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INSTITUT INTERNATIONAL DE CHIMIE SOLVAY

DIXIÈME CONSEIL DE CHIMIE
tenu à l'Université de Bruxelles
du 22 au 26 mai 1956

QUELQUES PROBLÈMES
DE
CHIMIE MINÉRALE

RAPPORTS ET DISCUSSIONS

publiés par les Secrétaires du Conseil
sous les auspices du Comité Scientifique de l'Institut

R. STOOPS
Editeur
76-78, COUDENBERG, BRUXELLES
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INTRODUCTION

Institut International de Chimie Solvay

EXTRAIT DES STATUTS.

Article premier. — Il a été fondé, à Bruxelles, à l'initiative de M. Ernest SOLVAY et pour une période de trente années, à partir du 1er mai 1913, un *Institut International de Chimie*.

La durée avait été prorogée jusqu'en 1949. Après le décès de M. Ernest Solvay, survenu le 26 mai 1922, M^{me} Ernest Solvay et ses enfants ont désiré assurer l'avenir de l'institut pour un temps plus long que celui qui avait été prévu. Dans ce but, une convention a été conclue entre les prénommés et l'Université de Bruxelles; en vertu de cette convention, l'avoir actuel de l'Institut est remis à l'Université en même temps que la somme nécessaire pour qu'à l'échéance prévue de 1949 le capital d'un million primitivement consacré par M. Ernest Solvay à l'Institut International de Chimie se trouve reconstitué.

L'Université assumera la gestion de cette somme en se conformant à toutes les dispositions des présents statuts.

Art. 2. — Le but de l'Institut est d'encourager des recherches qui soient de nature à étendre et surtout à approfondir la connaissance des phénomènes naturels à laquelle M. Ernest Solvay n'a cessé de s'intéresser.

L'Institut a principalement en vue les progrès de la Chimie, sans exclure cependant les problèmes appartenant à d'autres branches des sciences naturelles, pour autant, bien entendu, que ces problèmes se rattachent à la Chimie.

Art. 3. — L'Institut International de Chimie a son siège social à l'Université Libre de Bruxelles, qui met à la disposition de l'Institut les locaux nécessaires à la tenue des *Conseils de Chimie*.

Art. 4. — L'Institut est régi par une *Commission Administrative* comprenant *cinq* membres, belges de préférence, et par un *Comité Scientifique* international comprenant *huit* membres ordinaires auxquels peut être ajouté un membre extraordinaire ayant les mêmes droits qu'un membre ordinaire.

. . . .

Art. 9. — Le Fondateur a manifesté le désir qu'avant tout, l'Institut fasse preuve dans tous ses actes d'une parfaite impartialité; qu'il encourage les recherches entreprises dans un véritable esprit scientifique, et d'autant plus que, à valeur égale, ces recherches auront un caractère plus objectif. Il lui a semblé désirable que cette tendance se reflétât dans la composition du *Comité Scientifique*. Par conséquent s'il y avait des savants qui, sans occuper une haute position officielle, pourraient être considérés, en raison de leur talent, comme de dignes représentants de la Science, ils ne devront pas être oubliés par ceux qui désigneront les candidats aux places vacantes.

COMPOSITION DE LA COMMISSION ADMINISTRATIVE

MM. J. BORDET, Professeur honoraire et membre du Conseil d'Administration de l'Université Libre de Bruxelles, *Président*.

E.-J. SOLVAY, Gérant à la Société Solvay et Cie, membre du Conseil d'Administration de l'Université Libre de Bruxelles.

P. HEGER-GILBERT, Professeur honoraire à l'Université Libre de Bruxelles.

P. ERCULISSE, Professeur à l'Université Libre de Bruxelles.

F.-H. van den DUNGEN, Professeur à l'Université Libre de Bruxelles, *Secrétaire de la Commission administrative*.

R. LECLERCQ, Secrétaire de l'Université Libre de Bruxelles

10^e CONSEIL DE CHIMIE

22 au 26 mai 1956

LISTE DES PARTICIPANTS

A. Le Comité Scientifique.

MM. Paul KARRER, Prof. à l'Université (Zürich), *Président*, (Excusé).

H.-J. BACKER, Prof. à la Rijksuniversiteit (Gröningen).

Ch. DUFRAISSE Prof. au Collège de France (Paris), (Excusé).

K. LINDERSTRÖM-LANG Directeur du Carlsberg Laboratorium (Copenhague), (Excusé).

P. PASCAL Prof. à la Sorbonne (Paris), (Excusé).

Sir Robert ROBINSON Prof. à l'Université (Oxford), (Excusé).

A. R. UBBELHODE Prof. à l'Imperial College of Science (Londres).

H. WUYTS Prof. honoraire à l'Université Libre de Bruxelles, *secrétaire honoraire*.

Jean TIMMERMANS, Prof. honoraire à l'Université Libre de Bruxelles, *secrétaire*.

B. Les Membres rapporteurs.

MM. Prof. R. M. BARRER, Imperial College of Science, Departement of Chemistry, London.

Prof. J. BENARD, Faculté des Sciences de Paris.

R. COLLONGUES, Chef de Service au Centre d'Etudes de Chimie Métallurgique, Vitry s/Seine.

Prof. H. FORESTIER, Directeur de l'Ecole Nationale Supérieure de Chimie, Strasbourg.

Prof. J. A. HEDVALL, Institut for Silikatkemisk Forskning, Chalmers University, Göteborg.

Dr. Klixbüll JÖRGENSEN, Denmarks Tekniske Højskole, Copenhague.

Dr. R. LINDNER, Institut for Silikatkemisk Forskning, Chalmers University, Göteborg.

Prof. R. S. NYHOLM, University College, Department of Chemistry, London.

Dr. Leslie E. ORGEL, The Departement of Theoretical Chemistry, Cambridge, England.

Dr. H. M. POWELL, Chemical Crystallography Laboratory, University Museum, Oxford.

Prof. W. A. WEYL, Chairman, Division of Mineral Technology, Pennsylvania State University, University Park, PA.

C. Les Membres Invités.

MM. J. BJERRUM, Jr., Dr. Sc., Denmarks Tekniske Højskole, Copenhague.

V. CAGLIOTI, Directeur de l'Institut de Chimie Générale et Inorganique, Université (Rome).

J. CHATT, Dr. Sc., Akers Research Laboratories, Welwyn Herts.

G. CHAUDRON, Membre de l'Institut (Paris).

L. D'OR, Professeur à l'Université (Liège).

G. HÄGG, Professeur à l'Université (Uppsala).

W. KUHN, Professeur à l'Université (Bâle).

W. SCHLENK, Dr. Sc., Ammoniak-Laboratorium der Badischen Anilin und Sodafabrik, Ludwigshafen.

D. Les Membres Secrétaires.

M. J. TIMMERMANS, Professeur à l'Université Libre de Bruxelles, Secrétaire du Comité Scientifique de l'Institut.

Melle L. de BROUCKÈRE, Professeur à l'Université Libre de Bruxelles.

MM. R. DEFAY, Professeur à l'Université Libre de Bruxelles.

W. DE KEYSER, Professeur à l'Université Libre de Bruxelles.

F. BOUILLON, Assistant à la Faculté des Sciences.

I. LAFONTAINE, Licencié en Sciences Chimiques.

E. Auditeurs Invités.

MM. DECROLY, DESCAMPS, ERCULISSE, FLAMACHE, GOLDFINGER, GUILLISSEN, PRIGOGINE, Professeurs à l'Université Libre de Bruxelles.

ACTIVITÉS DU DIXIEME CONSEIL

Le dixième Conseil de Chimie Solvay s'est tenu à Bruxelles du 22 au 26 mai 1956 dans les locaux de l'Université Libre de Bruxelles.

Les travaux ont été ouverts le mardi 22 à 10 heures. En l'absence du Prof. Karrer, souffrant, le Prof. Backer a prononcé une allocution et la présidence du Conseil a été confiée au Prof. Ubbelohde.

Le mercredi 23 à 17 h 30, les autorités universitaires ont reçu les membres du Conseil dans le bâtiment central de l'Université.

Le vendredi 25, le banquet offert suivant la tradition par la famille Solvay et la Commission Administrative de l'Institut a réuni les membres du Conseil et les autorités universitaires. Au dessert, M. E.-J. Solvay qui présidait a donné la parole à M. De Groote, Président du Conseil d'Administration de l'Université, à M. Timmermans qui a lu une lettre du Prof Karrer et à M. Ubbelohde, Président du Conseil.

Le samedi 26 à 12 h 30, le Conseil a terminé ses travaux par une allocution du Prof. Hedvall.

Mmes. Timmermans et Erculisse ont très aimablement guidé les dames qui accompagnaient les membres dans leurs visites de la Ville de Bruxelles et de ses environs.

Message du Professeur P. Karrer

Président du Comité Scientifique de l'Institut

Mesdames et Messieurs,

Des raisons de santé m'ont interdit de prendre part au Dixième Conseil de Chimie Solvay. Je le regrette profondément, mais je ne veux tout de même pas manquer de vous transmettre par la voix de M. le Prof. Timmermans avec mes compliments l'expression de mes remerciements les plus cordiaux. Nos remerciements vont tout particulièrement à la famille Solvay, au Gouvernement belge et à l'Université Libre de Bruxelles qui a fondé l'Institut de Chimie Solvay et l'administre avec compétence. Nous ne manquerons pas d'y associer aussi les organisateurs de ce Dixième Conseil et tout spécialement M. le Prof. van den Dungen, secrétaire-administrateur, M. le Prof. Timmermans, secrétaire du Comité Scientifique et les membres secrétaires du Conseil.

En tant que président, j'ai l'honneur d'appartenir au Comité Scientifique depuis 1947 et j'ai toujours trouvé l'appui le plus constant et le plus dévoué auprès des membres de ce Comité. Que mes collègues en soient remerciés une fois de plus. Aujourd'hui, j'ai le plaisir de transmettre cette présidence à mon successeur le Prof. Ubbelohde. Je suis heureux qu'il ait accepté cette charge et lui souhaite la réussite la plus complète à son nouveau poste. Nous sommes persuadés qu'il exercera ses fonctions avec compétence et succès.

Depuis la fin de la deuxième guerre mondiale, il y a eu quatre Conseils de Chimie Solvay, en 1947, en 1950, en 1953, et en 1956. Le Septième Conseil de 1947 était consacré aux isotopes, le Huitième aux réactions d'oxydation, le Neuvième aux protéïnes et le Dixième aux combinaisons non stoechiométriques, aux sels complexes et à la réactivité des solides. Vous voyez combien le domaine scientifique auquel s'intéresse l'Institut International de Chimie Solvay est vaste. Malheureusement la biochimie manque à cet éventail coloré et ce *sera peut-être la tâche d'un futur Conseil de Chimie Solvay d'y consacrer une rencontre, car je n'ai pas besoin de signaler ici l'importance capitale des processus chimiques dans le captivant mystère de la vie. Il est certain que de telles rencontres donnent une impulsion nouvelle à la recherche scientifique et que cette impulsion contribue à la résolution de nombreux problèmes. On doit à Ernest Solvay, le fondateur de l'Institut de Chimie Solvay la maxime suivante : « La vérité sera la science ou elle ne sera pas ». Cette maxime exprime la foi inébranlable dans l'idéal de la science, seule capable d'ouvrir aux hommes les portes de la vérité, vérité n'acceptant ni maître, ni histoire mais seulement les résultats expérimentaux. Mais plus la science progresse et nous dévoile des secrets nouveaux et plus nous constatons qu'à elle seule elle ne peut apporter la paix et le bonheur à l'humanité.*

C'est encore à Ernest Solvay qu'on doit cette deuxième pensée sur la Société : « La Société est condamnée à la Justice sous peine de mort ».

Là encore Ernest Solvay apparaît comme un homme sage et avisé, ayant étudié les fondements des communautés humaines et ayant dégagé d'un coup d'œil infaillible l'essentiel de ces fondements. La justice est le fondement de toute société; ce fait est malheureusement trop souvent méconnu pour le plus grand dommage de la paix entre les hommes.

A ces considérations sur la vérité et sur la justice on doit ajouter une troisième maxime ayant trait au bonheur et à la paix intérieure des hommes. Elle a été formulée par un ami des enfants et des hommes : Heinrich Pestalozzi : « Rien n'est plus profitable que l'amour voué à son prochain ». Sans l'amour du prochain il manque à la science et à la justice le fondement moral qui anoblit et embellit la vie. Science et justice sont deux formules froides n'apportant aux hommes bonheur et prospérité que revêtues du manteau de l'amour. Nous espérons que la science moderne qui a obtenu de si remarquables succès dans tous les domaines n'oubliera pas ce précepte et comprendra que seule son association avec l'amour du prochain donnera son plein sens à la destinée humaine.

Et maintenant, Mesdames et Messieurs, je voudrais terminer ce court exposé en renouvelant une dernière fois mes remerciements les plus sincères à toutes les personnes ici présentes.

Discours de M. P. De Groote

Président du Comité d'Administration
de l'Université Libre de Bruxelles

BANQUET DU DIXIEME CONSEIL DE CHIMIE SOLVAY
du vendredi 25 mai 1956 au Métropole

Mesdames et Messieurs,

Il est de tradition que le Président de l'Université Libre de Bruxelles prenne la parole au cours du dîner qui accompagne chacune des sessions des Conseils Internationaux Solvay.

Je tiens à vous dire tout le prix que l'Université et moi-même, nous accordons à ce privilège qui donne l'occasion de vous exprimer nos sentiments et qui nous permet de remplir à l'égard de votre Institution nos devoirs de très sincère gratitude.

Vos travaux se développent sous le signe de l'objectivité et de la concision. Je ne dérogerai pas à cette règle, en ce qui me concerne, et je serai donc bref dans mes propos.

Je m'incline, tout d'abord, devant la mémoire d'Ernest Solvay, qui, en créant les Conseil Internationaux, a servi la science de façon particulièrement féconde et distinguée. Le hasard de mes lectures m'a fait connaître, il y a quatre jours à peine, le texte d'une lettre adressée par le Roi Albert à Ernest Solvay. J'en extrais le passage suivant : Je saisis cette circonstance pour vous adresser encore mes félicitations particulièrement chaleureuses à l'occasion de la récente fondation de l'Institut International des Sciences. Vous avez donné là un magnifique exemple en consacrant des sommes aussi importantes à l'établissement d'un véritable budget du progrès scientifique. Quant à moi (continue le Roi) je suis flatté d'être associé à une œuvre qui sert le bien de l'humanité et dont le succès est assuré par la valeur incontestée des hommes que vous avez appelés à concourir à la réalisation de votre remarquable initiative. »

Cette lettre porte la date du 8 octobre 1912.

Reportées à l'époque de la fondation des Conseils de Chimie et de Physique, les idées maîtresses des conceptions d'Ernest Solvay frappent par leur caractère original et leur parfaite appréciation des besoins ultérieurs des sciences en expension. Elles sont marquées de compréhension de l'homme et d'espoir dans les fonctions dévolues aux élites.

Confrontées, à quarante ans de distance, avec la réalité présente, la pensée du fondateur apparaît dans toute sa vigueur, son à-propos et son opportunité durable. Elle porte cette marque particulière du génie créateur qui fait durer les choses. Je prie Monsieur Solvay qui préside ce banquet, de recevoir l'expression de la déférente estime dans laquelle nous tous, nous resterons tenir la mémoire de son illustre grand-père.

Je m'adresse maintenant, aux membres du Conseil International de Chimie Solvay qui participent aux travaux de la présente session

Vos réunions se placent au niveau scientifique le plus élevé; elles réalisent, marquent ou précisent les étapes des progrès accomplis dans votre spécialité. Tout le monde de la science vous en sait gré et formule le vœu cordial de voir se poursuivre les activités de votre Institution dans la même fécondité, le même esprit et la même conscience. Il attend de vous, et c'est là une marque de confiance et d'égards, de nouveaux apports et de nouveaux enrichissements de notre patrimoine intellectuel commun.

Puis-je souligner que l'Université Libre de Bruxelles, intimement associée à l'organisation des Conseils Solvay, est votre lieu de réunion et votre foyer, qu'elle s'enorgueillit de la chose et que son désir demeure de se mettre à votre disposition pour vous apporter l'aide la plus complète et la plus appropriée.

Si votre Conseil entrevoyait des voies nouvelles suivant lesquelles l'Université pourrait développer ou renforcer sa collaboration en vue d'alléger vos devoirs ou d'intensifier votre action, nous ne ménagerons aucun effort, je vous demande d'en être assurés, pour répondre à vos vœux.

Messieurs,

Vous accomplissez dans la poursuite de vos recherches et dans l'association de leurs résultats, au cours de sessions comme celles des Conseils Solvay, une fonction éminente que comprennent et qu'appré-

cient tous les hommes soucieux de faire prévaloir le bien commun sur les intérêts personnels.

Vos activités se classent parmi les multiples manifestations de générosité humaine, parmi les cas de collaboration désintéressée que suscite la vie dans les domaines les plus divers. Mais à l'encontre des efforts visant aux réalisations sociales, politiques et internationales qui se développent à travers les écueils du verbalisme, des appréciations subjectives et de l'appauvrissement des compromis inévitables vos travaux, eux, se situent sur le plan de l'objectif et du concret, se poursuivent dans un climat moins ingrat peut-être, mais combien plus rigoureux, où les opinions se nivellent devant la réalité des faits et où les progrès engagés sont mis généreusement à la disposition de la communauté, sans monopoles ni restrictions.

Mais cette tâche qui est la vôtre et que vous accomplissez avec talent, revêt pour une large part sa pleine signification humaine du fait de sa continuité et de sa permanence, au-délà des personnalités particulières des savants qui se succèdent et se relaient. A cet égard puis-je évoquer devant vous un problème qui vous touche directement et qui suscite chez moi de réelles appréhensions pour l'avenir : le problème de l'insuffisance des moyens dont souffrent des universités de plus en plus nombreuses, spécialement en Europe. Vous qui êtes les artisans de la grande œuvre scientifique, vous comprenez mieux que quiconque l'angoisse montante que ressentent beaucoup d'établissements d'enseignement supérieur devant le manque ou la médiocrité des ressources dont ils disposent et devant les difficultés et les restrictions qui découlent de cet état de fait. Et cependant, ce sont ces mêmes institutions qui assument la responsabilité d'initier les jeunes hommes de science, appelés à animer les laboratoires, les écoles, les services de l'administration et de l'industrie, dans leurs échelons les plus élevés, ce sont ces mêmes universités qui ont la charge de former ces hommes de science qui, si leur valeur les y destine, feront dans l'aboutissement de leur carrière votre relève en temps opportun.

Bien sûr, la recherche scientifique suscite l'intérêt actif et la générosité des gouvernements et des mécènes, mais la tendance se manifeste de plus en plus de négliger dans ces soutiens, les besoins de base auxquels il doit être satisfait pour permettre la formation, par les universités, dans les meilleures conditions et dans le plus grand nombre, des jeunes hommes appelés à remplir des fonctions dans la recherche et l'ensei-

gnement. Si le toit de l'édifice scientifique reçoit généralement l'attention qu'il mérite, il n'en est pas de même des fondations, et ces fondations risquent s'il n'est pas porté remède à la situation, de se désagréger faute de ressources appropriées. On pourrait croire dès lors que les garanties de disposer d'une pépinière adéquate de chercheurs ne sont plus données. La parcimonie des moyens menace d'engendrer la médiocrité et de saper la fondation formative que les universités ont la charge d'accomplir.

Les contacts nationaux et internationaux que l'accomplissement de mes charges me ménage, me portent à juger que le mal que j'évoque est très général et tend à s'étendre. C'est ce qui justifie pour moi l'appel que je vous adresse. Des groupes de savants tels que le vôtre ne doivent pas être des épisodes dans la grande élaboration de la science. Ces groupes doivent se perpétuer. C'est dans vos successeurs que vous vous survivrez et c'est donc dans les garanties de formation de successeurs dignes de vous que vous trouverez les assurances de voir votre œuvre se poursuivre.

Je vous demande de nous aider, partout où cela est nécessaire, à mener une action vigoureuse pour combattre le dépérissement ou la stagnation dont sont menacés les établissements d'enseignement supérieur. Je requiers l'appui de toute votre autorité morale dans cette action. La science ne poursuivra ses progrès que si l'armature universitaire qui l'étaie et qui l'alimente en hommes, demeure forte et vivante.

Mesdames et Messieurs,

Je voudrais terminer cette intervention en saluant ceux des membres du Conseil que les circonstances ont empêché d'assister, partiellement ou totalement, à la présente session. Je remercie très cordialement M. le Prof. Backer qui, malgré son état déficient, a tenu à se rendre à l'appel du Conseil.

Je formule aussi mes vœux de bon rétablissement pour M. Karrer, et mets la circonstance à profit pour vous signaler qu'au cours de sa dernière séance, le Conseil d'Administration de l'Université de Bruxelles a conféré à M. Karrer, le titre de Docteur honoris causa de la Faculté des Sciences.

Discours de M. le Professeur Ubbelohde

Président du Dixième Conseil

Mesdames et Messieurs,

Vous venez d'écouter le message du Président du Conseil Scientifique de l'Institut Solvay. Nous regrettons tous que le Prof. Karrer n'ait pas pu être avec nous en personne. Je voudrais seulement ajouter quelques mots au sujet des travaux scientifiques du Dixième Conseil.

Ne vous alarmez pas. Je dois toutefois vous avertir que les corps solides ne sont plus du tout aussi inchangeants et aussi impénétrables que l'on pensait anciennement. Surtout à des températures élevées, il y a des migrations très considérables des éléments de structure dans les solides. En utilisant une grande variété de techniques nouvelles, la chimie a fait d'importants progrès dans l'étude des défauts de structures dans les corps solides et, dans la découverte des réactions chimiques à l'état solide. Ces développements de la chimie sont à la fois de haut intérêt scientifique, et de grande importance industrielle. C'est un plaisir de voir parmi les membres de ce Dixième Conseil de grands pionniers dans ces recherches tels que le Prof. Hedvall et le Prof. Chaudron. Mais tous les membres du Conseil qu'ils soient anciens ou nouveaux chercheurs dans cette nouvelle branche de chimie, ont profité des discussions germinatives qui ont eu lieu. Comme l'a dit une fois Sir Lawrence Bragg, il y a des discussions qui donnent une brulante envie de retourner immédiatement au laboratoire pour mettre des nouvelles idées à l'épreuve. Je crois pouvoir vous assurer que nos débats donneront un nouvel essor aux recherches dans la chimie des corps solides.

Nous avons également discuté les complexes inorganiques qui sont d'intérêt grandissant pour la théorie de la liaison chimique. Très certainement il y a un grand avenir pour l'étude de ces composés dans la chimie et dans la biochimie.

Tous les membres du Dixième Conseil apprécient l'organisation très efficace du congrès; cette organisation et l'hospitalité plénière, mais sans encombrements, a grandement aidé à soutenir nos discussions. Sans ce soutien, les débats auraient été durs à mener à bonne fin.

Nous remercions les fondateurs de l'Institut Solvay, le Comité Administratif, et l'Université Libre de Bruxelles pour le privilège qui nous a été donné de faire partie de ce Dixième Conseil. Je pense pouvoir promettre que ses résultats seront aussi importants et aussi fructueux que ceux des conseils précédents. Encore une fois merci.

Allocution de M. le Professeur Hedvall

à la clôture du Conseil Solvay

Mesdames et Messieurs,

Ayant terminé nos discussions sur la multiplicité des problèmes de l'Etat Solide, nous désirons exprimer notre profonde et respectueuse gratitude à tous ceux qui se sont occupés des préparatifs de ce Dixième Conseil Solvay, qui nous ont permis d'effectuer un travail extrêmement constructif.

Nous réalisons l'ampleur de l'effort qu'il vous a fallu fournir pour organiser ce Conseil. Nous vous félicitons cordialement d'avoir obtenu ce « produit » d'une qualité extraordinaire de vos actions et réactions, catalysées, nous l'espérons, par des phases liquides dont vous avez eu la bonté de verser pendant nos plantureux déjeuners et dîners.

Nous adressons nos remerciements à vous tous, mais nous sommes sûrs que vous n'objecterez pas que nous citions spécialement M. le Prof. Timmermans et M. le Prof. Ubbelohde. Celui-ci a dirigé, en tant que Président de notre assemblée, nos discussions avec une habilité et une capacité extraordinaire, profonde, amicale et circonstancielle.

Vous tous, vous nous avez donné un « screening » parfait. Nos imperfections se sont transformées en un état à la fois stable et actif, et les forces d'affinité se sont extrêmement renforcées, fait qui, pour sûr, n'est pas un phénomène superficiel.

Physical Chemistry of some Non-Stoicheiometric Phases

by **R. M. BARRER**

SUMMARY

A range of non-stoicheiometric phases has been classified and discussed, with particular reference to defect structures in which the defects take the form of included atoms or molecules. Systematisation is possible in terms of the idea of a " host " lattice with " guest " molecules. Structural features of various host lattices have been indicated, including some new data on two remarkable crystalline zeolites, with cavities able to accommodate ~ 29 and ~ 32 water molecules respectively.

The interpretation of occlusion or inclusion isotherms has been especially considered. These isotherms may be smooth curves, or they may have continuous regions separated by one or more steps. A general thermodynamic criterion for differentiating between continuous and discontinuous isotherms has been given, before proceeding to specific statistical thermodynamic interpretations. Particular attention has been paid to continuous occlusion isotherms in zeolites, and their quantitative interpretation. The standard entropy of occlusion for a successful isotherm model will fall in one or other of a series of entropy levels according to the degrees of freedom possessed by the occluded molecule. Partial molal entropies of the occluded molecules can be and have been employed to interpret the physical state of argon occluded within chabazite, and to obtain information regarding that of paraffins occluded within faujasite. The entropy function is shown to be of great usefulness in this direction.

1. In 1803 Berthollet published his "Essai de Statique Chimique". In it he expressed the opinion that the composition of a compound depended upon the conditions of its formation. This view drew the strongest opposition from Proust, whose work established the law of constant composition. Indeed for a long while the weight of chemical evidence grew in favour of Proust. Nevertheless we now know that both Proust and Berthollet were correct, each up to a point. Compounds of variable composition are now the concern of different industries as well as of more academic scientists. With the development of the wave mechanics of the solid state, and by the application of statistical thermodynamics to heterogeneous and homogeneous equilibria between and within phases, much insight has been obtained into the properties of Berthollide compounds.

Classifications of Berthollide compounds are more a matter of convenience than of rigorous distinctions. However we may give two categories :

(i) those showing small departures from stoicheiometry,

(ii) those which may show gross departures from stoicheiometry.

In group (i) are a number of oxides (Cu_2O, NiO, ZnO, FeO), sulphides (Ag_2S, PbS) and halides (NaCl, KCl, NaBr, KBr, AgCl, AgI), the compositions of which vary to a minor extent if concentrations of the anionic constituent, or on occasions of the cationic constituent, are maintained about the crystals (¹). In this group we may also place a range of phases the non-stoicheiometry of which is associated with the introduction of small amounts of foreign atoms or ions (¹). Examples are : $NaCl.\delta CdCl_2$; $AgCl.\delta CdCl_2$; $AgBr.\delta Ag_2S$; $NiO.\delta Li_2O$; $Ge_{1-\delta}Ga_\delta$; $Ge_{1-\delta}As_\delta$; $Al_{2-\delta}Cr_\delta O_3$. The quantity δ of added impurity may become considerable in some of these phases.

The second category of Berthollide compounds, exhibiting appreciable or large departures from stoicheiometry, is remarkably diverse both in range and in character. The following systems are typical :

(i) *Metallic and metalloid phases :*

a) Intermetallic alloys.

b) Interstitial phases (²) (H_2 in Pd, Pt, Fe, Ni, Ce, Zr, Ti, Th, U; O_2 in Zr, Ge, Ti; N_2 in Fe; C in some transition metals).

c) Interlamellar phases (²) (graphite with alkali metals, Br_2, F_2, $AlCl_3$, $FeCl_3$, CrO_2Cl_2, CrO_2F_2, $CuCl_2$, BCl_3, $ZrCl_4$, $MoCl_5$, WCl_6, ICl_3, etc.).

(ii) *Covalent systems :*

a) Interlamellar complexes of graphitic oxide (⁴) with organic penetrants.

(iii) *Ionic systems :*

a) TiO, PtS, CrS, FeS, Fe_2O_3 (¹).

b) Layer lattice basic salts (⁵) (e. g. basic Zn salts with H_2O, CH_3OH, C_2H_5OH, $C_2H_4(OH)_2$, CH_3CN, C_2H_5CN, $CH_2OH.CHOH.CH_2OH$).

c) Potassium benzene sulphonate (⁶) with H_2S, H_2O, NH_3 and many organic species.

(iv) *Polymerised ionic systems :*

a) Framework aluminosilicates exhibiting replacements (⁷) of types NaAl $\rightleftharpoons$ Si; Na $\rightleftharpoons$ K; Al $\rightleftharpoons$ Ga; Si $\rightleftharpoons$ Ge.

b) Open framework aluminosilicates with cavities (⁸) filled by neutral molecules (NH_3, H_2O, CO_2, S, I_2, hydrocarbons, hydrocarbon derivatives).

c) Open framework aluminosilicates (⁹) with cavities filled by ionic species (NaCl, KCl, $HgCl_2$, $BaCl_2$, $BaBr_2$, Na_2S_X, Na_2CO_3, Na_2SO_4, Na_2SeO_4, etc.).

d) Lamellar aluminosilicates such as montmorillonite ($^{10-10a}$) with inter-lamellar guest molecules (H_2O, NH_3, pyridine, CH_3OH, C_2H_5OH, $C_2H_4(OH)_2$ and many organic species).

(v) *Molecular systems :*

a) Dianin's compound (¹¹) (4-*p*-OH-phenyl-2:2:4-trimethyl chroman) forms inclusion complexes with I_2, SO_2, and a very wide range of organic species.

b) Urea and thio-urea form adducts (¹²) with many hydrocarbons and organic compounds.

c) Amylose, the straight chain fraction of starch forms complexes with I_2, and some n-fatty acids and alcohols (¹³).

d) Quinol forms clathrate compounds (14) with A, Kr, Xe, CH_3OH, C_2H_2, CO_2.

e) Water forms clathrate compounds (15) with simple organic species (CH_4, CH_3Cl, CH_2Cl_2, C_2H_6).

f) Schardinger's dextrin forms adducts (16) with I_2, Br_2, octanol, hexanol, trichlorethylene, p-nitrophenol, nitrosophenol and other species.

Some molecular complexes appear to be nearly stoicheiometric (e.g. those formed by nickel cyanide ammonia (17) with benzene, pyridine, quinoline, etc.). In any case the above list is not a detailed one.

Much attention has been devoted to crystals showing small stoicheiometric defect (1). Crystals may contain Schottky or Frenkel types of flaw; cation vacancies may be balanced electrically by an associated positive hole (e.g. a cation of higher valency); anion vacancies may be neutralised by the presence in them of an electron (F-centre) or pair of electrons (F′-centre); and the aggregation of F-centres may lead to the nucleation of a new phase. These and allied phenomena may govern the behaviour of semi-conductors; absorption and emission spectra of many crystals; and various catalyses and solid state reactions.

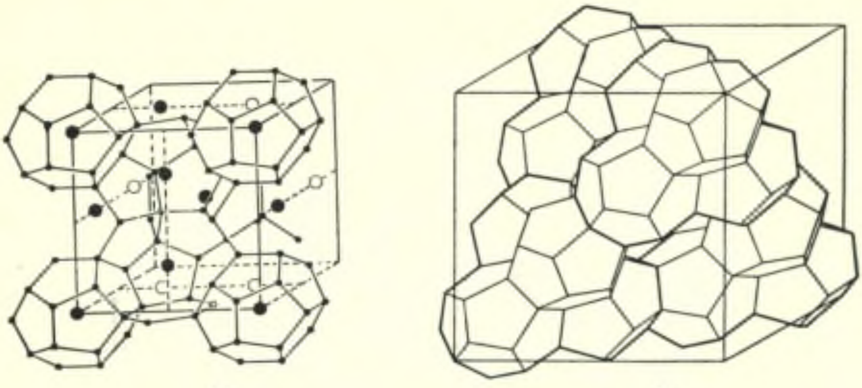
Many of the systems in category two of Berthollide compounds have been little investigated from the quantitative aspect at least. This has been remedied more recently in the case of intracrystalline occlusion by zeolites (8-18). Considerable attention of a quantitative kind is moreover now being given to intercalation by clays (10) and in various molecular complexes (19-6). At the same time much remains obscure, and an examination of some features of a few of the systems in category two is more than opportune, and will be made in the present paper.

2. The host lattice

In many interstitial solid solutions, interlamellar complexes, inclusion complexes of three-dimensional crystalline silicates and molecular adducts it is appropriate to speak of a *host lattice*. This may be thought of as a continuous lattice within which a second component is dispersed. In the water clathrate complexes (e.g. hydrocarbon hydrates) the water molecules are linked through hydrogen bonds into continuous systems of cages ([15]). The three-dimensional structures are based upon a tetrahedral arrangement of hydrogen atoms around each oxygen atom, part of the two fundamental networks being shown in Fig. 1. The cages so enclosed have 12 and 14 (Fig. 1*a*) and 12 and 16 faces (Fig. 1*b*) and are large enough to contain single guest molecules. Quinol ([14–20]), again by hydrogen bonding, forms two interpenetrating three-dimensional networks, in which each oxygen atom is at the centre of three diverging bonds. The interpenetrating networks enclose cavities in which small molecules are located (Fig. 2).

Dianin's compound ([11]) forms a six-membered ring by hydrogen bonding with other molecules of the same substance, and produces the structural unit formalised in Fig. 3. This unit can be further formalised as an hour glass truncated at each end. The packing of such units to give the crystal now provides substantial cavities which enclose guest molecules of considerable dimensions and of great diversity. Non-stoicheiometric proportions may occur between the numbers of guest molecules and those of the molecules composing the host lattices because the latter may exist even when some of the cavities they enclose are empty.

The concept of host lattice and of guest molecules is equally appropriate in the case of urea and thio-urea adducts ([12]) and of amylose ([13]) complexes. Here the host lattice consists of a spiral arrangement of hydrogen-bonded urea or thio-urea molecules, or of coiled amylose chains (Fig. 4). The guest molecules then lie along the axes of these spirals. Stoicheiometry is not found even if all the space along the axes of these spirals is occupied by the guest molecules, for the number of such molecules required depends only on their length. This is illustrated in Fig. 5 in which the number of moles of urea binding a mole of hydrocarbon is plotted against the number of C-atoms in the n-paraffin chain ([21]). The simple linear relationship is clearly seen. The paraffins are of necessity extended in their intra-crystalline environment, because there is no room for other configurations. In thiourea adducts, the thiourea molecules are also linked to form rather wider spirals still, which can occlude some branched chain paraffins



(a) (b)

Figs. 1*a* and 1*b*. — The two kinds of cage structure found in water-clathrates, after von Stackelberg (15). Structure (*a*) is composed of 12 and 14 faced polyhedra; structure (*b*) of 12 and 16 faced polyhedra. Only the dodecahedra are shown above.

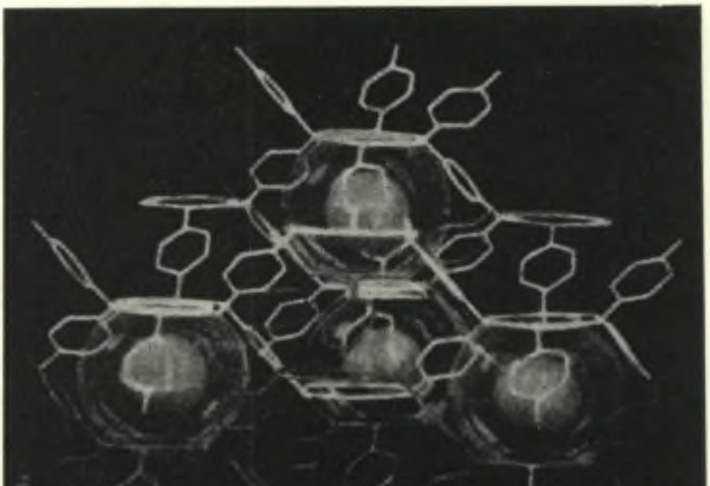


Fig. 2. — A model of the quinol clathrate structure (14) containing atoms such as argon (after Wells « The Third Dimension in Chemistry », Oxford, 1956).

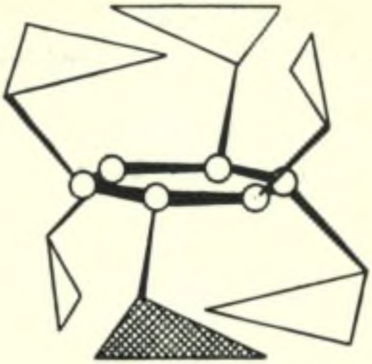


Fig. 3. — Formal representation, due to Powell and Wetters (11) of the space-enclosing unit based on six molecules of Dianin's compound.

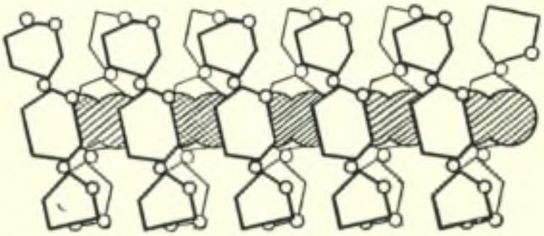


Fig. 4. — The configuration of the amylose complex with iodine. Iodine molecules lie along amylose helices [Rundle and Baldwin (13)].

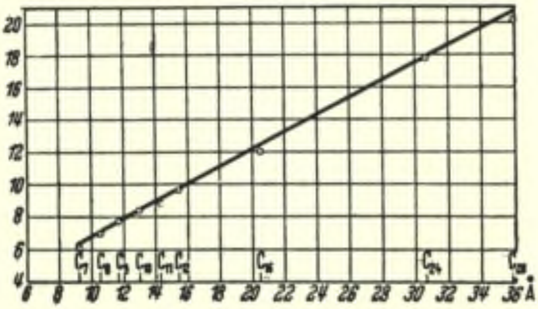


Fig. 5. — The dependance of the composition of urea-paraffin adducts upon the chain length of the paraffin [Cramer (12), after Schlenk (12)].
Ordinate : Moles of urea binding a mole of hydrocarbon.
Abscissa : Chain length of hydrocarbon.

and aromatics. The configurational restriction is still severe, but may be less marked for some molecules than in urea adducts.

When we consider the open framework aluminosilicates such as felspathoids and zeolites the concept of host lattice and guest molecules is particularly clear. A very sturdy anionic framework is often found (8−22), enclosing cavities joined into continuous channels by common windows (23). These channels cross other channels and very open frameworks then arise. The channel directions in several species are indicated without structural detail in Fig. 6 (24).

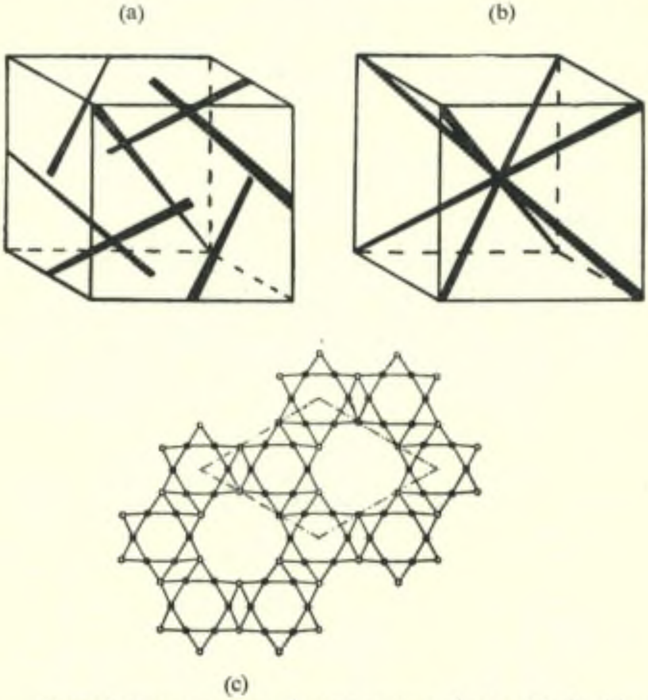


Fig. 6. — Formal representation of arrangement of channels in (*a*) analcite (*b*) chabazite and (*c*) cancrinite (normal to the place of the paper), [Barrer and Falconer (24)].

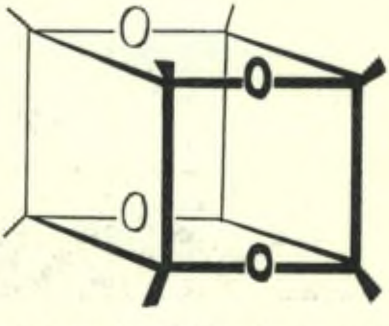
Framework aluminosilicates are based ultimately upon the tetrahedral $(Al,Si)O_4$ unit. However structural considerations of nets of tetrahedra can be much simplified for some open frameworks in the following way. The primary building units may be assembled to give secondary polyhedral building units, which can then be stacked in different ways in different co-ordinations. Fig. 7 (25) illustrates part of a polyhedron so formed. The complete polyhedron comprises eight rings of six tetrahedra and six rings of four tetrahedra and is a truncated octahedron. This unit has proved of great interest in aluminosilicate structures. We have found only three ways of assembling them, and have realised each in various syntheses. The resultant structures provide remarkable frameworks capable of forming non-stoicheiometric phases in great numbers. In each framework *every* O-atom is joined to each of two Si-atoms or to one Si- and one Al-atom.

In the *first structural type* the polyhedra are stacked in 8-fold co-ordination, by the sharing of the 8 × six-membered rings of a given central polyhedron with eight other polyhedra, one six-ring between each two polyhedra. The spatial arrangement is shown in Fig. 8, and is found in the following minerals :

Felspathoids :	*Zeolites :*
Sodalite	Chabazite
Nosean	Gmelinite (?)
Ultramarine	

In the felspathoids each polyhedron (or cage) contains amounts of salts (Na_2S_x, NaCl, Na_2SO_4, Na_2CO_3, NaOH, H_2O) in somewhat variable proportions. The zeolites contain water. The frameworks are capable of some distortion, so that the crystal symmetries may vary. We have synthesised nearly all the above crystals and a number of variants on them.

In the *second structural type* (26) the same polyhedra are stacked in 6-fold co-ordination, by union of each of their 6 × four membered rings with one such ring in another polyhedron. This union occurs through oxygen bridges as formalised below :



This mode of linking creates additional very small cages. However arranging the original polyhedra in this manner also encloses super-

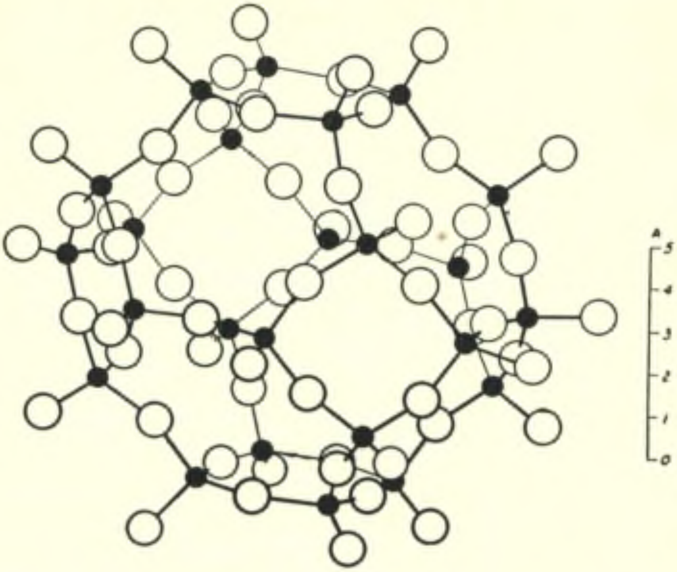


Fig. 7. — The structural polyhedron of importance in Figs. 8 and 9 and 10. It is a truncated octahedron with 14 faces.

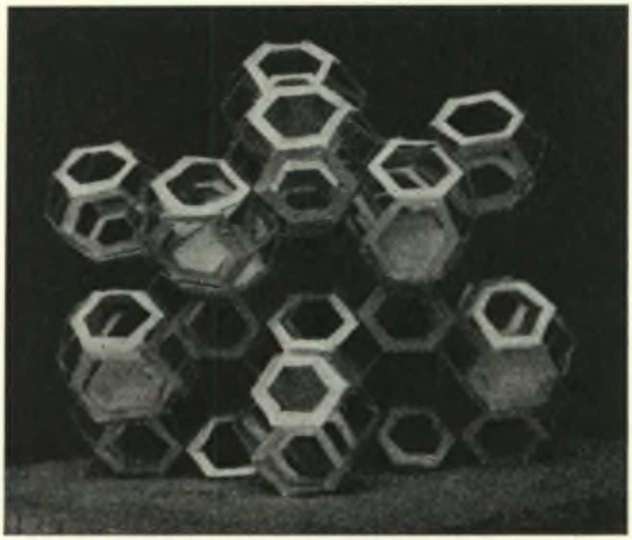


Fig. 8. — The structural units of Fig. 7 are stacked in 8-fold co-ordination to give a framework of chabazite type (27).

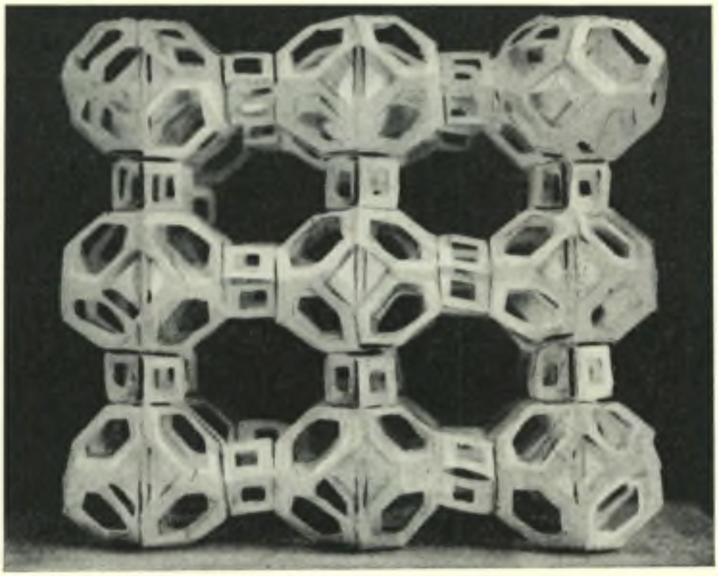


Fig. 9. — The structural units of Fig. 7 are stacked in 6-fold co-ordination to give the framework of a synthetic zeolite (26).

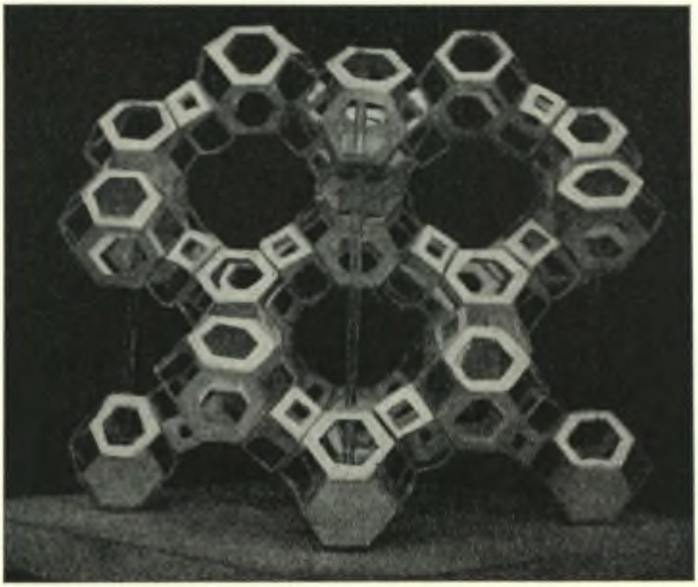
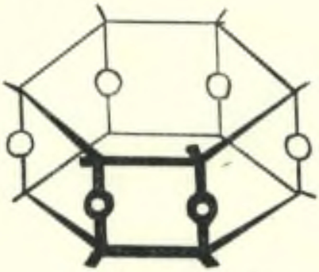


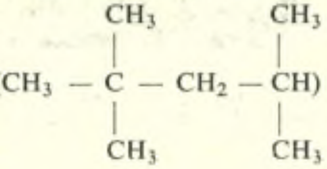
Fig. 10. — A third packing of the polyhedra of Fig. 7 to give a very open network characteristic of faujasite (27).

cages. The framework is shown in Fig. 9, and has been realised in a synthetic zeolite without natural counterpart.

In the *third structural type* (27) the polyhedra are stacked in 4-fold co-ordination, by union through oxygen bridges of four of the 8 × six-membered rings of a central polyhedron to one such ring in each of four other polyhedra :



This arrangement of the large polyhedra thus creates the additional small cages represented above. The large polyhedra are arranged like the atoms in diamond, and they enclose very large supercages indeed. This framework is shown in Fig. 10, and we have synthesised it in the form of faujasite-like crystals.

In Table I are given some characteristics of the crystals of the three structural types. The free diameters in column 3 are derived from the volumes of water which may be removed from the water-saturated crystals. It is further assumed that this water occupies the largest cavities only. The interstitial volumes in Column 7 are experimental values; and the numbers of molecules needed to saturate the largest cages (Column 6) are derived assuming only these cages to be filled. In chabazite, only one type of cage occurs; in the other two structures there are independent reasons for assuming only the larger cavities to be available, with the possible exception of water. Interstitial cations occupy positions in the cages, and it must be emphasised that the accessibility of cages to diffusing molecules may be influenced and even dominated by the situation of the cations. The faujasite lattice is thermally stable, yet it is the most open structure yet discovered, within which large molecules like iso-octane  $(CH_3 - \overset{CH_3}{\underset{CH_3}{C}} - CH_2 - \overset{CH_3}{\underset{CH_3}{CH}})$ can diffuse with the greatest ease (28). These zeolites, and others, provide almost perfect examples of host lattices, with a wide range in openness and accessibility to diffusing molecules.

As a final example of crystals acting as host lattices one may turn to an entirely different group of substances. Small non-metallic atoms such as hydrogen, oxygen, carbon and nitrogen may form interstitial solid solutions with a number of transition metals (2). The latter serve as host-lattices. In close-packed hexagonal or cubic crystals there are tetrahedral cavities, sometimes able to accommodate H atoms, and octahedral cavities, able to contain O, N and C atoms in some cases. Rundle (2) has shown that many interstitial carbides, oxides and nitrides have rock salt structures (Table II), but the siting of the interstitial atoms causes very little separation of the metal atoms, which then remain almost in contact and close packed.

TABLE I

Properties of open frameworks formed by stacking the cages of Fig. 7.

Structural type	Unit cell edge A^0	Free diameter of largest cage in A^0	Type of window joining largest cages into channels	Largest molecules admitted to dehydrated crystals	Nos. of molecules needed to fill the largest cages	Interstitial volume in cm^3 per cm^3 of crystal
1. (Fig. 8) Chabazite, Ca-form	9.5	$\sim$ 7.3	6-membered rings (eight in number)	n-paraffins (Cross-sectional diameter $\sim$4.9 A^0)	6-7 H_2O $\sim$3 A, N_2 or O_2	0.46
2. (Fig. 9) Synthetic zeolite, Ca-form	12.27	$\sim$11.8	8-membered rings (six in number)	n-paraffins	$\sim$29 H_2O 12-14 A, N_2 or O_2	0.46
3. (Fig. 10) Synthetic faujasite, Na-form	24.8	$\sim$12	12-membered rings (four in number)	n-, iso-, and neo-paraffins and aromatics readily occluded. Largest molecule not determined.	$\sim$32 H_2O 17-19 A, N_2 or O_2 $\sim$4.5 n-C_5H_{12} $\sim$3.5 n-C_7H_{16} $\sim$2.8 iso-C_8H_{18}	0.53

TABLE II

Metal-metal distances in metals and in interstitial phases.

Element	Distances between Metal atoms (in A^0)			
	Metal	Carbide	Nitride	Oxide
Sc	3.20 (A1)	—	3.14 (B1)	—
La	3.75 (A1)	—	3.73 (B1)	—
Ce	3.64 (A1)	—	3.54 (B1)	—
Pr	3.64 (A3)	—	3.65 (B1)	—
Nd	3.64 (A3)	—	3.64 (B1)	—
Ti	2.93 (A3)	3.05 (B1)	2.99 (B1)	2.99 (B1)
Zr	3.19 (A3)	3.32 (B1)	3.27 (B1)	—
Th	3.59 (A1)	3.75 (B1)	3.68 (B1)	3.71(?)(B1)
V	2.63 (A2)	3.03 (B1)	2.92 (B1)	2.91 (B1)
Cb	2.85 (A2)	3.16 (B1)	3.12 (B1)	2.96 (B1) distorted)
Ta	2.85 (A2)	3.14 (B1)	—	—
Cr	2.71 (A2)	—	2.75 (Hex) 2.93(?)(B1)	—
Mo	2.72 (A2,A3)	2.90 (Hex)	2.86 (Hex)	—
W	2.74 (A2)	2.91 (Hex)	2.86 (Hex?)	—

A1 = cubic close packed
A2 = body centred cubic
A3 = hexagonal close packed
B1 = sodium chloride
Hex = hexagonal

3. Stability of host lattices

It is useful for some considerations of inclusion to recognise three degrees of stability (29) of the host lattices :

(i) The host lattice becomes unstable as soon as the concentration of occluded guest molecules (or atoms) falls below a certain value (some complexes of potassium benzene sulphonate; clathrate compounds of quinol; hydrocarbon hydrates).

(ii) The host lattice retains some structural features, but changes in others as guest molecules are progressively withdrawn. This is often found in layer lattice intercalation complexes of substances such as montmorillonite, graphite and graphite oxide. Thus Fig. 11 gives the c-spacing of montmorillonite (30) as intercalated water is progressively removed or added. Fig. 12 indicates the way in which it has been suggested (31) that graphite bisulphate loses the interlamellar bisulphate ions.

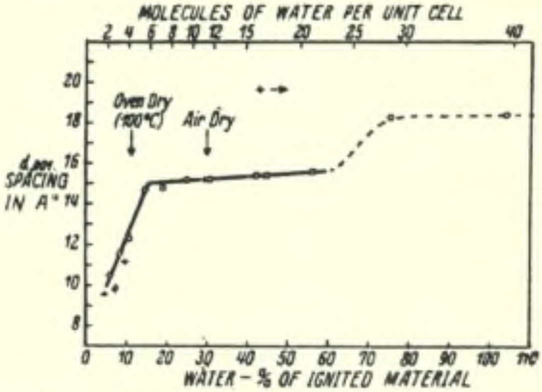


Fig. 11. — The one-dimensional swelling of montmorillonite on hydration (30).

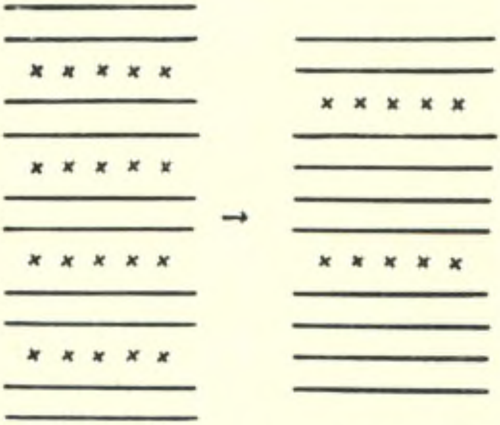


Fig. 12. — Suggested step-wise mode of loss of sulphate from graphite bisulphate (31).

(iii) The host lattice exists permanently whether intra-crystalline guest molecules are present or absent. This is the case in some interstitial alloys (2) of, for example, hydrogen in transition metals, or of dilute nitrogen solutions in iron, or oxygen in Zr, and even, it has recently been reported, of Ge(31a). It is also true of the robust framework zeolites (8–18), and of the molecular crystal of Dianin's compound (11). These examples are merely illustrations drawn from diverse molecular and atomic architectures and involving various types of bond between host lattice and guest molecule or atom.

4. Inclusion isotherms

Equilibrium isotherms of amount included *vs* equilibrium pressures can be measured by methods developed for studying adsorption of gases and vapours for all systems where the guest molecules are mobile within the host crystal and are volatile. These criteria are obeyed for many systems (hydrogen in metals; gases and vapours in zeolites, montmorillonite, graphite). Inclusion isotherms of three kinds have been observed :

(i) continuous curves (e.g. gases and vapours in zeolites ([28]), ammonia, ethylamine or ethanol in potassium benzene sulphonate ([6]),

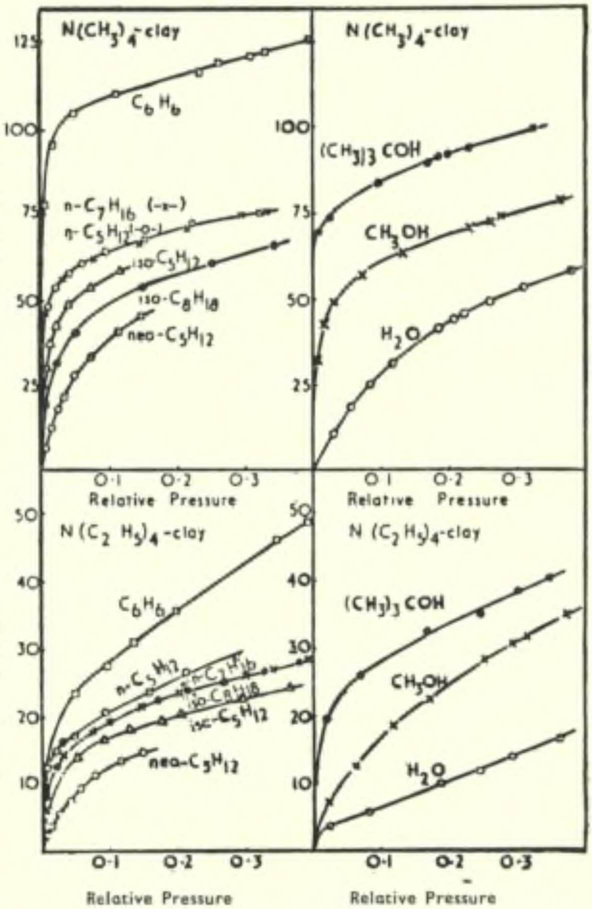


Fig. 13. — Typical continuous isotherms for intralamellar complexes of alkyl ammonium montmorillonite ([10]).

hydrogen above a critical temperature in some transition metals, hydrocarbons between lamellae of alkyl ammonium montmorillonites (10) (Fig. 13);

(ii) isotherms showing a step (e.g. benzene in potassium benzene sulphonate (6), methanol or ethanol in montmorillonite (32) (Fig. 14) and hydrogen below a critical temperature in some transition metals (33) (Fig. 15);

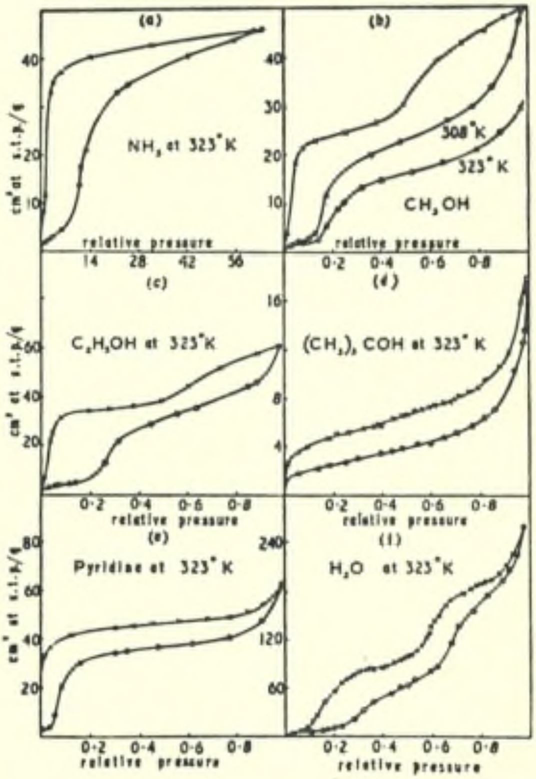


Fig. 14. — Typical isotherms for polar sorbates (32) in montmorillonite. ⊙ = adsorption points; x = desorption points.

(iii) isotherms showing two steps (e.g. water in potassium benzene sulphonate (6) and in montmorillonite (32) (Fig. 14), sulphur in PtS-PtS_2 phases (34) and hydrogen in O-Zr (35).

When isotherms exhibit steps these are often associated with perceptible and sharp lattice changes. In other systems however lattices changes are not associated with obvious isotherm discon-

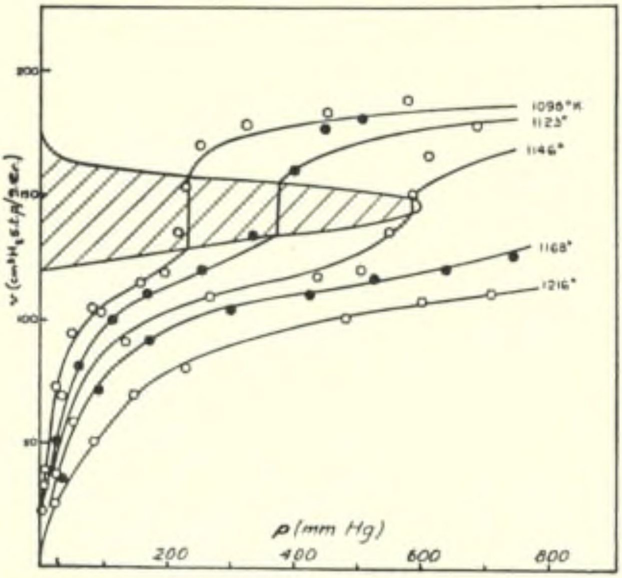


Fig. 15. — Stepwise isotherms for occlusion of hydrogen by zirconium metal (39).

tinuities, and the question arises as to when structural or other changes are associated with isotherm steps and when they are not. A thermodynamic criterion of the condition for stepwise or for continuous isotherms may be given as follows (36). We consider a system such as

$$xA_{(gas)} + A_{(1-x)}\,B$$

where A denotes a mole of the guest molecules and B a comparable amount of the host lattice. A fraction x of the mole of A is gaseous (or dissolved in an inert solvent) and a fraction $(1 - x)$ is included in the host lattice. Suppose the Gibbs free energies, G, of the system for different values of x are plotted as a function of temperature, T, and lie as in Fig. 16*a* so that the crossing points for decreasing x move from left to right. Then the envelope of lowest free energy corresponding to the stable state of the system touches each G — T curve at a single point only. As T rises x decreases continuously giving a continuous isobar (Fig. 16*c*).

On the other hand if the crossing points of the G — T curves for decreasing values of x move from right to left as in Fig. 16*b*, the curve of lowest free energy consists of two linear sections meeting

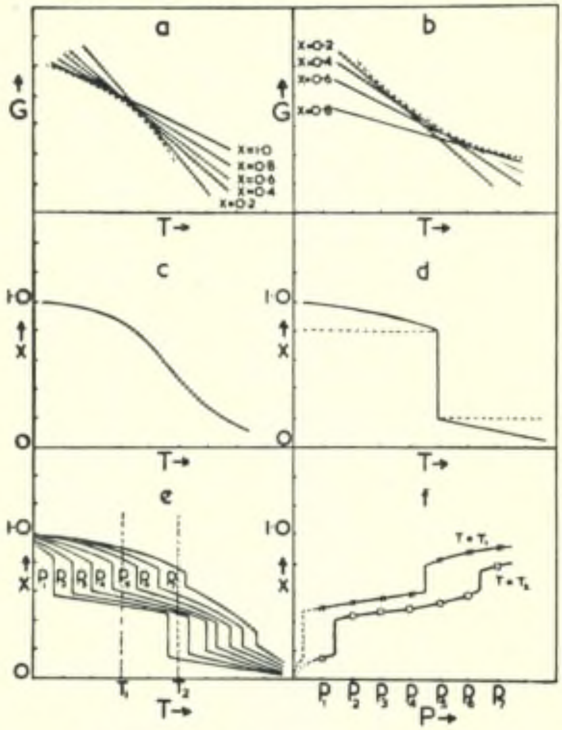


Fig. 16*a* and 16*b*, illustrating the thermodynamic requirement to obtain isobars which are continuous (Fig. 16*c*) or show a step (Fig.16*d*). Figs 16*e* and 16*f* show the way in which isobars with steps lead to isotherms with steps.

at a critical temperature Tc. In Fig. 16*b* x changes discontinuously from 0.8 to 0.2 at Tc. The isobar is now stepwise (Fig. 16 *d*).

Combinations of both types of behaviour may occur and regions of isobars both continuous and discontinuous then arise. Moreover a series of isobars will be obtained at a sequence of pressures $p_1 < p_2 < p_3 < p_4$, etc., as in Fig. 16 *e*, where two discontinuities are represented. From the isobars the isotherms may be constructed. Fig. 16*f* shows isotherms for $T = T_1$, $T = T_2$, and each has discontinuities, which reflect the behaviour of the isobars.

5. Theory of isotherms with both continuous regions and discontinuities

The next stage in the argument consists in setting up models for which in principle G — T curves may be calculated using the methods of statistical thermodynamics, and which reflect the types of behaviour illustrated in Fig. 16. We will postpone consideration of continuous isotherms and outline models which give continuous regions separated by one or more discontinuities. It is also convenient not to calculate families of G — T curves for different pressures and thence find the isotherms, but instead to derive the isotherms directly.

Three approaches have been developed. The first is that of Lacher (33), used for the interpretation of isotherms of hydrogen in palladium which show a single step below a critical temperature, Tc. The interstices in the Pd-lattice constitute sorption sites in the Langmuir sense, but distributed through the metal crystals instead of being confined to the surface. If there is no interaction between hydrogen atoms in these interstices then for a fraction θ occupied

$$p^{\frac{1}{2}} = \frac{K\theta}{(1-\theta)} \qquad 5.1$$

would define the equilibrium, K being a constant which can be evaluated by the statistical thermodynamic method. No isotherm step could then occur. However Lacher made the additional assumption that when two interstitial hydrogen atoms occupy adjacent sites there is an exothermal interaction, $\frac{2w}{Z}$ (the factor $\frac{2}{Z}$ being included for convenience and Z being the co-ordination number of a site). The number of pairs of adjacent H-atoms is approximately $\frac{ZN^2}{2N_s}$ or exactly $ZN\left(\frac{\theta}{2} - \frac{\theta(1-\theta)}{\beta+1}\right)$, where

$$\beta = \left\{1 - 4\theta(1-\theta)\left(1 - exp - \frac{2w}{ZkT}\right)\right\}^{1/2},$$

N is the number of H-atoms in interstices, and N_s is the saturation number of interstices. One may treat the interstitial H-atoms as oscillators and evaluate their partition function and hence their chemical potential. This can be equated at equilibrium to the chemical potential of gaseous H-atoms in equilibrium with molecular hydrogen. The isotherm equation then is

$$p^{\frac{1}{2}} = K\frac{\theta}{1-\theta}\exp\frac{2\theta w}{kT} \text{ (approximate treatment)} \qquad 5.2$$

$$p^{\frac{1}{2}} = K\frac{\theta}{(1-\theta)}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^{Z} \text{ (exact treatment)} \qquad 5.3$$

where the constants K are evaluated explicitly in the treatment and where p denotes the pressure of *molecular* gaseous hydrogen.

These equations have an interesting property. Provided $w < 0$ (exothermal interaction of adjacent H-atoms) there is a critical temperature $T_c = -\frac{w}{2k}$ for eq. 5.2 and $-\frac{w}{kZ\ln\frac{Z}{Z-2}}$ for eq. 5.3, for which with $Z = 6$, $T_c = -\frac{w}{2.43k}$.

At temperatures below T_c compositions near $\theta = 0.5$ are metastable and the solid phase splits into two phases with concentrations of hydrogen symmetrically related to $\theta = {}^1/_2$. Above but near T_c the isotherms show an inflection but no discontinuity while as $\frac{w}{kT}$ grows smaller the ideal Langmuir isotherm is more and more nearly approached. Lacher (33) was able to fit eq. 5.2 successfully to the experimental data of Sieverts (37) and of Gillespie (38).

Lacher's approach is essentially a treatment of a defect structure, the lattice defects being interstitial hydrogen atoms with the special property of interacting with one another. This treatment was taken further by Rees (1). He also started with a host lattice of A and treated all entering atoms, B, up to the limiting composition AB_n as interstitial atoms. The host lattice was supposed to remain unaltered during this process and the specific treatment envisaged three phases A, AB and AB_2. The occupation of one site per A atom by B atoms was supposed to produce a second kind of site. Thus the physical situation recalls that in the BET adsorption isotherm limited to the growth of two layers. However, unlike the BET isotherm interaction energies between pairs of B atoms were considered. The terminology used was

N = no. of A atoms in the crystal;

N^a = no. of sites of the first kind occupied;

N^b = no. of sites of the second kind occupied;

$-E^a$ = energy of a B atom in a site of the first kind, in its lowest quantum state relative to a free B atom in the gas phase;

$-E^b$ = the corresponding energy of a B atom in a site of the second kind;

$\frac{2E^{aa}}{Z}$ = interaction energy of a pair of adjacent B atoms in sites of the first kind;

$\frac{2E^{bb}}{Z}$ = this energy for sites of the second kind.

Interaction between occupied sites of the first and second kind is included in the energy difference $E^b - E^a$, so that cross terms E^{ab} need not be considered.

The approximate values were used for the number of pairs on sites of the first and second kind respectively :

$$N^{aa} = \frac{Z_a (N^a)^2}{2N}\ ;\ N^{bb} = \frac{Z_b (N^b)^2}{2N^a}$$

The same method of approach as used by Lacher (33) then gives for the isotherms

$$p^{\frac{1}{2}} = K_a \frac{\theta^a}{1 - \theta^a} \exp - \frac{2\ \theta^a\ E^{aa}}{kT} \qquad 5.4$$

$$p^{\frac{1}{2}} = K_b \frac{\theta^b/\theta^a}{1 - \theta^b/\theta^a} \exp - \frac{2\ (\theta^b/\theta^a)\ E^{bb}}{kT} \qquad 5.5$$

where K_a and K_b were evaluated explicitly and $\theta^a = {}^{N^a}/N$; $\theta^b = {}^{N^b}/N$.

The resultant isotherm shows two steps, separated by continuously varying compositions (Fig. 17). This treatment has been applied by Martin and Rees (39) to the H_2 — Zr system (Fig. 15). However one of the two critical temperatures must here be assumed low and the critical pressure to fall below the experimental pressure range.

An interesting point in the general treatment is that it appears possible to pass from one structure to another which may be of different symmetry without a change of phase, provided one is above the critical temperature T_c. This happens because the disordered parent lattice A with, for example, 33 % of interstitial atoms

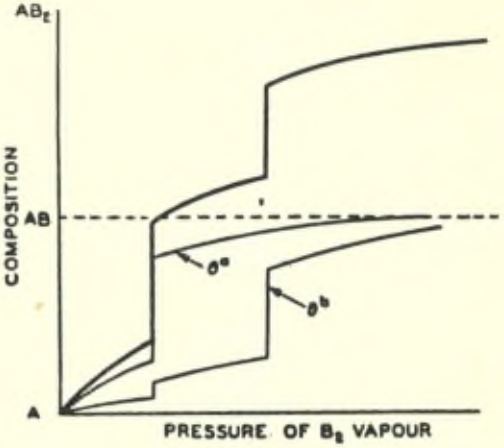


Fig. 17. — Construction of complete isotherm from component isotherms [Rees (1)].

of B is indistinguishable from the disordered lattice of AB of different symmetry containing 50% vacant B sites. Above the critical temperatures of the two phase regions there is no phase change in passing from A to AB to AB_2. Also if $T \gg T_c^a, T_c^b$, the two critical temperatures, then the disorder is such that no distinction arises between the two kinds of B-atom site.

Another point made is that if one introduces holes into the lattice of A atoms by removing A atoms from the interior to the surface of the crystal of A then the number of interstices suitable for occupancy by B atoms may be reduced. If the number of such Schottky defects in the A lattice is large, and since their number will normally increase as temperature rises, it could follow that the saturation content of B atoms in the A crystal decreases as the temperature rises. This argument has also been used in a discussion of the H_2 — Zr system.

The most difficult part of the above treatment perhaps lies in envisaging how the introduction of a B-atom into an "*a*" type site creates a "*b*" type site not previously there. There is a third treatment of isotherms exhibiting discontinuities, however, which is very general, and which was developed by Anderson (34). He was concerned with the conditions for co-existence of holes and of interstitial defects in the lattice of one of the component ions or atoms of a two component system. As is always necessary for discontinuous isotherms he again postulated an exothermic interaction between defects of the same kind.

If N^h_A and N^i_A denote respectively the numbers of holes vacated by atoms A and of interstitial A atoms in the crystal AB bathed in the diatomic gaseous species, A_2, then the number of pairs of holes and of interstitial atoms in juxtaposition are approximately

$$N^{hh} = \frac{Z_h\,(N^h_A)^2}{2N_B}\ ;\ N^{ii} = \frac{Z_i\,(N^i_A)^2}{2N_B}$$

Thus, if $\dfrac{2E^{hh}}{Z_h}$ and $\dfrac{2E^{ii}}{Z_i}$ are the interaction energies per pair, then the total interaction energies are respectively

$$\frac{(N^h_A)^2}{N_B}\,E^{hh}\ ;\ \frac{(N^i_A)^2}{N_B}\,E^{ii}$$

Here Z_i and Z_h are the co-ordination numbers of interstitial A-atoms and of holes in the A-atom lattice. The usual statistical thermodynamic procedure then leads to the two equations

$$p^{\frac{1}{2}} = K'_h\,\frac{\theta^h}{1-\theta^h}\,\exp\frac{2\theta^h E^{hh}}{kT} \qquad 5.6$$

$$p^{\frac{1}{2}} = K'_i\,\frac{\theta^i}{1-\theta^i}\,\exp\frac{2\theta^i E^{ii}}{kT} \qquad 5.7$$

where the constants K'_h, K'_i are evaluated specifically in the derivation. If p_o denotes the pressure of A_2 molecules at which the stoicheiometric composition AB exists in the crystal, then when $N_B > N_A$

$$\left(\frac{p}{p_o}\right)^{1/2} = K_h\,\frac{\theta^h}{1-\theta^h}\,\exp\frac{2\theta^h E^{hh}}{kT} \qquad 5.8$$

and when $N_B < N_A$

$$\left(\frac{p}{p_o}\right)^{1/2} = K_i\,\frac{\theta^i}{1-\theta^i}\,\exp\frac{2\theta^i E^{ii}}{kT} \qquad 5.9$$

where K_h and K_i are also evaluated specifically. Below critical temperatures T^h_c and T^i_c, defined by $T^h_c = \dfrac{-E^{hh}}{2k}$ and $T^i_c = \dfrac{-E^{ii}}{2k}$ these isotherms each show a two phase region, just as in the case of Lacher's and Rees's treatments. For any temperature $T < T_c^h, T_c^l$ the limits of the homogeneous composition ranges are given by the pressures for $\theta^h = 0.5 = \theta^l$. Then

$$\left(\frac{p_{1/2}^h}{p_o}\right)^{1/2} = K_h \exp\frac{E^{hh}}{kT}\,;\;\left(\frac{p_{1/2}^l}{p_o}\right)^{1/2} = K_l \exp\frac{E^{ll}}{kT} \qquad 5.10$$

Three cases may be visualised :

a) $p_{1/2}^h > p_o$; $p_{1/2}^l < p_o$. The stoicheiometric composition AB is stable, and the composition varies continuously on both sides of this composition before the upper and lower two phase regions appear (Fig. 18*a*).

b) $p_{1/2}^h < p_o$; $p_{1/2}^l < p_o$, but $p_{1/2}^h > p_{1/2}^l$. In this case the stoicheiometric composition AB falls in the two phase region (Fig. 18*b*)

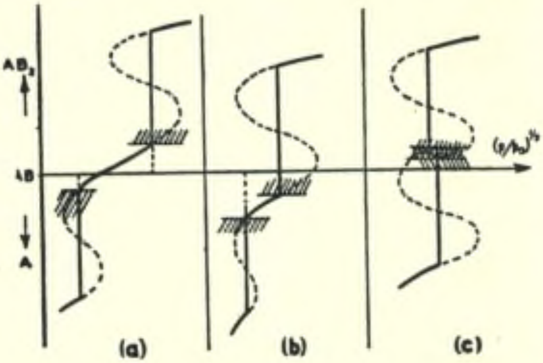


Fig. 18. — Isotherms illustrating possible behaviour of a system in the neighbourhood of a stoicheiometric composition AB [Rees (¹)].

c) $p_{1/2}^h < p_{1/2}^l$. No homogeneous range occurs in the neighbourhood of the stoicheiometric composition AB, and the two two-phase regions overlap (Fig. 18*c*). No crystal AB can exist. This situation is not physically possible, and in constructing isotherms the limiting condition must be $p_{1/2}^h = p_{1/2}^l$, giving a curve with only one step.

This treatment has been applied to the system Pt — PtS — PtS_2 (³⁴). While Anderson has in this case considered non-stoicheiometry in terms of interstitial S and of S-vacancies, in some non-stoicheiometric phases other defects are involved. For example δ-TiO (NaCl-type) varies continuously in composition from $TiO_{1.35}$ to $TiO_{0.60}$, the variation being due to anion vacancies trapping electrons and to Ti^{++}-cation vacancies trapping positive holes (Ti^{4+} ions). Even stoicheiometric TiO has 15 % unoccupied sites in each lattice (Table III).

TABLE III

Disorder in δ-TiO.

Composition	Ti sites occupied %	O sites occupied %
$TiO_{1.33}$	74	98
$TiO_{1.25}$	77	96
$TiO_{1.12}$	81	91
$TiO_{1.00}$	85	85
$TiO_{0.69}$	96	66

There is a strong element of similarity in the three treatments of Lacher, Rees and Anderson for in all these approaches the decisive factor in introducting steps into isotherms is the interaction between like defects, which may in turn be of several types.

6. **Hysteresis**

If isotherms show discontinuities there is often marked hysteresis associated with a sorption-desorption cycle. Such behaviour has been established in hydrogen-transition metal alloys (33) (H_2—Pd, H_2—U), in H_2O, NH_3, CH_3OH, C_2H_3OH-montmorillonite inclusion complexes (32), in Br_2-graphite (40), or in H_2O, C_6H_6, thiophen, toluene, xylene, naphthalene-potassium benzene sulphonate phases (6) (Fig. 19). The hysteresis phenomena have been attributed to the need to nucleate a second phase of host crystal and guest molecules on or in a parent phase. Suppose ΔG is the molar free energy for the reactions

$$pA_{gas} + B_{solid} \rightarrow A_pB_{solid}$$

$$\text{or} \quad pA_{gas} + A_nB_{solid} \rightarrow A_{p+n}B_{solid}$$

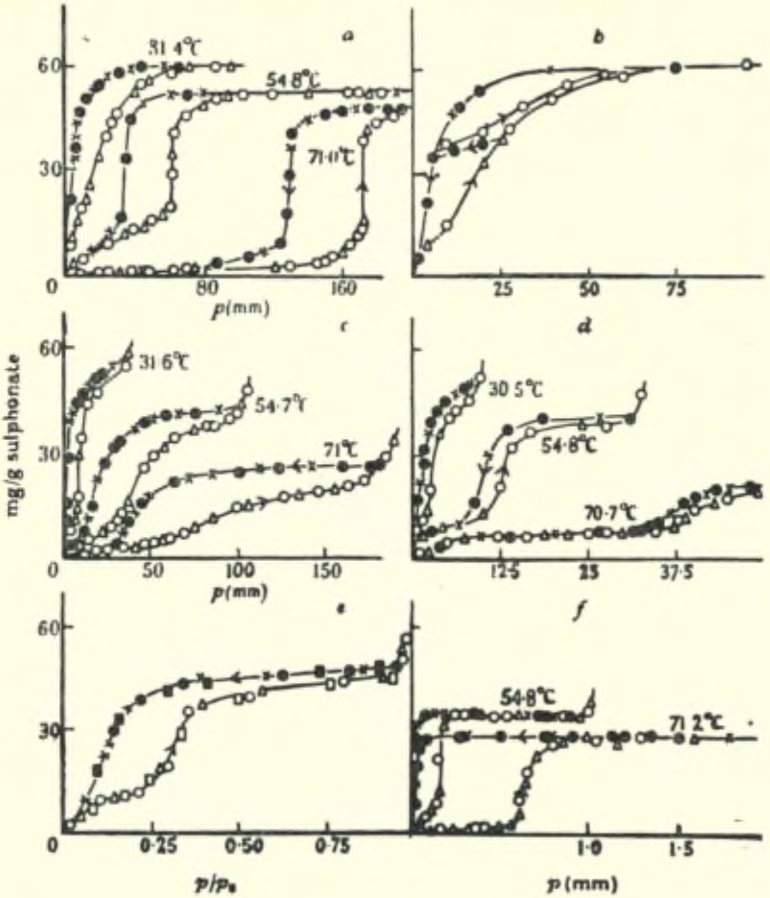


Fig. 19. — Sorption isotherms for some aromatic hydrocarbons. *a*, benzene, *b*, scanning loop for benzene at 31.4 °C, *c*, toluene, *d*, o-xylene, *e*, O, ●, o-xylene, 30.5 °C; Δ, *x*, p-xylene, 30.5 °C; □, ■, m-xylene, 30.5 °C. *f*, naphthalene. [Barrer, Drake and Whittam (6)].

However, when a germ-nucleus of the new phase richer in A forms on or in a matrix of the parent phase poorer in A then two additional free energy terms are involved, each of which is positive in sign. These are associated with surface free energy (Δg_σ) and with strain (Δg_s). Thus if the germ-nucleus comprising say *i* units A_pB forms on or in the matrix of B the actual free energy formation of the germ is

$$\Delta g_i = i\,\frac{\Delta G}{N_o} + \Delta g_\sigma + \Delta g_s \qquad 6.1$$

At the true thermodynamic equilibrium point, $\Delta G = 0$, but from 6.1, Δg_i is seen to be positive and so the germ-nucleus will not grow. However as the pressure of A grows, and the true thermodynamic equilibrium point is passed, ΔG becomes increasingly negative and reaction may set in. The further condition for this may be seen as follows.

One may suppose that Δg_σ = constant × area of germ-nucleus $= Ai^{2/3}$, and that Δg_s = constant × volume of germ-nucleus $= Bi$. Thus

$$\Delta g_i = i\frac{\Delta G}{N_0} + Ai^{2/3} + Bi \qquad 6.2$$

If we plot Δg_i against i, Δg_i is at first positive, but as i increases it reaches a maximum value and thereafter decreases. Any germ-nucleus reaching this critical size will then develop spontaneously.

At the maximum $\dfrac{d(\Delta g_i)}{di} = 0$ and so from eq. 6.2

$$i_m = -\frac{8A^3}{27\left(\frac{\Delta G}{N_0} + B\right)^3} \qquad 6.3$$

$$\Delta g_m = \frac{4A^3}{27\left(\frac{\Delta G}{N_0} + B\right)^2} \qquad 6.4$$

Through fluctuations there will be at first a steady state population of germ-nuclei of different sizes, but at pressures near the true thermodynamic equilibrium the number passing through the critical size i_m is negligible. As the pressure of A increases however the "current" of germ-nuclei exceeding the critical size rises very swiftly indeed, so that a threshold pressure is often found, below which the new phase does not appear and above which reaction is nearly complete.

On the desorption branch exactly the same kind of considerations delay the formation of crystallites of say B in or on a matrix of A_pB. Evidently then these considerations provide a very reasonable explanation of hysteresis, which may be made more realistic still when it is recalled that Δg_s and Δg_σ may depend on the shape of the germ-nuclei and their situation in the crystal (6). This means a spectrum of values of A and B, and the summation of groups of rectangular hysteresis loops which, as seen in Fig. 20, average to a sloping hysteresis loop such as is commonly observed.

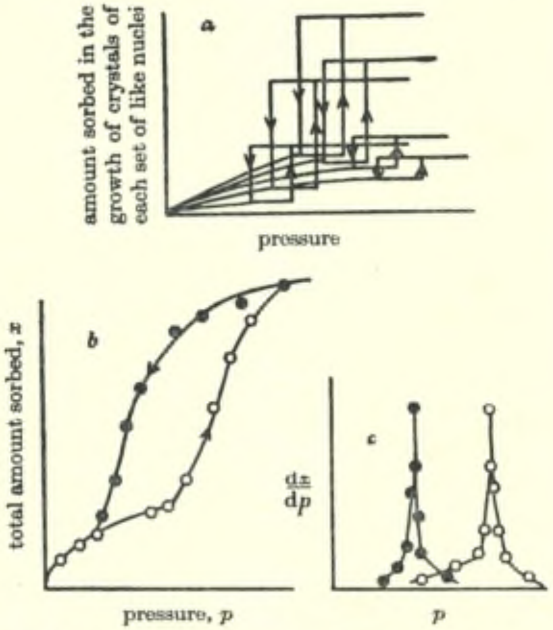


Fig. 20*a*, 20*b* and 20*c*. — The addition of the group of isotherms of 20*a* showing rectangular hysteresis loops gives the resultant isotherms in Fig. 20*b*. Fig. 20*c* then shows the curves of $\frac{dx}{dp}$ against p for sorption and desorption branches (6).

7. Non-stoicheiometric phases giving continuous isotherms

We return now to consider continuous isotherms. The possibility of having non-interacting or only slightly interacting defects, the number of which varies according to the environment of the phase, is realised in a variety of systems. If the empty host lattice is regarded as the parent structure, this lattice with the interstices partially filled with guest molecules or atoms is a defect structure. The equilibrium content of such molecules is normally determined by their concentration in the ambient atmosphere of gas or vapour. Some of these phases are non-stoicheiometric even when all available interstices or cavities are filled, e.g. those formed by occlusion in zeolites, or in certain alkyl ammonium ion exchanged forms of montmorillonite. These host lattices are stable in the complete absence of guest molecules.

In other systems the host lattice tolerates only a limited range of vacant cavities and if the content of guest molecules falls below this limit the host lattice decomposes, or at least becomes metastable ([29]). Examples include the quinol clathrate compounds and the hydrocarbon hydrates. Van der Waals ([41]) has discussed the true equilibrium occlusion isotherm in such systems with particular reference to the clathrate compounds, and has concluded that it should resemble the Langmuir isotherm. While van der Waals has outlined a possible method of measuring occlusion equilibrium within a given quinol clathrate this type of system offers some special experimental difficulties. These arise because the guest molecules are locked into the cavities of the host lattice at the moment of formation and so from then on cannot establish any fresh equilibrium vapour pressure. The only way guest molecules can escape is through the decomposition of the complex.

It may be that the stoicheiometric hydrates such as $CuSO_4.5H_2O$ also tolerate a small number of defects in the form of vacant water positions, and that this defect structure permits diffusion of water molecules. Experiments on such aspects of stoicheiometric hydrates do not appear to have been made. If water can diffuse then these hydrates could be thought of as zeolitic structures in which only a minute range of guest molecule concentrations is possible without nucleation of a new phase.

8. **Formulation of continuous inclusion isotherms**

We may formulate possible isotherms for systems in which the whole course of the isotherm may be realised. From this viewpoint the occlusion of gases and vapours by certain of the robust framework zeolites, such as those described in Section 2, is of most significance, because the frameworks of the host lattices are virtually unchanged by the inclusion process, and because the high intracrystalline mobility of guest molecules enables reversible equilibria to be established readily and measured accurately.

If we regard the crystal framework as inert, and consider the transfer of a mole of gaseous sorbate from the gas phase where its activity is a_g to an infinite amount of the zeolitic solution where its activity is a_z the free energy of transfer is

$$\Delta A = -RT\, ln \frac{(a_e)_z}{(a_e)_g} + RT\, ln \frac{a_z}{a_g} = -RT\, ln\, K + RT \ln \frac{a_z}{a_g} \quad 8.1$$

In this expression $(a_e)_z$, $(a_e)_g$ are respectively the activities of occluded and of gaseous sorbate and K is the equilibrium constant. If $a_z = a_g = 1$, then $\Delta A = \Delta A^0 = -RT\ ln\ K$, where ΔA^0 is the standard free energy of sorption, and $K = \frac{(a_e)_z}{(a_e)_g}$.

In an equilibrium system, $\Delta A = 0$, and so $\mu_g = \mu_z$ where μ denotes the chemical potential. For the gaseous sorbate

$$\frac{\mu_g}{kT} = ln \frac{p}{kT} - ln \frac{(2\pi mkT)^{3/2}}{h^3} - ln\, j(T) \quad 8.2$$

for molecules of mass m at a pressure p. $j(T)$ is the partition function for rotations, vibrations and electronic states of the molecule.

The chemical potential, μ_Z, of the intracrystalline molecules can only be defined if a model for the sorbed state is available. The whole intracrystalline volume V_i may for example be regarded as composed of N_s equal sites each able to accommodate one sorbate molecule, and that the situation corresponds to localised sorption as in Langmuir's isotherm. Then (33-19)

$$\frac{\mu_z}{kT} = ln \left[\frac{\theta}{1-\theta} \cdot \frac{1}{a(T)}\right] \quad 8.3$$

where θ is the fraction of sites occupied and $a(T)$ denotes the partition function for a sorbed molecule including its degrees of freedom relative to its intracrystalline environment. The equilibrium condition then gives

$$\frac{\theta}{p(1-\theta)} = K_1 \ ; \ \Delta A^0 = RT\, ln \frac{p(1-\theta)}{\theta} \quad 8.4$$

where

$$K_1 = kT \frac{(2\pi mkT)^{3/2}}{h^3} \frac{j(T)}{a(T)} \quad 8.5$$

We may test this relation by evaluating $RT\mathit{ln}\,\frac{p(1-\theta)}{\theta} = \Delta A^0$, and plotting this quantity against θ. In this way it was shown (42) that Langmuir's isotherm is only an approximate description of the equilibria between occluded $n-C_4H_{10}$, C_3H_8, C_2H_6 and H_2 in chabazite for $0 < \theta < 0.30$. Isotherms of C_2H_6 and of O_2 in " active analcite " are in better agreement with the above model. The departures from the localised model may be due to the trend in sorption heat, ΔH, with θ, so that all the sites are not homogeneous. Zeolites normally show the most marked change in ΔH with θ when the values of θ are not very great (42–43). We may accordingly re-examine the concept of localised sorption for large values of θ, when the trend in ΔH will be small and when the caging action of the molecules upon one another within the crystal framework further supports the idea of localisation. Table IV (28) gives values of $\frac{p(1-\theta)}{\theta}$ for high densities of *n*-butane occluded by faujasite from which it is apparent that the concept of localised sorption while not quantitatively exact is a reasonable qualitative description of the situation for $0.89 < \theta < 0.98$. We have observed similar qualitative agreement for other paraffins in faujasite in similar high concentration regions.

TABLE IV

Sorption of n-C_4H_{10} in faujasite at 50° C.

θ	$\frac{p(1-\theta)}{\theta}$
0.74	0.21
0.84	0.43
0.87_5	0.59
0.89_4	0.70
0.90_8	0.84
0.91_5	0.92
0.94_3	0.93
0.95_2	1.20
0.97_0	1.06
0.98_4	0.73

At the same time localised sorption may not be true in the strict Langmuir sense of sorption on a constant number of fixed sites.

In faujasite *n*-paraffins and other sorbates behave like liquids near saturation of the sorption volume V_l (28). The number of molecules required to saturate this volume decreases as the molecular volume increases. The coefficient of thermal expansion of sorbed fluid is parallel with this coefficient for the liquid sorbate, and the amounts of a given sorbate required to fill V_l at different temperatures are proportional to the densities of the liquid sorbates at the same temperatures. Attention has already been drawn to the large interstitial volume in faujasite, and to the exceptionally wide cavities ($\sim 16A^0$ free diameter) and the wide interconnecting windows leading from any one cavity to each of four others (Table I). In faujasite, the synthetic zeolite of Table I, and chabazite we have three crystals with decreasing size of cavity and inter-connecting windows. All three crystals however are open enough for the idea of localised sites in the strict Langmuir sense to be less easy to visualise. However this idea becomes physically very definite in the case of the interstitial hydrogen alloys of transition metals.

A development of localised sorption, in which interaction occurs between adjacent pairs of occluded atoms or molecules, has already been referred to (eqs. 5.2 and 5.3). When sorption occurs without dissociation eq. 5.3 takes the form (44)

$$K_2 = \frac{\theta}{p(1 - \theta)} \left(\frac{2 - 2\theta}{\beta + 1 - 2\theta}\right)^Z \qquad 8.6$$

In the cavities found in chabazite three argon atoms may occur (Table I), and so $Z = 2$. The interaction energy $\frac{2w}{Z} \sim -240$ cals per Avogadro number of interactions. Careful measurements of the heat of occlusion are able to demonstrate the reality of such inter-molecular potentials for simple gases in chabazite (Fig. 21). In faujasite and in the synthetic zeolite referred to in Table I, Z will exceed two, and the contribution due to self-potential of the occluded molecules may become greater.

Other models also require careful examination for inclusion within such open structures as the zeolites. In these the occluded molecules are assumed to have translational degrees of freedom. One, two, or possibly, in exceptional structures such as faujasite, even three translational degrees of freedom might be envisaged, with the appropriate molecular co-length, co-area or co-volume

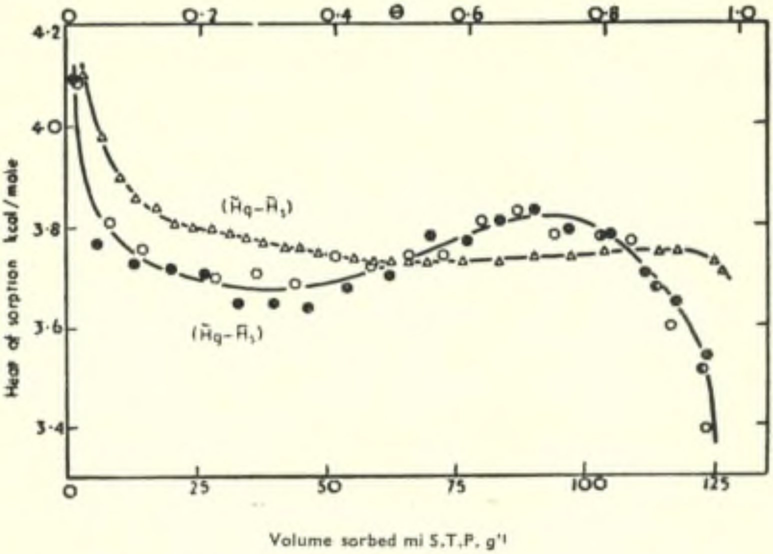


Fig. 21. — Heats of sorption or argon in natural chabazite at 90 °K. Isosteric heat, $q_{st} = \widetilde{H}_g - \overline{H}_s$; run 9, 0; run 9*d*, ●; run 9*b*, ◐; run 9*c*, ◑; integral molar heat, $(\widetilde{H}_g - \widetilde{H}_s)$, Δ. [Garden, Kington and Laing (18)].

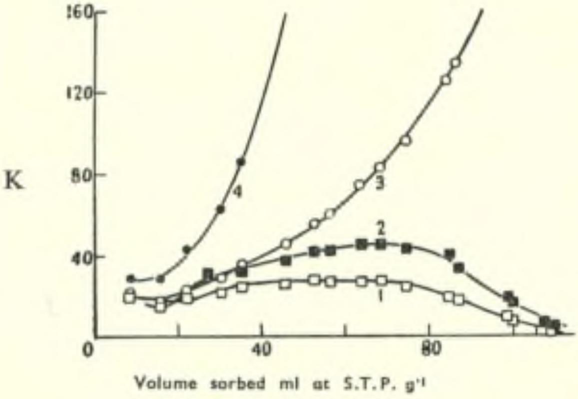


Fig. 22. — Argon in natural chabazite at 90.19 °K. Isotherm constants. Curve 1, mobile model; curve 2, mobile model with interactions; curve 3, localized model; curve 4, localized model with interactions (18).

of the sorbate, corresponding to the Volmer equation of state. The isotherm then takes the form (45)

$$K_3 = \frac{\theta}{p(1 - \theta)} \exp \frac{\theta}{1 - \theta} \qquad 8.7$$

Finally, the interaction potential between sorbate molecules may be allowed for, by using an equation of state for the occluded sorbate which is a one, two or three dimensional analogue of van der Waals equation. In this case (46)

$$K_4 = \frac{\theta}{p(1 - \theta)} \exp \left(\frac{\theta}{1 - \theta} - \alpha\theta\right) \qquad 8.8$$

where α is a constant, and is a measure of the interaction potential.

A careful examination of all these forms of isotherm equation has been made by Kington et al for oxygen, argon and nitrogen at liquid air temperatures (18). They used chabazite as sorbent, outgassed at 300 °C. The test was made by evaluating isotherms extremely carefully, making due correction for thermo-molecular pressures. From the experimental data the equilibrium constants were obtained. Thus for argon, $\frac{2w}{Z} = -240$ cals per Avogadro number of interactions, $Z = 2$, and the saturation sorption was taken as 130 cm^3 at N.T.P. per g. of chabazite. Finally, in the isotherm 8.8 α was taken as 1.0, corresponding approximately only to the above value of $\frac{2w}{Z}$. The values of K_1, K_2, K_3 and K_4 are shown as functions of θ in Fig. 22 (47). Quite clearly equation 8.7 gives easily the best representation over a substantial range in θ, followed by eq. 88. The models corresponding to localised sorption (eqs. 8.4 and 8.6.) give an unsatisfactory description of the occlusion of argon.

The foregoing probe into the state of the occluded guest molecules is a powerful one, which involves, however, the free energy relations of occlusion only. It is not possible on the basis of these relations to distinguish, for example, between the one, two or three translational degrees of freedom implied in the isotherm equations 8.7 and 8.8. A more delicate procedure which permits this requires the evaluation of the entropy of the occluded molecules and the specific interpretation of this in terms of configurational and thermal entropy contributions. This method will be developed subsequently. We may first give specific evaluations of the equilibrium constants K.

9. Specific evaluations of equilibrium constants

The equilibrium constant may be represented, whatever the degrees of freedom possessed by the included molecules, by the expression already given (Section 8, eq. 8.5). We now consider the values which may be taken by the partition function $a(\mathrm{T})$. First the term $\exp - \varkappa/\mathrm{RT}$ may be factorised from $a(\mathrm{T})$, where $\varkappa$ is the least energy required to remove a mole of sorbate from an infinite amount of zeolite + sorbate into the gas phase. Then

$$\mathrm{K} = k\mathrm{T}\,\frac{(2\pi mk\mathrm{T})^{3/2}}{h^3}\,\frac{j(\mathrm{T})}{j_a(\mathrm{T})}\,\exp \varkappa/\mathrm{RT} \qquad 9.1$$

where $j_a(\mathrm{T})$ is the partition function of the occluded molecule, for all its internal degrees of freedom and for its degrees of freedom relative to its intracrystalline environment. One then obtains the results given in Table V (*), assuming that all *internal* degrees of freedom of the guest molecule are unchanged by its inclusion. In Table V, T, V and R denote respectively a translational, a vibrational and a rotational degree of freedom. N'_s, N''_s and N'''_s in column 2 denote respectively the numbers of molecules required to fill completely 1 cm^3, 1 cm^2 or 1 cm of intracrystalline volume, area or length. ν and $\bar{\nu}$ are vibration frequency or mean vibration frequency respectively. I_1, I_2, I_3 denote the three principal moments of inertia of the occluded molecule and δ is its symmetry number.

The values of $\varkappa$ may be related to $\Delta\mathrm{H}$, the isosteric heat of sorption, obtained from the Clapeyron equation

$$\left(\frac{\delta lnp}{\delta \mathrm{T}}\right)_a = \frac{-\Delta\mathrm{H}}{\mathrm{RT}^2} \qquad 9.2$$

where the subscript "a" denotes a constant amount occluded and $-\Delta\mathrm{H}$ is the heat of desorption. We then have for the models (i) to (vii) inclusive of Table V

$$\left.\begin{array}{ll}
\text{(i)} & \Delta\mathrm{H} = -\varkappa - \mathrm{RT} \\
\text{(ii)} & \Delta\mathrm{H} = -\varkappa - {}^1/_2\mathrm{RT} \\
\text{(iii)} & \Delta\mathrm{H} = -\varkappa \\
\text{(iv)} & \Delta\mathrm{H} = -\varkappa + {}^1/_2\mathrm{RT} \\
\text{(v)} & \Delta\mathrm{H} = -\varkappa + \mathrm{RT} \\
\text{(vi)} & \Delta\mathrm{H} = -\varkappa + {}^3/_2\mathrm{RT} \\
\text{(vii)} & \Delta\mathrm{H} = -\varkappa + 2\mathrm{RT}
\end{array}\right\} \qquad 9.3$$

(*) In the expressions in column 2 of this table, if p is expressed in cm of Hg, k in the first term $\frac{1}{k\mathrm{T}}$ appearing throughout has the value 1.03×10^{-20}.

TABLE V

Values of equilibrium constants for different degrees of freedom of sorbate.

Degrees of freedom of occluded molecule relative to its environment	Equilibrium constants, K	Relevant isotherms
(i) 3T, 3R	$\frac{1}{kT}\frac{1}{N'_s}\exp \varkappa/RT$	$K_3 = \frac{\theta}{p(1-\theta)}\exp\frac{\theta}{1-\theta}$ or $K_4 = \frac{\theta}{p(1-\theta)}\exp\left(\frac{\theta}{1-\theta} - a\theta\right)$
(ii) V, 2T, 3R	$\frac{1}{kT}\frac{1}{N''_s}\left(\frac{kT}{2\pi m}\right)^{1/2}\frac{1}{\nu}\exp \varkappa/RT$	
(iii) 2V, T, 3R	$\frac{1}{kT}\cdot\frac{1}{N'''_s}\cdot\frac{kT}{2\pi m}\cdot\frac{1}{\bar{\nu}^2}\exp \varkappa/RT$	
(iv) 3V, 3R	$\frac{1}{kT}\cdot\left(\frac{kT}{2\pi m}\right)^{3/2}\frac{1}{\bar{\nu}^3}\exp \varkappa/RT$	$K_1 = \frac{\theta}{p(1-\theta)}$ or $K_2 = \frac{\theta}{p(1-\theta)}\left(\frac{2-2\theta}{\beta+1-2\theta}\right)^z$
(v) 4V, 2R	$\frac{1}{kT}\cdot\left(\frac{kT}{2\pi m}\right)^{3/2}\frac{1}{\bar{\nu}^4}\left(\frac{kT}{8\pi^3 I_1}\right)^{1/2}.\exp \varkappa/RT$	
(vi) 5V, R	$\frac{1}{kT}\cdot\left(\frac{kT}{2\pi m}\right)^{3/2}\frac{1}{\bar{\nu}^5}\frac{kT}{8\pi^3}\cdot\frac{1}{(I_1 I_2)^{1/2}}\exp \varkappa/RT$	
(vii) 6V	$\frac{1}{kT}\left(\frac{kT}{2\pi m}\right)^{3/2}\frac{1}{\bar{\nu}^6}\left(\frac{kT}{8\pi^2}\right)^{3/2}\frac{1}{(I_1I_2I_3)^{1/2}}\frac{\delta}{\pi^{1/2}}\exp \varkappa/RT$	

Moreover, the standard entropy of sorption ΔS^0 is given by $\Delta S^0 = \frac{\delta}{\delta T}(RT\, ln\, K) = R\, ln\, K + RT \frac{\delta\, ln\, K}{\delta T}$, and therefore for the seven models takes the value

$$\text{(i)}\quad \Delta S^0 = R\, ln \left(\frac{1}{kT} \frac{1}{N'_s}\right) - R$$

$$\text{(ii)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \cdot \frac{1}{N''_s} \cdot \left(\frac{kT}{2\pi m}\right)^{1/2} \cdot \frac{1}{\nu}\right] - 1/2\, R$$

$$\text{(iii)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \cdot \frac{1}{N'''_s} \cdot \frac{kT}{2\pi m} \cdot \frac{1}{\bar{\nu}^2}\right]$$

$$\text{(iv)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{3/2} \frac{1}{\bar{\nu}^3}\right] + 1/2\, R$$

$$\text{(v)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{3/2} \frac{1}{\bar{\nu}^4} \cdot \left(\frac{kT}{8\pi^3 I_1}\right)^{1/2}\right] + R$$

$$\text{(vi)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{3/2} \frac{1}{\bar{\nu}^5} \frac{kT}{8\pi^3} \frac{1}{(I_1 I_2)^{1/2}}\right] + 3/2\, R$$

$$\text{(vii)}\quad \Delta S^0 = R\, ln \left[\frac{1}{kT} \left(\frac{kT}{2\pi m}\right)^{3/2} \frac{1}{\bar{\nu}^6} \left(\frac{kT}{8\pi^2}\right)^{3/2} \frac{1}{(I_1 I_2 I_3)^{1/2}} \frac{\delta}{\sqrt{\pi}}\right] + 2R$$

Contained in the expressions for ΔS^0 is a requirement of a spread of entropy levels which should serve to characterise the (V, T, R) state of the occluded molecules (36). The spread in entropy over the seven models was about 16 e.u. (*) for a molecule of molecular weight 16 with $\nu = 6 \times 10^{12}$ sec^{-1} and I_1, I_2 and I_3 each equal to 10^{-39} c.g.s. units. An alternative method of investigating the degrees of freedom of occluded molecules has been developed by Kington and his co-workers (18) and is outlined below.

10. **Entropies of occluded molecules**

The isosteric heat of sorption, ΔH, may be determined either by direct calorimetry or from the change in equilibrium pressure with temperature $\left(\frac{\delta\, ln\, p}{\delta T}\right)_a = -\frac{\Delta H}{RT^2}$. The isosteric heat of sorption is however given by

$$\Delta H = \overline{H}_s - \widetilde{H}_g \qquad 10.1$$

(*) In the original paper the terms N_s were omitted from (i), (ii) and (iii). This was corrected later.

where $\overline{H}_s$ is the partial molal enthalpy of occluded molecules and $\widetilde{H}_g$ is the integral molal enthalpy of these molecules in the gas phase. From ΔH one may obtain an entropy of occlusion of the guest molecules :

$$\Delta S = \frac{\overline{H}_s - \widetilde{H}_g}{T} = \overline{S}_s - \widetilde{S}_g \qquad 10.2$$

where $\widetilde{S}_g$ and $\overline{S}_s$ are the molal entropy of the guest molecules in the gas phase and their partial molal entropy in the host crystals respectively. $\widetilde{S}_g$ is the entropy at the pressure p. Referred to the entropy $\widetilde{S}_{og}$ at a standard pressure, p^+,

$$\widetilde{S}_g = \widetilde{S}_{og} + R \, ln \, p^+/p \qquad 10.3$$

Accordingly by combining (*) 10.1, 10.2 and 10.3

$$\overline{S}_s = \widetilde{S}_{og} + R \, ln \, p^+/p + \frac{\Delta H}{T} \qquad 10.4$$

The standard pressure, p^+, for a gas is normally taken to be 1 atm.

Fig. 23 shows the partial molal entropy, $\overline{S}_s$, of argon occluded in a natural Ca-rich chabazite at 90.19 °K, as a function of θ. The entropy decreases steadily with increasing θ over a wide range in the values of θ. We now express $\overline{S}_s$ as the sum of two terms :

$$\overline{S}_s = \overline{S}_c + \overline{S}_{Th} \qquad 10.5$$

where $\overline{S}_c$ is the partial molal configurational entropy of the intracrystalline guest molecules which have undergone localised occlusion and $\overline{S}_{Th}$ is their differential thermal entropy. In the case of guest molecules possessing one or two translational degrees of freedom in their intracrystalline environment,

$$\overline{S}_s = {}_1\overline{S}_T + \overline{S}'_{Th} \qquad 10.6$$

and

$$\overline{S}_s = {}_2\overline{S}_T + \overline{S}''_{Th} \qquad 10.7$$

(*) Should correction for non-ideality of the gas be required we subtract a term αp from the above expression for $\overline{S}_s$, where approximately, $\alpha = \frac{27 R \; T_c^3}{32 P_c T^3}$. P_c and T_c are respectively the critical temperature and pressure.

TABLE VI

Isotherm equation	Entropies $\bar{S}_e$, ${}_1\bar{S}_T$, ${}_2\bar{S}_T$
eq. 8.4 : $K_1 = \frac{\theta}{p(1-\theta)}$	$\bar{S}_e = R\, ln \frac{(1-\theta)}{\theta}$
eq. 8.6 : $K_2 = \frac{\theta}{p(1-\theta)} \left(\frac{2-2\theta}{\beta+1-2\theta}\right)^z$	$\bar{S}_e = R\, ln \frac{(1-\theta)}{\theta} \left(\frac{2(1-\theta)}{\beta+1-2\theta}\right)^z + \frac{w}{T} \frac{(\beta-1+2\theta)}{\beta}$
eq. 8.7 : $K_3 = \frac{\theta}{p(1-\theta)} \exp \frac{\theta}{(1-\theta)}$ and eq. 8.8 : $K_4 = \frac{\theta}{p(1-\theta)} \exp \left(\frac{\theta}{1-\theta} - a\theta\right)$	${}_1\bar{S}_T = R\, ln \left[\frac{(2\pi mkT)^{1/2}}{h\, N_s'''} . \frac{(1-\theta)}{\theta}\right] + R \left[1 - \frac{\theta}{1-\theta}\right]$ ${}_2\bar{S}_T = R\, ln \left[\frac{2\pi mkT}{h^2\, N_s''} \frac{(1-\theta)}{\theta}\right] + R \left[1 - \frac{\theta}{1-\theta}\right]$

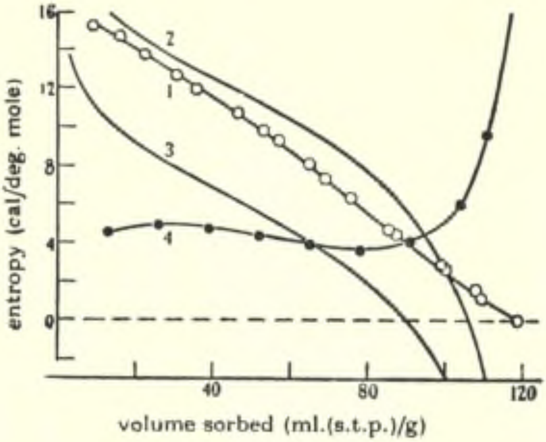


Fig. 23. — Comparison of experimentally observed differential entropy $\overline{S}_s$ of argon in natural chabazite with differential translational entropy of mobile models with one and two degrees of translational freedom. Curve 1, experimental $\overline{S}_s$; curve 2 ,${}_2\overline{S}_T$; curve 3, ${}_1\overline{S}_T$; curve 4, $\overline{S}_s - {}_1\overline{S}_T$ (18).

where ${}_1\overline{S}_T$ and ${}_2\overline{S}_T$ are the differential entropies of molecules possessing one or two translational degrees of freedom respectively, and $\overline{S}'_{Th}$, $\overline{S}''_{Th}$ are the residual differential thermal entropies of these molecules. In Table VI are given $\overline{S}_e$, ${}_1\overline{S}_T$ and ${}_2\overline{S}_T$ relevant to the appropriate isotherms 8.4, 8.6, 8.7 and 8.8. Now the test already carried out in which K_1, K_2, K_3 and K_4 were computed from experimental data and plotted as a function of the amount of argon occluded (Fig. 22) has already shown that isotherm equation 8.7 is the appropriate one. All that is now to be settled is whether the occluded argon atoms possess one or two translational degrees of freedom.

Fig. 23, in addition to the experimentally determined relation between $\overline{S}_s$ and θ (curve 1), also shows ${}_1\overline{S}_T$ and ${}_2\overline{S}_T$ calculated from the formulae in Table VI, as function of θ (respectively curves 3 and 2). If we subtract ${}_1\overline{S}_T$ and ${}_2\overline{S}_T$ from $\overline{S}_s$ we should, according to eqs. 10.6 and 10.7 obtain $\overline{S}'_{Th}$ and $\overline{S}''_{Th}$, the residual differential thermal entropies. These must be *positive quantities*, and in the range in θ for which the sorption model is valid they should be constants *independent of* θ. In fact, when ${}_2\overline{S}_T$ is substracted from $\overline{S}_S$ the difference is a negative quantity so that the occluded argon cannot possess two translational degrees of freedom. On the other hand when

${}_1\overline{S}_T$ is subtracted from $\overline{S}_s$ the difference is a positive quantity and is nearly constant at about 4 e.u. up to about 100 cm^3 at S.T.P./g of occluded argon (curve 4). Argon therefore possesses one translational degree of freedom within the chabazite crystals.

The quantity $\overline{S}_s - {}_1\overline{S}_{Th} = \overline{S}'_{Th}$ is the vibrational entropy of argon relative to its intracrystalline environment. Since the atom possesses one translational degree of freedom, it must have two vibrational degrees of freedom : $\overline{S}'_{Th} = {}_2S_V \sim 4$ e.u. For simple harmonic oscillations and for *each* vibrational degree of freedom

$$ {}_1S_V = R\,[u(e^u - 1)^{-1} - ln(1 - e^{-u})] \qquad 10.8 $$

where $u = \frac{h\,\nu}{kT}$. Up to about $\theta = 0.77$, ν ranges from 1.5 to 2.2×10^{12} sec^{-1}, which are physically reasonable values. The failure of the isotherm equation 8.7 above $\theta = 0.77$ was tentatively ascribed to a transition from mobile to localised sorption, due to caging action of the molecules of the denser intracrystalline argon fluid upon each other, as was also suggested for dense intracrystalline hydrocarbon fluids in faujasite.

In this region of dense intracrystalline fluid, where Langmuir's isotherm has been found to be reasonably valid (Table IV), partial molal entropies of paraffins have been obtained in faujasite ([28]). Table VII records such entropies, at 298°, and for $\theta = 0.90$ or 0.95.

TABLE VII

Some entropies in faujasite at 298° K.

Paraffin	θ	$\overline{S}_s$ (e.u.)	$\overline{S}_{Th}$ (e.u.)	$\widetilde{S}_l$ (e.u.)	$\widetilde{S}_l - \overline{S}_{Th}$ (e.u.)
n-C_4H_{10}	0.9	32.2	38.6	53.9	15.3
iso-C_4H_{10}	0.9	27.6	32.0	51.3	19.3
n-C_5H_{12}	0.95	33.4	39.3	63.5	24.2
iso-C_5H_{12}	0.95	29.7	34.6	63.1	28.5
neo-C_5H_{12}	0.95	31.5	37.4	53.7	16.3
n-C_6H_{14}	0.95	39.1	45.0	70.5	24.5
n-C_7H_{16}	0.95	44.6	50.5	77.9	27.4
iso-C_8H_{18}	0.95	44.5	50.4	79.7	29.3

From the values of $\bar{S}_s$ one may subtract $\bar{S}_c = R\textit{ln}\,\frac{(1-\theta)}{\theta}$, the differential configurational entropy, which is -4.4 and -5.9 e.u. at $\theta = 0.9$ and 0.95 respectively. This gives the thermal entropies of Column 4. In Column 5 are given the molar entropies of the liquid paraffins, and in the last column is recorded $(\tilde{S}_l - \bar{S}_{Th})$, a quantity of particular interest. $\tilde{S}_l = {}_l\tilde{S}_c + {}_l\tilde{S}_{Th}$ where ${}_l\tilde{S}_c$ and ${}_l\tilde{S}_{Th}$ are the molal configurational and thermal entropies of the liquid. According to Slater (48) the value of ${}_l\tilde{S}_c$ should be small (~ 0.33 e.u. in a typical case). Thus the thermal entropy of the liquid exceeds that of the occluded molecules by a substantial amount (*). This indicates that at $\theta = 0.9$ or 0.95 molecular freedom is much restricted. This is reasonable in view of the rigid anionic framework closely surrounding each small cluster of hydrocarbon molecules (cf. next section).

11. **Inclusion of long-chain molecules**

Occlusion of *n*-paraffins up to *n*-heptane has been followed in chabazite (42) and up to *n*-octane in faujasite (28), while it has been noted that a synthetic zeolite occludes tetradecane (49). Very long-chain molecules, through segmental rotation, may assume many configurations in the gas phase which would not be possible in the confinement of the intracrystalline channels and cavities. Accordingly, losses in entropy can be expected in addition to any considered in the previous section. No fully quantitative treatment of the configurational restraints is possible, but the order of magnitude of the entropy changes associated with them may be estimated (36). We assume long flexible chain molecules closely sheathed by intracrystalline channels, and so restricted to stretched out configurations.

We may let

r_{max} = the greatest possible distance between the terminal carbon atoms of the paraffin chain in gas phase or in zeolite.

r_{min} = the smallest possible distance between these atoms in the gas phase.

r_z = the smallest possible distance between these atoms for the molecule in its intracrystalline environment.

(*) In a range of θ values over which Langmuir's isotherm is valid, as is assumed in calculating $\bar{S}_c$ and is demonstrated for n-C_4H_{10} in Table IV, $\bar{S}_{Th}$ is equal to $\tilde{S}_{Th}$.

In general $r_{min} < r_z < r_{max}$. When P (r) denotes the probability of finding a given r, one has the following relations

$$\int_{r_{min}}^{r_{max}} P(r)\,dr = 1$$

$$\Delta S_{con} = R\,ln \left[\frac{\int_{r_z}^{r_{max}} P(r)\,dr}{\int_{r_{min}}^{r_{max}} P(r)\,dr} \right] = R\,ln \int_{r_z}^{r_{max}} P(r)\ \,dr \qquad 11.1$$

where ΔS_{con} denotes the entropy change associated with restrictions in configurations. The values of $P(r)$ within the zeolite will for longer chains differ from $P(r)$ in the gas phase, because for a give r_z some configurations possible in the gas may still be unrealisable in the zeolite. This however will merely increase $-\Delta S_{con}$. Evidently eq. 11.1 will give only a lower limit to the magnitude of $-\Delta S_{con}$.

Values of $P(r)$ for n-hydrocarbons are known for chains with 3-, 4- and 5-links and also approximately for chains with 10-, 20-, 40- and 80-link chains ([50]). The integrations of eq. 11.1 were carried out and the results are given in Fig. 24*a*, where the change in configurational entropy is plotted against $\rho = 100 \dfrac{\text{Actual range in } r}{\text{Maximum range in } r}$ for 3, 4, 5, 10, 20 and 30 link chains. In Fig. 24*b*, the complementary relation between $-\Delta S_{con}$ and chain length is shown for typical values of ρ.

It is seen that $-\Delta S_{con}$ may assume very large values indeed if the value of ρ is small. In particular :

(i) curves of $-\Delta S_{con}$ *vs* ρ cross at $\rho \simeq 20\ \%$ for 3, 4 and 5 link chains;

(ii) as chains grow longer $-\Delta S_{con}$ becomes rapidly greater for smaller values of ρ. When the chain is a long one configurational restraints thus substantially diminish the free energy of occlusion;

(iii) $-\Delta S_{con}$, for given ρ and for longer chains, becomes a nearly linear function of chain length.

According to this approach, in terms of Langmuir's isotherm,

$$\frac{\theta}{p\,(1-\theta)} = \mathrm{K} \int_{r_z}^{r_{\max}} \mathrm{P}(r)\,dr,$$ where K will be given by models such as (vii) or (vi) of Table V. ΔS_{con} will also play a considerable part in determining the free energy of formation of adducts of paraffins with urea or thio-urea where the hydrocarbons are stretched along the axes of spirals formed by hydrogen bonded urea or thio-urea molecules. Amylose chains also form spirals along the axes of which lie included molecules such as iodine, fatty acids, and n-alcohols.

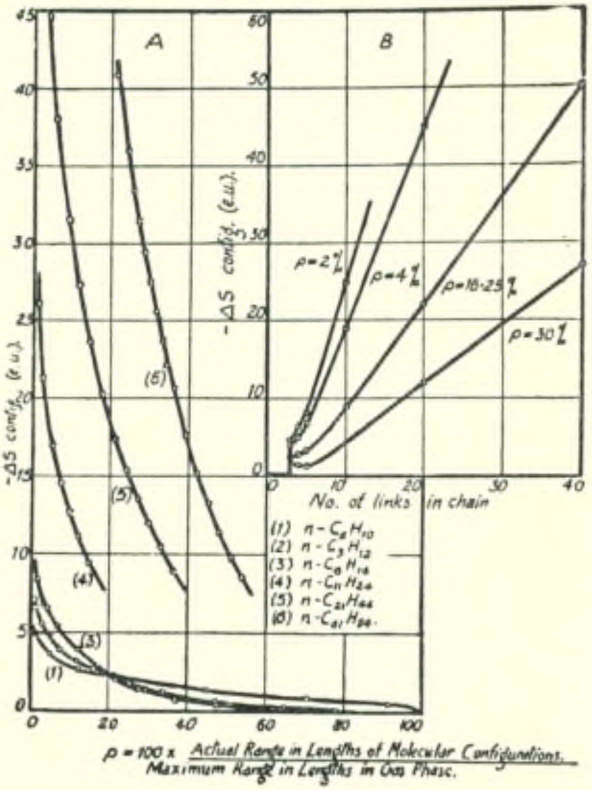


Fig. 24. — Calculated entropy effects for configurational restrictions of long chain molecules, such as might be found in zeolites or in urea-hydrocarbon adducts (36).

12. Concluding remarks

In this review no discussion has, for reasons of space, been given of the energetics of formation of Berthollide compounds of the host lattice-guest molecule type, although some extremely interesting work has been carried out in this direction. Similarly no examination has been made of the bond types formed, although here also considerable understanding has now been reached. Instead attention has been drawn to the generality of the statistical thermodynamic approach in interpreting equilibria between gases and vapours which act as guest molecules within host lattices. Our investigation of specific isotherm models indicates that even for continuous inclusion isotherms one physical model is not normally able to describe the entire course from $0 < \theta < 1$. Host crystals range from those which can accommodate only one atom per cavity (H_2 — Pd, Zr, Ti), those providing isolated cavities capable of containing one sizeable molecule (quinol clathrate compounds), and those which provide long cylindrical channels (urea adducts) to those in which big cages are interconnected by wide windows to give an intersecting network of channels (some zeolites). Individual cages may in the extreme case of faujasite be able to contain 32 water, 18 argon or 2.8 iso-octane molecules, and so become of remarkable dimensions. In interpreting some of the properties of the guest molecules in their intracrystalline environment there is great advantage in the measurement and interpretation of the entropy function for these molecules. This approach has accordingly been particularly developed with a view to demonstrating its potentialities.

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Discussion

M. Hedvall. — Je crois qu'il est nécessaire de définir plus exactement la notion stœchiométrie. Nous en avons — pour ainsi dire — deux conceptions : la forme classique basée seulement sur les facteurs analytiques et d'affinité dans les composés hétérogènes; la forme plus moderne où les structures des solides sont d'une importance fondamentale.

M. Barrer. — In the gaseous state stoicheiometry in the classical sense is appropriate : when atoms combine they do so in simple proportions by numbers. Perhaps this idea is at its best with the electron pair bond. Even for covalent species however, when two species are both present as complexes in the solid state, Dr. Powell's report draws attention to circumstances when compositions determined analytically may deviate from simple stoicheiometric ratios between the associated species.

In ionic lattices the idea of stoicheiometric proportions (eq Na : Cl = 1 : 1 in rock salt) may still have its uses, provided it is realised that in general departures from stoicheiometry may be encountered (even in NaCl). On the other hand, in the equilibrium state, departures from electrical neutrality throughout the crystal are not found, however gross the stoicheiometric defect. Equally, a stoicheiometric proportion between atoms does not always mean absence of lattice defects. It is believed for example that δ TiO (of NaCl structure) has 15 % vacancies, both anion and cation sites, at the stoicheiometric composition.

On the whole, I think the concept of electrical neutrality should replace the old idea of stoicheiometry in ionic crystals.

M. Powell. — My remarks on the word « stoicheiometric » were made in relation only to « organic non-stoicheiometric compounds » which at first seems not a rational term.

They do not seem relevant to the present question.

M. Defay. — J'ai été vivement intéressé, dans la communication du professeur Barrer, par le rôle joué par les surfaces intérieures du « host-lattice ».

Je voudrais poser deux questions à ce sujet :

Première question. — Les isothermes d'équilibre d'occlusion ou d'inclusion d'un gaz dans un solide sont à tous les points de vue si semblables à des isothermes d'adsorption que leur allure ne semble pas permettre de distinguer ces deux phénomènes. Je suppose qu'il serait possible de les distinguer en vérifiant si la quantité de gaz fixée par le solide est indépendante de la surface externe du solide et donc de son degré de pulvérisation.

Est-ce ainsi que l'on procède ou bien existe-t-il un autre mode de discrimination?

Seconde question. — L'explication du phénomène d'hystérèse par le retard de nucléation me paraît parfaitement valable. Il existe cependant dans les phénomènes d'adsorption des vapeurs par les corps poreux, une autre explication qui est également satisfaisante : c'est celle de la condensation capillaire dans des pores ayant un orifice étranglé. Dans ce cas, comme l'a suggéré Kraemer, si l'on considère un pore en forme de bouteille, l'hystérèse est due à ce que pendant la phase de sorption, la condensation commence dans la partie large de la bouteille, tandis que pendant la phase de désorption, la vaporisation doit commencer par le goulot de la bouteille.

Je voudrais demander au professeur Barrer s'il existe un moyen expérimental de savoir si l'on a affaire, soit à un phénomène de nucléation, soit à un phénomène de condensation capillaire.

M. Barrer. — In answer to professeur Defay's first question, I would say that it is in general not easy to distinguish between sorption on external surfaces and sorption within a substance. However, no difficulty presents itself in the case of the zeolitic crystals used by me. These are well crystallised, of $\sim 10^{-2}$ mm or even larger diameter as grown by hydrothermal technics, or as ground from natural crystals. They give excellent X-ray powder photographs. The estimated external surfaces (measured in some cases by the permeability method of Kozeny-Carman) are of the order of 1 m^2/g. The equivalent of the intra-crystalline sorption, when expressed as the monolayer value, v_m, of the Brunauer Emmelt Teller treatment may range from ca. 500 to ca. 1 000 m^2/g for different crystals. Accordingly in these cases virtually all the « surface » is intracrystalline. The amount of sorbed gas is indeed independent of the size of particules provided grinding is not carried to such an extent as to increase external surface beyond a few percent of the « internal surface ».

As regards the second question, it is perfectly possible to explain hysteresis in terms of capillary condensation in capillaries of suitable shape, as shown by Cohan, and by MacBain and Kraemer. For capillary condensation of liquids, I do not think one need postulate difficulties of nucleation as a cause of hysteresis, because an adsorbed monolayer, or a multilayer, film precedes formation of the more bulky capillary condensate, and the process may be thought to proceed smoothly through mono and multi-layer sorption stages.

In solids it is easy to demonstrate nucleation and growth of a new phase by X-ray or optical technics, but for liquid condensates in capillary systems, the use of such methods is not likely to help.

M. Ubbelohde. — The extreme cases of capillary condensation of a liquid and sorption of a gas can be clearly distinguished provided the range of molecular forces is short compared with the diameter of the « capillaries ». This question may be easy to satisfy in the case of molecular forces of short range such as the ordinary van der Waals interactions. There are however forces of longer range, for example between polynuclear aromatic molecules where the van der Waals interactions fall off less steeply than the sixth power, or in ionic fluids.

The range of effective forces between the walls of the capillary and the molecules may also extend beyond one molecular layer and may likewise become comparable with the capillary diameter.

In such cases, the concept of a liquid must be used with care. Any surface tension effective in capillaries can be very different from the surface tension of the bulk liquid.

M. Barrer. — Molecular forces may indeed be of considerable range. The dispersion or London energy of interaction falls off for a molecule interaction with a solid plane surface, according to the inverse cube of the distance from the molecule to the surface (this is seen by integrating, throughout the volume of the substrate, the expression for the interaction energy between an isolated surface atom and the molecule). I always regard the molecules occluded within the crystals of even the most open structure zeolites such as fanjasite as being subject to a powerful interaction with their environment. Clusters of molecules within a cage are then under the influence not only of this interaction, but also of the self-potential which they develop by interacting with each other. Such clusters may then be subject to interactions different in magnitude from those which a similar cluster would undergo in the interior of its own liquid. Also one must not forget the intracrystalline calories and framework charges. I tend to regard the zeolitic water as being in a state in some measure akin to that which would characterise water in a concentrated electrolyte solution, although of course there will also be very significant differences.

M. Kuhn. — How far are the hysteresis effects a phenomenon which is due to the limitation of time which the system is allowed to take for reaching equilibrium?

From the point of view of thermodynamics one might expect that the amount of material adsorbed or condensed at the surface will, if the vapour pressure is given, be entirely definite. No hysteresis would then occur provided the system is given enough time to reach equilibrium.

M. Barrer. — Hysteresis both in sorption processes and in processes involving nucleation of new species on or in a matrix of a parent phase may be entirely reproducible and independent of time (provided an adequate interval is allowed per point). This is fully understandable in terms of current treatments of hysteresis based for example upon domain theory. Very recent treatments of this type are contained in the papers of Everett and of Enderky published in the *Faraday Society Transactions*. An example of time-independent sorption hysteresis is provided by argon sorbed by « Nycer » porous glass (Barrer and Barrie, *Proc. Roy. Soc.*, 1952); an example of time-independent hysteresis involving nucleation of a new phase is provided by the formation and dissociation of the benzene-potassium benzene sulphonate complex (Barrer, Drake and Whittam, *Proc. Roy. Soc.*, 1953, A 219,32).

In other cases, points determined on the hysteresis loop may be independent of time, but the shape of the loop may depend upon the previous history of the sample, e.g. the number of hysteresis cycles around which the system has been taken. This may mean change in the relative number of nuclei for which A and B in my eq. 6.2 have one pair of values as compared with the number for which A and B have another pair of values. This is reflected in a change of the sizes of the component rectangular loops of figure 20*a*, and hence in a change in the shape of the resultant loop of my figure 20 *b*. This change in emphasis can arise if the parent crystallites progressively break up, as a result of the strains of nucleation, when the system is taken round successive hysteresis cycles. The proportion of edges to surfaces may then change, and nucleation of course is not likely to occur equally easily, at all crystallographic sites. This is one physical reason for a range of values of A and B (of fig. 20 *a*). This type of behaviour was observed in the p-dioxane-potassium benzene sulphonate system (Barrer, Drake and Whittam, *loc. cit.*).

Finally however we come to time-dependent hysteresis effects, such as professor Kuhn refers to. These arise for example in the sorption of penetrants in polymers, if the polymer possesses considerable internal stiffness and viscosity. These effects, in which the hysteresis loop in a sorption-desorption cycle depends upon the time scale of the experiments, we ascribe to slow visco-elastic relaxations within the polymer which modify its sorptive properties slowly.

The visco-elastic processes are set up by sorption of penetrant and swelling of polymer or by desorption and deswelling. Examples include the sorption of methanol, acetone or benzene by cellulose ether (Barrer and Barrie, in press).

M. Bénard. — 1. M. Barrer a attiré notre attention sur la distinction à faire entre le « host lattice » et les « guest molecules ». Cette distinction est parfaitement claire dans le cas des systèmes qu'il a étudiés personnellement, parce qu'il existe dans ces systèmes, une différence fondamentale entre le type de liaison qui assure la stabilité du réseau fondamental, et celui qui fixe les molécules étrangères dans ses intervalles. Mais il est bon de remarquer que dans bien des cas la distinction est beaucoup plus difficile à faire; en particulier, on peut assister dans certaines séries d'hydrates à un accroissement des forces de liaison entre le réseau et les molécules d'eau. A ce moment les possibilités d'écarts à la stœchiométrie diminuent et on arrive aux hydrates définis, dans lesquels le nombre des molécules d'eau qui peuvent être acceptées par le réseau est invariable. Comme corollaire, on constate que dans ces cas, il n'existe plus à proprement parler de « host lattice », puisque le type de structure caractéristique de l'hydrate ne peut exister lorsque l'eau a été éliminée.

2. Les tentatives de Lacher, d'Anderson et de Rees, pour retrouver par la thermodynamique statistique les résultats expérimentaux que l'on possède sur l'étendue des domaines monophasés et diphasés dans les systèmes non stœchiométriques sont extrêmement intéressantes car elles constituent les premieres tentatives effectuées pour obtenir des données quantitatives sur ce problème. Je pense cependant qu'à l'heure actuelle, il est impossible d'affirmer qu'il existe un accord satisfaisant entre la théorie et l'expérience, car les exemples cités (zirconium-hydrogène et soufre-platine) sont encore trop mal connus. Je pense par contre qu'il serait intéressant de suivre dès maintenant, une démarche inverse et d'utiliser certains résultats expérimentaux relatifs à des systèmes aujourd'hui bien connus, pour déterminer à l'aide de ces théories, les valeurs des énergies d'interaction des défauts.

M. Barrer. — The concept of host lattice and guest molecules is not to be used in all cases of association between a solid and a volatile component. Pr. Bénard refers to the so-called « stoicheiometric hydrates » eg. $CuSO_4.5\,H_2O$, $NiSO_4.7\,H_2O$. One could only speak of a $CuSO_4$ host lattice in such a system if the water-content were not in fact invariable. If, for example a definite small amount of water could be withdrawn without nucleation of a new phase, then vacant water positions would appear, and the idea of a host lattice could be acceptable. Whether there is a small non-stoicheiometric range of compositions of such crystallohydrates is not yet known, though we have some experiments in progress designed to test this point.

As regards Pr. Bénard's comment on the application of statistical mechanics to some stepwise isotherms (eg. H_2 — Pd below the critical temperature) I would be surprised indeed if anything approaching perfection in the treatments were yet achieved. The models used are the simplest possible ones, and their approximations, introduced for the purpose of retaining this simplicity, are well known to the authors and to others of us who have been interested in these problems. The degree of success achieved, combined with the simplicity, is indeed most encouraging provided one does not press the treatments too far in the quantitative sense. This proviso applies to Pr. Bénard's suggestion of using the theories in the converse sense to calculate defect interactions, though one should note that such calculations have been made.

M. Hedvall. — I am very glad to hear that Professor Barrer has so clearly pointed out the importance of the influence of all sorts of imperfections and surface properties, for the reactivity.

I have been all my life working in close contact with chemical industries and also from their view points, it is rather pressing, — for instance in powder metallurgy, powder ceramics and catalytically working factories — to know much more about these factors.

* * *

Professor Backer asked me to tell the history of the Aristotelian dogma *corpora non agunt nisi liquida.*

I was telling Professor Backer yesterday that the start of my work in this field was that I — still at that time, fifty years ago, a schoolboy — never believed in this dogma. One did not know very much about the build of crystals at that time, however it was possible to say that vibrations only did not imply any sort of transport, which of course is necessary for all reactions.

But if one could trap a solid and combine it with another solid reactant just *during* a transition state it might be possible to get real powder reactions. That was true and the systematical work started on this line. Before that, some testing experiments were carried out by Spring in this country.

Coming back to Professor Backer's question, a good friend of mine, Professor Düring of Göteborg, finally found what Aristoteles had said — of course he did not speak latin.

When lecturing once at the university of Athen, I told my Greek colleagues that the right form of the dogma was : « Ta hygra meikta malista ton somaton » i.e. in modern chemical language : It is *in the first line the fluid substances that can react*, a form which is much milder than the latin one.

It was the first time my Greek colleagues heard the original form!

M. Chatt. — If I may refer back to the first part of Professor Bénard's question regarding the stoicheiometry of hydrated aluminium sulphate, some twelve years ago Professor H. Bassett told me that in his study of the system SO_3 — Al_2O_3 — H_2O he found that in all his samples of hydrated aluminium sulphate, there was a slight deficiency of $SO_4^{=}$.

This was true even when crystallisation took place from strongly acid solutions. He also analysed a large number of samples of naturally occuring aluminium sulphate and found a similar deficiency of $SO_4^{=}$. He never found the exact stoicheiometric ratio of Al_2O_3 to SO_3.

M. Barrer. — This is an interesting observation, which suggests that there is incipient hydrolysis in the solid, to give some basic salt. Presumably, there is a concomitant requirement of some defect structure in the lattice. It would, in connection with Pr. Bénard's remark and my reply to it, be interesting to know whether there were also non-stoicheiometric proportions of molecular water in the crystal. One difficulty in establishing such non-stoicheiometric proportions for water would be that water might be adsorbed as well as incorporated within the crystal lattice. However, since large crystals are no doubt readily grown, the external surface could be reduced to a negligible value as far as adsorption of water is concerned.

M. Ubbelohde. — Are there any exact measurements on the proportion of defect sites that can be formed by removal of water from salt hydrates?

The formation of such defects can hardly require large energies and the usual calculations of independent lattice defects indicate that a considerable variation in the proportion of « water holes » should be attainable without collapse of the hydrate structure.

We have started to look for shrinkages of the lattice without collapse by precision X-ray measurements in certain organic acid hydrates, but have found it difficult so far to maintain equilibrium concentrations of water molecules in the crystal lattice.

M. Barrer. — No previous measurements are known to me. However we are attempting to investigate the possible occurrence of « water holes » in so-called stoicheiometric hydrates. The deuterated crystals, e. g. $CuSO_4.5\ D_2O$, are suspended by a silica spring in a light water vapour atmosphere, constantly renewed, and the attempt is being made to measure exchange and diffusion of H_2O and D_2O by weighing the crystal strength by the extension of the calibrated spring. The first runs, conducted at room temperature, have so far not shown interchange. At the same time this does not disproove the existence of « water holes » whose mobility may be very small at room temperature. These experiments will be suitably extended.

M. Kuhn. — The diffusion in ionic crystals is, according to the concepts of Schottky, Frenkel and others, mostly considered to be due to imperfections of the crystal lattice, i.e. either to particles placed in interstitial positions or to holes in the crystal lattice. It seems that in some instances at least, the diffusion might as well be ascribed to an exchange reaction between neighbouring molecules or atoms in the *normal* crystal lattice. This last conception seems especially to be an appropriate description in the case of the diffusion of ice, i.e. of ^{18}O and of D in ice. We have together with M. Thürkauf (1) recently determined the diffusion coefficient at about — 1° C. The diffusion coefficient was found to be about 10^{-10} cm^2 sec.$^{-1}$, i.e. about 10^{-5} times the diffusion coefficient in liquid water.

It is possible from this value of the diffusion coefficient to calculate the mean time t, needed for neighbouring molecules to exchange. It is thus found, that $t = 5.10^{-6}$ sec.; this means that a given water molecule in ice is changing position with one of its neighbours 2.10^5 times during one second.

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(1) Diss. Basel 1956.

It seems that in a case like this, the ability to diffuse might be described as a *normal property* of the *normal* constituents of the crystal lattice and not so much as a property of well defined defects of long life in the crystal lattice. There is certainly a continuous transition between the two modes of description. They coincide if the life-time of the crystal deficiencies assumed in the Schottky-Frenkel theory becomes of the order of magnitude of the mean time needed by one exchange reaction.

The concept of the crystal deficiency theory will therefore only be essentially different from the concept of direct exchange reaction in those cases where there is a definite reason to believe that the life-time of a crystal deficiency is of an order of magnitude longer than the mean time required for an exchange of neighbouring molecules.

M. Barrer. — In some crystals there is convincing evidence of defects of definite kinds and of long life, and their mobility can be measured or estimated. The processes of diffusion may then logically be ascribed to this mobility. In other media, the diffusion mechanisms have not been so clearly established. In metals for example while the bulk of the evidence points to vacancy diffusion, other possibilities have not been rigourously excluded, for example the ring mechanism of Zener :

The atoms 1, 2, 3 and 4 in the above diagram can move in unison in the directions of the arrows to give place changes with the minimum of disturbance of the surrounding lattice.

The direct interchange of atoms 5 and 6 as indicated would create a greater disturbance in the lattice. As I have said, much thought and experiment has been devoted to deciding between vacancy and other mechanisms in metals and the body of the evidence favours vacancy diffusion.

When we come to diffusion of liquids in one another, or diffusion of molecules dissolved in rubber, then I believe the place exchange mechanism comes into its own. Such structures are much looser and more irregular than are crystals and opportunities for interchange of molecules must be frequent. Incidently, for small clearing forces, I would expect a close correlation of molecular events resulting in unit acts of viscous flow and those resulting in unit acts of self diffusion.

M. Lindner. — I wonder if Professor Barrer would tell us something about the kinetics of the processes discussed by him. If the diffusion of the gas would need a sufficient activation energy, one might obtain information concerning an eventual real lattice diffusion of the gas atoms within the solid, as sometimes postulated in connection with the « emanation » technique; but obviously structures of that kind have not been investigated by Professor Barrer.

M. Barrer. — We have studied the diffusion of gases such as H_2, Ne, A, N_2, O_2 and other species into lattices of the zeolites, levynite, mordenite, sodium and calcium rich chabazites, and some synthetic zeolites. We have in some cases measured diffusion coefficients, and found these to depend, in a straight forward way, upon the cross-sections of the diffusing molecules, which have to squeeze through « windows », or restrictions, in the channel system. Energy barriers of several K cals up to 10 to 12 K cals were encountered in such diffusions.

Moreover the diffusions were sensitive in what was quite often a complex way to the number and dimensions of the cations distributed through the aluminosilicate frameworks. One must suppose that sometimes cations are placed like sentinels before the « windows » leading from one cage to another in what are otherwise very open structures indeed; that when so placed, they can block these windows and slow down diffusion or prevent it altogether. Ca-rich chabazites behave as though there were no sentinels or only a few, guarding the way through windows, while Na-rich chabazite behaves as a guarded structure. One then finds a virtually free diffusion of O_2, N_2, A, C_2H_6, etc., into Ca-rich chabazite, but a very much more restricted access into the lattice of Na-rich chabazite.

M. Ubbelohde. — The case of diffusion in ice referred to by Professor Kuhn is of very considerable interest, since it is possible to measure separately the proton or deuteron diffusion mechanism, and the diffusion of the molecule containing the oxygen atom. Are the two rates different?

I would also like to ask whether proton defect sites can be deliberately included by freezing acide molecules such as HCl into the lattice as it has been reported on the basis of experiments (in Germany)?

We have carried out ion migration experiments in various hydrated organic acids containing hydrogen bonds, with the object of correlating migration kinetics with the presence of short hydrogen bonds in the crystals. The results show a general correlation between cooperative systems of hydrogen bonds, and ease of migration, though it is too early to establish detailed conclusions.

M. Kuhn. — The question whether the mobility of D and that of ^{18}O in ice would be identical or not was given particular care.

It was not sure at all whether a difference should be expected or not. The question could be solved without ambiguity from the concentration differences chosen and from the transport of the different kinds of atoms determined by the mass spectrometer after the diffusion had taken place.

It was found that the diffusion coefficient was the same for D and for ^{18}O within the limit of accuracy of the experiment, say about 10 %. This means that the diffusion in ice is occurring by an exchange of water molecules and not, or nearly not, by an exchange of H and D through hydrogen bridges and not essentially by transport of ions.

M. Lindner. — I should like to ask a question concerning the experimental details of your procedure for measuring the self-diffusion of hydrogen and oxygen in ice.

I assume the time function is established and I may suggest a simultaneous measurement of (ionic) conductivity for further elucidation of the transport process. A direct place exchange of water molecules looks not too probable at first sight (as remarked already by Professor Barrer).

M. Kuhn. — In order to measure the self diffusion of ^{18}O and D in ice, we have prepared ice cylinders differing in their contents of $H_2\,^{16}O$, $H_2\,^{18}O$ and OH_2, OHD.

They were brought into contact with each other, either directly or with an air gap of about 10^{-2} cm. A calculation shows that an air gap of said magnitude is, as far as the resistance to migration of H_2O, etc., is concerned, equivalent to less than 10^{-4} mm of ice. Furthermore the results obtained in the case of direct contact and by the air gap method coincided. The cylinders were separated after being in contact with each other for 20, 30 days and then analysed with respect to H, D, ^{16}O and ^{18}O in a mass spectrometer.

As a result of these experiments it was found that the diffusion coefficients of ^{18}O and D coincided within the limits of the experimental error of a few percent. This indicates that the diffusion in ice is taking place by migration of water molecules, and not or not essentially by a migration of hydrogen ions.

M. Ubbelohde. — Has Dr. Linder observed actual examples of migration in molecular crystals?

M. Lindner. — We did not state a transport of molecules in a molecular lattice, but rather got evidence that in some cases of solid state reactions involving ionic compounds of higher orders as e.g. silicates, both ions of one component as e.g. $Pb^{2+} + O^{2-}$ are transported in the same direction, which nowadays is considered being an ionic transport rather than a molecular one.

M. Timmermans. — Je voudrais faire une remarque élémentaire sur les conflits de la stœchiométrie classique et sa forme contemporaine.

C'est que nos idées classiques sur la nature chimique intime des substances résultent surtout de l'étude des gaz et ne doivent pas nécessairement s'appliquer en tout cas aux solides; elles ne sont strictement valables que dans le domaine pour lequel elles sont vérifiées et dans les limites de la précision des expériences à différentes époques.

Les vues antinomiques de Proust et de Berthollet, qui ont si longtemps paru exclusives l'une de l'autre, tendent à faire place aujourd'hui, comme si souvent dans l'histoire des sciences, à une synthèse plus générale où chacune d'elles trouve sa place comme un aspect particulier des mêmes phénomènes; pour beaucoup d'entre nous, il faut faire un grand effort d'imagination pour s'adapter à ces théories nouvelles et c'est là ce qui fait notamment l'intérêt des discussions d'aujourd'hui.

Composés d'insertion des métaux de transition

par **Jacques BÉNARD**

LA NOTION DE COMPOSÉ D'INSERTION ET LA CONCEPTION DE HÄGG

Le terme *composé d'insertion* a été fréquemment utilisé pour désigner des catégories de composés très diverses : hydrures, carbures, zéolithes, clathrates, hydrates de gaz, etc. Le caractère commun généralement attribué à ces corps est la parenté de leur structure cristalline par rapport à un édifice primitif plus simple d'où ils semblent pouvoir se déduire par l'introduction d'atomes ou de groupes d'atomes dans certains vides de dimensions appréciables.

Nous nous bornerons à étudier ici les composés d'insertion pour lesquels l'édifice primitif est celui d'un métal de transition, c'est-à-dire possédant une sous-couche électronique *d* incomplète, et les particules insérées sont soit l'hydrogène, soit un élément électronégatif de la première période brève du tableau périodique : bore, carbone, azote, et éventuellement oxygène. Cette délimitation qui peut paraître à première vue arbitraire trouve sa justification dans le fait que la plupart des composés ainsi obtenus possèdent une physionomie particulière, non seulement du point de vue de la structure cristallographique mais encore du point de vue des propriétés physiques. Bon nombre de carbures, borures et nitrures des métaux de transition possèdent en effet, une conductibilité électrique de caractère métallique élevée, associée à une dureté et à une infusibilité exceptionnelles. Ces propriétés dont l'intérêt technique est considérable ont fait l'objet de nombreuses recherches qui trouvent leur origine dans l'œuvre magistrale élaborée il y a plus d'un demi siècle par Moissan et ses collaborateurs. Quant aux phases résultant de l'insertion d'atomes d'hydrogène dans un réseau métallique, bien que leurs propriétés physiques paraissent assez différentes de celles des composés précédents, leur étude est instructive car elle permet de mieux comprendre par comparaison, ce qui donne à ces derniers leur physionomie particulière.

Il ne saurait être question de décrire dans le présent rapport toutes les phases qui rentrent dans le cadre que nous venons de fixer. Cette description a d'ailleurs été faite au moins partiellement dans des monographies récentes auxquelles on pourra utilement se reporter ([1, 2, 3, 4, 5, 6]). Nous nous proposons plutôt d'examiner quelles sont, à la lumière des recherches accomplies au cours de ces dernières années, les réponses qui peuvent être données à un certain nombre de questions générales concernant la constitution et les propriétés de ces phases, et en particulier les suivantes :

1° Existe-t-il comme pourrait le laisser penser ce terme, une parenté étroite entre la structure des composés interstitiels et celle du métal d'où ils dérivent?

2° L'ensemble des propriétés physiques des composés interstitiels est-il suffisamment caractéristique pour qu'il soit possible de leur attribuer un mode de liaison particulier?

3° La variation de composition en phase homogène est-elle un caractère général des composés interstitiels?

Le problème de la constitution des composés interstitiels des métaux de transition a été abordé dans son ensemble, il y a plus de vingt ans, par Hägg ([7]). Si des modes d'interprétation nouveaux ont été introduits depuis quelques années, il n'en reste pas moins que les idées de cet auteur peuvent constituer encore maintenant un bon point de départ pour l'étude de ces composés .

L'étude de nombreux hydrures, nitrures et carbures des métaux de transition au moyen des rayons X, semble montrer d'après Hägg que la structure des composés interstitiels dépend avant tout du rapport du rayon atomique de l'élément léger à celui du métal. Si le rapport $R = \dfrac{r \text{ élément léger}}{r \text{ métal}}$ est inférieur à 0,59 la structure est généralement *simple* avec disposition compacte des atomes métalliques (cubique à faces centrées ou hexagonale compacte, plus rarement cubique centré) et répartition des atomes de l'élément léger dans les interstices laissés libres entre les atomes métalliques. Lorsque le rapport R dépasse la valeur critique 0,59 les composés formés possèdent des structures *complexes*. Tels sont les carbures de chrome, manganèse, fer, cobalt, nickel et la plupart des borures. A vrai dire, la signification générale de cette règle est singulièrement amoindrie si l'on remarque que le passage du rapport critique ne peut être observé que pour les carbures, tous les hydrures, oxydes et nitrures conduisant à des rapports inférieurs à 0,59. Le cas des borures doit être mis à part, car il est apparu postérieurement aux premiers travaux de Hägg que la structure de ces composés était plus complexe qu'il n'était prévu initialement (8) et ne pouvait par conséquent être incluse sans aménagements dans une systématique qui a pour objet de couvrir l'ensemble des composés interstitiels des métaux de transition.

Outre cette limite supérieure, essentiellement empirique du rapport R, au-delà de laquelle les structures *simples* ne sont plus observées, Hägg fut amené à postuler l'existence d'une limite inférieure au-dessous de laquelle ces structures deviennent également instables. L'instabilité apparaîtrait lorsque l'atome inséré possède des dimensions insuffisantes pour entrer simultanément en contact avec tous les atomes métalliques entourant une position interstitielle. La vérification du bien-fondé de cette dernière conclusion ne peut être tentée que dans le cas des hydrures et pour certains oxydes interstitiels, qui seuls conduisent à des rapports inférieurs à cette seconde valeur critique.

Nous examinerons maintenant comment se situent les données expérimentales actuellement à notre disposition par rapport à cette conception.

CARACTERES GÉNÉRAUX DES HYDRURES DES MÉTAUX DE TRANSITION

Au voisinage de la température ordinaire il existe dans un certain nombre de systèmes métal-hydrogène :

1° Une phase possédant la structure du métal pur et qui a été fréquemment considérée comme une solution solide d'hydrogène dans le métal (phase α) ;

2° Une ou plusieurs phases correspondant à des teneurs en hydrogène supérieures et dont les structures sont généralement différentes de celles du métal pur.

Les phases contiguës peuvent coexister deux à deux en équilibre à une température et sous une pression donnée, en formant des systèmes invariants à température donnée qui se signalent par des paliers sur les isothermes d'absorption. Les limites des domaines d'existence de ces phases, signalées par les extrémités de ces paliers, varient en fonction de la température et de la pression. Il en résulte que de façon générale, il est illusoire d'attribuer, comme on l'a fait trop souvent, une signification particulière à la concentration limite observée pour une phase donnée, dans des conditions de température et de pression particulières. Seules présentent dans une certaine mesure une signification les concentrations caractéristiques vers lesquelles tendent parfois les limites des phases lorsque les variables physiques se modifient d'une façon continue. Il s'en faut de beaucoup, cependant, qu'une telle tendance se manifeste d'une manière nette dans tous les cas.

Parmi les valeurs particulières de la concentration en hydrogène qui répondent à ce critère, la mieux marquée paraît être celle qui correspond aux compositions TiH_2, ZrH_2, HfH_2, vers lesquelles tend la phase solide lorsqu'on accroît la pression de l'hydrogène au-dessus du titane ([10, 11]), du zirconium ([12, 13]), ou du hafnium ([14]). Les phases correspondantes se présentent donc, non comme des composés définis mais comme des limites supérieures de domaines homogènes. Les phases limites TiH et Pd_2H apparaissent également dans les diagrammes titane-hydrogène ([11]) et palladium-hydrogène ([15, 16, 17]). Enfin une limite extrêmement bien marquée est celle qui correspond à la formule UH_3 dans le système uranium-hydrogène ([18, 19]).

Dans plusieurs systèmes l'étendue des domaines diphasés observés à la température ordinaire se rétrécit au point de disparaître lorsque la température et la pression d'hydrogène s'accroissent simultanément. On peut de cette façon réaliser aux pressions et températures élevées, des variations importantes de concentration en phase homogène dans les systèmes palladium-hydrogène, titane-hydrogène, zirconium-hydrogène. La fig. 1 indique à titre d'exemple la forme des isothermes d'absorption dans le système palladium-hydrogène, d'après Gillespie et Hall, qui montre la réunion progressive des domaines α et β; la fig. 2 montre, d'après McQuillan, ce même phénomène pour les phases α et β du système titane-hydrogène. On notera, par contre, que la phase γ de ce dernier système reste distincte dans tout le domaine de température et de pression exploré.

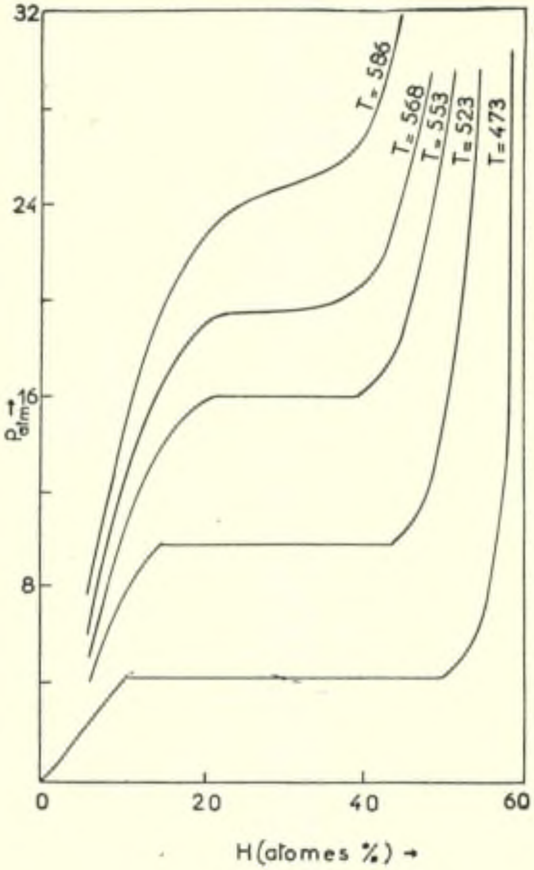

Fig. 1

Quelles sont les structures attribuées à ces phases?

Seul de tous les systèmes étudiés ici le système palladium-hydrogène ne comporte qu'un seul type de structure; les atomes de palladium conservent, en effet, quelle que soit la concentration en hydrogène, la disposition cubique à faces centrées qu'ils possèdent dans le métal pur (20). L'état diphasé observé aux températures et pressions peu élevées correspond à la coexistence de deux phases, présentant le même réseau métallique cubique à faces centrées des atomes de palladium, et qui ne diffèrent que par leur paramètre; cette différence tend d'ailleurs à s'atténuer lorsque la température et la pression augmentent simultanément, en accord avec les données indiquées plus haut.

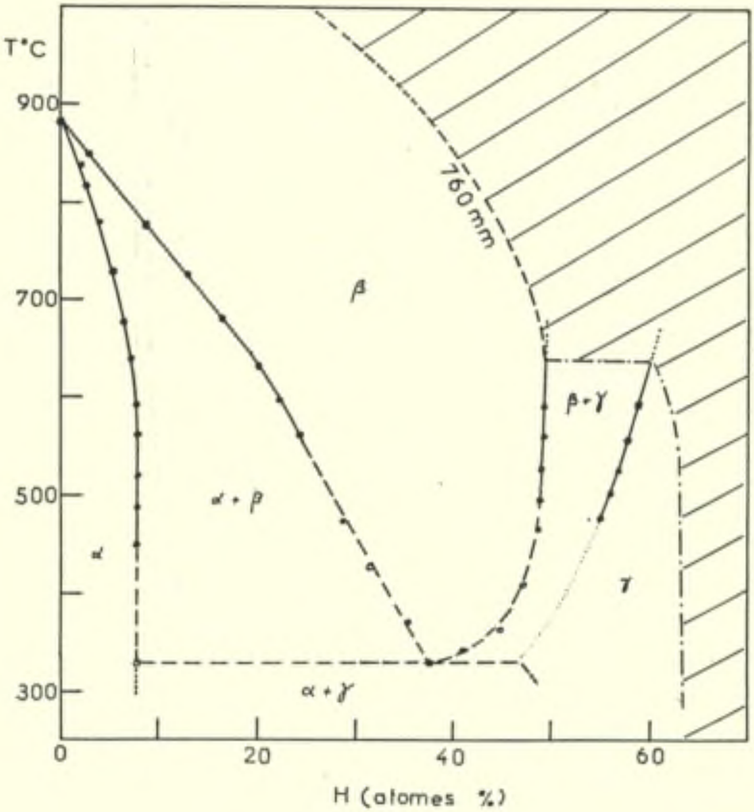

Fig. 2

Pour les autres systèmes, la disposition présentée par les atomes métalliques dans le métal pur n'est conservée que dans les solutions solides primaires, dont l'extension est parfois très faible à la température ordinaire.

Les phases plus riches en hydrogène possèdent encore des structures simples, mais qui sont généralement différentes de celle du métal pur. Tel est le cas de la phase γ du système titane-hydrogène dans laquelle les atomes de titane ont un arrangement cubique à faces centrées alors que le titane métallique est hexagonal compact ($\theta < 900$ °C) ou cubique centré (900 °C $< \theta$). Dans les systèmes zirconium-hydrogène et hafnium-hydrogène les phases proches de la formule ZrH_2 et HfH_2 ont un arrangement quadratique à faces centrées, alors que le métal est dans le premier cas hexagonal compact ($\theta < 862$ °C) ou cubique centré (862 °C $< \theta$) et dans le second cas hexagonal compact. La phase β du système tantale-hydrogène est hexagonale compacte alors que le métal est cubique centré.

L'affirmation selon laquelle les atomes métalliques posséderaient dans les hydrures des métaux de transition des configurations analogues à celle qu'ils possèdent dans ces métaux à l'état pur n'a donc pas, comme on le croit souvent, une valeur générale. La fréquence des structures compactes ou quasi-compactes observées dans la plupart de ces composés, qui a contribué à accréditer cette opinion, résulte en réalité de la grande différence des dimensions du métal de l'hydrogène, qui permet aux atomes métalliques de réaliser des configurations simples analogues à celles qu'ils ont tendance à adopter en l'absence d'atomes étrangers. Il est hors de doute que c'est l'impossibilité de localiser directement les atomes d'hydrogène par les rayons X qui a conduit inconsciemment les chercheurs à minimiser le rôle joué par ces atomes dans l'édification des phases hydrogénées.

LOCALISATION DES ATOMES D'HYDROGENE

Deux types de positions peuvent être envisagés pour des atomes d'hydrogène placés en insertion dans un assemblage quasi-compact d'atomes métalliques tel qu'on en rencontre dans bon nombre d'hydrures interstitiels : positions hexacoordinées (sites octaédriques) et positions tétracoordinées (sites tétraédriques) (figure 3). Si l'on admet à la suite de Hägg (7) que la phase d'insertion n'est stable que si tous les atomes antagonistes sont en contact, on doit conclure que les atomes d'hydrogène occupent toujours des positions tétracoordinées. En effet un raisonnement élémentaire montre que le contact entre l'atome inséré et les atomes métalliques contigus ne peut être assuré que si le rapport R du rayon de l'atome léger à celui de l'atome lourd est supérieur à la valeur critique 0,41. Si l'on prend pour dimension de l'atome d'hydrogène la valeur $r_H = 0{,}30$ Å adoptée initialement par Hägg les rapports caractéristiques de tous les hydrures des métaux de transition se situent entre les valeurs extrêmes $0{,}16 < R < 0{,}24$, toujours inférieures à la valeur critique.

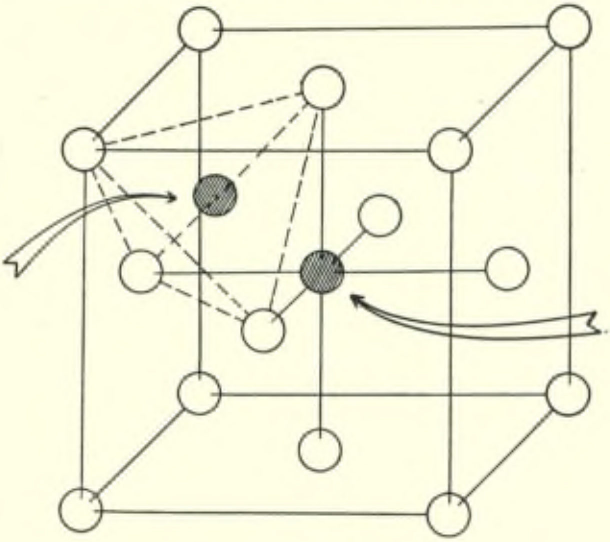

Fig. 3

En fait il ne semble pas possible de tirer de ces considérations des conclusions certaines quant à la position des atomes d'hydrogène dans le réseau métallique. En effet, les valeurs du rapport R sont subordonnées au choix d'une valeur pour le rayon atomique de l'hydrogène, choix qui présente encore un certain caractère arbitraire. Cet inconvénient serait d'ailleurs minime si l'on pouvait considérer cette valeur comme immuable dans tous les termes d'une série de composés homologues, mais il est certain que cette valeur se modifie en même temps que la nature des liaisons dans chaque série. Tout au plus semble-t-il donc possible de prévoir d'après ces raisonnements que dans les hydrures caractérisés par les rapports R les plus élevés, les atomes d'hydrogène ont tendance à occuper les positions tétracoordinées, tandis que pour les rapports les plus faibles l'hydrogène est dans les positions hexacoordinées.

On a d'autre part cherché à préciser la position des atomes d'hydrogène en se basant sur l'examen des compositions limites atteintes par les phases hydrogénées lorsqu'on fait varier la température et la pression. On pouvait espérer en particulier que les limites de phases observées correspondaient à l'occupation complète de différentes catégories de sites cristallographiques, ce qui aurait permis d'identifier ces sites par les valeurs des concentrations limites. Malheureusement il est fréquent que les limites caractéristiques observées ne peuvent être expliquées par l'occupation complète d'une catégorie déterminée de sites. C'est ainsi que si, dans la phase ZrH cubique à faces centrées, on localise à la suite de Hägg (7) et de Pauling et Ewing (21) les atomes d'hydrogène dans les sites tétracoordinés, on est conduit à admettre qu'à la saturation la moitié seulement de ces sites peuvent être occupés. De même quelles que soient les positions que l'on assigne aux atomes d'hydrogène dans TiH cubique centré, on doit envisager à la saturation une occupation qui n'est que partielle de ces positions. L'accord est meilleur dans les phases type TiH_2 cubiques à faces centrées, ou dérivées de ce système cristallin comme ZrH_2 quadratique à faces centrées ; on peut en effet considérer que dans ces cas, la saturation correspond à l'occupation de la totalité des sites tétraédriques disponibles.

Il n'en est pas moins vrai que dans l'ensemble, la considération des limites de phases ne permet pas, dans l'état actuel de nos connaissances, de localiser les atomes d'hydrogène. Le fait que des limites varient d'une façon considérable en fonction de la température et de la pression montre d'ailleurs très clairement qu'elles dépendent de nombreux facteurs autres que les facteurs géométriques. Il n'est même pas évident que les atomes soient localisés pour chaque phase dans une catégorie de sites déterminée et on pourrait envisager dans certains cas l'existence d'une répartition désordonnée des atomes d'hydrogène entre plusieurs catégories de sites. La tendance des phases différentes à se confondre, qui se manifeste dans certains systèmes lorsqu'on augmente la température et la pression correspondrait ainsi à la disparition de la localisation des atomes d'hydrogène et la réalisation progressive d'un état idéalement désordonné.

Il ne faut pas oublier enfin que le problème de la localisation des atomes d'hydrogène va se trouver d'ici peu entièrement renouvelé lorsque la diffraction des neutrons aura apporté un nombre suffisant de données. Nous citerons pour mémoire le très récent travail de Zachariasen et *alii* (22) qui ont déterminé par cette méthode la position des atomes d'hydrogène dans les phases du système cérium-hydrogène.

NATURE DE LA LIAISON DANS LES HYDRURES DES MÉTAUX DE TRANSITION

Le problème de la nature de la liaison dans les hydrures des métaux de transition ne semble pas encore avoir été traité dans son ensemble. Il paraît toutefois établi que l'hypothèse d'une dissolution de nature essentiellement physique doit être rejetée. A l'encontre de celle-ci plusieurs faits doivent être pris en considération:

1° *L'action de l'hydrogène sur ceux des métaux de transition qui absorbent ce gaz en quantité notable s'accompagne le plus souvent d'un dégagement de chaleur important*, dont l'ordre de grandeur (30 à 40 K/cal par mole H_2) ne diffère pas essentiellement de celui qui est mis en jeu dans la formation des hydrures ioniques. Seules font exception les phases hydrogénées du palladium, dont la chaleur de formation est beaucoup plus faible, de l'ordre de 10 K cal par mole d'hydrogène.

2° *Le paramagnétisme des métaux de transition qui résulte de la présence d'électrons solitaires, dans l'état métallique, décroît lorsque la teneur en hydrogène augmente*. Ceci prouve que les électrons apportés par l'hydrogène sont au moins en partie transférés dans le niveau *d* incomplet du métal. Dans le cas du palladium, le paramagnétisme disparaît totalement à la composition $PdH_{0,6}$ pour laquelle la totalité des niveaux *d* du métal se trouverait par conséquent occupé ([23]).

3° *Le transfert de l'électron de l'hydrogène au métal est confirmé par les expériences de diffusion de l'hydrogène dans les phases palladium-hydrogène sous l'influence d'un champ électrique* ([24, 25]). Ces expériences supposent en effet une ionisation électropositive au moins partielle des atomes d'hydrogène en insertion.

4° *Les variations parfois importantes des distances métal-métal lorsqu'on passe du métal pur aux phases hydrogénées ne peuvent s'expliquer que par un changement important dans la nature des forces de liaison.* Le changement du type de liaison se manifeste d'ailleurs dans chaque système, en fonction de la teneur en hydrogène, par l'altération progressive des propriétés physiques du métal. Alors que dans les phases primaires et même dans certaines phases intermédiaires déjà riches en hydrogène, l'atténuation du caractère métallique est relativement discrète et ne se traduit guère que par la diminution de la conductibilité électrique et l'apparition de la fragilité, les phases les plus riches en hydrogène comme ZrH_2 et TiH_2 perdent totalement le caractère métallique et s'apparentent par leur physionomie générale aux hydrures salins.

Se basant sur le fait que dans le système palladium-hydrogène le caractère métallique persiste aux concentrations en hydrogène les plus élevées, Ubbelohde (²⁶) a traité le problème de la liaison dans ces phases en les assimilant à des alliages dans lesquels l'hydrogène jouerait le rôle d'un métal. Cette conception paraît cadrer d'une manière assez satisfaisante avec les propriétés de ce système, mais il ne semble pas possible de l'étendre à l'ensemble des hydrures des éléments de transition, car le système palladium-hydrogène constitue un cas à bien des égards exceptionnel.

Une intéressante suggestion de Rundle (²⁷), reprise récemment par Pauling et Ewing (²¹) a été faite pour interpréter la *structure de l'hydrure d'uranium* dont la composition limite correspond à la formule UH_3. Bien que ce composé se situe par certains de ses caractères à la frontière des hydrures interstitiels et des hydrures salins, l'étude de sa constitution est instructive parce qu'elle souligne certaines particularités qui n'apparaissent qu'à l'état d'ébauche dans les hydrures interstitiels des métaux de transition des deux premières longues périodes. En effet UH_3 bien que conducteur de l'électricité, ne possède qu'un très petit nombre de liaisons métalliques comme il est facile de le constater en comparant les distance U — U dans sa structure aux distances correspondantes dans l'uranium métal. Cette structure comporte par contre un certain nombre de distances U — U qui sont trop grandes pour être des distances U — U normales et trop petites pour correspondre à l'insertion pure et simple d'un atome H entre deux atomes métalliques sans apparition d'une liaison nouvelle. Ces distances témoigneraient selon Rundle de l'existence d'une liaison U — H — U résultant du partage par moitié de l'orbitale *s* de l'atome d'hydrogène entre deux atomes d'uranium voisins et diamétralement opposés. L'existence de ces ponts hydrogène à liaison fractionnaire serait compatible avec l'existence des caractères métalliques et en particulier de la conductibilité électrique. Le caractère orienté de ces liaisons, comparables à cet égard à des liaisons de covalence, expliquerait d'autre part la grande fragilité du composé. Il est difficile de savoir dans quelle mesure leur présence peut être escomptée dans d'autres hydrures des métaux de transition. Seule une étude comparée approfondie des distances métal-métal dans ces hydrures et des mêmes distances dans le métal pur permettrait d'en décider.

Il ne saurait être question de rechercher un type unique d'interprétation pour définir l'ensemble des phases métal-hydrogène qui viennent d'être citées. Ces phases possèdent en effet une extrême diversité de propriétés, correspondant à des modes de liaisons manifestement différents et doivent s'intégrer dans une série évolutive. A l'une des extrémités de cette série se situe le palladium dans lequel la dissolution de l'hydrogène bien que couvrant un large domaine de concentration, n'altère que partiellement les caractères métalliques et ne modifie pas la configuration des atomes lourds. A l'autre extrémité un hydrure ionique comme CaH_2 auquel les caractères métalliques font totalement défaut et où la configuration des ions Ca^{2+} n'a aucun rapport avec celle des atomes dans le métal. Jalonnant la transition on pourrait d'une façon très approximative établir le classement suivant :

Pdα — Pdβ — Taα — Tiα et β — Zr ε et Ti γ — UH_3 — CaH_2

Cette évolution s'accompagne d'un accroissement de la chaleur de formation, d'une diminution de la conductibilité et de la disparition des variations de composition en phase homogène.

Il paraît nécessaire d'admettre de plus que le caractère de la liaison se modifie non seulement lorsqu'on passe d'une phase à une autre mais encore au sein d'une même phase en fonction de la concentration de l'hydrogène. Ceci permet d'expliquer en particulier que des phases présentant à basse température et sous la pression atmosphérique des structures et par conséquent des modes de liaison probablement différents, puissent arriver à se confondre en une phase unique de composition variable à plus haute température.

On ne peut manquer de rapprocher la situation attribuée à UH_3 dans ce classement, à la limite des hydrures à caractère métallique et des hydrures à caractère ionique, de la présence dans ce composé des ponts métal-hydrogène postulés par Rundle. Dans les phases hydrogénées métalliques type palladium-hydrogène, il paraît établi en effet que les électrons 1*s* de l'hydrogène, viennent remplir au moins partiellement les niveaux 4*d* du métal. L'opération peut être assimilée sous une forme schématique à un transfert d'électrons de l'hydrogène au métal. Dans les hydrures ioniques type LiH ou CaH_2, c'est le métal qui cède irréversiblement un électron à l'hydrogène pour compléter le niveau 1*s*, opération inverse de la précédente et qui conduit à la formation d'un anion H^-. Il n'est pas impossible de concevoir des couples métal-hydrogène intermédiaires dans lesquels la tendance de l'hydrogène à compléter son niveau 1*s* équilibrerait sensiblement la tendance du métal à compléter un ou plusieurs niveaux sous-jacents incomplets. Cette situation pourrait être favorable à l'apparition des ponts hydrogène et trouverait son illustration dans la structure de UH_3. Bien qu'on ne possède encore que peu de renseignements sur la structure de l'hydrure de thorium et des hydrures des lanthanides, on a tout lieu de penser que ces composés présentent des caractères analogues.

CARACTERES GÉNÉRAUX DES CARBURES, NITRURES ET OXYDES DES MÉTAUX DE TRANSITION

La plupart des carbures, nitrures et oxydes des éléments de transition possèdent un réseau métallique simple. Les seules exceptions sont constituées par les carbures de chrome, manganèse, fer, cobalt et nickel dont les structures sont complexes et pour lesquels le rapport du rayon atomique de l'élément léger à celui de l'élément lourd est supérieur à 0,59. En comparaison de la structure des hydrures, celle de ces phases apparaît comme beaucoup moins variée et se limite à un très petit nombre de configurations. Les phases répondant à la formule générale Me X constituent en particulier un ensemble extrêmement homogène dans lequel le métal de transition et l'élément léger alternent dans un réseau cubique type chlorure de sodium (fig. 4). Chaque sorte d'atome possède six voisins disposés aux sommets d'un octaèdre dont il occupe le centre. Ces phases sont traditionnellement citées comme exemples de composés interstitiels des métaux de transition. La liste en est donnée dans le tableau avec indication des structures et des distances métal-métal. Les phases Me_2X, qui ne se rencontrent que parmi les carbures et les nitrures, sont le plus souvent hexagonales compactes, à l'exception des composés W_2N et Mo_2N qui sont cubiques à faces centrées. Les phases Me_4X enfin, qui sont peu nombreuses (Mn_4N, Fe_4N), possèdent également une répartition des atomes métalliques sur les nœuds d'un réseau cubique à faces centrées.

La haute symétrie et la compacité de l'arrangement des atomes métalliques dans ces composés permettent-elles de les considérer comme résultant simplement de l'insertion d'atomes de carbone, d'azote ou d'oxygène dans les interstices de l'édifice cristallin du métal pur? L'examen du tableau montre que contrairement à une opinion communément admise, la configuration des atomes métalliques dans les composés d'insertion étudiés ici est le plus souvent différente de celle qu'ils adoptent dans le métal. La formation de ces composés entraîne donc une réorganisation complète de l'édifice du métal.

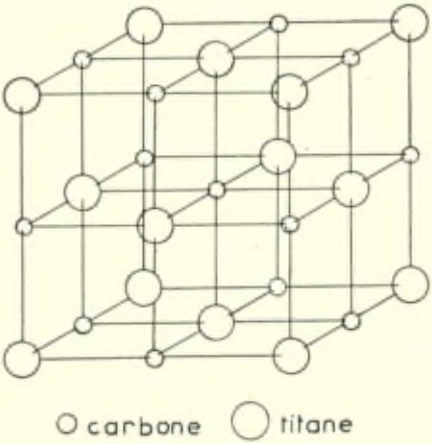

Fig. 4

L'union des métaux de transition au carbone et à l'azote ne provoque pas seulement un changement de la structure; elle s'accompagne en outre de *l'apparition de propriétés physiques entièrement nouvelles.* Tous possèdent une dureté élevée comparable à celle du diamant, dureté qui s'accompagne le plus souvent d'une grande fragilité. Leur infusibilité est également remarquable et les points de fusion, toujours supérieurs à 2.000°, atteignent fréquemment 3.000°. Il est remarquable de constater qu'en dépit de ces changements, certains caractères de l'état métallique subsistent, en particulier l'opacité, l'éclat métallique et une conductivité électronique appréciable avec un coefficient de température négatif.

Structures comparées de quelques carbures, nitrures et oxydes interstitiels des métaux de transition (lorsque aucune indication contraire n'est mentionnée les indications fournies se rapportent au composé MeX).

MÉTAUX			CARBURES			NITRURES			OXYDES		
	Maille	Distance Me-Me Å	Maille	Distance Me-Me Å	Expansion Me-Me Å	Maille	Distance Me-Me Å	Expansion Me-Me Å	Maille	Distance Me-Me Å	Expansion Me-Me Å
Ti	hex. c.	2,92	cub. fc.	3,04	0,12	cub. fc.	2,27	0,65	cub. fc.	2,99	0,07
Zr	hex. c.	3,12	cub. fc.	3,30	0,18	cub. fc.	3,21	0,09	cub. fc.		
Hf	cub. c. hex. c.	3,16	cub. fc.	3,27	0,11	cub. fc.			cub. fc.		
Th	cub. fc.	3,60	cub. fc.	3,76	0,16	cub fc.	3,66	0,06	cub. fc.		
V	cub. c.	2,60	cub. fc.	2,93	0,33	cub. fc.	2,90	0,30	cub. fc.	2,91	0,31
Nb	cub. c.	2,86	cub. fc.	3,14	0,28	cub. fc.	3,10	0,24	cub. fc. déformé		
Ta	cub. c.	2,86	cub. fc.	3,13	0,27	hex. (Ta_2N)	3,05	0,19	cub. fc.	3,13	0,27
Mo	cub. c. hex. c.	2,72	hex.	2,90	0,18	hex.	2,86	0,14			
W	cub. c.	2,72	hex.	2,90	0,18	cub. fc. (W_2N)					
U	cub. c. orth. rh.	2,76	cub. fc.	3,48	0,72	cub. fc.	3,44	0,68	cub. fc.		
Cr	cub. c.	2,50	cub. fc.			cub. fc.	2,92	0,42			

Le problème de la *localisation des atomes légers* dans la structure se pose, dans le cas des carbures, nitrures et oxydes, d'une façon beaucoup plus simple que dans celui des hydrures. L'encombrement des atomes de carbone, d'azote et d'oxygène est en effet, quel que soit l'état dans lequel ils se trouvent dans ces composés, nettement supérieur à celui de l'atome d'hydrogène. Il en résulte que pour ces atomes la position la plus probable est celle des sites hexacoordinés, dont la totalité se trouve occupée dans les composés MeX, et dont une partie seulement est occupée dans les composés Me_2X (la moitié) et Me_4X (le quart).

C'est sans doute l'une des raisons pour lesquelles les structures des carbures et nitrures et oxydes interstitiels des métaux de transition sont généralement plus simples que celles de leurs hydrures.

NATURE DES LIAISONS DANS LES CARBURES, NITRURES ET OXYDES DES MÉTAUX DE TRANSITION

Différentes tentatives ont été faites, pour interpréter l'ensemble des propriétés des composés d'insertion des éléments de transition d'après la nature des liaisons mises en jeu. La difficulté majeure à laquelle on se heurte est d'arriver à justifier dans ces composés la coexistence de caractères considérés comme spécifiques de types de liaison entièrement différents. Le problème est en effet compliqué dans le cas des carbures et des nitrures par l'apparition de la dureté et de l'infusibilité qui caractérisent habituellement les composés (ou éléments) possédant un réseau tridimensionnel de liaisons covalentes, tandis que la conductivité électrique et l'opacité jointes à l'éclat métallique témoignent d'un mode de liaison comparable à celui des métaux.

Umanski a repris en 1943 ([28]) la conception que Ubbelohde avait utilisée pour interpréter les propriétés du système palladium-hydrogène et l'a étendue aux carbures et nitrures interstitiels. Le carbone et l'azote dont les potentiels d'ionisation ne sont pas extrêmement différents de celui de l'hydrogène céderaient comme celui-ci une partie de leurs électrons au métal auquel ils se trouvent associés en formant des phases à caractère métallique. Cette conception trouve un appui dans les expériences de Seith et Kubachewski ([29])

qui ont montré qu'à 1.000° le carbone dissous dans le fer migre vers la cathode sous l'influence d'un champ électrique. Il est vrai que dans le système fer-azote, Seith et Dauer (30) avaient cru observer dans des conditions analogues une migration vers l'anode, mais ce résultat s'est trouvé infirmé par Prosvirin (31) qui a observé un transport électrolytique simultané du carbone et de l'azote vers la cathode dans les carbo-nitrures de fer.

La première difficulté à surmonter dans cette théorie est d'expliquer la réorganisation complète de la structure du métal à la suite de son union avec le carbone et l'azote. Comment comprendre en effet que l'introduction d'atomes supplémentaires de dimensions minimes puisse entraîner une perturbation importante de la structure, si la nature des liaisons ne se trouve pas entièrement modifiée du fait de cette introduction?

L'explication fournie par Umanski repose sur l'intervention des pressions internes élevées résultant de l'introduction des atomes étrangers, pressions dont l'existence serait prouvée par l'expansion des distances métal-métal, lorsqu'on passe du métal à la phase d'insertion, et qui provoquerait une véritable transformation allotropique du métal. Cette explication à laquelle Ubbelohde avait déjà fait appel dans le cas des hydrures, semble présenter dans le cas présent un caractère exclusivement formel.

Une autre difficulté est d'expliquer par cette théorie l'apparition de l'extrême dureté et de l'infusibilité. D'après Umanski la dureté élevée des composés d'insertion résulterait d'un mécanisme de blocage des plans de glissement du métal par les atomes interstitiels, analogue à celui qui fut invoqué à peu près à la même époque pour expliquer le phénomène de durcissement structural dans les alliages. Il ne fournit semble-t-il aucune explication de l'infusibilité.

On peut être surpris enfin de voir un échange électronique s'effectuer dans le sens prévu par cette théorie, entre deux catégories d'éléments dont les électronégativités sont telles que l'on escompterait plutôt un échange en sens inverse, à savoir un transfert électronique du métal à l'élément léger. Toutefois il n'est pas impossible que la présence des niveaux électroniques sous-jacents vacants dans les métaux vienne infirmer les prévisions que l'on peut faire en se basant sur la comparaison des électronégativités, lorsque ces dernières ont des ordres de grandeur voisins.

Rundle a développé en 1948 (32) une interprétation issue en partie des idées de Pauling (33). Cette interprétation au lieu de mettre l'accent comme les précédentes sur l'aspect métallique des liaisons, donne une importance plus grande à l'aspect covalent de celles-ci. Rundle fonde son raisonnement sur la remarque faite plus haut que dans la plupart des carbures, nitrures ou oxydes interstitiels répondant à la formule Me X, les atomes légers possèdent six voisins métal équidistants, échangeant avec ceux-ci six liaisons orientées suivant les sommets d'un octaèdre. La permanence de cette structure en dépit des variations nombreuses de valence et d'affinité que présentent les métaux de transition, jointe aux caractères physiques dont il a été question plus haut, tendrait à prouver, selon cet auteur, que ces liaisons ont des orientations imposées par leur nature même et possèdent par conséquent un certain caractère covalent. Il ne peut s'agir d'une liaison de covalence classique puisque les éléments légers : carbone, azote, oxygène, appartiennent à la première série brève du tableau périodique et ne peuvent mettre en jeu de ce fait que quatre orbitales alors que dans l'hypothèse de Rundle ils contractent six liaisons équivalentes. Le problème est donc de trouver une combinaison stable de trois ou quatre orbitales qui puissent se répartir uniformément entre six liaisons. Parmi les solutions possibles on peut mentionner l'intervention des trois orbitales 2 *px*, 2 *py*, 2 *pz* orientées suivant les arêtes d'un trièdre trirectangle et assurant par symétrie les six liaisons octaédriques équivalentes, mais ce n'est pas la seule possibilité qui puisse être envisagée. Quelle que soit la solution adoptée, cette interprétation suppose le partage par résonance de chaque doublet électronique entre plusieurs orbitales du métal. Ce partage s'accompagnerait d'une mobilité particulière des électrons et par suite de l'apparition de la conductibilité électrique; il n'irait pas cependant jusqu'à entraîner la délocalisation des liaisons comme cela est le cas dans les édifices métalliques typiques, de sorte que les propriétés physiques liées au caractère orienté des liaisons se trouveraient sauvegardées.

Rappelons que la notion de liaison covalente fractionnaire a été introduite par le même auteur pour expliquer l'existence d'une liaison uranium-hydrogène-uranium dans l'hydrure d'uranium. Elle semble trouver toutefois un champ d'application plus vaste dans les carbures, nitrures et oxydes que dans les hydrures, chez lesquels la permanence du caractère métallique est beaucoup plus grande par suite du caractère électropositif plus marqué de l'hydrogène. Cette conception a été étendue récemment par Krebs (^{34}) à un certain nombre de composés ioniques présentant simultanément le caractère métallique.

TRANSITION DE LA LIAISON DANS LES CARBURES ET NITRURES METALLIQUES

Pour mieux prendre conscience de la valeur des arguments invoqués à l'appui des théories que nous venons de passer en revue il est intéressant d'étudier par comparaison les carbures et nitrures métalliques dans lesquels les liaisons sont nettement différentes.

La transition des carbures interstitiels typiques cubiques à faces centrées (représentés par exemple par le monocarbure de titane) vers les carbures ioniques, ne semble se manifester dans aucun monocarbure. Par contre, plusieurs dicarbures des métaux de transition (LaC_2, ThC_2, UC_2) témoignent déjà d'une évolution vers l'état ionique; celle-ci se marque par un accroissement de l'activité chimique et par l'apparition d'une structure à basse symétrie monoclinique (^{35}). Dans ces composés les atomes de carbone se trouvent associés par paires dans les intervalles du réseau des atomes métalliques.

Avec les dicarbures des métaux très électropositifs du type $Ca\,C_2$, on a affaire à des composés franchement ioniques, comportant des ions C_2^- et facilement décomposables par l'eau avec formation de carbures d'hydrogène à deux atomes de carbone, parmi lesquels domine l'acétylène. L'association des atomes de carbone par paires dans ces composés est due au fait que si les atomes de carbone demeuraient isolés, la coordinence qui leur serait imposée deviendrait incompatible avec le diamètre élevé des ions métalliques qui sont appelés à les entourer. C'est également la raison pour laquelle, en dépit de leur électropositivité élevée, des métaux comme le sodium ou le potassium donnent des carbures du type Na_2C_2 et non pas du type Na_4C ($^{36, 37}$). Ceci constitue un bon exemple des restrictions que les facteurs d'ordre géométrique peuvent, dans ces composés, apporter à la réalisation des possibilités offertes par la constitution électronique des éléments en présence.

Si nous examinons d'autre part la transition des carbures interstitiels vers des formes de liaison spécifiquement métalliques, nous sommes amenés à constater qu'un bon exemple de système présentant ce mode intermédiaire de liaison est constitué par la solution solide de carbone dans la structure cubique à faces centrées du fer (austénite). Cette dissolution entraîne une dilatation progressive du volume de la maille (38) sans apporter de changement radical aux propriétés du métal pur sous l'état γ. La diminution progressive de la conductibilité électrique et l'altération de quelques autres propriétés en fonction de la teneur en carbone prouve cependant que l'introduction de cet élément en insertion modifie l'état électronique du métal. Si l'on se réfère aux résultats expérimentaux signalés plus haut concernant le transport du carbone dans le fer à l'état solide sous l'influence d'un champ électrique (29), il apparaît que dans cette phase la liaison résulte d'un transfert électronique du carbone vers le métal, ce qui, joint à l'absence des caractères de dureté exceptionnelle et d'infusibilité, conduit à la considérer comme authentiquement métallique. Les mêmes observations pourraient être faites au sujet de la solution solide d'azote dans le fer γ. Par contre le système fer-azote possède en outre une phase distincte, répondant sensiblement à la formule Fe_4N, et qui se rapproche beaucoup par ses caractères des composés interstitiels typiques (39, 40).

Il existe donc parmi les carbures et dans une certaine mesure parmi les nitrures, une filiation qui fait apparaître les composés interstitiels typiques du carbone et de l'azote avec les métaux de transition, comme des termes de passage entre des phases purement ioniques dans lesquelles l'élément léger joue le rôle d'un anion et des phases essentiellement métalliques.

Il semble ainsi possible de concilier dans une certaine mesure les différentes théories qui se proposent d'expliquer les caractères des composés d'insertion typiques, à l'exclusion toutefois de celles qui voudraient assimiler l'union de l'élément léger au métal de transition à une sorte de coexistence uniquement régie par les lois de la géométrie. Il est hors de doute que la conception de Ubbelohde-Umanski représente d'une manière satisfaisante les caractères du système palladium-hydrogène à partir duquel elle a été édifiée. Elle correspond également assez bien aux solutions solides primaires non seulement de l'hydrogène mais encore du carbone, de l'azote et de l'oxygène dans les métaux de transition, dans lesquelles l'élément léger semble effectivement adopter un état pseudo-métallique, et qui conservent l'essentiel des propriétés physiques du métal. Cette conception s'écarte par contre manifestement de la réalité lorsqu'elle prétend également expliquer la constitution des carbures et nitrures d'insertion, infusibles et de grande dureté, dont le type est le carbure de titane. Elle est en effet incapable de rendre compte de l'apparition des structures et des propriétés entièrement nouvelles qui caractérisent ce genre de composés.

Pour les composés de ce type la conception de Rundle mérite à son tour d'être prise en considération, car elle permet de justifier la coexistence des caractères covalents typiques qui s'y manifestent avec évidence et des caractères métalliques qui ne sont qu'en apparence hérités du métal d'origine. C'est en particulier à la formation d'un réseau tridimensionnel de liaisons quasi-covalentes que sont dues la dureté et l'infusibilité exceptionnelles de ces phases au même titre que dans le diamant et dans le carbure de silicium.

Il apparaît ainsi que les composés d'insertion typiques des métaux de transition doivent leur physionomie, bien moins à des relations d'ordre géométrique entre les atomes comme on l'avait pensé jadis, qu'à des particularités étroitement liées à la structure électronique à savoir :

1° Une faible différence d'électronégativité entre les partenaires, excluant la formation d'une liaison ionique et tendant à favoriser la liaison de covalence ;

2° L'existence dans le métal d'un nombre d'orbitales supérieur à celui des doublets disponibles, entrainant *ipso facto* le caractère métallique.

Ces considérations ne doivent pas inciter cependant à négliger les méthodes d'approche géométriques du problème, qui fournissent à toutes les théories la base concrète qui leur est indispensable. Les données de structure sont en effet susceptibles de donner des indications précieuses sur la nature des liaisons, et la voie indiquée par Hägg, il y a plus de vingt ans, conserve aujourd'hui encore toute sa valeur.

VARIATIONS DE COMPOSITION DANS LES COMPOSÉS D'INSERTION

Nous examinerons tout d'abord à ce point de vue les hydrures.

Les phases figurant dans les systèmes métal-hydrogène possèdent dans bon nombre de cas des domaines extrêmement étendus de variation de la concentration en phase homogène. Ces domaines s'accroissent lorsque la température et la pression d'hydrogène augmentent et il est difficile, comme il a été dit plus haut, d'attribuer une signification particulière aux concentrations limites observées par exemple à la température ordinaire. On peut tenter de justifier cette extension des domaines monophasés par le petit rayon de l'atome d'hydrogène mais cette explication est insuffisante puisqu'un métal comme le nickel, dont la structure est pourtant identique à celle du palladium ne fixe pas d'hydrogène dans le réseau cristallin (41). Tout au plus peut-on affirmer que les facteurs géométriques ne viennent pas, dans les systèmes métal de transition-hydrogène, restreindre les variations de concentration autorisées par les données électroniques. En ce qui concerne ces dernières, qui demeurent donc primordiales, on pourrait faire observer en se basant sur l'exemple du système palladium-hydrogène, que l'étendue maximum du domaine de concentration est fixée par le taux de remplissage des niveaux *d* vacants du métal par les électrons provenant de l'hydrogène. Dans l'état actuel de nos connaissances cette interprétation ne peut malheureusement pas être poussée très loin et nous en sommes réduits aux conjectures pour la plupart des autres systèmes.

Par une voie entièrement différente, Lacher (42) et Anderson (43)' puis Rees (44) ont tenté de retrouver *a priori* les valeurs des limites de phases en rattachant le passage des états monophasés aux états diphasés, à l'énergie d'interaction des atomes d'hydrogène dispersés dans le réseau du métal. Cette méthode, comme nous l'avons dit plus haut, a donné des résultats conformes à l'expérience dans les systèmes palladium-hydrogène (42), platine-soufre (43) et zirconium-hydrogène (45), mais ne semble pas avoir pu être étendue à d'autres systèmes. Ces larges variations de concentration ne s'observent que dans les phases hydrogénées qui conservent un caractère métallique marqué. L'apparition des premiers indices de liaison ionique s'accompagne d'une diminution brusque de l'étendue des domaines d'homogénéité comme c'est le cas pour l'hydrure d'uranium (18, 19).

Les variations de concentration des carbures des métaux de transition sont, à quelques exceptions près, beaucoup moins importantes que celles des hydrures. En ce qui concerne les solutions solides primaires tout d'abord, il est remarquable de constater qu'elles sont extrêmement réduites, sinon absentes, pour tous les métaux donnant des carbures interstitiels typiques (Zr, V, Mo, W, etc.). Seul le titane dissout le carbone jusqu'à atteindre la formule $\mathrm{Ti\,C_{0,05}}$ (46). Le fer, qui ne donne pas de carbure interstitiel typique, donne naissance dans l'état γ à la solution solide primaire austénitique dont la concentration peut atteindre 1,8 % à 1.100°, ce qui correspond à la formule $\mathrm{Fe\,C_{0,08}}$. L'existence des formes martensitiques instables dans lesquelles le carbone est placé dans les lacunes d'un réseau quadratique, et la solubilité pratiquement négligeable du carbone dans la ferrite témoignent d'une manière évidente de l'influence de la structure sur la solubilité. Néanmoins le facteur géométrique n'est certainement pas le seul à intervenir puisque, pour ne citer que cet exemple, le nickel dont la structure est la même que celle du fer γ et les dimensions très voisines ne dissout à la même température que 0,3 % C (47).

En ce qui concerne les *carbures interstitiels* proprement dits, les variations de composition sont particulièrement importantes pour le monocarbure de titane (de $\mathrm{Ti\,C_{0,28}}$ à Ti C) (46) et le monocarbure de vanadium (de $\mathrm{VC_{0,75}}$ à $\mathrm{VC_{1+\varepsilon}}$) (48). Les composés similaires du zirconium, du hafnium, du molybdène et du tungstène par contre ne présentent pas d'écarts à la stoechiométrie. Pour ce qui est des carbures de thorium et d'uranium, on a signalé (49, 50) un passage continu de Th C à $\mathrm{Th\,C_2}$ et de UC à $\mathrm{UC_2}$ aux températures élevées, sans que des précisions aient été données semble-t-il sur la façon dont la structure s'accommode de ces variations de concentration.

Les nitrures interstitiels typiques présentent des caractères similaires du point de vue des écarts à la stoechiométrie. La composition du nitrure de titane, de même structure cubique à faces centrées que le carbure, varie de $\mathrm{Ti\,N_{0,42}}$ à $\mathrm{Ti\,N_{1,05}}$. Le nitrure de vanadium présente des écarts moindres, quant aux autres nitrures les renseignements sont trop imprécis pour qu'il puisse en être fait état.

Les données concernant *les oxydes interstitiels* sont encore peu nombreuses. Le cas du monoxyde de titane est remarquable car ce composé présente des variations de composition depuis

$TiO_{0,58}$ jusqu'à $TiO_{1,33}$ sans autre changement de structure qu'une variation linéaire de l'arête de la maille en fonction du rapport du titane à l'oxygène. En se basant sur la mesure des densités, Ehrlich ([51]) a cru pouvoir affirmer qu'à la composition stoechiométrique Ti O le réseau comportait un nombre égal de sites vacants de chaque espèce, évalué à 15 % du nombre total des sites. Dans les phases riches en titane, le nombre des lacunes oxygène serait supérieur à celui des lacunes titane et inversement dans les phases riches en oxygène. Dans le cas du monoxyde de vanadium ([52]) la composition varierait de $VO_{0,8}$ à $VO_{1,2}$. Les données concernant ZrO, HfO, NbO, et VO ne permettent pas de conclure quant à l'étendue des variations de composition.

De l'ensemble des renseignements que l'on possède sur les écarts à la stoechiométrie des composés interstitiels typiques il résulte qu'il existe une analogie évidente à cet égard entre les carbures, nitrures et oxydes. Deux métaux : le titane, et à un degré moindre le vanadium présentent, quel que soit l'élément léger qui leur est associé, des variations de composition importantes de part et d'autre de la composition stoechiométrique du monoxyde. Etant donné le petit nombre des données expérimentales, il n'est pas certain qu'ils soient les seuls à posséder ce caractère. Toutefois, il ne semble pas possible d'affirmer, comme on l'a fait parfois, que l'existence de domaines importants de variations de concentration en phase homogène soit un caractère général propre aux composés d'insertion typiques. Si certains d'entre eux présentent effectivement des variations considérables, ils paraissent plutôt constituer des exceptions parmi l'ensemble des composés de ce type. Cette remarque ne concerne ni les systèmes métal-hydrogène dans lesquels les variations importantes de concentration sont de règle, ni les solutions solides primaires résultant de l'insertion d'atomes légers dans le réseau d'un métal.

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Composés ioniques non stoechiométriques

par **Jacques BÉNARD**

L'existence de composés minéraux susceptibles de présenter dans l'état solide des variations de la composition sans que le système cessât de demeurer monophasé a été signalée depuis longtemps. L'exemple le plus anciennement connu est celui des silicates naturels dans lesquels la proportion des différentes catégories d'atomes métalliques peut varier considérablement dans une même famille cristalline. Ce n'est qu'à une époque relativement récente que furent signalées dans certains composés ioniques binaires des variations du rapport $\frac{\text{métal}}{\text{non métal}}$. Plusieurs groupes de chercheurs s'efforcèrent de préciser l'étendue des domaines d'homogénéité de ces phases, parmi lesquels on peut citer principalement Schenck et ses collaborateurs en Allemagne, Jette et Foote aux Etats-Unis, Haraldsen et ses collaborateurs en Norvège, Hägg et ses collaborateurs en Suède, Chaudron et ses collaborateurs en France. On s'aperçut ainsi peu à peu que les premiers exemples sur lesquels on s'était appuyé pour édifier ces théories, loin de constituer des exceptions comme on l'avait pensé tout d'abord, n'étaient en fait que des manifestations exceptionnellement marquées, d'une propriété générale des composés ioniques solides. Grâce au perfectionnement des méthodes expérimentales d'investigation, un nombre sans cesse croissant de composés non stoechiométriques est maintenant signalé chaque année. (*)

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* Nous conviendrons d'appeler *composé non stoechiométrique* (Berthollide) tout composé dans lequel on peut faire varier de façon continue le rapport $\frac{\text{cation}}{\text{anion}}$ sans changement de phase.

D'après cette convention, le domaine de stabilité d'un composé non stoechiométrique peut inclure ou ne pas inclure le rapport stoechiométrique simple par lequel il est habituellement désigné.

Parallèlement à cette accumulation de données expérimentales le développement des études sur les imperfections des édifices cristallins vint apporter à cet ensemble la justification théorique qui lui faisait défaut. Généralisant, en effet, la conception introduite initialement par Frenkel et par Schottky pour expliquer la formation des défauts dans les composés stoechiométriques, plusieurs auteurs parmi lesquels il faut citer surtout Wagner et Hägg proposèrent différents mécanismes permettant de justifier les variations de composition observées dans les phases non stoechiométriques. Bien que ces interprétations comportent maintenant encore bien des aspects obscurs, elles constituent à l'heure actuelle un outil de travail extrêmement précieux.

Il est à noter que la physique a fait de son côté très largement appel à l'existence de défauts de ce genre pour justifier l'apparition de certaines propriétés dans les solides. L'abondance des défauts indiquée par ces propriétés étant toutefois très inférieure à celle qui correspondrait au seuil de sensibilité des méthodes de l'analyse chimique, il est le plus souvent impossible de contrôler directement la réalité des variations de composition postulées. Afin d'établir une ligne de démarcation entre ces deux ordres de recherches, nous nous limiterons ici à l'étude des composés non stoechiométriques dans lesquels les variations de composition peuvent être contrôlées par l'analyse chimique.

Il ne saurait être question de passer en revue, même brièvement, dans le cadre de ce rapport, tous les travaux qui ont été effectués depuis quelques années dans ce domaine. On trouvera dans une excellente mise au point due à Anderson (1), la plupart des références des publications antérieures à 1947; seules seront reprises ici celles d'entre elles qui offrent un intérêt pour l'interprétation générale des phénomènes en discussion. Notre bibliographie sera par contre plus explicite en ce qui concerne les publications postérieures à 1947. Nous avons rassemblé sous forme d'un tableau les composés binaires non stoechiométriques pour lesquels les variations de composition semblent les mieux établies. Ce tableau ne prétend pas être complet; n'y figurent pas en particulier les systèmes encore très controversés ou trop complexes pour s'accommoder de cette représentation schématique (système uranium-oxygène par exemple). On ne manquera pas de remarquer enfin que, bien que cette étude ne concerne en principe que des composés ioniques, le tableau comporte bon nombre de corps dans lesquels la liaison est sans aucun doute partiellement covalente ou métallique.

METHODES DE DÉTERMINATION DE L'ÉTENDUE DES DOMAINES

La détermination de l'étendue du domaine de variation de la concentration d'une phase non stoechiométrique peut se faire par des méthodes variées. La valeur des renseignements obtenus dépend dans une large mesure de la nature de la phase examinée.

Lorsque la variation de concentration s'accompagne d'une variation importante des paramètres cristallins, la méthode la plus sensible est la détermination des paramètres limites aux deux extrémités du domaine, au moyen de la diffraction des rayons X. Si l'on a déterminé au préalable la courbe de variation des paramètres en fonction de la concentration, on obtient immédiatement les valeurs des concentrations limites correspondantes. On est limité dans cette voie par la sensibilité des méthodes de mesure : pour les phases de symétrie cubique présentant un état de cristallisation optimum, la précision relative la meilleure que l'on puisse obtenir est semble-t-il voisine de 1/10.000 en employant la méthode en retour.

On ne peut espérer obtenir des résultats sérieux en se fondant sur la non évidence d'une seconde phase pour conclure qu'un échantillon est situé dans le domaine monophasé. La sensibilité des méthodes d'identification au moyen de microscope ou des rayons X ne dépasse pas en effet quelques unités pour cent. Seule la méthode magnétique peut assurer une grande sensibilité ([15a]) lorsque la seconde phase dont la présence est escomptée est ferromagnétique.

On a beaucoup utilisé la méthode basée sur l'étude des équilibres de réduction. Considérons par exemple le sulfure de nickel NiS, qui a fait l'objet d'un travail récent ([18]). Ce sulfure coexiste en équilibre à 600° soit avec le sulfure Ni_3S_2 (côté pauvre en soufre) soit avec le sulfure NiS_2 (côté riche en soufre). L'étude du domaine de variation de composition de cette phase peut se faire en partant d'un mélange $NiS_2 + NiS$ en équilibre avec une atmosphère H_2S/H_2 à cette température. Si l'on soustrait périodiquement de l'hydrogène sulfuré de la phase gazeuse, en mesurant après chaque soustraction la valeur du rapport pH_2S/pH_2 après rétablissement de l'équilibre, on obtient une courbe présentant la forme indiquée schématiquement dans la figure 1. La portion oblique correspond au domaine de variation continue de la composition de NiS dans lequel le système est monovariant à température et à pression données. Les limites de ce domaine correspondent aux abcisses des points anguleux de la courbe dont les valeurs sont en principe faciles à déterminer si l'on connaît la composition initiale du système et les quantités d'hydrogène sulfuré soustraites. Avec un composé rigoureusement stoechiométrique le passage d'un palier à l'autre s'effectuerait au contraire par une discontinuité verticale. Le danger de ce procédé réside dans le fait que la lenteur de la diffusion dans la masse solide tend à arrondir les courbes aux environs des points anguleux et peut laisser croire à une étendue du domaine monophasé plus grande qu'elle n'est réellement. En fait, il est très difficile de conclure par cette méthode à l'existence de domaines monophasés dont l'étendue est inférieure à 1 %. Pour ces derniers, la seule solution est de suivre les variations d'une grandeur physique liée à la concentration : point de Curie pour les ferromagnétiques, conductibilité électrique, etc. La sensibilité des variations de la conductibilité électrique est parfois considérable et a conduit à présumer de l'existence des variations de composition inappréciable par les méthodes chimiques classiques; elle offre toutefois l'inconvénient de ne pouvoir être rattachée directement à l'échelle des

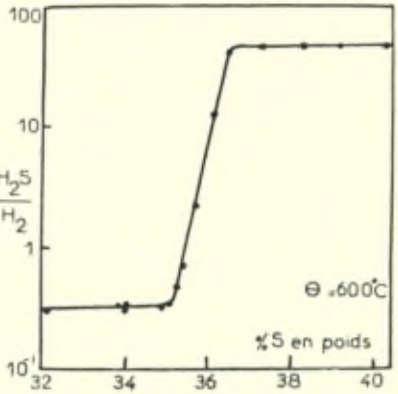


Figure 1. Equilibres de NiS avec les mélanges $H_2 + H_2S$ d'après Rosenqvist.

concentrations; de plus, comme toutes les méthodes très sensibles, elle peut être troublée par des facteurs secondaires difficiles à apprécier (impuretés, état de cristallisation, etc.).

A côté des méthodes qui se proposent de déceler l'étendue des variations de composition, il faut mentionner celles qui permettent d'identifier la nature des défauts de réseau qui en sont responsables. La densité tout d'abord qui, jointe à la mesure des paramètres cristallins, permet lorsqu'elle est mesurée avec précision de décider si la variation de la concentration est due à une soustraction d'atomes ou à une insertion d'atomes supplémentaires dans le réseau. Il convient toutefois de n'user qu'avec circonspection de l'argument densité, lorsqu'il s'agit de conclure comme l'ont fait certains auteurs à la présence d'une certaine proportion de défauts dans un composé rigoureusement stoechiométrique, en comparant les valeurs des densités déterminées expérimentalement à celles que l'on peut calculer à partir des dimensions de la maille cristalline. En ce qui concerne la polarité des défauts, la conductibilité électrique, le pouvoir thermoélectrique, et surtout l'effet Hall donnent des informations intéressantes. Plus récemment ont été mises à profit les méthodes magnétiques et la spectroscopie d'absorption pour l'étude des états électroniques des ions en présence.

DONNÉES GÉNÉRALES SUR LES DÉFAUTS DE RÉSEAU

Les interprétations, auxquelles on fait actuellement appel pour expliquer les variations de composition des phases ioniques non stoechiométriques, ont trouvé leur origine dans la théorie des défauts dans les composés stoechiométriques, qui fut édifiée jadis par Frenkel (49), Wagner et Schottky (50–51). Cette théorie a été maintes fois décrite depuis et il ne saurait être question de l'analyser ici dans tous ses détails. Nous retiendrons seulement pour clarifier la discussion qui va suivre qu'elle postule l'existence de deux sortes de défauts:

1° Un ion occupant initialement un site cristallographique normal peut venir occuper une position interstitielle normalement inoccupée dans le réseau idéal, en faisant apparaître une lacune réticulaire;

2° Un ion occupant initialement un site cristallographique normal peut venir occuper une position réticulaire normale, à la surface du solide, en faisant apparaître une lacune réticulaire comme dans le cas précédent.

Alors que le premier type de défaut ne peut en aucun cas entraîner un changement de composition, le second type de défaut ne répond à cette condition que s'il affecte en nombre égal les cations et les anions.

L'existence de ces deux catégories de défauts dans des composés qui doivent être considérés, d'après les critères de la chimie classique, comme des composés strictement stoechiométriques, est demeurée pendant de nombreuses années hypothétique. Le développement des recherches sur la conductibilité ionique des halogénures alcalins et la comparaison des résultats ainsi obtenus avec ceux de l'autodiffusion des éléments marqués dans ces composés ([53-54]) a conduit à en confirmer l'existence. L'argument essentiel réside en effet dans l'impossibilité où l'on se trouverait d'expliquer, dans l'hypothèse d'un réseau complet, les énergies d'activation de diffusion relativement peu élevées que l'on mesure. Bien que l'idée jadis émise par Smekal selon laquelle les migrations ioniques s'opéreraient grâce à la présence des défauts mosaïques des cristaux, ait bénéficié depuis quelques années d'un regain d'actualité à la suite du succès de la théorie des dislocations, rien n'indique qu'un changement des conceptions fondamentales soit à la veille de se produire dans ce domaine. Si l'on considère d'autre part qu'à une température donnée un cristal stoechiométrique en équilibre avec une atmosphère de composition déterminée comporte un certain nombre de défauts de chaque sorte, on peut admettre qu'il existe à l'intérieur du solide un équilibre entre les différentes catégories de défauts.

Comme les énergies de formation des différentes catégories de défauts sont inégales, l'une d'elles prédomine généralement dans un édifice cristallin déterminé à une température donnée. Les défauts de Schottky se forment de préférence dans les solides dans lesquels les ions antagonistes ont des dimensions voisines et l'énergie de Van der Waals peu élevée. Ces deux conditions se trouvent réalisées dans un certain nombre d'halogénures alcalins. Les défauts de Frenkel sont au contraire plus fréquents dans les solides présentant une grande disparité dans les dimensions des ions et mettant en jeu une énergie de Van der Waals importante. Différentes tentatives ont été faites pour calculer *a priori* les énergies de formation des défauts dans un réseau idéal ([55-56-57]). On a pu atteindre ainsi des ordres de grandeur dans le cas de formation des lacunes au sein d'un réseau simple.

mais il n'existe aucune méthode qui permette d'évaluer l'énergie de formation des défauts interstitiels.

A la lumière de ce qui précède la conception que l'on peut se faire des causes des variations progressives de la composition chimique d'un composé ionique binaire non stoechiométrique AB peut donc se ramener aux quatre mécanismes suivants :

1° Insertion d'atomes A supplémentaires dans le réseau de AB supposé complet;

2° Soustraction d'atomes B non compensée par celle d'un nombre égal d'atomes A;

3° Insertion d'atomes B supplémentaires;

4° Soustraction d'atomes A non compensée par celle d'un nombre égal d'atomes B.

Il convient de noter que les possibilités d'insertion et de soustraction posent des problèmes entièrement différents suivant qu'il s'agit de cations ou d'anions. Ce point marque la différence essentielle qui distingue les composés non stoechiométriques ioniques des composés intermétalliques dans lesquels les deux types d'atomes possèdent des électronégativités voisines et peuvent, de ce fait, être aisément permutés. On remarquera en particulier que nous avons éliminé *a priori* dans le cas présent la cause de variation de composition qui correspondrait à une substitution de A à B ou de B à A, une telle opération étant irréalisable dans un composé à liaison ionique marquée.

CONSTITUTION ELECTRONIQUE DES COMPOSÉS IONIQUES NON STOECHIOMÉTRIQUES

Les différents mécanismes qui viennent d'être envisagés comportent un certain nombre de conséquences d'ordre électronique, géométrique et thermodynamique. Nous examinerons tout d'abord l'aspect électronique du problème.

Considérons en premier lieu le cas le plus fréquent d'une soustraction de cations dans le réseau cristallin. Cette soustraction se traduit du point de vue de la composition chimique, par un accroissement de la teneur en l'élément non métallique au delà de la composition théorique qui correspond à l'occupation complète de tous les nœuds du réseau. Afin que soit maintenue la neutralité électrostatique de l'édifice, il est nécessaire qu'un certain nombre d'entre les ions restants modifient leur charge en conséquence. Ce résultat pourrait être atteint en principe aussi bien par une diminution de la charge négative des anions que par un accroissement de la charge positive des cations. La première solution n'est pas à envisager dans les halogénures, oxydes et sulfures métalliques parmi lesquels se rangent la plupart des composés non stoechiométriques. Reste la seconde qui est effectivement observée dans la plupart des oxydes des métaux de transition dans lesquels le métal ne se trouve pas à l'état de valence électropositive maximum. L'un des exemples les plus connus est celui de l'oxyde FeO dont le domaine de composition peut s'étendre jusqu'à $FeO_{1,19}$ à la température de 1.000° ([15a]). Jette et Foote ([15b]) furent les premiers à suggérer que pour chaque ion Fe^{2+} soustrait du réseau cristallin de FeO, deux ions Fe^{3+} devaient apparaître. Un peu plus tard cette hypothèse fut utilisée par Hägg pour expliquer la formation de $Fe_2O_3\gamma$ par soustraction d'ions Fe^{2+} dans le réseau de Fe_3O_4 avec passage simultané d'un nombre double d'ions Fe^{2+} à l'état de Fe^{3+} ([16]). Depuis lors, nombreux sont les exemples qui ont été cités de composés qui seraient le siège d'un équilibre ionique analogue. Dans tous ces cas l'écart à la stoechiométrie ne se manifeste, comme il est normal de le prévoir, que dans le sens correspondant à un excès du constituant non métallique. On pourrait citer à l'encontre de cette règle le cas des monoxydes de certains métaux à valence élevée parmi lesquels TiO, ZrO, VO, qui peuvent comporter des variations de composition correspondant à un excès de métal; nous verrons plus loin cependant qu'il s'agit de composés dans lesquels les configurations électroniques sont entièrement différentes de celles que l'on rencontre dans les oxydes supérieurs correspondants (TiO_2, ZrO_2, VO_2). La même remarque vaudrait pour de nombreux sous-sulfures des métaux de transition, parmi lesquels on peut citer la phase non stoechiométrique Ni_3S_2.

Le fait que la réalisation de ce type de défaut soit subordonnée à l'existence d'un état stable de valence supérieure du cation constitue, sur le plan des propriétés chimiques usuelles, l'expression d'une condition plus générale à savoir la possibilité pour celui-ci d'atteindre un état d'ionisation supérieur en ne mettant en jeu qu'une énergie minime. Cette condition est réalisée pour la plupart des éléments de transition dont les énergies d'ionisation successives ne sont pas extrêmement différentes. De ce point de vue il n'est nullement nécessaire que l'état d'ionisation impliqué dans la phase non stoechiométrique corresponde à un état de valence du métal apparaissant dans l'une de ses combinaisons stables. C'est ainsi que l'enrichissement en oxygène de la phase NiO entraîne l'apparition d'ions Ni^{3+} auxquels ne correspond semble-t-il aucun composé ionique connu.

On a supposé qu'un enrichissement en constituant non métallique pouvait encore se produire, à une échelle il est vrai beaucoup plus réduite, dans des composés comportant des cations qui ne possèdent pas la même aptitude à changer de valence. Tels sont les halogénures alcalins qui semblent pouvoir tolérer dans le réseau un très léger excès d'halogène. Il ne semble pas à vrai dire que la variation de composition correspondante ait pu être déterminée dans ce cas et seules les variations des propriétés physiques sont là pour en témoigner (58). Ceci nous amène à poser la question de savoir dans quelle mesure il existe une relation entre l'énergie qu'il faut mettre en jeu pour changer l'état d'ionisation des cations et l'étendue des domaines de variation de composition dans les composés non stoechiométriques à lacunes cationiques. L'exemple des halogénures alcalins, dans lesquels une énergie d'ionisation élevée se trouve associée à un domaine de variation de composition extrêmement faible, serait en faveur d'une telle relation mais, hormis ces cas extrêmes, il ne semble pas possible d'en confirmer l'existence. Le changement de l'état d'ionisation du cation constitue en effet une condition nécessaire mais non suffisante à l'existence d'une variation de composition selon le processus examiné ici, et d'autres facteurs parmi lesquels les interactions de défauts et les facteurs d'ordre géométrique doivent être pris en considération.

Bien que l'étude des propriétés physiques ne puisse être approfondie ici, il est intéressant de noter au passage que les composés non stoechiométriques à lacunes cationiques sont des semi-conducteurs du type *p*, dans lesquels la conductibilité est assurée par les trous positifs et croît avec la pression partielle de l'élément non métallique en équilibre avec le solide. Des études très complètes ont été faites d'autre part concernant l'incidence d'un excès d'halogène sur les spectres d'absorption des halogénures alcalins; des bandes apparaissent en particulier, dans le proche ultra-violet.

L'existence des écarts à la stoechiométrie par suite de la soustraction des anions a été reconnue plus tardivement que l'existence des écarts dus à la soustraction des cations. Du point de vue de l'équilibre électrostatique, la soustraction des anions exige en principe le passage d'un certain nombre de cations restants à un état inférieur de valence électropositive. Il y a lieu de prévoir que ce mécanisme doit apparaître en particulier dans les composés qui correspondent à la valence ionique la plus élevée d'un métal possédant plusieurs états de valence. Tel est le cas des dioxydes des métaux tétravalents : TiO_2, MnO_2, CeO_2, entre autres, qui peuvent perdre une partie de leur oxygène lorsqu'ils sont portés sous vide aux températures élevées ou traités en atmosphère réductrice. Ainsi le dioxyde de titane stoechiométrique qui est blanc lorsqu'il est chauffé aux températures moyennes en atmosphère fortement oxydante, perd de l'oxygène lorsqu'il est chauffé en atmosphère réductrice. La variation de composition qui en résulte conduit à la valeur limite $TiO_{1,9}$ (3); elle s'accompagne d'un accroissement considérable de la conductibilité électrique et d'un changement de teinte (passage au bleu-noir). Dans le cas du dioxyde de manganèse (14) la perte d'oxygène conduit à la composition limite $MnO_{1,8}$; dans le cas du dioxyde de cérium (32-33) jusqu'à la valeur limite $CeO_{1,5}$. Dans tous ces exemples on admet que la perte d'oxygène entraîne l'apparition de sites inoccupés dans le réseau des anions, un certain nombre d'ions tétravalents passant à l'état trivalent.

Les oxydes supérieurs des métaux de transition dont la valence maximum n'excède pas III semblent beaucoup moins sujets aux variations de composition par perte d'anions. Par exemple, le sesquioxyde de fer sous sa forme stable rhomboédrique présente des variations de composition qui exercent une certaine influence sur les propriétés physiques, et en particulier sur les propriétés magnétiques, mais qui sont difficilement appréciables par les méthodes chimiques.

La présence d'un excès de constituant métallique explicable par la présence d'un réseau anionique lacunaire ne se limite pas exclusivement aux composés de métaux de transition. Le cas de l'oxyde de baryum est instructif à cet égard. Chauffé à 1.000° dans la vapeur de baryum cet oxyde acquiert une teinte bleue (31). L'étude de la diffusion thermique de cette coloration conduit à un coefficient de diffusion très différent de celui de baryum dans BaO (59), ce qui laisse à penser qu'elle n'est pas due à la diffusion d'ions baryum. Les défauts résultant du traitement dans la vapeur de baryum seraient donc vraisemblablement des lacunes d'oxygène. La détermination de l'excès de baryum par la voie chimique conduit à 0,04 % Ba dans les oxydes traités à 1.100°. Il n'est pas surprenant que l'étendue du domaine de variation de la composition observée ici soit très inférieure à celle que l'on peut observer dans les composés des métaux qui se prêtent à un changement facile de valence. Le mécanisme de compensation électrostatique ne saurait être en effet ici le même puisque le baryum ne possède qu'une seule valence ionique stable. Il faut donc admettre qu'en présence de vapeur de baryum à haute température certains ions O^{2-} du réseau cristallin intérieur se portent vers la surface. Chaque fois qu'un atome de baryum supplémentaire issu de la phase vapeur s'agrège à la surface de l'oxyde après ionisation, un ion oxygène de l'intérieur du réseau migre à la surface en faisant apparaître une lacune anionique dans laquelle les deux électrons provenant de l'ionisation de l'atome de baryum sont captés. C'est à la présence de ces électrons dans les lacunes anioniques que serait due l'apparition d'une bande d'absorption dans le visible.

Cette conception due à Sproull, Bever et Libowitz ([31]) montre que la diminution de charge électropositive des cations restants n'est pas la seule voie par laquelle un composé ionique peut tolérer un accroissement de la teneur en métal. La différence entre les deux processus réside essentiellement dans le fait que dans l'un (cations à valence variable) les électrons provenant de l'ionisation des atomes métalliques supplémentaires sont captés par certains cations, tandis que dans l'autre (cations à valence fixe) les électrons viennent se fixer dans les lacunes du réseau anionique. Bien que dans ce dernier cas la présence des électrons dans les lacunes assure à celles-ci une relative stabilité, les variations de composition qui en résultent sont toujours de faible amplitude. Ce mécanisme est identique à celui qui est admis pour expliquer les colorations prises par certains halogénures alcalins chauffés dans la vapeur du métal correspondant ([60-61-62]). Par exemple, le chlorure de potassium chauffé vers 500° dans la vapeur de potassium devient violet par suite de la formation de lacunes anioniques occupées par les électrons (centres F) provenant de l'ionisation d'atomes de potassium supplémentaires fixés à la surface. Les variations de composition correspondantes sont toutefois trop faibles pour être perceptibles par l'analyse chimique, aussi ne nous étendrons-nous pas sur cette question si importante à d'autres égards.

La formation des lacunes ioniques occupées par des électrons, qui provoque l'apparition des bandes d'absorption dans le visible fait également apparaître des propriétés électriques entièrement différentes de celles du composé stoechiométrique. Si l'extraction des électrons des lacunes a lieu spontanément à température peu élevée, le solide est semi-conducteur avec un coefficient de température positif. Un grand nombre de phases non stoechiométriques, isolantes à la température ordinaire, acquièrent par ce mécanisme une conductibilité électronique appréciable lorsque la température s'élève, alors que les phases stoechiométriques correspondantes demeurent d'excellents isolants dans les mêmes conditions. L'extraction des électrons des lacunes anioniques peut également se produire par absorption d'énergie lumineuse et le composé non stoechiométrique manifeste alors la propriété de photo-conductivité.

Les variations de composition résultant de l'insertion d'ions supplémentaires dans les intervalles d'un réseau cristallin sont beaucoup moins fréquentes que celles qui résultent de la soutraction de certains ions.

Si l'on s'astreint à ne considérer comme nous l'avons fait jusqu'ici que les combinaisons binaires dans lesquelles la liaison possède un certain caractère ionique, c'est-à-dire si on élimine d'une part les hydrures, borures, carbures et nitrures des métaux de transition et d'autre part les composés d'insertion moléculaires, le nombre des composés non stoechiométriques interstitiels s'avère singulièrement réduit. L'insertion des anions autres que ceux qui viennent d'être cités est en effet peu probable si l'on tient compte du volume relativement élevé de la plupart d'entre eux. Seules ont été en fait observées quelques insertions de cations, n'entraînant d'ailleurs que des variations de concentration très minimes.

Un bon exemple en est donné par l'oxyde de zinc, qui est susceptible de dissoudre une petite quantité de zinc; on admet généralement que le zinc en excès se trouve en position interstitielle dans le réseau hexagonal de ZnO. Cette hypothèse, préférée à celle qui consisterait à attribuer la présence d'un excès de zinc à des lacunes d'oxygène, est fondée à la fois sur les études de structure ([30-63]) et sur les études de diffusion du zinc radioactif dans l'oxyde (64,65). Les écarts à la stoechiométrie entraînent l'apparition dans l'oxyde d'une conductibilité électronique élevée de type *n*, qui témoigne de l'état au moins partiellement ionisé des atomes de zinc en insertion. Les variations de la conductibilité électrique en fonction de la température et de la pression partielle d'oxygène qui règne au-dessus de l'oxyde ont fait l'objet de très nombreuses études mais il ne semble pas que l'étendue du domaine de variation de la concentration ait été déterminée avec certitude. L'existence de phases analogues semble avoir été également démontrée dans le cas de l'oxyde de cadmium et de l'oxyde d'argent (30) par des études de structure. Dans le cas de l'oxyde de cadmium la proportion des ions Cd^{2+} s'élèverait à 0,5 % de la masse de l'oxyde. La variation de composition serait plus importante dans le cas de l'oxyde d'argent et égale à 4 % à 200°.

La première remarque suggérée par l'étude de ces résultats est la faible étendue des variations de composition qui en résultent. Ceci est dû vraisemblablement aux énergies de répulsion élevée qui se manifestent dans le réseau à la suite de l'introduction des atomes interstitiels; dès que le nombre de défauts atteint une valeur même peu élevée, ceux-ci tendent à s'associer pour reconstituer la phase métallique après avoir récupéré les électrons cédés au moins partiellement à l'oxyde. La seconde remarque, corollaire de la précédente, concerne le fait que les trois exemples cités ici, qui sont véritablement les seuls à propos desquels on puisse parler avec quelque certitude d'insertion, se rapportent à des combinaisons dans lesquelles le cation (Zn^{2+}, Cd^{2+}, Ag^{+}) a la structure électronique à 18 électrons externes. On sait que ces ions sont extrêmement favorables au développement des forces de polarisation. L'insertion des ions supplémentaires serait donc rendue possible par la déformation des ions contigus.

Du point de vue de la chimie descriptive, l'existence de ces phases résoud d'une manière semble-t-il définitive la question des sous-oxydes de zinc, cadmium et argent dont on avait jadis admis l'existence. Les changements de teinte que l'on observe lorsque les oxydes normaux se trouvent en présence d'un excès de métal et qui avaient contribué pour une grande part à affirmer cette existence résultent simplement du déplacement des bandes d'absorption propres à l'oxyde stoechiométrique vers le visible par suite de l'introduction des défauts de réseau.

Avant de passer à l'étude géométrique de ces problèmes, il est nécessaire de faire remarquer que de nombreux écarts à la stoechiométrie ont été signalés dans la littérature sur la foi d'arguments indirects, parmi lesquels la variation de la conductibilité en présence d'un excès de l'un ou l'autre des éléments constitutifs est le plus souvent invoquée. Nous n'en ferons pas état ici pour rester fidèle à la règle que nous nous sommes imposée dans ce rapport de ne tenir compte que des systèmes dans lesquels l'existence d'une variation de composition a été démontrée par voie chimique. Il est hors de doute cependant que ces composés sont pour la plupart le siège de processus similaires à ceux que nous venons d'étudier. Seule la faible importance des variations de composition n'a pas permis encore de la confirmer et il serait souhaitable que des efforts soient faits pour mettre au point des méthodes microanalytiques appropriées à la résolution de ce genre de problème.

INCIDENCE DES VARIATIONS DE COMPOSITION SUR LA STRUCTURE

L'existence de variations de la composition chimique dans les composés ioniques ne soulève pas seulement des problèmes d'équilibre électronique. Les différents processus que nous avons envisagés pour expliquer ces variations de composition supposent en effet des réorganisations dans la nature et les positions des ions qui doivent être discutées du point de vue de la structure. Cette discussion se fonde actuellement sur deux ordres de renseignements : les résultats de l'analyse de structure par les rayons X et les mesures de densité.

Nous examinerons tout d'abord l'incidence des processus de formation de lacunes ou d'insertion sur les constantes cristallines. La présence d'un excès de l'un des constituants dans un composé ionique se traduit suivant les cas par un accroissement ou par une diminution du volume de la maille cristalline. On a toujours admis, jusqu'à maintenant, que l'accroissement du volume de la maille constituait une preuve de la position interstitielle des atomes en excès, tandis que la diminution du volume correspondait à la formation de lacunes. Il paraît certain que l'introduction d'atomes plus ou moins ionisés dans des interstices dont les dimensions sont insuffisantes pour leur faire place sans déformer les atomes contigus, entraine un accroissement des forces de répulsion qui doit provoquer un accroissement du volume de la maille cristalline. On trouvera dans la figure 2 la variation de la maille de l'oxyde de cadmium en fonction de la quantité de cadmium en excès dans le réseau. Les solutions interstitielles à caractère métallique ont aussi un volume de maille croissant en fonction de la teneur en élément supplémentaire, mais l'étendue des domaines homogènes est généralement plus grande dans ces systèmes.

Dans le cas des variations de composition par formation de lacunes, la diminution du volume de la maille est parfois importante (fig. 2). Il a été jusqu'à maintenant impossible d'établir une corrélation entre

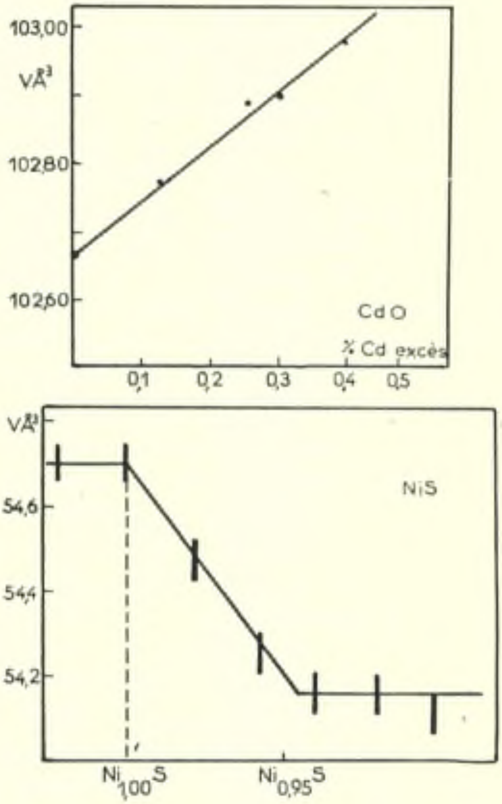


Figure 2. Variation du volume de la maille en fonction de la composition :
CdO d'après Faivre NiS d'après M. Laffitte et Bénard

les variations du volume de la maille et les rayons des ions soustraits, car de nombreux facteurs influent sur cette variation : énergie de réseau du composé à l'état stoechiométrique, changement de dimension des ions ayant été amenés à changer de valence, polarisation des ions.

L'incidence des variations de la composition des composés non stoechiométriques sur leur densité dépend elle aussi de la nautre du processus mis en jeu. Si la variation du rapport du nombre des anions à celui des cations n'entraînait aucune variation du volume de la maille, toute insertion s'accompagnerait d'une augmentation de la densité et toute soustraction d'une diminution de celle-ci. Mais les paramètres cristallins varient, de sorte qu'il faut tenir compte de cette variation pour décider de la nature des défauts du réseau d'après l'étude de la variation de la densité. En fait les insertions s'accompagnent toujours d'un accroissement de la densité, accroissement d'ailleurs minime si l'on tient compte de la faible étendue des domaines correspondants, tandis que la formation des lacunes peut entraîner suivant les cas une diminution ou un accroissement de la densité. La comparaison des variations de la densité mesurée et des variations calculées dans l'une ou l'autre hypothèse fournit donc en principe un critère de la nature des défauts de réseau responsables de la variation de composition. Ce critère a été fréquemment utilisé, mais pas toujours semble-t-il avec toute la prudence désirable. On sait, en effet, combien l'obtention de chiffres de densité ayant une réelle signification est difficile, et combien leur interprétation peut donner lieu à des erreurs. La technique de mesure semble autoriser une précision correspondant à quelques unités de la troisième décimale sous réserve de prendre les précautions d'usage : élimination préalable des gaz adsorbés et remplissage sous vide du vase pycnométrique en particulier. Mais les valeurs ainsi obtenues sont fonction de la température à laquelle a été préparé le solide, la densité étant d'autant plus élevée que la température de préparation est elle-même plus élevée. Il en résulte que les valeurs de densité ainsi obtenues sont très souvent inférieures, dans le cas du composé strictement stoechiométrique, à la densité calculée. On a reproduit dans la figure 3 quelques courbes de variations de la densité en fonction de la composition qui ont permis de décider de la nature des défauts dans des cas aujourd'hui classiques. On voit d'après ces exemples que si les valeurs absolues de la densité n'ont pas toujours une signification

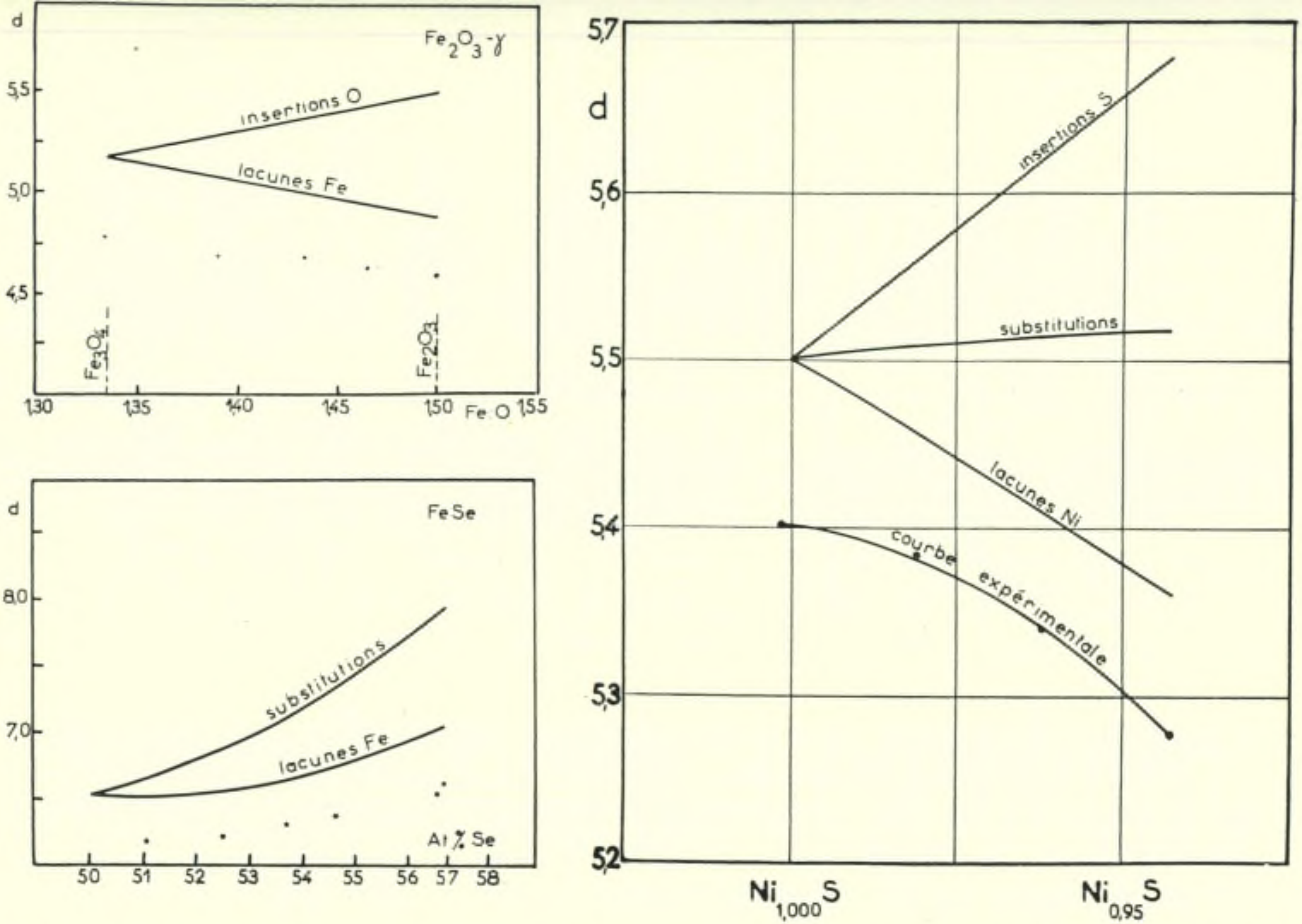


Figure 3. Variation de la densité en fonction de la composition: $Fe_2O_3\gamma$ d'après Hägg; FeSe d'après Hägg et Kindström; NiS d'après M. Laffitte et Bénard

indiscutable, le sens de la variation de la densité en fonction de la composition est généralement significatif si les échantillons comparés ont été préparés à la même température. En fait tous les cas dans lesquels l'argument densité a été décisif sont des cas de formation de lacunes qui sont les seuls à donner lieu à des variations de concentration relativement importantes et par conséquent à des variations de densité également importantes.

L'existence fréquente des écarts de densité par défaut dans les composés stoechiométriques eux-mêmes pose un problème qui mériterait d'être discuté. Ces écarts sont souvent dus, lorsque le solide a été préparé à une température relativement peu élevée par rapport à sa température de fusion, à des imperfections de cristallisation. Ces imperfections disparaissent parfois lorsque la température augmente, mais il y a des cas où la densité théorique n'est jamais atteinte. De là a attribuer l'écart de densité du composé stoechiométrique à la présence d'une proportion déterminée de lacunes ioniques des deux espèces il n'y a qu'un pas qui a été franchi par différents auteurs. L'exemple le plus caractéristique a été fourni par Ehrlich (3) à propos de l'oxyde TiO dans lequel il y aurait à la composition stoechiométrique 15 % environ de lacunes de chaque sorte, et des interprétations analogues ont été produites pour les oxydes similaires comme VO. Il y a lieu de noter toutefois que ces composés possèdent un type de liaison particulier, fort éloigné de la liaison ionique et l'on ne connaît en fait aucun exemple de composé purement ionique possédant un nombre aussi grand de lacunes symétriques.

ECARTS A LA STOECHIOMÉTRIE PAR SUBSTITUTION D'IONS DE VALENCE DIFFERENTE

Nous avons vu que la variation de composition dans une phase non stoechiométrique binaire s'accompagnait le plus souvent d'un changement de valence de certains cations restants. Il a été reconnu qu'inversement le remplacement progressif des ions du réseau normal par des ions étrangers possédant une valence fixe différente de celle des ions auxquels il se substituent, provoquait l'apparition d'écarts à la stoechiométrie grâce à la stabilisation d'un certain nombre de défauts de réseau. Nous nous bornerons à citer ici quelques cas typiques qui illustrent les différentes possibilités offertes par ces substitutions.

Zintl, Croatto et Hund ont montré par de nombreux travaux l'extraordinaire aptitude des réseaux cristallins du type fluorure de calcium à subir une variation du nombre des cations lorsqu'on remplace les cations du composé stoechiométrique par des cations de valence différente. Deux sortes de variations sont à envisager :

a) Lorsque les cations du réseau stoechiométrique normal sont remplacés par des ions de valence inférieure, la compensation des charges à lieu par la formation d'un certain nombre de lacunes dans le réseau anionique.

Tel est le cas des phases mixtes qui se forment dans les systèmes ZrO_2-CaO (66), ZrO_2-Y_2O_3 (67), UO_2-Y_2O_3 (68), CeO_2-La_2O_3 (69), ThO_2-La_2O_3 (70). On aura une idée de l'étendue des variations de composition qui peuvent être réalisées de cette façon en examinant le dernier cité de ces systèmes qui présente un domaine homogène jusqu'à la composition $ThLaO_{3,5}$ correspondant au remplacement de la moitié des ions Th^{4+} de ThO_2 par des ions La^{3+}, et à l'absence d'un ion O^{2-} sur quatre initialement contenus dans ThO_2.

b) Lorsque les cations du réseau stoechiométrique normal sont remplacés par des ions de valence supérieure, la compensation des charges a lieu par insertion d'un certain nombre d'anions supplémentaires dans les positions disponibles (4 par maille élémentaire) du réseau. Tel est le cas du système CaF_2-YF_3 dans lequel chaque substitution de Y^{3+} à Ca^{2+} entraîne l'insertion d'un ion F^- supplémentaire (71). Le même processus entre en jeu dans le système CaF_2-LaF_3.

Ces opérations sont rendues possibles grâce à la similitude des ions échangés, qui permet l'introduction massive des cations étrangers sans apporter de perturbation notable dans la structure. Mais il est hors de doute que la nature du réseau type du fluorure de calcium est pour beaucoup dans cette possibilité de variation du nombre des sites anioniques occupés dans un domaine aussi étendu. Rien ne permet semble-t-il d'expliquer actuellement cette aptitude tout à fait exceptionnelle parmi les composés ioniques. Tout au plus peut elle être comparée par son ampleur à celle que l'on rencontre dans les phases possédant la structure de l'arséniure de nickel (à l'exception de NiAs lui-même) ou au passage de Fe_3O_4 à $Fe_2O_3\gamma$ dans la structure spinelle.

Wagner, Hauffe et leurs collaborateurs ($^{72-73-74-75-76-77}$) ont postulé l'existence de phases non stoechiométriques résultant de substitutions d'ions divalents dans les halogénures des métaux monovalents. Par exemple la substitution d'un ion Cd^{2+} à Ag^+ dans le bromure d'argent entraîne la formation d'une lacune Ag^+; celle de Sr^{2+} à K^+ dans le chlorure de potassium entraîne la formation d'une lacune K^+. L'étendue des phases homogènes non stoechiométriques ainsi obtenues serait assez grande puisque d'après Teltow (^{78}) AgBr dissoudrait à 350° 25 mol % $CdBr_2$, 10 mol % $PbBr_2$ et 1 mol % $ZnBr_2$. L'existence de phases mixtes dont la formation résulterait de ce processus a été admise sur la foi des variations de la conductibilité électrique dans de nombreux autres systèmes. On peut citer dans le même ordre d'idées les phases mixtes intermédiaires entre les ferrites substituées $Fe_2^{3+}(Fe^{2+}, Me^{2+}O_4)$ de structure type spinelle et les oxydes mixtes correspondants dérivés du sesquioxyde γ de fer (^{79}) les phases mixtes entre Fe_2CoO_4 et $Fe_2O_3\gamma$ (^{80}) et celles entre FeO et $FeLiO_2$ (^{81}). Il convient de rappeler enfin que Verwey (^{82}) a été le premier à préconiser la mise à profit des substitutions pour stabiliser dans un édifice ionique une certaine proportion de défauts et obtenir ainsi des propriétés physiques déterminées.

DÉTERMINATION A PRIORI DE L'ÉTENDUE DES DOMAINES

Les bilans d'échanges électroniques qui ont été décrits dans les paragraphes précédents définissent des conditions nécessaires à la réalisation des variations de composition dans les phases non stoechiométriques, mais ne constituent qu'un des aspects de la question. Il est facile de se rendre compte en effet que le nombre maximum de défauts tolérés par un édifice peut accuser des différences considérables d'un système à l'autre sans qu'il soit toujours possible de relier ces différences aux énergies d'ionisation des cations figurant dans cet édifice. Tout au plus est-il possible d'énoncer la proposition suivante : les variations de composition des combinaisons ioniques sont *généralement* favorisées par :

1° Le passage facile des cations d'un état d'ionisation à un autre

2° La polarisabilité élevée des anions, elle-même reliée à leur grand diamètre

3° L'existence de certaines structures parmi lesquelles on peut citer celle de l'arséniure de nickel et celle du fluorure de calcium.

Pour ces raisons les chercheurs se sont orientés simultanément vers une étude globale de l'équilibre des défauts, ne préjugeant en aucune façon de la nature des forces, d'origines multiples qui concourent à l'établissement de cet équilibre et en déterminent les limites.

L'idée centrale est due à Wagner-Schottky ([51]), qui se sont placés dans le cas de solides présentant un nombre de défauts suffisamment petit pour qu'il soit possible de négliger leurs interactions; elle réside dans l'existence d'une relation entre la présence de défauts dans les solides répondant à la composition stoechiométrique (défauts intrinsèques) et l'aptitude de ces derniers à présenter des variations de composition en phase homogène. Il est admis au départ que tout composé ionique solide, stoechiométrique ou non, comporte un certain nombre de défauts qui coexistent en équilibre. La proportion des différents types de défauts qui participent à cet équilibre est fonction de la température et de la composition de l'atmosphère. Le caractère endothermique de la formation des défauts entraîne en l'absence de toute autre cause de variation de leur nombre un accroissement de celui-ci lorsque la température s'élève.

A une température donnée, une variation de la pression partielle du constituant volatil dans l'atmosphère peut provoquer dans certains cas une variation du rapport du nombre des défauts des différentes catégories, c'est-à-dire une variation continue de la composition. L'énergie libre du solide varie de ce fait et passe généralement par un minimum pour une valeur particulière de la composition qui correspond à un état de stabilité maximum. L'énergie mise en jeu dans la formation des défauts étant la même, que ces défauts entraînent ou non une variation de la composition, on conçoit que l'existence de nombreux défauts dans un édifice à rapport stoechiométrique simple soit favorable à l'apparition de variations de composition importantes lorsque les conditions du milieu s'y prêtent. Inversement un édifice dans lequel la répartition des ions est quasi-idéale à la composition stoechiométrique ne doit présenter que des variations de composition insignifiantes. Le calcul, conduit d'après cette idée, permet d'établir la relation qui existe à une température donnée entre la pression partielle p_n du constituant volatil dans l'atmosphère en équilibre avec le solide, (rapportée à la pression partielle p_o en équilibre avec le solide de composition théorique) et les écarts à la composition stoechiométrique exprimés par le nombre n de défauts non compensés. La phase dont la composition est la plus influencée par les variations de pression est celle dont l'état de désordre δ est le plus grand à l'état stoechiométrique (fig. 4).

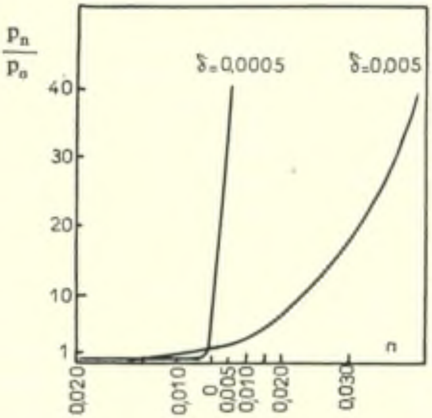


Figure 4 Relation entre les variations de composition et la pression partielle p_n du constituant volatil, pour différents états de désordres intrinsèques δ (d'après Anderson).

L'établissement *a priori* de ces courbes se heurte à de grandes difficultés. Il faudrait en effet connaître au préalable les énergies de formation des lacunes de différents types ainsi que la proportion des défauts intrinsèques de la phase stoechiométrique. Or ni l'une ni l'autre de ces grandeurs ne peut être appréciée d'une façon certaine dans l'état actuel de nos connaissances. Par contre, de telles relations devraient permettre, si elles étaient vérifiées, de déterminer la proportion des défauts dans les phases stoechiométriques d'après le tracé expérimental des courbes de variation de la composition en fonction de p/p_o qui n'offre aucune difficulté

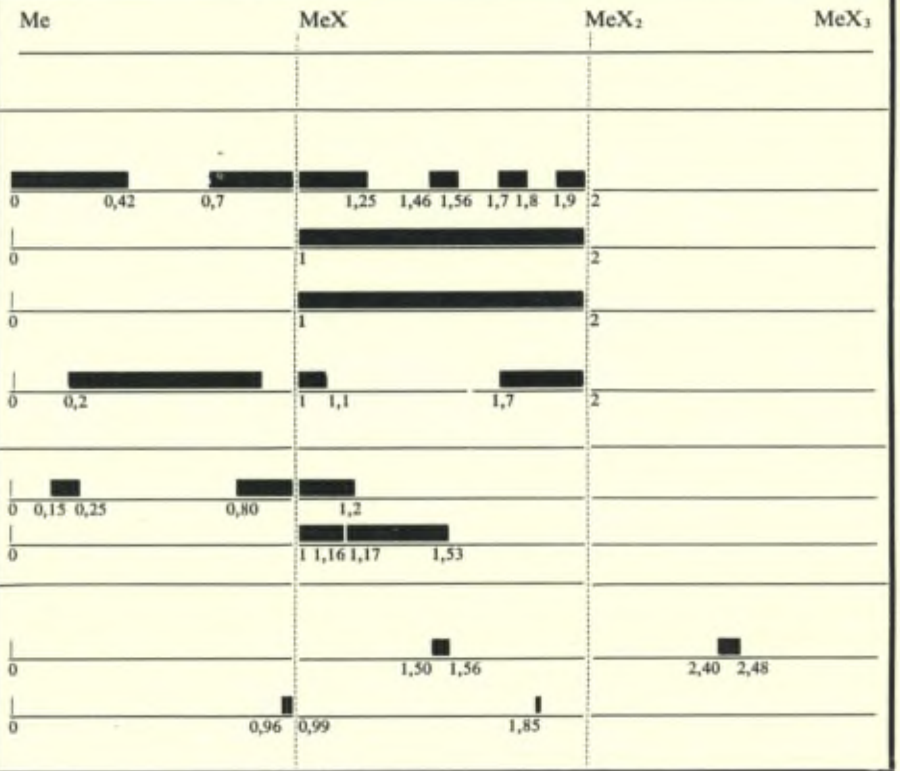
Dans tout ce qui précède les défauts responsables des variations de composition sont supposés en nombre suffisamment petit pour que leurs interactions soient négligeables. Cette hypothèse étant dans bon nombre de cas en contradiction avec les faits, différents auteurs parmi lesquels il faut citer dans l'ordre chronologique : Lacher ([83]), Anderson ([84]) et Rees ([85]), se sont efforcés de transposer le mode de raisonnement précédent en faisant intervenir les interactions entre défauts dans le cadre de la mécanique statistique. Bien que la plupart des exemples envisagés par ces auteurs concernent des phases métal-hydrogène totalement dénuées de caractère ionique, nous croyons nécessaire de mentionner ces tentatives car elles semblent *a priori* pouvoir s'appliquer à tous les systèmes non stoechiométriques.

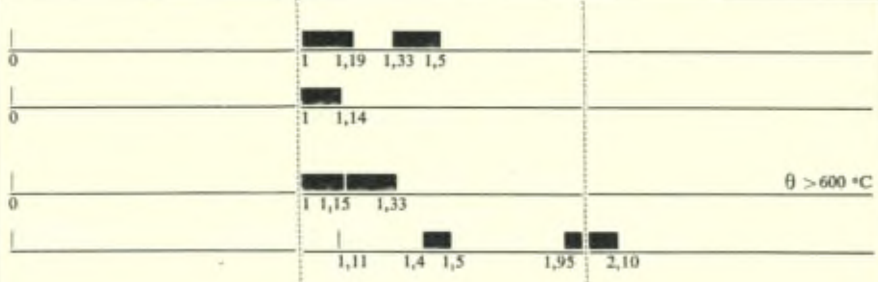
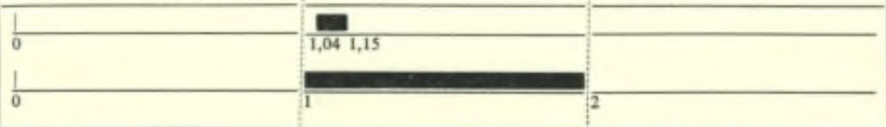
D'après ces auteurs, il est théoriquement possible en introduisant un certain nombre d'hypothèses sur la nature des interactions entre les différents types de défauts, de déterminer les valeurs des concentrations limites au-delà desquelles se produit une ségrégation des défauts avec apparition d'une nouvelle phase. Un excellent accord entre la théorie et les données expérimentales a été obtenu de cette façon par Lacher pour les phases palladium-hydrogène, par Anderson pour les phases platine-soufre et par Rees pour les phases zirconium-hydrogène. En ce qui concerne le dernier de ces systèmes, il paraît toutefois prématuré de considérer l'accord comme définitif, car l'étude expérimentale laisse encore place à bien des incertitudes.

Pour séduisantes que soient ces méthodes d'approche, il ne semble pas cependant qu'elles aient apporté jusqu'à maintenant beaucoup de résultats positifs. Le petit nombre des systèmes dans lesquels leur application a été tentée laisse planer un doute sur leur généralité. Elles n'en constituent pas moins des tentatives intéressantes qui pourront être reprises lorsque nous posséderons plus d'informations sur les caractères thermodynamiques des défauts réticulaires.

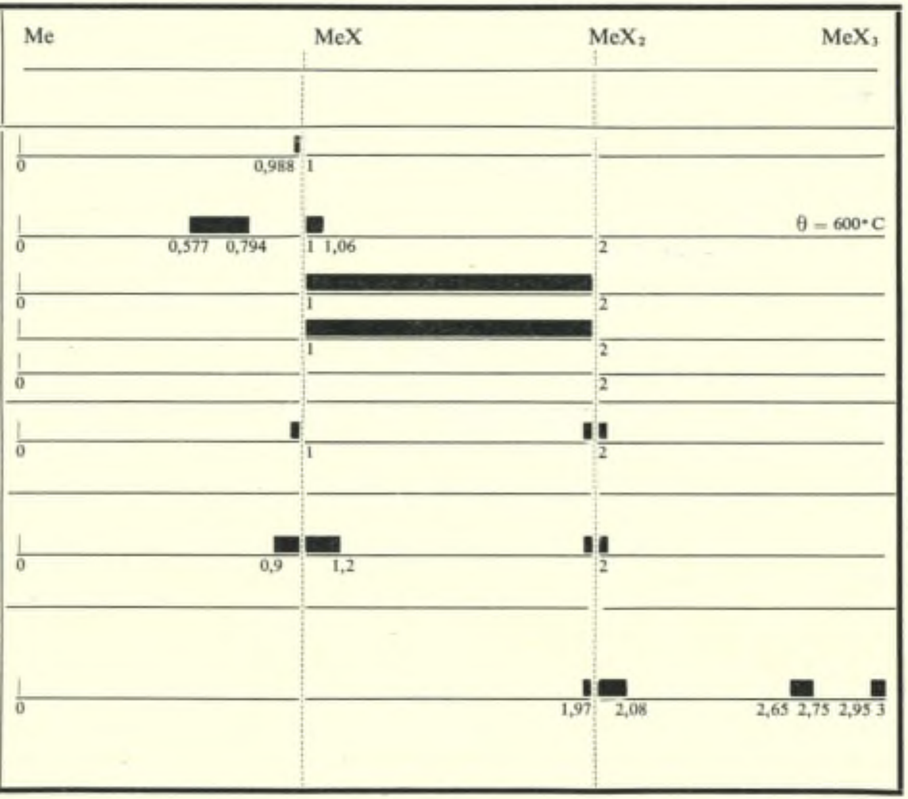
Nous avons attiré l'attention il y a un instant sur l'existence d'un minimum sur les courbes de variation de l'énergie libre d'une phase homogène présentant des variations de composition, en fonction de la composition. Il est logique d'admettre que le plus souvent la position de ce minimum dans l'échelle des concentrations doit correspondre à un rapport stoechiométrique simple puisque c'est pour ce rapport que chaque ion d'une espèce est entouré du nombre maximum d'ions de l'espèce antagoniste. Mais il convient de noter que l'étendue des domaines d'homogénéité de la phase à une température déterminée ne dépend pas exclusivement de la forme de la courbe d'énergie libre de cette phase. En effet, si une courbe d'énergie libre à minimum très accusé correspond nécessairement à un domaine étroit, une courbe à minimum très arrondi ne correspond pas nécessairement à un domaine large. La largeur du domaine est en effet déterminée dans ce second cas par la différence entre l'énergie libre du minimum de la phase considérée et celles des minima des phases adjacentes. On peut comprendre ainsi que dans certains cas le rapport stoechiométrique simple soit exclu du domaine de concentration à l'intérieur duquel la phase peut être observée dans un état stable.

Métal	Composé	Type de structure	Réf.
Ti	TiO	NaCl	(2) (3)
	Ti_2O_3	Cr_2O_3	(3)
	TiO_2	tétragonal	(3)
	TiSe	NiAs	(4)
	$TiSe_2$	CdI_2	(4)
	TiTe	NiAs	(4)
	$TiTe_2$	CdI_2	(4)
	Ti_2S		(5)
	TiS	NiAs	(5) (6)
	TiS_2	$Cd(OH)_2$	(5) (6)
V	$VO_{0,2}$	tétragonal	(7)
	VO	NaCl	(8)
	VS	NiAs	(9) (10)
Cr	$CrO_{2,4}$		(11)
	Cr_2O_3	rhombo-édrique	(12)
	CrSb	NiAs	(13)
	$CrSb_2$	marcassite	(13)

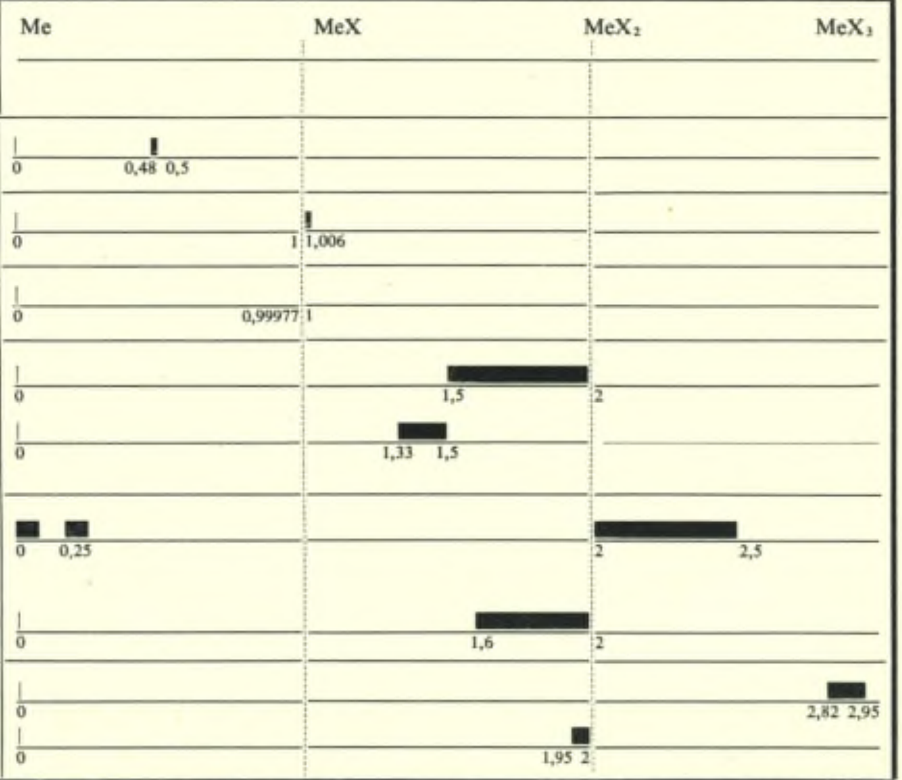


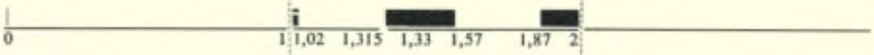
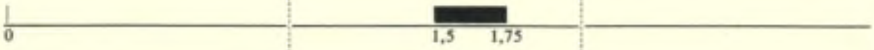
Métal	Composé	Type de structure	Réf.	Me MeX MeX_2 MeX_3
Mn	MnO	NaCl	(14)	
	Mn_3O_4	tétragonal	(14)	
	Mn_2O_3	cubique Tl_2O_3	(14)	
	MnO_2	SnO_2	(14)	
	Mn_2O_7	ortho-rhombique	(14)	
Fe	FeO	NaCl	(15 *a, b*)	
	Fe_3O_4	spinelle	(16)	
	$Fe_2O_3\gamma$	spinelle	(16)	
	FeS	NiAs	(17) (18)	
	FeSe	1-NiAs 2-monoclinique	(19) (20)	
	$Fe_{1-x}Te$	NiAs	(21)	
	$FeTe_{1,11}$	PbO	(21)	
	$FeTe_2$	marcassite	(21)	
Co	CoS	NiAs	(18)	
	CoTe	NiAs	(22)	
	$CoTe_2$	CdI_2	(22)	

Métal	Composé	Type de structure	Réf.
Ni	NiO	NaCl	(23)
	Ni_3S_2	rhomboédrique	(18)
	NiS	NiAs	(18) (24)
	NiS_2	pyrite	
	NiSe	NiAs	(22)
	$NiSe_2$	CdI_2	(22)
	NiTe	NiAs	(22)
	$NiTe_2$	CdI_2	(22) (25)
	NiAs	hexagonal	(26)
Zr	ZrS	AgZr	(6)
	ZrS_2	$Cd(OH)_2$	(6) (27)
Nb	$Nb_{1-x}S$	WC	(6)
	$Nb_{1+x}S$	NiAs	(6)
	NbS_2	$CdCl_2$	(6)
Mo	MoO_2	monoclinique	(28) (29)
	Mo_4O_{11}	orthorhombique	(28) (29)
	MoO_3	orthorhombique	(28) (29)



Métal	Composé	Type de structure	Réf.
Ag	Ag_2O	Cu_2O	(30)
Cd	CdO	NaCl	(30)
Ba	BaO	NaCl	(31)
Ce	Ce_2O_3	cubique	(32) (33)
	CeO_2	cubique	(32) (33)
	Ce_2S_3	Th_3P_4	(34)
	CeS_2	Th_3P_4	(34)
Ta	Ta_4O	ortho-rhombique	(35)
	TaO_2	ortho-rhombique	(35)
	TaS_2	$Cd(OH)_2$	(6)
W	WO_3	mono-clinique	(36) (37)
	WS_2	MoS_2	(38) (39)



Métal	Composé	Type de structure	Réf.	Me MeX MeX_2 MeX_3
Tl	Tl_4S_3		(44)	
Pb	PbO (rouge)	pseudo tétragonal	(41) (42) (43)	
	Pb_3O_4	tétragonal	(42) (43) (44) (45)	
	PbO_2	tétragonal	(42)	
Th	Th_7S_{12}	hexagonal	(46)	
Np	Np_3O_8	U_3O_8	(47)	
	Pu_2O_3	cubique faces centrées	(48)	

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(81) R. Collongues, *C. R. Acad. Sci.*, **231** (1950), p. 143.

(82) E. Verwey & F. Romeyn, *Chem. Weekblad*, **44** (1948), p. 705; E. Verwey, *Bull. Soc. Chim.* (1949), p. D 122; E. Verwey, « Oxidic Semiconductors », Butterworths Scientific Publications Ltd., London (1951), p. 151.

(83) J.R. Lacher, *Proc. Roy. Soc.*, A **161** (1937), p. 525.

(84) J. Anderson, *Proc. Roy. Soc.*, A **185** (1946), p. 69.

(85) A. Rees, *Trans. Farad. Soc.*, **50** (1954), p. 335.

Discussion

M. Timmermans. — Je voudrais soulever une question préjudicielle. Comment distinguer entre les composés non stoechiométriques et des systèmes à cristaux mixtes et où séparer le domaine de ces composés non stoechiométriques de celui des systèmes chimiques en voie d'évolution?

M. Bénard. — A l'origine, la notion de cristaux mixtes reposait essentiellement sur la possibilité que présentent deux phases distinctes de former des phases de compositions intermédiaires et variables, dont la structure est identique à celle des phases constitutives. La plupart des exemples cités étaient en fait des solutions solides de substitution dans lesquelles la variation de composition résultait du remplacement de certains ions du réseau par des ions de même charge. Depuis quelques années, de nombreux exemples de phases à composition variable ont été étudiés, dans lesquels la variation de composition résulte d'opérations plus complexes parmi lesquelles on peut citer en particulier les substitutions d'ions de valence différente (Li^+ substitué à Ni^{2+} dans NiO).

Dans l'état actuel de nos connaissances, il paraît sage de réserver le terme de cristaux mixtes aux phases à composition variable dans lesquelles la variation de composition résulte de la substitution isomorphique d'ions ou de radicaux équivalents, sous réserve que les composés extrêmes soient connus. Nous appellerons, au contraire, composés non stoechiométriques, les phases dans lesquelles on peut provoquer des variations de composition autres que celles qui peuvent résulter d'une simple substitution isomorphique. A cette catégorie appartiennent en particulier les composés ioniques binaires, dans lesquels on provoque une variation progressive du rapport du nombre des anions à celui des cations.

Le terme de solution solide me paraît devoir être employé seulement dans un sens extrêmement général, lorsqu'il n'est pas nécessaire de préciser l'origine des variations de la composition.

Pour ce qui est de la distinction à établir avec les systèmes en voie d'évolution, les composés non stoechiométriques étudiés ici correspondent en principe, à des états d'équilibre. A chaque composition particulière de la phase solide non stoechiométrique, il doit être possible de faire correspondre une atmosphère particulière qui soit en équilibre avec elle. Il est évident que dans bien des cas les études ont été faites sur des systèmes hors d'équilibre en raison de la lenteur des transformations dans le solide.

M. Hägg. — It may be appropriate to mention that cases have been found recently, where phases, which have since long been considered to have extended homogeneity ranges, are represented by a series of discrete phases with fixed compositions and closely related structures.

In the system V — O, Anderson has found a series of phases with compositions VO_x where $x = 1.67$, 1.75, 1.80, 1.84, 1.86, 1.87. All these phases have been previously considered to belong to an extended VO_2 phase. It is possible that they have have the general formule V_nO_{2n-1} ($n = 3$-8) and that their structure is related to the ideal VO_2 structure in principally the same way as the structures of the phases Me_nO_{3n-1} found by Magnéli in the system Mo — W — O, are related to the ReO_3 structure (the molybdenum oxides Mo_8O_{23} and Mo_9O_{26} are members of this series).

Unpublished experiments show that an analogous sequence of phases exists in the system TiO at oxygen contents closely below the composition TiO_2. The appearance of these phenomena seems to be connected with the pronounced tendencies of the central atoms to coordinate six oxygen atoms independent of charge variations.

M. Bénard. — Les observations rapportées par le Professeur Hägg sont extrêmement intéressantes et soulèvent un problème très général. Il est hors de doute que certains systèmes non stoechiométriques manifestent une tendance très marquée à se résoudre en phases distinctes dont les compositions sont apparemment très voisines. Aux exemples cités par l'auteur, j'ajouterai celui du système uranium-oxygène, dans lequel un certain nombre de phases distinctes ont été signalées entre l'oxyde UO_2 et l'oxyde UO_3. La question se pose toutefois de savoir s'il s'agit de véritables combinaisons définies excluant la possibilité d'existence de phases intermédiaires et excluant par conséquent l'idée même d'une continuité possible dans l'échelle des compositions, ou au contraire de compositions particulières dans la série des phases homogènes, compositions dont la stabilité serait légèrement supérieure à celle des phases de composition voisine. Nous avons en effet eu l'occasion fréquente d'observer avec le Decteur Robin que dans des séries de spinelles mixtes (Fe_2CoO_4 — Co_2CoO_4) certaines compositions apparaissent de préférence au cours de la formation de ces phases, sans que soit exclue l'existence d'une parfaite continuité, réalisable seulement à la suite de traitements thermiques prolongés. Dans l'état solide, la coexistence, même à des températures très élevées, de deux phases de même structure et de composition légèrement différente, est parfois insuffisante pour conclure définitivement à la présence d'une zone de non miscibilité entre ces phases. On peut, en effet, imaginer que dans une série de phases homogènes, certaines compositions puissent donner lieu à des phénomènes d'ordonnancement qui confèreraient aux phases correspondantes un léger supplément de stabilité rendant leur formation plus probable que celle des phases intermédiaires. Il s'agirait là, en fait, de la manifestation discrète d'une tendance à la formation d'un composé défini, mais n'excluant pas pour autant l'existence d'une continuité dans l'ensemble du système. Dans le cas où la variation d'énergie libre résultant de l'ordonnancement deviendrait suffisamment importante, la probabilité d'existence des phases de composition voisine deviendrait très faible et l'on se trouverait placé dans le cas d'un véritable composé défini.

M. Ubbelohde. — Has Professor Hägg any theories of the bond differences to account for the gaps in composition between oxides such as Mo_8O_{23} and Mo_9O_{26}? For example, it could be that functionally one molybdenum atom in eight in the unit cell of Mo_8O_{23} behaved as Mo^{IV} and the remaining seven as Mo^{VI}, but this would have to be apparent in the crystal structure. Alternatively are there Brillouin zone effects in the electronic energy of the crystals that would account for the gaps? Do the electronic conductivities of these oxides show gaps in activation energy or in mobility to correspond with gaps in the range of crystal compositions? I am assuming that the electrical conductivities obey semi-conductor equations of the type $\sigma = \sigma_0 \exp. (-E/KT)$ where σ is the conductivity and E the activation energy.

M. Hägg. — The occurrence of definite formulae has geometrical causes. If the phases have to be built of blocks of ReO_3 structure, joined in principally the same way, the formula depends on the thickness of these blocks. This thickness can only vary in steps, differing in magnitude by one MeO_6 octahedron at a time.

The oxides in question contain metal atoms of different charge but the charge seems to be distributed evenly over all metal atoms. The existence of « resonance » is indicated by the dark blue colour of the oxides.

M. Collongues. — Je voudrais faire une remarque sur la répartition des lacunes dans les composés non stoechiométriques très lacunaires. Cette remarque rejoint d'ailleurs celle du Professeur Hägg sur l'existence simultanée de deux composés non stoechiométriques de même structure.

Dans un travail récent, Bertaut, à Grenoble, a mis en évidence l'existence d'un ordre dans la répartition des lacunes du sulfure de fer FeS (1). L'établissement de cet ordre traduit la tendance des lacunes à se placer le plus loin possible les unes des autres. Il semble exister une température de transition entre des états ordonnés et désordonnés de FeS, mais l'accord sur cette température est assez médiocre.

D'autre part, on sait que le sesquioxyde de fer cubique $Fe_2O_3\gamma$ s'obtient par oxydation de la magnétite Fe_3O_4, par formation de lacunes et passage d'ions Fe^{++} à l'état Fe^{+++}. Le diagramme des rayons X de ce sesquioxyde est, en première approximation, identique à celui de la magnétite, à une petite variation de paramètres près ($a_{Fe_3O_4} = 8{,}378$ Å; $a_{Fe_2O_3\gamma} = 8{,}322$ Å).

Mais en utilisant des méthodes de rayons X extrêmement fines, nous avons mis en évidence sur le diagramme l'apparition de nombreuses raies supplémentaires de faible intensité (2). Ces raies s'interprètent très bien comme les interférences d'un réseau cubique simple de même maille que la magnétite. Ce phénomène conduit à penser que la répartition des lacunes dans la structure du sesquioxyde est ordonnée. Bien entendu, la détermination complète de la struc-

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(1) E. Bertaut, *Acta Cryst.*, 6, 557 (1953).

(2) R. Collongues, Thèse, Paris (1954).

ture exigerait la préparation de monocristaux, ce qui, étant donné l'instabilité du composé, paraît fort délicat.

Je voudrais demander à M. Bénard s'il a rencontré dans son travail beaucoup de composés lacunaires présentant un ordre dans la répartition des lacunes? S'agit-il là d'une règle générale?

D'autre part, je pense que lorsque deux phases de même structure et de compositions légèrement différentes coexistent, il n'est pas impossible que ces deux phases correspondent à des états d'ordre différents dans la répartition de leurs ions ou de leurs lacunes. On sait en effet aujourd'hui que la transformation ordre-désordre peut provoquer dans une phase des variations de composition.

M. Bénard. — Les remarques du Docteur Collongues concernant l'existence d'un ordonnancement des ions dans certaines phases non stoechiométriques viennent à l'appui de l'explication que je proposais il y a un instant. La question se pose seulement de savoir s'il est possible d'envisager dans des systèmes tels que ceux actuellement étudiés par le Professeur Hägg, la possibilité d'existence d'états ordonnés successifs correspondant à des différences de composition aussi faibles que celles qui nous sont décrites. Arrivé en ce point de la discussion, je constate qu'en fait il n'existe aucune incompatibilité entre l'interprétation du Professeur Hägg et celle que je proposais il y a un instant. La seule différence réside dans le fait que dans l'une des hypothèses, on exclut la possibilité d'existence des phases correspondant aux compositions intermédiaires, tandis que dans l'autre on admet seulement que ces phases ont une moindre tendance à se former. Il doit être possible en fait, de trouver des cas illustrant ces deux interprétations.

En ce qui concerne l'existence des phénomènes d'ordonnancement dans les réseaux lacunaires, les exemples bien étudiés sont très rares. Leur analyse suppose, en effet, une détermination très précise des variations des intensités des raies de diffraction des rayons-X, détermination encore très difficile dans l'état actuel de la technique.

M. Chaudron. — De nombreuses phases peuvent donner lieu au phénomène ordre $\leftrightarrows$ désordre. On peut penser que dans un certain nombre de cas, ces transformations sont accompagnées par un changement de composition. Des expériences récentes de Collongues et de Behar au laboratoire de Vitry (1) et (2) montrent l'importance de la transformation ordre ⇆ désordre dans le domaine des ferrites. La méthode micrographique a été précieuse pour l'étude des ferrites de lithium et de cuivre.

M. Barrer. — I would like to comment upon the significance of experiments made upon the electrolyte migration of hydrogen in palladium, by Duhm. At first he obtained a value of the effective positive charge on hydrogen of 1/500 that on a proton and later he corrected the charge to 1/25 of that value. However, the effective charge, relative to that on the other atomic nuclei, may not be established by migration experiments. The small hydrogen is so much more mobile than the large metal nuclei which compose the lattice of the host crystal. Perhaps if the mobility of the metal nuclei was equal to that of the hydrogen it would be found that most of the cationic transport was provided by the metal. I doubt therefore whether the relative effective positive charges on H and on metal can be established by migration experiments.

The photo-electric work function of a clean tungsten surface and of tungsten with a chemisorbed hydrogen layer has established a dipolar surface W — H bond in which hydrogen is negative with respect to tungsten. Experiments of this kind may give an insight into the relative tendency of hydrogen within the metal and the metal atoms themselves to contribute to the free electron pool of the crystal.

These remarks regarding the relative charges on the guest atom and the metal atom may apply also to the C — Fe system where C also migrates to the cathode. Arguments based on electronegativity of the two elements would suggest that carbon nuclei would be less positive than Fe-nuclei, assuming both elements to contribute to the free electron pool of the metal.

M. Ubbelohde. — Has it now been verified that the migration of hydrogen in palladium under the influence of an electric field is a true lattice effect? It has been suggested in cases where the hydrogen is introduced into the metal by cathodic treatment, that a very thin

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(1) R. Collongues, *Comptes rendus*, **241**, 1577 (1955).
(2) I. Behar, *Comptes rendus*, **242**, 2465 (1956).

film of electrolyte remain on the surface and in cracks of the metal and accounts for the proton migration observed under the influence of an electric field.

M. Bénard. — Je suis tout à fait d'accord avec le Professeur Barrer en ce qui concerne la prudence avec laquelle il faut interpréter les résultats de conductibilité électrique pour conclure à l'état d'ionisation de l'hydrogène dans les métaux. Je n'ai pas cru devoir passer sous silence ces mesures, mais je concède que leur interprétation peut donner lieu à des controverses. On peut déplorer de ne pas disposer à cet égard de plus de résultats expérimentaux récents.

En ce qui concerne l'évaluation du potentiel d'extraction des électrons, celui-ci pourrait en effet fournir des renseignements sur la nature des interactions hydrogène-métal. Ces renseignements risquent cependant d'être très qualitatifs, car, si mes souvenirs sont exacts, les valeurs des potentiels d'extraction annoncées par les différents auteurs sont assez dispersées. En outre, cette méthode fournit des renseignements sur l'émission des électrons par la surface, mais il n'est nullement certain que l'état électronique de la liaison chimisorptive telle qu'elle existe dans la couche superficielle soit identique à celui de la liaison métal-hydrogène en profondeur.

M. Orgel. — Are the experiments on electrodiffusion carried out in such a way that they definitely measure the charge on the hydrogen atom at its equilibrium position rather than at the transition state for the diffusion process?

M. Chaudron. — Je rappellerai des expériences faites dans mon laboratoire sur le système Pd-hydrogène, il y a maintenant une dizaine d'années (1) et (2).

L'extraction de l'hydrogène en insertion, dans le cas de la solution solide β, est très facile.

Au contraire, avec la solution α, la fixation est très forte. Pour constater l'existence de l'hydrogène après les traitements de dégazage, nous fûmes obligés d'utiliser la mesure du paramagnétisme.

Il y a là des faits qui montrent l'évolution du mode de liaison de l'hydrogène dans le Pd.

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(1) G. Chaudron, A. Michel et J. Bénard, *Comptes rendus*, **218**, 913 (1944).

(2) J. Bénard et Ph. Albert, *Colloque d'absorption cinétique hétérogène*, Lyon (1949), p. 207.

M. Hägg. — Professor Bénard has counted oxygen among the non-metals, which may form phases analogous to the metallic carbides and nitrides.

It is well known that, for instance, the phase TiO is very similar to the phases TiC and TiN and that these three phases can form solid solutions. But there are also analogies between certain complex carbides, nitrides and oxides.

N. Karlsson-Schönberg has found that the ternary carbides, having the ideal formula $Me'_3\,Me''_3C$ (of which the high speed steel carbide Fe_3W_3C is best known) possess both nitride and oxide analogues.

In the oxides, Me' may be any of the metals Cr — Cu but Me'' must have a place not too far to the right in the transition metal series. It seems to be a condition that the oxides which are similar to metallic carbides and nitrides, should contain transition metal atoms having a fairly uncompleted *d* shell.

I should also like to point out the existence of metallic « suboxides » like Cr_3O, Mo_3O, W_3O, of which the last one has been considered for many years to be a modification of tungsten (β — W).

M. Bénard. — L'existence de sous-oxydes à caractère métallique signalés par le Professeur Hägg vient enrichir la série des composés «d'insertion », dans lesquels l'oxygène jouerait un rôle analogue à celui du carbone et de l'azote, et qui ne comportait jusqu'à maintenant qu'un très petit nombre de termes. Il serait intéressant de savoir si ces oxydes pseudo-métalliques possèdent les mêmes caractères de dureté et d'infusibilité que les carbures et nitrures correspondants.

M. Hedvall. — Nous avons effectué, il y a environ vingt ans, quelques expériences connexes qui présentent peut-être un intérêt du point de vue de la catalyse.

Nous avons étudié l'influence des variations de la composition chimique de quelques préparations de HgS et de CdS avec ou sans excès de soufre. On a constaté que l'influence de ces variations sur la capacité d'adsorption des différents substrats est notable, ce qui est évident aujourd'hui.

Ce phénomène est important en catalyse du point de vue de l'interaction du catalyseur et de la couche adsorbée. Il se présente certainement pour les oxydes des métaux lourds, qui sont souvent utilisés comme catalyseurs.

Vous avez mentionné dans votre premier rapport que vous avez obtenu une couleur bleue en chauffant à 1.000° le BaO, dans la vapeur de Ba. Peut-être y a-t-il intérêt à mentionner que l'on obtient une couleur grise en chauffant le même oxyde dans H, à la même température.

Connaissez-vous l'explication de cette couleur. A mon avis, il ne s'agit pas d'une réduction même superficielle; ce sont plutôt les distorsions du réseau qui sont en cause.

M. Bénard. — Il est exact que des teintes très variées peuvent être obtenues avec l'oxyde de baryum porté à haute température dans des atmosphères réductrices. Il semble que ces variations de teinte soient dues à des états de ségrégation variables des défauts réticulaires, les interactions de ces défauts provoquant des déplacements du maximum d'absorption dans le visible. L'origine de ces phénomènes resterait cependant toujours la même, à savoir la présence de lacunes anioniques occupées par des électrons. J'ajouterai que les expériences que j'ai citées à ce propos n'ont pas été faites dans mon laboratoire.

M. Forestier. — Comment explique-t-on la conductibilité des carbures et nitrures des métaux lourds?

M. Bénard. — L'interprétation la plus récente de la conductibilité électrique des monocarbures et mononitrures des métaux lourds a été donnée par Rundle; elle repose sur l'idée qu'il existe dans tous ces composés une liaison d'un type particulier que j'ai tenté de décrire dans le rapport. Cette liaison tente de concilier dans une certaine mesure le caractère orienté des liaisons covalentes classiques et le partage des orbitales de l'atome léger entre plusieurs liaisons contractées par cet atome avec ses voisins. On peut considérer que cette conception justifie la conductibilité électrique de ces composés, dans la mesure même où l'on est disposé à admettre que la théorie de Pauling explique la conductibilité dans l'état métallique.

Il est hors de doute que la conductibilité électrique élevée de ces composés a été pour beaucoup dans leur assimilation trop hâtive aux phases métalliques typiques. Actuellement, le nombre des conducteurs électroniques non métalliques que l'on connaît est extrêmement élevé, et une telle assimilation ne se justifie plus.

M. Forestier. — W_3O peut-il être considéré comme un composé défini, ayant une conductibilité de type analogue à celui des carbures de métaux lourds?

M. Hägg. — The structure of W_3O presents a special difficulty in that the X-ray data can only be interpreted if some of the metal and oxygen atoms are assumed to be distributed at random over structurally equivalent positions. Under those circumstances it is too early to say anything about the bonds in this phase.

Les composés non stoechiométriques à caractère métallique. Phases intermétalliques

par **Robert COLLONGUES**

Le chimiste minéral qui a étudié les composés non stoechiométriques par suite de leur grand intérêt scientifique et de leurs nombreuses applications pratiques, ne peut pas ignorer le domaine des phases intermétalliques. Dans ce domaine, le composé défini est assez rare et la phase intermédiaire apparaît le plus souvent sous des aspects extrêmement variés. On peut se demander les raisons de cette multiplicité des phases et de la diversité de leurs propriétés. C'est à cette question que nous voulons répondre et, pour cela, nous avons analysé quelques uns des travaux les plus récents. Nous citerons tout particulièrement l'application des théories de Hume-Rothery à l'étude systématique des diagrammes d'équilibre (Hume-Rothery et Raynor) et les nombreuses déterminations de structures dues surtout à Bradley, Westgren, Taylor, Laves et Hägg.

CARACTERES GENERAUX DES PHASES INTERMEDIAIRES

Formation des phases intermédiaires

Considérons deux éléments quelconques de la classification périodique, le cuivre et l'aluminium par exemple, et préparons par fusion des alliages contenant des quantités croissantes d'aluminium. Lorsque l'addition d'aluminium est de faible importance, le diagramme de Debye-Scherrer du cuivre reste sensiblement inaltéré : on note seulement un léger déplacement des raies. Quelques atomes d'aluminium ont remplacé les atomes de cuivre dans le réseau de

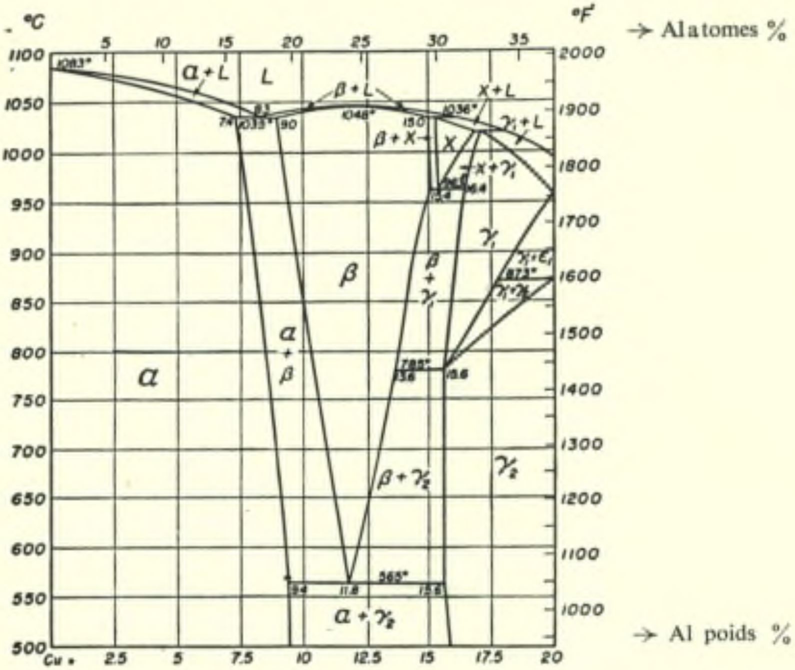

Fig. 1 Diagramme Cu-Al dans la région riche en cuivre.

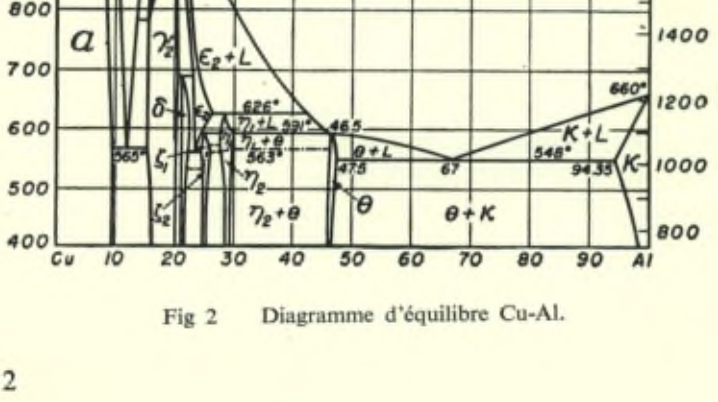

Fig 2 Diagramme d'équilibre Cu-Al.

ce métal d'une manière désordonnée. On obtient ainsi la solution solide primaire α (fig. 1). Or, les dimensions des deux atomes sont différentes ($r_{Cu} = 1{,}28$ Å; $r_{Al} = 1{,}43$ Å). L'introduction d'un nombre croissant d'atomes d'aluminium va donc provoquer une dilatation homothétique croissante du réseau du cuivre. Pour une teneur en atomes d'aluminium supérieure à 20 %, il existe un autre arrangement des deux sortes d'atomes plus stable que l'arrangement initial cubique à faces centrées. Un nouveau réseau se forme alors : c'est la phase intermédiaire β cubique centrée. Cette structure sera stable tant que la teneur en atomes d'aluminium ne dépassera pas 30 %. Pour des teneurs supérieures, la deuxième phase intermédiaire γ apparaît : elle est cubique mais sa structure est complexe (type laiton γ). Nous rencontrons ainsi sur le diagramme d'équilibre (1) (fig. 2) toute une série de phases intermédiaires (β, γ, δ, ε, ζ, η, θ) de structures différentes. Chaque structure représente l'arrangement le plus stable des deux sortes d'atomes dans un certain intervalle de composition et pour une certaine température.

Structure des phases intermédiaires

Les structures des phases intermédiaires peuvent être ordonnées ou désordonnées. Dans l'exemple choisi, la composition moyenne de la phase β correspond à Cu_3Al (20,3 à 30,8 % Al). Or, cette phase est cubique centrée (type chlorure de césium). La maille contenant deux atomes, il est impossible de répartir d'une manière ordonnée, dans une telle structure deux sortes d'atomes différents dans un rapport autre que $\frac{1}{1}$. La phase β est donc nécessairement désordonnée (2).

Au contraire, la phase δ du système nickel-aluminium est ordonnée. Sa structure est également cubique centrée (type chlorure de cérium) et sa composition moyenne corrspond à Ni Al (39, 9 à 54,75 %Al) (3) (fig. 3). Les atomes de nickel sont répartis aux sommets d'un cube dont le centre est occupé par un atome d'aluminium. Bradley (4) a mis en évidence l'apparition, sur le diagramme de Debye-Scherrer des raies de surstructure caractéristiques de cette répartition ordonnée.

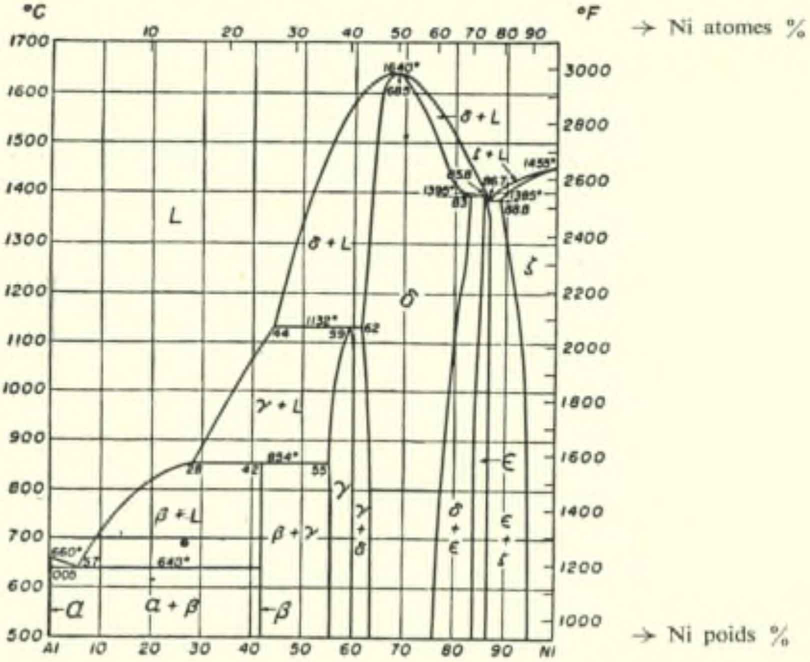

Fig. 3 Diagramme d'équilibre Al-Ni.

Conditions de formation d'une phase intermédiaire

La possibilité d'existence d'une ou plusieurs phases intermédiaires entre deux éléments A et B sera déterminée avant tout par les dimensions relatives des deux atomes (facteur de dimension $= \frac{r_A}{r_B}$) Nous avons représenté sur le diagramme (fig. 4 *a*) l'étendue du domaine d'homogénéité de toutes les phases intermédiaires formées entre l'argent et un autre métal (*). On constate que la formation d'une phase ne sera possible que si les deux éléments ont des dimensions suffisamment voisines. Les deux valeurs extrêmes

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(*) Pour établir ce diagramme, nous avons utilisé, le plus souvent possible, les valeurs des rayons atomiques déterminées expérimentalement dans les phases intermédiaires elles-mêmes. Les valeurs données dans les tables sont, en effet, généralement mesurées dans les éléments. Or, on sait (6) que la valeur du rayon atomique varie suivant l'état de coordination de l'atome. D'autre part, comme nous le verrons, les atomes peuvent être partiellement ionisés dans la structure de la phase intermédiaire.

du rapport des rayons atomiques sont : $\frac{r_{\mathrm{In}}}{r_{\mathrm{Ag}}} = 1{,}055$; $\frac{r_{\mathrm{Ag}}}{r_{\mathrm{Ga}}} = 1{,}15$. Cette valeur (1,15) constitue une valeur limite pour beaucoup de phases intermédiaires. Il est, du reste, important de signaler qu'on aboutirait aux mêmes conclusions et à la même valeur limite pour les solutions solides primaires α (5). Si le facteur de dimension est élevé, il apparaîtra à la place de la phase intermédiaire, un composé défini.

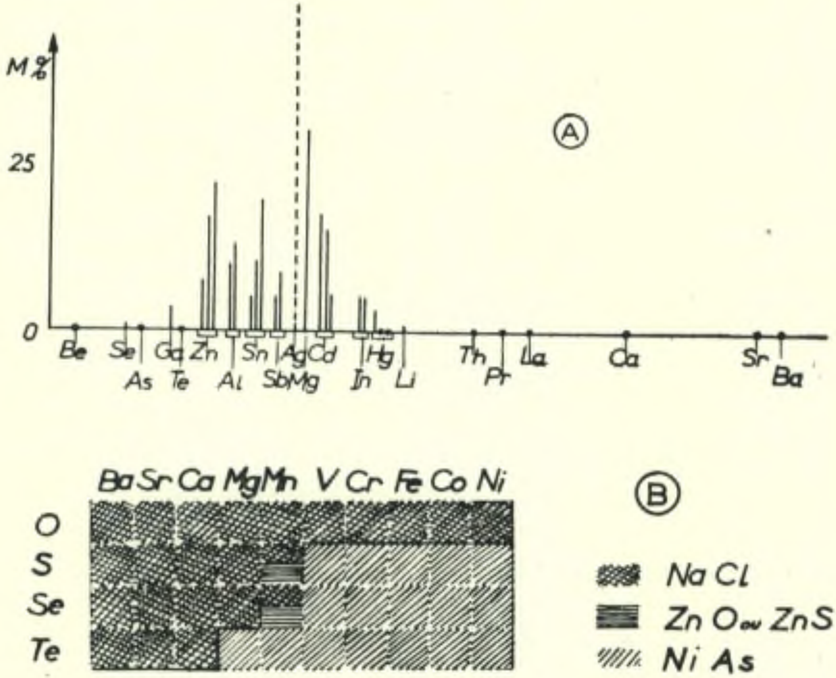


Fig. 4 *a)* Etendues des domaines d'homogénéité des phases intermédiaires formées entre l'argent et des métaux de rayons atomiques croissant.

b) Structures des phases ou composés A B formés entre des métaux d'électronégativité croissante et les éléments du groupe VI B.

L'électro-affinité des deux éléments interviendra également pour déterminer la structure de la phase et le mode de liaison des atomes (liaison ionique, covalente ou métallique). Nous avons indiqué sur le diagramme (fig. 4 *b*) les structures des phases ou des composés de formule générale AB formés entre des métaux d'électronégativité différente et les éléments du groupe VI B. On constate que les structures formées sont par ordre d'affinité décroissante

type NaCl → type ZnO ou ZnS → type NiAs

Lorsque les liaisons sont du type métallique, la structure dépendra, comme nous le verrons, de la concentration électronique, c'est-à-dire du nombre d'électrons associé à chaque atome de la phase intermédiaire.

Il est intéressant de noter que la structure de la phase intermédiaire peut parfois être déterminée par un seul de ces facteurs. Les composés de Laves (7), de formule générale AB_2, constituent des exemples, tout à fait remarquables de structures déterminées par le facteur de dimension : le rapport $\frac{r_A}{r_B}$ est voisin de 1,3 pour tous ces composés. Le rôle de l'électro-affinité des éléments dans la formation de ces composés semble tout à fait négligeable. On notera d'ailleurs qu'un même métal peut, suivant les dimensions de son partenaire, jouer le rôle de métal A ou de métal B : par exemple, le magnésium dans $MgCu_2$ et $CaMg_2$, le bismuth dans $BiAu_2$ et KBi_2, l'argent dans $AgBe_2$ et $CaAg_2$. D'autre part, il est important de remarquer que ces composés, dans lesquels la structure géométrique est capitale, ne peuvent s'expliquer par une concentration électronique globale.

Formule des phases intermédiaires

Les diagrammes Al-Cu et Al-Ni présentent, comme nous l'avons indiqué, un certain nombre de phases intermédiaires. Leur domaine d'existence peut être très étendu : par exemple, la composition de la phase β du système Al-Cu varie de 20,3 à 30,8 % d'aluminium. L'importance de ces variations a conduit certains auteurs à mettre en doute la signification d'une formule A_mB_n attribuée à de telles phases.

Glazunov (8) propose de distinguer deux types de phases intermédiaires :

1° les solutions solides dérivant d'un composé défini A_mB_n. La courbe représentant les variations, en fonction de la composition, d'une propriété quelconque de la phase, la température de fusion par exemple, présente alors un point singulier pour la composition A_mB_n. C'est le cas des phases β et des systèmes Al-Cu et Al-Ni dont le solidus et le liquidus présentent un maximum pour les compositions exactes Cu_3Al et NiAl.

2° les berthollides. Les courbes représentant les variations des propriétés en fonction de la composition ne possèdent pas de point singulier à l'intérieur du domaine d'homogénéité. C'est le cas des phases θ du système Al-Cu (9) et β du système Cr-Al par exemple. L'étude aux rayons X a cependant montré que la structure de cette dernière phase dérivait d'un manière évidente de celle du composé Cr_2Al (10) (fig. 5), quelques atomes de chrome étant remplacés par des atomes d'aluminium.

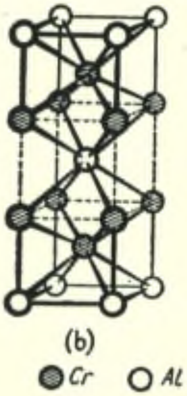
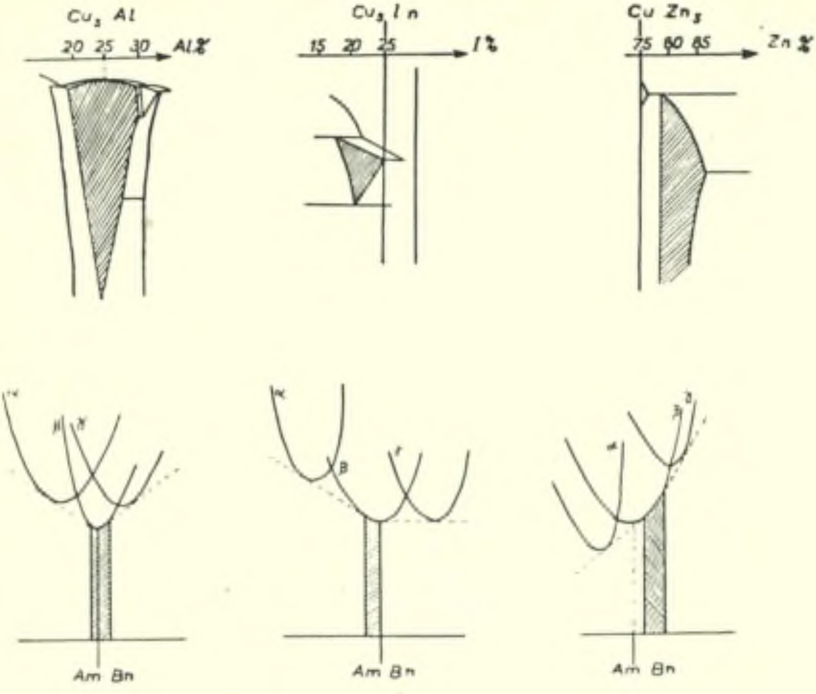


Fig. 5 Structure du composé Cr_2Al.

Mais la composition stoechiométrique ne fait pas nécessairement partie du domaine d'homogénéité de la phase. Trois cas peuvent se présenter (fig. 6) :

1° La composition stoechiométrique est à l'intérieur du domaine d'homogénéité de la phase. Nous citerons comme exemples : les phases β des systèmes Cu-Al (Cu_3Al) (fig. 6 *a*); Ag-Mg (AgMg); la phase δ du système Al-Ni (AlNi); les phases γ des systèmes Cu-Cd (Cu_5Cd_8), Cu-Zn (Cu_5Zn_{21}); les phases ε des systèmes Ag-Al (Ag_5Al_3), Ag-Zn ($AgZn_3$).

2° La composition stoechiométrique limite le domaine d'homogénéité. Nous citerons comme exemples : les phases β des systèmes



a b c

Fig. 6 Diverses positions possibles de la composition stoechiométrique par rapport au domaine d'homogénéité d'une phase intermédiaire.

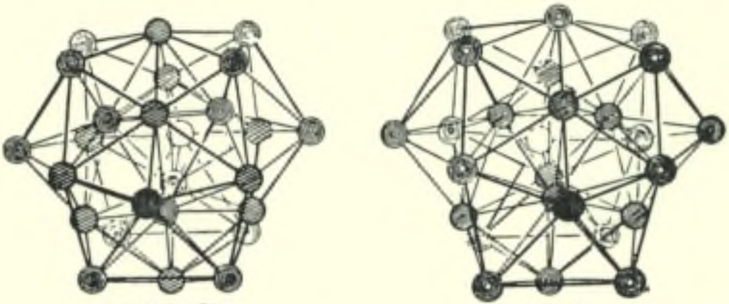


Fig. 7 Structures de Cu_5Zn_8 et Cu_5Cd_8. Les voisins de l'atome ● sont différents dans les deux structures.

Cu-In (Cu_3In) (fig. 6 *b*), Be-Cu (BeCu); de la phase γ du système Cu-Al (Cu_9Al_4) ainsi que de plusieurs phases non métalliques, par exemple FeO (11), NiS (12), etc.

3° La composition stoechiométrique est nettement extérieure au domaine d'homogénéité. Nous citerons comme exemples : la phase ε du système Cu-Zn ($CuZn_3$) (fig. 6 *c*), la phase γ du système Au-Zn (Au_5Zn_8), ainsi que plusieurs phases non métalliques, par exemple FeSe (13), FeS (14), etc...

Lipson et Wilson (15) pensent que ces différentes formes de diagrammes résultent des diverses positions relatives possibles des courbes d'énergie libre de la phase considérée et des phases voisines (fig. 6). On peut supposer que la courbe d'énergie libre d'une phase β présente un minimum pour un rapport atomique simple des constituants. Si l'ordonnée de ce minimum est inférieure à celles des minima des phases voisines, la composition stoechiométrique A_mB_n est à l'intérieur du domaine d'homogénéité de la phase β. Si l'ordonnée du minimum de la phase β est comprise entre celles des minima des phases voisines, la composition stoechiométrique est à l'extérieur du domaine d'homogénéité de la phase β. Il résulte de cette remarque que les propriétés d'une phase intermédiaire dépendent dans une large mesure des propriétés des phases voisines.

Il importe de remarquer que l'analogie de formule n'implique nullement une analogie de structure. Par exemple, les phases Cu_5Cd_8 et Cu_5Zn_8 possèdent des formules identiques et la même maille cristalline. Mais les analyses très précises de la structure effectuées par Bradley et ses collaborateurs (16, 17) ont montré que les répartitions des atomes à l'intérieur de la maille étaient différentes dans les deux cas. Les cinquante-deux positions possibles de la maille peuvent être divisées en quatre groupes de positions équivalentes contenant respectivement 8, 8, 12 et 24 atomes. Dans les deux phases considérées, les répartitions sont les suivantes :

groupes	I (8 atomes)	II (8 atomes)	III (12 atomes)	IV (24 atomes)
Cu_5Zn_8	Cu	Zn	Cu	Zn
Cu_5Cd_8	Cu	Cu	32 Cd + 4 Cu	

Les atomes de cadmium de la phase Cu_5Cd_8 ont donc des voisins différents des voisins du zinc de la phase Cu_5Zn_8 ([18]) (fig. 7).

ETUDE DES DIVERS TYPES DE PHASES INTERMEDIAIRES

La formation d'une phase dérivant d'un composé A_mB_n réel ou hypothétique (c'est-à-dire placé en dehors du domaine d'homogénéité de la phase) peut s'effectuer de plusieurs manières :

1° remplacement d'un certain nombre d'atomes de l'élément A par des atomes de l'élément B. On obtiendra ainsi une phase de substitution de formule $A_{m-\varepsilon}\ B_{n+\varepsilon}$;

2° élimination d'un certain nombre d'atomes de l'élément A, le réseau des atomes B restant inaltéré ou encore addition d'atomes de l'élément B dans les intervalles de la structure, le réseau A restant inaltéré. On obtiendra ainsi suivant les cas une phase lacunaire de formule $A_{m-\varepsilon}\ B_n$ ou une phase « interstitielle » de formule $A_m\ B_{n+\varepsilon}$.

L'utilisation simultanée des mesures précises du paramètre cristallin et de la densité permet, en général, de distinguer entre ces diverses possibilités.

Le premier processus ne pourra bien entendu intervenir que si les caractéristiques des deux atomes (en particulier rayon atomique et électro-négativité) sont très voisines (par exemple Ni-Zn). Au contraire, lorsque les deux éléments seront nettement différents (Ni-Se par exemple), toute substitution de l'un à l'autre sera impossible et, seule, la formation de lacunes pourra provoquer une variation de composition de la phase. Dans le cas intermédiaire (Ni-Al par exemple), les deux processus pourront se rencontrer dans la même phase.

Phases intermédiaires de substitution

Les phases intermédiaires de substitution se rencontrent presque uniquement dans les alliages formés :

1° soit entre deux métaux de transition;

2° soit entre un métal de transition et un élément des groupes II B, III B, IV B;

3° soit entre un élément du groupe I B et un élément des groupes II B, III B, IV B.

Dès 1926, Hume-Rothery (19) mettait en évidence l'existence d'une importante caractéristique commune aux alliages de cette dernière catégorie : pour toutes les phases β de ces alliages, la concentration électronique (rapport du nombre d'électrons de valence au nombre d'atomes) est égale à 3/2; pour toutes les phases γ, elle est égale à $\frac{21}{13}$ et pour toutes les phases ε à $\frac{7}{4}$. Ekman (20) montrait ensuite que les alliages de la seconde catégorie pouvaient satisfaire aux règles de Hume-Rothery à condition d'attribuer une valence nulle à l'élément de transition.

Nous signalerons quelques problèmes particulièrement intéressants qui se posent à propos de ces phases. Nous étudierons ensuite les principales phases intermédiaires des alliages formés entre deux métaux de transition : elles sont du type phase σ.

Nous montrerons enfin qu'il convient de considérer les surstructures comme des phases intermédiaires d'un type particulier.

Phases obéissant aux régles de Hume-Rothery

Les principales propriétés de ces phases ont été décrites en détail dans des ouvrages classiques de Hume-Rothery (21, 22, 23). Les règles de Hume-Rothery ont fait l'objet des études théoriques de Jones (24, 25), Dehlinger (26) et Slater (27, 28). Elles ont été remarquablement vérifiées par les déterminations de structures de Westgren (19, 30, 31), puis de Bradley (10, 16, 17, 32, 33).

Nous pensons qu'il convient d'insister sur les points suivants :

1° La valence apparente des éléments de transition. On sait que la troisième couche quantique des éléments de transition de la première longue période est incomplète. La structure électronique du nickel, par exemple, est la suivante :

n	1	2	3	4
Ni	2	2 6	2 6 8	2

D'après Ekman, cet élément présent dans une phase aura tendance à capter les électrons de son partenaire pour compléter sa troisième couche quantique. Il pourra ainsi fournir deux électrons de valence à la structure de la phase, mais il recevra également deux électrons de son partenaire. Sa valence apparente sera alors nulle. La phase intermédiaire sera donc dans ce cas partiellement ionisée. On constate en effet que sa formation s'accompagne d'une très nette contraction, les distances interatomiques observées étant inférieures à la somme des rayons atomiques (34).

Le fer et le cobalt devraient dans ces conditions posséder une valence négative, mais il est possible que l'élément de transition ne puisse recevoir qu'un nombre limité d'électrons de l'élément allié. Dans un travail récent (35) Douglas a mis en évidence l'absorption des électrons de valence par le métal de transition dans les phases Co_2Al_9, $MnAl_6$, $MnSi_3Al_9$: l'analyse de la structure montre que l'atome de cobalt possède une valence apparente négative voisine de — 2.

Dans sa théorie générale (36, 37) Pauling distingue des éléments « hyperélectroniques » (donneurs d'électrons), indifférents, et « hypoélectroniques » (accepteurs d'électrons). Les métaux de transition appartiennent à cette dernière catégorie. Chacun d'entre eux pourra capter un certain nombre d'électrons : au maximum 4,66 pour le chrome, 3,66 pour le manganèse, etc. Il est remarquable de constater que la valence maximum du cobalt déduite de la théorie de Pauling est — 1,71 voisine de la valeur expérimentale.

2° Il est intéressant de comparer la forme et l'étendue du domaine d'homogénéité des différentes phases β des alliages d'or, d'argent et de cuivre obéissant aux règles de Hume-Rothery (38) (fig. 8). Dans les alliages d'or, on remarque l'existence de nombreux points de fusion congruente et de plusieurs structures ordonnées. Au contraire, dans les alliages de cuivre, les structures ordonnées sont très rares et il apparaît de nombreux points eutectoïdes. Les alliages d'argent ont des caractères intermédiaires. Il semble que ces phénomènes doivent être attribués aux différences d'électronégativité entre les éléments alliés qui sont beaucoup plus élevées dans les alliages d'or que dans les alliages de cuivre.

Le rôle du facteur de dimension apparaît aussi très nettement. En général, l'étendue du domaine d'homogénéité diminue lorsque

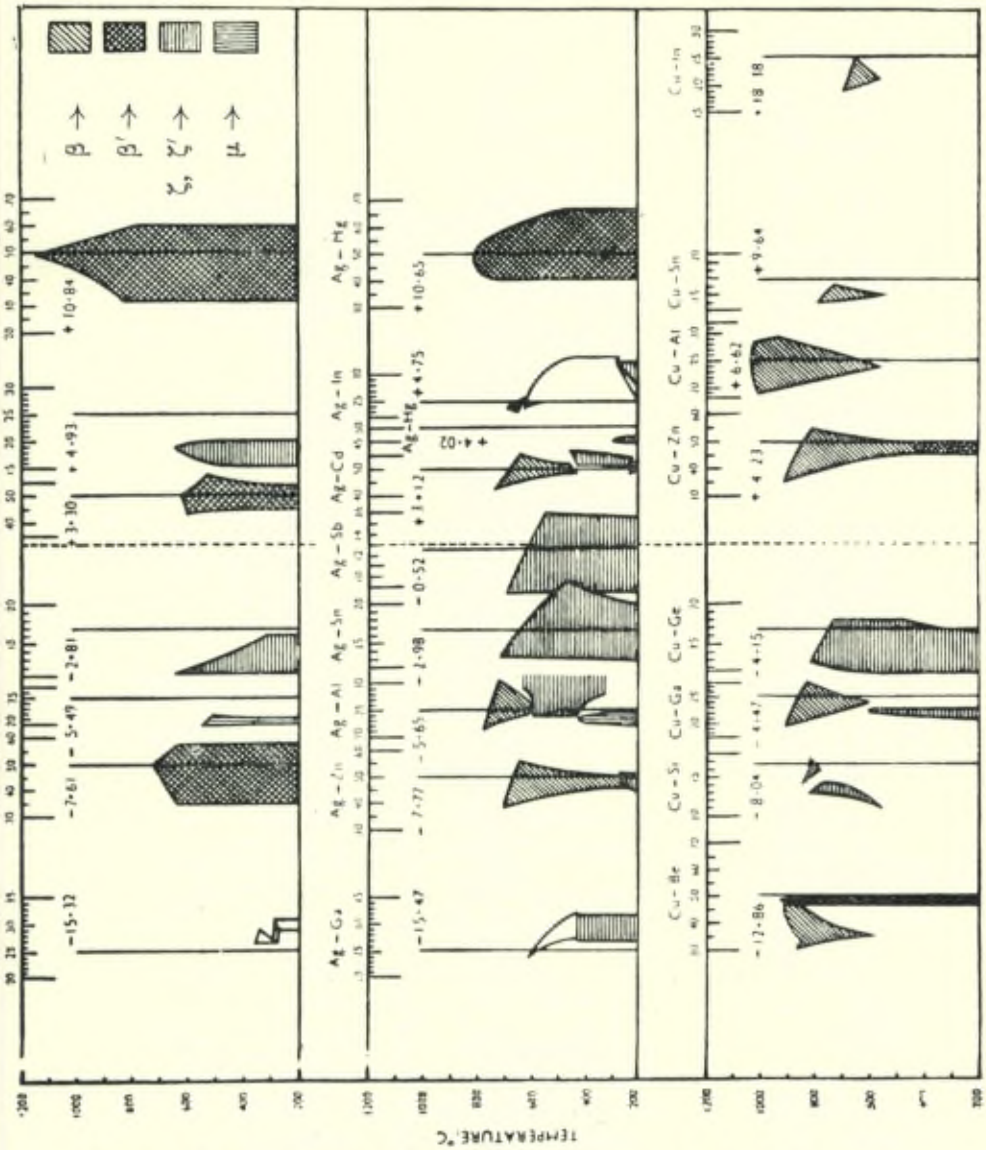


Fig. 8 Différentes formes des domaines d'homogénéité des phases obéissant aux règles de Hume-Rothery (en abscisses le facteur de dimension

$$100\left(\frac{r_M - r_{Ag}}{r_{Ag}}\right).$$

Nota. — L'étendue du domaine d'homogénéité des phases AgMg et AuMg n'est pas anormale : si l'on calcule le facteur de dimension à partir des rayons atomiques mesurés dans la phase elle-même, on trouve un facteur voisin de 3. Ces phases étendues devraient donc se trouver dans la partie centrale du diagramme.

le facteur de dimension augmente. Nous noterons, d'ailleurs, que l'étendue du domaine d'homogénéité des phases Au Mg et Ag Mg n'est nullement anormale à condition de définir le facteur de dimension comme le rapport des rayons atomiques des éléments déterminés dans la phase elle-même et non comme le rapport des rayons atomiques déterminés dans les éléments. La distance Ag-Mg mesurée dans la phase est en effet 2,92 Å, très voisine de la distance mesurée dans Ag-Cd (2,93 A), alors que la distance calculée ($r_{Ag} + r_{Mg}$) est 3,04 Å. Il en est de même pour la phase Au Mg .

Phases σ

Les phases σ et les surstructures se rencontrent souvent dans les mêmes systèmes et parfois pour la même composition. D'autre part, leurs conditions de formation sont assez voisines. C'est pourquoi dans certains alliages la formation de la phase σ a été assimilée à une transformation ordre-désordre. Plusieurs arguments s'opposent à cette conception :

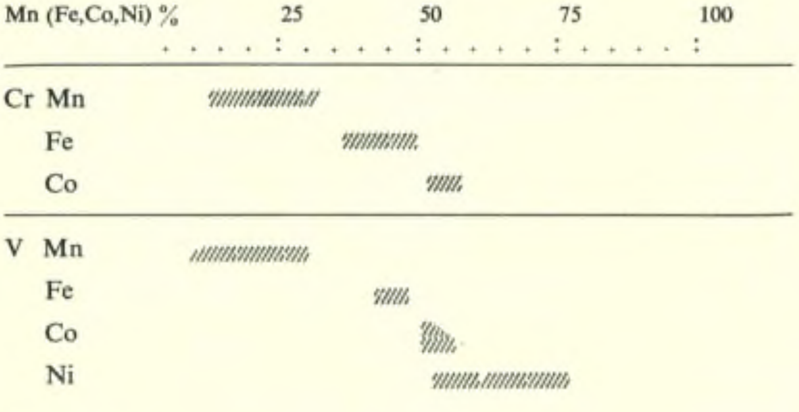
1° La complexité quasi générale de la structure des phases σ, qui n'a aucun rapport avec la structure de la phase mère.

2° le fait que la composition stoechiométrique (en général $\frac{1}{1}$) est parfois en dehors du domaine d'homogénéité de la phase σ; ce phénomène serait difficilement compréhensible si la phase σ dérivait simplement de la phase mère par une transformation ordre-désordre.

Dans un travail récent, Pomey (39) a pu étudier séparément les deux phénomènes dans l'alliage Fe-Cr. Il a trouvé pour les deux phases des domaines d'homogénéité très différents (43 à 50 % Cr pour la phase σ, 40 à 78 % Cr pour la phase ordonnée). De plus, la transformation α désordonné → α ordonné se produit dans une zone de température (500-600°) nettement inférieure à la zone de température correspondant à la transformation α désordonné → σ (825° environ). Enfin, Pomey a mis directement en évidence la transformation α ordonné → σ montrant ainsi que seule la structure σ est stable à la température ordinaire.

On sait aujourd'hui que les phases σ se forment dans de nombreux alliages binaires ou ternaires : Mn-V (40), Mn-Cr, Mn-Mo, Mn-Ti, Fe-Cr, Fe-V (41), Fe-Mo, Fe-W (42), Co- V(40), Co-Cr (43), Co-Mo, Co-W, Ni-V (44). En général, le domaine d'homogénéité entoure la composition $\frac{1}{1}$, mais quelques exceptions ont été signalées : Co-Mo (59-61 % Mo), Co-Cr (56-61 % Cr), Ni-V (55-61 % V), Mn-Cr et Mn-V à 75 % Mn. Toutes ces phases σ ont la même structure quadratique avec 30 atomes par maille. Un certain nombre de structures (phases ξ, μ) se rattachent aux phases σ.

Dans toutes ces phases, le facteur fondamental est le facteur de dimension : le rapport des rayons atomiques ne doit pas dépasser 1,08. Certains auteurs ont pensé qu'il était possible de considérer toutes les phases σ comme des phases ayant la même concentration électronique. Il semble fort délicat de prendre position sur un tel problème en raison de l'incertitude sur la valence des éléments de transition. Il est seulement intéressant de noter le déplacement du domaine d'homogénéité des phases σ en fonction de la position des éléments dans la classification périodique. Ce déplacement indique que le facteur concentration électronique doit jouer un rôle important dans la formation de ces phases.



Surstructures

Lorsqu'une phase ordonnée se sépare de la solution solide primaire, doit-on la considérer comme une phase distincte ayant sa place dans le diagramme d'équilibre? En général, les théoriciens n'ont pas envisagé la transformation ordre-désordre comme un véritable changement de phase dans lequel une structure subit une transformation discontinue ($^{45, 46}$). Dans la transformation ordre-désordre, la répartition des atomes semble varier de façon continue en fonction de la température.

Or, un groupe très important de travaux récents (en particulier, ceux de Newkirk et Smoluchowski sur le système Co-Pt) (^{47}) a conduit à réviser cette conception. Ces auteurs ont mis en évidence sur le diagramme d'équilibre l'existence d'une région biphasée entre les domaines ordonné et désordonné (fig. 9). L'examen micrographique montre la phase ordonnée précipitée à l'intérieur de la matrice désordonnée sous forme d'une structure de Widmanstätten. Les deux phases coexistant à l'équilibre ont des compositions légèrement différentes.

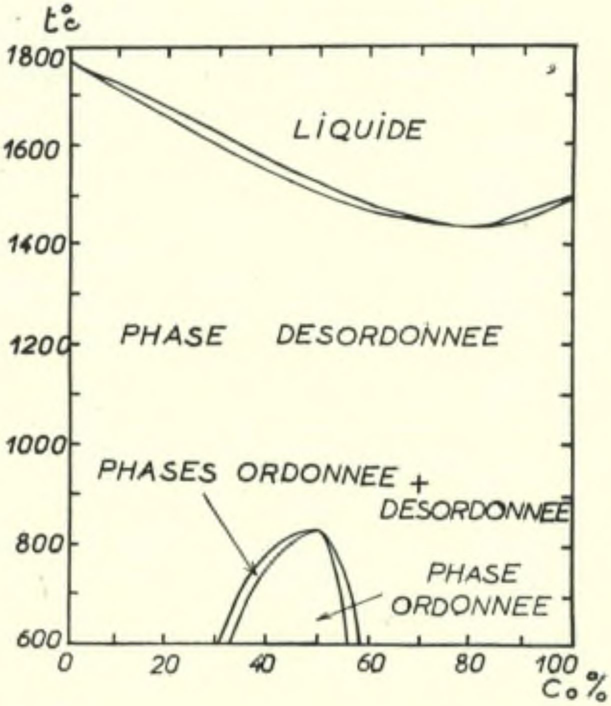


Fig. 9 Diagramme d'équilibre Co — Pt montrant l'existence d'un domaine à deux phases (ordonnée + désordonnée).

De même, dans l'exemple classique des surstructures Cu_3Au la coexistence des deux phases a été mise en évidence (48). De plus, dans ce cas, l'existence d'une différence de composition entre la phase ordonnée et la phase désordonnée a été nettement démontrée : l'augmentation de la teneur en cuivre de la phase désordonnée provoque une augmentation du paramètre, l'établissement de l'ordre provoque une diminution.

Le problème est loin d'être résolu. Nous pensons cependant que l'existence d'un domaine biphasé est aujourd'hui bien établie. Ce domaine peut, dans certains cas, être très étroit. Mais, c'est seulement à la composition stoechiométrique que la transformation peut être considérée comme un simple ré-arrangement atomique.

PHASES LACUNAIRES OU INTERSTITIELLES

Exemple d'un travail type

C'est Bradley et Taylor (49) qui, les premiers, mirent en évidence l'existence d'une phase lacunaire dans un système intermétallique : la phase Ni-Al. A la composition stoechiométrique, cette phase a la structure cubique centrée du chlorure de césium. Lorsque la teneur en nickel est supérieure à 50 %, quelques atomes d'aluminium sont remplacés par des atomes de nickel. Ceux-ci sont plus lourds et plus petits que les atomes d'aluminium : la densité augmente et le paramètre cristallin diminue (fig. 10). La limite de solubilité correspond à 61 atomes % de nickel. Inversement, quand on enrichit la phase Ni-Al en aluminium, on devrait s'attendre à une diminution de la densité et à une augmentation du paramètre. Or, on constate bien une diminution de la densité (beaucoup plus rapide d'ailleurs que celle résultant d'une simple substitution), mais aussi une diminution très rapide du paramètre. L'étude comparée des variations des densités mesurée et calculée conduit à supposer l'élimination d'atomes de nickel de leurs positions dans le réseau. L'accroissement de la teneur en aluminium de la phase se produit donc en réalité par extraction d'atomes de nickel avec formation de lacunes. La phase la plus pauvre en nickel (42,25 atomes %) contient 8 % de lacunes dans le réseau.

Cette hypothèse est confirmée directement par la mesure des intensités des raies du diagramme de rayons X. Une autre confir-

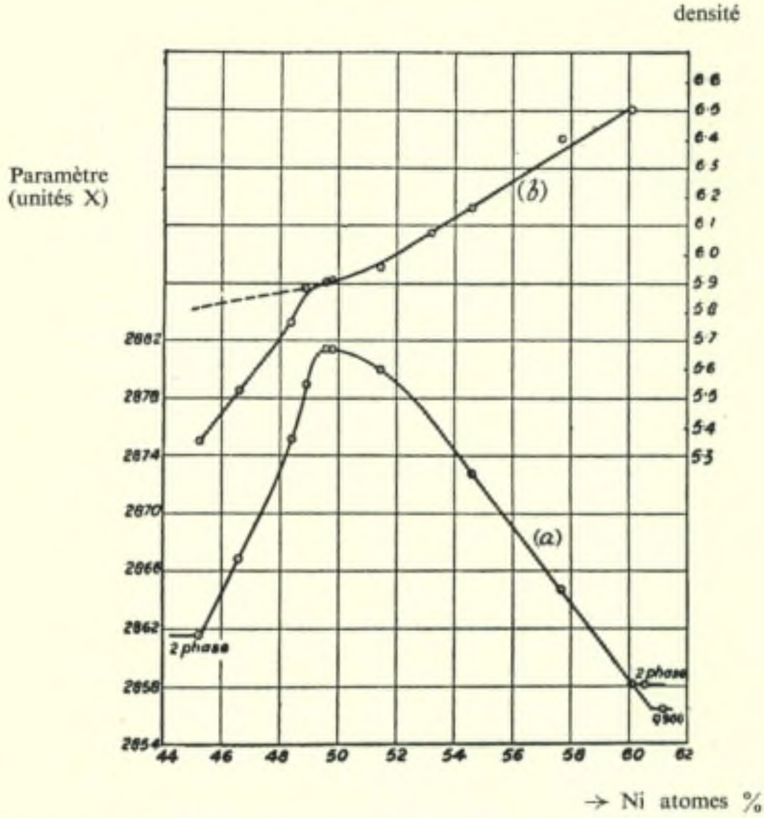


Fig. 10 Variations du paramètre *(a)* et de la densité *(b)* de la phase Ni-Al en fonction de la composition.

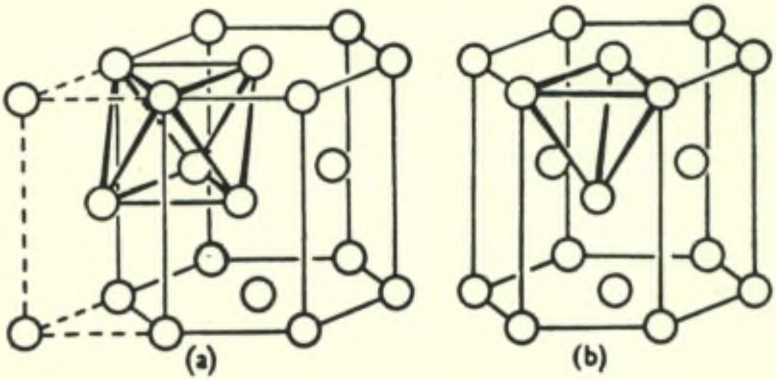


Fig. 11 Intervalles octaédriques *(a)* et tétraédriques *(b)* dans la structure Ni-As.

mation moins directe est l'étude de la diffusion dans la phase Ni-Al. La valeur élevée trouvée pour la vitesse de diffusion de ^{60}Co ne peut s'expliquer que par l'existence de nœuds réticulaires non occupés (^{50}).

A la suite de ce travail original, un grand nombre d'alliages d'aluminium binaires ou ternaires ont été étudiés. Des phases lacunaires ont été signalées dans les systèmes Co-Al (^{51}), Fe-Ni-Al (^{52}), Cu-Ni-Al (^{53}), Fe-Cu-Al (^{54}). Le composé $U\,Al_4$ dériverait du composé $U\,Al_3$ par formation de lacunes dans le réseau des atomes d'uranium (^{55}). Il est cependant difficile dans ce cas de préciser si la variation de composition s'effectue bien par ce processus ou par substitution d'atomes d'aluminium à des atomes d'uranium.

Les structures du type laiton γ contiennent aussi dans leur réseau un certain nombre de lacunes ($^{56, 57, 58}$). Nous citerons les exemples du laiton γ, des phases $NiGa_4$ (^{59}), $Ni_{28}In_{72}$, $PdIn_3$ ($^{60, 61}$). Certains auteurs ont insisté sur le caractère hétéropolaire de ces structures et envisagé la possibilité d'existence de molécules Ni_2Ga_3 et NiIn (^{59}).

Phases lacunaires de type NiAs

Mais c'est surtout dans les phases de type NiAs formées entre un métal de transition et un élement des groupes IV B, V B et VI B que de nombreuses phases lacunaires d'étendue importante ont été mises en évidence. Les atomes B forment un réseau hexagonal compact (fig. 11) délimitant des intervalles tétraédriques et octaédriques. Dans la structure du composé stoechiométrique, les intervalles octaédriques sont seuls occupés par des atomes A (^{13}). Mais un certain nombre d'atomes peuvent manquer provoquant ainsi la formation de lacunes. Le réseau B demeure inaltéré. Dans les cas extrêmes, la moitié des intervalles octaédriques peut être inoccupée : par exemple, dans les alliages Co-Se, Ni-Te, V-Se, Ti-Se, Ti-Te, on atteint à la limite et de façon continue les composés $CoSe_2$, $NiTe_2$, VSe_2 ($^{62, 63}$), $TiSe_2$, $TiTe_2$ ($^{64, 65}$). Inversement, la variation de composition peut être produite par insertion d'atomes A dans les intervalles tétraédriques normalement inoccupés de la structure. Ainsi, la phase NiSb peut contenir jusqu'à 54,4 % atomes de nickel. On peut dans certains cas atteindre la composition A_2B (Ni_2In).

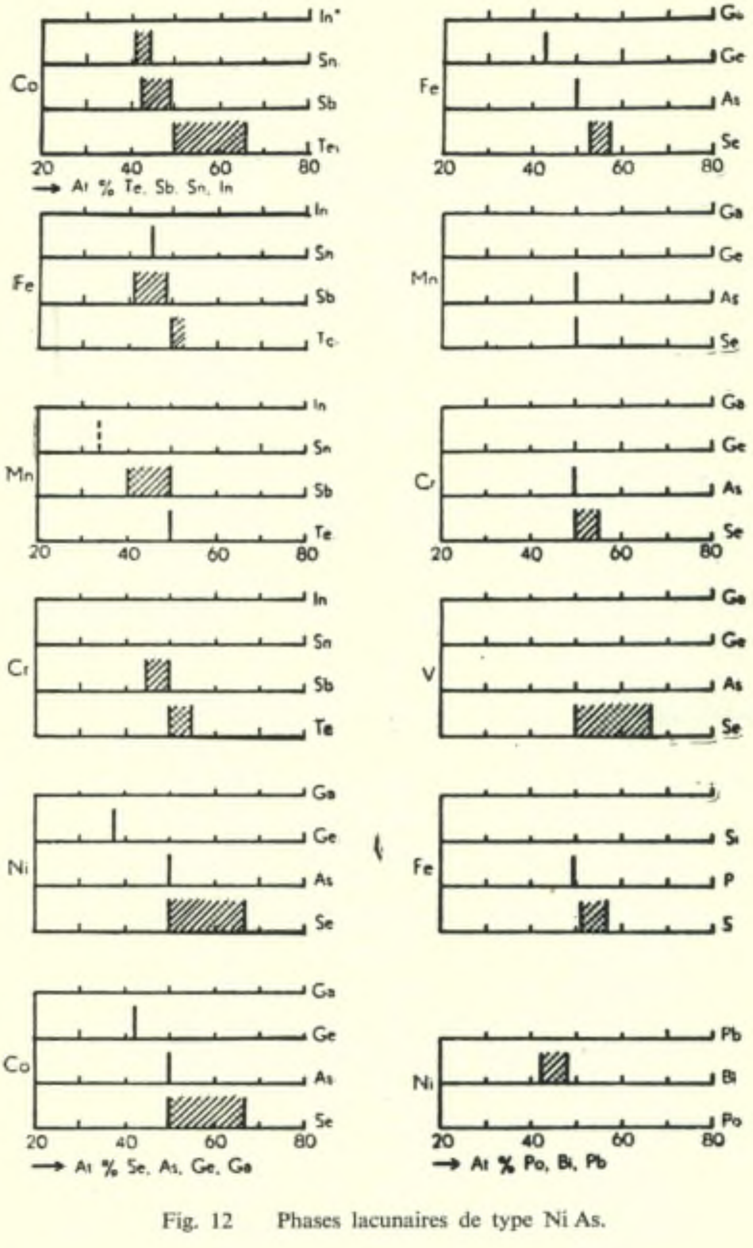


Fig. 12 Phases lacunaires de type Ni As.

La composition stoechiométrique peut ne pas faire partie du domaine d'homogénéité : c'est le cas par exemple pour FeSe, FeS, FeSb (52 à 58% atomes Fe) ([13, 14]).

L'examen de l'ensemble de ces phases (fig.12) révèle un certain nombre de phénomènes dont le plus curieux est certainement le déplacement du domaine d'homogénéité vers les fortes teneurs en élément A, lorsque le caractère métalloïdique de l'élément B diminue (fig. 13).

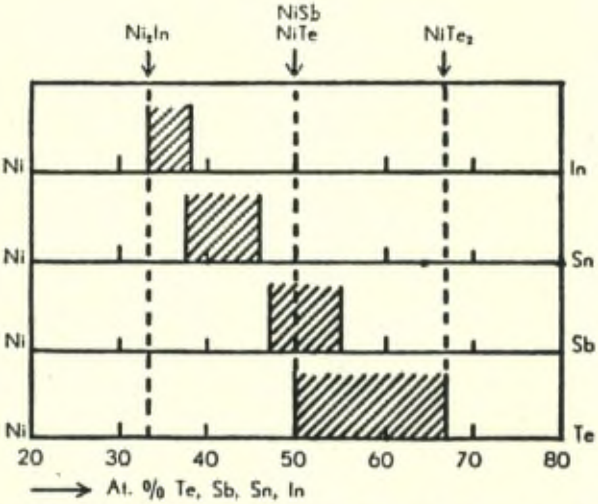


Fig. 13 Variation de la position du domaine d'homogénéité d'une phase lacunaire (type Ni-As) en fonction de l'élément B.

	Se	Te	As	Sb	Bi	Sn	In
Ni %	33,4-50	33,4-50	50	45-54	52-58	54-62	62-66,6
Co %	33,4-50	33,4-50	50	51-57		56-60	
Fe %	43-47	< 50	50	52-58		55	

Un autre phénomène très intéressant est la variation du rapport $\frac{c}{a}$ des axes de la maille hexagonale en fonction de l'électronégativité de l'élément A. ou de l'élément B. On remarque que le rapport $\frac{c}{a}$ décroît lorsque l'électronégativité de l'élément B diminue ($\frac{c}{a} = 1{,}55$ pour NiS; $\frac{c}{a} = 1{,}23$ pour NiIn) (fig. 14 *a*). Hume-Rothery (23)

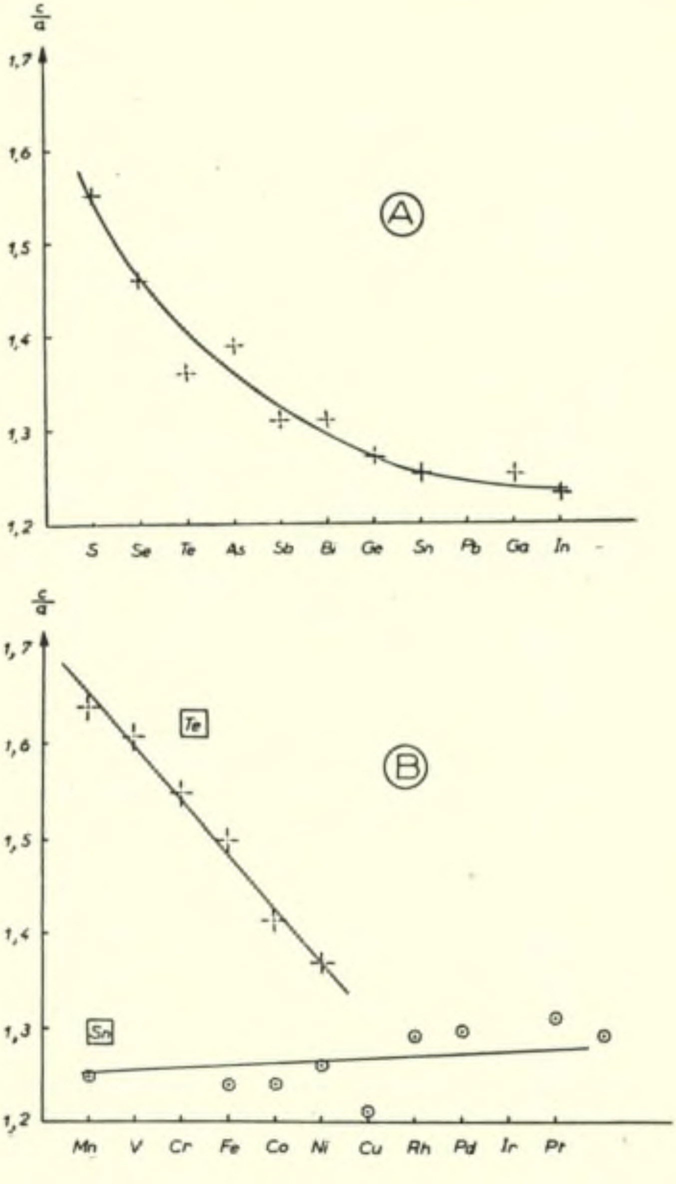


Fig. 14 Variation du rapport $\frac{c}{a}$ des axes de la maille hexagonale des phases de type Ni-As formées par :

A) Le nickel avec des éléments d'électonégativité décroissante ;

B) Le tellure et l'étain avec des éléments d'électronégativité croissante.

pense que ce phénomène résulte d'une variation continue du mode de liaison des atomes dans la structure. D'autre part, dans les phases de type A Te, le rapport $\frac{c}{a}$ diminue rapidement lorsque l'électronégativité de l'élément A diminue ($\frac{c}{a} = 1,66$ pour TiTe; $\frac{c}{a} = 1,36$ pour NiTe) (fig. 14 *b*). Au contraire, dans les phases de type ASn, le rapport $\frac{c}{a}$ est sensiblement indépendant de l'électronégativité du métal A. Les liaisons sont toujours, dans ce cas, de type métallique.

Autres exemples de phases lacunaires

Earley (66) a montré que le composé Cu_3Se_2 qui existe à l'état naturel, et qui peut aussi être préparé par fusion des constituants, était en réalité le composé limite d'une phase lacunaire $Cu_{4-x}Se_2$. La phase $RhSe_2$ est une phase mixte lacunaire et de substitution (67).

Enfin, des phases lacunaires se rencontrent dans certains alliages ternaires. Les phases LiZnAs, LiMgP, LiZnP ont une structure de type CaF_2 dans laquelle les atomes de lithium occupent les intervalles octaédriques. Certains d'entre eux peuvent manquer : il apparaît ainsi une phase lacunaire de formule $Li_{1-\varepsilon}ZnAs$ (68).

Ces phases nous paraissent occuper une position extrêmement importante : elles constituent vraiment les structures de transition entre les phases intermétalliques et les composés non stoechiométriques de la chimie minérale.

MODES DE LIAISON DANS LES PHASES INTERMEDIAIRES

Nous traiterons très succinctement ce problème important, mais nous nous proposons de développer ultérieurement notre étude.

Nous avons déjà montré qu'il pouvait exister, dans une série homologue de phases, une variation continue du mode de liaison entre atomes et nous avons cité l'exemple des phases lacunaires de type NiAs. On rencontre un phénomène analogue dans la série des composés Mg_2Si, Mg_2Ge, Mg_2Sn, Mg_2Pd, qui possèdent tous une structure cubique, anti-isomorphe de la structure de la fluorine. Le composé Mg_2Sn est un semi-conducteur : sa conductibilité croît exponentiellement en fonction de la température. Le composé Mg_2Pd est un conducteur métallique: sa résistivité croît linéairement en fonction de la température. De plus, à la température ordinaire, la résistivité Mg_2Sn est environ deux cents fois supérieure à la résistivité de Mg_2Pd (69). Ce phénomène indique nettement une différence notable entre les modes de liaison des atomes dans ces deux composés.

Mais on peut aussi rencontrer différents modes de liaison à l'intérieur d'une même phase. Nous avons signalé l'ionisation partielle des atomes dans les phases obéissant aux règles de Hume-Rothery, le caractère hétéropolaire des structures du laiton γ, des phases $NiGa_4$, $Ni_{28}In_{72}$, etc. Nous citerons maintenant quelques exemples particulièrement frappants.

Il nous paraît tout d'abord intéressant d'établir un parallèle entre deux composés, l'un intermétallique $PrGa_2$; l'autre bien connu en chimie minérale : le sous-fluorure d'argent Ag_2F. Le composé $Pr\,Ga_2$ a une structure hexagonale, constituée de couches d'atomes se succédant dans l'ordre suivant : Pr - Ga - Ga - Pr - Ga ...(70). L'étude aux rayons X a montré que la distance entre atomes de gallium était nettement inférieure au diamètre atomique de cet élément. La distance entre atomes de praséodyme est, au contraire, supérieure au diamètre atomique. Il semble nécessaire, pour expliquer une telle structure, d'admettre l'existence entre les atomes de gallium de liaisons plus fortes que les liaisons métalliques (liaisons de covalence par exemple). Ce composé possède d'ailleurs un point de fusion très élevé 1470^{o} ($t_{fGa} = 30^{o}$; $t_{fPr} = 940^{o}$) et sa stabilité chimique est notable.

Le sous-fluorure d'argent Ag_2F possède une structure du même type constituée de couches successives : Ag - Ag - F - Ag - Ag (71). La mesure des distances interatomiques montre que les liaisons entre atomes d'argent et de fluor sont du type ionique pur, alors que les liaisons entre atomes d'argent sont de type métallique. Les cristaux de ce corps possèdent en effet l'éclat métallique et sont fortement conducteurs. Ces deux composés $PrGa_2$ et AgF_2, en apparence si différents, possèdent un important caractère commun : leurs liaisons sont de type mixte. Il en résulte qu'ils possèdent à la fois les propriétés caractéristiques des composés minéraux et les propriétés de l'état métallique.

Nous signalerons enfin un exemple plus curieux encore que l'on rencontre dans le système Mg-Al (72). La phase de composition voisine de Mg_3Al_2 possède la structure du manganèse α, avec 58 atomes par maille répartis en trois groupes de 24, 24 et 10 atomes. Sa véritable formule doit donc être $Mg_{17}Al_{12}$ avec 2 $(Mg_{17}Al_{12})$ par maille. La mesure des distances interatomiques montre qu'en réalité les atomes d'aluminium sont groupés en doublets dans lesquels la distance entre deux atomes est nettement inférieure au diamètre de l'atome d'aluminium. Les deux atomes doivent donc être liés sous forme de groupements diatomiques par des liaisons homopolaires; les deux électrons supplémentaires nécessaires seraient fournis par l'ionisation des atomes de magnésium. Nous avons ainsi dans chaque maille : 12 « groupements » $[Al_2]^{--}$, 24 ions Mg^+ et 10 atomes de magnésium. La formule de la phase peut donc s'écrire $[Al_2]^{--}{}_{12}\ Mg^+{}_{24}\ Mg_{10}$.

Une bonne confirmation de cette structure est fournie par la mesure des distances entre un atome d'aluminium et les 34 atomes de magnésium de la maille : 24 d'entre elles (correspondant aux 24 ions Mg^+) sont nettement inférieures aux 10 autres (correspondant aux 10 atomes de magnésium). Dans cette structure interviennent donc des liaisons ioniques, homopolaires et métalliques.

CONCLUSION

L'ensemble des travaux que nous avons analysés permet de souligner l'intervention de plusieurs facteurs dans la formation des phases intermédiaires : le facteur de dimension, la concentration électronique et l'électro-affinité. La liaison des atomes dans ces phases nous apparaît, d'autre part, comme une synthèse de modes de liaison de caractères très différents.

On comprend alors la multiplicité des phases possibles dans un système et l'étendue souvent importante de leur domaine d'homogénéité, par suite de mécanismes variés de formation et de liaison. Au contraire, dans les parties de la chimie où prédomine très largement le caractère ionique des liaisons, les possibilités de formation et de structure d'une phase étendue sont nettement réduites. On expliquerait ainsi en première approximation le caractère stoechiométrique des composés ioniques. De toute manière, les transpositions d'idées d'un domaine à l'autre nous paraissent devoir être très précieuses pour le chercheur.

Je tiens à remercier très sincèrement Monsieur le Professeur Chaudron, Membre de l'Institut, Directeur de notre Laboratoire, pour l'intérêt constant qu'il a porté à ce travail et les conseils qu'il m'a prodigués au cours de nos conversations au Centre d'Etudes de Chimie Métallurgique.

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Discussion

M. Ubbelohde. — It seems rather important to define more precisely what is meant by « phase » in describing changes such as order-disorder in crystals. The classical phase rule is based on the possibility of describing the free energy G of, say, a simple substance entirely in terms of the variables P, V, T; $G = f(P, V, T)$.

At constant pressure, the curve relating G with T is infinitely thin. Modern theory of solids indicates that whilst this may still be a permissible approximation ordinarily, an important reservation is necessary near a transition between two structures. If these structures are quite independent and one solid is formed *in extenso* from the other, the classical phase rule indicates a *point* of intersection of the infinitely thin G, T curves.

From this, all the classical thermodynamic relationships, such as Clausius Clapeyron can be readily deduced. But examination e.g. by precision X-ray methods shows that for many transformations ① → ② in solids, provided the change of structure is small, regions of ① and ② coexist over a narrow interval of temperatures in the same matrix.

Suppose we start with structure ① and approach the transformation temperature ① → ②.

Regions of ② begin to appear within the matrix of ①. They are obviously in some state of strain, and in the matrix, the separation surface between ① and ② may involve appreciable internal surface energy. As a result, the free energy of ② appearing in ② can no longer be represented by the classical equation for an extensive phase $G_2 = f_2\ (P, V, T)$ (A) but two additional parameters to allow for strain energy ξ_{21} and surface energy η_{21} must be added

$$G_2' = f_2\ (P, V, T, \xi_{21}, \eta_{21})\ (A')$$

In the same way, starting with structure ② and approaching the transformation temperature, regions of ① begin to appear in the matrix of ② so that for its free energy, we must write instead of

$$G_1 = f_1\ (P, V, T)\ (B)$$

$$G_1' = f_1\ (P, V, T, \xi_{12}, \eta_{12})\ (B)'$$

Intersection of the thickened surfaces $A' + B'$ will no longer be at a transformation *point*, but over a smeared narrow region. This explains the following :

A. Hysteresis occurs since the intersection of G'_2 with G_1 does not follow the same path as the intersection of G'_1 with G_2 (the unprimed free energies refer to the values for structures undistorted by inclusions of the other).

B. There is a kind of rough contact or overlap over a narrow range of temperatures, between the G_1 and G_2. This appears to be the real structural explanation of many so called phase transformations of the « second order ». In reality these are examples of the *coexistence* of two structures in a common matrix over a narrow range of thermodynamic variables η and ξ.

Various structural tests proving coexistence have been reviewed for a variety of Λ point transitions, in a paper by me, shortly due to appear in the *British Journal of Applied Physics*, entitled : « Crystallography and the Phase Rule ».

These lambda point transitions all involve only small differences of structures between ① and ② such as « rotation » or « non-rotation » of NH_4^+ in a crystal lattice, positional order-disorder, etc.

In consequence regions of ② begin to form in ① but the mechanical strains do not exceed the breaking strength, so that the « hybrid » crystal lattice with regions of ② in a matrix of ① retains its crystal axes. We have actually followed certain apparently single crystals through a temperature cycle ① → ② → ① to test how far the crystal axes persist, but it would take too long to describe these in detail. The two main points to note are :

(*a*) instead of referring to « equilibrium between two phases » it is more correct in such cases to refer to « coexistence of two structures over a narrow region of temperatures and pressures ». Such transformations would theoretically be of the first order if the two phases were present *in extenso*. But because ② can only be formed within the matrix of ①, and vice versa, the extra parameters η and ξ automatically smear the transition point into a transition region.

(*b*) Generally speaking the free energy of small regions of ② formed in a matrix of ① will not be the same as that of ② as matrix, containing small inclusions of ①. This inevitably brings hysteresis into play, since what is nominally the same structure ② has a somewhat different free energy according to whether it has just been formed within ① as small regions, or whether it starts as the extensive matrix and merely contains small inclusions of ①.

M. Collongues. — Les remarques de M. Ubbelohde nous conduisent à préciser le mécanisme de la transformation ordre-désordre. Dans un travail récent (1) Kuczynski a étudié la transformation de l'alliage Au — Cu.

Il a mis en évidence l'existence entre 350 et 400° d'une période d'induction de la transformation d'autant plus longue que la température est plus élevée. D'autre part, il a pu établir pour cette transformation un diagramme TTT analogue à celui des réactions eutectoïdes par exemple. L'ensemble de ces résultats semble montrer que la transformation ordre-désordre s'effectue par un mécanisme de germination et de croissance. Or, dans un tel processus, il est impossible de négliger les variations d'énergie libre provoquées d'une part par la création d'un interface entre les phases 1 et 2 (paramètre η_{21}), d'autre part par la création de tensions dans la matrice au cours de la précipitation (paramètre ξ_{21}).

M. Timmermans. — Les vues de M. Ubbelhode confirment ce que nous savons des conditions où la loi des phases est d'application rigoureuse. Si une autre forme d'énergie intervient d'une manière notable, il faut introduire un paramètre supplémentaire; comme c'est le cas par exemple dans l'interprétation de l'opalescence critique dans les phénomènes critiques.

Pour compléter l'exposé de M. Collongues, je voudrais rappeler que l'existence d'un composé défini de base dans une série de cristaux mixtes ne doit pas nécessairement conduire à un *maximum* de la température de fusion pour la concentration stoechiométrique

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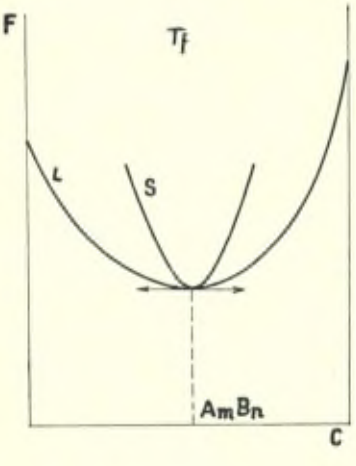
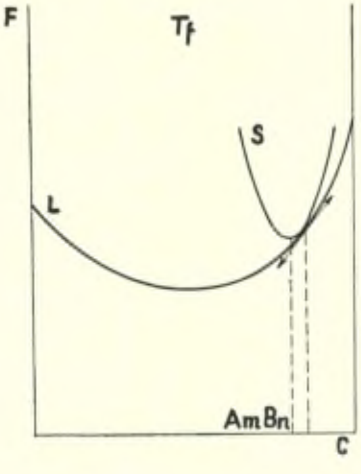
(1) Kuczynski, Hochman et Doyama, *J. Applied Physics.*, **26**, 871 (1955).

correspondante, mais peut produire un maximum à une concentration voisine, comme c'est le cas pour les maximums de température d'ébulition dans les solutions eau + acide nitrique (exemple classique de Proscoe et Dittmer.)

M. Collongues. — Il semble en effet que la température de fusion ne soit pas une grandeur physique très bien choisie pour caractériser le composé stoechiométrique dont dérive une phase. La température de fusion étant, par définition, la température d'équilibre entre les phases solide et liquide, sa variation ne dépend pas uniquement de la composition de la phase solide. Nous pouvons considérer les courbes d'énergie libre de la phase intermédiaire choisie et de la phase liquide et supposer, comme nous l'avons fait jusqu'ici, que la courbe d'énergie libre de la phase intermédiaire présente un minimum pour la composition stoechiométrique A_mB_n.





Pour que la température de fusion T_f soit maximum à la composition A_mB_n, il est nécessaire que les deux courbes d'énergie libre à la température T_f soient tangentes en leur point minimum. Ce n'est évidemment pas le cas général. Il n'existe donc aucune raison théorique pour que la composition correspondant au maximum de la température de fusion coïncide avec la composition stoechiométrique. L'expérience montre cependant que ces deux compositions sont en général extrêmement voisines, phénomène que l'on peut attribuer à la forme des courbes d'énergie libre (très ouverte pour la phase liquide, beaucoup plus fermée pour la phase solide).

La conductibilité électrique serait peut-être une grandeur physique permettant de mieux caractériser l'existence d'un composé défini à l'intérieur du domaine d'une phase.

M. Weyl. — It might interest here that in silicate systems similar phenomena can be observed. SiO_2 forms immiscible systems with CaO, MgO and other oxides. With Na_2O, K_2O, etc., no immiscibility is observed. Li_2O behaves as an intermediate and is usally described as having a « tendency towards immiscibility ». By adding a solid to such a system (Pt or Pd in colloidal subdivision) we were able to actually separate fused lithium silicate into two liquids.

M. Kuhn. — It has been proved recently that in the simple case of water the freezing point is not exclusively a function of temperature but also of the magnitude of the crystals which are mechanically possible in the system (1). It was observed that an aqueous gel containing 96 % of water and 4 % of a high polymer (polyacrylic acid and polyvinylalcohol) which has been allowed to swell to saturation in pure water and having exactly the same vapour pressure as water has a freezing point of e.g. — 0.9 or — 2.0° C instead of 0° C. The difference is due to the fact that the presence of the gel lattice prevents ice crystals to reach linear dimensions greater than the dimensions of the meshes of the network of the gel. Micro crystals have a lower melting point than macro crystals, due to the interfacial tension between liquid water and ice. This means that the activity of the ice phase and thereby the melting point depends not exclusively on the temperature but on the linear extension of the ice phase too.

Similar effects obviously exist in the case of phase transformation in solids where restrictions in the extension of phases may last for considerable lengths of time. In all these cases the free energy of a phase and, with it, the transformation point, must be considered to be, among other things, a function of the linear extension of the new phase.

(1) W. Kuhn u. H. Majer, *Z. physikal Chem.*, **3**, 330 (1955).

M. Bénard. — 1. Je crois qu'une des raisons pour lesquelles les changements de composition qui accompagnent les transformations ordre-désordre ont été antérieurement négligés, est que les chercheurs se sont placés de préférence, pour des raisons de commodité expérimentale, aux teneurs pour lesquelles la transformation ordre-désordre se produit aux températures les plus élevées. Or ces teneurs sont précisément celles pour lesquelles la transformation a lieu sans changement de composition. J'ajouterai cependant qu'il ne me paraît pas indispensable d'admettre que toutes les transformations ordre-désordre se produisent suivant le processus de nucléation et croissance. Ce processus ne doit apparaître en réalité que lorsque la différence d'énergie libre massique entre les domaines ordonnés et les domaines désordonnés est suffisamment grande pour compenser l'énergie nécessaire à la création d'un interface entre ces deux types de domaines. Cette condition sera d'autant mieux réalisée, semble-t-il, qu'il existe une plus grande différence d'électronégativité entre les deux espèces d'atomes en présence, dans le réseau.

Je crois qu'il est possible de pousser le raffinement plus loin encore que l'a fait le Professeur Ubbelohde. En effet, je crois qu'on est amené à envisager l'existence dans un certain domaine de température, non seulement d'équilibres entre deux états extrêmes, l'un ordonné, l'autre désordonné, mais entre une infinité d'états intermédiaires caractérisés par des états d'ordre intermédiaires. Ceci est à rapprocher de l'aspect structural de la transformation $\alpha \rightleftarrows \beta$ du cobalt dans laquelle les états extrêmes sont caractérisés par une succession de couches d'atomes en position A, B et C, suivant les séquences AB AB AB AB et ABC ABC ABC, correspondant à deux états d'ordre différents, mais où il existe en fait des états intermédiaires correspondant à la coexistence des deux types de séquences précédentes dans des domaines extrêmement petits.

M. Chaudron. — C'est un fait de grande importance et bien connu que les traitements thermiques peuvent modifier la structure des phases métalliques.

La phase métallique la plus importante par ses applications est sans aucun doute la phase austénite que l'on trouve dans le diagramme fer-carbone et qui est une solution solide de carbone dans le fer γ. Cette austénite possède un point eutectoïde à 720° pour une composition voisine de 0,8 % de carbone. L'ensemble des traitements thermiques peut-être représenté dans un diagramme TTT (diagramme de Bain). On peut également, à partir de la phase FeO, qui a son point eutectoïde à 570° : $4\ FeO \rightleftarrows Fe_3O_4 + Fe$, établir un diagramme tout à fait semblable. Nous avons pu, avec M. Collongues, mettre en évidence une transformation de type martensitique par trempe de FeO à basse température (1). On peut donc par traitement thermique obtenir une nouvelle phase comme dans le cas des alliages.

La transformation ordre-désordre doit également nous montrer l'intérêt pour le chimiste de tenir compte des traitements thermiques dans les domaines pourtant assez éloignés de l'état métallique.

M. Forestier. — Doit-on considérer comme applicable d'une manière générale le point de vue actuel sur le rapprochement entre la transformation du deuxième ordre et du premier ordre dans les cas examinés ici?

Cette question vaut aussi bien pour les alliages que pour les composés ioniques.

M. Collongues. — L'intervention du mécanisme de germination et croissance dans la transformation ordre-désordre a été démontrée d'une manière rigoureuse dans les alliages cobalt-platine (CoPt) et or-cuivre (Cu_3Au). Pour la phase CuAu, Borelius (1) considérait que la transformation s'effectuait d'une manière discontinue au voisinage de la température de transition et d'une manière continue à basse température. Mais récemment, Kuczynski (2) a mis en évidence l'intervention du processus de germination même à basse température. Au contraire, l'existence d'un mécanisme continu de transformation semble bien démontrée pour l'alliage cuivre-zinc (CuZn) (3). Mais il ne semble pas possible de prévoir *a priori* le type de transformation suivant la différence d'électronégativité des deux éléments, qui est considérable pour l'alliage CuZn.

La première transformation ordre-désordre signalée dans un composé partiellement ionique est celle de l'iodure double d'argent et de mercure Ag_2HgI_4 (4). Nous avons étudié plus spécialement les transformations des ferrites, en particulier celles des ferrites de lithium $FeLiO_2$ et Fe_5LiO_8. La différence des numéros atomiques

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(1) R. Collongues, Thèse, Paris (1954).

du fer et du lithium est en effet suffisamment élevée pour que la mise en évidence des raies de surstructure soit possible.

Dans les deux cas, nous avons mis en évidence la précipitation de l'une des phases (ordonnée ou désordonnée) à l'intérieur de l'autre.

1° La phase $FeLiO_2$ est cubique à haute température. Les ions Fe^{+++} et Li^+ sont répartis d'une manière désordonnée dans les positions cationiques d'un réseau de type NaCl. Au-dessous de 670°, ce ferrite subit une transformation qui conduit à l'établissement d'un ordre dans la répartition des cations. Les raies de surstructure apparaissent et la maille devient quadratique. L'étude aux rayons X révèle la coexistence des deux phases ordonnée et désordonnée et l'on observe au microscope la précipitation de la phase ordonnée à l'intérieur de la matrice désordonnée sous forme d'une structure de Widmanstätten (5).

2° Le ferrite Fe_5LiO_8 subit lui aussi une transformation ordre-désordre à 710° avec apparition de raies de surstructure, mais sans modification des dimensions de la maille cristalline. L'étude aux rayons X ne permet donc pas de révéler le mécanisme de la transformation. Mais on observe au microscope la croissance sous forme de dendrites de la phase désordonnée à l'intérieur de la matrice ordonnée (6).

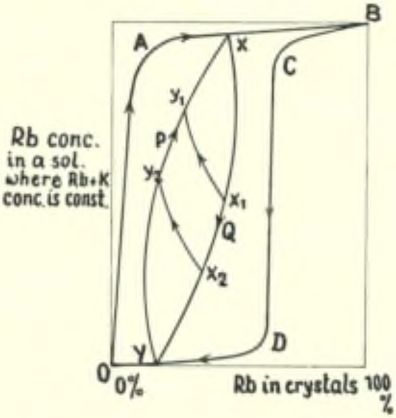
Nous pensons que ce processus discontinu de transformation se rencontre également dans d'autres ferrites, comme le ferrite de cuivre.

M. Barrer. — I have some observations bearing on the comments by Professor Ubbelohde upon the special free energy terms which arise when a new phase is nucleated on or in a matrix of a parent phase.

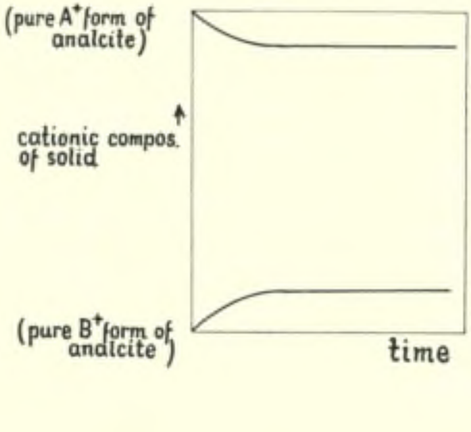
In my review I have indicaded how hysteresis can result from these extra free energy terms. However I would like to illustrate this by reference to some ion exchange experiments made with analcite $NaAlSi_2O_6H_2O$. This species can give a variety of exchanges such as $Na \rightleftarrows K$; $K \rightleftarrows Rb$; $Na \rightleftarrows Tl$, etc., which we have studied

(1) Borelius, *J. Inst. Metals*, **74**, 17 (1948).
(2) Kuczynski, Hochman et Doyama, *J. Applied Physics.*, **26**, 871 (1955).
(3) Beck et Smith, *Trans AIME*, **194**, 1079 (1952).
(4) Ketelaar, *Z. Phys. Chem.*, **26 B**, 327 (1934).
(5) R. Collongues, *Comptes rendus*, **241**, 1577 (1955).
(6) I. Behar, *Comptes rendus*, **242**, 2465 (1956).

rather fully. Some times one end member of exchanges (e.g. the pure form, $KAlSi_2O_6$) is not miscible over the whole composition range in the other form (e.g. the pure Rb form). We have demonstrated the appearance of a two phase region by optical and X-ray methods. One form (e.g. Rb rich) grows on or in a matrix of the other form (e.g. K rich) at a critical concentration Rb in the parent crystals. A very striking hysteresis loop OABCD was found in this case (fig. 1). The loop was also scanned (path XCYDX and paths $X X_1Y_1X$; $X X_2Y_2X$).



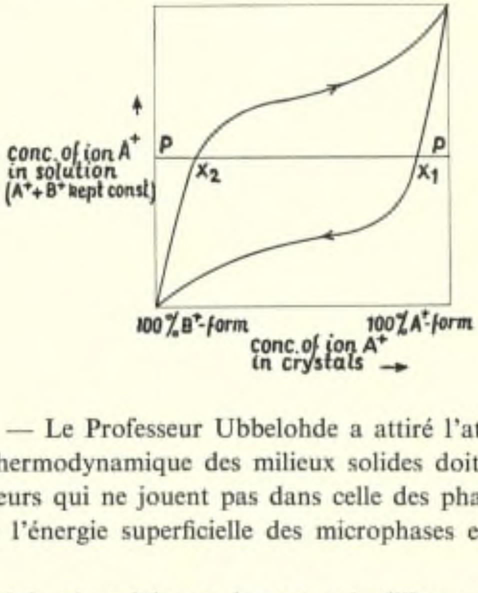
Another result of the nucleation process I have referred to is indicated in figure 2, which is representative of several of the exchanges studied in analcite.



Starting with a solution saturated with respect to each exchanging salt (e.g. KCl and RbCl) and exposing to this solution crystals of pure Rb and K analcite respectively different end points appeared.

By using solutions mutually saturated with respect to each exchanging ion A^+ and B^+ the concentrations of these ions in solution are held constant during the exchange.

The explanation follows at once from consideration of a typical hysteresis loop. Suppose PP represents constant concentration of A^+ in the electrolyte, where PP intersects the loop as shown. Then starting from the 100 % A^+ form the end point is clearly X_1 and starting from 100 % B^+ form the end point is obviously X_2. Reaction will never proceed past these two points in the electrolyte of composition represented by PP.



M. Defay. — Le Professeur Ubbelohde a attiré l'attention sur le fait que la thermodynamique des milieux solides doit tenir compte de deux facteurs qui ne jouent pas dans celle des phases ordinaires et qui sont : l'énergie superficielle des microphases et leur état de tension.

M. Ubbelohde n'emploie pas le mot « équilibre » pour les états stationnaires décrits par cette méthode. Il me semble que l'on peut parfaitement envisager ces problèmes comme problèmes d'équilibre, mais ce sont des états d'équilibre qui ne peuvent se décrire avec les seules variables T, V et concentrations; il faut au minimum adjoindre une variable liée à la dimension des microphases. Même lorsque le système présente le phénomène d'hystérèse, chacun des points de la courbe de montée comme chacun des points de la courbe de descente représente un véritable état d'équilibre. Cela se voit très bien dans l'hystérèse de condensation capillaire, où chaque point de la courbe d'hystérèse représente un état d'équilibre avec des pores de rayons déterminés.

L'exemple d'hystérèse des courbes de sorption d'un élément dans un solide, donné par le Professeur Barrer, est extrêmement instructif. L'explication la plus vraisemblable est celle des retards de nucléation, proposée par l'auteur dans son rapport. Mais étant donné que tout germe tend en général à croître indéfiniment dès qu'il a dépassé sa dimension critique, les courbes d'hystérèse ne seront chacune de vraies courbes d'équilibre que si quelque chose dans le réseau s'oppose à l'accroissement du germe. Dans la théorie du « host lattice », la dimension et l'environnement des cavités de diverses sortes déterminent cette limite. Elles jouent ainsi un rôle analogue à celui des rayons des pores dans la condensation capillaire, où ces rayons sont nombreux, différents mais fixes.

Je vois quelque difficulté à appliquer cette pensée à la nucléation ordre-désordre, car je ne vois pas, à première vue, ce qui va empêcher un germe de s'accroître indéfiniment et d'envahir toute la phase.

M. Ubbelohde. — Nuclei of small size have their free energy modified by the surface energy term, according to the well known Kelvin equation. But if they are free nuclei without any mechanical constraints they will have a true equilibrium point with another phase, determined by their dimensions.

In the smeared transitions in solids the nuclei or « regions » of ② are formed within the matrix of ①, and this sets up a system of mechanical strains as well as introducing surface energy terms. If any process could be devised in which solid ② could be formed from solid ①, as an extensive phase, one would expect the smeared transition to be replaced by a true first order transformation.

In the immediate neighbourhood of a transformation, mechanical strains of the kind described must have a relaxation time large compared with the time of experiment, since most examples of hysteresis are not suppressed by taking longer over the observations. The state of strain is « frozen in ». On passing beyond the transformation region, the differences between ① and ② become larger, so that relaxation of the transformation occurs and the change ① → ② or ② → ① is completed.

There is nothing novel about thermodynamic equilibria which are frozen in with respect to certain changes, whilst other changes set up true equilibrium. For example in a mixture of $H_2 + O_2$, at room temperature true equilibrium is rapidly set up with respect to temperature, and with respect to mixing of the molecules by diffusion.

On the other hand equilibrium with respect to the bond rearrangement : $2H_2 + O_2 \rightarrow 2\,H_2O$ is frozen in at room temperature because of the large activation energy required.

In the summation of states which determines the free energy, the factors referring to such frozen-in fluctuations retain an arbitrary value depending on the past history of the system, and are not minimised. Thus various mixtures of H_2, O_2 and H_2O can be discussed at room temperatures.

M. Bénard. — Un aspect particulièrement intéressant du problème des combinaisons intermétalliques paraît être la transition progressive de phases dans lesquelles la liaison est manifestement métallique à des phases dans lesquelles la liaison est sinon entièrement ionique, du moins largement polaire. Cette transition se manifeste dans des séries dans lesquelles le rapport stoechiométrique varie en donnant des phases successives de structures différentes.

Un bon exemple est donné par le système nickel-soufre dans lequel la phase Ni_3S_2 présente un caractère métallique très accusé, tandis que la phase NiS_2 présente un caractère salin, la phase NiS possédant des caractères intermédiaires. La transition se manifeste également lorsque dans une même série on remplace le soufre par les homogues supérieurs : sélénium et tellure. Je serais heureux de savoir si l'évolution des propriétés physiques dans ces différentes séries s'accompagne d'une diminution systématique de l'étendue des domaines homogènes lorsqu'on passe des phases type métallique aux phases type ionique. *A priori*, on pourrait en effet s'attendre à observer une telle variation au moins dans le second cas, puisque les possibilités d'échange entre les positions des deux types d'atomes constitutifs diminuent lorsque la différence d'électronégativité entre ces atomes s'accroît, entraînant de ce fait une réduction de la largeur de la courbe d'énergie libre de la phase en fonction de la composition. Il est évident cependant que les caractéristiques des phases adjacentes peuvent modifier l'étendue réelle du domaine d'homogénéité et masquer au moins partiellement cet effet.

M. Collongues. — Il ne semble pas possible d'établir une relation entre l'étendue des phases intermédiaires et la différence d'électronégativité des deux éléments. En effet, dans les phases de substitution, le facteur électroaffinité n'a qu'une importance secondaire vis à vis du facteur de dimension et du facteur concentration électronique. On peut cependant noter que l'étendue des domaines d'homogénéité des phases γ obéissant aux règles de Hume-Rothery est en général plus faible que l'étendue des phases β. Or les liaisons dans les phases β sont essentiellement métalliques; les phases γ au contraire sont fortement ionisées.

Dans les phases lacunaires, il est impossible de prévoir la variation de l'étendue du domaine d'homogénéité en fonction de la différence d'électronégativité des deux éléments, puisqu'il ne se produit pas d'échange entre les positions des deux types d'atomes. Dans le cas des phases de type NiAs, il est même assez curieux de constater que les domaines d'homogénéité semblent d'autant plus *étendus* que les différences d'électronégativité sont plus *grandes* (fig. 12 et 13) :

Co — Te	Co — Sb	Co — Sn	
16 %	7 %	3 %	
Ni — Te	Ni — Sb	Ni — Sn	Ni — In
16 %	7 %	7 %	4 %

M. Kuhn. — Quelles sont les méthodes par lesquelles le nombre d'électrons libres dans les métaux peut être déterminé.

M. D'Or. — Je crois que l'une des données qui renseignent le mieux de façon quantitative sur la densité en électrons « libres » dans un métal est la chaleur spécifique mesurée à de basses températures où la composante de réseau est devenue pratiquement nulle. Ceci se limite cependant au cas des métaux à structure électronique sous-jacente saturée; dans le cas des métaux de transition à couches *d* non saturées, la relation entre la composante électronique de la chaleur spécifique et la densité en électrons libres est en effet complexe.

M. Ubbelohde. — The fact that a metal such as palladium becomes diamagnetic for a given proportion of hydrogen atoms in solid solution does seem to imply that the *d* bond has been filled *at this concentration.* The number of electrons added is not immediately relevant for the number of vacancies in pure palladium, since the overlap of hypothetical atomic orbitals is likely to change as the interatomic distance expands in the crystal as hydrogen is added.

There is reason to believe that for some of the transitional metals the *d* bond is quite sensitive to interatomic separations.

Certain anomalous thermal expansions of alloys of transitional metals may arise in this way. The high solubility for hydrogen of certain alloys of palladium and silver likewise suggests that the model of electron transfer from the added hydrogen atoms to a *fixed* number of vacancies in a *d* bond in palladium is too simple to account for all the experimental findings.

M. Chaudron. — Il est possible d'expliquer la stabilisation de certains composés non stoechiométriques par l'application de la théorie lacunaire de Hägg. Le sesquioxyde de fer cubique pur est instable vers 200⁰ et même à plus basse température. Au contraire, par addition de sodium ce corps peut être obtenu au-delà de 700°. On peut écrire successivement :

$$3\ Fe^{2+} \rightarrow 2\ Fe^{3+} + \square \qquad \text{et} \qquad 2\ Fe^{2+} \rightarrow Fe^{3+} + Na^{+}$$

Ce problème a été repris récemment par M. Michel, de l'Université de Lille (1) : des ions tétravalents tels que Ti^{4+} qui se substituent dans la magnétite suivant le schéma :

$$2\ Fe^{3+} \rightarrow Ti^{4+} + Fe^{2+}$$

provoquent une augmentation du nombre des lacunes et on observe une diminution de la stabilité.

Dans le cas du protoxyde de fer, ce sont précisément les compositions de la phase FeO les plus riches en lacunes qui sont les plus instables. Je pense qu'il serait intéressant de créer sur certains composés, des défauts (lacunes) par bombardement. L'étude de ces composés artificiels serait d'un grand intérêt, mais elle présenterait certainement des difficultés techniques, dues probablement à une trop grande instabilité de ces composés. Enfin, il conviendrait de remarquer que la non-stoechiométrie établit une sorte de continuité entre les composés classiques de la chimie minérale. On ne peut plus dire que la chimie minérale est une chimie de prototypes; en effet, les solutions solides et la non-stoechiométrie sous ses multiples aspects donnent lieu à de nombreuses phases dont les propriétés peuvent varier d'une manière très importante.

(1) A. Michel, *Comptes rendus* (1956).

(2) G. Chaudron et J. Bénard, *Premier colloque des réactions dans l'état solide*, Paris (1948), p. 88.

Non-Stoicheiometric Organic Compounds

by **H. M. POWELL**

GENERAL CONSIDERATIONS

After the great success of Dalton's atomic theory which involved the idea of integral combining powers of atoms, chemists came to think that if elements combined they did so according to a simple plan. Any pure compound consisted of molecules containing definite and unalterable numbers of atoms of the elements involved. If all atoms of any one of the elements, A, B, C... are identical, the composition of a compound composed of molecules of formula $A_p B_q C_r$... where p, q, r... are integers, is constant. The weights of the elements that can unite to form one of the possible compounds that come from varying A, B, C... and the integers p, q, r... are simply related to the weights in other compounds. At first the integral values of p, q, r... were based on the compositions determined by analysis and any substance that did not obey the rule was suspected of being impure. Electronic theories of valency which have followed theories of atomic structure explain the integral values of p, q, r... by identifying chemical combination with the interaction of electrons which, in some sense at least, are regarded as entities and are ascribed in whole numbers to each atom. The definite compositions of molecules are explained if it is supposed that each atom involved in the formation of a chemical union must contribute a whole number of electrons for the process. When slightly modified to allow for isotopic variation in the elements these requirements of composition still hold for molecules or other complexes of finite groups of atoms such as may exist in the vapour and liquid states or in solutions. They also apply to many crystalline substances, but could no longer be maintained as unbreakable rules when crystal structures were examined by X-ray methods. Almost the first result of X-ray structure determination, which naturally was carried out on substances of the simplest chemical formulae, was to abolish the molecule for some compounds. After the atom or ion the next larger distinguishable entity in the structure was not the supposed molecule of a few atoms in the correct ratio to explain the composition, but the crystal as a whole or some other indefinitely extended complex. Integers p, q, r... may still arise from electronic requirements, but there are other possibilities. If one of the elements involved displays more than one valency, its compounds which exist in the form of finite molecules will obey the rules and have the compositions predicted from Dalton's laws. A substance of composition intermediate between two of those predicted from the law of multiple proportions may be described as a mixture of two or more molecular species capable, in principle, of separation into molecules of different weights. But when the molecule does not exist such a description has no meaning. In many crystalline inorganic compounds no molecules are found. Instead the structures are composed of ions or atoms linked in various ways.

Ideally the crystal is composed of a number of interpenetrating lattices all of the same dimensions. Ideally also the lattice points of each of these are occupied by a set of identical atoms. The crystal as a whole is made up of a finite number of these lattices, and thus it has a simple formula in accordance with Dalton's laws. Departures from these laws in crystalline compounds are commonly described therefore in terms of lattice defects. Many types of lattice defect are known and not all will affect the composition. The simple ratios between the numbers of atoms of the various elements that compose the crystal may arise from requirements such as the need for over-all electrical neutrality or for the formation of some definite number of electron-pair bonds. These requirements determine the relative numbers of the interpenetrating lattices. If a defect occurs, for example, by the ommission of an atom from one of these lattices, it may be balanced by some other defect, e.g. by an atom in an interstitial position or at the surface, or by the omission of an atom of another kind.

It is particularly when a crystal is in part composed of atoms of an element which can have more than one valency that the combining ratio of the atoms may vary. If some of the positions that formally are attributed to a set of identical atoms all in the same valency state are in fact occupied by atoms of the same element in a different valency state the number of combining atoms required in the complementary interpenetrating lattices is no longer that required by the simple formula. Vacant spaces may be left in the first lattice to compensate for those occupied by atoms in higher valency states, and the number of atoms in one or more of the interpenetrating lattices may vary according to the fraction of the possible positions occupied. In this way non-stoicheiometric compounds result; their existence has a simple structural explanation and the ranges of their compositions can be explained.

Some lattice defects do not affect the combining ratios of the atoms. For example crystalline silver cyanide consists of indefinitely extended chains of Ag-CN-Ag-CN-Ag in parallel array (1). The disorder which consists of irregular displacements of the chains in the direction of their lengths has no effect on chemical composition. The thermal oscillation or rotation of atoms or groups of atoms similarly has no effect.

A great many organic compounds can exist as single molecules identifiable in the gaseous, liquid or solid states or in solutions as entities separated from the surrounding matter by distances which are large in comparison with the normal distance of separation of atoms that are joined by a chemical bond.

If differences such as those due to isotopy and thermal motion are disregarded, a pure substance of this kind must consist of a set of identical molecules. The ratios of the constituent atoms are determined by the integral valencies of the combining elements. This is a property of the free molecules and is unaffected by crystallisation. Even if the crystal has more complex aggregates, e.g. by hydrogen bonding of molecules, or there are lattice defects involving whole molecules, the combining proportions of the elements are unaltered. It seems therefore that only when organic crystals contain two or more kinds of molecules can non-stoicheiometry arise.

A molecular crystal grows by using intermolecular attractions which add molecules to a regular stack. It is easy to see why this can proceed readily when all the molecules are identical. The chance that a mixture of two sorts of molecules will find some way of building a regular lattice pattern which contains them both in ordered array must be small, or substances could not be obtained pure from such mixtures, but particular pairs will form molecular compounds of this kind. A few substances seem especially given to this behaviour and any one of these may appear as a constituent common to a large number of related molecular compounds. Frequently, though not necessarily, there is a common structural basis in such a series. Enough intermolecular compounds are now known to make profitable a consideration of them as a whole with particular reference to their compositions. By analogy with inorganic structures it might be supposed that when analysis reveals a simple ratio of the molecular components the compound should be described as stoicheiometric, and non-stoicheiometric when it is otherwise. The case turns out to be more complex than this but provisionally the word " stoicheiometric " may be understood in this sense.

Some groups of molecular compounds depend on the similar chemical characteristics of their components. Thus of the large number of intermolecular compounds formed by aromatic polynitro compounds with other molecules (^{2}) many have in common the three nitro groups in one molecule and an aromatic system in the other. The formation of such compounds is affected by chemical factors such as the different electron-donating powers of different substituents, and in many of them there may be a strong localised interaction between particular parts of each molecule. These interactions require a special set of interatomic distances between the molecules. The set of contacts of each atom with other atoms in neighbouring molecules is part of the whole complex structural pattern. Lattice defects which could alter the ratio of the components are unlikely. Whole molecules might be missing but the proportion of spaces vacant is likely to be very small since large empty spaces would thus be formed. As will appear, organic crystals sometimes have large empty spaces but there are special reasons for it.

In other series there is no chemical similarity of a group of molecules that show similar behaviour in molecular coumpound formation. Thus β-quinol clathrates (^{3}) of ideal formula $3\,C_6H_4(OH)_2.M$ are formed where M is SO_2, H_2S, HCN, CH_3OH, $H.CO_2H$, C_2H_2, N_2, O_2, CO_2, A, Kr, and others. The binding, in some cases at least, is very weak and any similarities of the participating molecules are geometrical rather than chemical. Departure from the ideal formula is common in this series.

It is convenient for the present purpose to divide the structures of intermolecular compounds into two main classes. In the first class the component molecules M and N are intricately related so that the next larger distinguishable unit after the single molecule is some group composed of both M and N molecules in the same ratio as they occur in the crystal as a whole. For example the molecule may be arranged according to a pattern resembling the co-ordination structures of simple inorganic compounds in which after two individual atoms or ions a and b the next larger distinguishable group is the whole crystal of composition $a_n b_m$, n and m integral, each a being surrounded by a group of b's and each b being surrounded by a group of a's with co-ordination numbers determined by composition of the compound and other factors such as the dimensions of the particles. Alternatively the structural sub-unit of the same composition as the whole crystal may extend indefinitely in two dimensions or in one. Special interactions between particular atoms or groups of atoms in one molecule M, with some atom or groups in the component N are likely to give structures of this first class. In the second class structural sub-units may be distinguished which contain the component molecules in proportions different from those of the molecular compound as a whole, a special and common case being that in which a sub-unit of the structure is composed entirely of molecules of one kind. These sub-units could consist of a group containing a finite group of molecules all of the same kind or of indefinitely extended groups in 1, 2 or 3 dimensions, to give chains, sheets or 3-dimensional frame-works.

In the first class, compositions are determined by the particular interactions of one molecule with those of the other kind. It is not impossible for there to be lattice defects, for example by ommission of a complete molecule, but such defects are not likely to be numerous and the composition should not depart greatly from the ideal. Some kinds of lattice defects such as the displacement of a whole layer or chain component of such a structure would have no effect on the composition since these components of the structures have the composition of the crystal as a whole. In the second class, possibilities for non-stoicheiometric compounds arise in various ways. The structural part of the crystal composed entirely of molecules M may not be able to exist without its companion of composition N, though in some instances it does, but the fitting together of M with N may be governed by geometrical factors. If there is no strong localised bonding between the two different kinds of molecule, these geometrical factors may lead to simple proportions of M and N, but often they do not. The compositions of some intermolecular compounds of the second class will now be considered.

CHAIN AND LAYER STRUCTURES

Among crystalline intermolecular compounds already known to contain a complex made up of molecules of one component only several structural types may be distinguished. The complex may have a form that could be packed by itself to fill the space satisfactorily, and the molecular compound may be looked upon as built up of complexes containing molecules of the one kind together with other components which lie in between the complexes. These other components may be single molecules, finite groups of molecules, or may themselves also take on the geometrical character of an indefinitely extended complex. It there is no strong localised interaction between the two kinds of molecules, the composition of the molecular compound may be determined by geometrical conditions which have to be satisfied when the various components are fitted together into a structure. For example, suppose that one component forms a chain-like complex consisting of a stack of molecules regularly repeated along a lattice direction. Let the crystalline molecular compound consist of these chains arranged parallel, with regular lattice spacings between their long axes, together with molecules of the other component in positions between the chain complexes. These molecules between the chain complexes can fit some regular plan of repetition parallel to the chain lengths and might themselves constitute a second form of chain component. In the absence of strong localised bonding which will fix molecules of one kind in definite positions relative to the molecules of the first type of chain complex, there may be no simple relationship between the repeat lengths along the two kinds of chain. The ratio of one component to the other in the structure would then be determined by these repeat lengths, which in turn are related to the lengths of the molecules concerned and the intermolecular separations in the direction of the chain. An idealised form of structure of this sort can be imagined as composed of two arrays of cylinders which represent the packing dimensions of molecules. Imagine cylinders end-to-end in chain-like forms arranged parallel in a square pattern. Let a second and different set of cylinders be placed at the centres of the squares in the first. There is a definite 1 : 1 ratio of *chains* of the two kinds. If the cylinders of the two kinds are of unequal cross sections but of equal lengths they also have a definite 1 : 1 ratio, but if the two kinds are of known unequal lengths there will be a known relation between the number of *cylinders* of the one kind to those of the other, but this need not be a simple whole number ratio. If, for example, the cylinders of one kind had a length 1 and those of the other had a length $\sqrt{2}$, the composition, although definite, could not be expressed as a ratio. In practice any analytical result will be expressible as a ratio of sufficiently large numbers and to describe a compound as non-stoicheiometric simply because these numbers are large may be considered arbitrary. Without any essential change in the character of such a structure it might have a simple whole number ratio of the components. If a series of cylinders of different lengths can be imagined, e.g. because they represent members of homologous series, there will be some packing lengths which bear a simple ratio to the packing length of the other molecule. In this type of structure with parallel chain components, and its analogue with parallel layer components, the molecules therefore fill space satisfactorily and non-stoicheiometry may arise as described from incompatibility of the repeat distances in the one- or two-dimensional lattice patterns of the sub-units.

A further possible cause would be the failure of the chain or layer components to repeat in a regular manner, i.e. the chain or layer expected for regularity of the lattice might be sometimes replaced by the " wrong " component.

Known structures of this possible form are not numerous. The molecular compounds formed by hexamethylbenzene with the picryl halides may include examples ([4]). These compounds, although formally similar to the general class of molecular compounds between aromatic polynitro-compounds and other aromatic substances, have a structural characteristic which is not common among them. Both components occur in the compound as layers. That of the hexamethylbenzene differs only slighly from a layer in the structure of the normal anorthic form of the pure substance; it is almost identical with the layers in the less stable orthorhombic form (^{5}). The other component, picryl chloride, bromide, or iodide, forms a layer which does not, however, bear any simple resemblance to the structures, so far as they are known, of the pure picryl halides. The molecular compound consists of alternate layers and has, at least approximately, the 1 : 1 ratio.

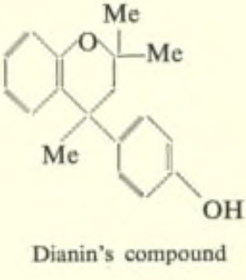
The molecular compounds with the chloride and bromide have orthorhombic pseudo unit cells roughly 14 × 9 × 15.3 A. There are, however, for the chloride faint continuous streaks in intermediate positions between the reciprocal lattice rows corresponding to this cell, and for the bromide more intense streaks and smudges which in certain positions have the appearance of fuzzy spots corresponding to a cell with thee b dimension three times enlarged to approximately 27 A. The direction of the streaks corresponds to an irregularity of spacing along a (14 A), i.e. perpendicular to the layers. In the iodide the irregular streaks and smudges are replaced by sharp spots which require the three times enlarged b spacing, but there is still some disorder since in place of the streaks there are discontinuous lines that break up into spots suggesting an enlargement of a. It is evident that these two layer components have a disordered sequence and possibly they do not make a good fit. It might be argued that if one of the three halides could form a layer structure to match that of the hexamethylbenzene then the other two, because of their slightly different dimensions, could not. This is, however, conferring too fixed a character on the hexamethylbenzene layer. This clearly can alter since there are two crystalline modifications and molecules which are linked by van der Waals forces will to some extent adapt their packing to fit the shapes of their partners in molecular compound formation. In agreement with this the dimensions of the three cells differ slightly, and most of the observations might be explained as due to an irregularity in the sequence of layers that may fit in several only slightly different positions. However, the compound with picryl iodide has been found to vary in other ways, the enlargement along the a dimension varying from crystal to crystal, although no deliberate variation of the conditions of formation has been made. From the existence of several distinct though related diffraction patterns there must be a number of molecular arrangements which may or may not have the same molecular ratio. The disorder effects which relate to the sequence of layers seem most likely to be caused through the identity of the hexamethylbenzene with the layer in the less stable orthorhombic form of this substance. One event that seems almost certain to occur is the deposition of a wrong layer, i.e. a hexamethylbenzene layer in place of the expected picryl halide layer. This must cause a departure from the simple molecular ratio. Disorder may be made apparent to X-rays with a comparatively small number of faults. This, combined with the difficulty of more than one crystal type being produced, makes a considerable analytical difficulty and the case has not been established as firmly as may be desired.

INCLUSION STRUCTURES

More numerous are the molecular compounds in which one structural component consists entirely of one kind of molecule but the form is such that it does not by itself fill space to the extent normally required for formation of a crystal. In addition to the unfilled small spaces that are left even by the closest packing of atoms or molecules there are comparatively large spaces available for the other component of the molecular compound. The type may be described as inclusion compounds, and there is not necessarily any strong localised interaction of the enclosing and included molecules. The binding, apart from some special cases, arises from the combination of a large number of van der Waals interactions. Whether the molecular compound has a simple molecular ratio is determined in part by geometrical considerations. To be enclosed by another structure a molecule must have size and shape suited to the enclosure, and it is convenient to divide the enclosures into those which may be considered as closed and those which are open. Of the two forms considered, one has a closed molecular cage limited in all directions and into which the second molecule must fit. The other has endless channels running through the structure so that although included molecules may be limited as to what may be called their cross sections, they are not geometrically restricted with regard to length. Since the molecular dimensions used to discuss these matters correspond to equilibrium values and do not have the invariability of the geometrical forms used to represent them, this division into two kinds, although practical, is an approximation only. A space which is effectively closed for a large molecule may be open and continuous with its neighbours for a smaller molecule.

A characteristic of structures with closed cavities is that there must be a fixed ratio of cavities to surrounding molecules. In the simplest case of a single enclosed molecule which occupies most of the available space in a cavity, the ideal formula is simple. Thus in the β-quinol clathrates where three molecules of quinol (Q) are required to form a single small cavity able to contain a single atom or small molecule (M), the ideal formula is 3Q.M. It is found when M is methanol or methyl cyanide, the molecular compound being formed by crystallisation of quinol from the solvent which in these cases itself provides the included molecules. A similar definite ratio of water molecules to others is found in the gas hydrates (^{6}). Departures from these ideal stoicheiometric formulae, however, may arise in at least two ways. The cavities are assumed to be subject to very little variation in size and shape for structural reasons. In the case of the quinol clathrates, for example, there is a hydrogen-bonding system which, although it does not forbid all variation, imposes severe limitations. This means that when only two components are present, the only alternative to a single atom or molecule in the cavity is a vacant space. Whether or not all the possible cavities are filled depends on the conditions of formation and in practice clathrates of a wide range of composition $3Q.xM$, x having values between 0 and 1, can be made.

A second case is that a closed cavity may be large enough to contain more than one molecule. This is the case with Dianin's compound (^{7}). There are a set of ideal limiting formulae of fixed numbers of enclosed to enclosing molecules. This is illustrated in Table I. The ideal formula depends on the size of the included molecule, and the actual composition can depart from these only through a deficiency of included material.



Dianin's compound

TABLE I

2 : 1 *	6 : 1
Methanol	Bromobenzene
	1 : 3-Dibromopropane
3 : 1	*m*-Dichlorobenzene
Acetic acid	*o*-Dichlorobenzene
Carbon tetrachloride	Ethylene dibromide
Methyl iodide	Iodobenzene
Nitromethane	Tetrachlorethylene
Sulphur dioxide	Argon

* Ratio of Dianin's compound to included molecule.

The ideal compositions are explained by the sizes of included molecules which are such that one, two, or three molecules may be included in each cavity. Adducts of carbon disulphide, chloroform, and iodine show deficiencies compared with the 3 :1 formula ; those of *p*-bromanisole and 2-bromopyridine are deficient compared to the 6 : 1 type. The argon compound shown in the table as having the 6 : 1 ratio should, in view of the relatively small size of the argon atom, be regarded as deficient with respect to the 2 : 1 type.

The deficiencies might be supposed to arise in the same way as in a singly occupied cavity through chance events when a cavity is closed, but there are differences. It is known that molecules in such cages have some freedom of movement (8). In this way they may occupy more than their normal space and thus a single one might have an effect in keeping out a second. A further factor which may apply to enantiomorphous pairs of molecules is mentioned later.

Best known of channel inclusion compounds are the adducts of urea and thio-urea (9). In these the space available for the other substance is without limit in one dimension. Possible compositions depend on whether the channels act as though uniform or non-uniform along their lengths. When there are no influences strong enough to attach included molecules to particular positions in the channels the molecular ratio is given by formulae such as :

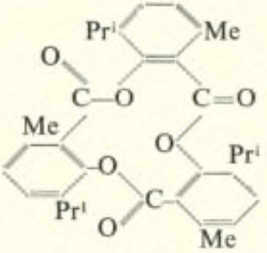
$$\frac{\mathrm{U}}{\mathrm{H}} = \frac{12\,[1.256\ (n - 1) + 4]}{2 \times 11.01} = 0.6848\,(n - 1) + 2.181$$

U = number of urea molecules, H = number of normal C_nH_{2n+2} molecules (10). The numerator, the effective length of hydrocarbon molecule, is divided by the constant length of the urea pattern parallel to the channel, and allowance is made for the number of urea molecules and channels per unit cell. These ideal compositions fit well with those found.

In adducts of thiourea with $\omega\omega'$ dicyclohexylalkanes there are noticeable periodic differences in intensity of interaction of the channel walls and included molecules. The included molecules do not follow one another at distances determined solely by their lengths. With molecules fixed in a less indiscriminate way, and sometimes repeating with periods related to those of the thiourea channels themselves, simple ratios of the component molecules arise. The same ratio may be found for three successive members of the series. For each included molecule there may be as much or more channel space as its packing length requires. There cannot be less, and steady increase in the molecular length according to the number of CH_2 groups eventually alters the proportion of components through intermediate values until a new simple ratio is reached.

It is certain that defects occur in cage compounds. They differ from some defects in inorganic non-stoicheiometric compounds in that the omission of an enclosed molecule does not require a compensating change in some other part of the structure. For some channel structures the agreement of compositions with formulae based on calculated lengths of included molecules shows that in these series effectively all the available space is filled. It may be that since the channels are open there is a greater chance of filling them. There is no difficulty corresponding to the closing of an empty cavity, in a clathrate, which will then never be filled, but the possibility of deficiencies in channel structures should not be overlooked. It is perhaps more difficult to detect than to understand such a deficiency.

Whether a given compound is stoicheiometric or not is determined by some form of analysis. Equilibrium diagrams may not always be easily obtained, and some organic intermolecular compounds present other difficulties. When enclosing structures are formed a relatively large amount of material is required for each space available for enclosed molecules. If both components are organic compounds some of the possible analytical quantities may be insensitive to change in the molecular ratio. Thus the compound formed by tri-*o*-thymotide with butanol would have $C = 74.4\ \%$, $H = 7.25\ \%$ for $2\,C_{33}H_{36}O_6.C_4H_9OH$ and $C = 74.1\ \%$, $H = 7.39\ \%$ for $2\,C_{33}H_{36}O_6.1\frac{1}{2}C_4H_9OH$. Differences finer than these must be measured to establish non-stoicheiometric compositions. In such cases it is better to analyse for the included component which amounts to 6.55 % in the 2 : 1 and 8.53 % in the 2 : 1 ½ formula, but a direct method, such as heating the material to find the loss of weight, may not be accurate. The enclosed material may be released only at a temperature far above its normal boiling point and even then it is not easy to know that all the included material has been driven off. To heat under vacuum is sometimes to risk possible losses due to volatilisation of enclosing component. In any case all losses due to whatever cause, such as decomposition, will appear to represent weight of the substance being estimated. When suitable atoms or groups are present in the included substance, determination of halogen, active hydrogen, and the like, may therefore give more reliable estimates of the molecular ratios. Estimation of the acid in urea adducts of aliphatic compounds provides a good example. There is, however, in all chemical methods,



Tri-*o*-thymotide

a difficulty concerning the material analysed. Frequently the included component is also the solvent used in its preparation. How a sample may be dried to render it suitable for analysis without loss of included material is uncertain.

In these circumstances a direct determination of the weight of material in the crystal unit cell has much to commend it. Unit cell dimensions may be measured fairly readily to an accuracy of one part in several thousands and a comparable accuracy in density is obtained without difficulty. The case may be illustrated by D. Lawton's measurements on the adducts of tri-*o*-thymotide $C_{33}H_{36}O_6$. Several series of inclusion compounds are formed by this substance. The compounds in some series are stoicheiometric, and have a close resemblance to clathrates. The lower members of the *n*-alcohols apparently fit one molecule per cavity. Thus the adduct with *n*-butanol has space group $P3_12$ and $a = 13.617 \pm 0.002$, $c = 30.603 \pm 0.002$ A. From the density (by a density column method) 1.146 g./c.c. the weight of the unit cell not accounted for by its six molecules of tri-*o*-thymotide, is 225 in molecular weight units. Three molecules of butanol require the value 222 showing that the molecular compounds fits a 2 : 1 ratio very closely.

One structural characteristic of channel structures may be used to reveal something about their composition in another method which depends on X-ray diffraction effects. If the molecules included in the channels can equally well occupy any position with respect to the repeat pattern of the surrounding structure and, in any one channel, follow each other at a regular distance determined by their packing lengths, they will produce an X-ray diffraction effect. In photographs this sometimes consists of streaks which, by suitable experimental procedure may be shown parallel to the layer lines of the main sharp pattern of spots due to the lattice of the enclosing structure. Effects of this kind have been observed with urea and thiourea adducts (11), the blue iodine adducts (12) and other substances. These streaks which resemble the effects of a one-dimensional lattice may be used to determine the repeat distance of the material in the channels. The length of the channels being parallel to the rotation axis of the crystal, and the number of them in a unit cell being known, the ratio of the two kinds of molecule is obtained simply by dividing one lattice constant into the other and allowing for the known number of enclosing molecules per

TABLE II

Tri-*o*-thymotide channel structures, containing alkyl halides. Hexagonal *c*-spacing from sharp layer lines = 29.04 Å.

Included molecule	Spacing from streaks parallel to layer lines (*c*-axis rotation)	29.04 divided by spacing of column 2	Number of molecules of alkyl halide to 6-tri-*o*-thymotide (by chemical analysis)
n-Heptyl iodide	12.72 A	2.26	2.1
n-Octyl iodide	14.5	2	2.0
n-Cetyl iodide	24	1.21	1.3
n-Cetyl bromide	24	1.21	1.1

unit cell. Table II gives some compositions calculated in this way. The third column shows the maximum permissible number of included molecules for every six tri-*o*-thymotide molecules, there being one channel per unit cell containing six tri-*o*-thymotide molecules. In this method there is no direct determination of the quantity of included material. That it is correct to divide the lattice constant by the figure calculated from the positions of the continuous streaks is made very probable by a comparison of the observed lengths with the probable dimensions of the included molecules. Thus the distances parallel to the *c*-axis between the centres of the terminal atoms of heptyl iodide, octyl iodide, and cetyl iodide, estimated from known bond lengths, and with the assumption that the molecule has the normal planar zigzag form, are 9.21, 10.46 and 20.5 A. To obtain the repeat distance allowance must be made for the packing space required by the terminal groups. In the absence of detailed knowledge of the structure this could be guessed as not much more than 4 A. It is simpler perhaps to take the spacings calculated from the continuous streaks and to subtract from each the appropriate value, 9.21 etc., when the remainder should represent the end packing effects. The values obtained are 3.51, 4.04, and 3.5 A for the compounds in the order given. The approximate constancy and the actual magnitude are in agreement with the assumptions made above. It thus appears that the repeat distance in the channel is correctly known but it is by no means certain that the whole of each channel is filled. The spread and diffuseness of the streaks in the direction perpendicular to the layer lines may be affected by other factors as well but in principle could be related to the regularity of the packing of molecules along the channels and the occurrence of vacant spaces. It is scarcely practicable to pursue this and the compositions estimated by the method above must therefore be regarded as giving for the included molecule a maximum value that in practice may not be attained.

In connection with these continuous streaks a distinction must be drawn between disorder and non-stoicheiometry. When the streaks lie at some arbitrary distance between the layer lines there is no simple ratio of the components if the space provided in the structure is filled as far as is possible with included molecules. However, the mere presence of the one-dimensional layer line streak does not mean that the compound is non-stoicheiometric. Thus in the case of octyl iodide-tri-*o*-thymotide continuous streaks coincide with the 2nd, 4th and 8th sharp layer lines for rotation about the *c* axis. This requires a simple ratio (1: 3) of octyl iodide to tri-*o*-thymotide molecules. When the repeat distance of the included material is the same as, or is simply related to, that of the tri-*o*-thymotide, disorder streaks may still arise because although the included material is regularly spaced along each channel it may be irregularly displaced relative to the tri-*o*-thymotide. The intermediate streaks may also occupy special positions between the layer lines, corresponding to enlargement of the unit cell in the direction of the channels to some simple multiple. This, with maximum filling by included molecules, also gives a simple ratio of included to enclosing molecules.

Measurement of the lattice constants of the surrounding structure and of the repeat distance for the enclosed material gives an ideal formula in the same way as complete structure determination for cage structures. In cage structures this ideal formula has a simple ratio of enclosing molecules to spaces; ideally these compounds should be stoicheiometric; vacant space defects may make them non-stoicheiometric. In channel structures the ideal formula, corresponding to all the possible space filled, may be stoicheiometric or not. If it is stoicheiometric vacant space defects will make the compound non-stoicheiometric. If it is non-stoicheiometric vacant space defects in the structure can alter the ratio of the components by lowering the proportion of included molecules. Thus from the layer streaks the ratio heptyl iodide to tri-*o*-thymotide in the completely filled form is calculated as 2.26 : 6. Vacant spaces would diminish this and it is possible that a value 2 : 6 could be obtained in this way. Thus a particular specimen of a channel-structure inclusion compound which ideally is non-stoicheiometric might through imperfections analyse as though it were stoicheiometric. This shows that no single way of investigating these compounds is by itself satisfactory. Both composition and structure must be examined. For the better examination of compositions it may be that analysis should be made more accurate. Possibly suitable isotopes should be used for this purpose.

OPTICALLY NON-STOICHEIOMETRIC COMPOUNDS

It was stated that non-stoicheiometric organic compounds will arise only when the compound can be regarded as formed from two or more molecular components, detectable by analytical methods which give their relative proportions. A form of non-stoicheiometry, however, can occur in what might be regarded as pure single substances. A very large number of synthetic organic compounds do not consist simply of identical molecules. They exist in two molecular forms which are the non-superposable mirror images of each other. Sometimes, although it has been comparatively rarely observed, the substance on crystallisation separates spontaneously into two non-superposable mirror image crystalline forms which are identical in nearly all their physical properties but are distinguishable by their shapes and some physical properties such as behaviour to polarised light. They can be separated by hand and in the examples so far discovered this separation constitutes a complete optical resolution of the molecules. It is known of a good many other substances that they crystallise as racemates, the crystal structure having symmetry elements which require the presence of equal numbers of the left and right mirror image forms. These racemates are so common as perhaps to be regarded as pure chemical substances, although it could be said that they are crystalline molecular compounds. Whether they are described in this way or not it remains that the lattice contains two different kinds of molecule. Any inequality in the number of right and left mirror image forms is in principle measurable since such a mixture can have an optical rotation varying between zero for the racemate to the full rotation given by either of the pure antipodes.

Disorders in crystalline structures which contain both mirror image forms could lead to non-stoicheiometric compounds in the optical sense, though they will not affect the atomic ratios. In this case disorders consisting of a vacant space could lead to optical activity in one of several ways. An ordinary racemic structure has space group positions in equal quantities for left and right mirror images. Vacant spaces would be expected to be of about equal frequency in the left and the right forms so that only a very small departure from the racemic mixture is likely. But other forms of crystal structure for optically active compounds are imaginable. In certain crystal structures molecules are found to occupy more than one space group position. For example 3 : 4 : 5 : 6 dibenzphenanthrene has space group A 2/a(13). Its unit cell contains 12 molecules: 8 of these occupy general positions in the space group which are crystallographically equivalent. The other 4 occupy a different set of space group positions. The group of 8 equivalent molecules do not use their possible symmetry in forming the structure, but each molecule of the group of 4 equivalents must show a two-fold symmetry axis. The compound *op*'dichlorodiphenyltrichloroethane (14) shows in exaggerated form what may be fairly common behaviour with molecules of sufficient complexity. Its anorthic unit cell contains 20 molecules. This unit cell being formally primitive these twenty require at least 10 crystallographically distinct sets of point positions each containing two molecules. Such complex arrangements of molecules to form a crystalline pattern are presumably due to difficulties in packing of awkward shapes. They are, therefore, in a general way more probable with unsymmetrical molecules which include those that are not superposable on their mirror images.

When molecules all of the same chemical constitution occupy several different sets of equivalent point positions in the space group, the relative numbers of molecules in the different groups cannot affect the composition except in the optical sense. Let a molecule be imagined in any general position of a non-enantiomorphous space group. If it is a dissymetric molecule its enantiomorph will occupy an equivalent position in accordance with the symmetry. No matter what other different sets, either of the general or the special positions may also be occupied, the same consideration applies to each and the crystal as a whole is racemic. The racemate is optically a stoicheiometric compound of 1 : 1 formula. Although this is the only kind known other optically stoicheiometric compounds are imaginable.

Let a molecule occupy a general position in an enantiomorphous space group. This molecule may have crystallographically equivalent molecules which are related to it by rotation- or screw-axes of symmetry. If it is dissymetric these equivalents are all of the same optical form. Suppose the structure as a whole contains other molecules occupying sets of equivalent positions. Each set consists of molecules all of the same optical kind, but there is no reason why all the different sets should have the same optical form. It is thus possible to imagine structures which contain the left- and the right-handed forms in various definite ratios. There could be a single set of equivalent molecules all of the one hand. Two forms of the structure will exist each being a mirror image of the other and containing one enantiomorphous form of the molecule. This is the kind of structure already known in crystals of resolved optically active substances. But in an enantiomorphous space group one set of equivalent positions could be occupied by the left-handed form of molecule and a crystallographically different set of the same number of equivalent positions could be occupied by the right-handed form of molecule. This structure would not be identical with its mirror image and there could exist both kinds of crystal. Each would display structural enantiomorphism but on dissolving either kind of crystal a racemic solution would be obtained. Defects in such a structure might lead to an optically non-stoicheiometric compound. Since the left- and right-handed molecules occupy structurally different positions a defect may be more likely to occur in one than in the other. There is not the same probability as in a racemic crystal that if, for example, molecules are missing from lattice positions, they will consist of equal numbers of left and right.

Similar considerations apply to other conceivable optically stoicheiometric compounds. If two or more sets of equivalent positions are occupied by molecules, each set having only those of one enantiomorphous kind, the crystal has an over-all composition D_nL_m where n and m are integers which need not be the same. There might be for example in space group $P6_2$ three equivalent L molecules in a special position requiring a two-fold symmetry axis in the molecule and a different set of six equivalent molecules, all D, in a general position. The unit cell would thus contain three L and six D molecules, the over-all composition being given by $n = 2$, $m = 1$. Two forms of crystal, the mirror images of each other, would exist, one corresponding to D_nL_m the other to D_mL_n. On dissolution these substances would show equal but opposite rotations of the plane of polarisation of light, and might be mistaken for *dextro* and *laevo* forms, unless some other means were available to show that the rotation is a definite fraction, in this case 1/3, of that of the completely resolved form. The ideal structures of such fractionally resolved materials are optically stoicheiometric. As in the preceding case departures from the strict stoicheiometric would occur if defects are more frequent for molecules in one set of positions than another. Such effects if they exist at all will be on a small scale and are not likely to be detected optically.

A defect which has not so far been considered is that in which some of the positions in an optically stoicheiometric structure are occupied by molecules of the wrong hand. This is ordinarily unlikely because in a well packed structure the wrong hand of molecule will not fit easily into the space left by omission of its enantiomorph. The case, however, is different when the optically active molecule is a component of an inclusion compound. The spaces in cage or channel structures are not so closely adapted to contain one particular molecule as is the space left by removal of a single molecule from the crystal structure of a pure substance. As all the known examples show, the enclosed molecule may be varied in shape. While the cavities, as revealed by lattice constant measurement, may remain unchanged the included molecule may be altered, e.g. propanol may be replaced by methanol in a closed cavity of a tri-*o*-thymotide clathrate structure. From this it is certain that in the case of the smaller molecule there must be free space in the cavity. It has been found that both the straight-chain aliphatic compounds and those with a hydrogen atom replaced by another atom or small group to form a slightly branched system may enter the same channel in some systems. Since there is room for the side group the unbranched molecule, which can sometimes be shown to be in its normal extended form, must fit rather loosely. For some purposes it has been convenient to regard the channels of inclusion structures as uniform hollow cylinders. These if they could contain one of two enantiomorphs could equally well contain the other; both forms may be regarded as fitting loosely, at least in the direction of the channel length. The proportion of left and right molecules that entered would be expected to be the same as that in the material used to prepare the inclusion compound.

The form of the spaces in inclusion compounds must, however, for this purpose be considered more closely. In enantiomorphous space groups they will not be superposable on their mirror images. In non-enantiomorphous space groups they will be superposable or they may occur in mirror image pairs.

The opposite extreme to the uniform cylinder which does not discriminate between left and right included forms is a space that can contain only one of these and rigorously excludes the other. It seems most likely to occur in clathrates where the cavity of defined shape may require the enclosed molecule to lie in a particular orientation. In a channel which is not regarded as a uniform cylinder but as a series of enantiomorphous but connected cavities there may be more freedom to displace the enclosed molecules and thus to find positions in which either right or left forms may be placed. The channel being imagined as composed of cavities all of the same enantiomorphous kind it may be geometrically possible to enclose both forms although there is a greater probability of fitting in one enantiomorph rather than the other.

Compositions in terms of enantiomorphous forms in molecular compounds can be of several kinds. An optically stoicheiometric form may result when there is a cage which is highly selective through close fitting to the enclosed molecule or molecules. This is illustrated by the adduct of tri-*o*-thymotide with secondary butyl bromide ([15]). From the racemic solvent any one crystal of the trigonal adduct has the composition $2\,C_{33}H_{36}O_6.C_4H_9Br$, all the butyl bromide being of one hand only, and similarly all the tri-*o*-thymotide being of one enantiomorphous form. The materials used to prepare this are both racemates but the yield can be obtained all in one form. Spontaneous optical resolution occurs and the rapid racemisation of the tri-*o*-thymotide in solution makes it possible through deliberate or accidental seeding to crystallise out one form only. Optically stoicheiometric compounds also result when the enclosing structure is centrosymmetric as in the adducts of Dianin's compound. Equal amounts of left and right forms of molecule are enclosed. The solutions of the molecular compounds give no optical rotation. Irrespective of the ratio of enclosed molecules to molecules of the Dianin's compound itself, there is a 1 : 1 ratio of the enclosed *dextro* and *laevo* forms.

Optically non-stoicheiometric forms may result when, as described above, there is a greater chance of fitting one enantiomorph rather than the other. Examples are cyclodextrin adducts ([16]) and urea adducts ([17]). The cavities in both these structures are not identical with their mirror images and when a racemic solvent is used to make adducts it is found that a partial optical resolution occurs. In the case of the cyclodextrins all the cavities are of one enantiomorphous form and it is found that the included solvent contains unequal amounts of left and right forms.

A special effect may be foreseen for cage structures where more than one molecule may be enclosed in a single cage. If, for example, Dianin's compound is crystallised from a racemic solvent, it may be expected that some of the cavities, which are centro-symmetic, will have a *dextro* and some a *laevo* enclosed molecule, or if the molecules are sufficiently small there may be cavities with one *dextro* and one *laevo* each. If the compound were formed from a *dextro* solvent the optical composition is necessarily simple, namely all *dextro*, but a curious effect on the composition may be expected in certain cases. Suppose that the dimensions are such that one *dextro* and one *laevo* molecule can be fitted into a cage. Once the cavity contains a *dextro* molecule the remaining space is the wrong mirror image form for a second *dextro* molecule which is the only form available. If this *dextro* form is as rigorously excluded as the wrong form of secondary butyl bromide in the spaces of the tri-*o*-thymotide adducts, this would mean that the molecular compound formed from the *dextro* solvent could include only half as much material as that obtained with racemic solvent. Partially resolved solvent should give molecular compounds of intermediate compositions, although it is not obvious that the included material should have the same optical composition as the starting solvent. There is, however, here a possibility that the ratio of molecules included to enclosing molecules may be linked with the optical composition of the solvent employed.

DESCRIPTION OF MOLECULAR COMPOUNDS

It remains to consider how molecular compounds may be described. One method would be to abandon attempts to understand or interpret compositions which could then be given as empirical. But variable or possibly misleading compositions can be understood if considered in relation to crystal structure. Many of the apparent complexities of mineral composition are simplified when attention is concentrated on the number and arrangement of the oxygen atoms which occupy much of the unit cell. Other inorganic compounds may be understood in terms of the packing of their halogen or other atoms; metallurgists clarify complex equilibrium diagrams by distinguishing phases which may include some which have ranges of inhomogeneity. A similar outlook on intermolecular compounds seems necessary. A formula for such a compound should be based on crystal structure. It might be related to the repetition, if regular, of either component but a choice will usually be simple. For example structural constants common to a series of molecular compounds formed by one substance like urea will be preferred to any quantity applicable only to a particular included component. From the structure as a whole an ideal formula is derived, based on some integral number of molecules of one component. The *ideal* formula may be described as *rational* when it requires a simple ratio of the components and *irrational* when it does not. This description does not by itself state whether the material examined is, on analysis, stoicheiometric. A particular structure may if necessary be further qualified as deficient, the deficiency being in the component on which the ideal formula is not based. As to the resulting composition it is perhaps better to consider constancy or variability rather than stoicheiometric character in the sense originally understood. An irrational molecular compound may be non-stoicheiometric but of such constancy of composition and properties that it may, for analytical purposes, be best compared to an ordinary pure chemical substance. A rational but deficient molecular compound is in general non-stoicheiometric and may have a range of composition and variable properties analogous to those of inorganic non-stoicheiometric compounds. An irrational and deficient molecular compound varies in the same way but might by accident analyse as stoicheiometric.

It may be appropriate to add whether the compound is disordered or not. Thus there are two closely related but distinguishable adducts of tri-*o*-thymotide and *n*-octyl iodide. That listed in Table II as having streaks coincident with sharp layer lines may be described as a rational non-deficient channel inclusion structure with displacement disorder in the channels. The other has the same channel structure but instead of streaks there are enhanced sharp spots on the corresponding layers. It is rational, non-deficient, and without displacement disorder. Both would be inadequately described as stoicheiometric of formula $3C_{33}H_{36}O_6.C_8H_{15}I$.

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Discussion

M. Schlenk. — 1. Is the inclusion-lattice of β quinol and that of Dianin's compound stable also without guest molecules, and if it is the case, how is the empty crystal to be got?

2. Can you tell some details regarding the structure of the tri-o-thymotide molecular compounds?

3. Is the structure of pure tri-o-thymotide without guest molecules known?

4. Have you succeeded in resolving other racemic mixtures than 2-bromobutane by means of tri-o-thymotide?

5. Is it possible to say, which of the two enantiomorphous forms of the inclusion-lattice of tri-o-thymotide belongs to the (+)-form of the host molecule? In the case of urea adducts it was possible to determine the relative configuration of corresponding (CH_3) —, (OH) —, (Cl) —, (NH_2) — and (SH) — compounds by including these compounds into one and the same form of the host-lattice.

M. Powell. — 1. Yes. The β-quinol structure without included molecules has been obtained by cooling solution of quinol in *n*-propyl alcohol to temperatures about — 20° C. It may also be obtained at room temperature from a solution, free of α-quinol seeds, by seeding with the β form or with the argon clathrate. Dianin's compound without included molecules may be obtained by sublimation. Another method is to dissolve it in sodium hydroxide solution — it is a phenol — and then to blow in, carbon dioxide. The Dianin's compound which is insoluble in water comes out, free of included material.

2. The detailed crystal structures, i.e. the exact location of atoms, have not been determined. They are very complex and of low symmetry in some cases. The general arrangement of molecules is known for two series.

In one, formed by molecules, such as *n*-alcohols and *n*-alkyl halides, provided the molecule does not exceed a certain length, there are closed cavities as in the quinol clathrates.

If longer molecules are used there is a slight rearrangement of the molecules to give channel structures very similar to the urea adducts.

If molecules either short enough for the first series, or too long to be accepted in it, are too much branched, they do not form adducts belonging to these series. But they are not simply rejected by the tri-o-thymotide, as urea rejects many branched molecules.

Instead they often form an adduct, but of a structure that may have no apparent relation to the two already mentioned.

3. The channel structure obtained when long molecules are included, is too open to form without guest molecules. The closely related structure, with closed cavities, obtained with short molecules, can form without guest molecules.

4. No, but there should not be great difficulties in the clathrate type. In the channel type, there have been obstacles such as failure of a particular adduct to grow a suitable crystal for seeding, or inefficiency of the seeding process.

5. This could be done by first using a molecule of known enantiomorphous form to determine the nature of the cavity. It is relevant that the surrounding cage of tri-o-thymotide must fit the guest molecule rather closely, since it entirely rejects one of the enantiomorphous forms.

M. Timmermans. — *a*) Les cristaux de complexes présentant une résolution spontanée, possèdent-ils des facettes hémiédriques et un pouvoir rotatoire mesurable?

b) La résolution est-elle vraiment spontanée, c'est-à-dire, se produit-elle en l'absence complète de germes énantiotropes?

M. Powell. — *a*) The crystals of those tri-o-thymotide adducts which are known from X-ray examination to belong to enantiomorphous space groups have so far not developed any faces that could reveal the hemihedrism. They have been examined for optical rotatory power since at one time it was necessary to determine whether they could be sorted into left and right forms by use of this property. The main series of adducts are uniaxial and thus favourable for such a procedure, but although the optical activity has been observed it is very weak.

Since other methods became available, the method was never attempted. Some of the crystals showed optical anomalies, possibly due to inhomogeneities of composition, and these might interfere.

b) It is scarcely possible to demonstrate that an experiment has been carried out so that no enantiomorphous material of any kind could have been present. Havinga carried out experiments with great care and obtained spontaneous resolution of a tetra substituted ammonium compound, but he mentions the difficulty.

M. Schlenk. — We have measured the rotation of urea-inclusion crystals. The optical rotation of the crystal is of the same order as that of β-quartz.

M. Bénard. — L'observation que je désire faire se rapporte, dans une certaine mesure, à celle qui vient d'être faite par le Professeur Timmermans. L'existence des composés moléculaires non stœchiométriques n'est pas, en effet, l'apanage des combinaisons organiques et l'on connaît maintenant de nombreux exemples de composés d'addition tels que iode-benzène, anhydride carbonique, protoxyde d'azote, iode-brome, etc. Dans ces systèmes l'étendue du domaine de variation de la composition paraît reliée d'une façon assez nette à la forme générale et aux dimensions des molécules qui sont appelées à se substituer les unes aux autres. Ainsi la miscibilité est totale, si mes souvenirs sont exacts, entre CO_2 et N_2O, dont les configurations sont très voisines. Il n'apparaît pas dans un tel système une composition particulière qui corresponde à un rapport moléculaire dicté par la géométrie du réseau, comme c'est le cas dans les composés décrits par le Docteur Powell.

M. Timmermans. — Un autre exemple de série continue entre cristaux énantiotropes est celui des carboximes $d + l$, dont la courbe de congélation passe par un maximum (pseudo-racémique, formant deux séries continues de cristaux mixtes avec chacun des antipodes).

Il serait très intéressant de rechercher si les antipodes ont des facettes hémiédriques et, éventuellement, à partir de quel pourcentage celles-ci disparaissent dans les cristaux mixtes.

M. Chaudron. — Les mécanismes d'inclusion permettent certaines séparations, par exemple de gaz rares.

Je voulais demander au Professeur Powell s'il a eu l'occasion de pousser ses recherches dans cette voie.

M. Powell. — Some of the host structures are indiscriminate in the selection of guest molecules. This is the case with Dianin's compound on account of its large cavities. Tri-o-thymotide forms adducts with nearly all the solvents that have been used for it.

Consequently it is not likely to be very useful for separating substances, except in the special case where it separates *dextro* and *laevo* molecules.

The urea and thio-urea inclusion compounds of Docteur Schlenk have been much used for separations based on molecular shapes. As a special case, the quinol clathrates have been used to separate the rare gases. The method does not depend on exclusion through shape or size, since both gases concerned form the clathrate. A 3 : 1 (volume) mixture of Kr and Xe gives crystals of quinol clathrate from which a 1 : 3 mixture is recovered.

M. Barrer. — I would like to ask Dr. Powell the following questions. In experiments in which solid thiourea was exposed to CCl_4 vapour, or solid potassium benzene sulphonate was exposed to various organic vapours, we have observed an induction period in formation of the complexes, an accelaration period and a slowing down of reaction, i.e. the typical auto-catalytic rate of formation of the complexes.

Tri-o-thymotide which recrystallises so readily to give diverse complexes seems to present an analogous case. Have such auto-catalytic kinetics of formation of complexes been observed?

My second question concerns the geometry of the cages in β-quinol or in Dianin's compound. The « windows » leading to and from these cages are rings of six — OH groups. What is the free diameter of these rings and have any measurements been made of rates of escape of small guest molecules through them?

Also what are the free volumes in cm³, per cm³ of crystal, in β-quinol and in Dianin's compound? It would be interesting to know these and to compare them with the free volumes found in zeolites, which may exceed 0.5 cm³ per cm³ of crystal in exceptional cases.

M. Powell. — *First question* : No.

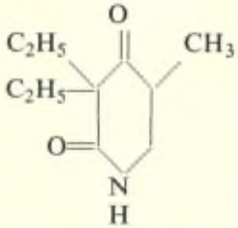
Second question : The distance across the hexagon between oxygen centres is 5.5 Å.

Allowance must be made for the effective radius of each oxygen in the hexagon.

This will not be less than 1.4 Å so that the diameter of the free space is not more than 5.5 — 2 × 1.4 = 2.7 Å.

Rates of escape have not been measured. The densities of empty β-quinol and the empty Dianin's compound are not very low in comparison with organic compounds of similar formulae. This is partly because although they have cavities they also have hydrogen bonds which bring some parts of the structures closer together than the normal intermolecular separations in organic crystals. From these densities it can be seen that the free volumes amount to a few per cent of the volume of crystal i.e. they are a good deal less than those mentioned by Professor Barrer.

M. Kuhn. — In connection with the remarks made by Professor Hägg and by Professor Timmermans with respect to spontaneous resultion and to a virtual continuity of the composition of crystals containing *d*- and *l*-molecules of optically active substances, it is of interest to mention that Docteur K. Vogler and Docteur M. Kofler in Basle have recently found an example of such a substance (1). It is a derivative of piperidine :



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(1) K. Vogl:r and M. Kofler; to appear in *Helvetica Chemica Acta.*

When this substance was synthesised from inactive material, a small optical activity was found, amounting to $(\alpha)_D^{20} = 4°$ in 5 % solution in water.

By about 400 crystallisations, the rotatory power was increased to $(\alpha)_D^{20} = 124°$. The melting point of the optically active compound was 84°, while the racemic substance melts at 74-76°. The melting point of the partly active substance varies continuously with optical purity with a flat minimum for the racemic mixture. The solidus and liquidus curves are separated over the whole range by about 1-2° C. The fact that it is not possible to obtain racemic crystals from a racemic solution and that the crystals separating from a racemic or from a partly optically active solution are neither pure antipodes, the degree of optical purity increasing slowly and continuously as the optical activity in the mother liquid increases, seems to indicate 1° : that the substance forms at room temperature two kinds of lattices, a *d*-lattice; and a *l*-lattice; 2° : that the *d*-lattice prefers to a certain extent *d*-molecules, present in the mother liquid, being at the same time a host for *l*-molecules which are taken up from the mother liquid, though relatively less than the *d*-molecules; 3° : that a continuous variation in the content from 50 % to 100 % *d*-molecules is thus possible for the crystallographic *d*-form and that a corresponding statement holds for the crystallographic *l*-form.

It should be remarked that according to the preference of the crystallographic *d*-form for *d*-molecules, a crystal of the crystallographic *d*-form containing e.g. 75 % *d*-molecules, will *not* be in thermodynamic equilibrium with a solution, or melt, containing 75 % *d*-molecules; a crystal with 75 % *d*-molecules would indeed grow from a solution containing e.g. 70 % of *d*-molecules. A corresponding statement would also hold for a crystal of the crystallographic *d*-form, containing about 50 % of *d*-molecules. It is possible that this might be the reason for the difference of solidus and liquidus curve mentioned.

M. Hägg. — There seems to exist another class of crystalline phases, which, according to Dr. Powell's definition, should be counted among the optically non-stoichiometric compounds. I refer to solid solutions between optical antipodes, which represent homogeneous phases with varying composition. Such solutions are rare, because the two antipodes must be so similar in size that they can replace each other in the lattice. They are, for instance, formed between optical antipodes of certain camphor derivatives as found by Knipping more than fifty years ago. In this case the similarity is probably due to rotation of the molecules in the lattice.

M. Timmermans. — Je désire attirer l'attention sur un groupe de systèmes qui ne rentrent pas à proprement parler dans la catégorie des combinaisons non stoéchiométriques, mais qui ne leur sont cependant pas complètement étrangers, en ce sens qu'il s'agit, comme dans les clathrates, de remplir certaines cavités du réseau d'une substance par les molécules d'une autre substance, comme dans les systèmes isomorphes.

Je veux parler tout d'abord des cristaux mixtes « anormaux » que forment entre eux des couples de composés globulaires. On sait que j'ai baptisé ainsi les substances organiques et minérales, dont l'entropie moléculaire de fusion est inférieure à 5, et qui présentent un grand nombre de particularités permettant de les classer à côté des liquides anisotropes, comme intermédiaires entre l'état cristallin et l'état liquide : pour un liquide anisotrope, à la température de fusion, le réseau disparaît, mais l'orientation moléculaire subsiste jusqu'à la température d'éclaircissement du liquide; dans les composés globulaires, l'orientation moléculaire disparaît déjà dans le cristal, à partir d'un point de transition énantiotrope, mais le réseau ne disparaît qu'au point de fusion.

Les phases globulaires, entre le point de fusion et le point de transformation, dont je viens de parler, cristallisent toutes dans le système cubique, et si leur grandeur moléculaire n'est pas trop différente, elles donnent des cristaux mixtes, quelle que soit leur constitution chimique : un exemple classique est celui de la série isomorphe méthane + argon. S'il s'agit d'antipodes optiques, ceux d'une même substance, mélangés en toutes proportions, ne donnent pas de racémique, mais une série continue de cristaux mixtes, qui ne se distinguent pas par leur point de fusion : c'est le cas des deux camphres $d + l$.

J'ai cru utile de signaler ici ce type de système curieux, dont la signification paraît avoir échappé jusqu'ici, surtout aux purs cristallographes.

M. Caglioti. — Je désire attirer l'attention sur la chimie des phosphates de calcium et particulièrement :

a) du phosphate tertiaire hydraté, qui présente un réseau lacunaire dans lequel peuvent trouver place des molécules d'eau ou de carbonate de calcium, etc.;

b) de l'hydroxyapatite, qui peut former avec les aminoacides et les protéïnes des complexes de surface, dont la formation est probablement facilitée par l'identité de certaines dimensions, phénomène qui joue un rôle essentiel dans la structure même des os.

Dans ce deuxième cas, nous sommes aux limites et nous ne pouvons plus parler de formation d'un composé d'insertion, mais nous devons plutôt supposer qu'il s'agit d'un cas d'épitaxie.

Complex Compounds of the Transition Metals

by R. S. NYHOLM

I. — INTRODUCTION

This report deals with the present state of the chemistry of the coordination compounds of the transition metals, with particular reference to developments which have taken place during the last two decades. During this period the approach to inorganic chemistry in general, and coordination chemistry in particular, has changed from an essentially preparative one to a more purposeful attack in which valency theory, structure and reactivity are of major interest. As will emerge from this, and other, reports the reason for this change is the application of physical methods of investigation and of the results of quantum mechanics — these two being largely complementary.

With the wealth of material available one must necessarily be selective if the report is not to be too long. Following this introduction, Part II will be devoted to a brief survey of the historical development of the subject of complex compounds tracing the reasons leading to the rapid growth of interest at the present time. In Part III a qualitative picture of the modern theory of valency as is relevant to discussion of complexes will be given. In particular the development of the present position will be discussed. Part IV deals with the magnetic behaviour of metal complexes. Finally in Part V we

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Statement on Report by R. S. Nyholm.

This report has been written in close collaboration with Dr. L. E. Orgel. It was agreed that a generalised introductory treatment of the part on valency in these complexes should be given in this paper, to be followed by a more detailed discussion on spectra by Dr. Orgel. I am very grateful to Dr. Orgel for his critical comments and advice in writing this section.

survey the data concerning transition metal complexes under each group with special reference to the *valence state*, *stereochemistry* and *magnetic behaviour*.

II. — HISTORICAL

It is convenient to regard the development of the chemistry of complex compounds as falling into four periods.

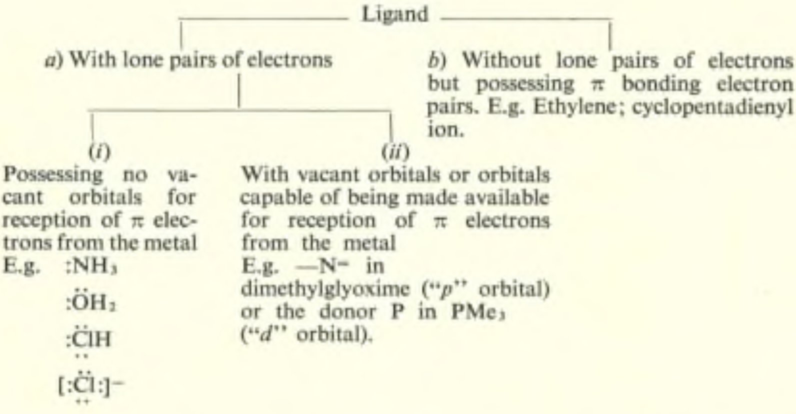
During the first of these, the *pre-Werner* period, a large number of what are now recognized as co-ordination compounds were isolated and analysed. They were recognized as "addition compounds" of greater or lesser stability resulting from the combination of two or more stable inorganic compounds. No satisfactory or acceptable theory to account for their structure was available. Then followed the *Werner* period during which time the essential principles of co-ordination number, direct metal to ligand bond and simple stereochemistry were laid down and developed. The octahedral, tetrahedral, planar and linear arrangements were visualised and the first three established more or less firmly by classical methods. Such an advance occurred during this period that experimental work outstripped the theoretical workers and in the absence of applicable physical techniques for further structural studies we pass into the *Quiescent* period extending until the nineteen thirties. During this time certain preparative and classical studies (e.g. optical resolution) of complexes continued, but no really striking advances occurred. From about 1932 onwards we move into the *Modern* period, of rapid advancement. The developments in quantum mechanics in the late nineteen twenties were applied by Pauling in particular to inorganic chemistry and although there have been modifications in detail since the early nineteen thirties, it is fair to say that Linus Pauling (1) enunciated the principles which provided the main stimulus for later developments. Of special importance was the fact that quantum mechanics gave a sense of purpose to physical measurements and enabled magnetic moments, electric dipole moments and spectral measurements to be correlated with structure. It is of interest to note that the basis of the crystal field theory was also laid down by Bethe (2), Penney and Schlapp (3) Van Vleck (4) and Gorter (5) in the late nineteen twenties and early nineteen thirties, but it is only during the past five years that this approach has found favour with many chemists.

III. — VALENCY THEORY

Before dealing with the complex compounds in the Periodic Table we summarise first the basis for discussion. Ligands can be classified conveniently as follows (Table I).

TABLE I

Types of ligand



Ligand

a) With lone pairs of electrons

(*i*) Possessing no vacant orbitals for reception of π electrons from the metal E.g. $:NH_3$, $:\ddot{O}H_2$, $:\underset{\cdot\cdot}{\ddot{Cl}}H$, $[:\underset{\cdot\cdot}{\ddot{Cl}}:]^-$

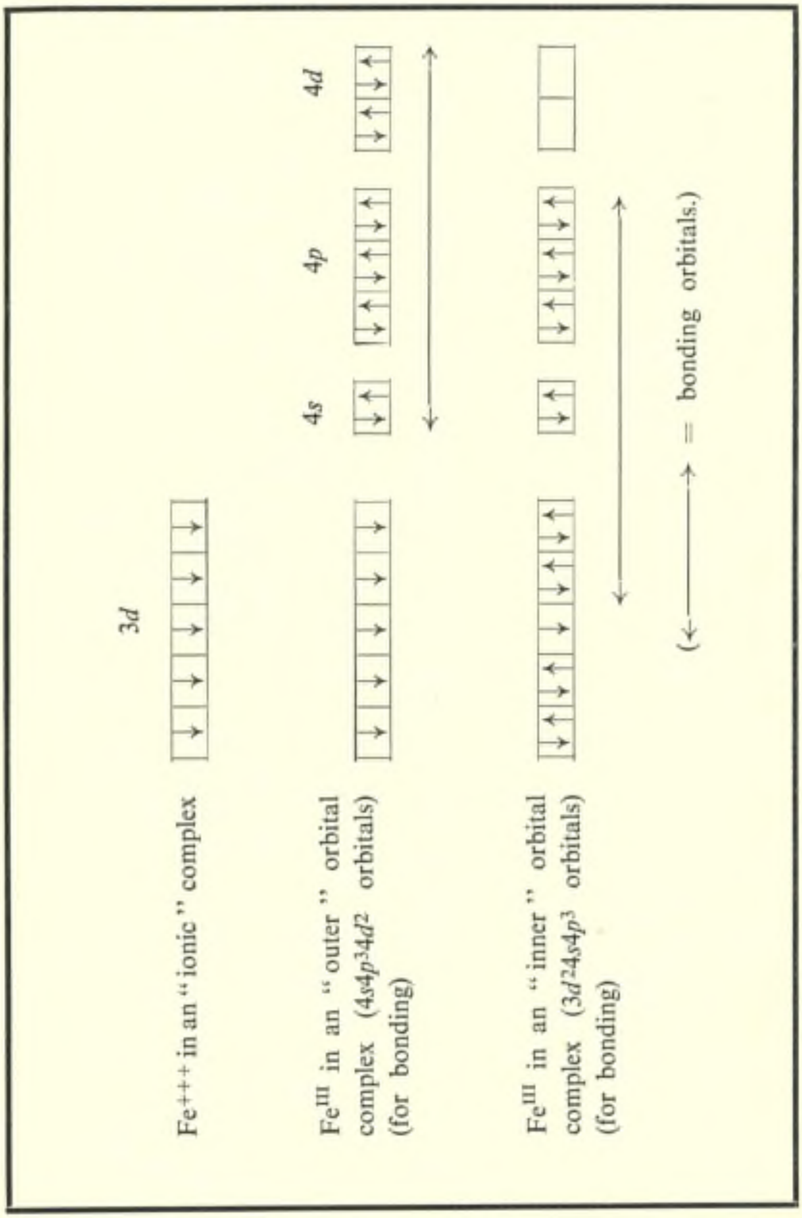
(*ii*) With vacant orbitals or orbitals capable of being made available for reception of π electrons from the metal E.g. $—N^=$ in dimethylglyoxime ("*p*" orbital) or the donor P in PMe_3 ("*d*" orbital).

b) Without lone pairs of electrons but possessing π bonding electron pairs. E.g. Ethylene; cyclopentadienyl ion.

In discussing the type of metal-ligand bond in complex compounds we must recognize that we are at an important stage of development in our views on this subject. For a long time chemists took the view that there were two main types of bond, and "electrostatic" or "ion-dipole" bond on the one hand, and one involving electron sharing — the so-called "covalent" bond — on the other. The metals of the first transition series were known to give two kinds of co-ordination compounds, "normal" and "penetration" complexes respectively. These were distinguished in ideal cases, e.g. Fe^{III}, by a difference in the number of unpaired non-bonding 3*d* electrons as determined by the magnetic moment. Then followed the view that in many instances in complex compounds the distinction was often not between " ionic " and " covalent " bonds but frequently between " outer orbital " complexes involving no electron pairing on the central metal atom, and " inner orbital " complexes with strong pairing on the other. Thus in comparing potassium ferrioxalate and potasium ferricyanide the electronic configuration of the Fe^{III}

atom in terms of " ionic ", " outer orbital " and " inner orbital " arrangements were regarded as in Fig. 1.

Fig. 1. — Electronic configuration of ferric atom in complexes.



In order to account for certain complexes in which electron pairing occurred but where an insufficient number of 3*d* orbitals were available to allow of inner " *d* " orbital binding the process of promotion of electrons was postulated. This was considered necessary in the case of octahedral " covalent " Co^{II} complex ions like $[Co(NO_2)_6]^{4-}$. The postulated electronic configuration of various Co^{II} complexes are shown in Fig. 2.

In addition to the necessity for promotion of electrons difficulties arose in certain compounds in deciding the stereochemistry of complexes wherein no electron pairing occurred. Thus the tetrahedral $[CoCl_4]^{--}$ and the square $[Cu(H_2O)_4]^{++}$ ions have respectively three and one unpaired electrons. In the first case there are two doubly and three singly filled 3*d* orbitals. This means that there are no vacant 3*d* orbitals available for bond-formation.(*) If in each case the empty orbitals immediately above these filled or partly filled non-bonding orbitals were used for bond formation we would in both compounds expect a tetrahedral arrangement based on the use of $4s4p^3$ bond orbitals. The fact that the four covalent complexes of Cu^{II} are square rather than tetrahedral shows that this rule is not of general validity.

The original Pauling theory made no serious attempt to decide which " outer " orbitals (if any) were employed when the number of unpaired electrons was the same in the complex as in the free ion. Generally speaking the bonds were regarded as " ionic " or essentially ionic using sp^3 bonds. Octahedral complexes were considered to involve either ionic binding although the possibility of some covalent character by allowing the four $4s4p^3$ bonds to resonate among the six positions was envisaged. The basic principles of the Pauling theory relation magnetic moment and stereochemistry in the first transition series are as follows.

1° For most purposes the number of unpaired electrons in an atom may be computed from the " spin only " formula,(**) i.e.

(*) We are not considering Pauling's (⁶) earlier suggestion that one 3*d* orbital might be used in bond formation by electron promotion. Although logical when first proposed there are sound objections on the basis of electronegativity of the ligand to this proposal. Ligands with donor atoms of *high* electronegativity give square Cu^{II} complexes. As will be discussed later the use of a 3*d* orbital should be favoured by the use of donor atoms of low electronegativity.

(**) The size of the orbital contribution rarely gives rise to any doubt as to the *number* of unpaired electrons.

Fig. 2. — Electronic configuration of cobaltous complexes.

Complex type of ion	Binding	Electronic configuration	Unpaired electrons	μ observed
Free ion i.e. Co^{++}		3*d* [↓↑][↓↑][↓][↓][↓]	3	5.6
Tetrahedral	" Ionic "	4*s* 4*p* [↓↑][↓↑][↓][↓][↓] [↓↑] [↓↑][↓↑][↓↑] ←——→ (4*s* 4*p*)	3	4.3-4.8
Octahedral	" Ionic "	4*d* [↑↓][↑↓][↓][↓][↓] [↑↓] [↑↓][↑↓][↑↓] [↑↓][↑↓] ←——→ (4*s* 4*p* 4*d*)	3	4.8-5.2
Planar	Covalent	[↓↑][↓↑][↓↑][↓][↓↑] [↓↑] [↓↑][↓↑][ ] ←——→ (3*d* 4*s* 4*p*)	1	2.1-2.9
Octahedral	Covalent	5*s* [↓↑][↓↑][↓↑][↓↑][↓↑] [↓↑] [↓↑][↓↑][↓↑] [↓] ←——→ (3*d* 4*s* 4*p*)	1	1.7-1.9

magnetic moment $\mu = \sqrt{n(n + 2)}$ Bohr Magnetons (B.M.) where n = number of unpaired electrons.

2° When the magnetic moment of a complex is essentially the same as that of the free ion (*) (i.e. no spin coupling occurs) the bonds do not involve $3d$ orbitals. In the Pauling terminology the binding is "ionic".

3° Spin coupling with a reduction of either two or four in the number of unpaired electrons indicates that $3d$ orbitals are being used for ("covalent") bond formation. This necessitates the transfer of unpaired electron(s) originally occupying the $3d$ orbital(s) now used for bond formation. Usually these displaced electron(s) pair off with other unpaired non-bonding $3d$ electrons.

4° If no vacant $3d$ orbital(s) are available to accommodate the displaced electron(s) referred to in 3 then electron(s) may be promoted to vacant orbital(s) above those used for bond formation.

5° The orbitals used for a bond formation are usually those immediately above those occupied by non-bonding electrons provided that these are a permissible combination for bond formation. This assumption is unreliable in certain cases where no electron pairing occurs (*cf* square Cu^{II} discussed above).

In the above theory the possible use of $4d$ orbitals was not considered. There were many, however, who considered that the properties of certain so-called "ionic" complexes warranted the view that some kind of covalent bonds were present. Thus Sugden (7) drew attention to the similarity of cobaltic and ferric tris-acetyacetone in their physical properties other than magnetism and suggested that some kind of covalent bonds were present in both cases. Earlier Huggins (8) had suggested that $4d$ orbitals might be involved in the binding of ligands in so-called "ionic" transition metal complexes. The idea was discussed by other workers, particularly Taube (9) in relation to reactivity of transition metal complexes and Burstall and Nyholm (10) in regard to magnetism. Then followed a theoretical study of the problem (11) and using the overlap integral

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(*) Provided that the free ion contains *more* than $3d$ electrons; this proviso is necessary because magnetic moments do not distinguish between $4s4p^34d^2$ and $3d^24s4p^3$ octahedral binding when three $3d$ electrons or less are present e.g. Cr^{III}.

as a criterion of covalent bond formation, based in turn, on reasonable postulates as to the nature of the wave functions involved, qualitative support for the view that 4*d* orbitals might be involved in σ binding was adduced. Noteworthy results included the conclusion that 4*d* orbits were much more elongated than the 3*d* type; this correlated with the well known fact that ligands of low electronegativity favour electron pairing and " inner " *d* orbital binding whereas those of high electronegativity favour the so-called " ionic " binding. It became apparent that the terms „ ionic " binding and „ overlap at a greater distance using 4*d* orbitals " were more similar than they might appear at first sight. Nevertheless exchange is implicit in the latter description but not in the former. Support for the view that d_π binding using non-bonding 3*d* electron pairs of the metal atom was feasible on the basis of the size of the overlap integral was also obtained. As expected this was found to be more favourable in " inner " rather than " outer " orbital complexes.

At this point it might fairly be said that the Pauling picture with additions to include the use of 4*d* orbitals could *explain* satisfactorily the stereochemistry and magnetism of both " covalent " and " ionic " complexes and also the reason why the ligands of low electronegativity tended to give " covalent " complexes and those of high electronegativity to give " ionic " complexes. Its chief limitations are :

a) failure to *predict* whether four-covalent " outer " orbital complexes would be tetrahedral (e.g. $[CoCl_4]^{--}$) or square planar (e.g. $[Cu(H_2O)_4]^{++}$) ;

b) inability to interpret spectra of metal complexes;

c) inability to explain quantitatively variation in magnetic moments when values in excess of spin only values are observed.

In short, it is limited to qualitative phemonena and does not account for quantitative features such as the intensity and observed frequency of spectral transitions.

At this stage chemists and physicists began to take a renewed interest in the Crystal Field Theory originally developed by Bethe, Penney and Schlapp and by Van Vleck. We shall be concerned here primarily with its application to stereo-chemistry and magnetism but some introductory discussion is called for. At the present time most inorganic chemists think in terms of valence bond theory. Books and papers in the field are based mainly on this approach and it is natural that there is some reluctance to think in terms of new concepts. We shall attempt to translate from the Valence Bond Theory and to emphasise that the similarities are quite substantial. In fact, once again it is a case of tackling a problem from two angles — one tending to use that approach which is most useful.

LIGAND FIELD THEORY

We shall begin by proposing use of the title *Ligand Field* (10*a*) instead of Crystal Field Theory. The latter tends to emphasise too much the relationship with *crystals* and *electrostatic* bonds. Actually we are concerned with the effects arising from the arrangement of electron pairs on charged or uncharged ligands around a metal atom. Furthermore the proximity of these electron pairs is frequently such as to warrant the concept of an ordinary covalent bond between metal and ligand.

The complexes with which we are concerned usually have a cubic or near cubic symmetry, that is to say the metal behaves as though it were in an electrical field of equal intensity along the three x, y and z axes. The octahedral and tetrahedral arrangement of ligands gives this type of field and the square planar and square pyramid may be regarded as imposing an extra component on the cubic field. In practice the deviations from cubic symmetry are very important in giving rise to effects such as variable orbital contribution in paramagnetic complexes.

Consider now a simple d electron in such slightly distorted cubic field. This single d electron may, when there is no field, be present in any one of 5 degenerate d levels. These are the d_{xy}, d_{yz} and d_{zx} orbitals ($d_\varepsilon$orbitals) on the one hand and the d_{z^2} and $d_{x^2-y^2}$ (d_γ orbitals) on the other (*). This first group of three orbitals are oriented as

(*) These d orbitals in terms of θ, and φ have the form :

$$d_{xy} = \frac{\sqrt{15}}{2} \sin^2\theta \sin 2\varphi$$

$$d_{xz} = \sqrt{15} \sin\theta \cos\theta \sin\varphi$$

$$d_{yz} = \sqrt{15} \sin\theta \cos\theta \cos\varphi$$

$$d_{z^2} = \frac{\sqrt{5}}{2} (3 \cos^2 \theta - 1)$$

$$d_{x^2-y^2} = \frac{\sqrt{15}}{2} \sin^2 \theta \cos 2\varphi$$

shown in Fig. 3, only one of the d_{xy}, d_{xz} and d_{yz} orbitals being shown (*).

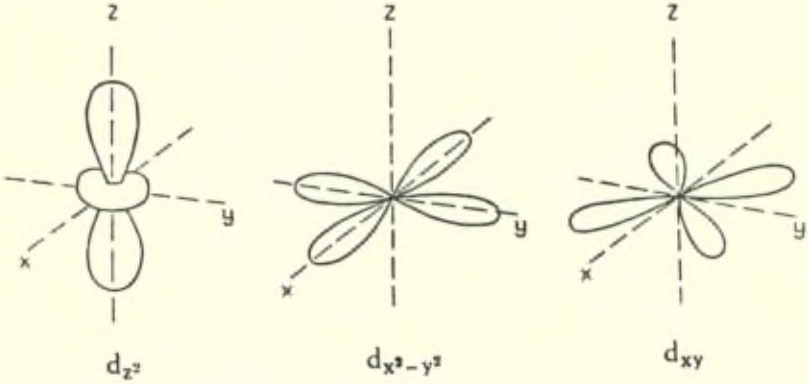
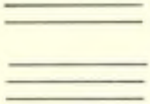


Fig. 3.

It will be seen that the d_ε orbitals are concentrated along the diagonals *between* the axes x, y and z, — along which the electron pairs of the ligands would be found in an octahedral complex. However, the d_{z^2} and $d_{x^2-y^2}$ orbitals are definitely concentrated along the three orthogonal axes as shown. Now under the influence of an essentially cubic field, such as is produced in an octahedral complex, these 5 degenerate d orbits are split apart as shown in Fig. 4, there being a lower triplet of the d_ε orbitals and an upper doublet known as d_γ orbitals. The more stable d_{xy}, d_{yz} and d_{xz} orbitals occupy the lower triplet whereas the less stable upper doublet consists of the two axial orbitals. Consider now what happens as we gradually add d electrons to an atom with five empty d orbitals :

Fig. 4. — Splitting of d levels in a nearly cubic field.



d_γ orbitals Axial — Pointing along bond directions.

d_ε orbitals Pointing along the bisectors of the x, y and z axes — between the bonds.

The first three will occupy the lower triplet level, one in each sub-level giving three unpaired electrons. This arrangement is expected naturally from a consideration of the requirements of

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(*) Reproduced from Orgel and Sutton ([10]*a*).

minimum electrostatic potential energy; in an octahedral complex there are six pairs of ligand electrons around the metal atom, one pair along each of the six co-ordinate axes. These will naturally tend to repel the $3d$ electrons of the metal which therefore go into the d_{xy}, d_{yz} and d_{xz} orbitals. On adding the fourth electron — as say in Cr^{++} this could go either into the lower of the two d orbitals or begin to pair off within the d_{ε} orbitals. If the bonds are such that the ligand pairs are not exerting a very strong repulsive effect the electron will go into a d_{γ} orbital giving 4 unpaired electrons. This is the situation in the $[Cr(H_2O)_6]^{++}$ ion. This state corresponds with Pauling's "ionic" bonds. If, however, the ligand electrons are very close to the metal as when strong "covalent" bonds are formed (*), the fourth electron might be forced to pair off in one of the d_{ε} orbitals resulting in two unpaired electrons only on the atom. This occurs in the $[Cr(Dipyridyl)_3]^{++}$ ion. Similarly with five $3d$ electrons we obtain either three singly occupied d_{ε} and two singly occupied d_{γ} orbitals or two filled and one singly occupied d_{ε} orbitals. The former situation corresponds with K_3FeF_6 and the latter with $K_3Fe(CN)_6$, there being 5 and one unpaired electrons respectively. An early criticism ([12]) of the Van Veck theory was based on the view that the F^- ion should create a stronger field than the CN^- ion and hence spin coupling might be expected more readily in K_3FeF_6 than in $K_3Fe(CN)_6$.

However it has been pointed out by Orgel ([13]) that polarisability of the ligand is of great importance; the capacity to produce high electron densities *close to the metal* is the all important factor and the "soft" CN^- ion can do just this. Factors which will favour this are naturally (i) a high positive charge on the metal ion (ii) low electronegativity on the part of the ligand atom (giving rise to readily polarised electron pairs) and (iii) the extent to which $d_{\pi} - p_{\pi}$ or $d_{\pi} - d_{\pi}$ bonds may be formed between metal and ligand.

In the example quoted ($K_3Fe(CN)_6$) $d_{\pi} - p_{\pi}$ binding making use of $3d_{\varepsilon}$ electron pairs of the Fe atom and a p_{π} orbital of the C atom must be very important. This gives rise to stronger binding between the Fe and C atoms resulting in a *shortening* of the Fe — C σ bond with a consequent increase in electron density close to the Fe

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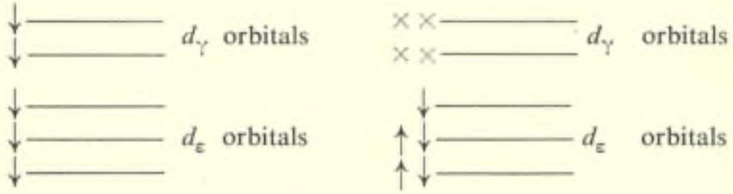
(*) This is equivalent to saying that the incoming electron pair of the ligand wish to make use of the $d\gamma$ orbital occupied by the unpaired electron.

atom along the x, y and z axes. This further enhances the tendency to *repel* non bonding electrons from the d_{z^2} and $d_{x^2-y^2}$ orbitals, i.e. to effect electron pairing.

It may be seen by reference to the d_{xy} orbitals in Fig. 3 that the shape of this is ideal for „ sideways " overlap with a vacant d orbital (or a p orbital which is made available) on the donor atom which forms a σ bond along the x, y or z axes in an octahedral or square planar complex. As discussed by Kimball (13a) simple geometry indicates that, provided that the metal atom has the requisite number of d_ε electron pairs we can expect a maximum of *three* strong d_π bonds from the metal atom in an octahedral complex and *two* in a square planar compound.

Fig. 5.



Electronic Configuration K_3FeF_6

Electronic Configuration of $K_3Fe(CN)_6$

×× Bonding Electron Pairs from Ligands

↓ Non-bonding Electrons from Fe^{+++} ion

It should be mentioned that the arrangement of the nondegenerate d orbital levels in Fig. 5 is inverted if the ligands are arranged tetrahedrally, for example as in the $[CoCl_4]^-$ ion. The separation of the levels, however, is much smaller. If one examines the arrangement of the orbitals with respect to the ligands it becomes clear that in a tetrahedral complex the electrons in the d_{xy}, d_{yz} and d_{zx} orbitals are those which are nearest to the ligands and hence become the least stable. The changeover from the octahedral arrangement as the more stable with ligand H_2O in $[Co(H_2O)_6]^{++}$ and tetrahedral as the more stable with ligand Cl^- in $[CoCl_4]^-$ indicates that there is a fine balance between size of charge on the ligand and the position of the ligands in deciding which is the more stable arrangement.

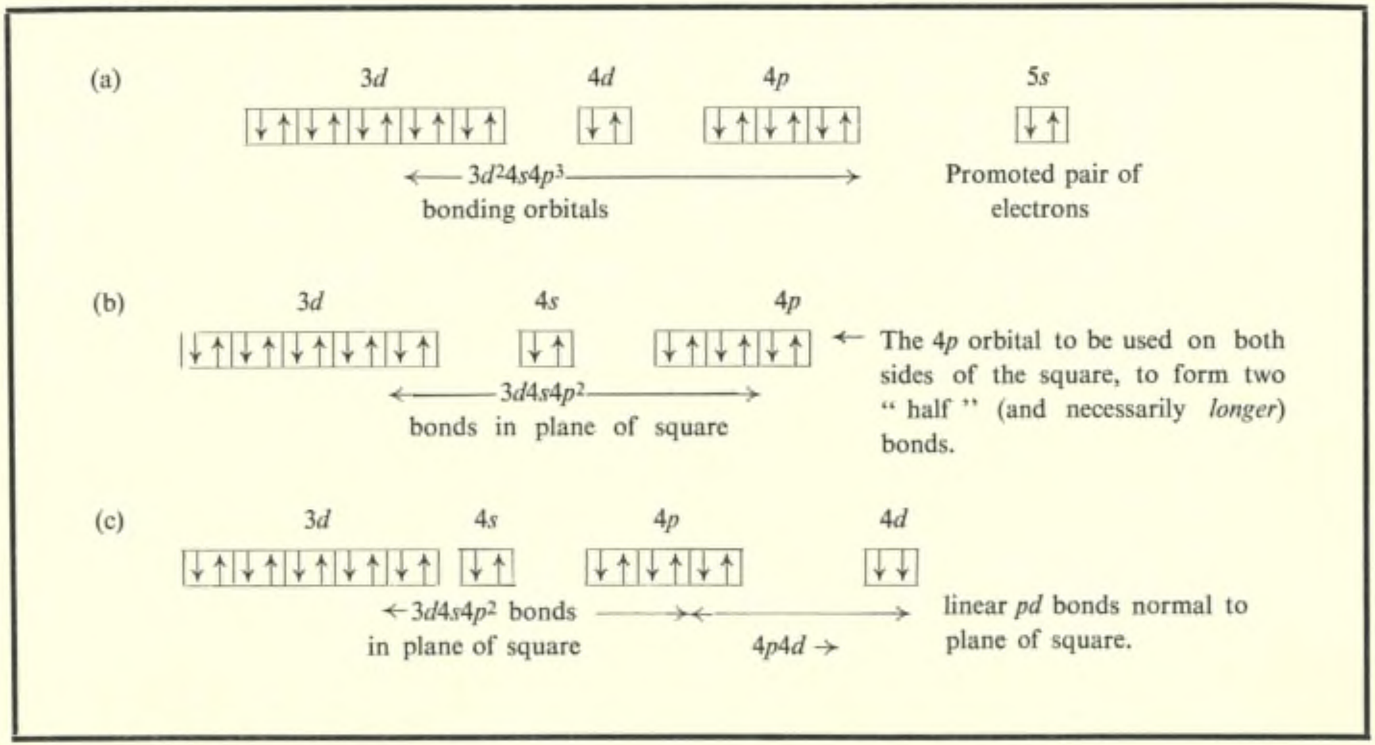
Returning to the case of electron pairing in the case of $K_3Fe(CN)_6$ it will be seen from Fig. 5 that two d_γ orbitals are made available as the result of electron pairing. These orbitals point in the direction of the ligands and are obviously the bonding orbitals of the Pauling theory. The two theories thus become very similar when discussing " covalent " complexes. However, it is important to realise that in applying the ligand field theory to complexes in which no electron pairing occurs, nothing has been said concerning the possible use of any *bonding* orbitals above the 3*d* orbitals. In a sense, like the Pauling theory, it offers no guidance on this point. In fact various workers reject altogether the idea of covalent bonds in this " ionic " type of complex. It seems to be largely a matter of opinion however whether out 4*s*, 4*p* and 4*d* orbitals are to be regarded as occupied. It is at least a convenient way of looking at the explanation of stereochemistry of these " ionic " complexes and in no way affects the previous arguments.

The results of x-ray spectroscopy need to be mentioned in this connection. Examination of the K x-ray absorption edge (15) shows that what is presumably the 1*s* → 4*p* transition is *absent* in $K_3Co(CN)_6$ but it may be observed in the $[Ni(NH_3)_6]^{++}$ ion and similar so-called " ionic " or " outer orbital ions ". This, however, may be taken to mean that the 4*p* orbitals are vacant part of the time — which is consistent with the work of Craig and alii (11) and paramagnetic resonance studies (20-21-22) since the latter work indicates that the binding is partially covalent. The overlap integral is smaller than in the spin-paired i.e., the " inner orbital " $K_3Co(CN)_6$ type complex.

A problem where the valence bond and the ligand field theory appear to be in some conflict is in connection with octahedral diamagnetic complexes of bivalent nickel. Examples of these include the $[Ni(Diarsine)_3]^{++}$ ion, the $[Ni(Tri\text{-}arsine)_2]^{++}$ ion and certain other Ni^{II} complexes (18). In these the nickel atom has a d^8 configuration and the usual octahedral coordination would suggest that there would be two unpaired electrons in the d_γ orbitals. On the Pauling theory one could explain the diamagnetism in one of the following three ways, as shown in Fig. 6.

Taking each of these in turn; the objection to (a) is the difficulty of promotion. This is expected to lead to electrons of high energy. Some support for this is to be adduced from the fact that oxidation occurs fairly readily. However exact values for the ionisation potential are difficult to assess. Explanations (b) and (c) really regard the com-

Fig. 6. — Possible electronic configurations of octahedral diamagnetic Ni^{II} complexes



plexes as derived basically from a square arrangement. The remaining two ligands are then attached on either side of the square by slightly longer bonds using either the single 4*p* orbital or a 4*p* and a 4*d* orbital. Support for this approach is provided by the existence of many apparently 5 covalent complexes of Pd^{II} (14) such as $[Pd(Diarsine)_2I]ClO_4$ and of Au^{III} e.g. $[Au(Diarsine)_2I][ClO_4]_2$. In the case of gold, however, one may also obtain six covalent complexes of the type $[Au(Diarsine)_2I_2][ClO_4]_2$ (15). These are iso-electronic (in the valency shell) with the $[Ni(Diarsine)_3]^{++}$ complex and in this case of these gold complexes there is no reason at all for postulating promotion of two electrons to the outer *s* orbital. It is probably most significant that in all of these complexes which show six-covalency the ligands are of low-electronegativity, the cation has a positive charge and double bonds from metal to ligand are feasible. The last two of these conditions favour a strong polarising effect on the ligand and the drawing out of lone pairs of the latter to form a covalent bond is a reasonable hypothesis.

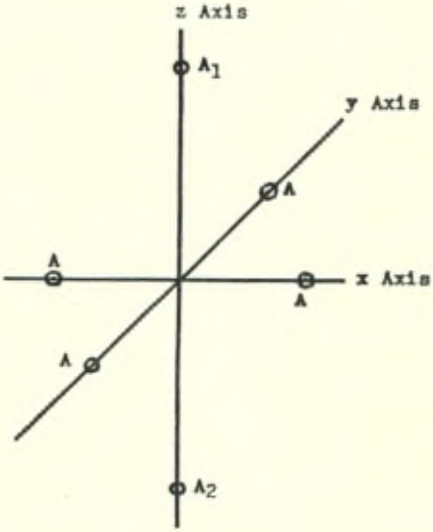
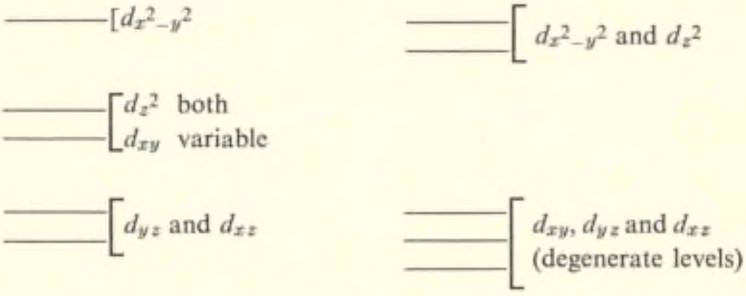


Figure VII

The ligand field theory would predict that for a regular octahedron there should be two unpaired electrons. If, however, the arrangement of the ligands departed from the perfect octahedral arrangement to one in which two longer co-axial bonds were present we would be dealing essentially with a square arrangement with some modifications. Consider the arrangement shown in Fig. 7. Place four equidistant A atoms in the plane *xy* along the *x* and *y* axes in a square. Also put two A atoms (A_1 and A_2) at a much longer distance along the *z* axis. Now consider the arrangement of the five *d* orbitals as A_1 and A_2 are steadily brought from a long distance until they form a regular octahedron around M. When a long way off the field at M is due almost entirely to the four A atoms in the *xy* plane. The orbital pointing *towards* these four, the $d_{x^2-y^2}$ orbital, is clearly destabilised, whereas the d_{z^2}, d_{xy}, d_{yz} and d_{xz} orbitals will not differ much in energy. At first sight the d_{z^2} orbitals might be expected to have the maximum stability, but as against this there is the small annular ring of charge density in the *xy* plane which will suffer some repulsion by the four A atoms (*). We represent the splitting of the five *d* orbitals then as in Fig. 8.

Fig. 8.



(*a*) Energy levels of *d* orbitals for square arrangement of ligands

(*b*) Energy levels of *d* orbitals for perfect octahedral arrangement

As A_1 and A_2 gradually move towards M the d_{z^2} level moves steadily upwards — becomes less stable — until we reach the perfect octahedral case again. The simplest ligand field explanation of the diamagnetism of the $[Ni(Diarsine)_3]^{++}$ compound is to suppose that the situation most nearly approximates to (*a*) in Fig. 8. The eight

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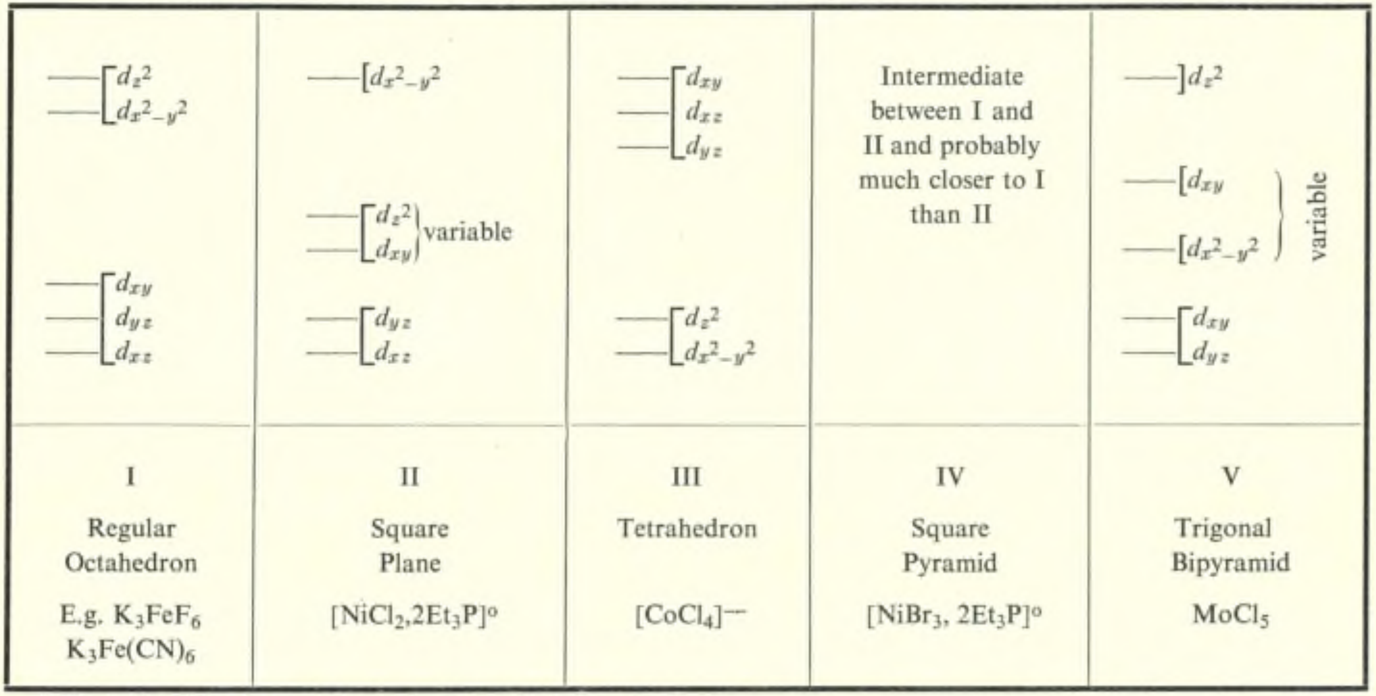
(*) Both Maccoll (16) and Orgel (17) estimates the amount of charge in the annular ring as about 35 % of the total charge in this d_{z^2} orbital.

Fig. 9.

Energy Levels of *d* Orbitals in Various Ligand Fields.



* The height of the $d_{x^2-y^2}$ relative to the other orbitals is uncertain.

3*d* electrons are then all paired in the d_{xy}, d_{yz}, d_{xz} and d_{z^2} orbitals leaving only one orbital $(d_{x^2-y^2})$ for bond formation. Agreement with (*b*) or (*c*) in Fig. 6 then becomes very close (*).

We now summarise in Fig. 9 the splitting of the levels which take place in various common types of stereochemical arrangement met with in transition metal complexes. In all cases it is assumed that all metal-ligand distances are equal and that all ligands are identical. For intermediate cases one would need to alter levels accordingly.

No attempt is made in the diagrams to represent the splitting in a quantitative manner. However in all cases of octahedral splitting the separation between the degenerate d_ε and d_γ levels is smaller when very electronegative ligands (e.g. F^-) are used than when covalent double bonding ligands like CN^- are present. Naturally a stage may be expected when the energy separation $d_\varepsilon \rightarrow d_\gamma$ is large enough to become equal to or greater than the energy required to pair electrons in d_ε orbitals and leave one or both d_γ orbitals free for bond formation.

This leads us naturally to a consideration of the effect of electronegativity upon spin-pairing.

A study of the magnetic behaviour of pentagonal bipyramidal molecules with from three to seven *d* electrons would therefore prove of great interest. The magnetic behaviour of RuF_5 (d^3) is being studied over a range of temperature as part of such an investigation ([51]).

SPIN PAIRING IN METAL COMPLEXES

We have referred previously to the various names given to the bonding complexes in which two kinds of magnetic behaviour are observed. Thus the terms "ionic" and "covalent", "outer" and "inner orbital complexes"; "higher" and "lower level covalent bonds"; "normal" and "penetration complexes". Henceforth we suggest that these names be dropped in favour of the terms "spin-free" and "spin-paired" complexes. Among the reasons for this are the following: (*a*) The terms "ionic", "outer orbital

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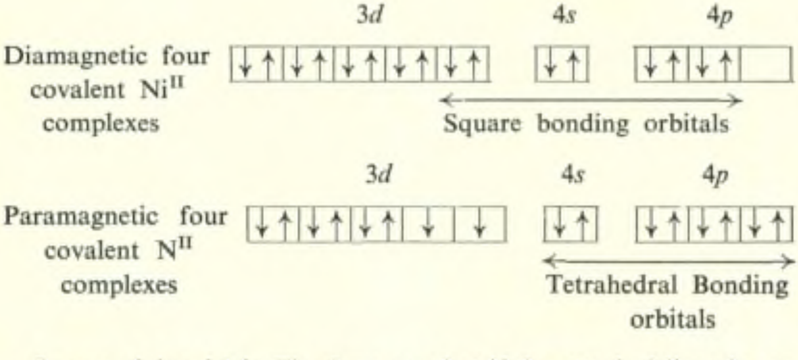
(*) Explanation (*a*) is compatible with ligand field theory if one postulates that the 5*s* level is *intermediate* between the d_ε and d_γ levels.

complex " etc. suffer from the defect that they group together *all* complexes in which no spin pairing occurs, irrespective of whether there is a possibility of covalent binding or not. Sometimes this dilemma is apparently avoided by saying "the term 'ionic' is used simply to imply that the magnetic moment is the same as that of the free ion ". This of course, is often not true. Thus the $[CoCl_4]^{=}$ and $[Co(H_2O)_6]^{++}$ ions with $\mu = 4.7$ B.M. and 5.2 B.M. respectively are both" ionic " in the sense that no spin pairing occurs but their moments are not the same as the free ion. (*b*) In certain cases more than two kinds of magnetic behaviour are observed. For example $[Cr^{II}(H_2O)_6]\,Cl_2$, $[Cr^{II}(Dipyridyl)_3]$, $[ClO_4]_2$ and $[Cr^{II}(CH_3COO)_2]_2$ contain 4, 2 and 0 unpaired electrons respectively. It seems best to differentiate between " spin-free " and " spin-paired " complexes first and then discuss the nature of the binding in each case as a separate problem.

Perhaps the most studied complexes wherein spin-pairing may occur are those of $Ni^{II}(d^8)$. Four-covalent complexes of two types are known, those which are diamagnetic, e.g. $K_2Ni(CN)_4$ and those which are paramagnetic with two spins e.g. (*) $[Ni(NO_3)_2\ 2Et_3P]_0$. On the Pauling theory these are represented as follows, (Fig. 10).

Fig. 10.



On examining (*a*) in Fig. 8 we see that if the attached ligands can get close enough to the Ni atom then the $d_{x^2-y^2}$ orbital — pointing in the direction of the ligands — can feasibly be used for bond forma-

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(*) Many of the supposedly four-covalent paramagnetic Ni^{II} complexes are probably octahedrally co-ordinated.

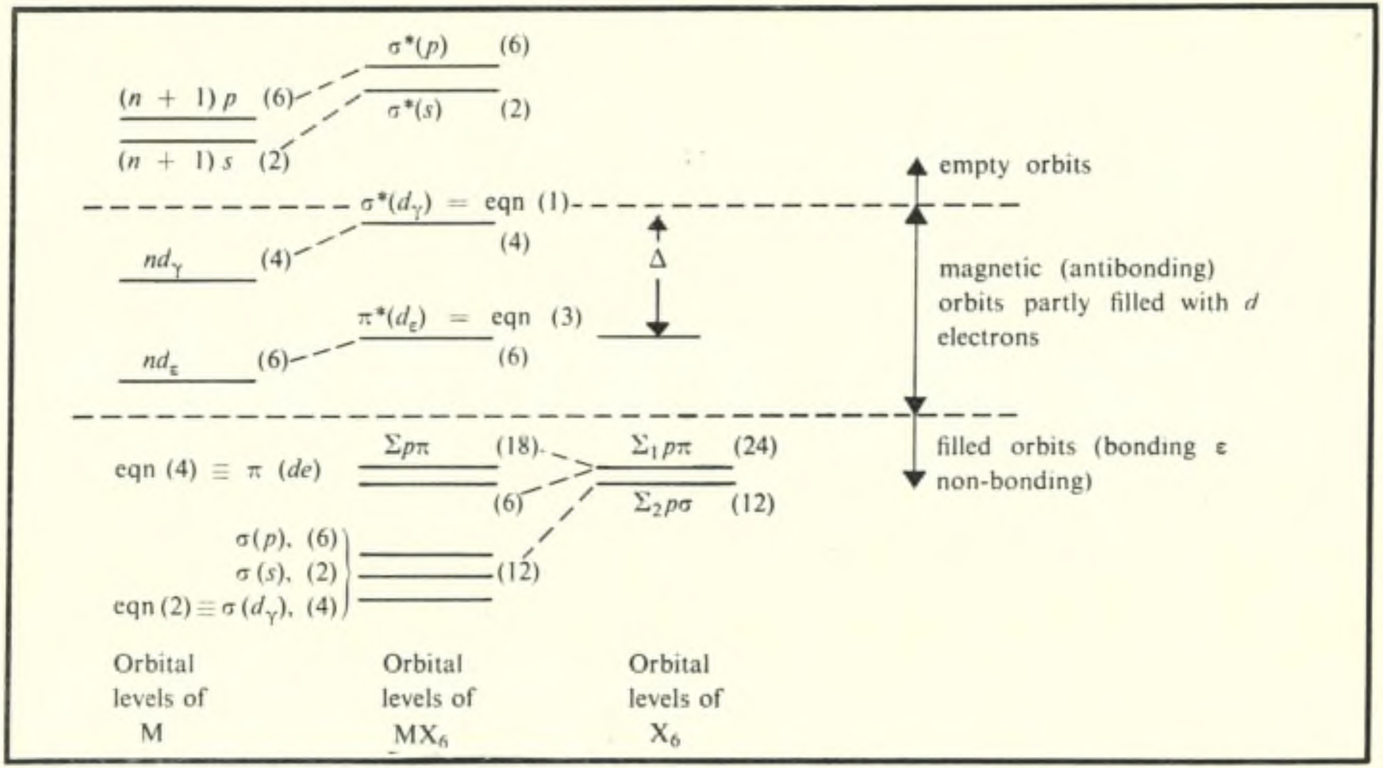
tion. This requires that the eight d electrons now be squeezed into the remaining four d levels giving diamagnetism. This use of the $d_{x^2-y^2}$ orbital for bond formation is indeed observed in practice, as expected, with ligands of low electronegativity (high polarisability) and good capacity for d_π bond formation. Thus the diamagnetic case corresponds closely with the Pauling picture. However on the ligand field theory, ligands of higher electronegativity — which leave the $d_{x^2-y^2}$ orbital available for non-bonding electrons — *could still be arranged in a square* and give rise to a complex with two spins. The author (18) has previously stressed that, pending confirmation, the assumption that four-covalent paramagnetic Ni^{II} complexes are tetrahedral is not at all proven. Even the high electric dipole moment of $Ni(NO_3)_2$, $2Et_3P$, which is indisputably a four-covalent complex (19), could be due to a *cis*-planar instead of a tetrahedral arrangement of the ligands. However both the ligand field and Pauling theories agree on the basic results for spin-paired complexes : in perfect octahedral complexes i.e. those in which the six metal ligand bonds are equal in length, *two* d_γ orbitals are left free for octahedral bond formation, whilst in square complexe *one* d_γ orbital is available to form square bonds with the ligands.

THE MOLECULAR ORBITAL APPROACH

A third approach to metal complexes is the method of molecular orbitals originally developed by Mulliken. This will be summarised briefly. Essentially this method treats the molecule formed by the union of two or more atoms as an assemblage of positive ions with various molecular orbitals, some bonding and some antibonding. These molecular orbitals are in turn formed by a combination of atomic orbitals. They are arranged in an energy sequence and will be filled by electrons in order to the relative potential energies of the orbitals. We shall confine our attention here to the combination of a metal ion (or atom) M with six ligands each represented by X. We shall follow the discussion given by Owen and Stevens (20, 21, 22) and confine our attention to the octahedral molecule or complex ion MX_6.

In Fig. 11 we represent on the left hand side the atomic orbitals of the metal atom or ion M and on the right those of the ligand. In the middle column are shown the molecular orbitals which result from a combination of these. With the metal atom only nd, $(n + 1)s$

Fig. 11 (*)



(*) I am grateful to Dr J. Owen (21) for permission to reproduce this diagram.

and $(n + 1)p$ atomic orbitals will be considered. The value of n is 3, 4 or 5 according as we are concerned with a metal of the first, second or third transition series. In the case of the ligand we are almost invariably concerned with a lone pair in a hybrid sp^3 orbital — c.f. Cl^-, H_2O, NH_3. For convenience we shall call this a p orbital of the ligand, but the above proviso is implicit. The lowest orbitals are the bonding σ orbitals which are of the usual d^2sp^3 type with which the Pauling theory has made us familiar. Next there are bonding π orbitals followed by the various antibonding orbitals.

Making molecular orbitals from linear combinations of the metal and ligand orbitals involves the use of a term $\sqrt{1 - \alpha^2}$ called the admixture coefficient; $\alpha^2 = 1$ if the binding is purely ionic and for a " purely covalent " bond $\alpha^2 = 0.5$. Paramagnetic resonance studies give valuable information about α^2. For this brief survey it is relevant to point out that in $[Ni(H_2O)_6]^{++}$ and $[Cu(H_2O)_6]^{++}$ paramagnetic resonance leads to values of $\alpha^2 = 0.83$ and 0.84... giving support for the view held on other grounds that the bonds in this hydrated ions have some covalent character. The effects of σ and π binding are summed up according to Owen as follows : *σ Bonds.* The net transfer of electrons from the six X atoms to the M atom evens out charge distribution and enhances stability. The magnetic properties are then affected,

1. By increasing the splitting between d_ε and d_γ levels;
2. By partial transfer of unpaired d_γ electrons from M to the six X atoms.

π Bonds. Considering only the d_ε orbitals which are suitably shaped for π binding, the contribution to the total binding from this source is smaller than with σ binding because overlap is smaller. Owen distinguishes between two cases; one in which ligands like Cl^-, H_2O, NH_3, etc., are employed for which there are no vacant orbitals available or capable of being made available. In this case partial transfer of p_π electrons from X to M and of d electrons from M to L is envisaged. With CN^-, however, transfer of d_ε electrons from M to X can be envisaged on a large scale. This, of course, is essentially the Pauling picture.

Perhaps a most important feature stressed by Owen is the effect of π binding upon the size of the orbital contribution to the magnetic moment. Partial transfer of a d_ε unpaired electron to a ligand atom L is expected to reduce the orbital contribution to the moment. The observed moment of $(NH_4)_2\,Ir\,Cl_6$, which is close to the spin only value for 1 unpaired electron, is attributed by Owen and Stevens (20) to this cause.

IV. MAGNETIC BEHAVIOUR OF TRANSITION METAL

Before discussing the complexes in each Group of the Periodic Table, a general survey of the types of magnetic behaviour which will be encountered is essential. These metals all contain 3*d* electrons and in those valency states wherein the binding involves no electron pairing or where the number of *d* electrons is odd, paramagnetism is generally observed. Even when electron pairing occurs paramagnetism is observed when there is an odd number of electrons, and in certain other cases. With the exception of type I, quoted as ideal, all the kinds of magnetism shown below are to be found among transition elements. They are summarised first and in certain cases will be discussed in more detail (see Nyholm (23) for detailed references on magnetochemistry).

Type 1. Rare Earth Type. — This is the ideal magnetic behaviour and arises (a) when the unpaired electrons responsible for paramagnetism are well shielded from external forces and (b) when the ground state of the atom is separated from the next higher excited state by an energy difference large compared with *k*T, i.e. $h\nu_{(J_0 \rightarrow J_1)}$(*) $\gg$ kT. The magnetic moment is then given by the equation $\mu = g\sqrt{J(J+1)}$. *g* is the Lande Splitting Factor given by the expression :

$$1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

For substances showing this type of magnetic behaviour μ is independent of the stereochemical environnement and the magnetic dilution. Magnetic moments of this type are not shown by the iron group elements but it is the ideal behaviour from which deviations occur to a greater or lesser extent.

(*) The expression $h\nu_{(J_0 \rightarrow J_1)}$ is used to indicate the energy interval between the lowest and next J values.

Type 2. Small Multiplet Separation. — When the energy separation between successive J values ($h\nu$) is very small compared with kT i.e. $h\nu_{(J_0 \rightarrow J_1)} \ll k\mathrm{T}$ it is found that L and S no longer couple together to give a resultant J but each reacts separately with an external field. Under these circumstances the calculated value of μ is given by $\sqrt{4\mathrm{S}(\mathrm{S}+1)+\mathrm{L}(\mathrm{L}+1)}$. This is the opposite extreme to case 1 and is the limit towards which μ approximates as $h\nu_{(J_0 \rightarrow J_1)}$ approaches zero.

Type 3. Intermediate Multiplet Separation.— i.e. $h\nu_{(J_0 \rightarrow J_1)}$ comparable with kT. When this situation arise, there is a distribution of the molecules over the various J values decided by the Boltzmann equation. Examples include NO, Sm^{+++} and Eu^{+++}.

Type 4. Iron Group Type. — It has been known for a long time that the magnetic moments of the irons of the elements of the first transition series (Ti → Cu) agree neither with the large multiplet separation formula $\mu = g\sqrt{\mathrm{J}(\mathrm{J}+1)}$ nor the very small multiplet separation formula $\mu = \sqrt{4\mathrm{S}(\mathrm{S}+1)+\mathrm{L}(\mathrm{L}+1)}$(*). Agreement between theory and experiment is best given by the simple expression $\mu = \sqrt{4\mathrm{S}(\mathrm{S}+1)}$, at least for the first half of the series, the whole of the orbital contribution L(L + 1) being ignored. This is shown in Table II on page 25. However, the quenching of this orbital contribution is often not complete and this deviation from the "spin-only" formula $\mu = \sqrt{4\mathrm{S}(\mathrm{S}+1)}$ can be used to assist in determining stereochemistry in ideal cases as discussed on page 27. The calculated values of μ for 1 to 5 unpaired electrons are given in Table II.

Type 5. Covalent Bond Type. — It is often found that the moments of certain complexes are much less than those predicted from Hund's rules on the spin-free formula. Thus, whereas the Fe^{+++} ion has the expected 5 unpaired electrons in $\mathrm{K_3FeF_6}$, in $\mathrm{K_3Fe(CN)_6}$ the moment of 2.34 B.M. indicates only one unpaired electron. This "electron pairing" occurs in many complexes of the first transition series with ligands of low electronegativity and is the norm for complexes, of the 2nd. and 3rd. transition series.

(*) Actually this formula does agree with the experimental μ_{eff} values for certain octahedral $\mathrm{Co^{II}}$ complexes. See p. 27.

TABLE II

Transition ion moments.

Term	Ion	Actual value of ν cm^{-1}	μ if $\nu = \infty$ i.e. $g\sqrt{J(J+1)}$	μ if $\nu = 0$ i.e. $\sqrt{4S(S+1) + L(L+1)}$	μ using actual value of ν	Spin only μ_{eff}	Observed $\mu_{eff.}$
$^2D_{3/2}$	Ti^{+++}	385	1.55	3.0	2.18	1.73	
$^3F_2$	V^{+++}		1.63	4.47	2.73	2.83	2.75 — 2.85
$^4F_{3/2}$	V^{++}	580	0.77	5.20	3.60	3.87	3.8 — 3.9
	Cr^{+++}	912	0.77	5.20	2.97	3.87	3.7 — 3.9
	Mn^{++++}	852	0.77	5.20	2.47	3.87	4.0
$^5D_0$	Cr^{++}	566	0.0	5.48	4.25	4.90	4.8 — 4.9
	Mn^{+++}	852	0.0	5.48	3.80	4.90	4.9 — 5.0
$^6S_{5/2}$	Mn^{++}		5.92	5.92	5.92	5.92	5.9 — 6.0
	Fe^{+++}		5.92	5.92	5.92	5.92	5.9 — 6.0
$^5D_4$	Fe^{++}	998	6.70	5.48	6.54	4.90	5.0 — 5.4
$^4F_{9/2}$	Co^{++}	1,890	6.64	5.20	6.56	3.87	4.3 — 5.2
$^3F_4$	Ni^{++}	2,347	5.59	4.47	5.56	2.83	2.9 — 3.4
$^2D_{5/2}$	Cu^{++}	2,130	3.55	3.0	3.53	1.73	1.7 — 2.2

Type 6. Heavy Atom Type. — In certain of the heavy atom complexes, e.g. K_2OsCl_6, the moment is less than the number of unpaired electrons predicted even for " covalent bond " formation. Thus Fe^{++}, Ru^{++} and Os^{++} ions have a d^4 configuration. If two *d* orbitals are left free for bond formation (using the Pauling picture) two unpaired *d* electrons are expected in the resulting complex, giving a moment of 2.8-2.9 B.M. However in K_2OsCl_6 the moment of 1.4 B.M. is much less than this. This is discussed further on page 49.

Type 7. Antiferromagnetism. — This behaviour is often found in certain types of lattice, e. g., the perovskite structure, when paramagnetic atoms are connected by $O^{=}$ or F^{-} ions. Good examples include the complex fluorides of type $KM^{II}F_3$ (24), where M = Cr, Mn, Fe, Co, Ni and Cu. They may be regarded as consisting of two interlacing ferromagnetic networks the spins of which point in exactly opposite directions. On gradually increasing the temperature from very low temperatures the susceptibility rises at first owing to the gradual destruction of the antiparallel cancelling spins. At higher temperatures the normal temperature dependence of paramagnetism is observed, which is characterised by a gradual fall in susceptibility, in accordance with the Curie-Weis law $\varkappa \propto \frac{1}{T + \Delta}$. This results in a maximum in the susceptibility-temperature curve, which is characteristic of antiferromagnetics.

Further Remarks on the Iron Group Type 4.

For a discussion of the moments of the first transition series Table II is relevant.

As mentioned earlier, the magnetic moments of the metal ions of the first transition series as a rule do not agree with the large $h\nu_{(J_0 \rightarrow J_1)}$ interval formula ($\mu_{eff} = g\sqrt{J(J+1)}$, with the small interval formula [$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)}$], nor with the more complicated formula wich uses the actual multiplet separation intervals. In general the moments are accounted for most satisfactorily by assuming that the orbital angular momentum [$L(L+1)$] is largly or completely quenched leaving only the spin momentum

TABLE III

Magnetic moments of first transition series.

Metal Ion	Ti^{++}	V^{++}	Cr^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{+++}	Cu^{++}
Spectroscopic state and unpaired electrons	F 2	F 3	D 4	S 5	D 4	F 3	F 2	D 1
μ_{eff}Calc. $\sqrt{4S(S+1)}$	2.83	3.88	4.90	5.92	4.90	3.88	2.83	1.73
μ_{eff} Observed		3.8–3.9	4.8–4.9	5.2–6.0	5.1–5.7	4.3–5.6	2.8–3.5	1.8–2.2 *
Metal ion	Ti^{+++}	V^{+++}	Cr^{+++}	Mn^{+++}	Fe^{+++}	Co^{+++}	Ni^{+++}	Cu^{+++}
Spectroscopic state and unpaired electrons	D 1	F 2	F 3	D 4	S 5	D 6	F 7	F 8
μ_{eff}Calc. $\sqrt{4S(S+1)}$	1.73	2.83	3.88	4.90	5.92	4.90	3.88	2.83
μ_{eff} Observed	1.7–1.9	2.7–2.9	3.8–3.9	4.7–5.0	5.4–6.0	—	—	2.8

operative. For bi- and tervalent ions agreement with the formula $\mu_{eff} = \sqrt{4S(S+1)}$ is very good for the first half of the series (i.e., Ti^{+++} to Mn^{++} or Fe^{+++}) but the deviation is much more marked for Fe^{++} and for the bi- and tervalent states of the metals Co, Ni and Cu. This is illustrated by the figures given in Table III.

In order to understand how the stereochemical arrangement of the ligands attached to the metal ion affect the size of the orbital contribution, it is first necessary for us to examine the way in wich the energy levels of an ion are affected by the electrical field produced by the charged groups surrounding the metal ion. The electrical

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(*) Certain recently discovered five-covalent Cu^{++} complexes have moments up to 2.6 BM. (see p. 59.)

field may be considered to arise mainly from the groups directly attached to, or in immediate proximity with, the metal ion, but longer range forces also appear to have a definite but smaller effect. We shall confine this discussion to the first of these two. Reference to Table II shows that for the ions of the first transition series, the spectroscopic ground states are S, D or F states (*). In the first of these the orbital angular momentum (L) is zero and hence there is no orbital contribution to the moment. For the ions in this S state the value of μ_{eff} is given by the spin only formula irrespective of the arrangement of the ligand around the metal ion; small deviations which do occur result in moments *less* than the spin only value. These involve effects (**) which are of no diagnostic value so far as inorganic stereochemistry is concerned. However, for both D and F states the position is quite different. In the following discussion we shall confine our attention mainly to Fe, Co, Ni and Cu, particularly when bivalent.

Let us consider first of all the simpler case, that of an ion in an F state, taking as our example the Co^{++} ion. The arrangement of electrically charged particles about a metal ion, e.g. the four Cl^- ions in the tetrahedral $[CoCl_4]^=$ complex ion, give rise to a ligand field about the central metal ion. This electrical field has two main effects (***). Firstly, the coupling of the L and S vectors is largely broken up so that the ion is no longer specified by a particular J value. Secondly, the $2L + 1$ sublevels associated with the particular L value, which are degenerate in the normal ion, with no electrical field superimposed, are usually split apart with separations between levels which have important effects upon the contribution which the orbital momentum makes to the magnetic moment. It should be recalled that for an ion with narrow multiplet separation, i.e. $h\nu_{(J_0 \rightarrow J_1)} \ll kT$, having no electrical field operating, the effect of an external magnetic field is to react separately with S and L lifting the degeneraties of these into their $2S + 1$ and $2L + 1$ sublevels. The distribution over the degenerate $2L + 1$ levels is what gives rise to the large orbital contribution to the magnetic

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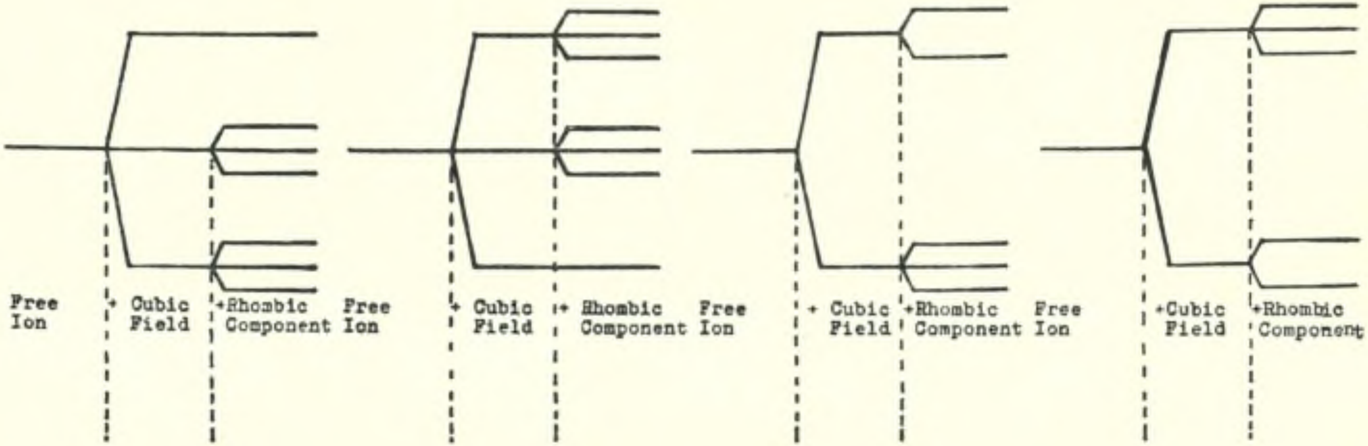
(*) The spectroscopic terms S, P, D and F refer to the value of L for the ion. The values are respectively 0, 1, 2, and 3.

(**) Both metal-metal interaction (as in the Hg_2^{++} ion) and antiferromagnetism can cause reduction in the moment of S state ions.

(***) For detailed reference to original work see Nyholm (23).

Fig. 12.



a

Octahedral Co^{++}

Cubic Field Constant D, Positive

Tetrahedral Ni^{++}

Cubic Field Constant D, Negative

b

Tetrahedral Co^{++}

Cubic Field Constant D, Negative

Octahedral Ni^{++}

Cubic Field Constant D, Positive

c

Octahedral Fe^{++}

Cubic Field Constant, D, Positive

Tetrahedral Cu^{++}

Cubic Field Constant D, Negative

d

Octahedral Cu^{++}

Cubic Field Constant D, Positive

Tetrahedral Fe^{++}

Cubic Field Constant, D, Negative

STARK PATTERNS FOR D AND F STATE IONS

moment in the formula $\mu = \sqrt{4S(S+1) + L(L+1)}$. Now if the ligand field should split the L value so that the separation between any two sublevels is large compared with kT, then only the lowest (or lower) levels will be populated. Furthermore, should this lowest level be only a singlet then the orbital contribution to the magnetic moment should be very small (*).

Penney and Schlapp (3) examined by group theory methods the effect of various kinds of electrical crystalline fields on F and D states for transition metal ions. They found that if an ion is in an F state, e.g. Co^{++} when at the centre of a cubic (**) electrical crystalline field, such as is produced when the Co^{++} ion is at the centre of a *perfect* octahedron of H_2O molecules, the single energy level is split into three new levels, the separation between successive levels being about 10^4 cm^{-1} (kT at 20 °C is approximately 204 cm^{-1}, small compared with 10^4 cm^{-1}).

Usually small departures from cubic symmetry occur owing to slight distortion of the octahedron. This may be regarded as equivalent to imposing on the field a small component of lower symmetry, e.g. tetragonal or rhombic. (***) This rhombic component causes a further splitting of two adjacent energy levels into triplets; the energy separation between the sub-levels of the triplet is of the order kT. This gives seven levels in all for an F state. An example of this kind of separation is given by $[Co(H_2O)_6]^{++}$ ion, shown in Figure XII. In this case the triplet level is lowest and the singlet is highest. This means that the populations of all three levels of the lowest lying triplet are appreciable whereas the intermediate triplet and upper singlet state have a negligible population. The distribution over the three sub-levels of the lowest lying triplet is according to the usual Boltzmann temperature dependent function.

(*) For a magnetic moment *degeneracy* of spin or orbital states is essential. The *spin* degeneracy can never be lifted by an electrical field alone however a sufficient splitting of orbital levels can destroy orbital magnetism entirely.

(**) Cubic field — three axes at right angles, all equal; tetragonal field — three axes ar right angles, two equal; rhombic field — three axes at right angles, all unequal. Trigonal field — two equal axes at 120° (X and Y) *NOT* equal to a third perpendicular to these two.

(***) The most usual distortion if for two co-linear metal — H_2O bonds to be slightly longer than the other four bonds in the plane at right angles to this axis.

TABLE V

Crystalline Field Effects on Ions of first transition series.

Ion	Ti^{+++}	Ti^{++} V^{+++}	V^{++} Cr^{+++}	Cr^{++} Mn^{+++}	Mn^{++} Fe^{+++}	Fe^{++} Co^{+++}	Co^{++} Ni^{+++}	Ni^{++} Cu^{+++}	Cu^{++}
Spectroscopic ground state.	${}^2D_{3/2}$	${}^3F_2$	${}^4F_{3/2}$	${}^5D_0$	${}^6S_{5/2}$	${}^5D_4$	${}^4F_{9/2}$	${}^3F_4$	${}^2D_{5/2}$
Unpaired 3*d* electrons.	1	2	3	4	5	4	3	2	1
L =	2	3	3	2	0	2	3	3	2
Lowest orbital level in cubic field (+ small rhombic component). Positive field constant, i.e. 6 octahedral charges.	Triplet	Triplet	Singlet	Non magnetic doublet (equiv. to singlet	Singlet	Triplet	Triplet	Singlet	Non magnetic doublet (equiv. to singlet)
Lowest orbital level in cubic field (+ small rhombic component). Negative field constant i.e. 4 tetrahedral charges.	Non magnetic doublet (equiv. to singlet)	Singlet	Triplet	Triplet	Singlet	Non-magnetic doublet (equiv. to singlet)	Singlet	Triplet	Triplet

Van Vleck (4), Penney and Schlapp (3), Bethe (2) and others (5) have attempted to explain quantitatively the splitting of the original single F level using expressions for the potential of the electrical crystalline field such as :

$$V = Ax^2 + By^2 - (A + B)z^2 + D(x^4 + y^4 + z^4).$$

A, B and D are constants which depend upon the charges on the ligands and their arrangement about the central metal ion. Usually the more simple expression $V = A(x^2 + y^2 - 2z^2) + D(x^4 + y^4 + z^4)$ suffices. This expression represents a field which is symmetrical about the z axis; the effects of more distant atoms and powers other than those shown are ignored. The term involving the fourth power of x, y and z represents the field of cubic symmetry which is responsible for the initial separation of an F state into three levels ($\sim 10^4$ cm apart). For the first transition series the constants A and B are of the order of 0 to 400 cm^{-1}, whilst D lies somewhere between 1,000 and 1,500 cm^{-1}. If one is dealing with an arrangement of negative charges about a metal ion it can be shown that D changes in sign in passing from the cubic field arising from six octahedral ligands to the cubic field due to four tetrahedral ligands. This change of sign results in an " Inversion of the Stark Pattern "; this is shown in Figure 12. The shape of the Stark pattern is also affected by the number x of d electrons; thus, if we consider the Ni^{++} ion instead of the Co^{++} ion the situation is exactly reserved, 12*a* arising from tetrahedral Ni^{++} and 12*b* arising from octahedral Ni^{++}. The patterns expected for the various bi- and tervalent first transition ions in a cubic field with a rhombic component are summarised in Table V.

For an ion in a D state the cubic crystalline field splits the orbital level into two levels, the separation between which is large, cf. with kT. These two levels are in turn split by a small rhombic component into a triplet and a doublet. Where the triplet lies lowest, as for example with the Fe^{++} ion (see Table V) when surrounded by six octahedrally co-ordinated negative charges, a large orbital contribution is expected. If the doublet is lowest, e.g. for Cu^{++} (Figure 12*d*) in the same field only a small orbital contribution can be expected because the doublet is said to be " non-magnetic ", for it behaves effectively as a singlet.

For the first half of the first transition series observed orbital contributions are negligible. For V^{++}, Cr^{+++}, Cr^{++} and Mn^{+++} this is in any case what we would expect for octahedral co-ordination. However, for octahedrally co-ordinated Ti^{++}, Ti^{+++}, and V^{+++}, which have a triplet lying lowest, a large orbital contribution might be expected. This has never been observed, moments corresponding to the spin only value being obtained; we may attribute this complete orbital quenching to the small and positive values of the spin orbit coupling which, together with a rhombic field, result in the separation even of the orbitally degenerate levels to widths large compared with kT.

For the ions of Fe, Co, Ni and Cu data are more interesting, most work having been done with Co^{++}. Octahedrally co-ordinated Fe^{++} and Co^{++} should have the large orbital contributions, which is in general true (see Table V). On the other hand, for octahedrally co-ordinated Ni^{++} and Cu^{++} small orbital contributions are expected; as shown by Table V this is, broadly speaking, what is found experimentally. For tetrahedrally co-ordinated Fe^{++} and Co^{++} a small orbital contribution would be predicted Data are not available for Fe^{++} but for Co^{++} it is correct to say that the orbital contribution is much smaller than in the octahedral complexes. In theory tetrahedral Co^{++} might be expected to have a μ_{eff} close to 3.88 B.M., since the singlet is lowest; Bose and Mitra ([25]) propose that high frequency contributions are partly responsible for the deviations from the spin only value in this case (*). They suggest that since kT becomes steadily larger as T increases, the high frequency contribution should increase with T and, in fact, be proportional to T. This implies that there should be a fall towards the spin only value of 3.88 B.M. as T decreases. Data are scarce but a definite decrease in μ_{eff} for the tetrahedral Co^{++} complexes as T decreases has been observed.

It is of interest to note that the large orbital contribution in octahedrally co-ordinated cobaltous salts, e.g. $[Co(H_2O)_6]\,Cl_2$, is associated with marked anisotropy in the susceptibility. On the

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(*) This orbital contribution is proportional to T/D; in addition another orbital contribution arises from λ, the spin-orbit coupling constant. This effect is proportional to $\frac{\lambda}{D}$.

other hand, the blue tetrahedrally co-ordinated salts are nearly isotropic. Thus, Krishnan and Mookherjie (26) found that anisotropy in blue Cs_2CoCl_4 was only about 5 %, whereas in the pink hexahydrated cobaltous salts it is of the order of 30 %. Data for tetrahedrally co-ordinated Ni^{++} are not available . Similarly, no certain case of tetrahedral co-ordination to Cu^{++} has been reported. However, some new five-covalent complexes of bivalent copper (14), which have a very large orbital contribution ($\mu_{eff} = 2.6$ B.M.) may be due to the ligand field resulting from a bipyramidal arrangement of five ligands.

As yet only in the case of bivalent cobalt complexes has any serious examination been made of the use of the orbital contributions as a guide to stereochemistry. Broadly speaking, a moment between 4.3 and 4.74 indicates tetrahedral co-ordination, whereas a moment in excess of 4.85 indicates an octahedral arrangement. It is obvious that uncertainty must remain for complexes having a μ_{eff} in the vicinity of 4.7-4.8 B.M. It has become increasingly apparent that, since the field constant is affected by several other factors besides the stereochemistry, these must be borne in mind. These factors include the charge on the complex ion, the attachment of heterogeneous groups, e.g. $CoCl_2X_2$, the electronegativity of attached groups, and the possibility of longer range electrical forces arising from atoms surrounding the complex. Data available at present suggest that the higher the electronegativity of the attached the larger the orbital contribution; thus the moments of the $[CoCl_4]^{=}$, $[CoBr_4]^{=}$ and $[CoI_4]^{=}$ ions are respectively 4.76, 4.62 and 4.56 B.M.

This may possibly be explained by the intensity of the ligand field increasing as electronegativity decreases. This will increase the energy interval between lowest lying singlet and next upper triplet.

A simple illustration of the application of these ideas to a stereochemical problem is provided by a study of the magnetic moments in the complexes of cobaltous halides with aniline, An. It is possible to prepare blue compounds having the formulae $CoCl_2.2An$, $CoBr_2.2An$ and $CoI_2.2An$. In addition, a pink di-alcoholate of the chloride $CoCl_2.2An.2EtOH$, and of the bromide can be isolated. If the alcohol in these really coordinated with the Co^{II} atom to form an octahedral complex, magnetic moments greater than 4.8 B.M. are expected. On the other hand, if the blue complexes Co X_2 An_2 are really tetrahedral then they should have moments ~ 4.7 B.M. The actual values given in Table VI indicate

TABLE VI

Magnetic moments and physical properties of cobaltous aniline complexes.

Complex	Colour in solid state	μ_{eff} in solid state
Co Cl_2 . 2 An	Blue	4.40
Co Br_2 . 2 An	Blue	4.46
CoI_2 . 2 An	Green-blue	4.61
Co Cl_2 . 2 An . 2 C_2H_5OH	Pink	5.0
Co Br_2 . 2 An . 2 C_2H_5OH	Pink	5.0
Co$(SCN)_2$. 2 An	Pink	5.11

that this is so and support the hypothesis that the Co X_2.2 An (X = Cl, Br and I) complexes are tetrahedral and the di-alcoholate octahedral. However, as an apparent exception to the above generalisations the thiocyanate Co$(SCN)_2$.2 An is found to be *pink* in the solid state and has the magnetic moment (5.11 B.M.) corresponding with an octahedral complex. This can be explained, however, by postulating that the Co$(SCN)_2$An is polymerised in the solid state, each -SCN group being co-ordinated to a second cobalt atom. This kind of behaviour occurs in the compound Hg Co$(CNS)_4$, the -CNS being co-ordinated to the mercury atom as well as the cobalt, although in this instance the Co atom retains its tetrahedral configuration. This hypothesis is being tested by studying the colour and magnetic moment and electrical conductivity of the Co(SCN).2 An complex in various solvents ([26a]) (*).

(*) μ_{eff} in acetone solution is 4.57 B.M., the solution being blue in colour as expected for tetrahedral complex.

Another interesting application is in connection with the structure of the *blue* and *violet* forms of cobaltous chloride bis-pyridine complex, $Co\,Cl_2.2\,Py$. The violet forms has a magnetic moment of 5.24 B.M. suggesting octahedral co-ordination. This form exists only in the solid state and cannot be dissoveld in solvents without a change over to the blue form taking place. The blue form, on the other hand, has a magnetic moment of 4.51 B.M. and 4.47 B.M. in the solid state and in nitrobenzene respectively. In the latter solvent it is monomeric and a non-electrolyte and undoubtedly exists as tetrahedral $Co\,Cl_2.2\,Py$ molecules. Under the circumstances, it is reasonable to suggest that the violet form has a polymeric structure with octahedrally co-ordinated cobaltous atoms connected together by halogen bridges in an infinite polymeric lattice (*).

It is probable that as more data on Fe, Cu and Ni salts bearing on the relationship between orbital contribution and stereochemistry become available the orbital contribution will serve as a useful guide to the stereochemistry of these ions also.

Further Remarks on Co-valent Bond Type — (Type 5).

To understand the magnetic behaviour of those complexes of the iron group in which electron pairing occurs, one can use the Pauling or Ligand Field theory and the same result is obtained. Thus we consider as examples two cases of octahedral co-ordination. The complexes of Cr^{II} in which no electron pairing occurs have four d electrons. These may be regarded on the ligand-field theory as giving rise to one doubly filled and two singly filled d_ε orbitals. This results in two unpaired electrons as in $[Cr(Dipyridyl)_3]^{++}$. On the Pauling picture, we get the same result. In the latter case the two d_γ orbitals are available for bond formation. As with the complexes of the iron group, in which no electron pairing occurs, some orbital contribution still remains. This is greater with some stereochemical rearrangements than with others. Thus spin-paired cobaltous complexes, if four-covalent, have large orbital contribu-

(*) *Note added in proof :* Preliminary investigations by X-ray crystallography of the violet form of $CoCl_2.2Py$ confirm the postulated halogen bridged polymer, the pyridine groups being *trans*. (^{26}b).

tions, μ being as high as 2.9 B.M. However with the (presumably) octahedral spin-paired Co^{II} complexes values closer to the spin only value of 1.73 B.M. are observed. In the absence of spin-orbit coupling data we shall not attempt to interpret these orbital contributions here.

Further Remarks on the Heavy Atom Type (Type 6).

As mentioned earlier it is often found that in the Pd and Pt groups the moments are even less than those expected by the Pauling or simple Ligand-Field theory*. Thus $K_2\,Os\,Cl_6$ has a moment of only 1.4 B.M. even though there are four *d* electrons in Os^{IV}, and the Pauling theory predicts $\mu = 2.83$ B.M. To understand the further reduction we must take into account the much larger spin-orbit coupling consequent upon the large value of z, the nuclear charge. This spin-orbit coupling constant is proportional to $(z - \sigma)^4$ where σ is the shielding correction. Under certain circumstances it is possible to lift even spin degeneracy by the application of an electrical field *via* the spin-orbit interaction. One naturally expects to find this effects most marked where spin-orbit coupling is greatest, i.e. for the heaviest transition elements. This lifting of spin degeneracy however, is governed by an important theorem due to Kramers. This states that spin degeneracy can be removed by an electrical field *only* if the number of unpaired electrons is even. This is related to the fact that the resultant spin in an atom can be zero only if all the spins cancel out. In an atom with an odd number of electrons the resultant spin is necessarily a half.

It is important at this point to emphasise that in certain molecules for which one spin only is expected diamagnetism may result from another effect — namely when the spin and orbital moments cancel. Thus for the NO molecule the ground state is diamagnetic ($a\,{}^2\pi_{1/2}$ state) whereas the first excited state has a moment of 2.00 B.M. ($a\,{}^2\pi_{3/2}$ state). In the ground state the orbital and spin momenta cancel to give no resultant momentum, and hence no resultant magnetic moment. However, in the upper state the L and S momenta

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(*) The magnetic moments of complex ions with $d_\varepsilon{}^1$ to $d_\varepsilon{}^6$ *non-bonding* electrons are discussed by Kotani (56) (see page 49), for a cubic field arising from an octahedral arrangement of ligands. For $d_\varepsilon{}^1$ and $d_\varepsilon{}^4$ μ_{eff} approxes zero as T approaches absolute zero. For $d_\varepsilon{}^2$ and $d_\varepsilon{}^5$ μ_{eff} approaches the finite values 1.22 BM and 1.73 BM as T approaches zero. For $d_\varepsilon{}^3$ the spin only value is expected at all temperatures.

combine vectorially to give a moment of 2.00 B.M. Since the separation between the states is only 120.9 cm^{-1} the observed moment is temperature dependent reaching a value of 1.84 B.M. at room temperatures and only slowly rising with T thereafter.

V. SURVEY OF VALENCE STATES, STEREOCHEMISTRY AND MAGNETISM OF TRANSITION METAL COMPLEXES

In this section we shall summarise the data available for complexes of the transitions metals shown in the modified Periodic Table hereafter. In this Table we list also the valency states which may be regarded as established beyond reasonable doubt. It would be impossible to deal with more than a fraction of the experimental data available and therefore we shall summarise with the following principles in mind.

(*i*) Valency states which have been established will be indicated and complexes of the 1st, 2nd and 3rd transition series compared.

(*ii*) Stereochemistry if differing from the usual octahedral arrangement will be discussed.

(*iii*) Magnetic behaviour will be indicated and in particular its importance in determing *a*) spin pairing, and *b*) stereochemistry as evidenced by orbital contribution, will be emphasised.

(*iv*) The relevance of the type of ligand so far as (*iii*) is concerned will be discussed.

In the Table hereafter zerovalency is found in most cases. As a rule this occurs most readily with carbonyls (See Table VIII) but other ligands of the same type will also give rise to zero-valency. We shall not attempt to discuss zerovalent compounds under the various groups but certain points of general interest should be mentioned.

The metal carbonyls are invariably diamagnetic; where the metal atom has an odd number of electrons the carbonyl dimerises in order to effect spin pairing. Thus both cobalt and manganese carbonyls are dimeric, e.g. $Co_2(CO)_8$, $Mn_2(CO)_{10}$.

Experimental data suggest that CO may have one or both of two roles in carbonyl complexes, as a terminal ligand as in $Ni(CO)_4$ or as a bridging ligand as in $Co_2(CO)_8$. In the latter compound one

TABLE VII

Transition metals.

Group	IV	V	VI	VII	VIII A	VIII B	VIII C	I *b*
1st	Ti	I V	Cr	Mn	Fe	Co	Ni	Cu
Series	II III IV	I II V III IV	O IV I V II VI III	O IV I V II VI III VII	O IV I VI II III	O IV I II III	O IV I VI II III	I II III
2nd	Zr	Cb	Mo	Tc	Ru	Rh	Pd	Ag
Series	III IV	II(?) III IV V	O V II VI III IV	↑ VI (and ↓ others)	O V I VI II VII III VIII IV	O I III IV	O I II IV III	I II III
3rd	Hf	Ta	W	Re	Os	Ir	Pt	Au
Series	III IV	II III IV V	O V II VI III IV	O(-1) III VI IV VII V	O V II VI III VII IV VIII	O III IV VI	O II IV VI	I III

finds two C-O absorption bonds in the infra-red spectrum which can be attributed to two different C-O stretching frequencies suggesting that in one case the carbon-atom is two covalent and in the other three covalent.

It is generally considered that a major reason for the stability of carbonyls is their capacity to form double bonds using *d* electrons of the metal. This not only results in stronger bonds owing to more overlap but removes an improbably high negative charge from the metal. Carbonyls are the best examples of a wide range of similar complexes formed by ligands capable of forming similar double bonds with the metal. Ligands of this type include isonitriles (e.g.C_6H_5NC), the phosphorous trihalides (PF_3, PCl_3), and certain complex cyanides e.g.$K_4Ni\,(CN)_4$. It is important to note that these

TABLE VIII

The metal carbonyls and their properties.

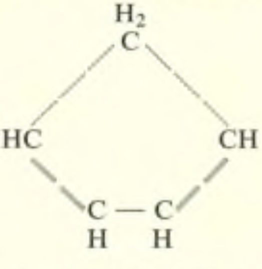
$Cr(d^4s^2)$	$Mn(d^5s^2)$	$Fe(d^6s^2)$	$Co(d^7s^2)$	$Ni(d^8s^2)$
$Cr(CO)_6$ Sublimes Colourless	$Mn_2(CO)_{10}$ M.P. 154-155° golden yellow	$Fe(CO)_5$ M.P. — 20° B.P. 103° yellow $Fe_2(CO)_9$ decomposes 100° golden yellow $Fe_3(CO)_{12}$ decomposes 140° dark green	$Co_2(CO)_8$ M.P. 51° golden yellow $(Co(CO)_3)_n$ decomposes 60° jet black	$Ni(CO)_4$ M.P. — 25° B.P. 43° colourless
Mo	Tc	Ru	Rh	Pd
$Mo(CO)_6$ sublimes colourless	——	$Ru(CO)_5$ M.P. — 22° colourless $Ru_2(CO)_9$ orange $Ru_3(CO)_{12}$	$Rh_2(CO)_8$ M.P. 76° (decomposes) orange $[Rh(CO)_3]_n$ red $[Rh_4(CO)_{11}]_m$ black	——
W	Re	Os	Ir	Pt
$W(CO)_6$ sublimes colourless	$Re_2(CO)_{10}$ M.P. 177° colourless	$Os(CO)_5$ M.P. — 15° colourless $Os_2(CO)_9$ M.P. 224° bright yellow	$Ir_2(CO)_8$ sublimes yellow-green $([Ir(CO)]_3)_n$ decomposes 210° yellow	——

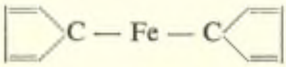
I am indebted to Professor R.K.Sheline for the compilation of this table.

ligands stabilise lower valency states, whereas many other common ligands like NH_3 fail to achieve this or do so only under very exceptional circumstances. There seems to be little doubt that the major reason for their ability to stabilise the zerovalent state is their capacity to *receive* electrons from the metal in forming $d\pi$ bonds. This had the effect of increasing the strength of the binding but more important still is the removal of negative charge from the metal. Thus in the compound $Ni(CO)_4$ the " formal " charge on the Ni atom if equal sharing of σ bonding pairs between Ni and C atoms occurs is -2 units. Even allowing for the difference in electronegativity between Ni and C the former would still have a charge of the order of -1 units. The formation of the $d\pi$ bonds can *return* some of this charge to the C and N atoms. In the process of making the Ni atom positively charged (or less negatively charged) a greater attraction for the σ bonding electrons is expected hence helping to strengthen the π bond. It is well known that carbonyls, isonitryls etc., are formed by the *transition* metals — a phenomenon which can be correlated with the presence of unpaired *d* electrons on the metal atom, available for $d\pi$ bond formation.

Cyclo-pentadienyl complexes.

Reference should also be made to the extensive recent literature upon complexes of cyclopentadiene (*). This molecule gives rise to compounds in which the cyclopentadienyl ion $[C_5H_5]^-$ is attached to metals. The simplest example is ferrocene $Fe(C_5H_5)_2$. At first sight a normal covalent Fe — C σ bond might be expected leading to the structure :





If this were correct the diamagnetism would suggest d^2 binding and hence two Fe — C bonds at right angles.

(*) For a review see Pauson (27).

However chemical properties and recent X-ray studies indicate quite definitely that this is the case; indeed the molecule involves a " sandwich " structure in which the Fe atom is placed in between two parallel C_5H_5 residues. Clearly a simple valence bond structure for this molecule cannot be visualised. There are, of course, no lone pairs of electrons in the resonance hybrid of the $[C_5H_5]^-$ ion(*) and we are clearly dealing with a bond of the type obtained in metal-olefine complexes in which π bonding pairs of electrons of the ligand are used to bond the ligand to the metal. A molecular orbital picture of the resulting structure has been put forward by Dunitz & Orgel ([28]). A large number of oxidation products such as the $[Fe(C_5H_5)_2]^+$ ion have been prepared and their properties investigated. At this stage the field is developing very rapidly and unless one can deal adequately with the conflicting views of the various workers in the field one cannot do the subject justice. We shall not therefore discuss these complexes further in this report.

GROUP IV (Ti, Zr, Hf)

These elements in the ground state have the configuration d^2s^2 the stable valency state of four corresponding to the loss of these four electrons.

Quadrivalent state. — Ti forms a large number of Ti^{IV} complexes in which the metal atom is octahedrally co-ordinated. These are exemplified by the halogeno complexes of the type K_2TiCl_6. However Zr and Hf, in addition to forming such six-covalent complexes give rise to seven-covalent compounds such as K_3ZrF_7. As all compounds are diamagnetic magnetic data give no help in deciding stereochemistry.

The tervalent state. — Titanous complexes appear to be primarily six-covalent and undoubtedly octahedral e.g. the hexahydrate $TiCl_3, 6H_3O$ ([29]). The single unpaired electron gives rise to a magnetic moment close to the spin-only value. In the cubic field arising from the octahedral arrangement a triplet should be lowest and hence a large orbital contribution might have been expected. The value of the multiplet interval (384.5 cm^{-1}) is small and we must presume that complete quenching of the L component takes place. If we assume ([30]) that there is a small asymmetric component superposed

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(*) If we consider a *single* resonance structure a *p* lone pair of electrons occure on one of the five carbon atoms. In the resonance hybrid, however, these becoms π bonding electrons.

on the cubic field the lower lying triplet is split into a doublet and a singlet of which the singlet lies lowest. This separation must be sufficient to account for almost entire destruction of the orbital contribution. Zr^{III} and Hf^{III} undoubtedly exist and have been prepared in impure compounds but as yet no well defined complexes have been described.

The bivalent state. — Ti^{II} is less stable than Ti^{III} but compounds have been prepared containing the required two unpaired electrons (31). Nothing is known of their stereochemistry; the anhydrous halides are most probably assemblages of ions. No Zr^{II} or Hf^{II} compounds are known.

GROUP V (V, Nb, Ta) d^3s^2

Pentavalent state. — In this valence state all complexes are diamagnetic. It is the most stable state in all cases and is best known in anionic complexes e.g. KVO_3 and K_3VO_4. Similar Nb and Ta compounds are formed but the tendency to polymerisation — already evident with V — is present to an even greater degree.

Quadrivalent state d^1. — A large number of V^{IV} complexes are known, ranging from the complex fluoride K_2VF_6 (μ_{eff} 1.5 — 1.8 B.M.) (32) to (presumably) five-covalent complexes such as VO (acetylacetone)$_2$ (33). The latter may also be obtained with one molecule of H_2O, NH_3, pyridine, etc., added. These latter complexes are then six-covalent. Their magnetic properties have been studied by Asmussen (33) who finds that μ_{eff} is close to the spin only value.

The anhydrous, presumably five covalent complexes, also have μ_{eff} values close to the spin only value. As with Ti^{III} all orbital contribution is clearly quenched and the moment is insensitive to the stereochemistry. Relatively little is known of the stereochemistry and magnetism of Nb and Ta.

The tervalent state d^2. — A large number of six covalent, presumably octahedral, V^{III} complexes are known e.g. $[V\,En_3]\,Cl_3$, $(NH_4)_3VF_6$, $[V(NH_3)_6]\,Cl_3$. Asmussen (33) reports that μ_{eff} is in all cases very close to the spin only value for 2 unpaired electrons. Little is known of the complexes of Nb and Ta. The magnetic behaviour of TaF_3 (32, 34) has been studied however; μ_{eff} is only 1.4 B.M. Since the figure of 2.55 B.M. is obtained for VF_3 it is apparent that the spin pairing in this instance may arise from exchange interaction between metal atoms consequent upon the high magnetic concentration.

Bivalent vanadium. — d^3 complexes of the type $K_4V(CN)_6$ and the double sulphates are known but are very unstable owing to the ease with which they may be oxidised. Their moments are close to the spin only value for 3 unpaired electrons (35). Little is known of the complexes Nb^{II} or Ta^{II} although simple salts such as $TaCl_2$ have been reported.

Univalent and zerovalent vanadium (d^4 and d^5). — Evidence for V^I has recently been obtained (36) as the compound $[V(dipyridyl)_3]I$. The corresponding V^0 complex $[V(dipyridyl)_3]^0$ has also been prepared. This has a moment of 1.9 B.M. indicating the single unpaired $3d$ electron expected for $3d^24s4p^3$ octahedral binding.

GROUP VI Cr, Mo and W(d^4s^2)

The univalent state (d^5). — This has been reported in the case of chromium only — as the tris-dipyridyl complex $[Cr(dipyridyl)_3][ClO_4]$ (37). The magnetic moment of 2.1 B.M. is consistent with the formation of a spin-paired complex in which $3d^24s4p^3$ bonds are present. The complex cation is then iso-electronic with the $[Fe(dipyridyl)_3]^{+++}$ ion. An unusual feature is the unexpected high-co-ordination number of 6 for such a low valency state. The corresponding Mo^I and W^I complexes are unknown.

The bivalent state (d^4). — Bivalent chromium gives rise to three kinds of magnetic behaviour in its complexes but in its stereochemistry it has a marked preference for sixfold coordination. The spin free complexes such as $[Cr(H_2O)_6]\,SO_4$ are paramagnetic with 4 unpaired electrons. The orbital contribution to the magnetic moment is negligible. If one uses CN^- or dipyridyl as the ligand complexes such as $K_4Cr(CN_6)$ and $[Cr(dipyridyl)_3]\,Br_2$ may be formed. These have two unpaired electrons only (34). This indicates that the 4 electrons give rise to two singly filled and one doubly filled d_ε orbitals. The two d_γ orbitals are free for bond formation and give the $3d^24s4p^3$ type of binding. Use of the acetate group in $Cr(CH_3COO)_2.4H_2O$ (38) gives a red feebly paramagnetic complex. The spin pairing in this complex is attributed to metal-metal interaction (39) — an hypothesis which is strongly supported by the short Cr-Cr distance found by X-ray crystallography (39, 40).

Except for the halides, which are themselves complex, no co-ordination compounds, as usually understood, are known of Mo and W.

The halides $(MoCl_2)_x$ and $(WCl_2)_x$ are diamagnetic (41) and in the case of the former, X-ray examination (42) indicates that the compound should be formulated as $[Mo_6Cl_8]\,Cl_4$. In this complex cation the Mo atom is four-covalent — but with nearly square co-ordination. From the diamagnetism we might expect the d_γ levels to be lowest — and well separated from the upper d_ε orbitals. However, for the latter inversion tetrahedral co-ordination is necessary. In connection with the diamagnetism it is of interest to point out that the Mo-Mo bond distance is consistent with metal-metal bonding; thus it is possible that the diamagnetism is accounted for in this way (as with Cr^{II} acetate) instead of by invoking a ligand-field explanation.

The tervalent state (d^3). — The octahedral complexes of Cr^{III} are so well known that we shall not discuss them here. The magnetic moment in all cases shows a value very close to the spin only value; the failure of CN^- in $K_3Cr(CN)_6$ to effect spin pairing is not surprising since two d_γ orbitals are available, if necessary, for bond formation irrespective of the type of ligand employed. Whereas even the simple salts of Cr^{III} show the paramagnetism characteristic of 3 unpaired electrons, the moments of $MoCl_3$ and $MoBr_3$ are only 0.7 and 1.23 B.M. respectively (41). Data for the trihalides of W are not available. The complexes of Mo^{III}, however, e.g. K_3MoCl_3 $(NH_4)_3Mo(SCN)_6$ have moments close to the spin only value for 3 unpaired electrons (3.7 — 3.9 B.M.). The only complex of W^{III}, $K_3W_2Cl_9$ has the very low moment of 0.5 B.M. As the latter would probably not arise from the spin-orbit coupling of W, metal-metal interaction is the more likely explanation. This probably takes place *via* the Cl atoms as in antiferromagnetism.

The quadrivalent state (d^2). — The best known chromium complex in this valency state is K_2CrF_6 prepared by E. Huss and W. Klemm (43). The magnetic moment of 2.8 B.M. is close to the spin only value for 2 spins. Mo^{IV} complexes are common and are illustrated by $K_4Mo(CN)_8$ which is diamagnetic (41). However the chloro-complexes are six-covalent and have the two unpaired electrons (41) in common with K_2CrF_6. This spin pairing when one uses CN^- and passes to an eight covalent state is noteworthy.

The pentavalent state (d^1). — In the case of Cr this valency state occurs in compounds such as $KCrOF_4$ which contain the expected single unpaired electron (34). For Mo^V an interesting situation is observed. Whereas the complexes $Rb_2Mo^{V}OCl_5$ $[PyH]_2Mo^{V}OCl_5$, $(PyH)_2Mo^{V}OBr_5$ all have moments close to 1.73 B.M. the complex anions $[Mo_2O_4Cl_4]^{=}$, $[Mo_2O_4(SCN)_6]$ and $[Mo_2O_4(C_2O_4)_2]^{=}$ are diamagnetic (41). In the diamagnetic compounds spin pairing presumably occurs between neighbouring Mo atoms. The complexes of W^{V} behave normally in having the expected one unpaired electron.

Hexavalent state (d^{0}). — Apart from the presence of unusually high paramagnetism ($\mu = \sim 1.4$ B.M.) in Cr^{VI} complexes (e.g. K_2CrO_4) the compounds of the hexavalent elements are diamagnetic. The paramagnetism of the chromates is generally attibuted to Van Veck paramagnetism — a temperature constant contribution arising from the high frequency contribution to the moment.

GROUP VII. Mn, Tc and Re (d^5s^2)

The univalent state (d^6). — The complex cyanide $K_5Mn(CN)_6$ has recently been prepared in a pure state by Treadwell and Rath. (44). It has the expected diamagnetism of a d^6, $3d^24s4p^3$ six-covalent spin-paired complex ion. The corresponding Tc valency state has not been investigated. No Re^{I} complexes are known. Mn^{I} is also known in complexes of the type $[Mn(RNC)_6]I$ where RNC is an isocyanide (44a).

The bivalent state (d^5). — Mn^{II} gives rise to spin-free (5 unpaired electrons) and spin paired complexes (1 unpaired electron). In the former category are complexes of apparently different co-ordination numbers e.g. the $[Mn(H_2O)_6]^{++}$ ion and $MnCl_2$, 2Py. Two forms of the last compound are known; these are no doubt similar to the corresponding Co^{II} complexes one being tetrahedral and the other octahedral co-ordinated as the result of chlorine bridging and polymerisation. However, in the absence of orbital contribution (Mn^{II}, d^5 is an S state) there is no simple way of supporting this. The spin-paired complexes are illustrated by $K_4Mn(CN)_6$. The bivalent state of Re and Tc is not yet established in any simple or complex compounds.

The tervalent state (d^4). — Mn^{III} forms spin free complexes such as $[Mn(acetylacetone)_3]^{0}$ with 4 unpaired electrons and spin paired complexes such as $K_3Mn(CN)_6$ with only two spins. Tc^{III} has not been investigated but Re^{III} complexes are diamagnetic or nearly so. This holds for both $(Re(NH_3)_6]Cl_3$ and $RbReCl_4$ (41, 45, 46). As pointed out by Orgel the diamagnetism of tetrahedral complexes is to be expected since the two d_γ levels will be lowest. However there is no certainty that the anion in $RbReCl_4$ is actually tetrahedral — it may be octahedral through polymerisation. Furthermore the diamagnetism of $[Re(NH_3)_6]\,Cl_3$ must clearly arise from some reason other than a tetrahedral arrangement of the attached ligands. In complexes of the type $[Re(Diarsine)_2Cl_2]\,Cl$, μ values of 1.6 — 1.8 B.M. are observed (47). Here the reduction from 2.83 B.M. is only partial. A temperature-susceptibility study of these complexes is being carried out (47). An interesting five-covalent Re^{III} complex $[ReCl_3, Diarsine]^0$ has been isolated. From the diamagnetism we conclude (see Fig. 9) that it is probably a trigonal bipyramid (47).

The quadrivalent state (d^3). — Mn^{IV} forms a complex fluoride $K_2Mn^{IV}F_6$ (48), the moment of which (3.9 B.M.) indicates the expected 3 unpaired electrons of a spin-free complex. No examples of Mn^{IV} with spin pairing are known. Both Tc and Re as their complex hexa-chlorides e.g. K_2ReCl_6 have moments which vary with temperature (45, 46). Thus, for K_2ReCl_6 μ_{eff} is 2.61 B.M. at 90°K, 3.05 B.M. at 195° K and 3.22 at 300° K. The Ag salt and the complex bromide behave similarly. It is apparent that the moment is approaching 3 spins as T increases. With a view to testing the effect of a change in the electronegativity on the moment Curtis and Nyholm (47) have recently studied complexes of the type $[Re(diarsine)_2Cl_2]$ $[ClO_4]_2$. These are diamagnetic; this can be explained readily by assuming large spin orbit coupling. The complex $K_4[Re_2OCl_{10}]$ is also being studied (47) (*). Like the *iso*-electronic Ru complex (which is diamagnetic) (49) one expects that this will contain one unpaired electron rather than three for the same reason as that which is believed to cause the diamagnetism of K_4RuOCl_{10} (47*b*) (see p. 49).

The pentavalent state (d^2). — Mn^V probably occurs in complex oxides of the type $Na_3Mn^VO_4.10H_2O$. The magnetic data (32) support the view that Mn^V and not a mixture of Mn^{IV} and Mn^{VI} is present. The subject is being vigourously studied at present (49*a*). Tc^V has not been investigated but Re^V is well known in complexes such as $K_2[Re^VOCl_5]$, $[Re^V(NH_3)_6]\,Cl_5$. The latter are diamagnetic

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(*) *Note added in proof :* It has been shown that in fact $K_4Re_2OCl_{10}$ is only very weakly paramagnetic and contains no unpaired electrons (47*a*), whereas μ_{eff} of $K_2[ReCl_5OH]$ is 3.3 B.M. The Orgel-Dunitz (47*b*) explanation is thus not applicable here since it should lead to *one* unpaired electron per Re atom.

(45, 46). Even with strong covalent bond formation the simple Pauling theory predicts 2 spins but in these Re complexes the coupling must be due to the large value of the spin-orbit coupling consequent on the value of $(Z - \sigma)^4$.

The Hexavalent state (d^1). — Where this has been observed in Manganates e.g. $BaMnO_4$ the expected unpaired electron is observed (50). Re^{IV} behaves in the same way (51).

The septavalent state (d^6). — Diamagnetism is expected for the complexes of this valency state but in the case of Mn^{VII} in permanganates weak temperature independent paramagnetism is observed.

The isolation of Re(— 1) (51*a*) as the hydrated potassium salt is of great interest. The weak paramagnetism of this compound corresponds to much less than one unpaired electron; the pure compound is presumably diamagnetic. This is taken to indicate that the Re(— 1) ion is square co-ordinated i.e. $K[Re(H_2O)_4]$. Re(— 1) is *iso*-electronic with Os^O, Ir^I and the well known square forming Pt^{II}.

GROUP VIII

a) Fe, Ru and Os Triad.

Uni-valency. This valence state has been claimed for certain nitrosyl complexes of Fe but real support is lacking. Recently W. Hieber and co-workers (cf. 52) have reported that $Fe^I(CO)_2I$ may be prepared and this on heating gives Fe^I. No data are yet available as to magnetism or stereochemistry. Ru^I is presumed to exist in the corresponding diamagnetic carbonyl Ru(CO)I. This is undoubtedly polymeric and of unknown complexity. The analogous Os compound is unknown.

Bi-valency. Two types of Fe^{II} complex are known (*) — those which contain four unpaired electrons and those which are diamagnetic. Compounds of the first type are either purely electrostatic e.g. $FeCl_2$, or involve " ionic or outer orbital " binding e.g. $[Fe(NH_3)_6]I_2$. Six-covalent octahedral complexes only have been reported so far

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(*) That is, where Fe^{II} is sixcovalent. Nothing is known of four-covalent Fe^{II} except in forced square configurations. The diamagnetic presumably four-covalent iso-nitrile complexes of the type $[Fe(CNR)_4][ClO_4]_2$ have, as yet, been little investigated.

but attemps to make tetrahedral complexes are being pursued. These should have a small orbital contribution owing to a low lying singlet. Diamagnetism is observed in complexes only e.g. $[Fe(Dipyridyl)_3]I_2$. These are invariably octahedral, consistent with the use of two d_γ type 3*d* orbitals for bonding. Ru^{II} and Os^{II} tend to ressemble the diamagnetic type complexes of Fe^{II} e.g. as their complex cyanides of type $K_4M^{II}(CN)_6$. However, in the case of the $[Ru(Dipyridyl)_3]^{++}$ ion Munro (54) reports 4 unpaired electrons; this paramagnetism is difficult to account for.

Ter-valency. Fe^{III} behaves similarly to Fe^{II} in giving both spin-free complexes with 5 unpaired electrons e.g. $[Fe(acetyl\text{-}acetone)_3]^o$ and spin paired complexe e.g. $K_3Fe(CN)_6$ containing 1 unpaired electron. They may be explained in the same way as for Fe^{II}. All known Ru^{III} and Os^{III} complexes are similar to those of "spin-paired" Fe^{III}. It is noteworthy, however, that the orbital contribution is much larger in the Fe^{III} complexes ($\mu_{eff} = 2.3\text{-}2.4$ B.M.) than in the Ru^{III} and Os^{III} complexes ($\mu_{eff} = 1.9$ B.M.).

The quadrivalent state d^4.

Fe^{IV} has been long suspected in complex oxides of the type $BaFe^{IV}O_3$ (52) (*). Recently the complex ion $[Fe(Diarsine)_2Cl_2]^{++}$ has been isolated by Nyholm and Parish (55) as its perchlorate, per-rhenate and ferrichloride. The moment of 2.9 B.M. indicates partial spin pairing of the four 3*d* electrons releasing the two d_γ orbitals for bond formation. The corresponding K_2RuCl_6 behaves similarly with a moment indicating 2 unpaired electrons. Considerable interest attaches to the diamagnetism of :

$$K_4[Cl_5\,Ru — O — Ru\,Cl_5]\ (^{49}).$$

The two linear bonds to the atom indicate *sp* bonds. If the O atom then uses 2*p* electron pairs for π bond formation with the two Ru atoms then each Ru atom must release a d_ε orbital to receive these electron pairs. This forces the four 4 *d* electrons into two only d_ε orbitals giving diamagnetism (47*b*). K_2OsCl_6 however is most unusual having a moment of 1.4 B.M. (49). The most reasonable explanation for the low moment of Os^{IV} is to be found in the work of Kotani (56)

(*) See also Scholder (52*a*).

who examined theoretically the susceptibilities arising from the configurations d_ε^1 to d_ε^6 under the perturbation of spin-orbit coupling. His calculations showed that for the configuration d_ε^4 at temperatures such that $\frac{kT}{\lambda} \sim 0.2$, μ_{eff} is proportional to $\sqrt{T}$.

At higher temperatures $\left(\frac{(kT}{\lambda} \sim 1\right)$ the moment reaches the value of 2.88 and remains constant at about that value. Although the spin-orbit coupling coefficient λ for Os is not known from spectral data, and indeed it is doubtful whether the term can be applied to the inter-electronic interactions in an element as heavy as Os, the effective value of it would be expected to be large — of the order of some thousands of cm^- — with kT at room temperature about 200 cm^{-1} — it is obvious that at these temperatures the condition $\frac{kT}{\lambda} \sim 0.2$ obtains and μ values < 2.88 occur. A recent measurement of $(NH_4)_2OsBr_6$ by Lindberg and Johannesen (57) admirably confirms Kotani's predictions (*). The moment of this compound is proportional to $\sqrt{T}$ from low temperatures up to room temperature. A value of $\lambda = 6{,}000$ was assumed in this work. The fluoride K_2OsF_6 (59) shows a similar moment (1.35 B.M.) at 20 °C.

The pentavalent state (d^3).

Fe^V has not been reported but Ru^V is well known in the simple fluoride RuF_5 and in complex fluorides such as $CsRuF_6$ (59). The moment of the latter (3.85) B.M. indicates 3 unpaired electrons, consistent with the d_ε^3 configuration with parallel spins. As with Cr^{III} this is clearly not diagnostic of bonding orbitals or stereochemistry. Os^V exists in $NaOsF_6$ (59) for which $\mu = 3.05$ B.M. The decrease in the moment from the spin only value of 3.88 B.M. is not easy to understand. On Kotani's theory for a *perfect* octahedron no reduction of moment from the spin only value for a d_ε^3 configuration is expected. Dwyer (60) has recently described complexes of the type $[Os(En-H)_3]I_2$ where En — H represents ethylene diamine *less* one proton from the N atom i.e. $H_2N.CH_2CH_2.NH$. These complexes contain one unpaired electron only and in this case the lower electronegativity of the N atom in the ligand must be assisting the process of spin pairing.

(*) Kotani's theory has also been confirmed for $K_3Mn(CN)_6$ (58).

Higher valency states.

Fe^{VI} is known in the complex ion $[Fe\,O_4]^{=}$. Hrostowski and Scott (61) succeeded in disentangling the ferro- and para-magnetic contributions to the moment and established the presence of two unpaired electrons. Nothing is known of the stereochemical arrangement of the O atoms. Ru^{VI} occurs in the corresponding ruthenates of type $M^{I}_2\,Ru\,O_4$. This contains the expected two unpaired electrons. $K_2\,Os\,O_4$ however once more shows diamagnetism presumably for the same reason as with $K_2\,Os\,Cl_6$ (62).

Fe^{VII} is unknown but perruthenates e.g. $K\,Ru\,O_4$ are undoubtedly tetrahedral and contain the expected unpaired electron. The corresponding Os^{VII} complex is unknown. As is to be expected Ru^{VIII} and Os^{VIII} complexes are diamagnetic, the hypothetical Ru^{VIII+} or Os^{VIII+} ions having lost all *d* electrons.

b) **Cobalt, Rhodium and Iridium.**

Uni-valent state (d^8).

Although the univalent state for these elements is iso-electronic with the well known and readily stabilised bivalent state for Ni, Pd and Pt it is only recently that stable complexes have been described. In the case of cobalt the simplest examples are complexes of the type $[Co(Ph\,NC)_5]\,Cl\,O_4$ using phenylisocyanide (63). In these they are diamagnetic compound the metal atom is five-covalent ; this means that the non-bonding electrons occupy the three dv and one d_γ orbital leaving one d_γ orbital for bonding. On the Pauling theory the binding is apparently dsp^3. No examples of spin-free Co^I compounds are known. Four covalent diamagnetic complexes (64) of Rh^I have been described of the type $[Rh(PhNC)_4]^+$ but the corresponding valence state of Ir is not yet definitely established. Chatt and Venanzi (64a) have also recently described Rh^I compounds. These complexes contain ethylene and are dimeric with halogen bridging.

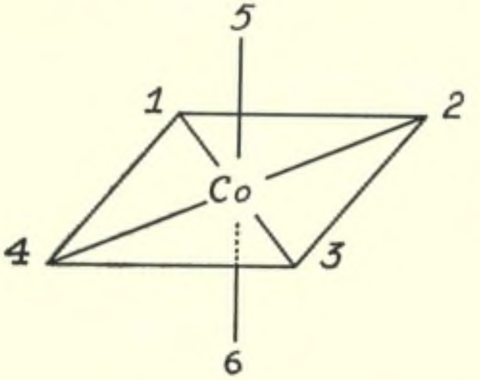
The bivalent state (d^7).

Bivalent cobalt gives rise to complexes of the spin-free and the spin-paired types. In the former category are (a) the ionic *salts* e.g. $Co\,Cl_2$ which form ionic lattices; (b) six-co-ordinated complexes such as $[Co(NH_3)_6]\,Cl_2$ wich are octahedral; (c) four-co-ordinated complexes in which the groups are arranged tetrahedrally around the Co atoms e.g. the $[CoCl_4]^{=}$ ion. The magnetic data indicates

3 unpaired electrons in all cases but moments vary from 4.3 to as high as 5.6. This variation is readily understood in terms of the effect of the different kinds of ligand field on the size of the orbital contribution.

As discussed on page 29 the octahedral arrangement gives rise to a lowest lying triplet and hence a large orbital component whereas the tetrahedral arrangement causes an inversion with a triplet lying lowest. This means that a much smaller orbital contribution can be expected. The situation in regard to ionic salts is complicated partly by the proximity of ions wich can give rise to exchange phenomena, and on occasions, antiferromagnetism, and partly owing to the complexity of the electric field perturbing the ions. Co^{II} complexes in which electron pairing occurs are of two types. The first of these, the four co-ordinated complexes, have a relatively large orbital contribution ($\mu = 2.1 - 2.9$ B.M.) Most of the spin-paired complexes fall into this class. Examples include Co^{II} phthalocyanine. The second class have moments of the order of 1.9 B.M.; these are mainly six-covalent e.g. K_2 Pb $Co(NO_2)_6$ but five-covalency is also observed e.g. K_3 $Co(CN)_5$. The six-covalent complexes are usually formulated as $3d^2\,4s\,4p^3$ complexes with one electron promoted to a $5s$ orbital. However other explanations for the moments of these compounds which does necessitate the promotion of an unpaired electron are available. The formulation of these complexes is a problem similar to that arising for the iso-electronic octahedral

Fig. 13. — Diagram of six-covalent spin paired Co^{II} complex.

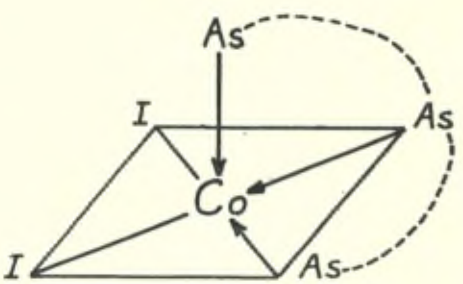


Bonds to 1, 2, 3 and 4 involve $3d4s4p^2$ hybrid orbitals. Bonds to 5 and 6 involve $4p4d$ hybrid orbitals.

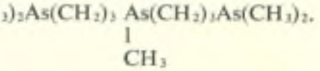
Ni^{III} complexes and for octahedral spin-paired Ni^{II} and Au^{III} complexes which have one more electron. The latter require the promotion of two electrons on the Pauling picture. For all of these complexes a satisfactory ligand-field formalution which reconciles the Pauling and Ligand-field theories is as follows. The seven *d* electrons of the Co^{II} (or eight of the Ni^{II} and Au^{III} complexes) are accommodated in the three d_ε and one d_γ orbital. We then use one d_γ orbital to form (with an *s* and two *p* orbitals) a square complex. Distinct from this combination are then two linear *pd* hybrids completing the octahedron (see also p. 13 *et seq.*).

The five-covalent complexes of Co^{II} are undoubtedly more common than hitherto suspected. Thus (67) the so-called "$[Co(CN)_6]^{4-}$" ion is actually $[Co(CN_5)]^{3-}$. In the solid state $K_3\,Co(CN)_5$ is diamagnetic but in aqueous solution the expected unpaired electron is observed. Although it is possible that the Co^{II} atom is six-covalent in the solid state with one molecule of co-ordinated water i.e. $[Co(CN)_5\,H_2O]^{3-}$ this is not considered likely. Other examples include $[Co\,I_2$, Triarsine] (*) (68). The latter on oxidation gives $[CoI_3$, Triarsine$]^0$ indicating that all three As atoms in the Co^{II} complex are almost certainly co-ordinated to the metal atom; otherwise the arsine would be preferentially oxidised on treatment with I_2. Since $Co\,I_2$, Triarsine behaves as a non-electrolyte in nitrobenzene solution and is monomeric in this solvent we conclude that it is probably to be formulated as shown in Figure 14.

Fig. 14.



(*) Triarsine has the formula


$(CH_3)_2As(CH_2)_3\underset{\overset{|}{CH_3}}{As}(CH_2)_3As(CH_3)_2$.

Another five-covalent Co^{II} complex is the cobalto-nitrite ion "$[Co(NO_2)_6]^{4-}$" in aqueous solution. Dwyer finds that this loses one NO_2^- group and becomes, unless an H_2O molecule enters, effectively five-covalent.

The bivalent state for Rh and Ir has been reported as existing in certain compounds where the analyses gave correct empirical formula e.g. $[Rh\,Cl_2, 3\,As\,R_3]_2$. However the diamagnetism of these makes this difficult to understand and it is now most likely (66) that these compounds should be formulated as complexes of Rh^I and Rh^{III} e.g. $[Rh^I(R_3\,As)_4][Rh^{III}\,Cl_4(AsR_3)_2]$

The tervalent state (d^6).

Co^{III} forms two types of complexes, the rare spin-free type exemplified by $K_3\,Co\,F_6$ with 4 unpaired electrons. One $3d$ orbital is doubly filled and four singly. The far more common octahedral diamagnetic complexes are readily explained on both the Pauling and ligand-field theories. Jensen (69) has reported a complex $Co\,Cl_3$, $2Et_3\,P$ which is found to contain two unpaired electrons. If, as seems likely, this five-covalent one can make an attempt at predicting the stereochemistry. The Pauling theory would suggest that only one $3d$ orbital is available for bond formation. If the combination $3d\,4s\,4p^3$ is used then on the Daudel and Bucher (70) argument (*) a square pyramid is probable. On the ligand-field theory again the square pyramid appears to be favoured. Both Rh^{III} and Ir^{III} are very similar to the spin-paired complexes of Co^{III} being invariably diamagnetic and octahedrally co-ordinated wherever structures have been determined.

The quadrivalent state (d^5).

As is to be expected this valency state increases in stability as we pass from Co → Rh → Ir. In all cases the known complexes are six-covalent and contain one unpaired electron the only doubtful case being $K_3\,Co\,F_7$ (43, cf. 52) the crystal structure of which has not been established.

(*) This theory proposes that $(n-1)d$ ns np^3 bonding orbitals gives rise to a *square pyramid* whereas ns np^3 nd bonding orbitals result in a trigonal bipyramidal arrangement.

The pentavalent state (d^4).

This occurs in Ir complexes of the type Na Ir F_6, Ag Ir F_6, K Ir F_6 the moments of which are of the order of 1.2-1.3 B.M. (^{59}). Assuming that the anion is octahedrally co-ordinated these compounds should, on the simple Pauling theory contain two unpaired electrons with a μ of at least 2.8 - 2.9 B.M. A similar prediction is made on the ligand-field theory. It is apparent that the same explanation holds as for Os^{IV}.

The hexavalent state (d_3).

Only one compound of this valency state has been established with certainly — the fluoride Ir F_6. This is almost certainly octahedral and once again both the Pauling and Ligand Field theory predict 3 unpaired electrons. The observed moment of 3.35 B.M. (^{71}) indicates that the departure from the spin-only value is small.

Zerovalency. It is of interest to note that G.W. Watt *et alii* (^{72}) have recently reported a zerovalent iridium complex of the formula $Ir(NH_3)_5$. Nothing is known of its stereochemistry. Similarly the Co^0 complex $K_4Co(CN)_4$ has recently been described by W. Hieber and C. Bartenstein (^{73}). From its diamagnetism we may safely conclude that the anion is probably dimeric, making it iso-electronic with the carbonyl $Co_2(CO)_8$.

GROUP VIIIC — Ni,Pd,Pt d^{10}

The zerovalent state d^{10}.

Reference is made to this valency for these elements because of the wide variety of ligands with which it may be stabilised, at least for Ni. The carbonyl of nickel $Ni(CO)_4$, which is diamagnetic, is tetrahedral. On the Pauling model this can be regarded as due to the use of $4s\,4p^3$ bonding orbitals. The CO may be replaced by PF_3, PCl_3, PBr_3 and isocyanides. These are all diamagnetic and presumably tetrahedral also. Of great interest is the complex cyanide $K_4Ni(CN)_4$ in which the Ni atom apparently has the same structure as in the carbonyl. The corresponding complex of Pd, $K_4Pd(CN)_4$ is known but not the platinum analogue. Other four-covalent Pd (^{0}) complexes have been described by Malatesta (^{74}), e.g. $Pd(CNPh)_4$. The presumably polymeric complex $Pd(CNPh)_2$ has also been described (^{74a}). A tetrammino Pt(^{0}) complex has also been claimed by G.W. Watt *et alii* (^{72}).

The univalent state d^9.

The best example of this is the complex cyanide of nickel of empirical formula $K_2Ni(CN)_3$. Since this is diamagnetic it is presumably dimeric. Nast and Pfab (75) have claimed that the Ni atoms are square co-ordinated there being two bridging and four terminal CN groups in the dimeric $[Ni_2(CN)_6]^{4-}$ anion. However infra-red spectral investigations (75^a). reveal only one C—N absorption band(*); this throws some doubt on the structural assignment by Nast and Pfab. Univalency has been suggested for one organo-palladium complex but no magnetic data are available (75^b). Univalency has not yet been definitely established in any platinum complex.

The bivalent state d^8.

This is the most stable valency for these elements. In the case of Ni four and six covalency are common and five-covalent complexes which have frequently been postulated as kinetic intermediates, has recently been fairly well substantiated, by other physical methods of investigation. The four-covalent complexes fall into two classes — the paramagnetic group containing two unpaired electrons and those which are diamagnetic. Wherever X-ray structural data or electric dipole moments are available the latter have been shown to be square planar. The diamagnetism indicates that one d_γ orbital is *not* used by non-bonding electrons and this orbital, together with a 4*s* and two 4*p* orbitals gives rise to the Pauling picture of four $3d\,4s\,4p^2$ bonds. The stereochemistry of the less common paramagnetic four-covalent complexes, however, is much less certain. Difficulty arises because most of the compounds in which the Ni^{II} atom is supposed to be four-covalent involve polymerisation in the solid state to make the Ni atom effectively octahedral. Nevertheless the green complex nitrate $[Ni(NO_3)_2, 2Et_3P]^o$ is definitely monomeric in benzene. Its magnetic moment indicates two unpaired electrons but the absence of a large orbital contribution is a little surprising. Reference to Figure 12 indicates that for a tetrahedral arrangement of the charges around a Ni^{II} atom the triplet lies lowest and hence a large orbital contribution is to be expected. However the surrounding groups are not all the same in this complex and the

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(*) Hence presumably only one C—N stretching frequency.

perturbing effects of the asymmetric field may give rise to further splitting of the triplet. The electric dipole moment (8.8 D) (76) indicates either a tetrahedral or a *cis*-planar arrangement. It is most important for us to obtain X-ray crystal structure determinations of compounds of this type. Since no $3d$ orbitals are available for bond formation it has been widely assumed that in the paramagnetic complexes the next four bonding orbitals $4s\,4p^3$ are used to give a tetrahedral complex. However, it is important to remember that the more electronegative ligands give rise to these paramagnetic complexes and, as with Cu^{II}, the square arrangement is just as feasible.

The six-covalent complexes are of two types, paramagnetic with 2 unpaired electrons e.g. $[Ni\,En_3]^{++}$ and $[Ni(Dipyridyl)_3]^{++}$ on the one hand and diamagnetic e.g. $[Ni(Diarsine)_3]^{++}$ on the other. The complex ion $[Ni(Dipyridyl)_3]^{++}$ has been resolved, thus confirming an octahedral (but not necessarily a *perfect* octahedral) arrangement of the ligands, and also showing that the complex is fairly " stable " in the kinetic sense of not reacting rapidly to give the racemate. In this *tris*-dipyridyl complex the binding is regarded by some as involving the use of $4s\,4p^3\,4d^2$ bonds on the Pauling model but strictly speaking the magnetic data really only tell one that no $3d$ orbitals are available for bond formation. Nevertheless this complex ion must be regarded as an example of covalent binding using " outer " orbitals. The diamagnetic six-covalent complexes however have, on the ligand-field theory treatment, only one d_γ orbital available for bond formation. As discussed on page 13 the six-covalency and diamagnetism are comparable provided that two co-axial bonds are assumed to be longer than the other four co-planar bonds. Five-covalent diamagnetic complexes are undoubtely much more common than hitherto supposed. The red colour produced by adding excess CN^- ion to the $Ni(CN)_4^{=}$ complex ion has been shown to involve a 1 : 1 combination and hence the formation of the $[Ni(CN)_5]^{3-}$ ion is indicated (77). It has also been shown that the $[Ni(Diarsine)_2]^{++}$ ion readily attaches another halogen atom to give the complex ion $[Ni(Diarsine)_2X]^+$ where $X = Cl$, Br and I (78). Similarly the physical and chemical properties of $[Ni\,Br_2$, Triarsine$]$ (68) (cf. the Co^{II} complex on page 53) indicate that the Ni^{II} atom is five-covalent. On the basis of the Pauling theory the use of the extra $4p$ orbital suggests a square pyramid.

The Daudel and Bucher (70) argument also leads to a square pyramid rather than a trigonal bipyramid.

Bivalent Pd and Pt form square complexes with great facility. No paramagnetic complexes of Pd^{II} or Pt^{II} are known. Five-covalency in complexes of the type $[Pd(Diarsine)_2X]\ Cl\ O_1$ (15) where $X = Cl$, Br and I is observed in the same way as with Ni^{II}. All known bivalent six-covalent complexes of these two elements are diamagnetic. Best known example is $[Pt(NH_3)_4(CH_3\ CN)_2]\ Cl_2$ (33). This is undoubtedly to be formulated in the same way as the $[Ni(Diarsine)_3]^{++}$ ion. The most significant feature about all of these five- and six-covalent diamagnetic complexes of Ni^{II}, Pd^{II} and Pt^{II} is the fact that in all cases they are formed with ligands which have a marked capacity for double bond formation using *d* electron pairs of the metal atom. In this way the otherwise improbably high negative change placed on the metal atom owing to the formation of so many dative σ bonds can be avoided.

It has recently been shown (78a) by X-ray methods that Pd(Diarsine) I_2 is octahedral in the *solid* state the two I atoms being *trans*. The length of the two Pd — I bonds is 3.52 Å. The calculated Pd — I bond distance in square Pd^{II} complexes is only 2.65 Å. This great increase in the bond length is attributed to the repulsion of the I atoms by the filled $d_z{}^2$ orbital. Work on $[Pd(Diarsine)_2\ I]\ Cl\ O_4$ is still proceeding.

The tervalent state (d^7).

Only in the case of Ni are complexes of this valency state known. $Pd\ F_3$ has been described and has paramagnetism indicating one unpaired electron (34) but no other Pd^{III} compounds are known. Ni^{III} occurs in the unusual five-covalent complex $Ni\ Br_3, 2\ Et_3P$ which contains one unpaired electron (79). The use of $3d\,4s\,4p^3$ bonds suggests a square pyramidal structure; this is supported by the small electric dipole moment but, in the absence of X-ray studies and in view of uncertainties as to atom polarisation its structure is still not absolutely certain. Six-covalency occurs in complexes such as $[Ni(Diarsine)_2Cl_2]^+$ which contain one unpaired electron (79). They are iso-electronic with spin paired octahedral Co^{II} complexes the structure of which are discussed on page 51.

The quadrivalent state (d^6).

With a few exceptions all complexes of Ni^{IV}, Pd^{IV} and Pt^{IV} are six-covalent and diamagnetic involving the two d_γ orbitals with s and three p orbitals for bond formation (80). Less is known of the complex oxides such as $Ba\,Ni\,O_3$ (81).

Higher valency states.

Pt^{VI} probably exists in complex oxides of the type $M^I_2Pt\,O_4$ but they have been but little studied.

GROUP IB, Cu, Ag, Au ($d^{10}s^1$)

The univalent state (d^{10}).

All three elements give rise to univalent complexes which are either two-covalent or four-covalent *. Although four is the preferred co-ordination number of Cu^I and Ag^I it is two for Au^I. However four-covalent Au^I complexes are now quite well established. On the Pauling picture the linear two covalent complexes can be regarded as arising from sp hydrid bonds and the tetrahedral four-covalent complexes from sp^3 hybrids. However it is interesting to point out that since there are no lone pairs in the valency shell ordinary electrostatic bond pair-bond pair repulsion would also lead to the linear and tetrahedral arrangements.

The bivalent state (d^9).

This is found only in the case of Cu and Ag. The Cu^{II} complexes are almost invariably four square planar bonds, e.g. as in the $[Cu(NH_3)_4]^{++}$ ion, but there is a strong tendency for two longer bonds to be formed to complete the distorted octahedron. These square complexes clearly do not involve electron promotion since they are resistant to oxidation. Furthermore use of a $3d$ orbital is not indicated on grounds of electronegativity of the ligand. The ligands which give rise to square Cu^{II} are of high electronegativity — the converse of what is required to give diamagnetic square Ni^{II}. Earlier, therefore it was suggested (23) that the binding involved $4s\,4p^2 4d$ orbitals — the use of an " outer " d orbital being indicated by the high electronegativity of the ligands. However, an alternative ligand field explanation which takes into account the Jahn-Teller theorem is discussed by Orgel. (13)

(*) Chatt (86) and Coates (87) have also adduced evidence in support of a co-ordination number of three for Silver (I).

Five-covalent Cu^{II} complexes have also been described e.g $[Cu(Dipyridyl)_2I] Cl O_4$. The very large orbital contribution found in these complexes ($\mu_{eff} = 2.8$ B.M.) is most readily explained by the postulate that the complexes are trigonal bipyramidal in shape (78). Bivalent silver, although rather less stable than bivalent copper gives rise to similar complexes.

The tervalent state (d^8).

Cu^{III} gives rise to both spin-free and spin-paired complexes. A good example of the former is $K_3Cu F_6$ (82 cf. 43) which contains the expected two unpaired electrons. $K Cu O_2$ however is diamagnetic (83) and since the Cu^{III} atom is iso-electronic with Ni^{II} the complexes are presumably square. Ag^{III} is best established in the diamagnetic complex fluoride $KAgF_4$ (85). It is interesting to notice the transition from paramagnetic K_3CuF_6 to diamagnetic $KAgF_4$ and $KAuF_4$. This is undoubtedly due to the greater electronegativity of Ag^{III} over Cu^{III}. The first ionisation potentials for Cu and Ag are respectively 7.72 and 7.57 volts whereas the *sum* of the first three ionisation potentials are 57.6 and 64.9 volts respectively. Au^{III} has a marked preference for forming four-covalent square co-ordinated complexes which are diamagnetic. Evidence has been available for some years to show that in solution at least the co-ordination number of gold may be increased beyond four. Thus Bjerrum (84) showed that the $Au(SCN)_6{}^{3-}$ ion existed in solution as long ago as 1918. More recently (14) complexes of the types $[Au(Diarsine)_2X]^{++}$ and $[Au(Diarsine)_2X_2]^+$ where X = Cl, Br and I have been isolated. Conductrimetric titration of $[Au(Diarsine)_2I]$ $[Cl O_4]_2$ with I^- ions in nitrobenzene solution results in a sharp end point after one equivalent of I^- ions have been added. These six-covalent complexes can be made to revert to square complexes again by suitable treatment — particularly in aqueous solution. In this solvent the hydration energy of more than sufficient to effect rupture of the Au-halogen bond. If we assume that two of the bonds are different from the other four these Au^{III} six-covalent complexes may be formulated in a manner similar to the six-covalent diamagnetic Ni^{II} and Pt^{II} complexes described earlier. To sum up, octahedral coordination requiring the use of four square planar bonds and two longer bonds normal to the plane offers a satisfactory explanation of the six-covalent complexes of Co^{II}, Ni^{II}, Pd^{II} and Pt^{II}, and of Au^{III}.

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Some Applications of Crystal-field Theory to Problems in Transition-Metal Chemistry.

by **L. E. ORGEL**

INTRODUCTION

Since the publication of Pauling's classic papers on the nature of the chemical bond(1) it has been customary to discuss the electronic structure of transition-metal compounds from the point of view of valence-bond theory. It was realized a long time ago that molecular-orbital and electrostatic theories could account equally well for many of the experimental observations (2), but these theories did not at first appeal to inorganic chemists. More recently it has become clear that the latter theories, which are almost equivalent in their mathematical formalism, are able to account quantitatively for the spectra and magnetic properties of divalent and trivalent transition-metal ions (3, 4, 5, 6). In Chapter I of this paper we shall extend a previous treatment of the stabilities of transition-metal compounds and show how they too depend on the crystal-field splitting. In Chapter II we shall discuss a number of more theoretical points concerned with the proper interpretation of the theory including, in particular, the effect of double-bonding. In Chapter III we shall make a number of applications of the conclusions of Chapter II. We shall use the language of the conventional electrostatic theory in Chapter I, although an alternative nomenclature will be suggested tentatively in Chapter II.

Very little introductory material has been included in this contribution. The reader is referred to the paper by Prof. R.S. Nyholm for an introduction to the theory.

CHAPTER I

The present Congress provides an occasion to put forward and try to justify the following, perhaps over-ambitious, claim :

The failure of the chemical properties of divalent and trivalent transition-metal ions of the first series to vary smoothly and systematically with the atomic number of the metal may be explained in terms of a single factor, namely, the dependence of the stabilization energy and *d* electron configuration of an ion in a field of given symmetry on the magnitude of the field and the number of *d*-electrons present.

If we wish to extend our discussion to the oxidation-reduction reactions of transition-metal complexes it is necessary to take account also of the third ionisation potentials of the free metal atoms.

HEATS OF HYDRATION

In a previous paper we have shown that while the heats of hydration of transition-metal ions vary rather erratically with the atomic number of the metal, the values obtained by subtracting the stabilization energies due to crystal-field effects from the observed heats of hydration rise steadily from the titanous ion to the divalent zinc ion ([7]). In Figs 1 and 2 we have plotted the measured and corrected heats of hydration of the divalent and trivalent transition-metal ions calculated by McClure from accurate data which has recently become available ([8]). The way in which the corrected values lie on smooth curves leaves no doubt that the coordinating power of the ions increases steadily with the atomic number once the discontinuous effects of crystal-field splitting have been eliminated. In this chapter we shall deal with two main topics, the theoretical basis for the observed correlation and its significance with regard to the stability of transition-metal complexes other than the hydrates.

Many authors have noted that the equilibrium constants for complex formation of a given ligand with the series of divalent transition-metal ions increase steadily from manganese to copper and then fall to zinc. The generality of this behaviour was emphasized by Irving and Williams, who also noted that the hydration energy varied in the same way ([9]). They pointed out that the sum of the first and second ionisation potentials of the metals, a quantity which they took to represent the electron affinity or electronegativity of the metal ion, also rises to a maximum at copper and then falls to zinc. From this they concluded that the stability of transition-metal complexes of a given ligand is in large measure determined by the ionisation energy of the metal. Similar conclusions were reached simultaneously by a number of other workers (10, 11).

We believe that this simple correlation is somewhat misleading. The electron affinity of the transition-metal ions which is relevant to their heats of hydration is the one which corresponds to the filling

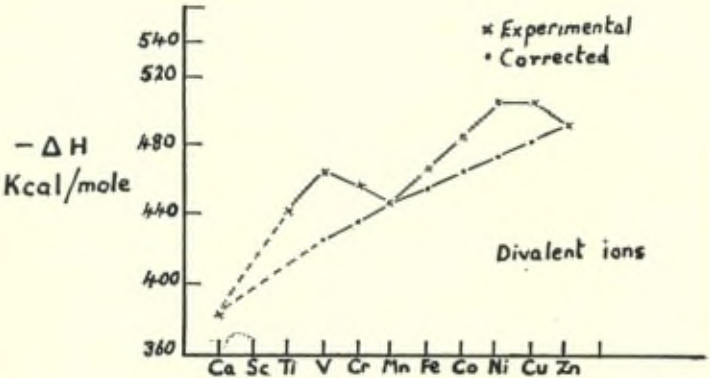

Fig. 1. — Experimental and corrected heats of hydration of divalent ions (8).

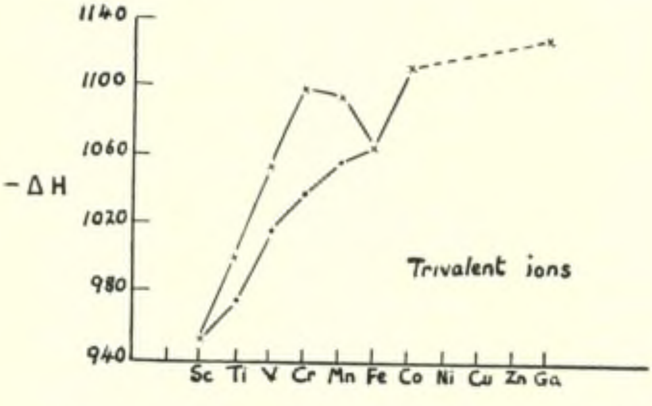

Fig. 2. — Experimental and corrected heats of hydration of trivalent ions (8).

of the 4s and 4p orbitals. It is true that the vacant 3d orbitals of e_g symmetry are also involved, but there is good reason to believe that they are less important as acceptors than the 4s and 4p orbitals ([12]). It follows that all electron affinities should be referred to some standard configuration, by far the most convenient of which is the $(3d)^n\,(4s)^2$ configuration, i.e. all electron affinities should be for the reaction

$$M^{++}\,(3d)^n + 2\varepsilon \longrightarrow M\,(3d)^n\,(4s)^2 \qquad (1)$$

where the ground state of the configuration is referred to on each side of (1). Electron affinities calculated in this way differ from the sums of the ionisation potentials for Cr^{++} and Cu^{++} since the chromium and copper atoms have $(3d)^4\,(4s)$ and $(3d)^9\,(4s)$ ground states, respectively ([13]). When the appropriate corrections of 7750 cm^{-1} for chromium and of 11200 cm^{-1} for copper are made, the electron affinities are found to rise steadily from the titanous ion to the divalent zinc ion. This indicates that it is the corrected heats of hydration and, as we shall show, the corrected heats of complex formation which should be correlated with the electron affinities of the metal ions.

The following additional argument supports the use of the electron affinity defined above, rather than the sum of the ionisation potentials, in correlating heats of complex formation with the electronic properties of the metal ion. Chromium and copper have d^5s and $d^{10}s$ rather than d^4s^2 and $d^9\,s^2$ ground states and hence larger ionization potentials because of the special stability of half-filled and filled electron shells (cf. the rare-earth ions). Now in the chromous, chromic and cupric ions the total number of d-electrons present does not permit the formation of these stable shells. It would therefore be unreasonable to attribute an extra stabilisation energy to the ionic complexes which corresponds to a feature of the electronic structure which can only be important in the free atoms. It might be argued that the special stability of the d^5 and d^{10} configurations is sufficient to lead to an increased donor-acceptor interaction of the type which leads to the capture of an electron from the ligands by the metal d orbitals. However, in divalent complexes, the bonding effect of the d orbitals, while by no means insignificant, is smaller than that of 4s and 4p orbitals ([12]). The excess stability, e.g. of cupric complexes over the corresponding nickel or zinc complexes is too large, in the author's opinion, to be accounted for by the greater electron affinity of the cupric ion for a 3*d* electron.

The use of the total electron affinity for the capture of two electrons (or three for the trivalent ions) rather than the simple first electron affinity is preferable for the following reasons :

a) The first electron affinities of divalent transition-metal ions often correspond to the processes

$$(3d)^n + \varepsilon \longrightarrow (3d)^{n+1} \tag{2}$$

rather than to the more relevant processes

$$(3d)^n + \varepsilon \longrightarrow (3d)^n\,(4s) \tag{3}$$

It would be possible to correct all values so that they refer to reaction (3) but even then an average would have to be taken over two electron affinities, those corresponding to the processes

$$^{n}X + \varepsilon \longrightarrow {}^{n+1}X \tag{4}$$

and

$$^{n}X + \varepsilon \longrightarrow {}^{n-1}X \tag{5}$$

where ^{n}X denotes the ground state of the ion, e.g. ^3F for Ni^{++}. This averaging is necessitated by the fact that in the complex the electrons shared between the ligand orbitals and the metal 4*s* orbitals are, apart from second-order effects, equally likely to have their spins in the same or the opposite directions to that of the resultant spin of the metal ion *d* electron core. For configurations $(3d)^n\,(4s)^2$ there is obviously no need to perform such an averaging.

b) The equivalent state of ionisation of a metal ion in a complex does not correspond to the formal valency. According to Pauling, the net charge on any ion is approximately zero ([14]). It is not easy to give a precise meaning to the net charge, and so to test this hypothesis, but it is clear that the metal ions are not in electronic states at all closely related to their free states since the 4*s* and 4*p* orbitals are partially occupied by ligand electrons. While the matter cannot be settled definitely at present it seems probable that for divalent ions the electron affinities for process (1) are nearer to the correct ones than those for capture of a single electron.

In order to understand the significance of the correlation between the corrected heat of hydration and the electron affinity of the metal ion we have to consider the behaviour of the $3d$ orbitals in the field of the octahedron of water molecules. It has often been shown that in such an environment the degeneracy of the five d orbitals is partially removed so that there results a stable triply degenerate t_{2g} orbital and a less stable doubly degenerate e_g orbital ([15]). The energy separation between these orbitals is defined to be 10 D_q. In the case of divalent and trivalent ions it is about 30 and 60 k cals, respectively. We shall return to the theoretical basis for this separation later; for the moment we are concerned with the sequence in which the orbitals are occupied.

In the series of divalent ions from titanium to zinc the configurations of the metal ion electrons are as shown in Table I. These configurations are exact except for Ti^{++} and Co^{++}, for each of which there is a small admixture of other configurations obtained by promoting one or more electrons from the t_{2g} to the e_g orbitals.

TABLE I.

The mode of occupation of the *d* orbitals in complexes with maximum spin multiplicity.

	t_{2g}	e_g
Ti^{++} (V^{+++})	↑↑	
V^{++} (Cr^{+++})	↑↑↑	
Cr^{++} (Mn^{+++})	↑↑↑	↑
Mn^{++} (Fe^{+++})	↑↑↑	↑↑
Fe^{++} (Co^{+++})	↑↓↑↑	↑↑
Co^{++}	↑↓↑↓↑	↑↑
Ni^{++}	↑↓↑↓↑↓	↑↑
Cu^{++}	↑↓↑↓↑↓	↑↓↑
Zn^{++}	↑↓↑↓↑↓	↑↓↑↓

If we consider that part of the electronic energy which is specifically connected with the mode of filling of the *d* orbitals it is clear that increasing the number of the electrons in t_{2g} orbitals favours the stability of the hydrates while increasing the number of electrons in the e_g orbitals leads to relative instability. We should, therefore, expect the stability to increase more or less steadily from Ca^{++} to V^{++} as electrons go into the t_{2g} orbital and then to decrease to Mn^{++} as the e_g orbital becomes occupied. At this point the stability should increase again until the t_{2g} orbital is filled at Ni^{++} and finally fall again until the e_g orbital is filled at Zn^{++}. It will be noted that these predictions are in error for the case of Cu^{++}, but we shall show that this is due to the non-octahedral nature of the hydrated cupric ion, which itself is readily explained by the theory.

In order to eliminate the disturbing effects which these discontinuities in the *d* electron energy have on the hydration energy we have first to define a *d* electron energy which is an average over the energies of all the states obtained by orienting the ground state of the free ion in different ways with respect to the octahedron of ligands. This mean energy can be determined empirically, once some or all of the states into which the ground state of the free ion is split have been identified in the electronic spectrum of the hydrate. The difference between it and the energy of the ground state of the hydrated ion is the crystal-field stabilization energy and must be subtracted from the observed hydration energy to obtain the corrected value. The corrected values in Figs 1 and 2 were obtained in this way (8). Slight differences between the corrections applied in this work and those given in reference (7) are due to the use of more accurate spectroscopic data which have recently become available.

We shall show for the simplest possible case, that of a single *d* electron in an octahedral field, how the averaging is carried out. There are only two different states which can be obtained, a triply degenerate T_{2g} state in which the electron is in the t_{2g} orbital and a less stable E_g state in which an e_g orbital is occupied. In the case e.g. of $[Ti(H_2O)_6]^{+++}$ there is a single absorption band with its maximum at $20400\ cm^{-1}$, showing that this is the t_{2g}—e_g separation. The mean energy for the five possible orientations of the *d* electron measured relative to the ground state of the ion is clearly

$$\frac{3 \times 0 + 2 \times 20{,}400}{5} = 8160 \text{ cm}^{-1}$$

and so this is the correction to the hydration energy of the Ti^{+++} ion. For other cases the averaging process is more complicated, but the method is the same.

The corrected heats of hydration are thus the heats of hydration which would be obtained if the free ions were not allowed to adjust to the field of the ligands. The fact that they increase steadily from Ti^{++} to Zn^{++} shows that the increase in stability due to the increasing electron affinity of the metal orbitals outweighs any decrease in stability due to the fact that each electron is treated as though it spent 40 % of the time in the e_g orbitals, which we shall show to be antibonding.

Many cupric compounds have been studied by means of x-ray crystallography, and it seems to be a general rule that the metal ion is surrounded by four nearest neighbours in a plane and two more distant neighbours which complete a distorted octahedron. The reason for this is probably the instability of degenerate electronic states of non-linear molecules first noted by Jahn and Teller ([16]). They showed that if the electronic state of a non-linear molecule is degenerate then there is always at least one vibrational coordinate along which the molecule may distort so as to lower its energy, i.e. they showed that a non-linear molecule will always distort if its ground state is degenerate. Jahn and Teller also pointed out that the extent of the distortion is proportional to the bonding or antibonding power of the degenerate electrons.

Van Vleck has studied the Jahn-Teller effect in Ti^{+++}, and V^{+++}, which have degenerate ground states and has found it to be small ([17]). This does not invalidate the suggestion that it is large in the hydrated cupric ion for in the cases studied by Van Vleck the degeneracy is due to t_{2g} electrons, while in our case it is due to an e_g electron. We shall show that in molecular-orbital theory the former orbitals are non-bonding while the latter are strongly antibonding. The only other case in which a strongly antibonding orbital is responsible for degeneracy in octahedral coordination is that of the chromous ion. We think it likely that chromous complexes will be found to show marked deviations from regular octahedral coordination. It seems relevant to this discussion that only the chromous ion of the divalent ions has been reported to form a dimeric diamagnetic acetate isomorphous with the cupric compound.

The physical basis of the Jahn-Teller stabilisation was explained in the following way (7). The e_g orbitals are the $d_{x^2-y^2}$ and d_{z^2} orbitals, the former pointing towards the ligands in the xy plane and the latter towards those along the z axis. If the four ligands in the xy plane move towards the metal ion and those along the z axis simultaneously move away then both in crystal-field theory and in molecular orbital theory the d_{z^2} orbital is stabilized and the $d_{x^2-y^2}$ orbital is destabilized to an approximately equal extent. The complex can thus achieve extra stability by leaving a gap in the $d_{x^2-y^2}$ orbital and filling up the d_{z^2} orbital as shown in Fig. 3. The distortion proceeds until the extra stability gained in this way is just balanced by the energy it requires to stretch and compress the bonds.

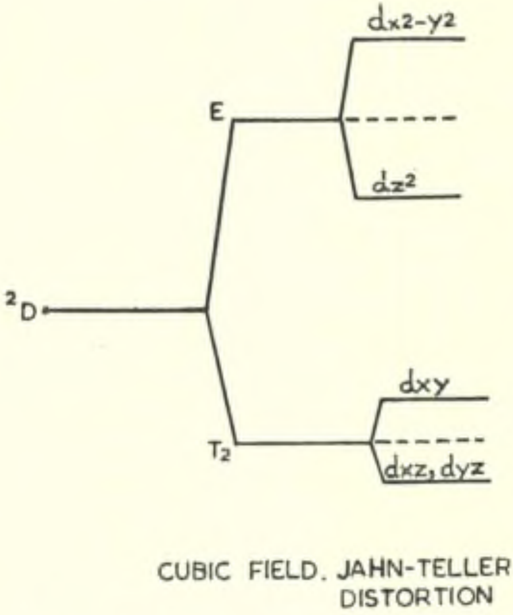

Fig. 3. — Orbital energy level scheme for octahedral and distorted octahedral cupric ions.

In the absence of a Jahn-Teller splitting the heat of hydration of the cupric ion would be almost half-way between those of the nickel and zinc ions. In fact it exceeds this value by about 8 k cals which we deduce is roughly equal to the Jahn-Teller stabilisation of the ion.

By an extension of the previous argument the formation of planar cupric compounds is readily seen to be due to the extra stabilization energy produced by the Jahn-Teller distortion increasing steadily until the fifth and sixth ligands are completely removed. It is possible, though probably not profitable, to regard the planar diamagnetic complexes of nickel as derived by a Jahn-Teller splitting of an excited state which causes it to cross the normal triplet ground state, since the latter is not stabilized at all by the Jahn-Teller distortion.

It should be noted that this explanation of the planarity or near planarity of cupric complexes is quite different from that given by Pauling, who described the metal configuration as $(3d)^8\,(4p)$. It seems to us that the resistance to further oxidation which is characteristic of the cupric ion is evidence against Pauling's suggestion ([14]).

THE STABILITY OF COMPLEXES IN SOLUTION

The experimental data on the complexes formed by ligands other than water are very incomplete. We shall therefore try to deduce how such systems should behave and compare our conclusions in detail with such experimental evidence as is available. Our general line of argument is that water is in no way exceptional as a ligand and so that we may generalise from the conclusions of the previous section. In particular it seems reasonable to assume.

1° That after correction for the crystal-field splitting the heats of formation of complexes of the type $[M^{++}X_6]$ increase smoothly from Ti^{++} to Zn^{++}, provided that no complicating factors such as changes in the nature of the ground state are encountered. We may expect this generalisation to work best for ligands like water, e.g. alcohols, amines, etc., which do not form strong π-bonds.

2° That the true heats of formation differ from those discussed in (1) due to crystal-field splittings the magnitude of which may be estimated from the observed spectra.

3° That the cupric complexes and possibly the chromous complexes will be unusually stable owing to large Jahn-Teller splittings of the ground state. We expect there to be a good deal of variation in the behaviour of these complexes since the Jahn-Teller effect depends rather critically on the variation of the electronic energy of the non-degenerate electrons with the distortion of the complex from a regular octahedron, and this must be determined by the nature of the ligand.

In practice very few heats of complex formation have been measured but many sets of values for formation constants in aqueous solution are available. In order to get any check on our theory we have therefore to make the further assumption that :

4° The variations in equilibrium constants K_i for the complexing of a given ligand with a sequence of metal ions reflect corresponding changes in the heats of reaction. A similar assumption is implicit in the earlier correlations of stability with electronic structure, for example those of Irving and Williams (9). Also, since it is only in exceptional cases that K_1, K_2, ... K_6 are all known, we shall assume that the deductions which we make about the relative stabilities of $[M^{++}X_6]$ ions apply equally to ions $[M^{++}(H_2O)_nX_{6-n}]$.

Our general hypothesis leads to the conclusion that, in the absence of crystal-field splittings, the heat of formation of complexes of a given ligand with different divalent metal ions should increase steadily from Ti^{++} to Zn^{++}. In view of the smooth increase in the corrected heat of hydration shown in Fig. 1 the corrected heat ΔH_{corr} of the solution reaction

$$[M^{++}(H_2O)_n] + X \longrightarrow [M^{++}(H_2O)_5X] + H_2O$$

should also increase (or possibly decrease) steadily with the atomic number of the metal, as shown in Figs 4*a* and 4*b*.

The crystal-field splitting will in general have different values for complexes from those for the hydrates. It follows that we may write the true heat of reaction ΔH in the form

$$\Delta H = \Delta H_{corr} + \Delta H_{cryst} \qquad (6)$$

where ΔH_{cryst} is the difference between the crystal-field stabilization of the complex and that of the hydrate.

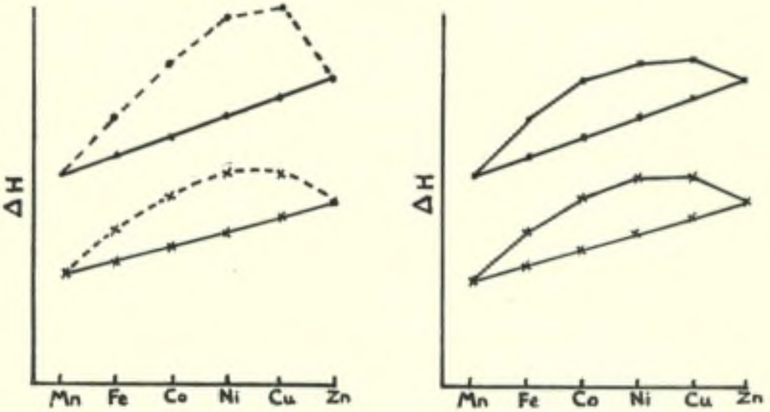

Fig. 4. — Heats of hydration and complex formation (*a*) for ligands with large crystal-field stabilizations, (*b*) for ligands with small crystal-field stabilizations. — x...x heat of hydration, ×—×—× corrected heat of hydration, ----- heat of complex formation, ———— corrected heat of complex formation.

ΔH_{cryst} vanishes for Mn^{++} and Zn^{++} so that in these cases ΔH may be equated to ΔH_{corr}. This enables us to estimate ΔH_{corr} for other ions by an interpolation method. The most suitable procedure would be to draw a curve through the values for Mn^{++} and Zn^{++} as nearly parallel to the curve for hydration energy as possible. However, in order to avoid any arbitrary procedure of this sort we have used linear interpolation throughout. We write

$$\Delta H_{corr}^{n} = \Delta H_{corr}^{Mn^{++}} + (n - 5)\,\frac{\Delta H_{corr}^{Zn^{++}} - \Delta H_{corr}^{Mn^{++}}}{5} \qquad (7)$$

where n is the number of d electrons and can vary from 0 — 10. This may be rewritten in the form

$$\Delta H_{corr}^{n} = \Delta H_{corr}^{Mn^{++}} + (n - 5)\,p \qquad (8)$$

where p is a quantity which characterizes a ligand.

Turning now to the second term in (6) we note that D_q for a given ligand does not vary much for the sequence of ions Fe^{++}, Co^{++}, Ni^{++}. Since crystal-field theory leads to stabilizations of

$4D_q$, $8D_q$ and $12D_q$ for six, seven and eight *d* electrons respectively we expect

$$\left.\begin{aligned}\Delta H_{\text{cryst}} &= 4\,(D_q{}^{L} - D_q{}^{o}) \qquad \text{Fe}^{++}\\ &= 8\,(D_q{}^{L} - D_q{}^{o}) \qquad \text{Co}^{++}\\ &= 12\,(D_q{}^{L} - D_q{}^{o}) \qquad \text{Ni}^{++}\end{aligned}\right\} \tag{9a}$$

where $D_q{}^{L}$ and $D_q{}^{o}$ are values for the ligand and for water respectively. ΔH_{cryst} for the cupric ion complexes cannot be treated so easily because of the effect of the ligand on the Jahn-Teller stabilization. For many complexes we find empirically that

$$\Delta H_{\text{cryst}} \sim 24\,(D_q{}^{L} - D_q{}^{o}) \qquad \text{Cu}^{++} \tag{9b}$$

but this result has a different status to (9a) which is based on theoretical arguments. We rewrite (9) in the form

$$\Delta H_{\text{cryst}} = mr \tag{10}$$

where m has the values 0, 1, 2, 3, 6, 0 for Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++} and Zn^{++}, respectively and r is a second parameter characterising the ligand and depending essentially on the magnitude of the crystal-field which the latter produces.

Combining (8) and (10) we have, finally

$$\Delta H^{n} = \Delta H^{Mn^{++}} + (n - 5)\,p + mr \tag{11}$$

where p and r are parameters which can be determined experimentally from thermochemical measurements on manganous and zinc complexes and from spectroscopic studies, respectively. If the latter have not been carried out the theory can still be checked by studying the consistency of the thermal data on Fe^{++}, Co^{++} and Ni^{++} complexes. Unfortunately no complete set of thermochemical data on the complexes of the six metals is available so we are obliged to make use of logarithms cf formation constants instead i.e. we use assumption (4). Since many of the ligands which we shall consider are chelating agents it is necessary to recall that $\log K_1$ for a chelating agent, in the present context, is equivalent to $\Sigma_t \log K_t$, where the summation is over all the co-ordinating groups employed, e.g. $\log K_1$ for ethylenediamine complexes is equivalent to $\log K_1 + \log K_2$ for simple amines.

The most studied ligand other than water seems to be ethylenediamine. The logarithms of the stability constants are given in Table 2*. The D_q values calculated from spectroscopic studies on ethylenediamine complexes are about 25 % higher than those for the hydrates. (The ratios lie in the range 1.17-1.31).

The sum of the logarithms for the three successive formation constants of tris-ethylenediamine complexes of Mn^{++} and Zn^{++} are 5.67 and 12.09 respectively. The corresponding "corrected" values for Fe^{++}, Co^{++}, Ni^{++} and Cu^{++} based on linear interpolation are 6.95, 8.24, 9.52 and 10.80 respectively. The divergences of the actual values from these, which we write as $\Delta \log K$ and attribute to crystal-field splitting, are 2.57, 5.58, 8.54 and 7.26 respectively. Before trying to interpret these in detail we must look at the corresponding $\Delta \log K_i$ separately. They are .85, 1.95, 3.00 and 5.44 for $\Delta \log K_1$; .62, 1.72, 2.66 and 4.51 for $\Delta \log K_2$; .94, 1.88, 2.88 and -1.11 for $\Delta \log K_3$. It is clear from these data that the extra stability of the Fe^{++}, Co^{++} and Ni^{++} complexes, for each stage separately and hence for the complete three-stage process can be explained by a crystal-field stabilization which increases steadily, from Fe^{++} to Ni^{++}. The extra stabilities in fact are quite close to being in the expected ratio 1 : 2 : 3. The stability constants for the cupric complexes are particularly interesting for they suggest that, on the same scale, the effect of crystal-field stabilization of Cu^{++} is about 6.5 for $\log K_1$, about 7.0 for $\log K_2$ and -1.3 for $\log K_3$. These data correlate remarkably with the spectroscopic evidence which shows that the first two ethylenediamine molecules coordinated to copper produce very large crystal-field splittings,

TABLE II.

Formation constants for ethylenediamine complexes.

	Mn	Fe	Co	Ni	Cu	Zn
$\log K_1$	2.73	4.28	5.89	7.52	10.55	5.71
$\log K_2$	2.06	3.25	4.83	6.28	9.05	4.66
$\log K_3$	0.88	1.99	3.10	4.26	—1.0	1.72

(*) All values for formation constants are taken from reference (9).

but that the third molecule actually *decreases* the crystal-field splitting in a unique fashion ([18]). Thus we can give a completely consistent account of the spectroscopic properties and stability constants of the ethylenediamine complexes. The first two ethylenediamine molecules stabilise the cupric ion through a large distortion of the kind already discussed for the hydrates. The $[Cu(en)_2(H_2O)_2]^{++}$ complex must consist of a planar $[Cu(en)_2]^{++}$ group attached weakly (if at all) to a further pair of water molecules. The addition of third ethylenediamine molecule causes the structure to change to a much more nearly regular octahedral complex with a resultant *decrease* in the crystal-field stabilization. This is the cause of the instability of $[Cu(en)_3]^{++}$ relative to $[Cu(en)_2(H_2O)_2]^{++}$, (but not relative to $[Cu(H_2O)_6]^{++}$). The fact that $[Cu(en)_3]^{++}$ is much more nearly cubic than $[Cu(En)_2(H_2O)_2]^{++}$ is itself readily understood. The amine forms stronger bonds to copper than does water and so by means of a Jahn-Teller distortion can almost push it out of the coordination sphere.

For tris-ethylenediamine nickel the spectroscopic D_q value is 1160 cm^{-1}, while the value for the hydrate is 880 cm^{-1}. We therefore expect an excess crystal field stabilisation over that of the hydrate of $12 \times 280 = 3{,}360$ cm^{-1} or 10 k cals. In fact the logarithm of the formation constant exceeds that to be expected in the absence of crystal-field splitting by 8.54 corresponding to about 12.3 k cals. In view of the unknown entropy factor which we have neglected and the approximations of the method this agreement is all that can be expected. It would be particularly interesting to see how the observed heat of reaction compares with that estimated from crystal-field theory.

Data on the simple amines are incomplete and in particular, the manganous complexes have not been studied. No detailed analysis of the results is thus possible, but the general impression is that they parallel those for the ethylenediamine complexes but with slightly smaller crystal-field splittings. This is consistent with the spectroscopic data.

Triethylenetetramine complexes of the metals from manganese to zinc have been studied and in each case log K_1 has been determined. The divergences of log K_1 from the values obtained by linear interpolation between manganese and zinc are 1.5, 3.3, 4.9 and 9.7 respectively. Comparison with $\Delta \log K_1 + \Delta \log K_2$ values for the ethylene-diamine complexes, which are 1.47, 3.68, 5.66 and 9.96 is interesting. The agreement is reasonable even for Cu^{++}, which must mean that the Cu^{++}-triethylenetetramine complex is as much stabilised by crystal-field effects as the ethylenediamine complex. This implies that the four nitrogen atoms are almost planar in the cupric compound, and that the complex is not destabilised by steric strain.

Triaminoethylamine complexes are generally similar to those of triethylenetetramine with respect to the deviations of log K from the interpolated values, except that the cupric complex is markedly less stable than would be expected. This must be attributed to the inability of the former molecule to occupy four sites in a plane. This is important in the cupric complex, but not elsewhere, for in the other complexes the spatial distribution of the four amino groups among the six coordination positions is relatively unimportant.

We turn next to molecules in which the chelating groups are oxygen donors. Salicylaldehyde, with the usual metals, gives $\Delta \log K_1$'s of .34, .59, 1.03 and 3.05 and $\Delta \log K_2$'s of .23, 35, 58 and 2.42. These values are only about 30 % of those for amines, due to the much lower crystal-field splittings of oxygen containing ligands. For malonic and oxalic acids the data are not in very good agreement with the theory but the crystal-field stabilizations are always appreciably smaller than for salicylaldehyde.

Finally we may discuss chelating agents with one nitrogen and one oxygen donor atom. The extensive data on amino-acid complexes give values for $\Delta \log K_1$ very close to those for simple nitrogen donors augmented by the small contribution from a carboxylate group. There are many anomalies in the log K values for hydroxypteridine, folic acid, etc. which we cannot easily explain.

We may also use the theory, particularly equation (11), to draw some more general conclusions about complex formation. It is immediately clear that in a complicated system containing many different kinds of ligands competing for a metal ion, the distribution of the metal ion will be determined largely by its behaviour in a crystal-field. Thus metal ions which are particularly sensitive to crystal-field stabilization will tend to coordinate with ligands which give large crystal-field splitting and metal ions which are insensitive will form *relatively* more stable complexes with ligands which produce small crystal-fields. In a system containing both amino and carboxylate groups, e.g. in a protein solution, cupric ion should be bound preferentially by the amino groups and the manganous ion about equally by both groups. Just such regularities have been found experimentally and have been reviewed by Williams (19). This point is illustrated in Figs 4*a* and 4*b* for the case of ligands producing large and small crystal-fields respectively.

The theory which we have developed for divalent ions should, with few alterations, be applicable to trivalent complexes. At present there is insufficient experimental evidence to justify giving the theory in detail.

LATTICE ENERGIES

It is quite clear that the crystal-field stabilization of a complex ion should be almost the same in a solid lattice as it is in a solution. The close correspondence between the solution and crystal spectra, e.g. of the transition-metal hydrates, shows that the crystal-field effects are indeed almost identical in the two environments. It is at first sight less clear that the crystal-field theory will be applicable more generally to solid transition-metal compounds, e.g. the binary halides, sulphides, etc., and so one must proceed more cautiously in these cases.

Stout (20) has shown that the spectrum of crystalline manganous fluoride, in which each manganous ion is surrounded by an almost regular octahedron of fluoride ions, is analogous to that of the hydrated manganous ion, and that the small differences in the wave-lenghts of the band maxima can be accounted for if D_q is slightly smaller for F^- in the crystal lattice than for H_2O in solution. The spectra of other crystalline halides do not seem to have been investigated.

In the absence of optical data for the halides we cannot proceed quite as we did for complex ions in solution, since there is no way if making sure that the stabilizations which we attribute to crystal-field splitting do not have some other origins. However the general consistency of the picture and the close correspondence between the behaviour of the lattice energies for the halides, despite some differences in crystal structure, and that of the heats of formation of discrete complexes gives us some confidence in our interpretation.

In Figs *5a* and *5b* the lattice energies of the divalent and trivalent halides have been plotted against the atomic number of the metal atom. The following facts are immediately clear :

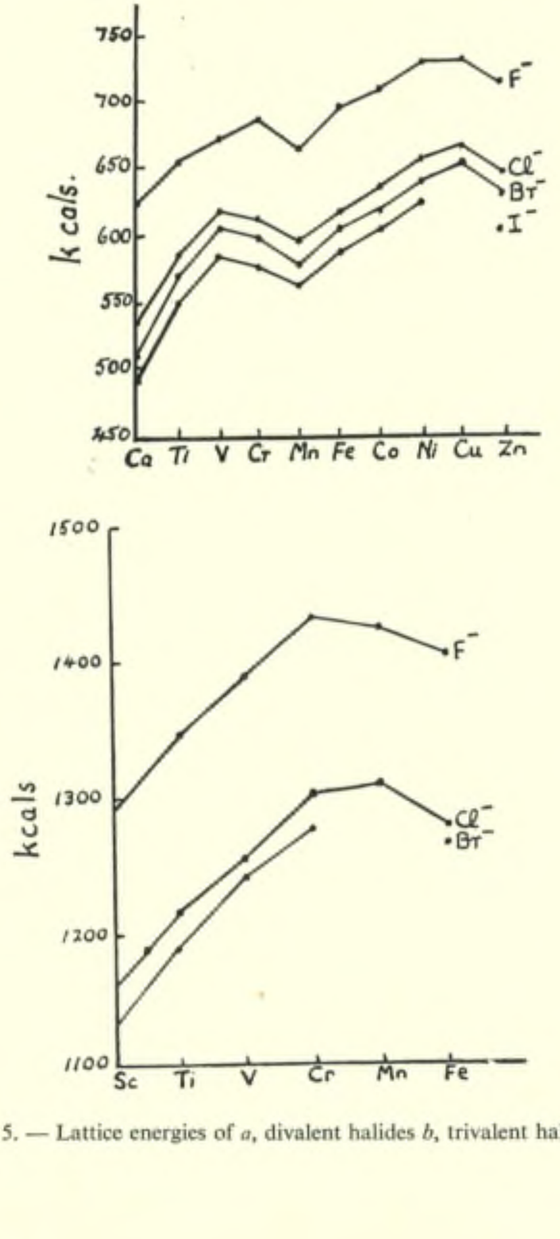

Fig. 5. — Lattice energies of *a*, divalent halides *b*, trivalent halides (8).

1° For the series of divalent ions there is a minimum in the lattice energy curve at manganese for each of the halides. If we suppose that divergences from linearity in the dependence of the lattice energy on the atomic number are due to crystal-field effects then these are of the order of magnitude of 10 — 40 K-cals, just as for complex ions;

2° For the series of trivalent fluorides the lattice energy falls to a minimum at the ferric ion, the ion with d^5 configuration. For the other halides the data are incomplete. The crystal-field effects are about twice as large as they are for trivalent ions, just as we have already found for the hydrates.

A number of features of Figs 5*a* and 5*b* require special comment. While the stabilizations of the Mn^{++}, Fe^{++}, Co^{++}, Ni^{++}, Cu^{++} and Zn^{++} ions follow the same pattern in the anhydrous chlorides, bromides and iodides as has become familiar in the treatment of complexes, there does seem to be a difference in the case of the anhydrous fluorides, for the lattice energy of CuF_2 is almost identical with that of NiF_2. We have already remarked that the Jahn-Teller effect which stabilises the cupric complexes is much more variable than the usual crystal-field splitting. It seems probable that the discrepancy indicates that the crystal-lattice of $Cu\,F_2$, which, significantly, is different from that of the other fluorides, is less deformable than the discrete complex ions so that the Jahn-Teller stabilization is smaller. If this is true one might hope that the absorption spectrum of anhydrous $Cu\,F_2$ would indicate a more nearly regular octahedral arrangement than occurs in the hydrates etc. A similar situation arises in the interpretation of the lattice energies of the V^{++}, Cr^{++} and Mn^{++} halides. The uncertainties in the lattice energies of the vanadous compounds is unfortunately large enough to prevent our reaching any definite conclusions, but the general trend of the results suggests that the Jahn-Teller effect is less important for Cr^{++} than for Cu^{++}.

THE RELATIVE STABILITIES OF TETRAHEDRAL AND OCTAHEDRAL COMPLEXES

The simple crystal-field theory shows that in tetrahedral complexes the set of *d* orbitals is split into a stable doubly degenerate *e* orbital and an unstable triply degenerate *t* orbital, e.g. the splitting is the reverse of that for octahedral complexes. The splitting and mixing of the states of atoms with several *d*-electrons differs considerably in detail from that for octahedral complexes with the single exception of the d^5 configuration which is perturbed in the same way by the two kinds of field.

Direct calculation of the electrostatic field of a set of ligands shows that the splitting in a tetrahedral complex is much smaller than in an equivalent octahedral complex. Molecular orbital theory shows that while the e_g metal orbitals are the only ones capable of forming bonding molecular orbitals of e_g symmetry for octahedral complexes; *d* orbitals must compete with the more favoured 4*p* orbitals in bond formation in tetrahedral complexes. This means that the antibonding *t* orbitals in tetrahedral complexes will be raised much less than the antibonding *e* orbitals in octahedral complexes. Thus both theories agree that the crystal-field splitting will be less in tetrahedral than in octahedral complexes. Experimentally this is shown to be true by the few available spectra of tetrahedral complexes and by the absence of spin pairing among the tetrahedral complexes of the first transition series.

It is interesting to ask wich configurations should particularly favor octahedral complex formation and which tetrahedral. We may use the argument of the introduction and state that in the absence of crystal-field splitting the tendency to form tetrahedral rather than octahedral complexes would increase steadily with atomic number through the transition series. However owing to crystal-field effects we shall find certain discontinuous changes superposed on this general trend. In Table III we give the crystal-

TABLE III.

Stabilizations of $d^1 — d^{10}$ configurations in crystal-fields.

	Octahedral	Tetrahedral
$d^5\ d^{10}$	0	0
$d^1\ d^6$	4 D_q	6 D_q
$d^2\ d^7$	8 D_q	12 D_q
$d^3\ d^8$	12 D_q	8 D_q
$d^4\ d^9$	6 D_q	4 D_q

field stabilizations for each electron configuration in each type of field. Since D_q is smaller for tetrahedral than for octahedral complexes this Table suggests, other things being equal :

1° That divalent manganese and zinc should form tetrahedral complexes more readily than the other divalent ions except perhaps titanous and cobaltous;

2° That ferric and thallic ions should form tetrahedral complexes more readily than other trivalent ions except perhaps vanadium;

3° That there should be a change favoring octahedral complexes on going from titanous to vanadous or from cobaltous to divalent nickel complexes of the spin-free type.

It is difficult to decide from the empirical formulae of substances which have been prepared much about absolute stabilities. Conclusion 3° seems definitely correct for cobaltous and divalent nickel. The ready formation of tetrahedral $[CoX_4]^{--}$ ions where X is a halogen or pseudohalogen is a characteristic feature of the chemistry of cobaltous cobalt, while few nickel complexes containing discrete tetrahedra $[NiX_4]^{--}$ groups seem to be known. Similarly $[FeCl_4]^{--}$ complexes are rare or unknown, hydrated (octahedral?) ions $[FeCl_4.2H_2O]^{--}$, $[FeCl_3, 2,3H_2O]^-$ and $[FeCl_6]^{4-}$ being obtained instead ([21]).

Conclusion 2° receives some support insofar as the $[FeCl_4]^-$ ion is stable under many conditions, although $[FeCl_6]^{3-}$ seems also to exist. There are no $[MnX_4]^-$ complexes known, the usual empirical formulae corresponding to $[MnX_5]^{2-}$ or $[MnX_5(H_2O)]^{2-}$. Also there seem to be no $[CoX_4]^-$ complexes. Aluminium seems to form both tetrahedral and octahedral complexes with great facility ([21]).

Conclusion 1° is also supported by very limited experimental evidence. Tetrahedral zinc complexes are quite common and there seem to be a few $[MnX_4]^{--}$ ions (but $MnCl_2$.2 pyridine which if it is monomeric we should certainly except to be tetrahedral is in fact claimed to be planar) ([21]).

All in all the experimental evidence suggests that crystal-field splittings are the important factors determining the relative stabilities of tetrahedrally and octahedrally co-ordinated metal ions. However these qualitative arguments, particularly those based only on empirical formulae may well prove deceptive. More structural and thermodynamic data are required to determine the scope of these methods.

These arguments may be applied to the metals of the second and third transition series, but they then lead to rather different results. In the later transition series D_q values for complexes are systematically larger than in the first series, while electron repulsion energies are systematically smaller. This leads to the well-known tendency to form spin-paired or "covalent" complexes. While in the first transition series the crystal-field effects are never large enough to cause spin pairing in tetrahedral complexes, we might expect it to be more favoured in the other series. If so it is clear that the configuration which would most likely form a spin-paired complex is the one with four *d*-electrons, for this allows the stable *e* orbital to be filled while leaving the *t* orbital empty.

This conclusion of crystal-field theory is supported by experimental evidence which does not easily receive an alternative explanation. Trivalent rhenium forms halogen complexes with the empirical formulae $M^+[ReX_4]^-$ (21). In this it seems to differ from related ions, e.g. trivalent manganese which, although a smaller ion, forms $[MnX_5]^{--}$ and $[MnX_5(H_2O)]^{--}$ or Re^{IV} which forms $[ReX_6]^{--}$. Since Re^{II} has just four *d*-electrons we suppose the complexes to be tetrahedral and attribute the existence of $[ReX_4]^-$ ions to the special stability of the configuration d^4 in strong tetrahedral fields. We therefore expect $[ReCl_4]^-$ and $[ReBr_4]^-$ to be diamagnetic.

While in the octahedral complexes of the first series electron pairing is the exception rather than the rule, the situation is reversed in the other series. This changes the position of maximum stability from the configurations d^8 and d^9 to the configuration d^6. We can deduce that in these cases the tetrahedral d^7 complexes are relatively the most stable, but there is little experimental evidence. There are probably no Pd^{III} or Pt^{III} complexes and only a few Rh^{II} or Ir^{II} complexes. Some of the latter are probably tetrahedral, e.g. $[Rh(SO_3)_2]^{2-}$ but the majority, surprisingly, seem to be octahedral (21), e.g. $[Ir(CN)_6]^{4-}$. We suspect that detailed x-ray work might show that, as in the case of the so-called "$[Co(CN)_6]^{4-}$" ion, some of the structures have been ascribed incorrectly.

CHAPTER II

It has been shown that there is a formal similarity between the electrostatic and molecular-orbital theories of transition-metal complexes which ensures that the general pattern of energy levels obtained is the same in the two theories, although there are quite definite differences in detail (12). Since many of the properties of the complexes, such as their relative stabilities and the broad features of their optical spectra, depend only on the energy level diagrams it is not easy to decide which theory gives the more accurate description of the electronic structure. The valence-bond method which, at first sight, is less closely related, in a formal sense, to the other theories can in fact be made equivalent to them by introducing the idea of three electron bonds in ionic complexes and by modifying certain conclusions about the promotion of electrons to highly excited orbitals. We shall examine more closely than hitherto the appropriateness of the electrostatic and molecular-orbital theories in different situations. The valence-bond method will not be discussed further.

In its most complete form the molecular-orbital theory includes all the electrostatic interactions between the electrons and nuclei of a molecule or ion. In this form it includes the electrostatic theory as a limiting case, that in which no mixing of metal and ligand orbitals occurs. It is therefore important to realize that it is the utility, not the correctness, of molecular-orbital theory which is at stake. If electrons are shared between metal and ligands the molecular-orbital method is useful, if not it has no advantages over the electrostatic method.

There are no general experimental techniques available, even in principle, whcih determine the distribution of a single molecular-orbital over the molecular framework. However, if one or more orbitals are distinguished from the majority by containing unpaired electrons then paramagnetic resonance absorption studies give fairly direct evidence about the distribution of the latter. Fortunately the key orbitals involved in the theory of transition-metal complexes are just the ones which can, in principle, be studied by this method.

The most direct method depends on the measurement of the nuclear hyperfine structure of the absorption line. The magnitude of the hyperfine splitting produced by a given nucleus is proportional to the density of unpaired electron near that nucleus. The proportionality constant can be determined fairly accurately by independent measurements, so that the actual density of unpaired electron on any nucleus which has a suitable nuclear spin can be determined. Owen and Stephens have applied this technique to the $[\mathrm{Ir\,Cl_6}]^{--}$ and $[\mathrm{Ir\,Br_6}]^{--}$ ions and have shown that the 5*d* electrons, usually thought of as isolated on the Ir atom, spend some 20 % of the time on the halogens (22,23). In principle this method could be applied to many other complexes, particularly those containing nitrogen, but this has not yet been done.

The results on the iridium salts do not tell us very much about complexes of the first transition series for two reasons. Firstly the lower ionization potentials and larger sizes of the later transition-series ions favour more extensive delocalization than in the first series. On the other hand the delocalization studied in these compounds can occur only through π bonding while in many complexes of the first transition series more extensive delocalization through σ bonding is to be expected. We may expect such delocalization to be greater than 10 %, but without further information cannot estimate its magnitude in this way.

Owen (6) has showed that a number of features of the paramagnetic resonance spectra of the hydrates and ammines of the first transition series cannot be explained by the simple electrostatic theory. In particular the spin-orbit coupling seems smaller in the complexes than in the free ions. This could be understood if the *d*-electrons spent only about 70-90 % of the time near the metal nucleus and the rest on the ligands. He finds that a consistent explanation of the hyperfine structure, the *g*-values, and of small deviations of the optical spectra from those predicted by theory can be given if delocalization is assumed. Alternative explanations of certain of the discrepancies between the simple theory and experiment are possible, but the consistency of Owen's results is convincing.

There is a great bulk of experimental evidence showing that if the ligands in transition-metal complexes have available empty π orbitals of even very moderate stability then extensive double-bonding involving the t_{2g} orbitals, occurs. This provides very strong evidence for the delocalization of t_{2g} electrons in a variety of simple complexes, e.g. those of pyridine. More important, it suggests that if the π electron delocalization is important even though the ligand π orbitals are much less stable than the metal orbitals, then the delocalization caused by the σ bonding, which involves metal and ligand orbitals of comparable stability, is likely to be very extensive.

This brings us to the theoretical approach of the problem. In general the condition necessary for orbitals on different atoms to be mixed together to form bonds is that they overlap strongly. Direct calculations of overlap integrals for typical transition-metal complexes have been carried out and indicate quite conclusively that the 3*d* orbitals of a metal ion overlap quite strongly with the *s* and *p* orbitals of typical ligands ([24,25]). It is difficult to avoid the conclusion that extensive mixing must occur.

We have now examined the evidence for mixing and must consider the arguments against it. The only one of any weight seems to be the success of *direct* calculations, from the electrostatic model, of the frequency of optical transitions. However, on closer examination it is seen that if the correct lengths are taken for the metal-ligand bonds then dipole moments much greater than the measured static dipole moments must be assumed for the ligands if agreement with experiment is to be achieved. These high moments may reasonably be attributed to the polarization of the ligands by the high field of the metal ion, but, apart from the arbitrariness of this procedure, in vieuw of the orthogonality requirement of quantum theory, this almost implies a mixing of the various metal orbitals and the ligand σ orbitals.

It seems to us that three rather different situations may be envisaged. In the first the σ orbitals of the ligands are sufficiently far from the electrons of the unfilled shell for overlap to be impossible or insignificant. In this case the electrostatic theory is applicable and nothing extra is achieved by the use of molecular-orbital theory. The rare-earth ions are the most important case of this kind. In the second extreme situation the mixing of metal and ligand electrons is so extensive that it is not even reasonable to assign configurations on the basis of a certain number of *d* electrons remaining on the metal ion and the rest being transferred to the ligands. In this situation only molecular-orbital (or valence-bond) theory is useful. Typical examples are the MnO_4^- or OsO_3N^- ions. Between these extremes there is a region in which mixing is more or less important, but not sufficiently extensive to remove the *utility* of the simple classification scheme based on the electrostatic picture, despite its only partial correspondence to the true electronic structure. We believe that the di- and trivalent complexes of the first, and probably the other transition series, and the actinide complexes lie in this intermediate range. The methods of the electrostatic theory lead to correct qualitative and sometimes even quantitative results but only because these approximate moderately closely to the results of molecular-orbital theory. If we are correct in this conjecture it would be wise to invent a new term to replace " crystal-field " theory which would indicate that " bonding " as well as electrostatic interactions are involved. The only name that we are able to suggest is " ligand-field theory ".

While the electrostatic theory is quite adequate for approximate calculations on the spectra and " bond types " of many simple complexes, it is not capable of extension to take into account the effect of π-bonding. Another drawback is that while it gives a good account of the internal spectra of the metal ions in complexes it can say very little about excited states in which charge is removed from the metal ion to the ligand or vice-versa. Thus in order to integrate the theories of double-bonding and of normal and photochemical oxidation-reduction reactions with the other aspects of transition-metal theory it is necessary to employ the molecular-orbital theory (2, 6, 12).

We shall discuss those metal complexes which have regular octahedral symmetry. The various orbitals of the central metal ion and of the ligands transform as representations of the octahedral group in the manner shown in Table IV. The system of numbering the ligands and the choice of axes is shown in Fig. 6. The orbitals are designated in the following way :

a) Metal orbitals are indicated by a symbols such as φ_{4s}. The subscripts refer to the usual classification of atomic orbitals ;

b) Molecular orbitals made up from ligand σ orbitals are indicated by symbols such as $\chi_{a_{1g}}$. The subscript refers to the symmetry species. If the representation is degenerate a further subscript is employed to show with which of the metal orbitals a particular member of a degenerate set will combine, e.g. $\chi_{t_{1u},x}$ will combine with φ_{p_x} but not with φ_{p_y} or φ_{p_z};

c) Molecular orbitals made up from ligand π orbitals are indicated by symbols such as $\pi_{t_{2g},xy}$, the use of subscripts being the same as in *b)*.

For the orbitals of individual ligands we have used the symbol σ_i for the σ orbital on the *i*'th ligand and the symbol π_{jx} for the π_x orbital on the *j*'th ligand, etc. The combined ligand molecular orbitals have been normalized assuming that individual ligand orbitals are mutually orthogonal.

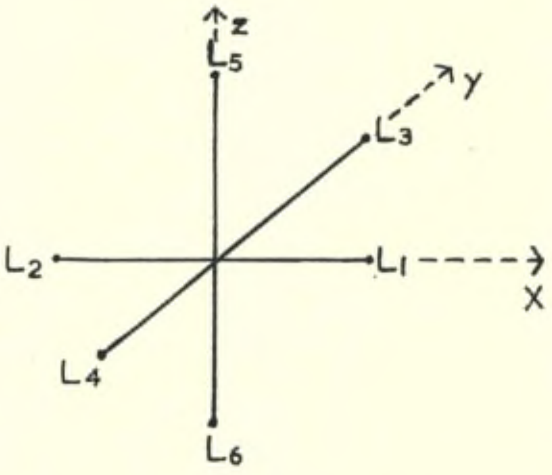

Fig. 6. — Numbering of ligands and choice of axes for octahedral complexes.

In the absence of π orbitals on the ligands and neglecting metal orbitals outside the 4*p* shell for the first transition series the most general molecular orbitals are of the forms shown in Table V. The normalising factors must be chosen in the usual way, e.g. $N_{a_{1g}} = \left(1 + \lambda^2 + 2\lambda S_{a_{1g}}\right)^{-1/2}$ where $S_{a_{1g}} = \int \varphi_{4s}\, \chi_{a_{1g}}\, dT$ is the overlap integral between φ_{4s} and $\chi_{a_{1g}}$. The requirement that the orbitals should be mutually orthogonal leads to a set of relations of the form

$$(\lambda' - \lambda'') + (1 - \lambda'\lambda'')\, S_{a_{1g}} = 0$$

TABLE IV.

Symmetry classification of orbitals for octahedral complexes (T_{1g} and T_{2u} orbitals neglected).

Metal		Ligand σ	Ligand π
A_{1g}	φ_{4s}	$\chi_{a_1} = \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$	
E_g	$\varphi_{3d_{z^2}}$	$\chi_{e_{g,z^2}} = \frac{1}{2\sqrt{3}}(2\sigma_5 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4)$	
	$\varphi_{3d_{x^2-y^2}}$	$\chi_{e_{g,x^2-y^2}} = \frac{1}{2}(\sigma_1 + \sigma_2 - \sigma_3 - \sigma_4)$	
T_{1u}	φ_{4p_x}	$\chi_{t_{1u},x} = \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_2)$	$\pi_{t_{1u},x} = \frac{1}{2}(\pi_{3x} + \pi_{4x} + \pi_{5x} + \pi_{6x})$
	φ_{4p_y}	$\chi_{t_{1u},y} = \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_4)$	$\pi_{t_{1u},y} = \frac{1}{2}(\pi_{1y} + \pi_{2y} + \pi_{5y} + \pi_{6y})$
	φ_{4p_z}	$\chi_{t_{1u},z} = \frac{1}{\sqrt{2}}(\sigma_5 - \sigma_6)$	$\pi_{t_{1u},z} = \frac{1}{2}(\pi_{1z} + \pi_{2z} + \pi_{3z} + \pi_{4z})$
T_{2g}	$\varphi_{3d_{xy}}$		$\pi_{t_{2g},xy} = \frac{1}{2}(\pi_{1y} - \pi_{2y} + \pi_{3x} - \pi_{4x})$
	$\varphi_{3d_{xz}}$		$\pi_{t_{2g},xz} = \frac{1}{2}(\pi_{1z} - \pi_{2z} + \pi_{5x} - \pi_{6x})$
	$\varphi_{3d_{yz}}$		$\pi_{t_{2g},yz} = \frac{1}{2}(\pi_{3z} - \pi_{4z} + \pi_{5y} - \pi_{6y})$

TABLE V.

Molecular-orbitals for octahedral complexes neglecting π bonding.

Symmetry Class	Bonding Orbitals	Non-Bonding Orbitals	Antibonding Orbitals
A_{1g}	$N'_{a_{1g}}\left(\varphi_{4s} + \lambda' \chi_{a_{1g}}\right)$		$N''\ \left(\chi_{a_{1g}} - \lambda'' \varphi_{4s}\right)$
T_{1u}	$N'_{t_{1u}}\left(\varphi_{4p_x} + \mu' \chi_{t_{1u},x}\right)$ $N'_{t_{1u}}\left(\varphi_{4p_y} + \mu' \chi_{t_{1u},y}\right)$ $N'_{t_{1u}}\left(\varphi_{4p_z} + \mu' \chi_{t_{1u},z}\right)$		$N''_{t_{1u}}\left(\chi_{t_{1u},x} - \mu'' \varphi_{4p_x}\right)$ $N''_{t_{1u}}\left(\chi_{t_{1u},y} - \mu'' \varphi_{4p_y}\right)$ $N''_{t_{1u}}\left(\chi_{t_{1u},z} - \mu'' \varphi_{4p_z}\right)$
E_g	$N'_{e_g}\ \left(\varphi_{3d_{x^2-y^2}} + \nu' \chi_{e_{g},x^2-y^2}\right)$ $N'_{e_g}\ \left(\varphi_{3d_{z^2}} + \nu' \chi_{e_{g},z^2}\right)$		$N''_{e_g}\ \left(\chi_{e_{g},x^2-y^2} - \nu'' \varphi_{3d_{x^2-y^2}}\right)$ $N''_{e_g}\ \left(\chi_{e_{g},z^2} - \nu'' \varphi_{3d_{z^2}}\right)$
T_{2g}		$\varphi_{3d_{xy}}$ $\varphi_{3d_{xz}}$ $\varphi_{3d_{yz}}$	

In order to explain the observed behaviour of transition-metal complexes it is necessary to assume that the order of levels is as shown in Fig. 7. This order is entirely consistent with the simplest theoretical considerations based on the energies of the different metal atomic orbitals and the magnitude of the overlap integrals. The separation between the t_{2g} and e_g orbitals is, of course, the critical separation 10 D_q on which most of the arguments of Chapter I depended.

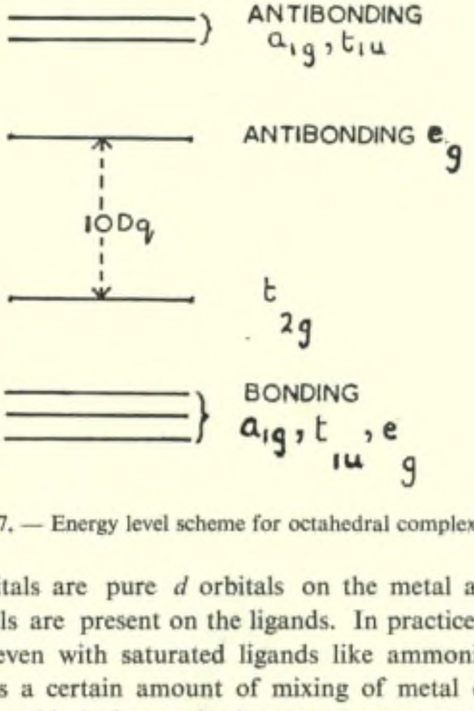

Fig. 7. — Energy level scheme for octahedral complexes.

The t_{2g} orbitals are pure *d* orbitals on the metal atom so long as no π orbitals are present on the ligands. In practice this is never the case, for even with saturated ligands like ammonia hyperconjugation allows a certain amount of mixing of metal orbitals with π type ligand orbitals in much the same way as methyl groups hyperconjugate with unsaturated systems. Nevertheless in this and related cases we can be sure that there is only very limited mixing between the t_{2g} orbitals of the metal and ligands. The case of the e_g orbitals is very different, for we have seen that mixing of metal and ligand orbitals is extensive, that is neither ν' or ν'' is negligible.

The bonding effect of the a_{1g} and t_{1u} orbitals must remain constant or vary continuously as the atomic number of the metal increases, for the same orbitals are occupied in every case. However while the e_g bonding orbital is filled by four electrons in all configurations its bonding effect is liable to be cancelled by the occupation of the e_g antibonding orbital. If we define the *d* orbital bond-number as the difference between the number of electrons in the bonding and antibonding orbitals it is obvious that it has the approximate values given in Table VI for different numbers of electrons in " ionic " and " covalent " complexes.

TABLE VI.

Bond numbers for d^n configurations in octahedral complexes.

No of *d* electrons . . .	1	2	3	4	5	6	7	8	9	10
Ionic complexes . . .	4	4	4	3	2	2	2	2	1	0
Covalent complexes. .	4	4	4	4	4	4	3	2	1	0

The bond-number defined in this way should not be confused with the bond-order usually employed in molecular-orbital theory. The bond-number is a measure of the occupation of bonding orbitals, not of the extent of binding which is achieved. We shall argue however that the bonding power per electron in the e_g orbitals is very roughly a constant, so that the bonding energy for ions of a given valency relative to their valence states increases steadily with the bond number. This allows us to translate into molecular orbital language the results of Van Santen and Van Weirengen (26) for we see that if the radii of transition-metal ions are plotted against the number of *d*-electrons they should decrease with the decreasing size of the *d* orbitals except when electrons are added to the antibonding e_g orbitals, e.g. in going from V^{++} to Mn^{++} and from Ni^{++} to Zn^{++}. In these cases the bond lengths should increases. This conclusion is in agreement with the experimental facts.

This idea is capable of considerable generalisation. It may readily be shown that for any state of an ion with *n* *d*-electrons the bond number defined in this way is related to the slope of the energy elvel diagrams in ref. (5). It was shown (12) that

$$\frac{dE}{d(Dq)} = 4n_1 - 6n_2 \qquad (12)$$

where n_1 and n_2 are the number of t_{2g} and antibonding e_g electrons respectively, so that n_1 can readily be determined for any excited state once the energy level diagram has been calculated and the approximate D_q value determined from optical spectra. The bond number is simply $4 - n_2$. It should be noticed that n_2 may not be even approximately integral, nor need it be approximately constant from one complex of a given metal to another for excited states as it is in the ground state. The calculation of the energy level diagram for excited states, or a knowledge of their electron configurations derived in some other way, thus enables one to predict bond lengths. This has proved useful in interpreting phosphorescence spectra ([27]), and as we shall show is important in understanding the effect of the Franck-Condon principle on the rates of electron exchange reactions.

Another application of the idea of bond number is to the change in ionic radius which occurs on going from an ion of maximum spin multiplicity, e.g. the Fe^{++} ion with four unpaired electrons, to an ion in which electrons have been paired in the t_{2g} orbital, e.g. diamagnetic $[Fe(CN)_6]^{4-}$. The bond number in this case changes from two to four and so there should be a very considerable decrease in the ionic radius. We shall return to this point later.

DOUBLE BONDING

Table VI shows that if the ligand have reasonably stable π orbitals then the t_{1u} and t_{2g} molecular orbitals of the metal ion and the σ framework can combine with them. The t_{1u} orbitals then become rather complicated, but fortunately this has little effect on those properties of the ground states of the complexes which are particularly dependent on the metal d orbitals, although it may lead to a systematic stabilization of all the metal complexes of a given ligand. If the ligand π orbital is isolated on a single atom the simple t_{2g} orbitals given in Table VII must be replaced by bonding and antibonding linear combinations. If the ligand has delocalized π orbitals the situation is more complicated.

When the ligand π orbital is unoccupied and rather unstable as it is in phosphines, arsines, mercaptans, etc. it is energetically

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(*) For a discussion of the magnetic criterion of bond type from the present point of view, see reference 11.

unstable relative to the metal orbitals so that the molecular orbitals have the forms

$$\left.\begin{array}{l} N'_{t_{2g}}\,(\varphi_{3d_{xy}} + k'\,\pi_{t_{2g,xy}}) \\ N'_{t_{2g}}\,(\varphi_{3d_{xz}} + k'\,\pi_{t_{2g,xz}}) \\ N'_{t_{2g}}\,(\varphi_{3d_{yz}} + k'\,\pi_{t_{2g,yz}}) \end{array}\right\} \qquad (13)$$

$$\left.\begin{array}{l} N''_{t_{2g}}\,(\pi_{t_{2g,xy}} - k''\,\varphi_{3d_{xy}}) \\ N''_{t_{2g}}\,(\pi_{t_{2g,xz}} - k''\,\varphi_{3d_{xz}}) \\ N''_{t_{2g}}\,(\pi_{t_{2g,yz}} - k''\,\varphi_{3d_{xz}}) \end{array}\right\} \qquad (14)$$

in which $k' < 1$ and $k'' < 1$. The first of these orbitals is bonding, i.e. it is stabilized relative to the *d* orbitals of the metal ion; the other is antibonding. Since the magnetic type of a complex is determined by the separation between the lower t_{2g} and the e_g levels and since this kind of double-bonding lowers the former and leaves the latter unchanged it follows that complexes in which it can occur are likely to be diamagnetic. We believe that the " covalency " of phosphine and arsine complexes is in large measure due to the effect of double-bonding on the occupied t_{2g} orbitals of the metal ion, rather than to a particularly strong interaction between the ligand and metal e_g orbitals. The importance of this kind of double-bonding in determining the stability of metal complexes has been recognized for some time (28) and has been discussed theoretically (24).

If the ligand π orbitals are of the stable occupied type, as for example in the halogen ions, then they are energetically more stable than the metal orbitals. The combined orbitals may still be described as in (13) and (14) but now $k' > 1$ and $k'' > 1$. The bonding orbital (13) is occupied by ligand electrons and any metal *d*-electrons are obliged to occupy the antibonding orbital (14). This results in a decrease in the $t_{2g} - e_g$ separation and hence a tendency to produce complexes with a maximum number of unpaired spins. Bonding of this kind does not seem to have been considered prior to the work of Stevens and Owen, but in the light of their results we may anticipate that it will prove to be very general. It should be noted that very similar double-bonding must occur in the hydrates even though they have only one occupied π orbital which can combine with the metal orbitals.

Double bonding between metal ions and molecules with delocalized systems of π orbitals has been considered in a number of instances, e.g. in β-diketone complexes of cupric copper and in the complexes of heterocyclic nitrogen compounds with transition-metal ions ([21]).

CHARGE-TRANSFER SPECTRA

Most metal complexes have absorption bands in the visible or ultraviolet region which are distinguished from the internal transitions of the metal ion by their dependence on the ease of oxidation or reduction of the ligand and often by an unusually high intensity. Although there is much evidence showing that the final chemical result of the absorption is often the oxidation or reduction of the ligands there is no general agreement as to the nature of the upper orbitals involved. The molecular-orbital theory enables one to describe the transitions in a satisfactory fashion.

The internal transitions of the metal ions dealt with in crystal-field theory are essentially $d - d$ transitions. It is to be expected that the next lowest electron transitions will be from the occupied d orbitals into the lowest empty orbitals, namely the antibonding a_{1g} and t_{1u} orbitals, and empty ligand π orbitals, and from the least stable orbitals beneath the d orbitals, namely the bonding a_g and t_{1u} orbitals, and perhaps from occupied π orbitals, into any empty d orbitals which are present. There will be other transitions from the bonding a_{1g} and t_{1u} orbitals, to the corresponding antibonding orbitals but these will usually be at shorter wave-lenghts than the transitions involving d-electrons, except perhaps in Zn^{++} and other highly charged positive ions with filled d shells.

A great variety of transitions is possible. They may be spin-forbidden or spin-allowed, orbitally forbidden or orbitally allowed; they may involve mainly one ligand as in $[Fe(H_2O)_5I]^{++}$ or all equally as in $[Cr(H_2O)_6]^{+++}$. The theory has hardly begun to be developed and the experimental evidence is also very incomplete. We shall make some general remarks here, and deal with one case in detail later.

The metal t_{2g} d orbitals are usually fairly well localized and the e_g orbitals not delocalized by more than 20-30 %. The metal $4s$ and $4p$ orbitals are likely to be delocalized to a greater extent. It follows that all of the transitions other than those within the d shell involve more or less transfer of charge. The most intense transitions must be $g - u$ in character, so that the lowest intense transitions of readily oxidised ions will usually be from the top occupied d orbital into the lowest empty t_{1u} or t_{2u} orbital, e.g. in a spin-paired ferrous complex, e.g. $[Fe(dipyridyl)_3]^{++}$ this would be from a moderately localized t_{2g} d orbital to a delocalized t_{1u} orbital, partly ligand π and σ and partly metal $4p$ in character. This is essentially a mixed charge-transfer and $3d - 4p$ transition. The corresponding transitions to the a_{1g} σ antibonding orbital must occur in the same general region but they will be much less intense, perhaps not much stronger than the internal $d - d$ transitions. Jorgensen ([30]) has suggested that certain transitions of the divalent transition metal ions classified by Dainton ([31]) and by the author ([32]) as charge-transfer transitions, are in fact $3d - 4s$ transitions. We are inclined to agree that the $3d - 4s$ character of these transitions is large and that Jorgensen's classification is perhaps the closer to the truth.

The lowest transitions other than d-d transitions, in complexes of oxidising anions are likely to be from the bonding a_{1g} and t_{1u} orbitals into the empty d-orbitals. These transitions are indeed largely charge-transfer in character, since they involve the removal of an electron from a delocalized orbital, largely on the ligands, into a d orbital almost localized on the metal atom. They will vary widely in intensity, those from the t_{1u} orbital being very intense and the others much less so.

The classification of these transitions involving the transfer of electrons from the d orbitals to empty antibonding orbitals, etc. is capable of giving very extensive and useful information about the energy level diagrams of complex ions and hence about their chemical properties, e.g. in the case of the planar complexes of palladium and platinum we have identified the position of the vacant $5d$ and $6p$ orbitals and have been able to study $d - p$ mixing by following the change in position and intensity of the $5d_{z^2} - 6p_z$ transition as the ligands are changed ([33]).

CHAPTER III

The molecular-orbital method developed in the last section can be applied both in a qualitative and a quantitative way to a variety of problems in transition-metal chemistry. We shall discuss a number of examples. It must be emphasized that similar results may in some cases be obtained by other methods. In particular the treatment of some of the examples owes much to the work of Taube ([34]). We hope to show that just as in the treatment of the spectra and magnetic properties of complexes the ligand-field method makes possible rather exact predictions about the effects of changes in the ligands on the chemical properties of complexes.

THE TRANSITION FROM " IONIC " TO " COVALENT " COMPLEXES

We have shown in a previous paper that the transition from complexes with maximum spin multiplicity to ones in which the spins are paired takes place when the separation between the t_{2g} and e_g orbitals exceeds a certain critical energy which can be calculated approximately. We shall take up this topic again from the point of view of molecular-orbital theory and discuss in detail the behaviour to be expected near the transition point, i.e. for ligands which produce crystal-field splittings very close to the critical one at which the cross-over occurs.

The change from a complex with maximum spin-multiplicity to one in which spins are paired is invariably associated with the transfer of electrons from the e_g antibonding orbital to the t_{2g} orbital. For definiteness we shall discuss the case of the ferrous ion, in which two electrons are transferred when the spin-multiplicity changes. The removal of electrons from the antibonding orbital must cause a decrease in the radius of the ferrous ion, so that the metal-ligand distance must also decrease. This agrees with the conclusion of valence-bond theory. The potential energy curves for the two states are shown diagramatically in Fig. 8. Two cases are considered, namely that in which the spin-paired state is more stable and that in which it is less stable than the state of maximum multiplicity. In the former case the compound will be diamagnetic at sufficiently low temperatures; in the latter it will have a normal paramagnetic susceptibility. If the energy separation between the two minima is of the same order as kT a very interesting situation arises since a thermal equilibrium between the two forms should exist. The magnetic susceptibility should be a weighted average of the susceptibilities of the two forms ([34]) and the absorption spectrum should be composite, including bands from each form.

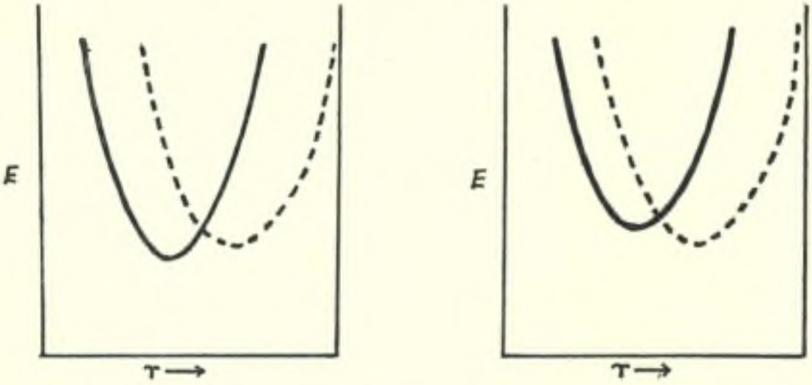

Fig. 8 *a* and *b*. — Energy level scheme for octahedral complexes near crossover point.

The change in radius which occurs at the cross-over point has important consequences. Any feature of the ligand's structure which favours the formation of long metal-ligand bonds will, other things being equal, favour the complex of maximum spin multiplicity and vice-versa.

A theoretical consequence of the change in radius with change in spin multiplicity is that while a single Dq is sufficient to describe the ground state and the spectroscopically excited states we must expect Dq to change when the ground state of the ion changes. It is clear from Fig. 8 that the change-over will always occur for values of Dq smaller than that calculated on the basis of a fixed Dq. Unfortunately it is difficult to calculate how big this effect will be.

The one major discrepancy between the calculated and predicted spin multiplicity of simple transition-metal complexes occurred for the tris-phenanthroline complex of ferrous ion which is diamagnetic, although according to the simple calculations, it should be paramagnetic. The author is grateful to R.J.P. Williams for pointing out that the complex of tris 2-methylphenanthroline is paramagnetic and much less stable than the simple phenanthroline complex owing to steric hindrance. Shortening of the Fe-N bonds would so compress the structure that the 2-methyl groups would interfere with the neighbouring molecules. Instead the complex remains in the state of maximum spin multiplicity. This provides a rather direct proof that the source of discrepancies between the calculated and observed cross-over points is in some cases due to the change in bond length, and hence D*q*, which occurs when the spin multiplicity changes.

We must next ask for what range of D*q* values an appreciable thermal mixing of the two types of ground state is likely. Suppose that the crossover occurs at some definite value $\mathrm{D}q^{\mathrm{o}}$. The crystal-field stabilizations for the types of ground state differ by 20D*q* so that, neglecting other effects, we must have $|20(\mathrm{D}q^{\mathrm{o}} - \mathrm{D}q)| \sim \mathrm{KT}$ where D*q* is the value for the ligand. At room temperature we may expect a tenth of the material to be in the less stable form if $|\mathrm{D}q^{\mathrm{o}} - \mathrm{D}q| \gtrsim 30\ \mathrm{cm}^{-1}$. While there are many reasons why this result should be inaccurate, it should not be out by more than a factor of 2. Thus ligands whose D*q*'s fall in a rather small range about the critical value will have anomalous magnetic properties. It is clear that most ligands must give either predominantly paramagnetic or predominantly diamagnetic complexes but that if one deliberately chooses a ligand giving complexes close to the cross-over point then by modifying it slightly complexes with very different properties can be obtained. We have already mentioned one example, that of the ferrous complexes of phenanthroline and 2-methyl phenanthroline.

Many of the most important examples of this behaviour near a cross-over point are concerned not with regular octahedral complexes, but with octahedral complexes containing more than one kind of ligand and with planar complexes. The principles however are exactly the same.

Calvin has studied the magnetic susceptibilities of a variety of planar cobaltous complexes ([35]). The interpretation of much of his data is complicated by the fact that planar cobaltous complexes in which the coordinating groups are nitrogen atoms lie very close to the cross-over point from complexes with one unpaired spin to those with three. The temperature dependence of the susceptibility has been measured for a selection of these compounds and it is found that some obey Curie's law over the whole temperature range studied while others have susceptibilities corresponding to one unpaired spin at low temperatures and to a greater number of unpaired spins at higher temperatures, although there is no change in the crystal form. Clearly the former group are well clear of the cross-over point while the latter group are very close to it. As is to be expected from the theory very small modifications in the ligand effect very large changes in the magnetic susceptibilities.

A similar situation exists in the case of complexes of ferrous iron with planar four-coordinating ligands such as porphyrins and phthalocyanines. Ferrous protoporphyrin has a magnetic moment corresponding to four unpaired electrons at all temperatures but ferrous phthalocyanine has a moment of intermediate size at room temperature (36). At low temperatures the apparent magnetic moment falls even further and it is fairly clear that the material would finally become diamagnetic. Clearly there is a paramagnetic excited state only a few hundred calories above the diamagnetic ground state.

Perhaps the most important group of compounds which have two lowest states of comparable stability are the ferrous and ferric porphyrins and their complexes with further ligands. Octahedral ferrous and ferric complexes in which four co-ordination positions in a plane are occupied by the nitrogen atoms of the pyrrole rings of protoporphyrin or related porphyrins and the fifth and sixth are filled by water have maximum spin multiplicity. Replacement of the water molecules by ligands which produce strong crystal fields such as cyanide ion or carbon monoxide invariably produces spin-paired complexes. Ligands of intermediate character such as simple and conjugated amines, hydroxide ions and azide ions form complexes the properties of which depend on the nature of *each* of the two groups and are surprisingly sensitive to very small changes in either. We attribute the remarkable versatility of the iron protoporphyrin prosthetic group in the various haemoproteins in part to the dependence of the ground states of its complexes with simple ligands such as hydroxide or hydrogen peroxide on the detailed nature of the haem-protein linkage. A small change, e.g. the replacement of a histidine nitrogen atom by the aliphatic amino group of lysine would be quite sufficient to change the ground-state of the complex and hence its magnetic and spectroscopic properties. The anomalous magnetic moment of methaemoglobin hydroxide, which has been interpreted by Pauling as due to partial spin pairing leaving three unpaired electrons is, we believe, due to an equilibrium between complexes with one and five unpaired spins, respectively ([37]). Similarly we believe that the great complexity of the visible spectra of many ferrous and ferric porphyrin complexes, which is in contrast to the very simple nature of other metallo-porphyrin spectra, is due in part to equilibria between different forms, although the occurrence of charge-transfer bands at long wavelengths is also almost certain.

Magnetic measurements do not easily detect the presence of an equilibrium mixture of states unless the two forms are present in comparable amounts. If the conditions are chosen carefully optical measurements can be much more sensitive. The ideal case is that of manganous and ferric complexes, for, in the spin-free form, these have no spin-allowed internal transitions. The spin-paired complexes on the other hand always have spin-allowed internal transitions at least one hundred times more intense than the spin forbidden ones. In ideal cases they may also have charge-transfer spectra up to one hundred thousand times stronger than spin-forbidden internal transitions. It follows that it should be possible to detect .001 %-1 % of spin-paired complex by optical methods, i.e. one should be able, in ideal cases, to detect spin-paired complex even if $\mathrm{D}q^{0} - \mathrm{D}q \gtrsim 150\ \mathrm{cm}^{-1}$. This should provide a very sensitive tool for studying the effect of small changes in a ligand on the ligand-field splitting which it produces.

Detailed calculations have shown that for octahedral trivalent ions the crossover point is expected to occur at lowest D*q* values for Co^{+++}, at much higher D*q* values for Fe^{+++} and at intermediate values for Mn^{+++}. We are carrying out similar calculations for planar complexes but, since the crystal field can now be described only by using three parameters, the results are not so simple. The most interesting conclusion is that while divalent planar cobalt and nickel complexes require similar crystal fields to achieve spin-pairing, the manganous ion requires a much larger crystal field. The ferrous ion requires a field of intermediate size. A study of spin-paired divalent planar nickel complexes shows that the ligand fields are somewhat greater than in trivalent octahedral complexes, i.e. more than twice those in divalent octahedral complexes. This, at first sight, surprising result is connected with the much less efficient shielding of the ligands by the $3d$ electrons in the planar complexes. Another way of putting this is to say that the ligands are more strongly polarized or form stronger, more " covalent ", bonds, a point of vieuw which is supported by much experimental evidence (14).

THE MECHANISM OF SOME ELECTRON-TRANSFER REACTIONS

Libby (38) has pointed out that the Franck-Condon principle requires that a reaction involving the transfer of an electron between the same element in different valency-states, e.g.

$$[\mathrm{M}^*(aqu)]^{\mathrm{n}+} + [\mathrm{M}(aqu)]^{(\mathrm{n}+1)+} \rightarrow [\mathrm{M}^*(aqu)]^{(\mathrm{n}+1)} + [\mathrm{M}(aqu)]^{\mathrm{n}+}$$

must proceed via a symmetrical transition state. We shall investigate the activation energy required for such a transfer process from the point of view of molecular-orbital theory and then examine in detail those reactions which proceed via bridged binuclear complexes.

Let us suppose that the radii of the di- and trivalent ions of a metal which forms octahedral complexes in both valencies are r^{II} and r^{III} respectively, and let K_{II} and $\mathrm{K}_{\mathrm{III}}$ be the force constants for the metal-ligand bonds. Then the tranfer of an electron from M^{II} to $\mathrm{M}^{\mathrm{III}}$, while maintaining the internuclear distance at the values corresponding to the forms present before transfer, requires the expenditure of an energy $3(\mathrm{K}_{\mathrm{II}} + \mathrm{K}_{\mathrm{III}})(r^{\mathrm{II}} - r^{\mathrm{III}})^2$. This is the energy which would be required for a direct photo chemical oxidation-reduction reaction. Thermal electron exchange can proceed much more readily via a transition-state in which each ion adjusts prior to the reaction. The activation energy for this process is roughly $3(\mathrm{K}_{\mathrm{II}}+\mathrm{K}_{\mathrm{III}})\left(\frac{r^{\mathrm{II}} - r^{\mathrm{III}}}{2}\right)^2$ i.e. it is about $^1/_4$ of the energy absorbed in the corresponding photochemical reaction.

We can see from the expression for the activation energy for thermal electron-transfer that a direct exchange of the kind contemplated is most likely to occur rapidly if $(r^{\mathrm{II}} - r^{\mathrm{III}})$ is small. Now $(r^{\mathrm{II}} - r^{\mathrm{III}})$ will depend very largely on whether the electron transferred comes from an e_g or a t_{2g} orbital. In the former case

($r^{II} - r^{III}$) will tend to be larger than in the latter, since the e_g orbital is antibonding. Thus we expect reactions such as the exchange between ferrous and ferric ion to be relatively rapid whether the ions are spin-paired or not. In the former case the reaction can be written

$$\mathrm{Fe}^{++}(t_{2g})^4(e_g)^2 + \mathrm{Fe}^{+++}(t_{2g})^3(e_g)^2 \rightarrow \mathrm{Fe}^{+++}(t_{2g})^3(e_g)^2 + \mathrm{Fe}^{++}(t_{2g})^4(e_g)^2$$

and in the latter

$$\mathrm{Fe}^{++}(t_{2g})^6 + \mathrm{Fe}^{+++}(t_{2g})^5 \rightarrow \mathrm{Fe}^{+++}(t_{2g})^5 + \mathrm{Fe}^{++}(t_{2g})^6$$

On other hand the reaction between chromous and chromic ions should be much slower since it can be formulated as

$$\mathrm{Cr}^{++}(t_{2g})^3(e_g) + \mathrm{Cr}^{+++}(t_{2g})^3 \rightarrow \mathrm{Cr}^{+++}(t_{2g})^3 + \mathrm{Cr}(t_{2g})^3(e_g)$$

Similarly the cobaltous-cobaltic exchange reaction should be slow since it may be written

$$\mathrm{Co}^{++}(t_{2g})^5(e_g)^2 + \mathrm{Co}^{+++}(t_{2g})^6 \rightarrow \mathrm{Co}^{+++}(t_{2g})^6 + \mathrm{Co}^{++}(t_{2g})^5(e_g)^2$$

This reaction, it will be noticed, involves not only the transfer of an electron but also the rearrangement of the other *d* electrons of both ions. It is partially spin-forbidden and should proceed very slowly indeed.

In fact most electron-transfer reactions involve bridged binuclear intermediates (39). However, in these too the same general considerations should apply, namely that if an e_g electron is transferred the reaction should go more slowly than otherwise. Experimentally there is one serious exception to this rule, namely that the manganous and manganic ions exchange much more rapidly than we should have expected. On the whole, however, Libby's suggestion that it is the Franck-Condon principle that is responsible for the energy barrier to electron exchange seems to account for most of the evidence if it is supposed that the ionic radius depends on the number of electrons in the e_g orbitals [cf. Taube, ref.(34)].

In a bridged chromium complex of the type shown in Fig. 9 the electron distribution can be determined with some confidence.

The chromic ion is in the configuration $(t_{2g})^3$ or more precisely $(d_{xy})^1\ (d_{xz})^1\ (d_{yz})^1$, with all electron spins parallel. The chromous ion has the configuration $(t_{2g})^3\ (e_g)$ in the particular state $(d_{xy})^1\ (d_{xz})^1\ (d_{yz})^1\ (d_{z^2})^1$ also with all electron spins parallel. The first three electrons automatically go into the t_{2g} orbitals in the way shown. The d_{z^2} orbital is occupied rather than the $d_{x^2-y^2}$ because the chloride ion produces a smaller ligand field than the H_2O molecule, particularly as it is being polarised by a positive Cr^{III}, so that the d_{z^2} orbital is destabilised to a smaller extent than the $d_{x^2-y^2}$ by the ligands.

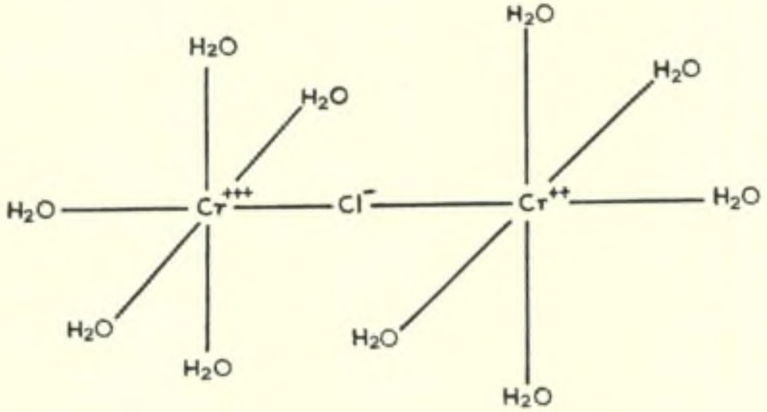

Fig. 9. — The structure of binuclear intermediates in electron-exchange reactions.

Direct transfer of an electron from Cr^{II} to Cr^{III} would, as we have seen, require an unnecessarily large activation energy. It is far more economical to create a symmetrized complex before transferring the electron. The transfer involves the simple removal of an electron from the Cr^{II} d_{z^2} orbital to the Cr^{III} d_{z^2} orbital, so that we can neglect all the other d electrons.

The assumption that the d_{z^2} electron is isolated on one chromium atom or the other is only approximately justified. When the chloride ion is at its equilibrium position the approximation is quite good, but as the ion approaches a position half-way between the chromium atoms it becomes less valid until when the complex is symmetrical the electron is equally likely to be on either metal atom. In Fig. 10 we show the energy level diagram for the two critical orbitals as a function of the displacement of the chloride ion from its equilibrium position, it being assumed that the other bond lengths adjust to the equilibrium values for each position of the chloride ion.

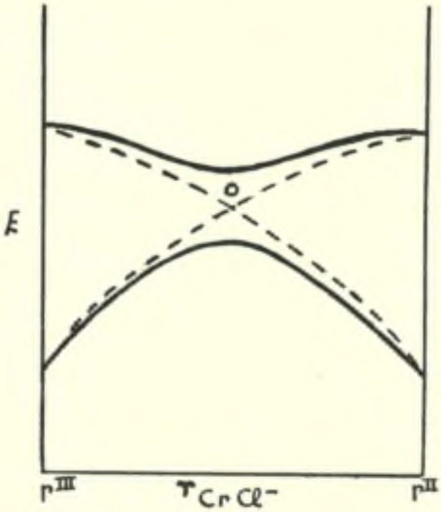

Fig. 10. — The orbital energy scheme for electron-exchange reactions.

The left-hand side of the diagram shows the Cr^{II} d_{z^2} orbital stable and the Cr^{III} d_{z^2} orbital unstable. The distance E is the activation energy for direct electron transfer. As the chloride ion approaches the symmetric position the two orbitals become more nearly equal in energy and may become mixed together if the interaction between them is strong. In the absence of mixing the two levels would cross at the symmetric position O, but if mixing can occur then the two curves repel each other as shown in the diagram.

The course of the reaction can now be understood in some detail. As the chloride ion moves from left to right, the electron moves from right to left. In the symmetric configuration the d_{z^2} electron is equally distributed between the two chromium atoms. Two things can now happen : either the chloride ion moves back to its original position and the electron proceeds in the opposite direction, so that no reaction occurs, or the chloride ion continues moving to the right and finally reaches the equilibrium position for $Cr^{III} + Cr^{II}$, the electron meanwhile having been transferred in the opposite direction. This mechanism explains why the bridging group is transferred in an electron-exchange reaction of this type, as was shown by Taube. It can be summed up by saying that the electron always prefers to stay as far away as possible from the bridging chloride ion; if the latter moves in one direction the former move in the opposite direction.

One might next ask what effect substituents would have on this process; for example, would oxidation-reduction reactions go more quickly with a cis or trans isomer in the pair of reactions

$$\left.\begin{array}{l}\text{cis}\\ \text{trans}\end{array}\right\} \qquad [Cr(NH_3)_4\,(H_2O)\,Cl]^{++} + [Cr(NH_3)_6]^{++} \rightarrow$$

$$[Cr(NH_3)_5\,(H_2O)]^{++} + [Cr(NH_3)_5\;Cl]^{++}$$

if they are assumed to go via bridged intermediates.

To solve this problem we must consider the energy level diagram in some detail. Since the ligand field of a water molecule is smaller than that of ammonia in the trans position it stabilizes the d_{z^2} orbital rather strongly and the $d_{x^2-y^2}$ orbital rather little. A water molecule in the cis position has little effect on the critical d_{z^2} orbital. It is seen that the reaction with the trans form should be more rapid than that with the cis form. Similar considerations also apply to the equilibrium properties of complexes and enable one to make certain predictions about the relative stability of cis and trans forms of those ions which have degenerate ground-states in a regular octahedral field.

It is very important to realize that while methods of this kind are quite general they must be applied very carefully to each particular system. Quite different rules might apply, e.g., in the electron exchange reaction between V^{+++} and V^{++}, since in this case it is a t_{2g} electron which is transferred. Similarly in the case of cis-trans isomers the exchange reaction should be slower for the trans isomer than for the cis in a reaction such as

$$[Cr(H_2O)_4\,(NH_3)\,Cl]^{++} + [Cr(H_2O)_6]^{++} \rightarrow [Cr(H_2O)_5\,(NH_3)]^{++}$$

$$+\;[Cr(H_2O)_5\;Cl]^{++}$$

since NH_3 molecule, having a *larger* ligand field than the H_2O molecule, destabilizes the orbital pointing towards it.

We shall deal with one more class of electron-transfer reactions, since it involves further theoretical considerations of some interest. During the reduction of spin-paired cobaltic complexes, such as the $[Co(NH_3)_6]^{+++}$ ion, not only is an electron tranferred to the cobalt, but in addition the arrangement of the electrons already present is altered. In fact, as we have seen, the reaction is

$$\mathrm{Co}\,(t_{2g})^6 + e \rightarrow \mathrm{Co}\,(t_{2g})^5\,(e_g)^2$$

A reaction of this sort should be extremely slow both on account of the great change in bond length to be expected when two electrons are introduced into the e_g orbital and on account of the change in spin multiplicity from one to four.

There is a second mechanism which could be considered for some reactions of cobaltic cobalt, namely one which produces the cobaltous ion in an excited state :

$$\mathrm{Co}\,(t_{2g})^6 + e \rightarrow \mathrm{Co}\,(t_{2g})^6\,(e_g)$$

This reaction is favoured for two different reasons, namely because the Franck-Condon principle is violated to a much lesser extent since only one extra electron is placed in the e_g orbital, and because there is no violation of the spin selection rules. On the other hand the promotion energy from the $(t_{2g})^5\,(e_g)^2$ to the $(t_{2g})^6\,(e_g)$ state will often be large, and so increase the activation energy.

It is not possible to make exact predictions about the relative importance of the two mechanisms in any particular case, but the general variation as ligands with progressively greater ligand fields are used can be anticipated. If the ligand is such that the cobaltic salt is spin-paired, but the cobaltous salt is far from being spin-paired, then the first mechanism will predominate. It will have a very low frequency factor and a high activation energy. If the ligand is such that the cobaltous complex is very close to the crossover point to a spin-paired complex (perhaps phenanthroline) then the second reaction should predominate. It should have a normal frequency factor and an activation energy comparable to that for reduction of chromic complexes. In between there should be a range of ligands such that the cobaltic complexes react by both mechanisms with comparable speeds. Such anomalous behaviour might be revealed by a study of the temperature dependence of the reaction rate. Finally, if the ligand field is such that both the cobaltous and the cobaltic ions are spin-paired, then the reaction should proceed by the second mechanism, and the reduced complex be formed in its ground-state, i.e. in the spin-paired state.

CHARGE-TRANSFER SPECTRA

We have already remarked that a great variety of charge-transfer transitions is to be anticipated. We shall discuss only two types of molecule, the pentammine halides of trivalent chromium and cobalt, which are fairly typical complexes of oxidizing cations. We have chosen these systems mainly because a great deal of experimental evidence is available. The methods employed are general and could be applied to many other systems, e.g. cupric, cuprous or ferric complexes with oxidizable or reducible inorganic or organic molecules or ions.

The simple hexammine cobaltic ion has two moderately weak absorption bands in the visible and near ultraviolet and one very strong band further in the ultraviolet at about 2000 Å ([40]). It is generally believed that the latter is associated with the transfer of an electron from the ligands to the metal ion, reducing the latter to the divalent state. As we have seen, a more accurate description of this transition is given by molecular orbital theory, which describes it as being from one of the occupied bonding orbitals into the antibonding e_g orbital which is actually largely d orbital in character. In view of the high intensity of the band we believe it to be fully allowed so that it must involve the t_{1u} bonding orbital which has a high density on the ligands. Our description of the transition is therefore substantially the same as the conventional one, the transfer of charge in the transition being considerable, and from the ammonia molecules to the metal. We believe this to be the most probable assignment, but it must be noted that it is entirely based on theory, and the experimental evidence does not exclude, e.g. the transfer of an electron from the filled t_{2g} shell of the cobalt ion to the empty antibonding t_{1u} orbitals.

The situation is a good deal clearer in the pentammine cobaltic halides. The fluoride has substantially the same spectrum as the hexammine, but the chloride, bromide and iodide have intense absorption bands at much longer wavelengths, the wavelengths increasing from chloride to bromide to iodide. There can be little doubt that these bands are connected with a transition in which an electron is removed from an orbital concentrated on the halogen and transferred to one concentrated on the metal ion.

A closer inspection of the spectra reveals that the intense absorption is not due to a single band but to pairs of bands at 26000 and 35000 cm^{-1} in the iodide, at 32000 and 39000 cm^{-1} in the bromide and at 36000 and 44000 cm^{-1} in the chloride. In each halide the longer wavelength band is much weaker than the other (40).

There are a number of possible explanations for the appearance of two bands under these conditions. They might correspond to the formation of the halogen atom in the $2P_1/_2$ and $2P_3/_2$ states respectively, to the removal of different kinds of electrons from the halogen, e.g. σ and π, to the transfer of an electron to two different kinds of empty orbital, or to a pair of transitions arising from different kinds of empty orbital, or to a pair of transitions arising from different states of a single configuration. The first possibility is ruled out by the appearance of a pair of bands in the chloride separated by several thousand wave-numbers, since the separation between ${}^2P_1/_2$ and ${}^2P_3/_2$ states of chlorine is only 880 cm^{-1}. The fact that transitions of this type occur at long wavelengths only in trivalent transition-metal complexes and not, for instance, in trivalent aluminium or gallium complexes suggests that the acceptor orbital involves the metal d orbitals. Since the t_{2g} d orbitals are already filled in trivalent cobalt it seems almost certain that the e_g antibonding orbital is the acceptor in each case.

The donor orbitals on the halide ion are of two types, almost localised π orbitals and largely delocalized σ orbitals. The former group are less stable than the latter and so might be expected to be involved in the longest wavelength transition. It would be plausible therefore to assign the first band to the almost completely charge-transfer transition from a halogen π orbital to a metal e_g orbital and the second to a less completely charge-transfer transition from the bonding σ orbital of the cobalt-halogen bond, to a metal e_g orbital. A closer study of the problem shows that, if we define the z axis to be in the cobalt-halogen direction, it is predominantly the d_{z^2} orbital which acts as acceptor in each case.

This theoretical assignment is consistent with the observation that the long wavelength band is always weaker of the two. The intensity of a transition will be large only if the donor and acceptor orbitals overlap strongly. Detailed calculation here shows that in most cases σ overlap is larger than π. It seems likely qualitatively that the transition moment is larger for the σ than for the π transition. It is interesting that the longer wavelength transitions should be polarized in the x and y directions and the shorter ones in the z direction.

In the pentammine chromic halides there is one new feature which must be considered in the theory, namely the occurence of vacancies in the t_{2g} orbital. These vacancies make possible two new types of transition, from the halogen σ and π orbitals to the t_{2g} orbital. In fact the charge-transfer bands of the chromic complexes are extremely similar to those of the cobaltic ones, except for a systematic shift to shorter wavelengths which is caused by the greater resistance to reduction of the chromic ion. This suggests that in the chromic complexes, even though the t_{2g} orbital is available, it is not used in the lowest energy transitions, but the e_g orbital is used instead. The energy required for spin pairing of the electrons in the t_{2g} orbital, more than balances the extra energy obtained by putting an electron in one of the stable orbitals. This is consistent with the fact that chromous complexes are usually spin-free.

The nature of the transitions of lowest energy in the spectra of complexes of this kind is relevant to the mechanisms of spontaneous oxidation-reduction reactions. In each case an electron is transferred from the least stable orbital concentrated on the ligand to the most stable one on the metal. It follows that a detailed experimental and theoretical examination of the charge-transfer spectra of stable complexes should throw a great deal of light on the precise electronic changes which take place, e.g. in the reaction of Cu^{++} with I^-.

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Discussion des rapports de R. S. Nyholm et de L. G. Orgel

M. Bjerrum. — I should like to add some comments to the paper of Prof. Nyholm.

1) The fact that we have some kind of directed chemical bonds in more labile transition complexes as well as in the robust Co^{III}complexes has been recognized by several chemists for the last twenty years. Therefore, I agree with Nyholm that names as "ionic" and "covalent", "outer" and "inner orbital complexes", etc., are inadequate, and should be dropped in favour of terms as "spin-free" and "spin-paired" complexes which directly refer to experimental facts.

2) I also agree with Nyholm that ligand field is a better name than crystal field in so far as molecules and ions in the second sphere contribute but very little to the colour of the substances. In fact, this more adequate name has already been proposed several times. (Sutton and Orgel, 1953; Ballhausen, 1954, etc.) but until now with little success.

3) In his contribution Prof. Nyholm mentions (e.g. p. 258), that the intensity of the ligand field increases as the electronegativity of the ligand decreases. This statement, however, is not compatible with the position of the ligand in the famous Tsuchida series : $J^- < Br^- < Cl^- < OH^- < F^- < H_2O < SCN^- < NH_3 < en < NO_2^- < phen < CN^-$ which empirically has been found to determine the intensity of the ligand field.

4) Prof. Nyholm mentions that considerable interest is attached to the diamagnetism of $K_4(Cl_5Ru—O—RuCl_5)$ which is after all a d^4-system. In this connection I may mention that Dr Schäffer in my laboratory has found that the basic rhodo complex $[(NH_3)_5Cr—O—Cr(NH_3)_5]^{4+}$ first prepared by S.M. Jørgensen is either diamagnetic or very close to be so; it is very hard to under-

stand that a d^{3-} complex can be diamagnetic, and I should like to ask Prof. Nyholm if he is able to explain this fact. I may add that Selwood in a recent paper (*J. Am. Chem. Soc.*, **76**, 6207, 1954) has found diamagnetism of what he supposes to be $[aq_4\,Fe\genfrac{}{}{0pt}{}{OH}{OH}Fe\,aq_4]^{4+}$ in a hydrolysed ferric solution. In our opinion this suggests that the complex also has an oxygen bridge, i.e. it has the constitution $[aq_5\ Fe{-}O{-}Fe\ aq_5]^{4+}$.

M. Nyholm. — In reply to Prof. Bjerrum I would like to emphasize that the electronegativity of the ligand is only one factor influencing the strength of the ligand field.

As mentioned on p 258 other factors are also important; these include double bond formation. They are discussed by Dr Orgel. The diamagnetism of the $[(NH_3)_5Cr{-}O{-}Cr(NH_3)_5]^{4+}$ ion is indeed surprising, since the simple theory applied to the Ruthenium case would suggest that one unpaired electron per Cr atom would still be present unless some kind of coupling akin to antiferromagnetic exchange occurs; I cannot suggest a simple explanation.

M. Orgel. — Prof. Wilmeel claims that a quite large moment is observed for $[(NH_3)_5Cr{-}O{-}Cr(NH_3)_5]^{++++}$ at room temperature, although it is much less magnetic than simple chromic complexes.

M. Bjerrum. — I have studied Orgel's contribution and especially his section on " The stability of complexes in solution " with great interest. At the conference on coordination chemistry in Amsterdam last year I put forward similar ideas, but the paper worked out in cooperation with Jørgensen to be published in *Rec. Trav. Chim. Pays-Bas* has not yet appeared.

Dr Orgel discusses the values of the complexity constants for the ethylenediamine systems determined by me. In Table I the gross stability constants of these conplexes are compared with gross constants for other selected systems. In case of the ethylenediaminetetraacetate, ethylenediamine and o-phenanthroline systems the ligand field stabilization is estimated in a way similar to that employed by Orgel. According to the ligand field theory the stabilization for octahedral complexes should be for Fe^{II} 1/3, for $Co^{II} < 2/3$ and for Cu^{II} 1/2 of the stabilization found for Ni^{II}. The stabilities

TABLE I.

Gross complexity constants for some systems of transition metal ions

(from Prof. Bjerrum, Tables of complexity constants).

$$K_{1-N} = K_1.K_2...K_N = \frac{[MA]_N}{[M]\,[A]^N}$$

	d^0	d^2	d^3	d^5	d^6	d^7	d^8	d^9	d^{10}
	Ca^{++}		V^{++}	Mn^{++}	Fe^{++}	Co^{++}	Ni^{++}	Cu^{++}	Zn^{++}
enta : log K^1	10.6		12.7	13.4	14.2	16.1	18.5	18.4	16.2
stabilization			0.4		0.2	1.6	3.4	2.8	
gly : log K_{1-3}						10.9	14.2	~16	11.5
NH^3 : log K_{1+6}	—5.7					5.1	8.7	10	
en : log K_{1-3}				5.7	9.5	13.8	18.1	18.6	12.1
stabilization					2.5	5.5	8.6	7.8	
den : log K_{1-2}					10.3	14.6	18.9	21.3	14.4
dip : log K_{1-3}				~ 6.3	17			17.0	13.3
phen : log K_{1-3}				~ 7.4	21.3		18.3	18.0	17.0
stabilization					12.0		5.2	2.9	
	Sc^{+++}	V^{+++}		Fe^{+++}					
enta : log K_1	23.1	25.9		25.1					

enta = ethylenediaminetetraacetate
gly = aminoacetate
en = ethylenediamine
tn = trimethylenediamine

den = diethylenediamine
dip = α, α'-dipyridyl
phen = o-phenanthroline

are of the right order of magnitude, and the data show the strong tetragonal distortion normally found in cupric systems. Only the Cu^{II}-phen system seems to be very nearly octahedral, and this is in complete agreement with the spectra as shown by Jørgensen. Table II gives some data for the ratios between the consecutive constants. The data given for the ammonia systems show that the nickel ion has six, and the cupric ion four uniform coordination places. This is in agreement with what is to be expected from the ligand field theory. For the cobaltous ion a weak rhombic distortion of the octahedron should be expected, and the irregularities found in the residual effects are not in disagreement with such an interpretation. The negative values of the residual effects in the zinc ammonia system are due to a change from octahedral configuration of the hexaquo ion to tetrahedral configuration of $Zn(NH_3)_4^{++}$, and the abnormally high stability found in the Fe^{II} systems of the aromatic diamines are due to the pairing of the spins by the uptake of the third ligand. In the ethylenediamine systems the data show

TABLE II.

Total effect ($T_{n,n+1}$), statistical effect ($S_{n,n+1}$) and residual effect ($R_{n,n+1}$) for some metal amine systems.

$$T_{n,n+1} = S_{n,n+1} + R_{n,n+1} = \log \frac{K_n}{K_{n+1}}$$

$S_{1,2} = S_{5,6} = 0.38$, $S_{2,3} = S_{4,5} = 0.27$, $S_{3,4} = 0.25$

	$R_{1,2}$	$R_{2,3}$	$R_{3,4}$	$R_{4,5}$	$R_{5,6}$
Co^{++}, NH_3	0.10	0.21	0.04	0.31	0.42
Ni^{++}, NH_3	0.18	0.24	0.29	0.17	0.34

$S_{1,2} = S_{3,4} = 0.43$ $S_{2,3} = 0.35$

	$R_{1,2}$	$R_{2,3}$	$R_{4,5}$	$T_{4,5}$	$T_{5,6}$
Cu^{++}, NH_3	0.22	0.26	0.33	2.76	~ 2.3
Zn^{++}, NH_3	— 0.5	— 0.4	— 0.1	—	—

$S_{1,2} = 0.68$, $S_{2,3} = 0.97$

	Mn^{++}, en	Fe^{++}, en	Co^{++}, en	Ni^{++}, en	Cu^{++}, en	Zn^{++}, en
$T_{1,2}$	0.67	1.03	1.06	1.16	1.41	0.77
$T_{2,3}$	1.18	1.26	1.73	1.93	10.3	3.29

		Fe^{++}, dip		Ni^{++}, tn	Cu^{++}, phen	Zn^{++}, phen
$T_{1,2}$		$\overset{\sim}{<} 0$		2.00	0.15	0.71
$T_{2,3}$		$\overset{\sim}{<} -3$		3.16	0.65	0.87

that steric strain increases from Mn^{++} to Zn^{++} and from the nickel ethylenediamine to the nickel trimethylenediamine system. In the cupric and the zinc o-phenanthroline systems there seems to be less steric strain than in the corresponding ethylenediamine systems, but this is not sufficient to explain that the tetragonal distortion has dissappeared in the $\mathrm{Cu}^{\mathrm{II}}$-phen system, and I should like to ask Dr Orgel for an explanation. I have discussed the matter with Dr C.E. Schäffer in my laboratory, and one could think of the possibility that the strong π-bonding in this case stabilitzes the cis-configuration of the bis-diamine complex to a higher extent than the trans-configuration?

M. Orgel. — In the trans form of diaquobispyridyl Cu^{++} only one π bond can be formed, but in the cis form two are possible. Perhaps this factor is sufficient to account for the difference between the complexes of the simple and conjugating amines.

M. Kuhn. — Is the magnetic moment rigidly connected to the framework of the molecule or is the central atom carrying the magnetic moment free to rotate inside the rest of the molecule? Paramagnetism is due to an orientation of the electric moment present in the atom or molecule with respect to a magnetic field applied from outside.

Which is then the unity whcih undergoes orientation?

Are there cases in which orientation of the magnetic moment implies orientation of the *entire* molecule?

M. Nyholm. — Both spin angular momentum and orbital angular momentum contribute to the total angular momentum hence the effective magnetic moment. In so far as we separate these the moment arising from the former is anisotropic; and thus Fe^{III} compounds have moments arising from spin only, hence no orientation with the magnetic field is expected. However the vector, when present, is oriented by the molecular field, and hence magnetic anisotropy occurs, e.g. as in octahedral CO^{II} complexes. Molecules of the latter do, therefore orient in a magnetic field.

M. Bénard. — Le Prof. Bjerrum nous a dit, il y a un instant, que la commission de nomenclature de l'Union Internationale de Chimie avait décidé d'adopter pour l'élément W le nom wolfram à l'exclusion de tout autre. En tant que membre de cette commission, je crois nécessaire de préciser que la situation ne correspond pas exactement à cela. En fait, au cours des réunions qui eurent lieu ces dix dernières années, à Amsterdam, New York et Stockholm en particulier, de longues discussions eurent lieu sur cette question, et il est exact que dans certains textes provisoires, la solution à laquelle le Prof. Bjerrum fait allusion, fut préconisée. Mais une opposition très forte s'éleva entretemps dans certains pays. Aussi fut-il décidé à la dernière réunion de cette commisison (Reading, avril 1956) de laisser la question en discussion, jusqu'à nouvel ordre.

M. Bjerrum. — I agree with Dr Orgel that changes in enthalpy give a more correct measure of the ligand field stabilization than changes in free energy. Until now the heats of complex formation have been determined only in a few cases, and it is therefore desirable that more thermochemical measurements be made in the nearest future. It should be mentioned that the heats are less dependent upon the salt concentration than are the free energies and it is further a possibility that they can be determined also in reactions with robust complexes where equilibrium in most cases cannot be established.

M. Chatt. — Our experience in platinum (II) chemistry indicates that the halogen atoms, especially iodine, have a definite tendency to form double bonds with the metal. The π type bond might occur either by a drift of p-electrons from the halogen to the metal or of d-electrons from the metal to the halogen. The evidence at present points to the latter in platinous and similar complexes, and indicates that the strength of π type bonding increases in passing along the halogen series from chlorine to iodine.

The formation of halide complexes with silver ion, which has been studied by Dr Ido Leden, also indicates that rather strong double bonding occurs with the iodide ion. In the stepwise formation of silver complexes in aqueous solution the first molecule of ligand (L) to be taken up by silver ion is followed almost at once by the second to give stable $(AgL_2)^+$ complexes. These are known to be linear in such ions as $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$ in the solid state. When a ligand which can form strong d_π-bonds is taken up, however, its use of two of the d_ε-orbitals in the silver ion will reduce the availability of the same d_ε-orbitals for attaching the second molecule of ligand in the position diametrically opposed to the first. Thus we may expect the second molecule of a d_π-bonding ligand to be taken up less readily than the first. We (Ahrland, Chatt, Davies and Williams, unpublished) find this to be true when the ligand is a phosphine where strong d_π-bonding between silver and phosphorus is to be expected. Leden finds that iodide ion behaves similarly, the first complex ($\bar{n} = 1$) being very stable relative to the second ($\bar{n} = 2$). This we consider to be evidence of strong n-type bonding between the silver and iodine atoms; the third complex ($\bar{n} = 3$) is also surprisingly stable and the formation of mononuclear complexes continues to $\bar{n} = 4$. Probably the relatively great stability of this third complex is also caused by double bonding, although the exact reason is not clear; it may be connected in some way with the use of d^2p hybrid orbitals for the formation of dative

π-bonds from a trigonally sp^2 hybridised silver ion (cf. Ahrland and Chatt, *Chem. and Ind.*, 1955, **96**).

Dr Orgel has admirably synthesized from crystal field theory and molecular orbital theory a very satisfactory theory of bonding in metal complexes and I wish to emphasize that the great success of cristal field theory alone in interpreting the ultra-violet spectra and magnetic properties of transition metal complexes must not blind us to the importance of covalent bonding. Therefore I wish to present data which are difficult to explain on the basis of an electrostatic theory of bonding in complexes. We have recently examined the formation of silver complexes by water-soluble organic derivatives of nitrogen, phosphorus, arsenic, oxygen, sulphur and selenium. We found a great variety of formation curves. These are shown in the figure together with a list of the ligands studied. The " normal " curve of complex formation with ammonia taken from J. Bjerrum's thesis, and Leden's curve showing complex formation with chloride ion are also included for comparison. The latter has an inflection at $\bar{n} = 2$. None of the new curves show the inflection, which was thought to be characteristic of the formation curves of the complexes of silver and related ions, at $\bar{n} = 2$. The variation in the curves is not connected so far as we know with the pairing or unpairing of electrons in the *d*-shell and depends largely on the donor atoms involved. Silver (I) has just sufficient electrons to fill all its *d*-orbitals and to leave only *s* and *p*-orbitals for σ-bond formation. These may be used as sp, sp^2 or sp^3 hybrids to give linear, trigonal or tetrahedral complexes respectively. The d_ε orbitals are available for dative π bonding which would be enhanced by some *p*-hybridisation in the linear and trigonal complexes. This means that silver (I) can give a great variety of complex types according to the electronegativities and double bonding tendencies of the donor atoms. The change in the relative stabilities of these different complex types with change in the covalent bonding characteristics of the donor atoms undoubtedly accounts for the variety of formation curves which we have found.

The " arsine curve " is peculiar in having a very strong inflection or a final " stop " at $n = 1$. No further complex formation took place at the highest concentrations of the sulphonated arsine which it was possible to investigate. This " stop " at $\bar{n} = 1$ may be caused by the high negative charge carried by the ligand, $As(C_6H_4SO_3^-)_3$.

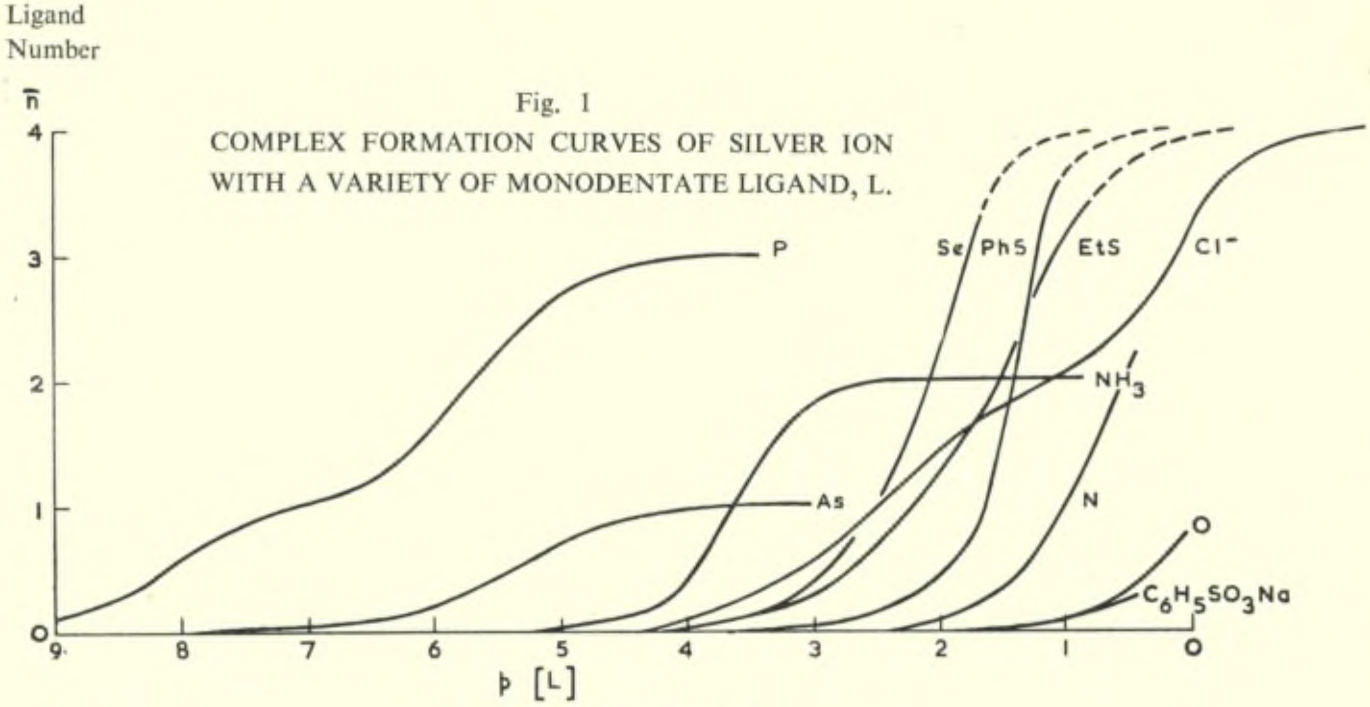

Fig. 1

COMPLEX FORMATION CURVES OF SILVER ION WITH A VARIETY OF MONODENTATE LIGAND, L.

LIGANDS, L.

P = 3 - $\underline{P}$ $Ph_2C_6H_4SO_3Na$
As = $\underline{As}$ $(3 - C_6H_4SO_3Na)_3$
Se = 4 - $\underline{Se}$ Ph $C_6H_4SO_3Na$

Et S = 4 - $\underline{S}$ Et $C_6H_4SO_3Na$
Ph S = 4 - $\underline{S}$ Ph $C_6H_4SO_3Na$
N = 3 - $\underline{N}$ $H_2C_6H_4SO_3Na$

NH_3 = Ammonia
Cl^- = Chloride Ion
O = Anisole - 4 - Sulphonate

The first complex $(AgL)^-$ carries two negative charges, and the second complex $(AgL_2)^{5-}$, if it were formed, would involve the addition to this of another three negative charges. This may account for the evident difficulty in attaching a second molecule of the sulphonated arsine. The arsine is not strictly comparable with the other ligands studied, but owing to difficulty in synthesising the sulphonates it was not possible to get a strictly comparable series.

The relative magnitudes of the first stability constants K_1, relating to the complex formation equilibria

$$Ag^+ + L = AgL^+$$
$$\text{and } Cd^{2+} + L = CdL^{2+}$$

are also indicative of the covalent character of the bonds.

The constants relating to Ag^+ are listed in Table I.

TABLE I.

Stability Constants, K_1, of the Ligands, L, with Silver Ion in Aqueous Solution at Ionic Strength, $\mu(NaClO_4)$ and 25°.

Ligand L	μ	K_1
$PhSO_3Na^+$	1.0	0.9
3—$\underline{N}H_2C_6H_4SO_3Na^*$	1.0	17
4—$\underline{N}H_2C_6H_4SO_3Na^*$	0.1	14
4—$\underline{N}Me_2C_6H_4SO_3Na^*$	0.1	5.7
3—$\underline{P}Ph_2C_6H_4SO_3Na^*$	0.1	1.4×10^8
$\underline{As}$(3—$C_6H_4SO_3Na)^*$	0.2	2×10^5
4—$OMeC_6H_4SO_3Na^+$	1.0	0.76
4—$\underline{S}EtC_6H_4SO_3Na^*$	0.1	415
	0.2	390
4—$\underline{S}PhC_6H_4SO_3Na^*$	0.1	47
$\underline{S}$(4—$C_6H_4SO_3Na)_2^*$	0.2	25
4—$\underline{Se}PhC_6H_4SO_3Na^*$	0.1	430

+ = The co-ordinating atom is not known with certainty, but it is probably an 0 atom of the sulphonate group.
* = the co-ordinating atom is underlined.

The important points about these stability constants are the much greater affinities of the silver ion for the heavier donor atoms than for nitrogen and oxygen, and the very great differences between the constants for the ligands containing nitrogen and those containing phosphorus and arsenic. If the entropy factors remain constant, the difference between the constants indicates a difference of bond energy between the Ag — N and the Ag — P bonds of the order of 11 k cal. If the differences between the stabilities of the amine and phosphine complexes are due to dative π-bonding in the Ag — P bond, we might expect the difference between the corresponding complexes in the cadmium series to be much smaller. This we find to be so.

The cadmium ion is isoelectronic with the silver ion, but because of the greater positive charge on the nucleus we might expect electrons from its $d\varepsilon$-orbitals to be much less readily available for dative π-bond formation than in the case of silver. We therefore measured the first stability constants in the system :

$$Cd^{2+} + NH_2C_6H_4SO_3^- \text{ and } Cd^{2+} + PPh_2C_6H_4SO_3^-.$$

Both ligands are weak complexing agents with cadmium, and the constants, K^1, are of the order 10 in each case. This contrast between silver and cadmium cannot be explained on any electrostatic theory of complex formation, but is very strong evidence that covalent bonding, and especially double bonding, is important in the complexes of silver with the heavier donor atoms.

M. Jørgensen. — 1. By what methods is the trigonal bipyramidal configuration of (Cu dip_2J) ClO_4 supported? In the rare cases, where four nitrogen atoms are not bound co-planar to copper (II), the spectra (of Cu $tren^{++}$, Cu $phen_2^{++}$, Cu dip_2^{++} and Cu $tren^{++}$ with one or two ammonia molecules) might rather suggest a cis-octahedral configuration. However, due to the Jahn-Teller effect, the tetrahedral complexes of copper (II) [and of nickel (II)] may be distorted such that they resemble cis-octahedral complexes much.

2. If RuF_5 is monomeric and trigonal-bipyramidal, it is one of the few cases where a d^3 system is not a 6-coordinated in a regular octahedron. Is there anything known about its absorption spectrum?

3. General remarks of nomenclature :

I agree that "ligand field theory" is a better name than "crystal field theory" but will the two words be used synonymously, or will the "crystal field theory" denote the electrostatic theory with pure *d*-orbitals, which are not intermixed with the orbitals of the ligands? A name does not necessarily have the intrinsic significance of its parts; thus, I do not agree with Voltaire in his criticism of the Holy Roman Empire, which was neither holy, nor roman, nor an empire. Thus the name "crystal field theory" does not necessarily imply a connection with crystals. However, the exclusive importance of the first co-ordination sphere for the energy levels of transition group complexes suggests much the better name "ligand field theory". The energy difference between the two levels of a *d*-electron in an octahedral complex is denoted by 10 Dq by Schlapp and Penney, $(E_1 - E_2)$ by Ilse and Hartmann, $\frac{10}{21}$ K by Owen, Q by Williams, and Δ by Owen and Griffith. The first symbol seems too complicated, since the factors 10, D and *q* no longer have a clear meaning. $(E_1 - E_2)$ might be substituted by $(E_3 - E_5)$ as the energy difference between γ_3^- and γ_5^- electrons. However, it would probably be better to choose a single letter for the quantity, and Δ is proposed.

I hope that we all agree in Mulliken's proposal to use capital letters for the quantum numbers of systems (atoms, ions, molecules) and small letters for electrons and orbitals.

Finally, it may be discussed, if the Mulliken nomenclature a_1, a_2, e, t_1 and t_2 is to be substituted for the Bethe nomenclature γ_1, γ_2, γ_3, γ_4 and γ_5 for orbitals in complexes with the cubic symmetry O_h. It is the only point where I hesitate to conform with the viewpoint of Dr Orgel, since γ_n is an useful expression for an arbitrary orbital, and since the majority of ligand field theoreticists (Van Vleck, Van Santen and van Wieringen, Hellwege, in later papers Hartmann, and the chemical physicists of Copenhagen) actually utilizes the quantum numbers γ_n which reminds an atomic spectroscopist of the angular momentum quantum number 1. However, it can cordially be recommended to refer to both sets of quantum numbers in papers, which are on the border-line to infra-red spectroscopy and general molecular theory.

M. Nyholm. — I shall reply to the points raised in turn.

1. As yet all know of $(Cu\ Dipy_2\ I)\ ClO_4$ is that the Cu^{II} atom is five covalent in nitrobenzene (unless a $PhNO_2$ molecule occupies

the sixth position) *and* that a moment of 2.8. B.M. is observed. According to Prof. D.P. Craig, the large orbital contribution in the latter is not expected in a square, an octohedral or a square pyramidal molecule. It is however expected in a trigonal bipyramidal molecule. Unless we have X-ray evidence our suggested structure must be regarded as tentative.

2. Nothing is known of the absorption spectrum of RuF_5, at least to my knowledge.

3. One of my reasons for suggesting that we use the term " ligand field " instead of " crystal field " theory is to overcome the very serious effects that it has on those first looking into the field.

There is a great need for the presentation of quantum mechanical ideas to chemists who are unfamiliar with the more mathematical details that any phrases which are likely to give erroneous first impressions are best avoided. I certainly agree with the need for a generally accepted symbol for the energy separation between the $d\varepsilon$ and $d\gamma$ orbitals in a cubic field. Personnaly I prefer Δ.

M. D'Or. — Je voudrais demander aux spécialistes du domaine des complexes formés par les métaux de transition si de nouveaux travaux ont été effectués récemment au sujet des interactions entre ions centraux dans les cristaux de complexes paramagnétiques et notamment si l'effet du champ magnétique dû aux ions métalliques se marque par une démultiplication observable du niveau fondamental de ces ions lorsque l'on passe d'une solution solide diluée du complexe avec une substance diamagnétique, au complexe pris à l'état de cristal pur.

M. Orgel. — I am not aware of any recent work on this subject. There is a good deal of work on the interaction of ions in magnetically concentrated solids. In general one gets a broadening rather than a splitting of the paramagnetic resonance absorption, although there are a few cases where bonds are split. These interactions desappear if the paramagnetic ion is diluted by forming a solid solution in a diamagnetic crystal.

M. Ubbelohde.

Introducing various discussions — " Stable " — " Stability ".

1. It would be useful if a clear distinction were made between various meanings of the words " stable " and " stability ". From the quantitative aspect, " stability " could be measured for complex compounds either in terms of free energy differences, or entropy differences, or enthalpy differences. Whilst the last of these is probably most directly related to bond problems, a clear statement as to which measure is being used would be preferable to the rather vague use of " stability ".

2. *Crystal field and ligand field.*

Can contributors agree whether a clear distinction should be made between the terms ligand field theory and crystal field theory, and if so, what is the distinction? Alternatively, are the two expressions best used interchangeably?

M. Nyholm. — When dealing with complex ions like $[Co(NH_3)_6]^{+++}$ or complex molecules like $(PtCl_2, 2NH_3)^0$ where we are concerned only with the field arising from the attached ligands, I prefer the term " ligand field ". However I agree that in those ionic crystals wherein the field arises from interactions throughout the whole crystal (or domain) the term crystal field theory is rightly applicable.

M. Ubbelhode. — In the case of the interlamellar compounds of graphite, the magnetic findings can probably be interpreted in terms of a transfer of electrons between the added molecules and the layers of fused aromatic nuclei. This transfer may take place either way. If graphite is regarded as a crystal with one full electron band separated by zero energy gap from the next empty band, an approximate representation is to regard electron donor additives, such as potassium, as transferring electrons to the empty band, whilst acceptor additives, such as bromine, probably abstract electrons from the full band forming positive holes. Either process leads to a marked increase in electrical conductivity, which is what is actually observed.

For additives of simple electronic structure, such as bromine or potassium, or other alkali metals, measurements of the changes of electrical properties throw important additional light on the transfer mechanism.

Measurements of the Kall effect verify that bromine abstracts electrons and potassium adds electrons to the aromatic macromolecules. However, the transfer is statistical and cannot be regarded as localised at particular groups. From obvious analogies with the Pauling model for metals we have termed these quasi-metallic bonds, involving cooperative process extending statistically over many aromatic groups in the crystal.

This brings one to a closer examination of the interesting differences described by Prof. Nyholm, relating to complexes of cobalt sulphocyanide in the solid state and in solution.

The fact that polymer bonds are observed in the solid, but not in the solutions described, raised the interesting and crucial question as to what would happen in really strong solutions. It must be stressed that two quite different kinds of behaviour can be foreseen, the distinction between which has a bearing on a real discrimination between " crystal fields " and " ligand fields ". Either :

(1) the strong solutions will show " polymer bonds " of the type —Co—CNS—Co— in which case true ligand field effects can be discussed in terms of what happens around each CNS group independently of next nearest neighbours;

Or (2) polymer bonds only develop to any appreciable extent in an ordered cooperative system, i.e. the crystal lattice, in which case a true *cooperative crystal field* is required.

An analogous instance of how the change from the ordered environment in a crystal lattice to the disordered arrangement in a melt or solution affects ligand fields can be found in the behaviour of certain acid hydrates, such as nitric acid monohydrate H_2O, HNO_3. In the crystals, infra-red and other studies indicate that the structure can be described as $NO_3^-OH_3^+$ whereas in the melt the molecules are predominantly H_2O, and HNO_3. Here the order in the crystal lattice ensures a cooperative crystal field of quite high symmetry around each NO_3^- and OH_3^+. This permits the ligand stability of OH_3^+ to be exerted. But on melting the action of neighbours on OH_3^+ is much less symmetrical and the HNO_3 molecule has a higher stability than NO_3^- under such conditions.

M. Nyholm. — We are at present studying the effect of concentration upon the magnetic behaviour of solutions of —NCS complexes wherein association is possible.

M. Hägg. — Referring to the thiocyanate group being coordinated to two metal atoms I want to mention that Lindqvist in my laboratory has found that the silver thiocyanate structure contains chains —Ag—SCN—Ag—SCN—.

M. Bjerrum. — To Dr Chatt I should remark that I still consider normal for the silver ion to have the characteristic coordination number two and the maximum coordination number four. So far as I know the silver ion exibits these coordination numbers towards ligands as Cl^-, SCN^- and CN^-, and has very distinctly the coordination number two towards the ligands to which it is bound through oxygen or nitrogen atoms. Only in case of ligands as e.g. phosphines, arsines,etc. giving special possibilities of strong π-bonding, the conditions may be changed. I should also like to emphasize that this applies still more to Au^+, Cu^+ and Hg^{++} and that I do not remenber any cases, where these metal ions deviate from having the characteristic coordination number two.

Absorption Spectra of Complexes with Unfilled *d*-Shells

Chr. KLIXBÜLL JÖRGENSEN

The complexes of the transition group metals absorb light in the wavenumber range 8.000 - 40.000 cm^{-1}. The transition group ions are characterized either by having in a shell from one to nine of the ten possible *d*-electrons with the same principal quantum number 3, 4, or 5, or by having from one to thirteen of the fourteen possible 4*f*- or 5*f*-electrons (the lanthanides and actinides). The absorption bands of ions with partly filled *f*-shells are very narrow and their positions do not shift much, when the ligands are changed. These bands are comparable with the spectral lines of gaseous atoms and ions, and the bands may be identified as transitions from the groundstate to a set of excited levels as predicted by application of quantum mechanics to f^n-electron configurations (19-25-28-32-41-45-54-67-68-72-73-75-78-122-130-131-138-143-144).

The situation is markedly different for d^n-systems, which will be the main subject of this paper. It is known that cobalt (III) or nickel (II) form complexes of green, blue, purple, red, and yellow colours. But when the absorption spectra are measured, they are seen to consist of a low number of absorption bands, 2-3 in the case of cobalt (III) and 4 in the case of nickel (II), which are shifted when the ligands are changed. The spectra are determined almost unequivocally by the first co-ordination sphere, i.e. the nearest environment of atoms from the ligands, which « touch » the central metal ion. Tsuchida (148) has arranged the ligands in a spectrochemical series according to their shifting effect on the spectra. This series is the same regardless of the central ion, and the order of ligands is roughly determined by the ligand atom nearest to the central ion :

$$\mathrm{Br} < \mathrm{Cl} < \mathrm{F} < \mathrm{O} < \mathrm{N}$$

Highly polarizable anions such as NO_2^- and CN^- are situated further towards the right-hand side. Secondly, a rule of « average environment » can be established : the ligands corresponding to a mixed complex such as $Ni(NH_3)_4(H_2O)_2^{++}$ has an effective place in the spectrochemical series at the position found by taking the average of the positions of the single ligands. In the case of some mixed complexes, the absorption bands are split into several components.

The presence of an unfilled *d*-shell is no necessary condition for colour; thus, the iodo complexes of silver (I), mercury (II) or bismuth (III) are intensely coloured.

Also, some of the strong absorption bands (with the molar extinction coefficient ε = 1.000 - 10.000) of transition group complexes can be ascribed to an electron transfer from the ligand to the central ion. This process is possible also in d^0- and d^{10}-systems and in complexes, containing the same element in different oxidation states ($^{90-110}$). The electron transfer requires less energy, the more reducing the ligand, and oxidizing the metal ion. In the excited state, the central ion thus achieves a lower oxidation number. While the strongly coloured complexes MnO_4^- and CrO_4^{--} do not contain *d*-electrons in their groundstate, they may thus be expected to do so in their excited states ($^{55-56}$).

The following sections will concentrate upon the weaker bands (with ε from 0.01 to 200) which are caused by internal transitions between the levels of the d^n-configurations. Bethe (^{18}) elaborated a theory of the action of crystal fields on a partly filled shell in an ion. Since the perturbations in question decrease so rapidly with the distance from the central ion, the immediate environment, i.e. the first co-ordination sphere is sufficient, also in solution, to maintain similar electrostatic fields as in the lattice of a crystal. It is interesting that the central ions in most transition group complexes are surrounded by ligands, arranged in regular or distorted octahedrons. Since the number and relative positions of the levels of an electron configuration are determined by the symmetry of the crystal field, most d^n-complexes are much more similar in behaviour than expected. However, the crystal field in f^n-complexes can have much lower symmetry.

Even though Finkelstein and Van Vleck (38) applied Bethe's theory to the spin-forbidden absorption bands of chromium (III), e.g. in the ruby, and Abragam and Pryce (1) discussed cobalt (II) spectra, most applications before 1951 of the crystal field theory was made to magnetochemical problems (66-127-132-149-150-152). Then, Ilse and Hartmann (62) interpreted the weak band of titanium (III) hexaaquo ions as caused by the transition between the levels formed by splitting of the ^{2}D-level of the free ion.

In the following five years, a very large number of publications have appeared on the interpretation of absorption spectra. Table III is a review arranged according to the number of *d*-electrons in the complex. In the following, the quantum numbers of a single electron (l, γ_n, ...) will be denoted by small letters and of a system (an atom, an ion or a molecule) by capital letters (L, S, Γ_n, ...). Bethe (18) found for crystal fields of symmetry O_h (found in regularly octahedral complexes) that five types of levels are possible: Γ_1, Γ_2, Γ_3, Γ_4, and Γ_5, which are 1, 1, 2, 3, 3 times orbitally degenerate respectively. They are denoted by A_1, A_2, E, T_1, and T_2 by Mulliken (106). In atoms with Russell-Saunders coupling (28) the multiplet terms can be described by the electron configuration and the two quantum numbers S and L (representing the total spin and the total angular momentum). The analogous description for an ion in a crystal field is : electron configuration, S, Γ_n. Bethe (18) found the possible levels Γ_n originating from a term with a given L in the free ion (or of γ_n from a given l) e.g. for O_h :

L	Spectroscopic notation	Bethe's quantum numbers
0	S	Γ_1
1	P	Γ_4
2	D	$\Gamma_3 + \Gamma_5$
3	F	$\Gamma_2 + \Gamma_4 + \Gamma_5$
4	G	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$
5	H	$\Gamma_3 + 2\Gamma_4 + \Gamma_5$
.....		......

Thus, a *d*-electron (l = 2) has two possible energy levels, γ_3 and γ_5, of which the former has the higher energy, when the six ligands are negatively charged or polarized by the positive central ion. (Geometrically, this can be visualized by γ_3-electrons being concentrated in space near the six ligands, while γ_5-electrons have lower potential energy in the eight directions between the ligands). The energy difference is denoted by $(E_1 - E_2)$ or 10 Dq. In systems with more than one *d*-electron, the levels Γ_n can either be described by sub-shell configurations $\gamma_5{}^a\gamma_3{}^b$ or by the original term L in the free ion. If *q* of these levels have the same S and Γ_n (denoted by ${}^{2S+1}\Gamma_n$) their energy can be given as the eigen-values of a matrix of *q*'th degree. The non-diagonal elements of this matrix can either contain multipla of $(E_1 - E_2)$ (cf. 38-111) or term differences, e.g. expressed in Slater-Condon-Shortley or Racah parameters (cf. 9-109-146). It is proposed to name the two types of matrices weak-field-diagonal and strong-field-diagonal matrices according to the asymptotes represented by the diagonal elements. The final results of the two types of calculation are of course equivalent, but the concepts " weak " and " strong " crystal field have been much applied in literature for the approximation introduced by using the diagonal elements of the appropriate matrices only. If the term differences are not changed from their free ion values, and if other electron configurations are not intermixed, the energy levels in O_h will vary as a function of one crystal field strength $(E_1 - E_2)$ only. More parameters are necessary in crystal fields of lower symmetry.

Tanabe and Sugano (146) completed the electrostatic calculations on d^n-systems in O_h by giving the full strong-field-diagonal matrices. In Table I are given the diagonal elements of energy for the lowest levels to which transitions from the groundstate can be observed as absorption bands. The levels are arranged in groups with identical sub-shell configuration and hence with equal values of the coefficient *a* in the energy expression $a\,(E_1 - E_2) + bB + cC$. In the cases, where for small values of $(E_1 - E_2)$ the connection of a level with a given value of L is obvious, the term is given in parenthesis after the appropriate level, viz. ${}^3\Gamma_2(F)$. The Racah parameters B $(= F_2 - 5F_4$ after Slater, Condon, Shortley) and C $(= 35F_4)$ describe the energy differences between the terms in the free ion, and Table II gives a representative set of terms for some systems. The ratio F_2/F_4 is at least 9 and is for hydrogen-like 3*d*-wave functions 14, corresponding to $C/B = 8.75$ and 3.89, respectively. Generally, C/B is assumed to vary between 5 and 4.

As pointed out by van Santen and van Wieringen (129) d^4-, d^5-, d^6- and d^7-systems can exhibit different groundstates with differing

TABLE I

The energy of the lowest $\gamma_5^a\gamma_3^b$ levels in octahedral complexes expressed in the Racah parameters B and C of electrostatic interaction between *d*-electrons and the crystal field strength $(E_1 - E_2)$. The corresponding Slater-Condon-Shortley parameters (28) are $B = F_2 - 5\,F_4$ and $C = 35\,F_4$. The energy difference between the actual level and the groundstate in the gaseous ion is given. The non-diagonal elements between levels with the same Γ_n of different sub-shell configurations $\gamma_5^a\gamma_3^b$ are not considered. The table can be implied from the results of Tanabe and Sugano (146), but the content has earlier partly been discussed by many authors (9-18-38-42-47-71-74-109-111-116).

Electron configuration	Sub-shell configuration	Level	$a(E_1 - E_2)$	$+ b$ B	$+ c$ C
d^1	γ_5	$^2\Gamma_5$ (D)	-0.4	0	0
	γ_3	$^2\Gamma_3$ (D)	$+0.6$	0	0
d^2	γ_5^2	$^3\Gamma_4$ (F)	-0.8	$+3$	0
		$^1\Gamma_3$ (D)	-0.8	$+9$	$+2$
		$^1\Gamma_5$ (D)	-0.8	$+9$	$+2$
		$^1\Gamma_1$ (G)	-0.8	$+18$	$+5$
	$\gamma_5\gamma_3$	$^3\Gamma_5$ (F)	$+0.2$	0	0
		$^3\Gamma_4$ (P)	$+0.2$	$+12$	0
		. . .			
	γ_3^2	$^3\Gamma_2$ (F)	$+1.2$	0	0
		. . .			
d^3	γ_5^3	$^4\Gamma_2$ (F)	-1.2	0	0
		$^2\Gamma_3$	-1.2	$+9$	$+3$
		$^2\Gamma_4$	-1.2	$+9$	$+3$
		$^2\Gamma_5$	-1.2	$+15$	$+5$
	$\gamma_5^2\gamma_3$	$^4\Gamma_5$ (F)	-0.2	0	0
		$^4\Gamma_4$ (F)	-0.2	$+12$	0
		. . .			
	$\gamma_5\gamma_3^2$	$^4\Gamma_4$ (P)	$+0.8$	$+3$	0
	. . .	. . .			
d^4	γ_5^4	$^3\Gamma_4$	-1.6	$+6$	$+5$
		. . .			
	$\gamma_5^3\gamma_3$	$^5\Gamma_3$ (D)	-0.6	0	0
		. . .			
	$\gamma_5^2\gamma_3^2$	$^5\Gamma_5$ (D)	$+0.4$	0	0
	. . .	. . .			

TABLE 1 *(continued)*

Electron configuration	Sub-shell configuration	Level	$a(\mathrm{E}_1 - \mathrm{E}_2)$	$+ b\,\mathrm{B}$	$+ c\,\mathrm{C}$
d^5	γ_5^5	$^{2}\Gamma_5$	-2.0	$+15$	$+10$
	$\gamma_5^4\gamma_3$	$^{4}\Gamma_4$ (G)	-1.0	$+10$	$+6$
		$^{4}\Gamma_5$ (G)	-1.0	$+18$	$+6$
		. . .			
	$\gamma_5^3\gamma_3^2$	$^{6}\Gamma_1$ (S)	0.0	0	0
		$^{4}\Gamma_1$ (G)	0.0	$+10$	$+5$
		$^{4}\Gamma_3$ (G)	0.0	$+10$	$+5$
		$^{4}\Gamma_5$ (D)	0.0	$+13$	$+5$
		$^{4}\Gamma_3$ (D)	0.0	$+17$	$+5$
		$^{4}\Gamma_4$ (P)	0.0	$+19$	$+7$
		$^{4}\Gamma_2$ (F)	0.0	$+22$	$+7$
		. . .			
	$\gamma_5^2\gamma_3^3$	$^{4}\Gamma_4$ (F)	$+1.0$	$+10$	$+6$
		$^{4}\Gamma_5$ (F)	$+1.0$	$+18$	$+6$
	. . .	. . .			
d^6	γ_5^6	$^{1}\Gamma_1$	-2.4	$+5$	$+8$
	$\gamma_5^5\gamma_3$	$^{3}\Gamma_4$	-1.4	$+5$	$+5$
		$^{3}\Gamma_5$	-1.4	$+13$	$+5$
		$^{1}\Gamma_4$	-1.4	$+5$	$+7$
		$^{1}\Gamma_5$	-1.4	$+21$	$+7$
	$\gamma_5^4\gamma_3^2$	$^{5}\Gamma_5$ (D)	-0.4	0	0
		. . .			
	$\gamma_5^3\gamma_3^3$	$^{5}\Gamma_3$ (D)	$+0.6$	0	0
	. . .	. . .			
d^7	$\gamma_5^6\gamma_3$	$^{2}\Gamma_3$	-1.8	$+7$	$+4$
	$\gamma_5^5\gamma_3^2$	$^{4}\Gamma_4$ (F)	-0.8	$+3$	0
		. . .			
	$\gamma_5^4\gamma_3^3$	$^{4}\Gamma_5$ (F)	$+0.2$	0	0
		$^{4}\Gamma_4$ (P)	$+0.2$	$+12$	0
		. . .			
	$\gamma_5^3\gamma_3^4$	$^{4}\Gamma_2$ (F)	$+1.2$	0	0
		. . .			
d^8	$\gamma_5^6\gamma_3^2$	$^{3}\Gamma_2$ (F)	-1.2	0	0
		$^{1}\Gamma_3$ (D)	-1.2	$+8$	$+2$
		$^{1}\Gamma_1$ (G)	-1.2	$+16$	$+4$
	$\gamma_5^5\gamma_3^3$	$^{3}\Gamma_5$ (F)	-0.2	0	0
		$^{3}\Gamma_4$ (F)	-0.2	$+12$	0
		$^{1}\Gamma_5$ (D)	-0.2	$+8$	$+2$
		$^{1}\Gamma_4$ (G)	-0.2	$+12$	$+2$
	$\gamma_5^4\gamma_3^4$	$^{3}\Gamma_4$ (P)	$+0.8$	$+3$	0
		. . .			

S values (which determines the magnetic properties). This can be explained from the purely electrostatic crystal field theory (even though covalency, i.e. intermixing of molecular orbitals, may be actually important) by the competition between the levels :

d^4 : ${}^5\Gamma_3(D)$ and ${}^3\Gamma_4$
d^5 : ${}^6\Gamma_1(S)$ and ${}^2\Gamma_5$
d^6 : ${}^5\Gamma_5(D)$ and ${}^1\Gamma_1$
d^7 : ${}^4\Gamma_4(F)$ and ${}^2\Gamma_3$

It is seen from Table I that for increasing values of the crystal field strength ($E_1 - E_2$), the magnetically anomalous states with lower

TABLE II

Energy levels in the free gaseous ions, expressed in Racah's parameters B and C of electrostatic interaction between *d*-electrons. The energy is given with the groundstate as zero-point. In multiplet terms with several levels with various J. the energy refers to the centre of gravity (21). In actual cases, C ≅ 4 B (141).

$d^2 \equiv d^8$	${}^3F$	0
	${}^1D$	5 B + 2 C
	${}^3P$	15 B
	${}^1G$	12 B + 2 C
	${}^1S$	22 B + 7 C
$d^3 \equiv d^7$	${}^4F$	0
	${}^2G$	4 B + 3 C
	${}^4P$	15 B
	${}^2P$	9 B + 3 C
	${}^2H$ . . .	9 B + 3 C
d^5	${}^6S$	0
	${}^4G$	10 B + 5 C
	${}^4P$	7 B + 7 C
	${}^4D$	17 B + 5 C
	${}^4F$ . . .	22 B + 7 C

TABLE III

Absorption Bands of Transition Group Complexes with one to nine *d*-electrons. In each group with the same number of *d*-electrons, the ions are arranged according to increasing atomic number.

The following abbreviations will be used for the ligands :

ox^{--} = oxalate
gly^{-} = aminoacetate
ata^{-3} = nitrogentriacetate
enta^{-4} = ethylenediaminetetraacetate

en = ethylenediamine
temeen = C, C, C', C' tetramethyl-ethylenediamine
tren = β, β', β'' tris(ethylamino) amine
py = pyridine

dip = α, α'-dipyridyl
phen = o-phenanthroline

Electron configuration	Ion	Ligands	Wavenumbers of maxima and assignment of excited level	Remarks	References
$3d^1$	Titanium (III)	6 H_2O	20300 $^2\Gamma_3(D)$	rhombic splitting	49, 62, 77
		enta^{-4}	18400		82
		3 SCN^-, 3 H_2O?	18900		88
$3d^1$	Vanadium (IV)	2 OH^-, xH_2O	13100, (15800)	not octahedral	39, 125
		enta^{-4}, O^{--}(?)	12800, 17200	unknown structure	82
		2 ox^{--}, O^{--} (?)	12600, 16200	»	51
		SCN^-, O^{--}	13900, 17200	»	39
		4 Cl^-	9000	tetrahedral	111
$3d^1$	Manganese (VI)	4 O^{--}	electron transfer bands	»	30
$4d^1$	Niobium (IV)	?, 13 MHCl	20900		30
		?, 8 MHCl	14300		30
$4d^1$	Molybdenum (V)	O^{--}, 5 Cl^-	14000 tetragonal splitting of cubic $^2\Gamma_5(D)$		58, 59
$4d^1$	Ruthenium (VI)	4 O^{--}	electron transfer bands	tetrahedral	29
$3d^2$	Vanadium (III)	6 H_2O	17700 $^3\Gamma_5(F)$, 25600 $^3\Gamma_4(P)$		47, 48, 109
		3 ox^{--}	16500 $^3\Gamma_5(F)$, 23500 $^3\Gamma_4(P)$		51
		enta^{-4}	$<$ 8000?, 12500, 19400, 22600	peculiar	82
		5 H_2O, OH^-	second band at 23200 very high		39
		6 SCN^-	16700 $^3\Gamma_5(F)$		39
$4d^2$	Niobium (III)	?, 10 MHCl	15400, 18900, 22500	cf. Venta$^-$	30
$4d^2$	Ruthenium (VI)	4 O^{--}	electron transfer bands	tetrahedral	29
$5d^2$	Wolfram (IV)	? ,12 MHCl	19100 ($\varepsilon \sim 600$)	electron transfer?	88, 108
$3d^3$	Vanadium (II)	6 H_2O	12600 $^4\Gamma_5(F)$, 18200 $^4\Gamma_4(F)$, 26500 $^4\Gamma_4(P)$		9, 71, 89, 110, 111, 116

$3\,d^3$	Chromium (III)	$6\ H_2O$	17400 $^4\Gamma_5$(F), 24700 $^4\Gamma_4$(F), 37000 $^4\Gamma_4$(P)		9, 53, 74, 109, 111, 137
		$6\ O^{--}$(ruby)	15000 $^2\Gamma_3$, 15500 $^2\Gamma_4$, 18500 $^4\Gamma_4$(F), 22000 $^2\Gamma_5$, 24400 $^4\Gamma_4$(F)		38, 137
		3 en	21900 $^4\Gamma_5$(F), 28600 $^4\Gamma_4$(F)		74, 137
		3 ox^{---}	14350 $^2\Gamma_3$, 17400 $^4\Gamma_5$(F), 24000 $^4\Gamma_4$(F)		51, 71, 104, 137
		various ligands	very large number of spectra interpreted		53, 97, 137
$3\,d^3$	Manganese (IV)	$6\ O^{--}$ (heteropoly-molybdate)	14300 $^2\Gamma_3$, 21400 $^4\Gamma_5$(F)		140
		$6\ F^-$	13200, 14200, 15200, 16700 $^2\Gamma_3$, $^2\Gamma_4$		88, 137
$4\,d^3$	Niobium (III)	?, 10 MHCl	13700 (?) $^2\Gamma_3$, 22700 $^4\Gamma_5$(F)		30
$4\,d^3$	Molybdenum (III)	$6\ Cl^-$	14800 $^2\Gamma_3$, 19200 $^4\Gamma_5$(F), 24200 $^4\Gamma_4$(F)		27, 51
$4\,d^3$	Ruthenium (V)	$6\ F^-$, $5\ F^-$	predicted from colour : 16000 $^2\Gamma_3$		57, 93
$5\,d^3$	Wolfram (III)	$Cl^-(W_2Cl_9^{-3})$	13200 ($\varepsilon \sim 25$) $^2\Gamma_3$, 16300 ($\varepsilon \sim 40$) $^2\Gamma_4$, 22200 ($\varepsilon \sim 1200$)		88, 94
$5\,d^3$	Rhenium (IV)	$6\ Cl^-$	14200 $^2\Gamma_3$, 15700 $^2\Gamma_4$, electron transfer	vibrational structure	79, 102, 126
		$6\ Br^-$	13200 $^2\Gamma_3$, 15100 $^2\Gamma_4$, electron transfer bands		79, 126
$3\,d^4$	Chromium (II)	$6\ H_2O$	13900 $^5\Gamma_5$(D)		71, 89, 146
		$5\ SCN^-$?	16500 $^5\Gamma_5$(D)		3, 88
$3\,d^4$	Manganese (III)	$6\ H_2O$	21000 $^5\Gamma_5$(D)		48
		3 ox^{---}	10300 $^3\Gamma$, 20100 $^5\Gamma_5$(D)		88
		$6\ CN^-$	21000, electron transfer bands	groundstate $^2\Gamma_5$	128
$4\,d^4$	Ruthenium (IV)	?	mainly electron transfer bands		153, 154
$4\,d^4$	Rhodium (V)	?	electron transfer bands		4, 5, 44
$5\,d^4$	Rhenium (III)	$4\ Cl^-$	19600	the band can split	15
$3\,d^5$	Manganese (II)	$6\ H_2O$	18800 $^4\Gamma_4$(G), 23000 $^4\Gamma_5$(G), 24900 $^4\Gamma_3$(G), 25150 $^4\Gamma_1$(G), 28000 $^4\Gamma_5$(D), 29700 $^4\Gamma_3$(D), 32400 $^4\Gamma_4$(P), 35400 $^4\Gamma_2$(F), 36900 $^4\Gamma_4$(F), 40600 $^4\Gamma_5$(F)		40, 71, 80, 89, 111, 113 114,134
		$2\ Cl^-$, $4\ H_2O$	19300 $^4\Gamma_4$(G), 23400 $^4\Gamma_5$(G), 24600 $^4\Gamma_3$(G) and $^4\Gamma_1$(G), 27600 $^4\Gamma_5$(D), 29200 $^4\Gamma_3$(D), 31600 $^4\Gamma_4$(P),		88, 134
		enta^{-4}	18800 $^4\Gamma_4$(G), 21300 $^4\Gamma_5$(G), 23800 $^4\Gamma_3$(G), 24300 $^4\Gamma_1$(G), 27200 $^4\Gamma_5$(D), 29200 $^4\Gamma_3$ (D)		88
		3 en	15900 $^4\Gamma_4$(G), 20500 $^4\Gamma_5$(G), 23800 $^4\Gamma_3$(G) and $^4\Gamma_1$ (G)		88
$3\,d^5$	Iron (III)	$6\ H_2O$	12600 $^4\Gamma_4$(G), 18500 $^4\Gamma_5$(G), 24300 and 24600 $^4\Gamma_1$ and $^4\Gamma_3$(G),		71, 111, 121
		$x\ Cl^-$	electron transfer bands		121, 133
		$6\ CN^-$	six electron transfer bands	groundstate $^2\Gamma_5$	84
$3\,d^5$	Ruthenium (III)	$6\ Cl^-$?	19200, four electron transfer bands	»	26, 84, 154
$3\,d^5$	Iridium (IV)	$6\ Cl^-$	electron transfer bands at 17400, 20450, 23200, 24200	»	84
		$6\ Br^-$	electron transfer bands at 13600, 14300, 14800, 17200, 18400, 19600	»	84
$3\,d^6$	Manganese (I)	$6\ CN^-$	from colour : > 25000	groundstate $^1\Gamma_1$	99, 147
$3\,d^6$	Iron (II)	$6\ H_2O$	10400 $^5\Gamma_3$(D), 14400 ?, 19800, 21100, 22200,25900 all $^3\Gamma$		71
		enta^{-4}	9700 $^5\Gamma_3$(D)		82
		$6\ CN^-$	31000 $^1\Gamma_4$, 37000 ? $^1\Gamma_5$	groundstate $^1\Gamma_1$	88

TABLE III *(continued)*

Electron configuration	Ion	Ligands	Wavenumbers of maxima and assignment of excited level	Remarks	References
3 d^6	Cobalt (III)	6 F^-	predicted from colour : 18000 $^5\Gamma_3(D)$	groundstate $^5\Gamma_5(D)$	71, 93
		6 H_2O	16600 $^1\Gamma_4$, 24900 $^1\Gamma_5$	all other cobalt (III) have $^1\Gamma_1$	3, 137
		3 ox^{--}	16500 $^1\Gamma_4$, 23800 $^1\Gamma_5$		104
		3 CO_3^{--}	15700 $^1\Gamma_4$, 22800 $^1\Gamma_5$		82, 137
		6 NH_3	13000 $^3\Gamma_4$, 21000 $^1\Gamma_4$, 29500 $^1\Gamma_5$		82, 109, 146
		3 en	13700 $^3\Gamma_4$, 21400 $^1\Gamma_4$, 29600 $^1\Gamma_5$		81, 82, 109, 146
		6 CN^-	32200 $^1\Gamma_4$, 38600 $^1\Gamma_5$		92
		various ligands	a large number of absorption spectra interpreted		9, 13, 14, 16, 50, 64, 82, 96, 97, 101, 104, 109, 111, ,137, 146 148, 158
3 d^6	Nickel (IV)	6 F^-	predicted from colour : 20000 $^1\Gamma_4$, 28000 $^1\Gamma_5$		93
4 d^6	Ruthenium (II)	?	strong bands	tetragonal groundstate $^3\Gamma$?	84
4 d^6	Rhodium (III)	6 Br^-	18100 $^1\Gamma_4$, 22200 $^1\Gamma_5$	All groundstate $^1\Gamma_1$	83
		6 Cl^-	14700 $^3\Gamma_4$, 19300 $^1\Gamma_4$, 24300 $^1\Gamma_5$		83
		6 H_2O	25500 $^1\Gamma_4$, 32800 $^1\Gamma_5$		83
		3 ox$^-$	19200 $^3\Gamma_4$, 25100 $^1\Gamma_4$, 30000 ? $^1\Gamma_5$		83
		5 NH_3, Cl^-	28700 $^1\Gamma_4$, 36100 $^1\Gamma_5$		83
		5 NH_3, OH^-	31200 $^1\Gamma_4$, 36000 $^1\Gamma_5$		83
		5 NH_3, H_2O	31600 $^1\Gamma_4$, 38100 $^1\Gamma_5$		83
		6 NH_3	32700 $^1\Gamma_4$, 39100 $^1\Gamma_5$		83
		3 en	33200 $^1\Gamma_4$, 39600 $^1\Gamma_5$		83, 95
		trans-2ox^{--}, 2 Cl^-	21300, 25100	tetragonal splitting of $^1\Gamma_4$	86
		cis - 2 ox^{--}, 2 Cl^-	23000 $^1\Gamma_4$, 28400 $^1\Gamma_5$		86
		trans-2 py, 4 Cl^-	20000, 23200	tetragonal splitting of $^1\Gamma_4$	86
		cis - 2py, 4 Cl^-	22400 $^1\Gamma_4$, 28700 $^1\Gamma_5$		86
		trans-4py, 2 Cl^-	24300		86
4 d^6	Palladium (IV)	6 F^-	predicted : 26000 and 32000		93
5 d^6	Iridium (III)	6 Br^-	16800 $^3\Gamma_4$, 22400 $^1\Gamma_4$, 25800 $^1\Gamma_5$	All groundstate $^1\Gamma_1$	83
		6 Cl^-	16300, 17900 $^3\Gamma_4$, 24100 $^1\Gamma_4$, 28100 $^1\Gamma_5$		83
		5 NH_3, Cl^-	27800 $^3\Gamma_4$, 35000 $^1\Gamma_4$		83

		3 en	33100 $^3\Gamma_4$, 40200 $^1\Gamma_4$	83
		py, 5 Cl^-	18500 $^3\Gamma_4$	86
		trans-2py, 4 Cl^-	19400 $^3\Gamma_4$	86
		cis - 2 py, 4 Cl^-	21600 $^3\Gamma_4$	86
		various ligands	complexes prepared by M. Delépine	86
5 d^6	Platinum (IV)	6 Br^-	19100 $^3\Gamma_4$, 23000 ? $^1\Gamma_4$, electron transfer bands	84
		6 Cl^-	22100 $^3\Gamma_4$, 28300 $^1\Gamma_4$, 38200 ($\varepsilon \sim 25000$ electron transfer)	84
		6 F^-	31500, 36400 $^1\Gamma_4$ and $^1\Gamma_5$?	156
		5 NH_3, Cl^-	35000 $^3\Gamma_4$?	84
		trans-2 en, 2 Cl^-	30000 $^3\Gamma$?. 38000 $^1\Gamma$?	12
		various amines		46, 84
		NH_2^-, Cl^-, OH^-	partly electron transfer in anion complexes	46, 84
3 d^7	Cobalt (II)	6 H_2O	8100 $^4\Gamma_5(F)$, 11300 $^2\Gamma_3$, 16000 $^4\Gamma_2(F)$, 19400 and 21550 $^4\Gamma_4(P)$	1, 10, 70 71, 111, 146
		$enta^{-4}$	9100 $^4\Gamma_5(F)$, 16300 $^4\Gamma_2(F)$, 19900, 20600, 21500 $^4\Gamma_4(P)$	82
		6 NH_3	9000 $^4\Gamma_5(F)$, 18500 $^4\Gamma_2(F)$,21100 $^4\Gamma_4(P)$	10
		3 en	9800 $^4\Gamma_5(F)$, 18700 $^4\Gamma_2(F)$, 21700 $^4\Gamma_4(P)$	10
		4 Cl^-	6300 $^4\Gamma_4(F)$, 14300-16400 $^4\Gamma_4(P)$, many $^2\Gamma$ tetrahedral	10, 33, 91, 111
3 d^8	Nickel (II)	6 H_2O	8500 $^3\Gamma_5(F)$, 13500 $^3\Gamma_4(F)$, 15400 $^1\Gamma_3(D)$, 18400 $^1\Gamma$, 22000 $^1\Gamma$, 25300 $^3\Gamma_4(P)$	8, 20, 24, 33, 40 43, 52, 70, 71, 74, 77, 80, 82, 85, 109, 111, 116 124, 127, 146,
		3 gly^-	10100 $^3\Gamma_5(F)$, 13100 $^1\Gamma_3(D)$, 16600 $^3\Gamma_4(F)$, 27600 $^3\Gamma_4(P)$	82
		6 NH_3	10750 $^3\Gamma_5(F)$, 13150 $^1\Gamma_3(D)$, 17500 $^3\Gamma_4(F)$, 28200 $^3\Gamma_4(P)$	20, 82, 111, 124
		3 en	11200 $^3\Gamma_5(F)$, 12400 $^1\Gamma_3(D)$, 18350 $^3\Gamma_4(F)$, 24000 $^1\Gamma$, 29000 $^3\Gamma_4(P)$	8, 70, 74 82, 111, 124
		3 dip	11500 $^1\Gamma_3(D)$, 12650 $^3\Gamma_5(F)$, 19200 $^3\Gamma_4(F)$	82
		3 phen	11550 $^1\Gamma_3(D)$, 12700 $^3\Gamma_5(F)$, 19300 $^3\Gamma_4(F)$	82, 124
		$enta^{-4}$	10100 $^3\Gamma_5(F)$, 12700 $^1\Gamma_3(D)$, 17000 $^3\Gamma_4(F)$, 26200 $^3\Gamma_4(P)$	82
		$enta^{-4}$, NH_3	10200 $^3\Gamma_5(F)$, 12700 $^1\Gamma_3(D)$, 17200 $^3\Gamma_4(F)$, 26900 $^3\Gamma_4(P)$	85, 135
		ata^{-3}	9500 $^3\Gamma_5(F)$, 13300 $^1\Gamma_3(D)$, 16000 $^3\Gamma_4(F)$, 25600 $^3\Gamma_4(P)$	85
		2 ata^{-3}	10400 $^3\Gamma_5(F)$, 13000 $^1\Gamma_3(D)$, 17400 $^3\Gamma_4(F)$, 27000 and 28600 $^3\Gamma_4(P)$	85
		ata^{-3}, en	9400 $^3\Gamma_5(F)$, 13100 $^1\Gamma_3(D)$, 16900 $^3\Gamma_4(F)$, 27200 $^3\Gamma_4(P)$	85
		tren, 2 H_2O	10500 $^3\Gamma_5(F)$, 12800 $^1\Gamma_3(D)$, 17800 $^3\Gamma_4(F)$, 27800 $^3\Gamma_4(P)$	85
		tren, 2 NH_3	11000 $^3\Gamma_5(F)$, 12750 $^1\Gamma_3(D)$, 18200 $^3\Gamma_4(F)$, 28200 $^3\Gamma_4(P)$	85
		tren, en	11000 $^3\Gamma_5(F)$, 12500 $^1\Gamma_3(D)$, 18700 $^3\Gamma_4(F)$, 29000 $^3\Gamma_4(P)$	85
		tren, gly^-	11200 $^3\Gamma_5(F)$, 12600 $^1\Gamma_3(D)$, 18800 $^3\Gamma_4(F)$, 28200 $^3\Gamma_4(P)$	85
		en, 2 gly^-	10500 $^3\Gamma_5(F)$, 13000 $^1\Gamma_3(D)$, 17300 $^3\Gamma_4(F)$, 28100 $^3\Gamma_4(P)$	85
		2 en, gly^-	10800 $^3\Gamma_5(F)$, 12650 $^1\Gamma_3(D)$, 17900 $^3\Gamma_4(F)$, 28600 $^3\Gamma_4(P)$	85
		en, 4 H_2O	10200 $^3\Gamma_5(F)$, 13600 $^1\Gamma_3(D)$, 15600 $^3\Gamma_4(F)$, 27000 $^3\Gamma_4(P)$	8,85
		2 en, 2 H_2O	10000, 11100 $^3\Gamma_5$ (F), 17500, 18200 $^3\Gamma_4(F)$, 29400 $^3\Gamma_4(P)$	8

TABLE III *(continued)*

Electron configuration	Ion	Ligands	Wavenumbers of maxima and assignment of excited level	Remarks	References
		2 temeen	23100	groundstate $^1\Gamma t_1$	8, 9, 15, 52, 87, 109
$3\ d^8$	Copper (III)	6 F^-	pale green	»	93
		2 JO_6^{-5}	electron transfer absorption	»	98
$4\ d^8$	Palladium (II)	4 Cl^-	23800	»	145, 159
		6 Cl^-	21000	»	145
		6 H_2O	26300	»	145
$5\ d^8$	Platinum (II)	4 Br^-	16600 $^3\Gamma$, 19900 $^3\Gamma$, 24300 $^1\Gamma$	»	6, 87
		4 Cl^-	17700 $^3\Gamma$, 21000 $^3\Gamma$, 25600 $^1\Gamma$, 30300 $^1\Gamma$	»	6, 87, 159, 160
		4 NH_3	35400	»	6, 87
		2 en	35800	»	87
		4 CN^-	very strong bands : 35700, 38700, 39200, 41300	»	87, 95
$3\ d^9$	Copper (II)	6 H_2O	(9400), 12600		7, 22, 111
		4 NH_3, 2 H_2O	16900		7, 22
		6 NH_3	(11700), 15100		7, 22
		2 en, 2 H_2O	18200		21, 22
		3 en	(11800), 16400		21, 22
		2 dip, 2 H_2O	10500, 13900		23, 82
		3 dip	14700		23, 82
		2 phen, 2 H_2O	10200, 13300		23, 82
		3 phen	14700		23, 82
		tren, 2 H_2O	(9600), 11600, (14700)		85
		tren, 1 or 2 NH_3	(11100), 12700, (15400)		85
		2 temeen	18300		85
		$enta^{-4}$	13600		82
		$enta^{-4}$, NH_3	13800		85, 135
		ata^{-3}	11400, 12900		85
		2 ata^{-3}	15200		85
		acetylacetonates with	various solvate ligands		17
		2 gly^-	15800		82
		3 gly	~ 15100		82
$4\ d^9$	Silver (II)	2 dip 4 py	>25000, electron transfer		87, 111

values of S will eventually be the groundstates, because the promotion energy $bB + cC$ does not increase, but rather decreases relative to the values for the free ion.

From the absorption spectra in Table III and the theoretical predictions in Table I, values of $(E_1 - E_2)$ which are given in Table IV can be inferred. It is seen from Table IV that Tsuchida's spectrochemical series can be quantitatively treated, the position being determined by the ratios between the values of $(E_1 - E_2)$ for the considered

TABLE IV

Values of the crystal field strength $(E_1 - E_2)$, also denoted 10 Dq, in octahedral complexes, estimated from absorption spectra. In cases of strong intrinsic tetragonality, viz. in d^4 - and d^9 - systems, the value of $(E_1 - E_2)$ has not been corrected for tetragonal contributions, demonstrating the anomalous conditions. Literature : [24–47–48–71–74–82–83–84–109–111–116–146].

		6 Br^-	6 Cl^-	6 H_2O	6 NH_3	3 en	6 CN^-
3 d^1	Titanium (III)	—	—	20300	—	—	—
3 d^2	Vanadium (III)	—	—	18600	—	—	—
3 d^3	Vanadium (II)	—	—	12600	—	—	—
	Chromium (III)	—	13300	17400	21600	21900	26300
4 d^3	Molybdenum (III)	—	19200	—	—	—	—
3 d^4	Chromium (II)	—	—	13900	—	—	—
	Manganese (III)	—	—	21000	—	—	—
3 d^5	Manganese (II)	—	—	7800	—	9100	—
	Iron (III)	—	—	13700	—	—	—
3 d^6	Iron (II)	—	—	10400	—	—	33000
	Cobalt (III)	—	—	19100	23500	24000	34100
4 d^6	Rhodium (III)	19300	20800	27700	34600	35300	—
5 d^6	Iridium(III)	23400	25300	—	—	41800	—
	Platinum (IV)	25000	30000	—	—	—	—
3 d^7	Cobalt (II)	—	—	9700	10500	11300	—
3 d^8	Nickel (II)	6000	6500	8500	10800	11600	—
3 d^9	Copper (II)	—	—	12600	15100	16400	—

complex and for the hexaaquo ion. Thus, for a given central ion, the value of this ratio is for the hexabromo complex 71 %, and for the hexachloro complex 76 % of the value found for the hexaaquo ion. The corresponding ratios for the ammine complexes are 125-130 %, and for the hexacyanide complex, it varies between 150-300 %. Excepting the irregular cyanide complexes, the values of $(E_1 - E_2)$ are generally 40-80 % higher for a trivalent ion then for the isoelectronic divalent ion. A quadrivalent ion has an even higher crystal field strength. For the same oxidation state, the values of $(E_1 - E_2)$ do not vary very much within a given transition group, except when the tetragonality effect discussed below is significant. For different transition groups (*3d*, *4d*, *5d*) the values of $(E_1 - E_2)$ increase generally in the ratio 1 : 1.54 : 1.90. The decrease of Racah parameters B and C in the later transition groups amplifies the tendency towards magnetic anomaly exhibited by the complexes of the platinum metals.

Several chemical conclusions can be drawn from the crystal field theory. Already Orgel (109) pointed out that ~ 5 % of the absolute heat of formation of hexaaquo ions in d^n-systems ($n \neq 0, 5, 10$) can be ascribed to the energy decrease of the groundstate (see Table I). Crystal field stabilizations have later been studied (23-42-76-85-137). The chelate effect on formation constants, which can mainly be ascribed to changes of entropy (2-63-85-120-136) is also caused by crystal field stabilization of complexes with partly filled *d*-shells (21-85-120). However, in the following only four problems of general interest to the future development of the theory of the transition group complexes will be discussed.

I.

DEVIATIONS FROM THE HOLOEDRIC OCTAHEDRAL SYMMETRY

Van Vleck (152) emphasized that the Jahn-Teller effect implies that all groundstates shall be only once orbitally degenerate. Thus, only Γ_1 and Γ_2 can exhibit regular octahedral symmetry, while Γ_3 must be distorted to tetragonal and Γ_4 and Γ_5 to rhombic or tetragonal symmetry. Thus, only the systems without crystal field stabilization (d^0, $d^5\ {}^6\Gamma_1$, d^{10}) and a few others (d^3, $d^6\ {}^1\Gamma_1$, and d^8) will retain regularly octahedral configuration. The latter class of complexes are remarkable by forming robust complexes (i.e. with high activation energy) when ($E_1 - E_2$) is sufficiently large ([23-76]). On the other hand, characteristic co-ordination numbers below 6 occur only in the non-regular systems ([20]). The tendency of tetragonal symmetry is especially pronounced in the cases of d^4- and d^9- systems. The absorption spectra in Table III indicate excessively large wavenumbers for these complexes. Table III also demonstrates the " pentamine effect " ([20-22]), the fact that mixed complexes with strong crystal field from four planar bound ligands will have spectra with higher wavenumbers than the complexes with six ligands with equally late position in the spectrochemical series. The latter effect can be explained as a systematical depression of the groundstate with unsymmetrical substitution of ligands.

In the first transition group, the values of ($E_1 - E_2$) in the divalent hexaaquo ions decrease regularly from 12 600 cm^{-1} for vanadium (II) to 8 500 cm^{-1} for nickel (II), except for chromium (II) which seems to give some 2 000 cm^{-1} higher values than thus expected (and it is just a d^4-system). Then, in copper (II) the high value 12 600 cm^{-1} appears. The cubic contribution ([9]) in the latter case is probably rather near to that of nickel (II), and the author ([82]) has proposed to use as a measure of tetragonality the wavenumber ratio ν_{Cu}/ν_{Ni}. Table V therefore demonstrates that this ratio is highly varying for different types of complexes. In the case of strong tetragonality ($\nu_{Cu}/\nu_{Ni} \sim 1.7$), the condition, strongly bound nitrogen atoms in the tetragonal plane, is satisfied. When all six atoms in the first co-ordination sphere of copper (II) are equal, moderate values of the tetragonality (~ 1.45) are obtained. Similar results are produced by several amino-acids (see Table V), which for steric reasons cannot be bound exclusively in the plane. Finally, some amine complexes are nearly cubic ($\nu_{Cu}/\nu_{Ni} = 1.1$). In case of aliphatic amines, such as tren = β, β′, β″-tris (ethylamino) amine, steric hindrance necessitates the formation of cis-octahedral complexes. More peculiar is the behaviour of bis- and tris-complexes of heterocyclic diamines such as α, α′-dipyridyl and *o*-phenanthroline. From the absorption spectra of Cu $dip_2(H_2O)_2^{++}$ and Cu $phen_2(H_2O)_2^{++}$, it can be concluded that the trans-isomer is nearly absent. The opposite is the case by Cu $en_2(H_2O)_2^{++}$. This behaviour seems to be dependent on the ionic radius, since the complexes of silver (II) : Ag py_4^{++} and Ag dip_2^{++} are distinctly planar, just as Cu py_4^{++}.

TABLE V

Relative tetragonality of copper (II) complexes from the ratio ν_{Cu}/ν_{Ni} between the wavenumbers of the principal band in copper (II) and nickel (II) complexes with equal set of ligands, i.e. the apparent values of ($E_1 - E_2$). Literature : 82,85.

Low tetragonality		Medium tetragonality		Strong tetragonality	
tren, 2 H_2O	1.08	6 H_2O	1.48	4 NH_3, $2H_2O$	1.7
tren, 2 NH_3	1.11	6 NH_3	1.45	2 en, 2 H_2O	1.72
2 dip, 2 H_2O	1.1	3 en	1.46	2 gly^-, 2 H_2O	1.60
3 dip	1.21	3 gly^-	1.5	2 acetylacetonate	2.06
2 phen, 2 H_2O	1.15	$enta^{-4}$, H_2O	1.36		
3 phen	1.21	$enta^{-4}$, NH_3	1.35		
		ata^{-3}	1.29		
		2 ata^{-3}	1.46		

Diamagnetism (groundstate ${}^1\Gamma_1$) is shown by nickel (II) complexes with very strong crystal fields of tetragonal symmetry (8–9–15–52 109–112–118). It is evident that particularly weak bonding on the axis perpendicular to the plane is a necessary condition. The solid [Ni en_2] [Ag Br $J]_2$ and Ni $temeen_2^{++}$ are diamagnetic, while Ni $en_2(H_2O)_2^{++}$ and Ni $phen_2(H_2O)_2^{++}$ are paramagnetic, according to the absorption spectra. However, intermixing with the orbitals of the ligands seems to be important, since the Schiff'base-anions with two nitrogen and two oxygen atoms in the tetragonal plane would not be expected to be situated very lately in the spectrochemical series. However, six equal ligands can actually form diamagnetic d^8-complexes, which must be assumed to be tetragonally distorted as copper (II) complexes. Thus, $Ni(CN)_4^{--}$ takes one (and presumably two) CN^- up in strong cyanide solutions. These complexes, and Pd Cl_6^{----}, and the solids $K_3Cu\ F_6$ and Pt tren J_2 are all diamagnetic.

Another result of tetragonal distortion in octahedral complexes is increased acidity. The causes of increased acid strength of a complex are often very complicated. Thus, the intermixing of molecular orbitals seems to enhance acidity of strongly oxidizing metal ions. It is also evident that d^4- and d^9-systems are inter alia more acidic than other complexes. Copper (II) and manganese (III) hexaaquo ions are e.g. much stronger acids than the neighbour ions and recently (35) ethylenediamine in the d^4- system Os en_3^{+4} was found to be an acid with $pK < 0$ and $pK = 8.2$. Corresponding values are $pK = 5.5$ and 9.2 for Pt en_3^{+4}. It is further known (26) that the d^4-system ruthenium (IV) has a much higher tendency of forming hydroxo complexes than the d^6-system platinum (IV).

Besides the intrinsic tetragonality, mixed ligands of highly different position in the spectrochemical series may produce tetragonal splitting of the levels in d^3-and diamagnetic d^6-systems. These effects will not be discussed here [Table III gives some examples for rhodium (III)], they are generally smaller than expected and often deviate from the predictions based on the electrostatic crystal field models (1-7-8-9-13-16-17 18-22-51-52-53-62-82-86-96-97-101-109-111-116-137-148-158).

Another deviation from the symmetry O_h is the demolition of the centre of inversion, whereby crystal fields of hemiedric instead of holoedric symmetry are created. Complexes without a centre of inversion e.g. cis-MA_4B_2 and tetrahedral MA_4, have often somewhat higher absorption bands than complexes with a centre of inversion, e.g. MA_6 or trans-MA_4B_2 (16-77-137). It is rather surprising that the differences in band intensities are not even larger. In a gaseous ion or in a system with a centre of inversion, the parity Q of a level is a strictly defined quantum number, even or odd [usually denoted by subscripts g (= gerade) and u (= ungerade)]. While electron configurations with different parities q of the single electrons may freely intermix, it is necessary that the sum Q is either odd or even for all interacting configurations. Laporte's rule states that transitions as electric dipole radiation are only possible between levels with opposite Q. Since the observed absorption bands are too strong to be due to other types of radiation, e.g. magnetic dipole or electric quadrupole radiation, it is not easily explained why internal d^n-transitions (where all levels are even, since $1 = 2$ is even) can be observed at all. Actually, the oscillator strengths P are only 10^{-5} to 10^{-3} for spin-allowed d^n-transitions, while the corresponding values for electron transfer bands where one of the electrons is odd or for the $5f^n \rightarrow 5f^{n-1}\,6d$ bands in the actinides are 10^{-1} to 1. The intermixing of about 10^{-4} odd states to the even d^n-levels has been ascribed either to static hemiedry or to coupling with vibrations

(11-16-25-62-77-146-151). The former type of explanation necessitates to assume the intermixing of odd molecular orbitals into the groundstate, decreasing the energy slightly according to the principle of variation.

II.

THE PHYSICAL SIGNIFICANCE OF $(E_1 - E_2)$

The absorption spectra can be interpreted by use of the parameter $(E_1 - E_2)$, which varies in a regular way among the complexes (Table IV). It is possible to explain the energy difference between the γ_3- and γ_5-orbitals by different models, the most prominent of which have been the molecular orbital theory and the electrostatic crystal field model with pure *d*-orbitals. At the moment, there seems to be no possibility of predicting the value of $(E_1 - E_2)$ within a few hundred %, except from the empirical regularities of Table IV.

Already van Vleck (150) pointed out that the molecular orbital theory and the crystal field theory both lead to a considerable energy difference $(E_1 - E_2)$ between the γ_3- and γ_5-orbitals. The former theory considers the intermixing of orbitals with identical γ_n and parity *q*. Thus, in octahedral complexes, the σ-bonding orbitals from the ligands (even γ_1, odd γ_4 and even γ_3) intermix with 4*s*, 4*p* and 3*d*, respectively, when the first transition group is considered. It is interesting to note that 50 % intermixing in each of the three pairs of orbitals corresponds exactly to the Pauling d^2sp^3-hybridization (117-118). Thus, the molecular orbital theory affords the possibility to describe any case between the pure d^n-systems in the electrostatical model and Pauling's type of covalency by choice of three independent parameters. This development can continue beyond 50 % intermixing, corresponding to electron transfer from the central ion to the ligands. This probably occurs in some cases of π-bonding. Many authors have used this intermixing of molecular orbitals to explain a part of the energy difference $(E_1 - E_2)$ (17-42-50-112-116-155) or even the whole of it, neglecting the electrostatic contribution (64). It can be questioned if the molecular orbital theory is very adequate for the transition group complexes without a study of interaction of configurations for each level. Slater (142) and Mc Weeny (103) emphasized that configuration interaction is very important in systems with a positive value of S (e.g. O_2), especially in cases with larger nuclear distances. These are just the conditions, prevailing in most transition group complexes. Several chemical physicists interested in the groundstate of simple molecules, apply one molecular orbital configuration with only one singlet state, while $\gamma_5^a\gamma_3^b$ mostly contains more levels, as seen from Table 1. The energy depressions from other configurations are e.g. in the range 0 — 37.000 cm^{-1} in the simple molecule HCN (61). Actually, the deviations of absorption bands from the crystal field theory predictions are usually less than 2.000 cm^{-1}, and the spectra would be totally irrecognizable, if displacements as large as 20.000 cm^{-1} often occurred. This agreement with single configuration treatment may be ascribed to some tendency of depressing all the levels of a complex by nearly the same amount. In the next section it will be discussed, if the deviations can be ascribed to varying values of the Racah parameters B and C of electrostatic interaction between *d*-electrons, the crystal field theory thus being rescued. It would be interesting to see experimental evidence for the intermixing of *d*-electrons with the ligand's orbitals. Curiously, the clearest fact applies to π-bonding in $IrCl_6^{--}$ and $IrBr_6^{--}$ rather than to any case of σ-bonding, namely that the γ_5-electrons in these ions are situated $\sim$ 80 % of the time near the iridium nucleus and $\sim$ 3 % of the time near to each of the halogen nuclei, as found from the hyperfine structure of paramagnetic resonance (115). As discussed below in the section on intermediate coupling, Owen (116) maintains the presence of $\sim$ 20 % σ-bonding of γ_3-electrons because of the decreased values of the Landé factor ζ_{nd}. Generally, it can be said that the γ_3-part of *d*-electrons and γ_3-ligand electrons are subject to some kind of intermixing at low inter-nuclear distances resulting from orthogonalization alone. However, with orthogonalized orbitals, the interaction does not intermix orbitals with the same γ_n, but rather levels with the same ${}^{2S+1}\Gamma_n$, originating from different configurations $\gamma_n^a\gamma_m^b$... Thus, the final calculations tend to be complicated. However, the results would be very interesting.

Ilse and Hartmann (62) proposed a crystal field model, which has been used by several authors (7-8-22-47-52-53-134). A hydrogen-like 3*d* wavefunction with the effective charge Z, proposed by Slater (141) is perturbed by 6 point charges or point dipoles in the distance R from the nucleus of the central ion. Any hydrogen-like wavefunction will of course be approximative, since Z varies from e.g. 28 in the centre of a nickel (II) ion to 3 on the surface, while Slater assumes $Z = 7.55$. But these screening values are only good for internal electrons, while the values for external electrons are very uncertain. Further, the ionization potential for Ni^{++} in vacuo, 36.16 eV, suggests $Z = 4.9$. On the other hand this gives for the density maximum of the radial wavefunction the improbably high value of 0.96 Å, while the ionic radius in crystals is only 0.7 Å.

It may be argued that by calculations from perturbation theory, the energy value is often determined much more correctly than the wavefunction. However, a first-order perturbation cannot be very reliable, when the radius is predicted ~ 80 % too large. Even worse, it is the outer parts of the wavefunction which are most perturbed by the crystal field and which are the most uncertainly determined in the hydrogen-like approximation. Belford (^{17}) proposes a Hartree's self-consistent wavefunction, which gives smaller crystal field contributions for copper (II).

The concept of point dipole moments is entirely meaningless, since the negative end of a dipole molecule contributes from 10 to 100 times more to $(E_1 - E_2)$ than the opposite effect of the positive end. The concept of point charges might seem more reasonable, since we are accustomed to regard the action of the charge of non-polarized anion as identical with the action of the same charge, placed in the centre of the anion. But this assumption is valid only for R^{-1} potentials (^{77}). Mr. O. Bostrup has kindly informed me that an integration of the negative charge distribution on e.g. a chloride ion can give 4-10 times higher values of $(E_1 - E_2)$ than the point charge^{-1}. Generally $(E_1 - E_2)$ is highly dependent on the radius of the central ion and is inversely proportional to the radius of the anion, when similar charge distributions are considered (^{24}). This resolves the old paradox, why neutral molecules such as H_2O and NH_3 can induce larger values of $(E_1 - E_2)$ than anions such as Cl^- and Br^-.

Thus, there remains only the semi-quantitative expression that in atomic units : (the energy unit = 2 Rydberg = 219 000 cm^{-1})

$$(E_1 - E_2) \cong \frac{5}{3} q \cdot \frac{\overline{r^4}}{R^5}$$

where $\overline{r^4}$ is the average value of r^4 (r is the distance nucleus-electron) and R the distances from the nucleus to the six charges q. This expression may be integrated for given charge distributions of q, having the symmetry O_h, by multiplication with the angular dependence factor. Thus, the electrostatic model can be made compatible with all the observed facts, but that is of course no proof of its validity. Most peculiar is the fact (116) that trivalent ions have 1.4 — 1.8 times higher values of $(E_1 - E_2)$ than the isoelectronic divalent ions. If the ligands are not much more polarized, this result can only be explained by treatments taking intermixing of molecular orbitals into account.

III.

THE PARAMETERS B AND C OF ELECTROSTATIC INTERACTION BETWEEN d-ELECTRONS AS MEASURED FOR COMPLEXES

Orgel (111–113), Owen (116), and Tanabe and Sugano (146) pointed out that the parameters of electrostatic interaction may be smaller in the complexes than in the gaseous ions, as determined from atomic spectra. This assumption can explain the deviations from the Orgel diagram in which the energy levels are supposed to be a function of $(E_1 - E_2)$ only [see Table III, where the first bands $Cr(H_2O)_6^{+++}$ and Cr ox_3^{---} to $^4\Gamma_5(F)$ have identical wavenumbers, while the band to $^4\Gamma_4(F)$ is situated 700 cm^{-1} lower for the tris (oxalate) complex than for the hexaaquo ion]. Mr. C. E. Schäffer pointed out to me that the distance between the first and the second band is highly varying in chromium (III) complexes. If this distance is assumed to be 12 B (Table I), then B = 500 — 600 cm^{-1}, while the value for gaseous Cr^{+++} is B = 950 cm^{-1}. Analogously, the first two excited singlet levels in diamagnetic d^6-systems, $^1\Gamma_4$ and $^1\Gamma_5$, have the asymptotical distance 16 B, implying B $\sim$ 500 cm^{-1} for cobalt (III), 300-450 cm^{-1} for rhodium (III) and 250 cm^{-1} for iridium (III) complexes. This is roughly half the expected values for the gaseous ions, since the 4d-group generally (60) has slightly lower values of B than the 3d-group. It is obvious that anions [such as tris (oxalate) and hexacyanide complexes] seem to have lower values of B than the positively charged complexes. But it is not easy to distinguish a direct charge effect from a tendency to form covalent bonds as far the anions are concerned. It is known from the intensities that oxalate and thiocyanate complexes certainly contain small intermixings of odd molecular orbitals, but it is much more difficult to estimate the possibly much larger intermixing of even molecular orbitals. From the viewpoint of an atomic spectroscopist, the decreased values of B suggest a broader wavefunction, since the parameters of electrostatic interaction are inversely proportional to the average radius for isomorphous electron distributions. This decrease of B can only be explained by the perturbation theory, if more negative charge is present between the nucleus and the considered electron in the complex than in the gaseous ion, e.g. even γ_1 or odd γ_4 electrons from the ligands. On the other hand, any transfer of electrons to the ligands, conforming to an " electroneutrality " principle, will lower B. If only $(1 - X)$ of the original electrons remains in the central ion, the value of B would be expected to be roughly proportional to $(1 - X)^2$, since the more remote parts of the electrons do not contribute much to the parameter. However, another complication arises from the ratio C/B, which would be 8.75 for electrons concentrated on a spherical surface, and which is actually 4-5 in the gaseous ions (146). By expansion of the electron cloud, the Slater-Condon-Shortley parameter F_2 decreases relatively more slowly than F_4, giving a smaller ratio $C/B = 35F_4/(F_2 - 5F_4)$. Therefore the observed decrease of B suggests an even stronger decrease of F_4.

In case of nickel (II) complexes, the non-diagonal element 6B between $^3\Gamma_4(F)$ and $^3\Gamma_4(P)$ and the non-diagonal element $-2\sqrt{3}B$ between $^1\Gamma_3(D)$ and $^1\Gamma_3(G)$ are significant. Hence, the straight lines of Table 1 are strongly distorted for small values of $(E_1 - E_2)$. But due to the diagonal sum rule, the sum of the energies of $^3\Gamma_4(F)$ and $^3\Gamma_4(P)$ should still be $0.6\,(E_1 - E_2) + 15B$, and with good approximation, $^1\Gamma_3(D)$ has the energy given in Table I, $-1.2(E_1 - E_2) + 8B + 2C$, while the latter energy for the free ion is $\frac{4}{7}\,(^1D) + \frac{3}{7}\,(^1G) - (^3F) = 17.900\ \text{cm}^{-1}$. Table VI gives a list of the energy differences, found from nickel (II) complexes. The maxima in Table III are often displaced 200 cm^{-1} in the cases of unsymmetrical bands, when the midpoint of area is taken. In the case of $^1\Gamma_3(D)$, correction is made for the shift due to effects of intermediate coupling, as discussed in the next section.

TABLE VI

Effective term distances in nickel (II) complexes in cm^{-1}.

Values implied by excited level		$^3\Gamma_5(F)$	$^3\Gamma_4(F) + {}^3\Gamma_4(P)$	$^1\Gamma_3(D)$
of the parameter		$(E_1 - E_2)$	$15\,B = (^3P) - (^3F)$	$8\,B + 2\,C = \frac{4}{7}(^1D) + \frac{3}{7}(^1G) - (^3F)$
Ligands	Number of nitrogen atoms in the environment			
free ion	—	0	16900	17900
6 H_2O	0	8500	14100	14800
ata^{-3}, x H_2O	1	9500	12800	13300
$enta^{-4}$, H_2O	2	10100	13000	12700
3 gly^-	3	10100	13900	13100
en, 4 H_2O	2	10200	12000	13600
$enta^{-4}$, NH_3	3	10200	13500	12700
2 ata^{-3}	2	10400	13400	13000
en, 2 gly^-	4	10700	13500	12800
6 NH_3	6	10800	13400	13100
2 en, gly^-	5	11300	12600	12200
tren, 2 H_2O	4	11300	11700	12000
3 en	6	11600	12600	12000
tren, 2 NH_3	6	11700	11300	12000
tren, en	6	11700	12600	11800
tren, gly^-	5	11800	11500	11900

It is seen from Table VI that the effective term distances do not decrease monotoneously with (E_1 — E_2). This is partly connected with the definition of this parameter as the corrected wavenumber of the first absorption band. However, it is clearly seen that B eventually decreases to ~ 70 % of its value in the gaseous ion, and there is slight evidence that C/B eventually decreases to a value ~ 3.5 as predicted above.

As far as term differences in nickel (II) complexes are concerned, the discussion is made somewhat uncertain by the fact that four absorption bands shall deliver the three parameters (E_1 — E_2), B, and C. It is interesting to note that ten absorption bands are known in the manganese (II) hexaaquo ion. As pointed out by Orgel (^{113}), the terms in the free ion (^{105}) which are ^{4}G : 26,800, ^{4}P : 29,200, ^{4}D : 32,300, and ^{4}F : 43,600 cm^{-1}, are decreased about 8 % in the hexaaquo ion (and 10 % in Mn enta^{--}), while the corresponding decrease is 18 % for the nickel (II) hexaaquo ion (Table VI) and ~ 40 % for the chromium (III) and cobalt (III) complexes. While it cannot be excluded that these changes are subtle effects of covalent bonding, it seems at the moment more probable that the electrostatic crystal field theory actually is applicable with (E_1 — E_2) as empirical parameter together with smaller electronic repulsion parameters.

IV.

EFFECTS OF INTERMEDIATE COUPLING

In gaseous ions, the Russel-Saunders' coupling with definite values of L and S for the terms may break down, when individual levels each with a definite value of J (the quantized vector sum of L and S) differ much in energy. This behaviour is evident in heavier atoms ($^{25-28-72-73-78-81-123}$) and can be described by increasing values of Lande's multiplet splitting factor ζ_{nl}. As in the case of (S, Γ_n) levels discussed above, the q levels with identical J of an electron configuration can be described by a matrix of q'th degree. The non-diagonal elements of this matrix have the order of magnitude ζ_{nl}. The values for l = 2, viz. ζ_{nd} are strongly increasing with three quantities : the external charge Z_0 — 1; the number of equivalent d-electrons; and the principal quantum number n. Thus,

ζ_{nd} is roughly proportional to Z_0^2, and the following relationship is approximately valid for the three transition groups :

$$\zeta_{5d} \cong 2\,\zeta_{4d} \cong 5\,\zeta_{3d}$$

The absorption spectra of complexes support strongly the analogous influence of ζ_{nd}, which is greatest at the end of the transition groups and increases with *n*. Levels with S differing by one unit are intermixed in the squares of the wavefunctions to the extent $\cong \left(\frac{k\ \zeta_{nd}}{\Delta}\right)^2$, where Δ is the distance between the two levels, and *k* is about 1 and approximately constant for different complexes of the same ion. The selection rule that transitions are only allowed between levels with the same S is mitigated to the degree as the groundstate and the excited level achieve the same S by intermixing induced by intermediate coupling. For group-theoretical reasons, levels can only be intermixed with the same value Γ_j of the internal vector product $\Gamma_S \times \Gamma_n = \Sigma\Gamma_j$, but it has not yet been possible to observe with certainty the Γ_j-components of the Γ_n-levels, except in the tetrahedral $Co\,Cl_4^{--}$.

In some cases levels with different S have nearly the same values of Δ for all ligands, because the levels have the same sub-shell configuration, cf. iridium (III). In other cases, e.g. in chromium (III) and nickel (II), Δ assumes all possible values down to the lower limit $2k\zeta_{nd}$ with resulting very high intermixing in some of the complexes. (82-85-137). As Δ varies the intensity ratio of the intermixed bands behaves as predicted. A special case seems to occur in manganese (II), where the oscillator strength P is $\sim 0.5\ \%$ of that of spin-allowed bands in iron (II) or nickel (II). Since ζ_{3d} can be interpolated from Table VII to be 300 cm^{-1}, the spin-forbidden bands were expected to have $P \cong \left(\frac{300}{20.000}\right)^2 = 0.02\ \%$ only of the ordinary P-value, if the distance to the interacting sextet level (either the groundstate $^6\Gamma_1$ or a level from some other electron configuration) is assumed to be $\sim 20.000\ cm^{-1}$. The discrepancy can be explained by admixed odd states, which perhaps have a less strictly defined S.

Owen (116) concludes from the *g*-values from magnetochemical measurements that ζ_{nd} is diminished between 17 and 40 %, compared to the free ion. It is not possible to infer differences of this size from

TABLE VII

The Landé multiplet splitting factor ζ_{nd} from atomic spectroscopy and the interaction constants $k\,\zeta_{nd}$ from absorption spectra of complexes, all in cm.$^{-1}$.

Number of *d*-electrons		1	2	3	4	6	7	8	9
$3d^n$, divalent :	$\zeta 3d$	79	123	169	229	408	530	630	829
	$k\,\zeta 3d$	—	—	—	—	—	—	500, 800	—
trivalent :	$\zeta 3d$	154	217	275	352	—	—	—	—
	$k\,\zeta 3d$	—	—	200, 300	—	500	—	—	—
$4d^n$, divalent :	$\zeta 4d$	290	468	560	—	—	—	—	1843
trivalent :	$\zeta 4d$	500	800	800	—	—	—	—	2325
	$k\,\zeta 4d$	—	—	900	—	900	—	—	—
$5d^n$, divalent :	$k\,\zeta 5d$	—	—	—	—	—	—	2000	—
trivalent :	$k\,\zeta 5d$	—	—	—	—	2000	—	—	—
quadrivalent :	$k\,\zeta 5d$	—	—	—	—	2500	—	—	—

Table VII, but they may be explained by the expansion of the d^n-electron cloud, discussed above. Hence, it is not absolutely necessary to describe this phenomenon in terms of covalency. The intermixing of S in the groundstates of e.g. diamagnetic d^6-systems has no consequences for the magnetic moment in Bohr magnetons ([107]) but the excited states contribute to the temperature-independent paramagnetism and might also be compared with optical data.

CONCLUSION

In the period 1951-1956, the absorption spectra of transition group complexes have been investigated much more intensely than previously. It is generally believed that the crystal field theory gives a reliable description of the levels in terms of the crystal field strength [in octahedral complexes $(E_1 - E_2)$], and the parameters of electrostatic interaction between *d*-electrons B and C, also applied in atomic spectroscopy. However, the value of $(E_1 - E_2)$ in a given complex can only be predicted by empirical interpolation from other complexes. Although the electrostatic model explains this behaviour very well, it is not yet clear how important molecular orbitals are for the bonding of the complex. But the absorption spectra of complexes from all three transition groups have given a much more unified picture than predicted from sharp distinctions between "ionic" and "covalent" complexes, and the actual situation resembles much the successful application of concepts from the atomic spectroscopy to the spectra of lanthanide and actinide ions. Many chemical conclusions can be drawn from this theory of d^n-systems.

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Discussion

M. Orgel. Is there any evidence from optical absorption spectra for the reduction of the spin-orbit coupling constant in complexes relative to its value for the free ions?

M. Jørgensen. — The non-diagonal element $k\xi_{nl}$ can be found from adsorption spectra, from the relative intensities and in some cases the mutual repulsion of the energy levels, when their distance approaches $2k\xi_{nl}$. Thus, if theoretical estimates could be made of the number $k \sim 1$, it would be possible to determine the actual value of ξ_{nl} in the complex. Even though such calculations have not been performed. I guess that at least the platinum metals exhibit considerable decrease of ξ_{nl}, if k is not systematically small.

Thus, ξ_{5d} can be estimated from several gaseous ions to be larger than $k\xi_{5d}$ 2.000 cm^{-1} observed in iridium (III) and planitum (II) complexes :

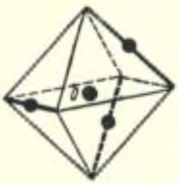
Platinum (0)	$5d^96s$	4.050 cm^{-1}
	$5d^86s^2$	~4.000
Gold (I)	$5d^96s$	5.100
	$5d^86s^2$	~5.000
Mercury (II)	$5d^96s$	6.200
	$5d^86s^2$	~6.000
Thallium (III)	$5d^96s$	7.450

M. Nyholm. — It is now well established that the number of tetrahedral Ni^{II} complexes, if any, is much fewer than was formerly believed to be the case.

However the compound $[\text{Ni(NO}_3)_2\text{, 2 Et}_3\text{P]}^\text{o}$ is monomeric in benzene solution. It has a high electric dipole moment. Would Dr Jørgensen give his views as to the probable structure of this compound?

M. Jørgensen. — This compound is not necessarily tetrahedral or cis-octahedral, but may show a distorted structure with two oxygen atoms co-ordinated of each nitrate group, or with very loosely bound solvent molecules on the residual positions. Due to the Jahn-Teller effect, a tetrahedral structure must distort, and there may be raised similar questions as to whether $Cucl_4^{--}$ in solid K_2CuCl_4 is distorted planar or distorted tetrahedral. However, the inversion in sign of the energy difference between γ_3 and γ_5 orbitals by going from the symmetry on to T_d would lead to a rather complicated behaviour of the energy levels of the intermediate cases. Actually, Prof. Asmussen and M. Soling have kindly presented me with a sample of the complex, whcih did show two bands with rather high intensities ($\varepsilon \sim 40$ and $\varepsilon \sim 20$) at nearly the positions known from octahedral $Ni(H_2O)_6^{++}$. Prof. K.A. Jensen has kindly informed me that yellow solvation products seem to be diamagnetic, and that the relatively very pale blue-green colour is only obtained in pure non-polar media.

M. Kuhn. — The absorption properties of complex molecules are not only characterised by the frequency and the intensity of the absorption bands; a further fundamental quality being the distribution of the vibrating electric moment over the molecule. Important information about this can be obtained from measurements of optical activity. We have been especially interested in this respect in the behaviour of substances like Triethylenediamincobaltibromide $[Co(en)_3]Br$ and Trioxalatopotassium cobaltiate $[Co(ox)_3]K_3$. In those compounds the cobalt atom is found at the centre, the three bivalent substituents on 3 edges of a normal octahedron.



If the vibrating electric moment of the absorption bands of these compounds were localised at the central atom, no optical activity, i.e. no Cotton effect would be observed. A Cotton effect only occurs if the vibrating moment of the bands has components in distant parts of the molecule. The optical active behaviour of a band or a part of it is best characterised by the quotient

$$g = \frac{\varepsilon_l - \varepsilon_r}{\varepsilon}$$

where ε_l, ε_r and ε are the absorption coefficients for left and right hand circular and for ordinary light; g has been termed anisotropy factor. The value of g depends on the distribution of intensity and direction of the components of the vibrating moment over the various parts of the molecule. The numerical evaluation of the g-values and the intensity show that in the case of the molecules mentioned the vibrating moment must have components a few Ångstrøm units apart, a result which is well in agreement with the enouncement in Orgels, Nyholms and Jørgensens papers according to which there must strong interaction between the peripheral substituents and the central atom.

In order to give an approximate description of the distribution of the electric moment over the molecule, we have represented the central atom as a threedimensional isotropic oscillator in a first approximation and attributed the peripheral substituents a preferential polarisability in the direction of the long axis of ethylenediamine, etc., i.e. in the direction of the octohedral edge occupied by the molecule (1). In this case, the coupling between the central atom and the peripheral substituents removes the degeneracy. The original absorption band splits up in 2 or 3 parts, differing somewhat in frequency and differing considerably in g-value. This is a consequence which has been corroborated by experimental facts : the determination of g-values in the region of the long wave absorption bands of the $Co(en)_3$-ion and the $Co(ox)_3$-ion as well has shown that g varies to a great extent inside the band, revealing that the distribution and orientation of the components of the vibrating moment are different for the various parts of the absorption band. It can therefore be considered to be proved that the long wave absorption band is as a matter of fact *a superposition of several* neighbouring *bands*.

While the *mean* value of g keeps its sign if the central atom is exchanged, the arrangement of the peripheral substituents beeing kept constant, the *relative distribution* of the g-values observed in the long wave and the short wave part of the absorption band changes considerably.

In the case of very week coupling (rather unstable) compound $[Cr(ox)_3]K_3$ g is slightly negative in the long wave part and strongly positive in the mean part of the band; in the case of *medium* coupling in $[Co(ox)_3]K_3$ the *g* value in the long wave part is strongly, in the mean band less strongly positive; and in the case of strong coupling, i.e., in $[Co(en)_3]Br_3$ the *g* value is strongly positive in the long wave part and slightly negative in the short wave part of the first absorption band; this all is in agreement with theoretical calculations made on the basis outlined (¹).

It is found experimentally that the next absorption band in the compounds mentioned is of similar intensity as a first mentioned absorption band, i.e., its *f*-value is 10^{-3} to 10^{-4} approximately. At a variance with the first band, the *g*-value is in all the compounds investigated very much smaller in absolute value in the second than it was in the first absorption band; *g* is however found to vary inside the second band too, indicating that this band also is in reality a superposition and not a truly simple absorption band.

M. Jørgensen. — It is very interesting to me to hear the information, given by Prof. Kuhn and Prof. Orgel. I may only add that according to the calculations of Tanabe and Sugano, the spin-forbidden transition to ${}^3\Gamma_5$ (in Mulliken's notation ${}^3T_2$) is situated at nearly the same wavenumber as the first spin allowed transition to ${}^1\Gamma_4({}^1T_1)$ in diamagnetic d^6 systems. Thus, the complicated behaviour, mentioned by Prof. Kuhn, might be connected with this superposition and the effects of intermediate coupling. My colleague, M. Schäffer, has found some evidence for such a structure in the first strong band of cobalt (III) complexes. The non-diagonal elements of intermediate coupling seem to be rather strong in tetragonal and lower symmetries of the complex. Thus it is rather difficult in many cases to distinguish between band splittings due to tetragonal distortions and to intermediate coupling. It would probably be interesting to study the optical rotation dispersion curves of such complexes; it is rather paradoxical that the angular deviations of $Co(en)_3^{+++}$ (Saito, Nakats, Shiro and Kuroya, *Acta Cryst.*, **8**, 1955, p. 729) from a regular octahedron do not correspond to larger deviations of the absorption spectrum from that of $Co(NH_3)_6^{+++}$.

M. Orgel. — Prof. Moffitt at Harvard has shown that, in cobaltic complexes, theory predicts that the long wavelength band will be

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(*) See an oversight by D. Kuhn in *Angew. Chemie* **68**, *93* (1956).

optically active and the shorter wavelength band much less so. He has calculated the magnitude of the effect. I had reached a similar qualitative conclusion independently.

With regard to the splitting of bands, this is understandable since the states of T_{1g} and T_{2g} symmetry in octahedral complexes are split in the lower C_3 symmetry of the ethylenediamine complexes. I am not certain, but I suspect that the two states into which the lower state is split would have different optical properties, one perhaps being much less active than the other.

M. Ubbelhode. — Do the bands shift appreciably with changes of temperature?

What happens at liquid hydrogen temperatures in the solids?

M. Jørgensen. — While the influence of low temperatures on the spectra of lanthanide compounds has been much studied, there is not much information available on transition group complexes. There seems to be an increase of the wave number of the band maxima, amounting to about three percent for each 100° cooling, and the intensities do not seem to change drastically (cf. some recent measurements by some Japanese authors).

M. C.E. Schäffer, M. Arne Jensen and the present author have observed similar effects in the opposite direction by warming solutions from 20 °C to 80 °C. Qualitatively, the coloured transition group salts may exhibit beautiful hysochromic effects by cooling with liquid air; rose-red cobalt (II) salts turn yellow and green nickel (II) salts sky-blue. This corresponds to an increased value of the parameter ($E_1 — E_2$), analogous to the exchange of water with ammonia at room temperature.

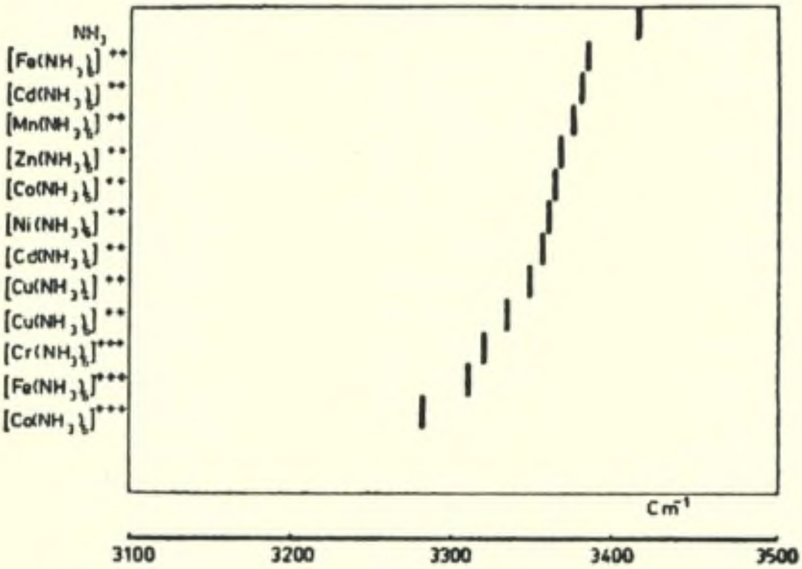
M. Cagliotti. — Les questions sont si compliquées dans la spectographie ordinaire, que je ne sais s'il est possible d'apporter une contribution effective à ce domaine, au cours d'une étude de spectographie infrarouge.

Dans mon laboratoire, on a étudié avec M. Sartori et M. Silvestroni les spectres infrarouge de quelques complexes hexaminées et tétraminés pour essayer de relever des relations entre la position de la bande correspondant à la ν_3 " stretching band " de l'ammoniac et la stabilité de la liaison Me—N dans les complexes.

Nous avons relevé les spectrogrammes de plusieurs complexes à l'état solide. Nous avons choisi l'oscillation ν_3 qui correspond, comme ont pu montrer Lecomte et Duval, Kobayashi, Mizushima et plus récemment Quagliona, à la " Schwingungenergie " la plus élevée et que l'on peut considérer la moins perturbée.

Nous avons ordonné les complexes en fonction décroissante des valeurs des fréquences ν_3.

Les spectres à l'état solide sont bien plus compliqués que les spectres que nous relevons, lorsque c'est possible, en solution. Mais si on a soin de choisir les bandes les moins perturbées, telles que la ν_3, on peut relever que les complexes se placent, sauf quelques exceptions, dans un ordre qui correspond qualitativement à la stabilité croissante de la liaison Me-N (fig. 1).



Après cet accord qualitativement satisfaisant, nous avons essayé encore d'appliquer, dans les cas où l'on pouvait attribuer avec suffisamment de certitude les quatre fréquences, la relation de Lechner, pour calculer dans les complexes, la valeur de l'angle qui vient d'être formé par la liaison N—H avec l'axe de la molécule deNH_3.

On voit que cet angle devient plus petit en fonction de la grandeur de la stabilité du complexe, c'est-à-dire, que le volume deNH_3 décroît avec la stabilité du complexe même.

M. Jørgensen. — Votre observation des fréquences ν_3 des complexes ammoniacales, entre les valeurs qui caractérisent NH_3 libre et NH_4^+, est très intéressante; on peut proposer d'étudier les complexes encore plus stables comme $Rh(NH_3)_6^{+++}$, $Ir(NH_3)_6^{+++}$ ou $Pt(NH_3)_6^{++++}$ (que l'on peut préparer selon les données de Tronev et Shumilina, *Doklady Akad. Nauk SSSR*, **101**, 1955, p. 499). On espère qu'il sera possible de trouver un cas, où l'influence de l'ion central sur NH_3 est plus grande que l'influence du quatrième proton de NH_4^+. Il serait aussi intéressant d'étudier les spectres de vibration de l'eau dans les ions hexahydratés des métaux.

M. D'Or. — Les spectres d'absorption d'origine électronique des complexes considérés ici sont généralement relevés sur des solutions. Je pense cependant que, de même que la nature du solvant n'a probablement qu'un effet peu important sur le spectre, le spectre de la substance à l'état cristallin ne doit pas différer essentiellement du spectre des solutions.

S'il en est bien ainsi, et que d'autre part, selon les indications de M. Jørgensen, une variation de la température a pour effet de produire un léger déplacement des bandes dans l'échelle des longueurs d'onde et non une modification de la forme des bandes, il semble que la largeur des bandes est due non à un effet direct de l'agitation thermique, mais à un effet d'élargissement des niveaux électroniques dû en partie à la variation de la distance entre l'atome central et les groupes coordonnés, au cours de la vibration, en partie au champ créé par ceux-ci. Le déplacement des bandes sous l'effet de la température serait dû au caractère anharmonique de la vibration des groupes coordonnés par rapport à l'atome central.

M. Jørgensen. — Je suis parfaitement d'accord avec vous sur la faible influence de la température. Les cristaux semblent avoir presque les mêmes spectres que les solutions, mais le paramètre $(E_1 - E_2)$ est souvent plus grand de 2 %, comme mon collègue, M. Ole Bostrup, a trouvé pour les sels du nickel (II). Parfois, il est possible d'observer l'effet visuellement. Les sels Tutton, comme

$(NH_4)_2Ni(SO_4)_26H_2O$ sont bleu-verdâtres et $Ni(H_2O)_6^{++}$ en solution est d'un vert un peu jaunâtre. On peut les comparer avec les effets de solvation (J. Bjerrum, A.W. Adamson et O. Bostrup, *Acta Chem. Scand.*, **10**, 1956, 329).

M. Chatt. — With reference to the use of infra-red spectra for the examination of electronic effects in complex compounds, we (Chatt, Duncanson and Venanzi, *J. Chem. Soc.*, in the press), have examined the spectra of a series of simple monoamines and monoamine complexes in carbon tetrachloride solution and also in the solid state. Although this series includes the simplest possible amines (*viz.* monoamines), we found that the spectra in the region of N-H stretching frequencies (ν_{N-H}) are complicated by intermolecular hydrogen bonding. All the N-hydrogen atoms are hydrogen bonded in such substances as *trans*-$[PR_3,NH_3PtCl_2]$ in the solid state. The complexes of primary amines are similar. However, in the complexes of secondary amines, *e.g.* of piperidine, very little, if any, hydrogen bonding occurs and the N-H stretching mode of vibration causes a single sharp absorption band both in solution and in the solid state. ν_{N-H} in the solid state is only some 20 — 30 cm^{-1} lower than in solution, yet when the complexes *trans*-(L, piperidine, $PtCl_2$) (L = an unchanged ligand) were placed in the order of increasing ν_{N-H} measured in carbon tetrachloride solution and of increasing ν_{N-H} measured in the solid state, the two sequences were slightly different. It is most probable that the sequence observed in solution is the one relating the electronic effects of the different L's, and that obtained from measurements in the solid state is perturbed as a result of slightly different crystal forces acting on the N-H bond. These results indicate that great caution is necessary in interpreting small differences in ν_{N-H} measured in the solid state, and that crystal forces may outweigh intra-molecular electronic effects in their effect on ν_{N-H}, even in the absence of such strongly perturbing effects as hydrogen bonding.

M. Cagliotti. — L'observation de M. Chatt est exacte : à l'état solide en effet, il y a des bandes supplémentaires, dues probablement aux phénomènes d'association : mais nous avons eu le soin de choisir la fréquence ν_3 qui est la moins perturbée et nous avons comparé tous les composés à l'état solide.

Il faut remarquer que les complexes examinés ont tous le même " Ligand " coordonné, c'est-à-dire NH_3.

Les valeurs observées présentent des variations très importantes, comme on peut le relever des nombres sous-indiqués (Tableau I).

De toute façon, les relations que nous trouvons ont la valeur d'indication.

TABLE I.

	V_3
NH_3	3.415
$Fe(NH_3)_6^{++}$	3.384 f
$Cd(NH_3)_6^{++}$	3.380 f
$Mn(NH_3)_6^{++}$	3.375 f
$Zn(NH_3)_6^{++}$	3.365 f
$Co(NH_3)_6^{++}$	3.364 f
$Ni(NH_3)_6^{++}$	3.360 f
$Cd(NH_3)_4^{++}$	3.355 f
$Cu(NH_3)_4^{++}$	3.347 f
$Cu(NH_3)_6^{++}$	3.335 f
$Cr(NH_3)_6^{+++}$	3.320
$Fe(NH_3)_6^{+++}$	3.310
$Co(NH_3)_6^{+++}$	3.280 f

M. Jørgensen. — 1. Since gaseous ions with from two to eight d-electrons present several multiplet terms of the same electron configuration, the lowest of these will have lower energy than the average of all the terms. This produces a special stabilization of the groundstate of a gaseous ion, which is the same in d^n and d^{10-n} system and reaches its maximum value in d^{5-} systems (which is the explanation of the stability of half-filled shells, often mentioned in chemical textbooks). However, this stabilization of the groundstate is not so large as might be predicted from the large number of levels, since the " centre of gravity " of the configuration is found by weighing with the total number of states $(2S + 1)\ (2L + 1)$ in each term with a given value of S and L. Since the term differences decrease in complexes, relative to the gaseous ion, the energy of the groundstate of complexes will be increased by this special effect. Has Dr Orgel observed any decrease of the ligand field stabilization, which might be interpreted as caused by this counter-acting influence of the decrease of term distances in complexes? Probably, the σ-bonding of γ_1 and γ_4-orbitals is slightly stronger in nickel (II) complexes than interpolated from the behaviour of manganese (II) and zinc (II) complexes, since the distances from the central ion to the ligands are relatively too small in the nickel (II) complex. Thus the observed ligand field stabilization which often is 20 % larger than predicted from the simple theory, may contain two further corrections : a positive contribution from the bonding orbitals, which do not contain *d*-electrons in their linear combinations, and a negative contribution, caused by the decreased values of the parameters of electrostatic interaction between the electrons in the partly filled shell. However, the first effect will to a high degree be linear in the number of γ_3-electrons and thus participate in $(E_1 - E_2)$ without being distinguished. Unfortunately, I had not yet found the following argument for partly intermixing of *d*-electrons with the ligands' orbitals, when I delivered the manuscript for the report. From the effective term distances, it is possible to determine the integrals F^K of the theory of Condon and Shortley (*Theory of Atomic Spectra*, Cambridge, 1953).

The arguments will be presented in a paper in *Danske Videnskab. Selskab, Mat. Fys. Medd.* that it is possible to extrapolate from F^2 and F^2 to the integral :

$$W = e^2 \int_0^\infty \frac{R^2}{r} dr$$

where e is the electronic charge and R^2 the square of the radial function. For reasonable shapes of the wavefunction, $F^2 \sim 0.5$ W, From W it is possible to define an average radius :

$$r_0 = \frac{e^2}{W}$$

which is given for metal ions in gaseous state (in the case of the lanthanide ions for the aquo ions) and in complexes :

3 d^3	Chromium (III)	0.75 Å	0.97 — 1.35 Å	0.55 Å
3 d^5	Manganese (II)	0.83	0.89 — 0.94	0.80
3 d^6	Cobalt (III)	0.64	0.92 — 1.6	0.47
3 d^8	Nickel (II)	0.78	0.91 — 1.12	0.68
4 d^6	Rhodium (III)	0.72	1.2 — 2.4	0.69
4 f^2	Praseodymium (III)	0.84	0.84 — 0.89	1.16
4 f^3	Neodymium (III)	0.80	0.80 — 0.83	1.15
4 f^5	Samarium (III)	0.80	0.80 — 0.83	1.13
4 f^7	Gadolinium (III)	0.76	0.76	1.11
4 f^9	Dysprosium (III)	0.74	0.74	1.07
4 f^{12}	Thulium (III)	0.59	0.59	1.04

Thus, while 4*f*-electrons are screened in trivalent lanthanides (but not so much as assumed by many authors) the effective radius

r_0 of the *d*-shell is definitely larger than the ionic radius. In my opinion, this is strong evidence for partly covalent bonding, not only of γ_1 and γ_4 orbitals, but also of γ_3 orbitals containing *d*-electrons contributions.

Eventhough the molecular orbital theory thus has proven its superiority over the limiting case : the electrostatic theory with pure *d*-orbitals, it is interesting to notice the differences between the application of the molecular orbital theory to transition group complexes and to other types of molecules such as π-electron systems. In the latter case, the excited levels generally agree very modestly with calculations, and it is necessary to take large effects of intermixing of configurations of molecular orbitals into account, as pointed out by Coulson, Craig and Jacobs, *Proc. Roy. Soc.*, **A 206**, 1951, p. 297.

The calculations on transition group complexes generally agree within 3 %, when the parameter $(E_1 - E_2)$ in octahedral complexes and the somewhat decreased term distances are applied.

Eventhough the group-theoretical results cannot be connected with the electrostatic model originally used, the theory of transition group complexes must still be considered as much more unified than earlier distinctions between " ionic " and " covalent " complexes might have allowed.

The most prominent failure of the earlier theory is in my opinion the concentration of interest on the groundstate of the complex only, with resulting desire for a single valence bond formula of the type encountered in CH_4 or NH_3. It is very fortunate for the chemical physicists that there exist complexes with a partly filled shell, where each electron configuration correspond to more than one level. These cases are liable to yield much more information about the electronic structure than the closed shells which exist in only one state.

M. Bjerrum. — In his paper Dr Orgel also discusses " the mechanism of some electrontransfer reactions " and I should like to ask Dr Orgel how it can be that the transfer of an electron from the tris-ethylenediamine cobalt (II) ion to the corresponding luteo ion is much more rapid than the electron transfer in the corresponding cobalt ammonia system?

One might have expected the opposite, but perhaps the explanation is that $Co(en)_3^{++}$ is more close to be spin-paired than $Co(NH_3)_6^{++}$ so that the spin rearrangement occurs more easily in case of the ethylenediamine system.

M. Orgel. — When I talk of stability, I am referring to heats of formation. Often only free energy data are available.

In such cases I assume, optimistically, that trends in free energy parallel those in heats of formation in series of related compounds. The reason for preferring the heat of formation is simply that it is this quantity which can be calculated.

M. Nyholm. — When discussing stabilities of metal complexes one would prefer to have values of enthalpy (ΔH) for the heterolytic fission of the metal ligand bond (i.e. $M \leftarrow L \longrightarrow M + :L$) rather than free energy values (ΔG) . Pending the accumulation of many more ΔG and ΔS data we are forced to use free energy values in discussing metal complex stability rather than ΔH.

It must be borne in mind, however, that biological workers and those interested in the separation of metal ions in analytical chemistry and in industrial processes are concerned mainly with the extent of dissociation of complex ions in solution. For these workers free energy values are the more important.

What one needs very badly is some direct means of examining the relative strengths of metal — ligand bonds directly. For this purpose infra-red absorption spectroscopy in the 100 cm^{-1} region will prove most valuable. A grating spectrograph is necessary for this work.

We propose to work on this subject in the near future.

M. Chatt. — With reference to Prof. Nyholm's remark about the development of infra-red spectroscopic methods to examine the region of the spectrum where metal-ligand bond stretching occurs, my colleague Dr L.A. Duncanson is at present constructing apparatus for that purpose.

The entropy differences between isomeric complex compounds can be quite large. Some while ago we (Chatt and Wilkins, *J. Chem. Soc.*, 1952, 4300; 1955, 525) measured the entropy changes during some isomerisation reactions of the type *cis*-$[L_2PtCl_2]$ — *trans*-

[L_2PtCl_2]. The differences were of the order 10-15 cal. mol.$^{-1}$ deg.$^{-1}$. Actual examples are; when L = PEt_3, $\Delta S = 13.3$; when L = $AsEt_3$, $\Delta S = 14.2$; when L = $SbEt_3$, $\Delta S = 9.4$, all within oneen tropy unit.

We speculate that these large differences are due to the very great dipole moments of the *cis*-isomers (10 D), and that the moments cause a much greater solvation of the *cis*- than of the *trans*-isomer. It is an effect which might be found in any complex system where large dipole moments occur, and I mention it because these differences in ΔS are much greater than are usually found between isomeric substances.

M. Barrer. — From the thermodynamic point of view, the standard free energy of a reaction is $\Delta G^o = -RT \ln Ka$ where Ka is the thermodynamic equilibrium constant. The termodynamic equilibrium constant is the quotient of *activities* of resultants and reactants, whereas the stability constants, K, are the corresponding quotients of *concentrations*. Thus the stability constants do not give any rigorous measure of ΔG^o. Also $\frac{\delta}{\delta T}(RT \ln K)$ does not give a rigorous measure of ΔS^o nor $\frac{RT^2\ \delta \ln K}{\delta T}$ a rigorous measure of the heat of the reaction. One must be careful in introducing the terminology of thermodynamics that it be done exactly, since thermodynamics is an exact branch of science, and much confusion may eventually result from its qualitative or incorrect use.

M. Jørgensen. — So far crystal field theory shall denote the electrostatic model with pure *d*-wavefunctions, it might be questioned if " ligand field theory " does not simply mean " molecular orbital theory ". However, the partly covalent bonding also of *d*-electrons in complexes might be visualized as a result of the electrostatic perturbation on the partly filled *d*-shell. In most complexes outside the transition groups (except the p^2 systems, bromine (III), iodine (III) and polonium (II) which exhibit the tetragonal symmetry predicted from the Jahn-Teller effect) there is no electrostatic field separating the energy levels of a partly filled shell. Thus, the " ligand field " seems to be a good name for these co-operating effects with resulting partly covalent bonding.

M. Nyholm. — I believe that at first sight the term "crystal field" gives rise to a mental picture of an electrical field extending throughout a whole *crystal*. However in complex chemistry the field with which we are concerned is that arising from the ligands directly attached to the metal atom ; the second order effects of more distant ligands may be ignored as a first approximation. Thus in a sense a *ligand field* is a special kind of *crystal* field but the difference between these is importat since complex ions eg $[Co(NH_3)_6]^{+++}$ or molecules *eg* $[Co(NO_2)_3(NH_3)_3]^o$ may exist in solution when no "crystals" are present. There are occasions, of course, when both the ligand field and the crystal field may be involved. This appears to be true of certain crytalline metal complexes eg Cs_3CoCl_5 where the main effect upon the magnetic suceptibility arises from the four Cl^- ions which are attached to the Co (II) atom but longer range forces appear also to be operating.

Application of the Screening Theory to Chemical Reactions Involving Non-Metallic Solids

by **W. A. WEYL**

I. INTRODUCTION

For the past eight years the Office of Naval Research has sponsored basic research on various aspects of solid state chemistry in the author's laboratory. The results of this experimental program has led to a new concept of the polymerization of molecules and of the formation of solids. In solid state chemistry, e.g., in the determination of crystal structures, the principle of electroneutrality in the smallest possible volume is well established. To this first principle of chemistry a second one is now being added. The author assumes that the nuclei of most atoms require screening by a larger number of electrons than that which neutralizes their positive charges. The author considers this need for additional screening to be the second principle which governs the chemistry of the solid state.

In solid state chemistry it is not possible to operate with the conventional concept of the valency of an atom. Sodium is monovalent, but its reaction with chlorine is not terminated after each sodium ion has combined with one chlorine ion, a reaction which produces 120 Kcal. The reaction continues until each sodium ion is screened by six chlorine ions. The formation of solid NaCl from NaCl molecules gives an additional 60 Kcal. The condensation of NaCl molecules and the formation of solid NaCl is the result of the coordination requirement or the screening demand of the cation.

The fact that NaCl and AgCl have widely different properties (melting point, solubility in water) in spite of having identical structures, charges of the ions, and internuclear distances, ha. been explained in two ways. One way to account for the difference is by the assumption of different " degrees of covalency ". It became customary to describe the $Ag^+ — Cl^-$ bond as being more, and the $Na^+ — Cl^-$ bond as being less covalent. Another way has been suggested by K. Fajans (1) who describes these crystals as arrays of ions with different degrees of " mutual polarization ". The Ag^+ ion with its 18 electron shell is more interpenetrable for electrons and exerts a stronger polarizing effect upon the Cl^- ions than the Na^+ ion with its octet shell.

It is rather unfortunate that in crystal chemistry the terms " ion " and " ionic size ", etc. are used even for units such as P^{5+}, Si^{4+}, O^{2-}, N^{3-}, etc. These symbols are used to designate the quantum state of these elements. The use of the term O^{2-} " ion " means only that the oxygen participates in a crystal structure with eight eletrons quantized with respect to its core. This quantum state or the " quanticule " O^{2-} (K. Fajans) (2) does not exist in the free state nor is it stable as a hydrated ion, but it requires stabilization by strong positive fields, a fact which is most important in surface chemistry because in a surface the O^{2-} ions may lack the positive environment which is essential for their stabilization.

It has become customary to describe matter as consisting of atoms. In spite of the fact that we know little or nothing about the properties and the behavior of atoms of some of the most common elements, e.g., carbon, sulfur, and phosphorus, the atomic concept has proved very useful in chemistry, especially in organic chemistry.

There is only one rigorously correct approach to chemical reactions, namely, the description of the reacting systems in terms of nuclei and electrons. This idea is the basis of the quantum mechanical treatment of compounds and their reactions. As it is too cumbersome and too complicated to use this approach even for relatively simple chemical reactions, one depends upon approximations. The polarizability of the electron clouds and their deformation by adjacent electrical fields gives at least a qualitative picture of what may actually happen.

Recently (3) (Fritz Ephraim 1954), the Fajans approach to chemical binding forces, i.e., the " Quanticule Theory ", has found its way into a textbook of chemistry. We have chosen this concept for our approach to solid state chemistry because it offers several advantages over more conventional descriptions of chemical binding.

1. According to K. Fajans' quanticule theory an experimentally unique molecular species is represented by one electronic formula.

2. The Fajans' theory does not mix the two incompatible concepts, i.e., the classical valence bond (e.g., $O=C=O$) and the concept of charged particles (e.g., $(CO_3)^{2-}$).

3. The Fajans' concept of the mutual deformation of ions makes it obvious that in a solid the chemical bond between two atoms must be affected by any change which takes place in a remote part of the molecule. This "depth action" of chemical binding does not involve long range forces but is the result of a change in the state of polarization of the constituents which is relayed over long distances.

Our concept of the screening demand of positive cores and its decrease with increasing temperature made it possible to explain a number of phenomena for which, in the past no proper approach was available. Thus, E. C. Marboe and W. A. Weyl (4) explained the widely different viscosities of simple glasses in which cations were replaced by others of different sizes and different electronic configurations. A study of the glassy state was of particular value for the development of this concept because glasses offer the advantage over the crystalline state of permitting one to change the composition gradually. Replacing in a glass one ion by another one which has a different charge does not produce the kind of defect which is so characteristic for crystals, i. e., the change of insulators into semiconductors. Once the general rules which govern the screening of cations were established, it became possible to use them for the interpretation of the melting points of simple compounds (5) and for their hardnesses (6). As the screening of a cation improves with the size and the polarizability of the surrounding anions and as these parameters are decreased under hydrostatic pressure, it also became possible to explain the structural changes of crystals and glasses which had been found to occur under high pressures (7).

It is the object of this report to apply the screening concept to the rates of solid reactions. For this purpose the author postulates that the activation energy of solid state reactions which do not involve electronic transfer, i.e., change of the oxidation numbers of elements, is the result of the need for partially unscreening cations before they can be rearranged into the new lattices. This atomistic picture of the activation energy of solid state reactions makes it possible to understand reaction rates in a qualitative way and to explain the characteristic properties of the intermediate phases which have been called " Active Zwischenzustände ", by G. F. Hüttig (8).

II. THE SCREENING THEORY

The author's concept of the screening demand of positive cores is based on the following facts :

1. Most elements are solids at ordinary temperature.

2. Only the noble gases exist as atoms under ordinary conditions. In order to obtain atoms of other elements under normal pressure the energy of the system has to be raised. For some of the most common elements, e.g., carbon, sulfur, and phosphorus, a temperature of even 2 000 °C is too low for producing a gas which under normal pressure consists of atoms.

3. Other forms of energy, e.g., electrical discharges or radiation, can take the place of heat and produce atoms at ordinary temperature.

In order to account for these facts the author postulates that the formation of the elements took place under energy conditions (temperature, radiation) which were very different from those prevailing on our planet today. As the energy density changed, only the atoms of the noble gases remained single. In these elements the nuclei are sufficiently screened by the number of electrons which neutralize their charges. The octet shell seems to play an important role in the screening power of an electron cloud :

$$\mathrm{Ne}^{10+}\,(e^-)_{2,8}\,.$$

In the neon atom the nucleus Ne^{10+} is well screened by a group of 10 electrons, two belonging to the K shell and eight forming the very stable L shell. It seems, however, that other elements could not arrange their electrons in a fashion which provided sufficient screening for their nuclei.

These elements began to interact in order to improve the screening of their positive cores when the energy density level dropped. One of the most effective means for improving the screening of cores consists of the sharing of some electrons by a very large number of atoms. Some of the electrons of the individual atoms form and participate in a continuous three-dimensional atmosphere of electrons; the degenerated electron gas of metals. Metallicity can be assumed only if the number of atoms is very large. In metals the electron gas screens the nuclei of a three-dimensional array of atoms in a way which permits each core to be surrounded by electrons. This method of screening seems to be very effective : not only are most elements metals, but a large number of non-metallic compounds, e.g., UO_2, PbS, etc., imitate metallicity.

The formation of molecules which imitate the structure of a noble gas atom is another method for improving the screening of cores. In some molecules a small number of atoms combine and rearrange their electrons so that they are quantized with respect to two or more cores. According to K. Fajans, two nitrogen atoms assume the configuration of neon and form the N_2 molecule in which the two positive cores, N^{5+}, screen themselves by ten electrons which move in orbits quantized with respect to the two cores :

$$N^{5+}\,(e^-)_{10}\,N^{5+}\,.$$

The Fajans' quanticule theory gives us the expression :

$$C^{4+}\,(e^-)_{10}\,O^{6+}$$

for carbon monoxide. This formula indicates that the positive cores of carbon and oxygen are screened by an electron cloud which is quantized with respect to both cores. The close similarity between CO and N_2 molecules (the same van der Waals' constant) and their chemical inertness is expressed in this formula which can be derived from that of a neon atom by replacing the one core Ne^{10+} by two cores. In these and similar molecules (Cl_2, P_2, P_4, S_8) the number of cores is usually small and the electrons which are quantized with respect to these cores are not available for carrying a current.

In metallic tin the positive cores are screened by the electron gas. Tin can form a low temperature modification (gray tin) which is not metallic. We assume that in this form the Sn^{4+} cores are screened by an environment of anions Sn^{4-}. We treat gray tin as a " stannide ", $Sn^{4+} Sn^{4-}$; elemental germanium as the germanide, $Ge^{4+} Ge^{4-}$; and diamond as the carbide, $C^{4+} C^{4-}$. This regrouping of electrons and formation of cations and anions, e.g., $Na^+ Cl^-$, is one of the main reasons for the existence of the solid state. In order to properly screen all cations the array should be three-dimensional and infinitely extending. Indeed, a surface of a crystal has to be treated as defective and its chemical properties might be considerably at variance with those of the bulk.

The concept of screening or shielding of atoms has been used for structural considerations of compounds by several scientists, e.g., J. J. van Laar, W. Kossel and, more recently, by A. E. van Arkel. Especially van Arkel (9) went very far in using the screening concept and he even suggested that the mutual polarization of the ions should be introduced as a further refinement. This is being done in our approach. Another improvement over earlier attempts to use the screening concept is the reference to the core of atoms rather than to their oxidation number. Sulfur, for example, is always treated as the S^{6+} core, no matter whether it is hexavalent as in SO_3 or tetravalent as in SO_2. The use of the oxidation number instead of the core of an atom was one of the major stumbling blocks in earlier attempts to use the screening concept as can be seen from the questions which van Arkel raises in his book. For example, why is SO_2 not a linear molecule resembling CO_2? We use the Fajans' quanticule formula $S^{6+} (e_2^-) (O^{2-})_2$ in order to describe the molecule SO_2. This formula explains why the O—S—O bond angle in SO_2 is the same as in SO_3. The Fajans' quanticule formula makes it obvious that the oxidation of SO_2 to SO_3 is a process which does not involve the addition of atomic oxygen but the exchange between the quanticules (e_2^-) and O^{2-}. This is of particular importance for the understanding of the role of semiconductors as catalysts for this reaction.

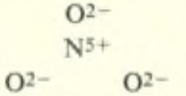
For most chemical reactions of the compounds of divalent lead it is perfectly satisfactory to refer to the Pb^{2+} ion, because in aqueous solutions the Pb^{2+} ion is surrounded by water in a highly symmetrical fashion. However, $PbBr_2$ is not linear and the bond angle Br-Pb-Br of this molecule in the vapor phase reminds us that the core is Pb^{4+} with an eighteen shell, so that it would be better to write $Pb^{4+} (e_2^-) Br_2^-$ rather than $Pb^{2+} Br_2^-$. Using this expression for describing the lead ion we can understand why in solid PbO the lead ion does not occupy the center of the prism which is formed by its surrounding eight O^{2-} ions, but is much closer to one group of four O^{2-} ions than to the other.

Keeping in mind the fact that divalent lead is actually $Pb^{4+}(e_2^-)$ explains the reaction of lead chloride with Grignard reagent :

$$2\,Pb^{4+}(e_2^-)\,Cl_2^- + 4\,CH_3^-MgBr^- = Pb^{4+}(CH_3^-)_4^- + Pb^{o} + 2\,MgBr_2 + 2\,MgCl_2$$

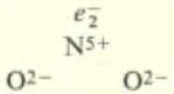
Otherwise this disproportionation of divalent lead into metallic lead and tetramethyl lead is difficult to understand.

K. Fajans treats nitrates and nitrites in a similar fashion. The NO_3^- and the NO_2^- groups contain the core of nitrogen N^{5+} screened by three quanticules, namely :



$$\begin{matrix} & O^{2-} & \\ & N^{5+} & \\ O^{2-} & & O^{2-} \end{matrix}$$

and



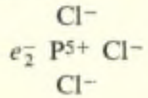
$$\begin{matrix} & e_2^- & \\ & N^{5+} & \\ O^{2-} & & O^{2-} \end{matrix}$$

In aqueous chemistry it is not very important to emphasize the quantization of the nitrogen and one may use the oxidation number instead. In solid state chemistry this is not satisfactory. If one neutralizes the $N^{5+}(e_2^-)(O^{2-})_2$ groups with interpenetrable cations, e.g., Ag^+ ions, one obtains a solid in which the cation is linked to the nitrogen by the quanticule (e_2^-). The less interpenetrable Na^+ ion, however, will be linked to the nitrogen by an O^{2-} ion. This difference, namely,

$$(O^{2-})_2\,N^{5+}\,(e_2^-)\,Ag^+ \quad \text{and}$$
$$(e_2^-)\,N^{5+}\,(O^{2-})_2\,Na^+$$

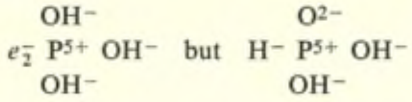
does not exist in aqueous solution where these salts are ionized but it becomes significant for the solid state. The reaction of the two solid nitrites with C_2H_5I leads to ethyl nitrite for the $NaNO_2$ but to nitroethane for $AgNO_2$. In the nitrite the ethyl group is linked to nitrogen by oxygen; in nitroethane it is linked "directly" to the nitrogen atom or, in the way we express it, the two cores N^{5+} and C^{4+} are linked together by the quanticule (e_2^-).

Trivalent phosphorus or trivalent arsenic is treated in the same fashion as trivalent nitrogen. The quanticule formula of phosphorus trichloride is, therefore,



$$\begin{matrix} & & Cl^- \\ e_2^- & P^{5+} & Cl^- \\ & & Cl^- \end{matrix}$$

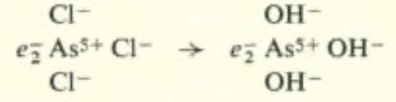
Its hydrolysis does not produce



$$e_2^-\,\underset{\mathrm{OH^-}}{\overset{\mathrm{OH^-}}{\mathrm{P^{5+}}}}\,\mathrm{OH^-} \quad \text{but} \quad \mathrm{H^-}\,\underset{\mathrm{OH^-}}{\overset{\mathrm{O^{2-}}}{\mathrm{P^{5+}}}}\,\mathrm{OH^-}$$

because the proton is better screened in the quanticule e_2^- than in the quanticule O^{2-}.

The corresponding $AsCl_3$, however, gives $(e_2^-)\ As^{5+}\ (OH)_3^-$ when hydrolyzed. This brings out the fact that the quanticule e_2^- is not as good a screener as an O^{2-} ion when both are polarized by positive cores which are more interpenetrable than noble gas-type cores. The greater interpenetrability of the As^{5+} core causes the substance $AsCl_3$ to behave in a " normal " fashion :



$$e_2^-\,\underset{\mathrm{Cl^-}}{\overset{\mathrm{Cl^-}}{\mathrm{As^{5+}}}}\,\mathrm{Cl^-} \rightarrow e_2^-\,\underset{\mathrm{OH^-}}{\overset{\mathrm{OH^-}}{\mathrm{As^{5+}}}}\,\mathrm{OH^-}$$

These few examples may suffice to illustrate the importance of referring to cores and electrons rather than to the oxidation number of an element.

III. CHARACTERISTIC FEATURES OF SOLID STATE CHEMISTRY

In this section the main features are discussed which the author considers characteristic for solid state chemistry.

1. The basic principles

The author postulates that the chemistry of the condensed state is governed by two basic principles, namely, the trends of a system toward establishing electroneutrality in the smallest possible volume and the desire to provide the maximum screening of the nuclei. Polymerization, i.e., the sharing of anions, and crystallization, i.e., the establishment of a symmetrical environment of anions around cations, are means by which a system can improve the screening of its nuclei. Sometimes electroneutrality is sacrificed in order to improve screening. The reaction between equal numbers of molecules of KI and $AgNO_3$ in water leads to negatively charged particles of AgI. The system has improved the screening of the Ag^+ ions at the surface of the solid at the expense of electroneutrality.

At its melting point a crystal is in equilibrium with a liquid phase which has a higher entropy but which provides less screening for its cations. This difference in screening can give rise to electrical potentials between a solid and a liquid. In systems containing protons, e.g., the system ice-water or the system crystalline-fused salol, E. J. Workman and S. E. Reynolds (10) found electrical potentials up to 60 volts, the solid being positive. Protons leave the less screening liquid phase in order to enter the better screening solid. This shift of protons also produces pH changes which have been observed by the same authors.

These facts should not be interpreted as indicating that electroneutrality is of lesser importance than screening. Water is unique as an ionizing solvent not because of its superior screening power (liquid NH_3 is a better screener) or because of its high dielectric constant (the dielectric constant of anhydrous HCN is 50 % higher than that of H_2O), but because it can establish electroneutrality around cations and anions of high charge. No other liquid can dissolve and ionize the sulfates of aluminium or thorium. No matter how high the dipole moment of a molecule and how many solvent molecules surround an Al^{3+} ion, the excess charge remains in this solvate unless a shift of protons in the water in the direction away from the Al^{3+} ion brings this volume element closer to electroneutrality.

The principle of establishing electroneutrality in the smallest possible volume is well recognized by workers in the field of solid state reactions. Those who have theorized on the nature of the "diffusing unit", e.g., J. A. Hedvall (11), agree that the particles which diffuse should be electrically neutral or nearly so. In their thinking they eliminated the possibility that P^{5+} or W^{6+} ions migrate as such; they preferred to speak of P_2O_5 or WO_3 molecules. This concept seems to be supported by experiments whenever experimental techniques made it possible to draw conclusions on the nature of the diffusing unit.

We have added to this principle of electroneutrality a second one, namely, that of the screening demand of positive cores. With decreasing temperature or, more generally speaking, with decreasing energy density, the nuclei of most elements require more electrons for screening than are necessary for neutralizing their positive charges.

The screening demand of cations depends upon their electronic configurations. For noble gas-type ions it increases with their field strengths, i.e., the screening demand of the cations is directly proportional to their excess charges and inversely proportional to their sizes. This can be seen from the boiling and melting points of the fluorides of the alkalies. The greater the field strength of the cation — i.e., for constant charge, the smaller their radii — the greater is their demand for screening by a symmetrical environment of anions. Fused CsF can maintain its more probable liquid state down to a temperature of 700 °C but NaF loses entropy at 1,000 °C in order to improve the screening of the smaller Na^+ ions. If one plots the melting points of the compounds CsF, RbF, KF, and NaF versus the radii of the cations, one finds a straight line relationship. One can describe the melting point as the temperature at which two phases are in equilibrium, one having the higher entropy and another having a less probable, more symmetrical structure but better screened ions. Screening is improved in a crystal by surrounding the cations with anions in a symmetrical fashion.

Increasing the field strength by increasing the charge of the cation, i.e., going from Na^+ to Mg^{2+} and Al^{3+}, etc., has a similar effect upon the screening demand. However, as the excess charge of the cation increases, more anions are required for neutralizing their charge so that the demand for additional screening decreases. These two antagonistic changes cause the melting point of the fluorides

NaF	MgF_2	AlF_3	SiF_4
980 °C	1,400 °C	1,040 °C	—77

to go through a maximum. The gases SiF_4, PF_5, and SF_6 consist of molecules in which the positive cores are well screened. The anion to cation ratio is the most important parameter which determines the screening of a cation.

Up to a certain point it is possible to treat solids as consisting of electrically charged rigid spheres. One can use the principle of electroneutrality in the smallest possible volume and deduce that a solid mixture of LiCl and KF will not be in equilibrium. The combination of the small cation (Li^+) with the small anion (F^-) and the large cation (K^+) with the large anion (Cl^-) would provide a more economical packing and thus produce electroneutrality in a smaller volume. Indeed, the lattice energies of these halides reveal that the mixture of $LiF + KCl$ has a lower free energy and higher lattice energy than one of $LiCl + KF$:

$LiCl +$	$KF =$	$LiF +$	KCl	
192	187	239	163	Lattice Energy in Kcal
381		402		Total Energy of Mixture.

This simple treatment has its limitations when the mutual polarization becomes an important factor. The system $CoO + BaS$ is not in equilibrium in spite of the fact that the sizes of the ions would suggest that this is the most economical packing. The small Co^{2+} ion, however, has an incomplete electron shell and, consequently, it is much more interpenetrable for electrons than the noble gas-like Ba^{2+} ion. As a result, a mixture of $CoO + BaS$ can lower its free energy by reshuffling its ions and combining the most interpenetrable ion with the most polarizable, i.e., the largest, anion. For this reason cobalt occurs in nature in sulfidic ores rather than in silicates. Platinum and gold occur in nature only in forms which have highly polarizable anions, either the electron gas of the metals or as telluride (calaverite, $AuTe_2$) and arsenide (sperrylite, $PtAs_2$).

Cations of the non-noble gas-type also are more polarizable, i.e., they have a more deformable electron cloud, than those of the noble gas-type. This, too, affects their screening demand. Whereas a Mg^{2+} ion requires complete screening in space, non-noble gas-type ions of the same size and charge can be satisfactorily screened by an environment of anions in a plane rather than in space.

Mg^{2+} and Be^{2+} ions, like other divalent ions, can be forced into a planar configuration by the phthalocyanine group which in its center has two H^+ ions which can be replaced by a divalent ion. However, the Be and Mg compounds hydrate readily, taking up $2\,H_2O$ molecules, in order to complete their screening in space, but the corresponding Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, and Pt^{2+} complexes do not.

This difference in the screening demands with respect to the distribution of anions around cations of the noble and non-noble gas-type has a direct bearing on the formation of the solid state. K. Fajans considers the volatile boron hydride B_2H_6 as having a structure similar to the molecule Al_2Cl_6 which is present in the vapor of aluminum chloride :

$$\begin{array}{ccccccccccc} \mathrm{H}^- & & \mathrm{H}^- & & \mathrm{H}^- & & \mathrm{Cl}^- & & \mathrm{Cl}^- & & \mathrm{Cl}^- \\ & \mathrm{B}^{3+} & & \mathrm{B}^{3+} & & \text{and} & & \mathrm{Al}^{3+} & & \mathrm{Al}^{3+} & \\ \mathrm{H}^- & & \mathrm{H}^- & & \mathrm{H}^- & & \mathrm{Cl}^- & & \mathrm{Cl}^- & & \mathrm{Cl}^- \end{array}$$

Dimerization through the sharing of anions gives each cation the coordination number four, i.e., it can be screened by four anions in tetrahedral arrangement. The fact that the hydride of aluminum is solid can be explained on the basis that the Al^{3+} ion is larger than the B^{3+} ion so that the cations cannot be screened in the dimer. However, it is not only the larger size of the Al^{3+} ion but also its low polarizability which is responsible for its need to continue its polymerization and to form a three-dimensional structure. This can be seen from the fact that the larger Ga^{3+} with its greater polarizability (18 outer electrons) forms a volatile hydride Ga_2H_6.

Methyl and ethyl groups are better screeners than H^- ions. $Al(CH_3)_3$ and $Al(C_2H_5)_3$ form dimers in the vapor phase but the corresponding gallium and even the indium compounds are monomeric.

The fact that the polarizability of the anion is as important for the screening as the polarizability of the cations can be seen from the melting points of the sodium halides which decrease with increasing polarizability of the anion :

	NaF	NaCl	NaBr	NaI	Na metal
M. P.	980	801	755	651	98 °C

Also, whereas SiO_2 in its various stable modifications has to form a three-dimensional network, the corresponding SiS_2 polymerizes only in one direction (chain structure).

The screening theory is based on the postulate that the screening demand of cores increases with decreasing temperature. The cations of high temperature modifications frequently have a lower coordination number than those of the low temperature forms.

The effect of hydrostatic pressure on the screening demand of cations is less obvious than that of temperature. Up to the present time physical chemists have paid little attention to pressure as a parameter beyond its effect upon concentration. Today high pressure reactions have become of technical importance and it might be interesting, therefore, to examine the effect of hydrostatic pressure on the screening demands of cations and, with it, the atomic structure of substances.

1. All ions are compressed, i.e., their electron clouds are forced closer to their respective nuclei so that their sizes and polarizabilities decrease. As a rule, anions, because of their larger sizes, are more compressible than cations.

2. The compression of an ion tightens the electron clouds. As a result of this tightening, the refractive index of a solid under hydrostatic pressure does not increase to the same extent as its density.

3. The loss of polarizability of the anions lowers their screening power with respect to the cations. For this reason, many solids undergo structural changes which improve the screening of their cations by increasing their coordination number. RbCl has NaCl structure under normal pressure (C.N. = 6) but assumes CsCl structure (C.N. = 8) under high pressures. AgI changes its coordination from 4 to 6. P. W. Bridgman (12) found that CS_2, a liquid which consists of molecules in which the carbon cores are well screened by two large and polarizable S^{2-} ions, polymerizes under pressure and changes into a solid which is supposed to have the structure of SiO_2.

4. Modifications which are formed under high pressures are metastable at normal pressure. In spite of their higher energy content the high pressure forms can be less reactive. Their lower reaction rates are the result of the lower polarizability of their ions. The solid CS_2 obtained by P. W. Bridgman is barely inflammable. A high pressure modification of silica obtained by L. Coes (13) is not attacked by hydrofluoric acid.

2. The depth action of chemical binding

The leaders in the field of solid state reactions, in particular H. Forestier (14) and J. A. Hedvall (15), are aware of the influence of the atmosphere upon the rate of solid state reactions. These scientists encountered effects of gases on the chemical reactivity, phase transformation, and melting of solids which are difficult to interpret on the basis of conventional physical chemistry. These phenomena seem to indicate that adsorbed molecules, even if they are chemically inert like N_2 or the rare gases, must affect the electronic structure and, with it, the binding forces of the solid to a considerable depth.

We can assume that the present description of atoms and ions is essentially correct; they can be compared with tiny solar systems in which the gravitational forces are replaced by electrical forces. Solids accordingly represent a three-dimensional array of these solar systems in close proximity. Astronomers would deny the possibility that the effect of a disturbance in one solar system would be limited to its nearest neighbors. Nevertheless, many physical chemists still attempt to describe events at the surface of a solid, say chemisorption, in terms which are limited to certain lattice sites or active centers and they prefer to sacrifice the concept of a " depth action " in order to be able to derive a quantitative treatment of an interaction between two atoms. Astronomers who would firmly refuse to accept the idea of a localized disturbance would also frankly admit that they are not in a position to mathematically derive the extent and the magnitude of the disturbances in remote solar systems. The mathematics is too complicated if it involves many bodies.

The Fajans' concept of the mutual polarization of ions provides a physical picture of the way in which the effect of a disturbance is relayed from one lattice site to another: induction of dipoles and changes in their magnitude and their direction. The screening concept explains the reason for the interaction of surfaces with the electron clouds of inert molecules such as N_2 or noble gas atoms. It seems that the concept of a constant " chemical bond " is the main reason for certain difficulties in solid state chemistry.

Workers in various industries are well aware of this " depth action ". The role of the " cooling liquid " in grinding, milling, and drilling operations is too well known to be discussed here. The mechanical strength and the hardness of substances depend upon their environment, a technical know-how which is well supported by laboratory experiments. W. von Engelhardt (16) published several papers on the abrasion hardness of quartz as a function of the " cooling liquid ". Experiments of C. Benedicks (17) reveal that silica glass fibers and thin platinum wires undergo volume changes in contact with liquids (liquestriction). C. Benedicks and G. Rubens (18) found that the strength of steel, especially its fatigue strength, is strongly dependent on the nature of the wetting liquid. The effect of the environment upon the mechanical properties of a solid, its volume, hardness, tensile strength and fatigue makes it obvious that electronic and chemical properties also must be affected.

M. Faraday (19) in his classical treatise " Experimental Relations of Gold and Other Metals to Light " describes reversible color changes of gold dispersions as the result of alternate drying and wetting. In the manufacture of pigments (Guinet Green, Iron Oxides) it is well appreciated how particle size and surface structure affect the color. G. F. Hüttig (20) uses the color of reacting systems, e.g., $Fe_2O_3 + ZnO$, to characterize the state of reaction. Disturbances emanating at a surface or interface are relayed into the interior and affect the state of polarization of the Fe^{3+} ions to a considerable depth as the color does not depend upon surface ions only.

Guided by the hypothesis that the visible fluorescence of CdS is due to asymmetrical units, e.g., Cd^{2+} ions which are located between S^{2-} and say O^{2-} ions in glasses, J. K. Inman, A. M. Mraz and W. A. Weyl (21) produced luminescent materials by precipitating cadmium sulfide on suitable carriers, for example, alkali halides. Both intensity and frequency of the emitted light was found to decrease in progressing from KCl to KBr to KI. The more polarizable the anion of the halide the more it resembles the S^{2-} ion and the less asymmetrical becomes the unit S^{2-} - Cd^{2+} - Halogen. Also, by choosing the suitable environment (e.g., aluminium stearate in xylene) the sulfides of tin, thallium, and mercury could be excited to visible fluorescence. None of these sulfides shows visible fluorescence when precipitated without a carrier from aqueous solutions.

Of particular interest is the observation of W. Braunbeck (22) because it shows that even the chemically inert gases, helium and argon, can screen a surface and thus mobilize electrons. He found that the conductivity of a thin platinum foil has its lowest value in vacuo and that it increases when gases are admitted. Helium increases the electrical conductivity by only 0.1 % but argon increases it by 0.3 % and oxygen by 0.5 %.

With respect to the chemical properties of substances this depth action in solids has three implications.

a) For any substance the chemical reactivity changes if subdivision is carried out to an extent that one, two or all three dimensions decrease beyond the range of the depth action. The interactions of some clay minerals with water, i.e., ionic exchange and rheological properties, depend more upon the thickness of the layers of these minerals than upon their chemical composition.

R. Schenck (^{23}) emphasized the fact that the particle size of a metal or of an oxide not only affects the reaction rate but also the equilibrium with gases. For palladium oxide the dissociation pressure at a given temperature increases with decreasing particle size. For iron oxides a similar dependence on the subdivision was discovered for their equilibria with CO_2 - CO mixtures.

G. Rienäcker and associates (^{24}) found that sintering of fine metal powders decreases the surface area steadily but their catalytic activities go through a maximum.

b) A second manifestation of this depth action is the influence of a " carrier " upon the chemical properties of substances. In heterogeneous catalysis this phenomenon is so well known that there is no need for going into details.

F. Feigl (^{25}) gives numerous examples for abnormal solubilities of substances when precipitated on certain " carriers " : " Numerous cases are known in which a solid loses its normal reactivity toward certain reagents because it is associated with a second solid which thus plays the part of a masking agent. Sulfide precipitates offer a veritable treasure trove of such abnormalities. "

c) A third manifestation of the " depth action " concerns the interaction between solids and gases. It is well established that a molecule chemisorbed at a solid has different optical and chemical properties than the same molecule in the gaseous state or in a solution. However, it is not yet fully appreciated that the chemisorbed particle also affects the electronic structure of the surface of the solid and that this effect goes far beyond the adjacent lattice sites. Combining the principle of " depth action " with that of " actio est par reactione " we may express our thoughts on this subject drastically by saying : A crystal of metallic nickel or of zinc oxide which has a molecule of hydrogen chemisorbed at its surface has changed into a different chemical individual and, consequently, its reactivity toward a second hydrogen molecule is different. This difference, e.g., the change in the heat of absorption with increasing numbers of chemisorbed gas molecules, is, of course, known, but it is usually attributed to the existence of lattice sites which had different activities from the very beginning. No doubt, this possibility exists, but it is not necessarily the right explanation for the phenomenon. Again we may assume that the depth action will be a maximum for the polarizable metals and for sulfides and a minimum for oxides and fluorides containing noble gas ions. Even for the latter group, however, it cannot be ignored as we can see from the fact that quartz is affected by adsorbed gases. P. Stahl (26) found that the temperature of the α-β-inversion of fine quartz powder changes with the nature of the ambient atmosphere. Such an inversion requires a cooperative maneuver and a change in the chemical bonding within only one atomic layer in the surface could have no effect upon the nucleation of a new modification.

H. W. Kohlschütter (27) found that the nature of the ambient gas has a pronounced influence upon the rate of inversion of the yellow into the red modification of mercuric iodide. W. A. Weyl and D. P. Enright (28) studied the transition of the metastable yellow into the red stable form on cooling. Irradiation and mechanical shear forces accelerate the transition and, depending upon the nature of adsorbed ions, the transition can be accelerated or delayed. Also, yellow HgI_2 precipitated from a hydrocarbon transforms immediately into the red form but it takes minutes when precipitated from a more polarizable solvent such as alcohol and hours from acetone. Yellow HgI_2, embedded in a matrix of rosin saturated with HgI_2, did not change into the red form at room temperature over a period of years. Ordinarily the red form transforms into the yellow form at 126 °C but treatment of the surface with Pb^{2+} or Tl^{+} ions made it possible to superheat the red form to 131 °C.

3. **Formation of defective structures**

Foreign atoms or other lattice defects affect the stability of a crystal in two ways. Firstly, they lower the free energy of the system by increasing its entropy. With increasing temperature this contribution becomes increasingly important. Secondly, any disturbance increases the potential energy of a crystal. The extent to which it increases this energy term decreases with increasing polarizability of all constituents. The polarizability of an ion can be looked upon as its ability to adjust its own force field to suit its environment. A lattice vacancy, for example, produces asymmetrical fields but such a defect raises the energy of a polarizable crystal less than that of a crystal which contains noble gas-type cations and anions of low polarizability. In nature we find sulfidic ores of great complexity rather than pure heavy metal sulfides. Calcium carbonate, calcium fluoride, cryolite or silica, on the other hand, often occur as very pure specimens.

The degree of defectiveness which a given crystal assumes depends upon the temperature, the composition of the atmosphere, and the presence of foreign atoms. Of particular interest to us is the fact that foreign atoms not only can induce lattice vacancies but they can also prevent their formation.

4. Glasses versus crystals

Glasses represent the most generalized arrays of ions. The glassy state has a higher entropy than the crystalline state because it has no long range order. The short range order around major cations is essentially the same in both states so that there is no major energy difference between a glass and a crystal. If the need for screening of the cations of a fused system is very high (MgO, Al_2O_3 or MgF_2) the melt crystallizes on cooling in order to surround each cation by anions in a highly symmetrical fashion. If the cations are well screened by the number of anions which neutralize their charges, independent molecules are formed (SF_6, PF_5 or SiF_4) and their condensation at low temperature is the result of van der Waals' forces. The rearrangement of the liquid into crystals is too fast to permit the formation of stable glasses. Glasses can form from a melt in which the screening of the major cations is intermediate between these two extremes (SiO_2, P_2O_5, or BeF_2).

The chemistry of glasses offers several features which can lead to a better understanding of the solid state. The author could derive a great deal of information concerning solid state chemistry from studies of glasses because :

a) The chemical composition of glasses can be changed gradually and continuously.

b) By chilling a glass from high temperature it is possible to "freeze in" and to examine at normal temperature some of its high temperature structure, e.g., a coordination of cations which is stable at high temperature only.

c) Elements which form several states of oxidation (Fe^{2+} - Fe^{3+}, Cr^{3+} - Cr^{6+}) can form equilibria between these states in a glass so that it is possible to study the effect of composition, temperature, and atmosphere upon the state of oxidation of elements.

d) The absence of long range order makes it impossible for glasses to form semiconductors and, as a result, their chemical properties are not as sensitive to "impurities" as those of crystals.

As an example for the usefulness of the constitution of glasses for answering basic questions in the field of solid state chemistry we will discuss the factors which determine the screening demands and, with it, the coordination numbers of cations which have field strengths sufficient to exert a major influence on the structure.

W. A. Weyl and E. Thümen ([29]) developed an optical method for following coordination changes in glass. The Ni^{2+} ion was found to be particularly suitable for this purpose. When introduced into silicate glasses, Ni^{2+} ions form two distinct types of color centers which could be attributed to Ni^{2+} ions in sixfold and fourfold coordination. In sodium silicate glasses an equilibrium is formed between the yellow center (Fig. 1A) characteristic for the NiO_6 group and the purple center (Fig. 1B) characteristic for the NiO_4 group. These glasses are gray because their absorption extends over the whole visible spectrum. Any change in composition which decreases the polarizability of the O^{2-} ions favors sixfold coordination of the Ni^{2+} ions and shifts the color of such a glass toward yellow. For example :

1. Replacing some Na^+ ions by the more polarizing Li^+ ions. The gray color of this glass is shifted toward yellow.

2. Replacing Si^{4+} ions by P^{5+} ions. Nickel oxide produces yellow colors in a $NaPO_3$ glass or in vitreous metaphosphoric acid.

3. Replacing some O^{2-} ions by less polarizable F^- ions. Complex fluoberyllate glasses containing Ni^{2+} ions are yellow.

4. Replacing O^{2-} ions by the less polarizable OH^- ions. Exposure

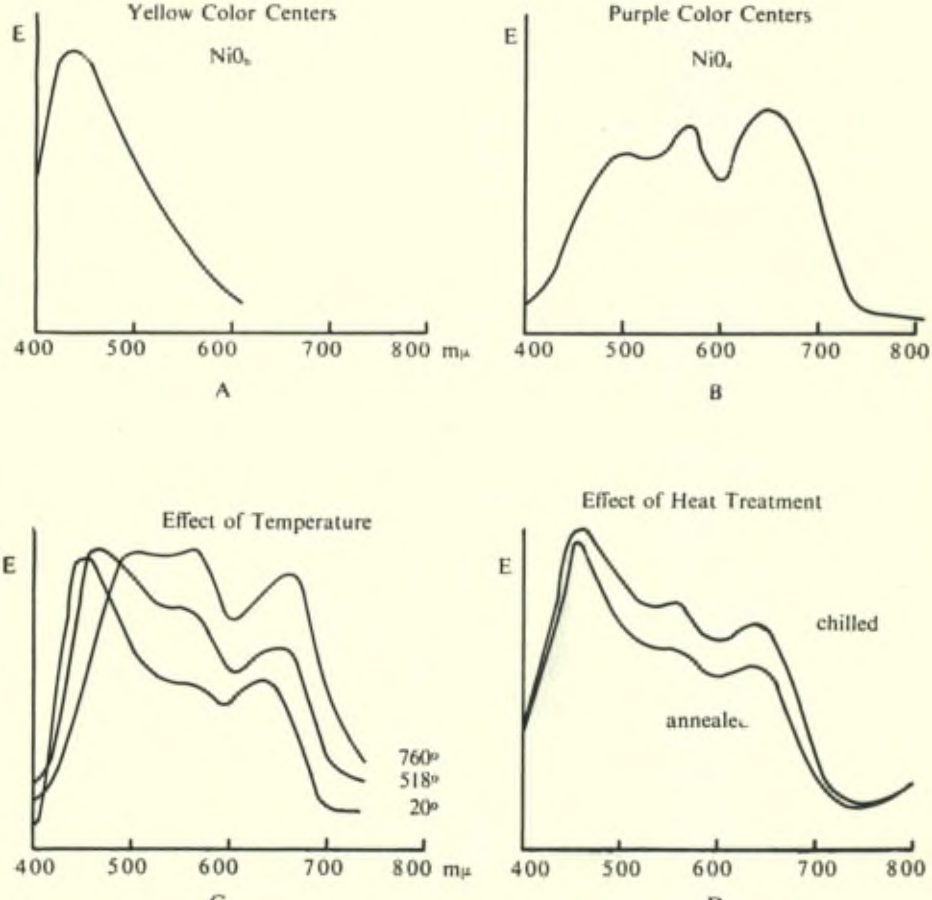

Yellow Color Centers
NiO_6
E
400
500
600
700
800 mμ
A
Purple Color Centers
NiO_4
E
400
500
600
700
800
B
Effect of Temperature
E
760°
518°
20°
400
500
600
700
800 mμ
C
Effect of Heat Treatment
E
chilled
annealed
400
500
600
700
800
D

Fig. 1.

of alkali silicate glasses containing Ni^{2+} ions (K^+ - silicate) to water vapor over extended periods of time causes H_2O to diffuse into the glass and, as the diffusion of H_2O proceeds, zones are produced in which the purple color has changed into yellow.

The opposite effect, namely, the change of the yellow and gray colors toward purple corresponding to the change of the coordination from six to four, is observed if the polarizability of the O^{2-} ions is increased. For example :

1. Replacing some Na^+ ions of sodium silicate glass by the weaker or less polarizing K^+ or Rb^+ ions. Rubidium silicate glasses containing NiO are pure purple and their absorption spectra reveal the absence of yellow color centers.

2) Increasing the polarizability of the O^{2-} ions by raising the temperature. Due to thermal expansion the average internuclear distances are increased and the state of deformation of the O^{2-} ions decreases. Increasing the temperature shifts the equilibrium from the yellow NiO_6 groups toward the purple NiO_4 group (Fig. 1C).

3. Chilling a glass rapidly from a high temperature " freezes in " a high temperature modification which is characterized by a lower density and a greater polarizability of its anions. A chilled glass is more purple than the same glass after annealing (Fig. 1D).

Hydrostatic pressure decreases the polarizability of the anions and, with it, their screening power. T. Förland, in the author's laboratory, found that a purple-gray alkali silicate glass changes into a yellow one permanently when exposed to high pressure (30,000 atm.) at temperatures around 450 °C. These observations agree with those of geochemists who associate the occurrence of aluminium in minerals in the higher coordination, i.e., sixfold, with their formation under high pressures.

IV. ATOMISTIC INTERPRETATION OF SOME SOLID STATE REACTIONS

The concepts which were developed in the preceding chapters make it possible to present an atomistic picture of the activated state of chemical reactions. It is postulated that the activated state corresponds to a state in which the cations are screened to a lesser extent than in the reactants and in the reaction product. The activation energy of a solid state reaction is the energy which is necessary to temporarily increase the volume of the reactants and to partly unscreen cations. This concept applies to phase transformations of the reconstructive type, to sintering and recrystallization as well as to chemical reactions between solids.

1. **Phase transformations**

The spectacular differences which exist between the fast α-β-inversion of quartz and the sluggish inversion of quartz into tridymite or cristobalite and the pseudo-stability of cristobalite in nature led to a classification of phase transformations into two groups, " displacive " and " reconstruction " transformations. M. J. Buerger (^{30}) suggested that fast transformations involve a displacement of non-contacting atoms with respect to one another without the need for disrupting the linkage of the three-dimensional network and the formation of a new one. With respect to the reconstructive transformation he writes : " It necessarily involves a temporary breaking of first coordination bonds. This represents a very high energy barrier. Evidently this transformation must proceed in a sluggish fashion indeed. "

The geometry of the transformation is, no doubt, important but it is not the only rate determining factor. The red form of mercuric iodide, for example, cannot be overheated to an appreciable extent. Within a few degrees above 126 °C it changes into the yellow modification which is stable above this temperature. The yellow form contains Hg^{2+} ions surrounded by six I^- ions in a distorted octahedral arrangement. The red modification has a layer structure which is quite different from that of the structure of the yellow modification. The Hg^{2+} ions in red HgI_2 are surrounded tetrahedrally by four equidistant I^- ions. The formation of such a layer structure may be treated as the first step toward the transition from a three-dimensional infinitely-extending network into independent molecules. In this first step electrically neutral layers are formed which extend infinitely only in two dimensions.

Considering the geometry one would expect that the change of the low temperature form of HgI_2 into the high temperature form would be a sluggish transformation. This change and similar changes of complex iodides, however, are so fast that they are used as temperature indicators (silver mercuric iodide, copper mercuric iodide). In order to understand the mechanism of these modification changes and, generally speaking, of the rates of solid state reactions, we must abandon concepts such as those of " breaking a bond " and " formation of a new bond " because they have no physical significance in solid state chemistry.

The activation energy of phase transformations of the reconstructive type is given primarily by the energy necessary to partly unscreen the cation. In these iodides containing polarizable cations this energy term is very low.

2. Recrystallization and sintering

The driving force in sintering or recrystallization is the lowering of the free energy of the system by decreasing the surface area and, with it, the surface free energy. P. A. Marshall, Jr. in the author's laboratory studied the sintering of CaF_2 and BaF_2 pellets. The volume change of these pellets on heating reveals that CaF_2 begins to sinter at a temperature 100 °C lower than BaF_2 in spite of the fact that BaF_2 has a lower melting point than CaF_2. The low polarizability and the relatively high field strength of the Ca^{2+} ions causes CaF_2 to have a higher surface energy than BaF_2. This provides a greater driving force for CaF_2 to lower its free energy by decreasing the surface area and, with it, the number of incompletely screened cations. These experiments show that in sintering, the rate of the reaction can be proportional to the driving force and inversely proportional to the resistance of the reacting system. However, one has to keep in mind that the " driving force " of a reaction determines its rate only in those cases where the equilibrium is actually an oscillation in which small volume elements switch back and forth between both configurations, a situation which has been called " microscopic reversibility " by S. R. De Groot ([31]).

Non-noble gas-type cations because of their greater polarizability can lower the surface energy of a crystal which contains noble gas-type ions. Thus, two solids in contact, e.g., $Al_2O_3 + Cr_2O_3$, may lower their free energy by covering the one with the least polarizable cation (Al_2O_3) with the one which has the more polarizable cation (Cr_2O_3). G. F. Hüttig ([32]) observed this " creep " of one oxide over another, a process which lowers the driving force for sintering.

P. W. Clark and J. White (33) found that the addition of 4 % Cr_2O_3 to Al_2O_3 prior to pressing slowed down the rate of sintering of the alumina without affecting the ultimate shrinkage.

W. E. Brownell (34) in the author's laboratory made a quantitative analysis of solid state reactions producing different spinels. He found that the addition of PbO slows down the rate of the reaction between MgO and Al_2O_3.

The stabilization of a system by lowering its surface free energy is the driving force for sintering. The energy barrier or the activation energy of this process can be attributed to the partial unscreening of cations and the repulsive forces which come into play if one cation has to pass another cation. For example, if a sodium ion has to move through the lattice of NaCl during thermal diffusion or in an electrical field, it has to squeeze through between other Na^+ ions and Cl^- ions. In this position it will be strongly attracted by the Cl^- ion and repelled by the Na^+ ion. We emphasize in our approach the repulsive forces between cations more than those between anions because anions exert weaker forces upon each other because of their mutual polarization. Many crystals can be described as arrays of anions which touch one another and which are held together by cations. However, noble gas-type cations as neighbors are not likely to occur in crystal structures.

The volume expansion which accompanies the melting of the alkali halides is an indication of the repulsion between the cations. This has been discussed previously (35) and V. Zackay (36) pointed out that this volume effect during melting decreases with increasing polarizability of the cations as well as of the anions so that it is a minimum for the alkali metals. One might suspect that there is a simple relation between diffusion processes, e.g., sintering, and the absolute melting temperature. This, however, is not the case because of the paramount importance of vacant lattice sites for diffusion.

Zinc oxide (M.P. 1975 °C) sinters at 700 °C because this crystal can form a defective structure. On heating, ZnO cleaves off oxygen and forms anion vacancies :

$$Zn^{2+}\,O^{2-} = Zn^{2+}\,(e^-)_{2x}\,(A.V.)_x\,O^{2-}_{1-x} + x\,O.$$

The defective crystal has anion vacancies which make rapid diffusion possible.

The very low polarizability of the Mg^{2+} ion is responsible for the fact that MgO forms lattice vacancies only at much higher temperatures. However, in the presence of cations which have a higher (Fe^{3+}) or a lower (Li^{+}) charge than the Mg^{2+} ion the gain in entropy causes MgO to form a solid solution at lower temperature (~ 1,500 °C) which contains cation vacancies or anion vacancies respectively :

$$Mg^{2+}_{1-1.5x}\ Fe^{3+}_{x}\ (C.V.)_{0.5x}\ O^{2-} \quad \text{and}$$

$$Mg^{2+}_{1-x}\ Li^{+}_{x}\ (A.V.)_{0.5x}\ O^{2-}_{1-0.5x}$$

The addition of iron oxide to magnesite is used in the manufacture of magnesite refractories.

The sintering of zinc oxide can be enhanced by the addition of Li_2O (more anion vacancies) and delayed by the addition of Ga_2O_3 or Al_2O_3 because the latter additions prevent the lattice from developing anion vacancies at a temperature where the zinc oxide partly dissociates.

Sintering and recrystallization processes are closely related to chemical reactions and the following two examples illustrate that foreign atoms can enhance and prevent chemical reactions in exactly the same way as they can affect sintering.

The reaction of calcium carbide with nitrogen to form cyanamide is very slow even at 1,000 °C but it can be greatly accelerated if calcium chloride or fluoride is added. According to G. Bredig (37) $CaCl_2$ or NaCl catalyze the reaction but Na_2CO_3 and $CaCO_3$ do not. At 1,000 °C the CaC_2 crystal can gain entropy by forming a solid solution in which some $(C_2)^{2-}$ ions are replaced by singly charged F^- or Cl^- ions so that the lattice develops cation vacancies.

$$Ca^{2+}\ (C_2)^{2-} \rightarrow Ca^{2+}_{1-x}\ (C.V.)_x\ (C_2)^{2-}_{1-2x}\ Cl^{-}_{2x}$$

Replacing $2x$ $(C_2)^{2-}$ ions in the carbide by the same number of singly charged Cl^- ions produces x cation vacancies per mol.

The additions of foreign atoms may accelerate a chemical reaction but they can also delay and even prevent it. NiO of stoichiometric composition is green but on heating in air it forms a defective structure, a higher oxide which is black. As one would expect, the black oxide can react with metallic nickel and form the green stoichiometric NiO.

Addition of Li_2O is another way to change the green NiO into the black form. The two black oxides, one obtained by oxidation, the other by substitution, have identical electronic properties. This is expressed in their formulae by indicating that both structures lack x electrons per mol. The $(+)$ sign indicates one " missing electron " per mol.

$$Ni^{2+}_{1-5.5x}\ (+)_x\ (C.V.)_{0.5x}\ O^{2-} \quad \text{and}$$

$$Ni^{2+}_{1-x}\ Li^{+}_{x}\ (+)_x\ O^{2-}$$

The oxidized NiO contains cation vacancies and is chemically reactive. The Li^+ substituted NiO does not contain cation vacancies and, consequently, it does not react with metallic nickel to form the green NiO.

3. **Decomposition reactions**

The fact that CO_2 is a gas at ordinary temperature indicates that the core of carbon C^{4+} is well screened by two O^{2-} ions. A carbon core, however, may require three or four O^{2-} ions if the latter are less polarizable. In carbonates a part of the excess charges of the O^{2-} ions are neutralized by weak cations, e.g., Na^+, K^+, Ba^{2+}, etc., therefore, the planar $(CO_3)^{2-}$ group becomes stable. As the field strength of the contrapolarizing cations and, with it, the tightening of the electron clouds of the O^{2-} ions increases, the carbonate becomes less stable. In this case the carbon is better screened either by having two O^{2-} ions of its own or it expands its coordination to four less polarizable O^{2-} ions. The latter configuration exists in the esters of the orthocarbonic acid in which each O^{2-} ion is tightened by two carbon cores. The configuration $(CO_4)^{4-}$ can also be obtained under high pressure because hydrostatic pressure decreases the polarizability of anions. W. Skaliks (38) thus prepared a potassium magnesium carbonate glass and W. A. Weyl (39) melted sodium carbonate-silicate glasses in which CO_4 and SiO_4 groups are interlinked.

The equilibria between carbonates and oxides plus CO_2 illustrate how the screening power of an anion is affected by surrounding positive fields. Table I gives the stability of some carbonates. $BeCO_3$ decomposes at 100 °C whereas $BaCO_3$ has a stability which compares with those of the alkali carbonates. The stabilities of the carbonates of Mg, Ca, and Sr are intermediate between these two extremes. The weaker the field of the contrapolarizing cation the greater is the stability of the $(CO_3)^{2-}$ group. Table I also shows that the Pb^{2+} ion and the Zn^{2+} ion have stronger polarizing effects upon the O^{2-} ions of the CO^{2-} group than noble gas-type ions of similar size and the same charge.

If one goes to more highly charged cations one finds that only the large La^{3+} ion in La_2O_3 provides O^{2-} ions of sufficient polarizability to allow a direct reaction with gaseous CO_2. No carbonate of aluminium has been prepared.

The stability of the $(CO_3)^{2-}$ complex decreases with decreasing

TABLE I

Stability of some carbonates

Compound	Size of cation	Heat of formation	Decomposition temperature °C
Cs_2CO_3	1.65 Å	97 Kcal	very high
Rb_2CO_3	1.49	97	very high
K_2CO_3	1.33	95	very high
Na_2CO_3	0.98	78	very high
Li_2CO_3	0.78	56	1270
$BaCO_3$	1.43	64	1360
$SrCO_3$	1.27	57	1275
$CaCO_3$	1.06	44	812
$MgCO_3$	0.78	28	500
$BeCO_3$	0.34	—	100
$PbCO_3$	1.32	23	350
$ZnCO_3$	0.83	16	300
Ag_2CO_3	1.13	20	220

polarizability of its O^{2-} ions. The polarizability of the O^{2-} ions decreases with

1. increasing charge of the contrapolarizing cation, i.e., in the order Na^+, Mg^{2+}, Al^{3+};

2. decreasing size of the cation, i.e., in the order Ba^{2+}, Sr^{2+}, Ca^{2+};

3. changing electronic configuration of the cation from noble gas-type (Mg^{2+}) to those with 18 outer electrons (Zn^{2+}) and, finally, to those with incomplete electron shells (Cu^{2+}).

Some metals which cannot form stable carbonates can form basic carbonates. In these compounds the anion to cation ratio and, with it, the screening of the metal ions is increased so that the electron cloud of the $(CO_3)^{2-}$ group is less deformed. $Cu^{2+}(CO_3)^{2-}$ is not stable but $Cu_2^{2+}(CO_3)^{2-}(OH)_2^-$, malachite, and $Cu_3^{2+}(CO_3)_2^{2-}(OH)_2^-$, azurite, occur in nature. Because of the single charge of the OH^- ion the basic carbonates of copper have an anion to cation ratio which is greater than 1:1.

With increasing thermal motion a Mg^{2+} ion in $MgCO_3$ distorts the $(CO_3)^{2-}$ group to such an extent that the carbon core is better screened by two independent O^{2-} ions. Leaving an O^{2-} ion behind, a gaseous CO_2 molecule escapes and the system gains entropy; firstly, because of the formation of a gas, secondly, because of the disorder which is introduced into the magnesium carbonate crystal. Equations such as

$$MgCO_3 = MgO + CO_2$$

do not properly describe the reaction; as a matter of fact, they have been misleading. They do not indicate that the process occurs in two steps, namely, first the formation of a defective structure

$$Mg^{2+}(CO_3)^{2-} = Mg^{2+}(CO_3)_{1-x}^{2-}(O^{2-})_x + x\,CO_2$$

in which a small fraction of the $(CO_3)^{2-}$ anions are replaced by O^{2-} ions and, secondly, the formation of MgO nuclei. The poor reproducibility of experimental data and the discrepancy between experimental and theoretical dissociation temperatures and pressures have annoyed physical chemists for a long time. Recently, E. Cremer (40) demonstrated that only under experimental conditions which keep the volume of the gas phase very small do the dissociation pressures of $MgCO_3$ agree with the values obtained from thermodynamic data.

A magnesium carbonate crystal consists of anions and cations which have a low polarizability so that it can lose only a very small quantity of CO_2 and still retain its original structure. Thermodynamic data fix the dissociation pressure of one atmosphere at a temperature of 350 °C. This temperature is approximately 200 °C lower than the average of the widely scattered experimental data which were accumulated by various workers ever since H. Le Chatelier (1887) made the first comprehensive study on the decomposition of this carbonate.

The thermodynamic treatment does not take into consideration the fact that the first MgO nuclei which form as an independent phase require a high energy for nucleation. By choosing the proper experimental conditions, in particular a small volume of the reaction vessel, one restricts the reaction to the formation of defective magnesite and, thus, eliminates the nucleation of periclase. By this method E. Cremer obtained dissociation pressures for $MgCO_3$ which are close to the theoretical value and which did not change with time.

4. Metathetical reactions

When heating a mixture of BaO and $CaCO_3$, J. A. Hedvall and J. Heuberger ([41]) observed an exothermic effect at 345 °C. The endothermic effect at 900 °C which was expected from the dissociation of $CaCO_3$ was absent because the mixtures had reacted at 345 °C according to

$$CaCO_3 + BaO = BaCO_3 + CaO.$$

In this reaction the large anion $(CO_3)^{2-}$ combines with the large cation Ba^{2+} and the small Ca^{2+} ion (greater polarizing power) combines with the small more polarizable O^{2-} ion. Therefore the C^{4+} core of the $(CO_3)^{2-}$ group improves its screening because the more contrapolarizing Ca^{2+} ion is replaced by the weaker Ba^{2+} ion.

The reactions studied by Hedvall and Heuberger (Säureplatz wechsel reaktionen) are well suited for illustrating the application of the screening theory to the equilibria and to the rates of metathetical reactions in the solid state. The temperatures were determined

TABLE II

Solid state reactions

(After J. A. Hedvall an J. Heuberger)

Salt	Reaction with CaO		Reaction with SrO		Reaction with BaO	
	Reaction products	Temp.	Reaction products	Temp.	Reaction products	Temp.
$SrCO_3$	No reaction	—	No reaction	—	$BaCO_3 + SrO$	395 °
$CaCO_3$	No reaction	—	$SrCO_3 + CaO$	465 °	$BaCO_3 + CaO$	345 °
$MgCO_3$	$CaCO_3 + MgO$	525 °	$SrCO_3 + MgO$	455 °	$BaCO_3 + MgO$	345 °
$SrSO_4$	No reaction	—	No reaction	—	$BaSO_4 + SrO$	370 °
$CaSO_4$	No reaction	—	$SrSO_4 + CaO$	450 °	$BaSO_4 + CaO$	370 °
$MgSO_4$	$CaSO_4 + MgO$	540 °	$SrSO_4 + MgO$	440 °	$BaSO_4 + MgO$	370 °
$ZnSO_4$	$CaSO_4 + ZnO$	520 °	$SrSO_4 + ZnO$	425 °	$BaSO_4 + ZnO$	340 °
$CuSO_4$	$CaSO_4 + CuO$	515 °	$SrSO_4 + CuO$	420 °	$BaSO_4 + CuO$	345 °
$Sr_3(PO_4)_2$	No reaction	—	No reaction	—	$Ba_3(PO_4)_2 + SrO$	350 °
$Ca_3(PO_4)_2$	No reaction	—	$Sr_3(PO_4)_2 + CaO$	450 °	$Ba_3(PO_4)_2 + CaO$	340 °
$Pb_3(PO_4)_2$	$Ca_3(PO_4)_2 + PbO$	525 °	$Sr_3(PO_4)_2 + PbO$	455 °	$Ba_3(PO_4)_2 + PbO$	355 °
$Co_3(PO_4)_2$	$Ca_3(PO_4)_2 + CoO$	520 °	$Sr_3(PO_4)_2 + CoO$	465 °	$Ba_3(PO_4)_2 + CoO$	355 °

at which the oxides of the alkaline earths began to react with carbonates, sulfates and phosphates (Table II). In all of these reactions an oxide of an alkaline earth reacts with a salt which contains a cation of greater field strength (greater polarizing power) than that of the oxide. The anion of the salt is larger and has a low polarizability because its O^{2-} ions are strongly tightened by a central core of high field strength, C^{4+}, P^{5+} and S^{6+}. The driving force of this group of reactions is the gain in energy by combining the smallest, i.e., the most polarizing, cation with the most polarizable anion, the O^{2-} ion. If the cation of the salt is of the non-noble gas-type, there can be an additional energy gain through the formation of a defect structure. CuO, for example, which forms from the mixture of $CuSO_4 + BaO$ does not have a stoichiometric composition but takes up an excess of oxygen, thus forming a semiconductor with a higher entropy. It is this gain in entropy through the formation of defective crystals which stabilizes the wustite phase in a temperature region where the " perfect " FeO should disproportionate into Fe and Fe_3O_4, according to the heats of formation.

T. Förland and W. A. Weyl (42) pointed out the importance of the increase of mutual polarization as a " driving force " in glass technology and in geochemistry. As the temperature of our planet decreased, elements which are more interpenetrable, e.g., cobalt, combined in the original magma with the most polarizable anions, e.g., S^{2-}, As^{3-}, etc., and formed the ore bodies, whereas the less interpenetrable noble gas-type ions formed silicates, carbonates, etc. The separation which took place in our planet on a gigantic scale is used commercially for producing certain colored glass, e.g., selenium ruby. In such a glass, small amounts of a non-noble gas-type cation (Cd^{2+}) and of large polarizable anions (S^{2-}, Se^{2-}) are introduced. At high temperature the distribution of the anions is a random one, but as the glass cools or is reheated it " strikes ". The Cd^{2+} ions now surround themselves preferentially with S^{2-} and Se^{2-} ions, thus, producing the red pigment of this ruby glass.

Let us now turn to the rates of these reactions or to the " temperature of beginning reactivity ". J. A. Hedvall and J. Heuberger found that each alkaline earth oxide began to react within a relatively small and characteristic temperature region. Surprisingly, the nature of the salt with which the oxide reacted had little influence upon its reactivity. Barium oxide began to react between 350 and 400 °C and it was immaterial whether the other reactant was a sulfate, a carbonate, a silicate or a phosphate. Strontium oxide required a higher temperature, namely 450-500 °C, and calcium oxide a still higher temperature, 500-550 °C, in order to react. These temperature ranges of beginning reactivity are fairly well defined and are sufficiently far apart so that they must be significant.

The reactions chosen by J. A. Hedvall and J. Heuberger are truly solid state reactions and do not involve reactions through the vapor phase or through a polyeutectic melt. This leaves surface diffusion and volume diffusion as the only possible mechanisms. For reasons which were discussed earlier, crystals such as CaO or $MgCO_3$ are not likely to form a large number of vacant lattice sites in the temperature region where their reactivity was observed. This minimizes the contribution of volume diffusion and makes it likely that most of these reactions begin with surface diffusion. This raises two questions : What are the diffusing units? What are the energy barriers?

The first reaction listed in Table II, namely,

$$MgCO_3 + CaO = MgO + CaCO_3,$$

becomes noticeable at 525 °C. At this temperature $MgCO_3$ dissociates and the CO_2 creeps over the surface of the CaO where it lowers the surface energy. This creep probably takes place even at lower temperature but the temperature of 525 °C is the one where the CaO becomes sufficiently reactive in order to form nuclei of $CaCO_3$. In contrast to the film formation in tarnishing reactions, these nuclei grow into independent crystals and do not coat and separate the reactants. The diffusing units are electrically neutral or nearly so. The central cores of these complex anions, so to speak, carry along sufficient O^{2-} ions to be neutral or weakly charged (CO_2, SO_3, PO_3^-, SiO_3^{2-}) and complete their coordination with the surface O^{2-} ions of the oxide. According to this picture, a creeping SO_3 group can always be described as an SO_4^{2-} ion. The surface ions of the oxide participate in the screening of the S^{6+} core and the diffusion process does not involve " breaking of bonds " and formation of new bonds. During motion the interaction of the S^{6+} core is merely shifted from one O^{2-} ion of the oxide surface to its neighbor. This concept of a gradual change of the state of polarization and, with it, of the binding forces has been developed by the author in order to understand the viscosity of glasses.

The crucial moment in these reactions comes with the removal of $(CO_3)^{2-}$ or $(SO_4)^{2-}$ groups from the surface of the oxide and their arrangement into a new phase. This process leaves the cations of the oxide partly unscreened. This temporary unscreening of the cations of the alkaline earth oxides is considered to be the major energy barrier of these metathetical reactions.

This concept is akin to the ideas of J. A. Hedvall not only with respect to the low charge of the diffusing units but also to his " predissociation " of compounds.

5. Reaction between acidic and basic oxides

The author considers the acidity of a system to be inversely proportional to the degree of screening of its cations. The acidity of SF_6 is zero because the S^{6+} core in this molecule is completely screened.

It has become customary to use pure water as a neutral point and call systems in which the proton is better screened bases and those in which it is less screened acids. We found that the screening concept can be easily coordinated with other systems of acidity without leading to contradictions.

According to our concept, the acidity of a reacting mixture of MgO and Al_2O_3 goes through a maximum as the degree of screening goes through a minimum in the active intermediate state. The screening approach more than any other concept of acidity impresses upon us the deep meaning of Sir Humphrey Davy's remark that the acidity depends upon a " peculiar arrangement of various substances" (1814). One of the most important proton-donating catalysts, the alumina-silica catalyst, owes its high acidity to the peculiar arrangement of Al^{3+} and O^{2-} ions. Dehydration of the coprecipitated gel forces the Al^{3+} ions to assume the coordination number of four without permitting the Al-O distances to become as small as they are in stable AlO_4 groups.

If we keep in mind that acidity and basicity are relative and that SiO_2 is an acid with respect to CaO but a base with respect to P_2O_5, we may still follow the established custom and talk about reactions between acidic and basic compounds, e.g.,

$$CaO + SiO_2 = CaSiO_3$$

Numerous reactions between basic and acidic oxides, e.g., $CaO + SiO_2$ or $CaO + UO_3$, have been examined by G. Tammann and his school. The driving force of these reactions is the improvement of screening of the cations of the acidic oxide by surrounding them with anions of greater polarizability.

These solid state reactions, e.g., the formation of the uranates of the alkaline earth oxides from the acid UO_3 and the base MgO

$$MgO + UO_3 = MgUO_4,$$

can be treated in the same fashion as the metathetical reactions. Indeed, G. Tammann and W. Rosenthal ([43]) found BaO to be more reactive than CaO and CaO more reactive than MgO.

Here, too, we can assume that neutral UO_3 molecules creep over the surface of the oxides utilizing surface O^{2-} ions in order to complete their screening. At relatively low temperature this creep coats the oxides with UO_4^{2-} groups which lower the surface energy. Again, the beginning of the reactivity is determined by the alkaline earth oxide. These reactions between an acid and a base or between two salts (metathetical reactions) have two features in common.

1. The anion becomes mobile at relatively low temperature because it can meet the requirements of the two basic principles : forming electrically neutral or weakly charged groups in which the central core is sufficiently screened as long as it can utilize the surface anions of the other reactant for additional screening.

2. The reaction temperatures are relatively low and are determined by the energy necessary to partly unscreen the alkaline earth ions.

Other reactions involving alkaline earth oxides require much higher temperatures. As compared with the formation of calcium uranate (600 °C), the formation of calcium zirconate begins at 1000 °C. The high temperature modification of ZrO_2 (fluorite structure) reveals that each Zr^{4+} ion must be surrounded by eight O^{2-} ions in order to be properly screened. The large Zr^{4+} ion cannot possibly migrate with less than six anions and even if we assume that one of the six O^{2-} ions belongs to the surface of CaO it still hasto " carry along " five O^{2-} ions whereas the Zr^{4+} ion neutralizes only two O^{2-} ions. The diffusion of a highly charged unit such as a $(ZrO_4)^{4-}$ or $(ZrO_5)^{6-}$ group is not likely to occur at 600 °C. As a result, the reaction proceeds only at a much higher temperature where the screening demands are less. In reactions with oxides of the general formula $X^{4+}\ O_2^{2-}$ it is not the alkaline earth oxide alone which determines the beginning of reactivity. The temporary unscreening of an X^{4+} ion requires a temperature which increases with increasing coordination number of X^{4+}. The screening demand of these cations increases with increasing atomic weight and ionic size as can be seen from their coordination numbers :

C^{4+} 2, Si^{4+} 4, Ti^{4+} 6, Sn^{4+} 6, Zr^{4+} 8.

CaO begins to react with SiO_2 at 400 °C, with TiO_2 at 675 °C, with SnO_2 at 900 °C, and with ZrO_2 at 1000 °C. The screening power of the O^{2-} ions for a Si^{4+} or a Ti^{4+} ion increases with increasing polarizability. For this reason one finds that more basic compounds, e.g., Ca_2SiO_4, form faster even if the acid oxide is present in a large excess. O^{2-} ions contrapolarized by Ca^{2+} ions are better screeners than those exposed to another Si^{4+} ion. The greater the $R^{2+}\ O^{2-} : X^{4+}\ O_2^{2-}$ ratio, the lower is the energy barrier of the reaction.

Mixtures of oxides such as BeO, MgO, Al_2O_3, ZrO_2 and SiO_2 react only at very high temperatures because the screening demand of the cations is strong and the oxygen to cation ratio is rather low. For this reason it is not possible to synthesize beryl, $Be_3Al_2Si_6O_{18}$, without a catalyst (additional screener, H_2O). All of the eleven cations of this molecule have a high field strength and they are neutralized by only 18 O^{2-} ions. In order to cause such a system to react, temperatures would be required which are above the stability region of the beryl (1450 °C).

6. **The nature of Hüttig's " Active Intermediate State "**

The formation of Ag_2HgI_4 from AgI and HgI_2 is one of the few solid state reactions for which the quantitative data are in good agreement with the theory ([44]). In contrast to reactions involving solids with highly polarizable cations and anions such as iodides and sulfides, the reactions between the oxides MgO, Al_2O_3, and SiO_2 seem to offer greater difficulties with respect to the interpretation of their rates. Those who are active in the field of solid state reactions are well aware of the experimental difficulties which are involved if one wants to follow quantitatively the formation of a spinel. However, aside from the general difficulties which lie in the nature of reactions between powders with poorly defined shape and surface area, the formulation of some solid state reactions is more complicated than of others. In the reactions which were chosen by C. Wagner and his school, the state of affairs at any moment can be described by the quantities of the reactants and that of the reaction product.

For other reactions, however, such a description is not applicable. The formation of spinel from MgO and Al_2O_3 produces phases which are different from both the reactants and the reaction product. These phases which may have very characteristic physical and chemical properties have been called " Active Zwischenzustände " by F. Hüttig who has contributed much to their identification.

The formation of spinels has been studied by several workers and this reaction provides a good example for the unusual properties of the metastable intermediate state. W. Jander and K. Bunde (^{45}) studied the reaction of the mixture $ZnO + Al_2O_3$ in the ratio 1:1 by heating it stepwise to increasing temperatures until a well crystallized spinel $ZnAl_2O_4$ had formed. Each step was examined with respect to its catalytic activity (CO-O_2 combustion), its sorbing power for an azo dye dissolved in benzene, and the solubilities of ZnO and Al_2O_3 in NH_4Cl, HCl, and H_2SO_4. All of these chemical reactivities went through maxima for mixtures which had been treated in the temperature range between 600° and 900 °C.

In a later paper with H. Pfister (^{46}) W. Jander states : " We must not forget that we know absolutely nothing about the state and the energy of the active film ". In reality W. Jander and other workers in this field were amazingly well informed about the conditions which affect the formation of an active intermediate state. Thus, for example, W. Jander mentioned that elements which form several states of valency are not conducive to produce a highly active intermediate state. According to our views, the polarizability is the missing link for the understanding of the active state. The ions of elements, e.g., Fe or Cr, which occur in different valencies are more polarizable than those of the noble gas-type. As a rule, elements which form noble gas-type ions have only one valency over a wide temperature region.

W. Jander also mentioned the possibility that Cr^{3+} at a surface may form CrO_4^- groups even if the quantity of chromate ions is too small to be detected analytically. Again he had the right intuition. We were able to prove that oxidation of Cr^{3+} to Cr^{6+} and of Co^{2+} to Co^{3+} occurs when these ions are adsorbed on the surface of silica gel and the system heated in air to 300-400 °C.

The formation of the magnesia spinel, $MgAl_2O_4$, from the oxides shows essentially the same features as that of the zinc spinel. The reactivity as a function of heat treatment seems to follow a simpler pattern than that of the system ZnO-Al_2O_3 probably because in the latter the probability of forming electronic defects is greater. Around 800 °C a state is obtained in which the mixture of $MgO + Al_2O_3$ has its maximum reactivity. Especially the occurrence of a maximum in the dyestuff adsorption and a maximum in the hygroscopicity are direct proofs for the unscreened nature of the active state. The incomplete screening of cations also increases the cation-cation repulsion so that one must expect that the volume of the reacting system also goes through a maximum.

Now we can answer W. Jander's question concerning the structure of the active intermediate state : A mixture of oxides which contain cations with a strong screening demand, e.g., Mg^{2+}, Al^{3+}, or Si^{4+}, has to go through an " active state " in order to react in the solid state because of the volume expansion (first principle) and the unscreening (second principle) which are necessary before the cation can occupy new equilibrium positions. In this active state the system exhibits a chemical reactivity which is greater than those of both the reactants and the reaction product. The reaction with H_2O from the atmosphere (hygroscopicity) lowers the free energy of the system by increasing the anion to cation ratio, i.e., by changing some O^{2-} ions into twice the number of OH^- ions. From a poorly screening liquid (benzene) the active phase attracts and chemisorbs polar dye molecules in order to improve the screening of surface cations.

We mentioned earlier that the acidity of a system is inversely proportional to the degree of screening of its cations. On this basis we can understand another characteristic feature of the active intermediate state, namely, its ability to donate protons. This property is utilized in the cracking and isomerization catalysts, e.g., the alumina-silica type, which are obtained from oxides or hydroxides which, by themselves, are not good catalysts. Neither B_2O_3, SiO_2, MgO, Al_2O_3 nor ZrO_2 are useful cracking catalysts by themselves. Coprecipitation of two of these oxides, however, produces a solid which has the ability to donate protons at about 500 °C. In their partly reacted state these oxides undergo a reaction with H_2O and organic molecules which can be described as an " oscillation of the coordination number " in the same fashion as one can describe the catalytic activity of vanadium or iron oxide with respect to the oxidation of SO_2 to SO_3 as an " oscillation of the valency ". In the course of the proton donation reaction a surface cation improves its screening by changing an $(OH)^-$ ion into a better screening O^{2-} ion. This process leads to charged particles.

W. Jander also raises a question concerning the energy relations of these intermediate states. This question can be answered on the basis of two recent papers, one on the apparent surface energy of crushed quartz and the other on the heat of reaction of thoroughly degassed alumina. A. Bondi (47) called attention to the discrepancy which exists between the energy requirements for producing a quartz surface by fracture and the chemical potential of this surface. The energy consumed in the crushing of very brittle substances might be ascribable to the energy required for the creation for new surfaces only since energy processes are probably negligible. Hence, the energy absorbed in crushing per unit of surface generated ought to be a measure of the total surface energy. The crushing of quartz led to a value of the total surface energy of 70-80000 ergs/cm^2 by measurement of crushing energy, and of 107000 ergs/cm^2 by ball mill calorimetry, numbers which are out of proportion to the data for liquid silica (200-260 ergs/cm^2).

These large " surface energies " may, however, constitute the amount of energy stored in the surface as a result of the scission of chemical bonds and the local lattice deformation. Referred to a layer depth of one SiO_2 molecule (3.2 A.U.) the calorimetric value gives 3.3×10^{12} ergs/cm^2 = 93 e.v. per mole of silica in the surface an altogether impossible magnitude. But, even if one assumes the energy to be stored in the three molecular layers nearest the surface, the energy would still be of the order of 20 e.v. per mole, i.e., of the order of ionization energies.

According to our concepts the potential energy in the quartz is stored in a surface film which is several hundred atoms deep, the distortion of which is strongest in the surface but tapers off very gradually toward the interior.

From the viewpoint of screening, the energy requirement for producing 1 cm^2 of a new surface must be greatest if the quartz is crushed in vacuo and it must decrease with increasing ability of the environment to screen the fields of the Si^{4+} ions.

E. B. Cornelius, T. H. Milliken, G. A. Mills and A. G. Oblad ([48]) dehydrated alumina and found that the heat of reaction for the first 0.3 wt. % of water is greater than 105 Kcal/mole, i.e., of the same magnitude as the reactions between chlorine and alkali metals. The heat of reaction drops off with increasing water content and reaches 10 Kcal/mole for alumina with 3 % water.

Arrays of cations with insufficient screening corresponding to Hüttig's intermediate state can be obtained in several ways :

1. Mixing of oxides and allowing the mixture to react under conditions (time, temperature) which do not permit the reaction to go to completion (F. Hüttig, W. Jander).

2. Dehydration of a coprecipitated gel of hydroxides, e.g., $Al(OH)_3 + Si(OH)_4$, under conditions which decrease the anion to cation ratio by the reaction

$$2\,(OH)^- = O^{2-} + H_2O.$$

An Al^{3+} ion can be satisfactorily screened either by six or by four O^{2-} ions. In the latter case, however, the four O^{2-} ions have to come closer to the Al^{3+} ions so that they can be more strongly deformed. By coprecipitating $Al(OH)_3$ with silica, the rigid silica network prevents the O^{2-} ions from moving into such a position so that all cations remain insufficiently screened.

3. Dehydration of a hydrated clay mineral under conditions which decrease the anion to cation ratio by changing OH^- into O^{2-} ions (gain in entropy) without giving the system a chance to form the equilibrium structure which would be mullite plus silica.

L. Tscheichwili, W. Büssem and W. A. Weyl (49) found that the dehydration of kaolin leads to a defective lattice in which the Al^{3+} ions are in fourfold coordination. Dehydration takes place at a temperature which is characteristic for the particular clay mineral. When carried out carefully the dehydration of kaolin can lead to a highly reactive, metastable phase which has been called " metakaolin ". If this phase is prepared at a temperature not exceeding 600-700 °C it can be partly rehydrated.

The chemical characteristics of the metaphases, e.g., the solubility of alumina in HCl and the reactivity of metakaolin with $Ca(OH)_2$, resemble those of Hüttig's active intermediate phases. The same applies to the physical characteristics. The distortion of the lattices produces a rather diffuse X-ray scattering. The cation-cation repulsive forces of the incompletely screened Al^{3+} and Si^{4+} is responsible for their low densities. The volume expansion of clay minerals which accompanies the dehydration is so characteristic that it can be used for their quantitative determination.

Above 700 °C the lattice of metakaolin breaks down into Al_2O_3 and SiO_2 which at higher temperatures form mullite. Water vapor catalyzes this rearrangement of the metaphase into the more stable lattices of gamma alumina and cristobalite as can be seen from the experiments of G. F. Hüttig and E. Hermann (50) who found that under optimum heating conditions in oxygen or nitrogen approximately 12 % alumina became soluble in HCl. Dehydration of the kaolin in an atmosphere of water vapor, however, caused the maximum acid soluble alumina to drop to 8 % because the water catalyzes the formation of acid-insoluble aluminium oxide. In order to make dehydration and rehydration reversible both processes should be carried out at the lowest possible temperature.

7. **Catalysts for solid state reactions**

In the preceding chapter an atomistic picture has been presented of the energy barrier which has to be overcome by a mixture of MgO and Al_2O_3 in order to form the spinel. A reaction of this type can be described as a reshuffling of Al^{3+}, Mg^{2+}, and O^{2-} ions. The energy barrier consists of the overcoming of the Coulomb attractive forces between Al^{3+} and O^{2-} as well as between Mg^{2+} and O^{2-}. In addition these cations have to be temporarily unscreened.

The partial unscreening of Mg^{2+} and Al^{3+} ions suggests that additions to the mixture which can provide temporary screening should lower the energy barrier. In some industrially important reactions this is done by means of a flux which changes the solid state reaction into one involving a liquid phase. However, screening can also be achieved by a suitable gas phase. The most effective way to temporarily screen Al^{3+} and Mg^{2+} ions consists of increasing the anion to cation ratio by a surface chemical reaction with HF, HCl or H_2O. The protons of these molecules enter the electron clouds of surface O^{2-} ions changing them into OH^- ions and the rest of the molecules attach themselves to cations which need the screening most. The effectiveness of these gaseous molecules as catalysts for the reaction of an oxide is due to their twofold action, namely, lowering the Coloumb forces between cations and O^{2-} ions by changing the latter temporarily into singly charged OH^- ions, and by providing additional temporary screeners, i.e., Cl^-, OH^- or F^- ions which temporarily increase the anion to cation ratio.

To many chemists the formation of " hydroxides ", even temporarily, may seem to be strange; however, these facts are well established.

Whereas the dehydration of $Al(OH)_3$ is rather complete around 1,000 °C, alumina above its melting point reacts with water because the Al^{3+} ions lose screening when their symmetrical environment of O^{2-} ions is replaced by a more random one. H. von Wartenberg (51) made this observation when he fused corundum in different flames some of which contained H_2O $(H_2 + O_2)$ and others $(CO + O_2)$ not. In the latter case alumina did not volatilize, but in the presence of H_2O it did.

At its melting point two phases of Al_2O_3 are in equilibrium; the crystal is better screened, but the liquid has the higher entropy and its cations are less screened. Through its reaction with H_2O an oxide can increase its entropy without losing too much screening. This is the principle of using H_2O as a catalyst in the method of hydrothermal synthesis.

The catalytic effect of H_2O and HF which accelerate the formation of spinels, silicates, etc. can be described in conventional terms. However, some gases have an effect on the rates of solid state reactions which makes it difficult to formulate the interaction in the conventional chemical terminology.

Our concept that reaction rates can be increased by the presence of screening electron clouds leads to the conclusion that chemically inert molecules such as N_2 and even the noble gases, e.g., argon, can be catalysts. Noble gas atoms can enhance reactions by "lending" electrons to cations which require temporary screening in order to move into new positions.

The volatility of silicates and of alumina in the presence of H_2O is the result of the improved screening of the Si^{4+} and Al^{3+} ions which causes depolymerization. As the screening of cations can also be improved by the electron clouds of inert molecules, one may expect that the volatility of an oxide is a function of the atmosphere and that it increases from helium to xenon.

J. A. Hedvall and O. Runehagen(52) were probably the first to observe and to have the courage to publish the effects of apparently inert gases such as SO_2, O_2, and N_2 on the reactivity between different forms of silica with CaO. Recently, H. Forestier (14) presented additional pertinent experimental material. The formation of the spinel $NiFe_2O_4$ from the oxides was found to be slowest in vacuo and fastest in an atmosphere of H_2O and CO_2. This fact can be explained on a conventional basis by attributing the catalytic effect to the temporary formation of "carbonates" and "hydrates". However, H. Forestier also found that this reaction is faster in an atmosphere of argon than in one of helium

From the viewpoint of screening, there is no need to distinguish between the noble gas atoms on the one hand and O_2 or N_2 molecules on the other. The polarizability of the electron clouds is the only parameter which determines their screening power. The fact that nitrogen or oxygen can form several valence states whereas argon cannot, has no influence upon this catalytic activity. We assume that during the rearrangement of Ni^{2+}, Fe^{3+}, and O^{2-} ions constellations arise in which cations need additional screening in order to move from one equilibrium position into another. This temporary screening can be achieved either by hydration or by "borrowing" an electron cloud from an atom or molecule which is sufficiently polarizable. An adsorption process of very short duration due to van der Waals' interaction may help an ion to overcome a certain energy barrier; van der Waals' interaction thus can accelerate solid state reactions.

The fact that the electron cloud of an argon atom can act as a screener in a manner similar to that of a nitrogen molecule is completely in line with the findings of H. S. Frank and M. W. Evans ([53]) who found a relatively high entropy loss when argon was dissolved in water. The electron cloud of the argon atom acts as a screener for some protons of the water, and this process immobilizes a certain volume of water around the solute (iceberg formation).

V. SUMMARY AND CONCLUSIONS

In order to understand the existence of solids at ordinary temperature, the author postulates that under normal energy conditions the nuclei of most elements require a more complete screening by electrons than can be achieved by the number of electrons which neutralize the nuclear charge. In order to improve their screening and still conform with the basic principle of electroneutrality in the smallest possible volume, many molecules, e. g., NaCl, SiO_2, Al_2O_3, etc., do not assume their most probable state under ordinary conditions but lose entropy and undergo polymerization or condensation.

The principle of maximum possible screening has been added to the principle of electroneutrality and it is shown in this paper how the two principles cooperate and govern the chemistry of solids. The main factors which determine the screening of a cation, e.g., the anion to cation ratio, the symmetry of the environment, and the polarizability of the anions, are discussed.

In order to use the screening theory for explaining solid state reactions, one has to relinquish a concept which has been useful when dealing with gaseous molecules, namely, that of a constant chemical bond between atoms. We prefer to use the concepts of K. Fajans who speaks of " binding forces " rather than of " bonds ". The binding forces are changed over large distances if a surface or a defect in the interior of a crystal produces a disturbance. This concept of a " depth action " becomes important if one wants to understand the influence which a carrier exerts upon a catalyst or that of adsorbed gases upon the properties of solids.

The variance of data on the CO_2 pressure of $MgCO_3$ as a function of the temperature and the discrepancy between the experimental data and the theoretical values for the dissociation temperature of this carbonate are used to demonstrate how the formation of defects can obscure phenomena which occur in crystals. For this reason the author studied the fundamental relations governing the condensed state in the glassy rather than in the crystalline state. The advantages offered by the glassy state are demonstrated for the coordination or screening requirements of Ni^{2+} ions as a function of composition, temperature and pressure.

Using the concepts developed in the first part of this paper a few selected solid state reactions are analyzed with respect to the nature of their " driving forces " and their " energy barriers ". A physical picture of the " active state " and the " energy barrier " of solid state reactions is derived and the various features of Hüttig's active intermediate state are interpreted on that basis. Our definition of the energy barrier of solid state reactions as the energy requirement for partial unscreening of cations was used to explain the mechanism of catalysts, for example, the findings of H. Forestier that even noble gases, e.g., argon, can catalyze spinel formation.

Our atomistic approach to solid state reactions made it possible to explain the mechanism of hydrothermal synthesis as well as the mineralizing action of gases such as HF, HCl and H_2O. These phenomena are of interest to physical chemists, geochemists and geologists. The action of these gaseous molecules is twofold. They send protons into the electron clouds of oxygen ions in silica or silicates. This changes the structure

$$\ldots\ Si^{4+}\,O^{2-}\,Si^{4+}\,O^{2-}\,Si^{4+}\ \ldots$$

temporarily into one in which the Si^{4+} ions are bonded together by OH^- ions rather than by O^{2-} ions. We rightly expect two fluorides, e.g.,

$$2\ NaF + BeF_2 = Na_2BeF_4$$

to react at a much lower temperature than two oxides

$$2\ CaO + SiO_2 = Ca_2SiO_4.$$

This, after all, is the basic idea of V.M. Goldschmidt's model structures. The fluorides, i.e., the weakened models, are more reactive because their valence sums are only one-half of those of the oxides.

Thus, the change of O^{2-} ions into singly charged OH^- ions lowers the reaction temperature. In addition to this weakening of the Si-O-Si-O "bonds" by the protons, the F^-, Cl^-, and OH^- ions increase the screening of the Si^{4+} ions by temporarily increasing the anion to cation ratio, thus aiding depolymerization.

This purely ionic picture is applicable not only to oxide systems but even to organic compounds, in particular to hydrocarbons when we use the quanticule theory of chemical binding. K. Fajans pictures a hydrocarbon chain as a row of C^{4+} cores, the repulsive forces of which are overcome by the quanticules (e_2^-), a pair of electrons quantized with respect to two neighboring cores

$$\ldots\ (e_2^-)\ C^{4+}\ (e_2^-)\ C^{4+}\ (e_2^-)\ C^{4+}\ \ldots$$

In order to reshuffle such a chain either relatively high temperatures are required (thermal cracking) or the Coulomb forces have to be weakened by sending protons into the (e_2^-) quanticules. Isomerization, aromatization, polymerization, and cracking can be carried out at lower temperature in the presence of acids and proton donating catalysts. Thus, the extreme ionic concept and the quanticule theory make it possible to treat the reshuffling of oxides and of hydrocarbons on a par.

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Discussion

M. Hedvall. — The ideas presented by Prof. Weyl are of course very interesting especially because they try to give so to say a broad and general concept or picture of the many peculiarities of the solid state of matter. Prof. Weyl has in his publications often used the word " picture ". He has also mentioned the close connection of his ideas with those of Fajans and V. M. Goldschmidt.

There are different ways we have to go in order to solve the problems of matter. You can start directly from the problems of the nuclei and their electron shells and no doubt these are places where you by means of mathematical methods, using quantum mechanical and wave mechanical calculations, will gradually find the many enigmas answered.

But you can also start in another way, the way which Prof. Weyl has chosen. And this way of thinking and working is very welcome to all those who do not master the pure mathematical sort of thinking. It is welcome because it is materializing the notions of which many chemists have and will keep to have a need. Especially of course investigators working in contact with industries, wanting and having the task to develop technical applications. We have heard that Prof. Weyl is the first to emphasize that his ideas do not explain the mechanism of reactions or of lattice structure in details. But no doubt they are valuable and promising as a sort of germs, from which the growth will go down to deeper layers and details. Intimate results will be achieved when differend kinds of thinking meet and complete each other.

After this more principal introductory remarks I should like to come back to discussion of definite " solid problems ". However I shall limit myself to put only one question, leaving the other ones to my collaborator Dr Lindner, who since many years occupies himself with studying the reaction mechanism by means of radio isotopes.

I should like to ask you whether you consider the imperfections you have talked about in ZnO as corresponding to equilibria or not. And I think you mentioned something like that also for some spinel systems?

I think it is not necessary to add that from that point of view the formulas do not tell us very much, because the structure is of course always depending on the conditions (starting material, temperature, time of heating, etc.) you have chosen for the production of the substance.

Considering this, it must also be emphasized that it is not always easy to compare the qualities of different substances in exactly corresponding states.

M. Weyl. — It is not easy to give a definite answer to your question concerning defective crystals and equilibria. A defect raises the potential energy of a crystal but it also increases its entropy. As the entropy enters this expression of the free energy as a factor multiplied by the absolute temperature, one can assume that a true equilibrium is established with the number of defects increasing with the temperature. However at low temperature the diffusion of defects might become so slow that one deals with crystals whose defects correspond to " frozen in " equilibria. Indeed one finds that this disorder of many crystals is a function of their past chemical and thermal history.

The terminology which Fajans introduced in order to describe e.g. SO_2 as $(e^-{}_2)$ $S^{6+}(O^{2-})_2$ has the advantage over other description that it is obvious that this oxidation of SO_2 to SO_3 can be catalyzed by V_2O_5, etc. because it consists of an exchange of an $(e^-{}_2)$ quanticule for an O^{2-} quanticule. Crystals like V_2O_5 can easily exchange O^{2-} ions for electrons and vice versa so that they become catalysts. It has been reported that ozone does not oxidize SO_2 to SO_3 so that this oxidation reaction is not an addition of an O atom. I agree With Dr Hägg that in many cases the Fajans description which I use is not essentially different from other description but it has the advantage of clearly showing the values of the binding forces.

M. Hägg. — Prof. Weyl has given a report which treats a great many important problems related to solid state reactions. I am sure that Prof. Weyl's statement of such problems will be of great value to all working in this field because of its great stimulating effect.

But I don't think that the language chosen by Prof. Weyl in describing the chemical bond is quite suitable. It is very important that there can be given an elementary description of the quantum mechanical ideas of chemical bonds. But such a description can certainly be brought to conform more closely to the present state of these ideas than does Prof. Weyl's. It can thus be made much more useful but need not be more difficult to understand nor harder to visualize.

Prof. Weyl has, for instance, showed how the " quanticule " method could be applied to the bonding in SO_3 and SO^2. But is it more difficult to apply the valence bond method, using sp^2 hybrid orbitals? This gives immediately the shape of both molecules. In addition, it explains the appearance of a non-localized π bond.

Several solid state reactions, in which Prof. Weyl uses the concept of screening, can be easily treated after the relative lattice energies of the phases have been estimated, according to usual elementary ideas.

In some cases the " quanticule " language is obviously dangerous. A drastic example is the diamond lattice, where it requires the existence of two non-equivalent kinds of carbon atoms.

M. Weyl. — 1. I do not think that it is generally possible to replace the " screening concept " by the " lattice energy ". In many cases, of course, they both convey the same idea, but the screening applies to polymerization e.g. formation of $Al_2\,Cl_6$ molecules in the gas phase or to di-, tri-chromic acid anions in aqueous solution, when the lattice concept could not be in order.

I fully agree with Prof. Hägg's comment concerning the description of the diamond. If this were an isolated case no necessity would arise to describe this form of carbon as $C^{4+}C^{4-}$ until an experiment proves that not all carbons are identical. However the high melting point and the high hardness become obvious if this element is treated formally as being a carbide. I distinctly remember that earlier workers had serious difficulties to explain that in series such as

NaF ZnS AlN Ge

the hardness increased in a way which did not indicate an abrupt change of chemical binding. The electronic properties of Ge can be so much better understood if the element is treated as the germanide of germanium $Ge^{4+}Ge^{4-}$ analogous to $In^{3+}Sb^{3-}$ and similar compounds.

2. The change of TiO_2 and WO_3, etc. into defective structure can be described as a lowering of the valency of the metals. However such a description does not account for the extremely high dielectric constant, for the semi-conductivity and other electronic properties, at least not in an obvious manner. For this reason I prefer to describe these compounds as crystals in which some O^{2-} ions are replaced by electrons and where the electrons cannot be " located " but are quantized with respect to a number of cations.

M. Jørgensen. — 1. One of the most interesting results of Prof. Weyl's investigations of metal ions in silicate glasses is the discovery of tetrahedrally co-ordinated nickel (II) complexes, since only anhydrous nickel (II) salicylaldehyde is known as a dubious case. Do you think that other metal ions, which always are octahedrally co-ordinated in solution, such as chromium (III) might be provoked into tetrahedral positions in some kind of glass?

2. You mention the much higher heat of formation of solid NaCl than of gaseous NaCl molecules and ascribe it to the much larger screening of the sodium ions each by six chloride ions. Why do you not emphasize as much the reciprocal influence of each chloride ion being surrounded by six sodium ions?

3. You point out the importance of electroneutrality in the smallest possible value. Since the electrostatic energy of a sphere is Z^2/r (where Z is the charge and r is the radius) it is sixteen times more difficult to understand the auto-ionization of diamond to C^{4+} and C^{4-} than the auto-ionization of an analogous monovalent system. Your argument that Al_4C_3 and SiC resemble much diamond does not suggest that diamond is a carbon carbide, but rather that the carbides have the same type of covalent bonding as diamond. Do you agree that diamond might be described better as C^{4+} cores surrounded by quanticules e_2^- analogous to an infinite hydrocarbon structure? I must point out that the latter quanticules, which in the theory of Fajans have played the role of electron pairs in Pauling's

theory of covalent bonding, are not responsible for the bonding solely by reasons of electrostatic potentials. Thus, the bonding state of a hydrogen molecule must be described by quantum mechanics in a manner, which necessitates the extension of your theory with imaginary charges, attracting each other in some of the states. I do not know your opinion of a possible electrostatic model with complex charges.

4. I am very happy that you recognize nuclei and electrons as the actual particles applied by quantum mechanics. Thus, your concept of cores and quanticules such as electron pairs is only expedient method of classification into distinct units of the particles in a system, and it cannot be assigned an absolute validity in all cases. When the concepts of your report are translated into the language of the theory of molecular orbitals, your electron distributions correspond to the single configurations for a molecule. I do not agree with the first of the three principles *p*3 that an experimentally unique molecular species is represented by one electronic formula. I may guess that you would assume the presence of a quanticule, containing e.g. 6 electrons, in benzene for avoiding the consideration of the two Kékulé structures. This would be equivalent to a linear combination of two of the possible sets of molecular orbitals, which co-operate in the complete description of the benzene molecule.

The transition group complexes, which have been discussed also by Dr Orgel and Prof. Nyholm, exhibit many cases, where it would not be very adequate to ascribe a certain limiting electronic configuration, such as the pure electrostatic case or the d^2sp^3-hybridization of Pauling to e.g. the hexaaquo ions of trivalent metals. I hope that you agree in the relative inadequacy of the Fajans' theory for these cases.

5. It is very interesting that the ion O^{--} cannot exist without strong electrostatic fields from cations in lattices. I can here remind that the Fermi-Thomas statistical model for atoms, assuming spherical symmetry and no distinction between the shells, implies increasing radii for the metal ions for decreasing external charge, i.e. the difference between the nuclear charge and the number of electrons. Even after certain assumptions, the neutral atom is the last case, whcih is predicted to exist by Fermi-Thomas' statistics; the electron distribution diverges for anions as function of the

distance. This may perhaps be the explanation that cations are so much more common in the periodical system than anions, which only occur in the halogen and chalcogen groups. While the ligands with tendency of σ and π-bonding in the direction from the ligands towards the central ion, prefer high oxidation states of the metals (where the actual charge is decreased by the bonding), the ligands such as *o*-phenanthroline or cyanide with tendency towards π-bonding in the opposite direction, as discussed by Dr Orgel, stabilize the metals with low oxidation states, such as iron (II) or vanadium (II). However, the lattice energy (which stabilizes the dioxides with fluorite structure of actinides, which not elsewise is easy to have in quadrivalent state) and the relative difficulty of liberating elementary oxygen and fluorine may co-operate in the stabilization of some oxidation states.

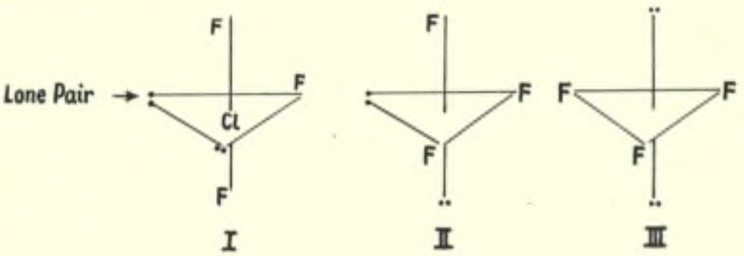
M. Weyl. — 1. Unfortunately we have no experimental evidence for the existence of Cr^{3+} ions having fourfold co-ordination in glasses. As a rule, the co-ordination number of a cation decreases with increasing polarizability of the O^{2-} ions i.e. from B_2O_3 glass to alkaliborate glasses or from a lithium silicate to a potassium or rubidium silicate? However these changes from six fold to four fold co-ordination are easily observable only for Ni^{2+} and Co^{2+} ions because here they produce drastic color changes.

2. It is out of energy considerations that I center my screening theory amid the co-ordination requirements of the cations. A cation of the noble gas type rarely changes its co-ordination number with respect to O^{2-} ions. Some elements like Al form AlO_4 and AlO_6 groups. However major changes of this co-ordination number of O^{2-} ions are frequently observed. O^{2-} ions in silica are exposed to two Si^{4+} ions. In Rutile the co-ordination number of oxygen is three and in periclase (Mgo) it is six.

M. Ubbelohde. — In the particular case of sodium chloride, the straightforward summation of electrostatic attractions and repulsions shows that there is a large decrease in potential energy on passing from the gaseous ion NaCl to the crystalline assembly with 6 nearest neighbours around each ion. As Prof. Weyl says, there is no clear cut distinction between " chemical combination " in the gas and " physical interaction " in the crystal, for the case of sodium chloride. However, the specific polarizability contribution to the potentiel energy does not constitude more than 1 or 2 % for sodium chloride crystals. There are other crystals where the polarisability contribution is much larger fraction of the lattice energy.

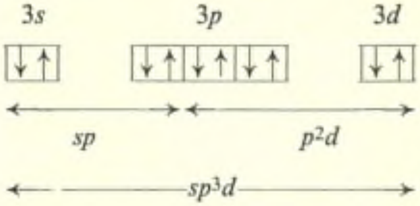
M. Nyholm. — It would be very interesting to study the magnetic susceptibilities of the glasses containing various transition metal ions which Prof. Weyl has made. In particular the " freezing in " of the tetrahedral configuration of the oxygen atoms around Ni^{II} is expected to result in a triplet as the ground state in the Stark splitting of the orbital levels by the ligand field. We are very glad to be able to measure these moments on compounds to be supplied by Prof. Weyl.

Also one feels that the screening theory, whatever be its value in connection with electrostatic substances, appears to have a very limited application to covalent compounds. Thus it would be interesting to see how far it enables one to understand the shape of a molecule such as ClF_3 which contains three bonding pairs and two lone pairs of electrons. On the basis of simple electrostatic repulsion structures I, II and III are possible :



of which III *might* be thought the more likely since the lone pairs are furthest apart in the structure. However I is closest to the correct structure; this can be understood in terms of a valency bond description.

In the latter we regard the structure as intermediate between that obtained by hybridising bonding orbitals (p^2d) and non-bonding orbitals (Sp) separately and that obtaining by mixing all of these together in an Sp^3d pentagonal bipyramidal arrangement. This means that the lone pairs have a good deal of S character hence that they are to be located in the trigonal plane.



M. Weyl. — If one applies the screening theory to a compound such as ClF_3 one has to assume that the positive core of the chlorine, Cl^{7+}, is screened by three F^- ions and two pairs of electrons, (e_2^-). In this case the structure III is not likely because of the large size of the F^- ions as compared with the very small Cl^{7+} core. It is impossible for the Cl^{7+} core to be close to all five negative particles. From electrostatic consideration it is, therefore, most reasonable to assume that the doubly charged (e_2^-) quanticules will be closest to the Cl^{7+} (1.598 A.U.) and the other two have to assume positions which are more remote (1.698 A.U.). This arrangement corresponding to formula I seems to give the lowest electrostatic energy of any arrangement between a Cl^{7+} core, two (e_2^-) quanticules and three F^- ions. That this arrangement is not very satisfactory and that it produces strong repulsion forces between the five negative quanticules expresses itself in the extreme chemical reactivity of the compound ClF_3 which resembles that of elemental fluorine.

M. Lindner. — I should like to make some comments to professor Weyl's paper, especially concerning the connections with solid state reactions :

1. Perhaps one should not overemphasize the importance of electroneutrality in the smallest possible volume in solids as it became known lately that space charges can occur and are in fact most essential for the first stage of some solid state reactions as oxidation of metals.

2. The newer interpretation of the mechanism of reactions between solids as forwarded by Hedvall and his school, does neither overemphasize the electroneutrality of diffusing particles. In some cases metal and oxygen seem to be mobile in the solid lattice, which

can more conveniently be described as a simultaneous transport of ions, possibly by means of associated vacancies.

3. The experimental proofs for the "creeping" of one oxide over another during a solid state reaction cannot yet be considered sufficient. As far as I know no direct surface transport of that kind has been measured, but indirect conclusions have been drawn from experimental observations, which can be explained on a simpler basis. Several examples can be named : thus a reaction layer of zinc ferrite formed by reaction between the oxides of zinc and iron is always attached to the iron oxide although it is formed by a migration of both zinc and iron ions within the reaction layer. In the case of the reaction between the oxides of aluminum and chromium, the higher vapour pressure of chromic oxide may explain the covering of the alumina.

4. As outlined in our paper during this conference there is actually a relation between self-diffusion and melting temperature in the form that the self-diffusion of cations in oxides at melting temperatures shows conforming values for practically all oxides investigated thus far.

5. As to our knowledge anion vacancies in zinc oxide have not been reproved experimentally. The difference in defect concentrations between the oxides of zinc and magnesium may not be so essential, as the values for self-diffusion in the oxides indicate the possiblity of comparable defect concentrations (cf. our paper, presented during this conference).

6. For the so-called place exchange reactions as investigated by Hedvall and his school, an interesting mechanism has been suggested by C. Wagner (*Z. anorg. Chem.*, **236**, 322, 1938) avoiding the necessity of diffusion transport of bigger complex ions.

7. It may perhaps not be generally valid that reactions between an acid and a base in the solid state proceed by predominant diffusion of the anion. In the case of silicate formation e.g. no sufficient mobility of silicon or silicate ions could be found. On the other hand self-diffusion values for Ca in Ca_2SiO_4 are nearly comparable to those for the formation reaction. Within the temperature range usually investigated, the self-diffusion within the orthosilicate surpasses the values obtained for lower basic silicates, which may

explain sufficiently the predominant formation of the high basic silicate.

8. There may be a certain danger with an oversimplified picture of solid state reactions. It is doubtful if a more qualitative conception like the screening demand of cations actually is sufficient for a deeper understanding of the reaction mechanism. Naturally it is an ultimate aim to deduce a complete picture of solid state reactions from atomic properties. These are finally rate determinations by determining differences in chemical potential and energies necessary for defect formation and migration. Even if a detailed description of crystals and their energy distribution would be possible, it may not be sufficient. The actual solid state reaction is strongly influenced by defects which to a lesser extent have been subject of exact calculation as e.g. dislocations. A sensible approach to the whole field of solid state reactions is the endeavour to investigate in detail the different parameters and to establish quantitative relations.

M. Forestier. — Je serais heureux de savoir si l'on peut admettre que le «screening effect » est lié à la stabilité de l'état d'ordre ou de désordre; il semblerait en effet que l'état d'ordre demande un screening plus élevé que l'état de désordre (exemple : le phénomène de fusion). Peut-on relier les transformations ordre-désordre à cet effet ?

M. Bénard. — Je tiens tout d'abord à dire l'intérêt que je porte aux conceptions du Prof. Weyl, dont le plus grand mérite est semble-t-il d'avoir attiré l'attention sur l'importance des phénomènes de polarisation dans le comportement des solides. C'est surtout, semble-t-il, pour la compréhension des phénomènes de surface que le rôle de ce facteur est le plus grand. Par contre, il me paraît difficile de suivre le Prof. Weyl lorsqu'il attribue au « screening » une importance égale dans la formation des structures lacunaires telles qu'on les rencontre dans certaines phases non stoechiométriques.

Je ne me fais bien entendu aucune illusion sur le caractère, au moins partiellement formel, du langage que nous utilisons lorsque nous attribuons aux ions des charges discrètes. Cette représentation qui n'est probablement pas très éloignée de la réalité lorsqu'on considère les oxydes des métaux comme le sodium ou le calcium, s'en éloigne lorsqu'on passe des oxydes aux sulfures et des sulfures aux séléniures, dans les réseaux cristallins desquels la contribution de l'énergie de polarisation est importante. Il en est de même avec un élément déterminé, lorsqu'on compare des phases dans lesquelles celui-ci est associé à un nombre variable d'anions, le caractère ionique s'atténuant lorsque le nombre des anions diminue (passage TiO_2 à TiO par exemple). Mais j'éprouve l'impression que le Prof. Weyl nous propose de substituer à un formalisme auquel nous sommes habitués, un autre formalisme qui, pour le cas des phases non stoechiométriques, ne semble pas apporter des facilités nouvelles d'interprétation.

Il paraît en particulier difficile d'expliquer les différences importantes observées dans l'étendue des phases non stoechiométriques sans faire appel aux différences d'énergie qui existent entre les différents états d'ionisation des cations, toute formation de lacune cationique devant en effet s'accompagner d'un changement dans l'état quantique des cations restants, et étant par conséquent subordonnée à la possibilité d'effectuer ce changement avec une dépense d'énergie raisonnable. Adopter ce point de vue n'équivaut d'ailleurs pas à admettre une localisation des ions de valence anormale dans la structure, la répartition des charges anormales pouvant être considérée comme répartie statistiquement sur l'ensemble des sites cristallographiques aptes à les accueillir.

Avec ce point de vue, l'apparition de la conductibilité électrique et de bandes d'absorption dans le visible trouve une explication satisfaisante.

Un autre point sur lequel j'aurais voulu attirer l'attention est l'influence que le Prof. Weyl attribue au phénomène de « screening » sur la cinétique des transformations dans l'état solide. Il est aisé de comprendre, dès que l'on a adopté les hypothèses de base de l'auteur, que le « screening » puisse être un facteur déterminant dans le sens de la variation d'énergie libre qui accompagne une transformation solide A $\rightleftarrows$ solide B. Il me paraît par contre difficile de le considérer comme facteur déterminant de la cinétique. En effet, toute explication de la cinétique de telles transformations doit, pout être prise en considération, établir la distinction entre le processus de nucléation et celui de croissance. L'un et l'autre possèdent des énergies d'activation qui dépendent de facteurs multiples autres que le « screening » et qui ne sont pas nécessairement identiques.

Some Problems of Solid State Chemistry

(With special regard to diffusion and reaction in oxide systems.)

by Roland Lindner

INTRODUCTION

One aim of modern solid state chemistry is the elucidation of the mechanism of solid state reactions. Very extensive work has been laid down on the investigation of the diffusion stage of some typical and important solid state reactions such as :

1° the oxidation of some metals at high temperatures and

2° the formations of " oxide compounds of higher order " as silicates and spinels by reaction between the respective oxides in the solid state.

A question of special importance in this connection is the state of the reaction layers at high temperatures. The deviation from stoichiometric composition and the degree of reversible lattice disorder, i.e. the concentration of vacancies and interstitial atoms and its dependence on temperature, impurities and changes in the surrounding gas atmosphere, has to be investigated by special experiments, which, besides, contribute to the knowledge of the solid state itself.

During recent years new techniques as e.g. the measurement of the dielectric loss and of the nuclear magnetic resonance spectrum have been developed. As direct and comparatively easy and reliable methods, the measurement of atomic mobility with radioactive tracers and by evaluation of electronic and ionic conductivity can, however, still be considered to be the most important ones.

In the following an attempt is made to illustrate the present situation in this field with a detailed discussion of some of the most prominent solid systems. Reference will be made to some unpublished results, and this summary should consequently not be considered as final, but rather as a report on the present situation and as a survey on results, some of them not fully established and still open to discussion. The author is indebted to several colleagues, especially in the USA (C. Wagner, W.J. Moore, E. Gulbransen) for discussions during his recent visits.

In the following the available information about lattice disorder and self diffusion in some oxides will be discussed as well as the correlation of these results with the oxidation of the respective metals (reactions : solid - gas). In the second half of this paper the same procedure shall be applied to reactions between solids.

The systems discussed can be divided into the following groups :

1. *a)* alkaline earths (MgO, CaO and BaO)
   b) ZnO as example of a *n*-conducting metal oxidation layer
   c) *p*-conducting oxides (Cu_2O, FeO, CoO and NiO)
2. *a)* Atomic mobility and solid state reactions in systems SiO_2 + PbO and CaO respectively.
   b) Self diffusion and reaction in various spinel systems.

METAL OXIDES AND METAL OXIDATION

All available information on self diffusion in oxides is assembled in Table I and repeated reference to this table will be made. The constants for the temperature dependence of the self diffusion coefficient $D = D_0 \exp (Q/RT)$ viz. the preexponential (frequency) factor D_0 and the experimental activation energy (heat of activation) are presented. Informations about crystal structure and melting point are given in connection with the evaluation of the self diffusion coefficients at the melting point (to be discussed later).

The alkaline earths have hardly any importance as oxidation reaction layers, as the oxidation of alkaline earths metals usually does not result in coherent protective oxide layers (with the possible exception of magnesium at low temperatures). Nevertheless the knowledge of lattice disorder and self-diffusion in alkaline earths contributes to the general picture of the behaviour of oxides (and has, besides, some bearing on problems connected with alkaline earth cathodes and their electron emission).

The self-diffusion of Mg^{28} in MgO has been measured in *single crystals* (1), whilst practically all other investigations have been made on polycrystalline material.

Only a very tentative *direct* determination of the ionic conductivity has been made and a small value (a few percent at 1,300 °C) for the transfer number could be estimated. The indirect determination by comparison of diffusion measurements with conductivity measurements (in air) (2) on crystals from the same source leads to the same order of magnitude. Measurements of the thermoelectric power (3) indicate hole conduction in Mg O, which should normally be accompanied by Mg-vacancies, although interstitials are also assumed.

The self-diffusion of Ca^{45} in sintered samples of CaO shows an activation energy very similar to that for MgO. Conductivity and transfer numbers, i.e. the ionic conductivity has also been measured over a large range of temperature and been found to increase from about 1 % at 1,200 °C to about 10 % at 1,400 °C, which means that all conductivity should be practically ionic near the melting point (4). The ionic conductivity and the self-diffusion coefficient, correlated by the Nernst-Einstein relation, are in fair agreement, which indicates that practically all ionic transport is due to calcium ions.

The self-diffusion of Ba^{140} in single crystals of BaO has been measured by Redington (5). The values for the activation energy at elevated temperatures are, however, astonishingly high ($\sim$ 250 Kcal) and should in the present author's opinion be considered with reservation. If these values are not accepted, measurements of the migration of excess barium in colourless barium oxide (6) crystals could be considered to give an estimate for the self-diffusion of barium with an activation energy of 65 kcal, which tentatively had been ascribed to the diffusion of oxygen vacancies.

Surveying the measurements on alkaline earths it can be stated that an activation energy of about 80 kcal represents an average value for the self-diffusion of the cations in these comparatively simply built oxides. The self-diffusion values can possibly be predicted empirically from the melting temperatures as will be described later.

Zn O AS EXAMPLE OF AN EXCESS CONDUCTING METAL OXIDATION PRODUCT

Zn O is a substance of manifold interest as luminescent, catalyst, and metal oxidation layer. It has been investigated very thoroughly during the last twenty years, but no complete and consistent picture of its basic kinetic qualities has been obtained yet. ZnO is considered to be a typical *n*-conductor, the excess of zinc in deviation from stoichiometric composition being accommodated in the form of interstitial zinc ions and electrons. The alternative possibility of oxygen vacancies seem somewhat less probable because of recent x-ray investigations by Gray ([7]). Primarily interstitial zinc ions are considered to be the main vehicles for atomic transport under self-diffusion and oxidation of zinc metal.

Table I contains two different investigations with practically the same values for the temperature function of the self-diffusion coefficient of zinc. This coincidence is, however, surprising as in the first case polycrystalline samples in air were investigated ([8]), whereas in the second case the exchange between radioactive zinc oxide crystals and zinc metal vapour at 1 atmosphere pressure was measured ([9]). In this last case the formation of interstitials zinc ions should require less energy (by solution of the metal in the oxide) than by dissociation of zinc oxide in the first case, and consequently a lower activation energy for self-diffusion (37 kcal for Zn^{++} and 22 kcal for Zn^{+} formation and diffusion) would be expected ([10]). In fact, however, the self-diffusion was practically unaffected by the presence of zinc vapour under the specific experimental conditions used (probably diffusion against an overall gradient of zinc). In this connection experiments ([11]) are to be mentioned which indicated that the diffusion constant during the exchange of radioactive zinc metal vapour with zinc oxide crystals is strongly con-

TABLE 1

Self-diffusion in oxides

	D^0 (cm sec^{-1})	Q (kcal mole^{-1})	T^m (^{0}C)	log DT^m	Ref.
MgO	0,23	78.7	2800	— 6,22	I
CaO	0,4	81	2570	— 6,62	II
Cu_2O	4,4 .10^{-2}	36.1	1235	— 6,61	III
ZnO	1,3	74	1975	— 7,06	IV
	4,8	73	1975	— 6,42	V
FeO	1,4 .10^{-2}	30.2	1420	— 5,75	VI
CoO	2,15 .10^{-3}	34.5	1935	— 6,09	VII
Cr_2O_3	4 .10^{3}	100	1990	— 6,05	VIII
Fe_2O_3	4 .10^{5}	112	1570	— 7,7	IX
SnO_2	10^6	119	1930	— 5,95	X
PbO	10^6	69	890	— 7,00	XI
NiO	0,24	62	2090	— 6,35	XII

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centration dependent, suggesting vacancy diffusion as rate determining, when the excess zinc (metal) concentration is high. Similar experiments with radioactive zinc vapour, performed in this laboratory by Spicar (12), showed over a large range of temperature an activation energy of 85 kcal. Preliminary diffusion experiments on sintered pellets performed by Moore and Secco indicated about the same value (90 kcal).

Some observations concerning the colour of zinc oxide heated to high temperatures or exposed to zinc metal vapour are of interest in connection with diffusion measurements. Sometimes the assumption is made, that the colour is a direct measurement of the concentration of excess zinc in the form of interstitial ions. This is, however, by no means certain. According to preliminary results obtained by Lander at Bell Telephone Laboratories the activation energy for the diffusion of a reducing agent in zinc oxide crystals, possibly excess zinc, requires a considerably higher activation energy than the diffusion of the coloration (about 90 against 50 kcal/mole) (13).

Endeavours were made by E. Spicar to determine the diffusion of interstitial zinc in zinc oxide by following the change in conductivity after quenching (12). This change proceeds according to a diffusion law. Of course an essential experiment is the investigation of zinc self-diffusion as a function of oxygen pressure, which should establish a differentiation between interstitial and vacancy diffusion. Certain conclusions can already be drawn from experiments by Roberts (14), who found that self-diffusion of zinc is enhanced by factor of 4, by the substitution of oxygen for an argon atmosphere.

After this short discussion of diffusion data the oxidation of zinc metal is considered. The kinetics have been investigated by Wagner and Grünewald (15) and in newer work by Moore and Lee (16), who measured the oxidation of zinc foil at different oxygen pressures and obtained at the highest pressure used (10 cm Hg) as the temperature dependence of the parabolic rate constant $k = 3.3 \times 10^{-7} \exp(-28{,}000/RT)$ cm^2 sec^{-1}, whilst a decrease in oxygen pressure of two orders of magnitude increased the activation energy by about a factor 2, which brings it near the self-diffusion activation energy. The preexponential factor is, however, 10^5 times higher than D_0 and the values for k at 400 °C 10^8 times higher than for the (extrapolated) D. It should be noted that the low preexponential factor indicates a negative activation entropy, which is usually considered as being proof of prevailing grain boundary diffusion.

In contrast to the deficit (*p*—) conductors discussed below, agreement between oxidation and self-diffusion was not to be expected, as the formation of interstitial zinc ions, should require less energy in the case of metal oxidation, and the activation energy for diffusion of zinc in zinc oxide in equilibrium with solid metal was calculated to 47 kcal (10), which figure is considerably lower than the one experimentally found for diffusion in zinc oxide in air but still higher than that observed for the oxidation.

Direct measurements of the self-diffusion of zinc in zinc oxidation layers has been tried independently by both Moore (10) and Lindner (17), who found that this diffusion coefficient has the order of magnitude 10^{-16} cm^2 sec^{-1} at 400 °C, which is in sufficient accordance with the oxidation rate at that temperature. Thus the original assumption that the diffusion of interstitial zinc ions determines the oxidation rate looks sufficiently established.

The fact that the activation energy for self-diffusion in zinc oxide was not considerably influenced by the presence of zinc metal vapour but well by the presence of solid zinc casts a new light on the theories of atomic mobility in zinc oxide. It does not invalidate the assumption mentioned above, that the oxidation proceeds mainly by diffusion of zinc ions (although a participation of oxygen cannot yet be excluded) but indicates that grain boundary diffusion may be prevailant as already indicated by a negative entropy of activation for the oxidation constant. Lattice diffusion besides, may eventually not proceed by interstitial migration mainly and a certain indication for this possibility has been given by the results obtained by Münnich (11). He found in his experiments, as mentioned a marked decrease in the diffusion coefficient with increasing excess zinc concentration in the crystals. The conclusion is drawn, that at low concentrations the considerably faster interstitial diffusion prevails, whilst at higher concentrations vacancy diffusion becomes rate determining. The interstitial transport may be decisive and responsible for the lesser activation energy of the oxidation reactions, as in this case a continuous consumption of zinc ions takes place at the zinc oxide oxygen interface. This preserves a concentration gradient for interstitials and favours this transport as compared with vacancy transport.

The extensive work on Zn O, originated by the effort to elucidate the oxidation of zinc, has lead to a rather complex picture and some more crucial experiments seem necessary. Such experiments are amongst others : measurement of an eventual anisotropy for the self-diffusion, experiments in zinc oxidation layers over a larger range of temperature, experiments in order to establish equilibrium condition at the surface of zinc oxide crystals. An essential point is the detailed investigation of interstitial diffusion by following the migration of an excess zinc interstitial concentration forced upon the crystal by treatment with zinc vapour or by generation at high temperatures and subsequent quenching. The preliminary results by Lander (13) would give a rather high activation energy for interstitial diffusion and should be repeated as soon as pure crystals of sufficient size become available.

In spite of all complications (experiments with gas adsorption and diffusion through the oxide also contribute to the picture) there is no convincing evidence that the Wagner mechanism (18) of prevailant cation diffusion through the oxidation layer is not rate determining for the oxidation of zinc.

P-CONDUCTING OXIDES AS REACTION LAYERS

In the following some *p*-conducting oxides shall be treated by comparison of oxidation and diffusion constants. *The self-diffusion in cuprous oxide* (Cu_2O) has been investigated by Moore (19) and co-workers as shown in Table I. The comparison of the results with oxidation data obtained by Lee and Moore, shows that the activation energy for both is the same and the values of the constants are in the relation $k/D \sim 2$. This indicates that there is a *uniform* distribution of vacancies throughout the oxide layer, (as e.g. in the case of a linear concentration gradient the ration k/D would be 4). This contradicts results obtained by Bardeen, Brattain and Shockley (20), who assumed a gradient of vacancy concentration in a cuprous oxide reaction layer and a diffusion coefficient for cuprous ions proportional to that gradient. Their experimental evidence may not be quite sufficient and according to Moore the possibility must be considered that no vacancy gradient is maintained in a growing cuprous oxide layer (grain boundaries and dislocations acting as sources and sinks for vacancies), or that otherwise the diffusion is based on another mechanism. According to Moore (21) even the participation of copper-oxygen vacancy pairs cannot be excluded as indicated by direct measurement of the diffusion of oxygen-18 in cuprous oxide. The conditions are further complicated by the observed plastic flow of oxide layers during oxidation of copper, which makes any marker experiments for the determination of the prevailant migrating ionic species very difficult.

The question of vacancy concentration gradients in oxide layers arises in other cases of *p*-conducting oxides where sufficient agreement between self-diffusion and oxidation is found. Thus the diffusion coefficient for ferrous ions in *ferrous oxyde*, according to Himmel, Birchenall and Mehl (22), increases linearly with increasing vacancy concentration, which latter can be easily determined, as in this case the deviation from stoichiometric composition is large. This evidence is, however, mainly based on experiments at the highest temperature used (1000 °C). The measurements of Carter and Richardson of the self-diffusion in wustite agree, as shown above, very well with those by Himmel, Birchenall and Mehl, although these authors report a practically unchanged composition of the wustite, equivalent to a constant vacancy concentration over the temperature range 700 ° — 1000 °C.

In *cobaltous oxide* (Co O), however, oxygen excess is found to increase with temperature and with about the 1/3 power of oxygen pressure (23), which indicates considerable association between cobaltic ions and vacancies. Such a phenomenon, i.e. that the vacancy formed is bound by an ion of deviating valency may be common and contribute little to diffusion, which argument would invalidate the calculation of vacancies from deviations of stoichiometric composition.

The investigation of the oxidation of the cobalt metal by Richardson and Carter (24) shows that although the oxidation rates agree with the Wagner oxidation theory the distribution of cobalt in growing oxide layers is different from that predicted by Wagner. The tracer distribution in growing oxide films corresponds to a constant diffusion coefficient for approximately two thirds of the layer and falls towards zero at the oxide metal interface. In any case, the diffusion coefficient does not vary linearly with distance and there is indication that the concentration of vacancies near the gas/oxide interface is less than the equilibrium value for oxide in equilibrium with the oxidizing atmosphere.

Summing up the evidence concerning the detailed mechanism of the growth of *p*-conducting oxide layers on metals we can state that although the simple assumption of a linear concentration gradient for vacancies through the oxide film seems to have been proved by experiments by Bardeen and co-workers ([20]) as well as by Himmel, Birchenall, and Mehl ([22]), contradictory evidence has been found by Moore and co-workers as well as by Richardson and Carter ([23]).

Another case of the oxidation of a transition metal is that of nickel. The activation energy for oxidation is according to Moore and Lee 38,4 kcal ([25]) and according to Kubaschewski and Goldbeck ([26]) 45-60 kcal/mol. The electric conductivity shows an activation energy of 23 kcal with σ proportional to $p(O_2)^{1/4}$ which indicates that only one hole is dissociated from the cation vacancy. Other observations by Baumbach and Wagner ([27]) indicate that the activation energy for diffusion of *oxygen* should be about 45 kcal (concluded from the change of conductivity as a function of change in oxygen pressure).

Direct measurement of nickel self-diffusion in NiO are still incomplete. The preliminary value for the activation energy, contained in Table I and obtained for the diffusion of radioactive nickel in nickel oxide crystals does not, however, coincide with the oxidation rates at lower temperatures, in which case grain boundary diffusion may have been prevailant. (This would, however, be in contrast to the results of Richardson and Carter ([23]) for the diffusion in cobaltous oxide films, where no grain boundary diffusion has been found). Thus it would be possible that the activation energy for the oxidation rate changes with temperature. Some indication for this has been found in unpublished experiments by Gulbransen ([29]), who quotes an activation energy of about 60 kcal at temperatures between 1000 ° and 1200 °C [a similar value is given by Goldbeck ([26])]. Extensive work has still to be done. Thus the dependence of the self-diffusion coefficient of nickel on the composition of the oxide and on the oxygen pressure has to be investigated in detail. Experiments with pure nickel oxide single crystals are under work both in the laboratory of W.J. Moore and in our Gothenburg laboratory.

The last example we shall shortly consider is the oxidation of lead metal which has been investigated by a number of authors. The activation energy for oxidation seems to be about the same as for the self-diffusion of lead in PbO (30). The self-diffusion is not appreciably affected by the presence of underlying metal (31), which indicates that PbO is a *p*-conductor as should be expected. The quantitative comparison of oxidation and diffusion rates, however, shows that the oxidation rates are about three orders of magnitude higher, i.e. the ratio k/D is about 10^3. This can hardly be reconciled with the assumption of a linear concentration gradient for lead vacancies in the oxide layer. The concentration gradient for radioactive lead in layers of oxidized metal ought to be investigated experimentally and even the possibility of oxygen diffusion should be considered in this oxide where the ionic sizes of cations and anions are comparable.

When surveying the field of metal oxidation mechanisms as described in this paper the impression is obtained that an originally clear picture has become more and more indistinct as experimental progress has been made. This is, however, no disadvantage and will finally lead to a much deeper knowledge of the oxidation mechanism as well as of the oxides concerned.

2 REACTIONS BETWEEN SOLIDS

The experimental material for establishing definite reaction mechanisms is scarce compared with the amount of analogous work on tarnishing reactions. Carl Wagner assumed the diffusion of cations through the formation of " ionic compounds of higher order " (32). This could be verified in the case of the formation of silver-mercury-iodide (33), which is a pure ionic conductor with a high mobility of silver and mercury ions and practically no mobility of iodide ions. This proof, already established in 1936, was to be the only one for a long time.

Based on the material about ionic mobility in silicates which was available at that time Wagner suggested that the same mechanism (cation diffusion through the reaction layer and immobile anions) should be valid also for the formation of high melting compounds such as silicates and spinels. Investigations by Jagitsch and co-workers in the Hedvall institute, however, already showed in the years 1946-1947 that the experimental results found with the formation of lead silicates (34) and zinc aluminium spinel (35) were not consistent with the Wagner theory. The evidence was not based on the comparison of diffusion and reaction data, but on a very simple and effective technique, that of the marked original interface between the reactants. The markers, small particles of noble metal, not participating in the reaction, would be imbedded in the reaction layer, if the layer grows by diffusion of the two cation species in opposite direction. This was, however, not found to be the case in the two reactions mentioned, where all transport obviously was due to the motion of lead and zinc ions respectively together with oxygen ions in the same direction.

The two groups of high melting oxidic compounds, viz. silicates and spinels have been the subject of a larger research program using radioactive tracers and being under work in the Hedvall institute during the last eight years (36). We intended to make full use of the technique of radioactive tracer atoms, which became increasingly available during this time.

2*a*. SILICATES OF LEAD AND CALCIUM (37)

The formation of silicates by reaction between a metal oxide and silica in the solid state is a rather intricate reaction as several compounds are simultaneously found in varying concentrations. Usually one has to reckon with the formation of 3 $MeO.SiO_2$, 2 $MeO.SiO_2$, 3 $MeO.2SiO_2$, and $MeO.SiO_2$. All four silicates exist in the best investigated cases, viz. the systems $PbO + SiO_2$ and $CaO + SiO_2$. This means that not only the direct reaction between the oxides but also intermediate reactions between different silicates must be considered. This complicates studies of silicate formation as compared with the formation of spinels, where only one reaction product exists. Fortunately, in the beginning of the diffusion stage only orthosilicates (2 $MeO.SiO_2$) are formed with a yield surpassing that of the others. In any case, however, a quantitative analysis of the process is rather difficult and our research has only reached semiquantitative results.

LEAD SILICATES

Our aim was to measure the self-diffusion coefficients for lead in ortho- and metasilicate (and if possible also the diffusion of silicon) and compare them with exact determinations of the reaction rates. It contrast to metal oxidation the transport of one atomic species through the reaction layer is not sufficient for the reaction to proceed. Consequently, diffusion of two different cation species in opposite directions (Wagner) or the diffusion of oxygen and metal ions in the same direction is necessary. Experiments to find a mobility of silicon in lead silicates were not successful. Silicon-31, the only tracer available at that time, has, however, a comparatively short half life and is produced with a yield small compared with that of usually present impurities as sodium. This limits the precision of the measurements and it could only be stated that the self-diffusion of silicon, if any, must be considerably lower than that for lead ions at the comparable temperatures. (In the meantime longlived Silicon-32 has become available and a reinvestigation of the diffusion in silicates as well as in silica itself is planned.)

A rechecking of Jagitsch's results concerning the formation of orthosilicate by reaction between lead oxide and lead metasilicate led qualitatively to the same results, i.e. the activation energy of the reaction rate is not identical with that of the self-diffusion of lead ions, but higher, as should be expected if a simultaneous transport of oxygen takes place during reaction. The assumption by Jagitsch that diffusion of oxygen participates in lead silicate formation could not be devaluated and has to be investigated direct.

CALCIUM SILICATES

No very exact measurements of the reaction rates in this system are available, and the best data are still those by Jander and Hoffmann ([38]), who measured the rate of the powder reaction between calcium oxide and silica. Powder reactions, in spite of their technical and scientific importance, are far from fully explored and the participation of phase boundary reactions and surface diffusion has not yet been sufficiently investigated. The last phase of powder reactions is rate determined by diffusion through the reaction layer and, with the contact phases area sufficiently well known, reaction constants can be evaluated according to a procedure suggested by Serin and Ellickson (39).

In principle rate determinations by reactions between e.g. plane crystals of the reactants are to be preferred; although the instability of the calcium orthosilicate formed usually as a loose powder (as consequence of a crystallographic transformtaion and increase in volume) makes it difficult to follow the reaction through repeated intervals.

The same effect complicates the measurement of self-diffusion in calcium orthosilicate samples. (The " surface decrease " method has to be used with radioactivity measurements *during* diffusion.) The self-diffusion of Ca-45 in $CaO.SiO_2$ and $3CaO.2SiO_2$ has also been measured and the following activation energies have been obtained :

$2CaO.SiO_2$: α-modif. 55 kcal, β-modif. 65 kcal;

$3CaO.2\,SiO_2$: α-modif. (58 kcal), β-modif. 73 kcal;

$CaO.SiO_2$: α-modif. 112 kcal, β-modif. (78 kcal). Comparison with the rate of the reaction $CaO + SiO_2$ favours the self-diffusion in $2\,CaO.SiO_2$ in accordance with the predominant formation of this silicate. Neither in this case was it possible to find an appreciable transport of radioactive silicon, although diffusion experiments with silicon-32 will be necessary to obtain final results. Thus oxygen diffusion has to be considered and to be experimentally investigated by means of 0-18 as a tracer isotope.

THE FORMATION OF SPINELS BY REACTION IN THE SOLID STATE (28)

Spinels, i.e. solids with the same crystal structure as the mineral spinel $MgAl_2O_4$, should be expected to display markedly the characteristics of atomic mobility in the solid state because of their specific structure. The spinel structure (shown by ferrites, chromites, and aluminates of certain bivalent metals) is a comparatively " loose " structure, as the interstices of the oxygen lattice are only partly occupied with cations. In the case of a " normal " spinel each cation species is confined to a type of position, i.e. tetrahedral or octahedral sites. If the non-occupied lattice sites constituted vacancies in the sense of the theory of reversible lattice disorder, considerable diffusion in the solid state would be expected, with an activation energy practically identical with that for the motion of lattice defects (as no energy for vacancy formation would be required). In fact, the self-diffusion of cations in spinels is usually higher than in the pure oxides but the diffusion rates are nevertheless still low at not too high temperatures, as would be expected when considering the fact that some spinels act as protective layers in the case of high temperature oxidation of alloys. The activation energies for self-diffusion in spinels is comparable with that for self-diffusion in oxides (Table II). (The respective measurements are made on sintered compacts of nearly stoichiometric composition; some of them will be repeated using single crystals which recently became available.) In ferrites and chromites both cations are mobile with comparable activation energy. In the case of aluminates Jagitsch's method of marking the original interface between the reacting oxides had to be used. Thus Jagitsch's results for zinc aluminate could be repro-

TABLE II

Self-diffusion in Spinels

$D = D_0 \exp(-Q/RT)$

	D_0 (cm^2 sec^{-1})	Q (kcal mole^{-1})
(Mg in $MgAl_2O_4$	2 .10^2	86)
Zn in $ZnAl_2O_4$	2.5.10^2	78
(Ni in $NiAl_2O_4$	3 .10^{-4}	55)
Zn in $ZnFe_2O_4$	8.8.10^2	86
Fe in $ZnFe_2O_4$	8.5.10^2	82
Zn in $ZnCr_2O_4$	60	85
Cr in $ZnCr_2O_4$	9	81
Ni in $NiCr_2O_4$	0.85	75
Cr in $NiCr_2O_4$	0.75	73
Sn in $SnZn_2O_4$	2.3.10^5	109
Zn in $SnZn_2O_4$	37	76

duced and also nickel aluminate (with a much smaller reaction rate) seems to show the same mechanism. Here the diffusion of both cations in opposite direction is obviously not rate determining, but the diffusion of oxygen within the aluminate lattice has to be considered and will be measured direct, which, however, may be a rather difficult experimental task, because of small rates and high temperatures.

In the case of ferrites and chromites the comparable diffusion coefficients and the nearly identical activation energies indicate a sufficient mobility for both cations to justify the assumption of a Wagner mechanism. Both may even diffuse by the same mechanism because of the nearly identical activation energies, which of course would mean a certain exchange or even a statistical distribution between tetrahedral and octahedral positions ("inversion") at high temperatures.

A detailed comparison of reaction and diffusion rates in order to prove the Wagner mechanism quantitatively has been tried in the case of zinc ferrite, zinc chromite and nickel chromite. The agreement is rather good; the independent determination of the change in free energy for the reactions considered by measurements of electromotoric forces has still to be made.

The situation is somewhat puzzling : in spite of the same structure (as low temperature X-ray measurements indicate) ionic mobility and reaction mechanism in ferrite and chromite systems are different from those in aluminate systems.

Investigations of atomic mobilities in spinels with deviations from stoichiometric composition are of special interst in this connection. In a close packed lattice with comparatively few vacancies the introduction of impurities with valencies different from that of the ionic constituents of the pure crystal should strongly influence the vacancy concentration as shown by Koch and Wagner (40). The impurity atom might even associate with vacancies and form a complex of deviating mobility. The question is now, whether similar considerations are valid for the case of spinels in which geometrically a very high concentration of vacant lattice sites is assumed?

If a spinel — contrary to conditions revealed by X-ray diffraction at low temperatures — is regarded as a structure with nearly completely occupied cation sites, the substitution of a bivalent ion by a trivalent one would, for electrostatical reasons, increase the vacancy concentration of the bivalent ions and increase their diffusion and possibly even enhance the diffusion of trivalent ions associated with the generated vacancies to a sort of a complex. The essential formal difference between the ternary spinels and binary compounds is of course that such a change is in the first case only a change from stoichiometric composition and does not imply the introduction of impurity atoms as in the second case. As, however, the spinel cation sites are far from completely occupied and, besides, different types of lattice sites are assumed for the two different cationic species one should not assume a priori an increase in atomic mobility if the addition is within reasonable limits. Experiment, however, shows than an increase of concentration of iron (probably as ferric ions) of about 3 - 5 % in zinc ferrite ($Zn^{2+}Fe_2^{3+}O_4$) increases the diffusion coefficient of iron by about a factor 10, but does not affect appreciably the self-diffusion coefficient for zinc ([41]). The same has been found for the case of zinc chromite where the addition of 3.7 % chromium increased the self-diffusion coefficient for chromium by about one order of magnitude.

Speculative assumptions concerning the increase in mobility of the trivalent ions can be made. For reasons as yet unknown the excess of the trivalent ions may partially or completely be accommodated on tetrahedral sites as favoured paths for atomic transport (" inversion " of the spinel). The tetrahedral sites which usually are occupied only to 1/8 of their capacity are only at lower temperatures considered to be smaller than the octahedral ones, whereas X-ray measurements at high temperatures (and possibly a detailed calculation of the potential functions within the different spinel lattices at hig temperatures) would be necessary to obtain sufficient information concerning this question. In this connection, a paper presented by Flood and Hill at the Third International Meeting on the Reactivity of solids, Madrid 1956, is of great interest. The concentrations of ferric and ferrous ions in the spinel magnetite ($FeFe_2O_4$) can be calculated (with the assumption of vacancy formation by oxidation) as function of oxygen pressure and are found to fit experimental results. Obviously the Wagner-Koch ([40]) procedure can be applied. The influence of the two different types of cation sites (if they are preserved at high temperature) on atomic mobility ought to be elucidated. A consistent theory of the kinetics in spinels will have to explain the changes in self-diffusion coefficients with deviation from stoichiometric composition and will also have to explain why aluminium ions should be so much less mobile than chromic or ferric ions. In the latter case hardly differences in ionic sizes can be used for explanation, a better approach would be to consider the eventual existence of bivalent iron and chromium ions which may be generated by an electron exchange; this is less probable in the case of aluminium ions.

When surveying the available data on atomic mobility in oxides (Table I), the question arises, if there is a feature common to all systems investigated. The activation energies can vary within wide limits (maximum ratio nearly 4), so do the preexponential factors D_0 (variation over 10 orders of magnitude).

The values for the cation self-diffusion coefficients extrapolated to the (sometimes not too well known) melting points of the oxides (42) lie, however, within comparatively narrow limits around a mean value $\log D_0 = -6.5 \pm 0.8$ (with a deviation for Fe_2O_3, whose latter value might possibly change somewhat with improved experimental technique).

The deviation in $\log D_{MP}$ is smallest for the cubic oxides of Mg, Ca, Co, and Cu^I (the values for the cubic NiO still being somewhat uncertain) and larger for the trigonal Fe_2O_3 and Cr_2O_3 and the tetragonal PbO and SnO_2, whilst the hexagonal ZnO shows a $\log D_{MP}$ very near to -6.5, if the values of Moore and Secco are used.

The molar ratio metal/oxygen varies from 2 (Cu_2O) to 0.5 ($Sn\ O_2$). Obviously the only thing in common to all syst ms are oxygen ions which are considerably larger (with the exception of PbO) than the metal ions. The question is how to ascribe the values for cation self-diffusion at the melting points to corresponding qualities of the collapsing oxygen lattice.

Any self-diffusion coefficient represents the product of the lattice defect concentration and the mobility of disordered particles. The separation of the two terms has been possible only in a few cases and more determinations for oxides (Hall effect measurements) look highly desirable. There is not yet any quantitative basis for an argument like the assumption of corresponding values for cation defect concentration and finally corresponding instability of the oxide lattice. [Similar ideas can be found in literature and are treated e.g. by Frenkel (43)]. A qualitative " cooperation effect ", in grouping vacancies to dislocations with consequent decreased resistivity to shear (= melting), has been suggested by Rothstein (44).

In this connection, ideas presented by Nachtrieb and Handler (45) are of interest. A relation between the latent heat of fusion and the activation energy for self-diffusion in face and body centered cubic metals induced those authors to assume a " relaxion " model for self-diffusion, the essential part of which is the inward relaxation of the atoms nearest to a vacancy. In the case of Na-metal, about 0.4 % of all atoms are assumed to belong to relaxions immediately under the melting point. A higher concentration obviously leads to melting. A similar model might possibly explain the influence of cation vacancies on the stability of the oxygen partial lattice in oxides, although here the relation $\Delta H/L_M = \text{const.}$ is not fulfilled.

Concluding this paper, it should be stated once more, that it is intended as a report on research in progress. It contains only a part (although an essential one) of modern solid state chemistry and leads to the following picture :

Continued research has led to an ever increasing complexity in the treatment of the field. The basic conceptions concerning the mechanisms of solid state reactions have been few and ought to be enlarged in order to explain all experimental results, although considerable progress has been made during the last few years. There is, however, no reason why the mechanism of the most prominent solid state reactions should not be completely elucidated in a comparatively short time.

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Etat actuel et évolution des recherches et de l'application technique dans le domaine de la réactivité des corps solides

par **J. ARVID HEDVALL**

A la fin du siècle dernier, quelques expériences préliminaires de *Spring*, *Cobb* et *Roberts-Austen* démontrèrent la possibilité de transport de matière à l'état solide. Ce n'est qu'au début de ce siècle que l'étude de ce domaine, jusqu'alors inexploré, fut entreprise de façon systématique. A ce moment, les connaissances concernant le réseau cristallin étaient nulles : elles se sont développées ultérieurement grâce à la méthode de Rœntgen.

Les recherches ont d'abord porté sur une série de substances oxygénées, choisies à cause de leur importance pratique considérable. Ce choix est considéré aujourd'hui comme un heureux hasard. Les principaux résultats des expériences exécutées dans le but d'établir les limites « topographiques » de ce nouveau domaine de la chimie, furent les suivants :

1° Les réactions donnant lieu à la formation de *composés ou de solutions solides* peuvent se faire avec une vitesse considérable, à des températures de plusieurs centaines de degrés en dessous de la température de fusion ou sublimation.

2° La vitesse de la réaction est fortement influencée par le traitement préalable, le mode de liaison et, en général, par les facteurs cristallographiques des différents constituants.

3° Des maxima de réactivité se manifestent lorsque de nouvelles phases apparaissent, lors de décompositions thermiques ou de modifications cristallographiques, par exemple. Ces maxima correspondent à un excès d'énergie ou à un état de déséquilibre.

Ces résultats, parmi d'autres, formaient la base des considérations théoriques concernant les états lacunaires réversibles et irréversibles. Celles-ci ont pu être développées par *Frenkel*, *Schottky* et *Wagner*, grâce au développement de la Rœntgenographie.

4° On a découvert de nouveaux types de réactions, qui peuvent être schématisés de la façon suivante :

a) $M'O + M''XO_n = M''O + M'XO_n$

b) $M'O + M''X = M'X + M''O$

$M'O$ et $M''O$ sont des oxydes, $M'XO_n$ et $M''XO_n$ des sels d'oxacides et $M'X$ et $M''X$ des halogénures, sulfures, carbures, phosphures, siliciures, borures, etc. De telles réactions, effectuées au départ de substances appropriées, peuvent être déclenchées à des températures étonnamment basses et se déroulent avec des vitesses très grandes. Ceci se présente lorsque la différence d'énergie entre le mélange réactionnel et les produits formés est grande. Les réactions du type *a)* présentent des régularités étonnantes quant aux températures de début de réaction. Celles-ci sont indépendantes du sel ($M''XO_n$) et déterminées par l'oxyde ($M'O$). Ces régularités ont suscité les premières discussions animées au sujet de la nature des particules de transport. Pour expliquer de telles régularités, il s'avère nécessaire de faire intervenir des migrations en surface, de groupes d'atomes autres que les ions. Par contre, dans la majorité des cas, les réactions du type *b)* commencent aux températures auxquelles les halogénures utilisés deviennent conducteurs électrolytiques. *Weyl* aussi a confirmé ce point de vue dans ses travaux.

On a montré, que dans les deux cas *a)* et *b)*, des écarts à ces régularités apparaissent lorsque le mélange des poudres renferme un composé qui subit un changement de structure cristallographique avant d'atteindre la température normale de la réaction. Dans ce cas, la réaction débute à la température de transformation.

5° En métallographie, on connaissait depuis longtemps l'influence de traces de substances étrangères sur le comportement physicochimique. On a démontré que ce phénomène était général. Les atomes étrangers encastrés dans le réseau du solide influencent ainsi l'activité du cristal à cause de leurs déviations au volume, à la charge et à la structure des couches électroniques. De même, les gaz ambiants, chimiquement inertes, peuvent influencer la réactivité par leur présence dans le réseau cristallin.

6° Après avoir constaté l'influence de chacune des perturbations du réseau cristallin sur l'activité physico-chimique et sur la mobilité interne des particules, il devenait passionnant de voir si une action semblable pouvait être provoquée par un changement d'état purement énergétique, sans perturbation structurale directe. D'autant plus, que pendant les vingt années antérieures, la cristallographie roentgenographique s'était développée et affinée pour devenir un outil indispensable.

Suite à des discussions et à des échanges de correspondance, je sais qu'il n'est pas exagéré de dire que les théoriciens étaient étonnés par les grands changements de réactivité, d'activité catalytique ou d'adsorption que peuvent provoquer des variations *d'états magnétiques, électriques et de rayonnement*. Ceci sous-entend une compréhension large et approfondie des termes magnéto-, électro-, photo- et phono (ultrasons) -chimie, qui ne se limitent plus à des substances isolées.

Des travaux purement théoriques se sont développés, en rapport direct et en contact étroit avec les études précédentes. L'utilisation des méthodes roentgenographiques a permis de mettre en évidence, de façon précise, les différences existant entre les réseaux cristallins idéaux et ceux présentant des défauts de structure de diverses natures. On a introduit et démontré théoriquement des notions importantes connues: places inter-réticulaires, vides, formation d'assemblages moléculaires par polarisation, équilibre thermodynamique entre concentrations d'assemblages normaux et déformés dans les réseaux. On a prévu l'influence de ces facteurs sur des effets de diffusion, de transformation et de conductibilité électrique. Les défauts de structure ont été divisés en deux groupes, défauts réversibles ou d'équilibre et perturbations de structure irréversibles. Ces derniers défauts ne correspondent pas à un équilibre et, de ce fait, les réseaux possèdent un excès d'énergie. Ils comprennent des perturbations provenant de défauts héréditaires de structure, de transformations incomplètes ou de particules étrangères réparties de façon désordonnée. La réactivité des solides appartenant à ce dernier type peut être prévue à l'avance. De ce fait, leur connaissance est importante pour l'industrie en général et, tout particulièrement, pour celle utilisant la catalyse ou l'adsorption.

Dans ce bref résumé du développement de ce domaine relativement neuf de la chimie, on n'a marqué que les dates importantes.

Soulignons que les résultats obtenus ne constituent qu'une porte entrouverte sur un vaste domaine, resté longtemps non prospecté. Les particularités de la chimie des solides sont sans doute plus nombreuses que celles des autres états de la matière, étant donné que les influences structurales sont naturellement plus diverses.

Il sera donné, dans la partie suivante, un bref résumé des réalisations techniques existantes, des groupes de problèmes théoriques et, ensuite, quelques exemples de recherche et de réalisation les plus urgentes. Il n'existe évidemment plus de différences de principe, actuellement, entre le travail théorique et pratique, étant donné que l'industrie moderne ne peut plus travailler sans connaître exactement les matériaux, les réactions et les méthodes, sous peine de s'exposer à des pertes de temps et d'argent. Ces connaissances ne peuvent s'acquérir que par la recherche approfondie.

Un fait important, observé dans la chimie des silicates, en métallurgie et, en général, chaque fois que l'on travaille avec des solides, est que les réactions effectuées au départ de poudres, commencent à des températures beaucoup plus basses qu'on ne le pensait auparavant. De ce fait, il y a formation de produits de réaction qui agissent, non seulement directement sur la température d'effondrement ou de fusion, mais qui, par la suite, influencent l'évolution de la réaction totale. En effet, les produits formés à des températures plus basses, par effet de diffusion, sont différents de ceux qui se formeraient normalement, à des températures plus élevées.

Le fait de savoir que chaque forme de transformation ou d'état incomplet, correspond à un maximum relatif d'activité — que ce soit une attaque ou une prédisposition à l'attaque — a donné à l'industrie la possibilité d'éviter des destructions de matériaux, provenant de transformations cristallographiques. Ainsi, le quartz ou la sillimanite, utilisés pour le revêtement des fours, doivent être préalablement transformés en cristobalite et en mullite.

La présence de petites quantités de substances étrangères dans la matière première, peut influencer les propriétés physico-chimiques de cette dernière. Ceci a permis d'expliquer le comportement différent, considéré longtemps comme énigmatique, de matériaux de compositions chimiques à peu près identiques.

L'industrie a compris l'importance capitale des propriétés structurales, dépassant souvent celle des analyses chimiques dont elle se contentait précédemment.

La réactivité des solides est fortement influencée par des variations de composition du gaz ambiant, ne réagissant pas chimiquement. Ceci est valable non seulement lors du chauffage au four, mais aussi lors du broyage, au cours duquel la formation de couches de grains fins, freinant les chocs autour des particules non ramolies, dépend de la teneur en humidité de l'atmosphère du moulin.

Notons encore que les nouveaux types de réactions cités, qui ont été appelés, plus ou moins heureusement, *réactions d'échange* ont permis d'expliquer le déroulement de divers procédés, utilisés depuis longtemps dans l'industrie; par exemple, les procédés de grillage et frittage ou la méthode de Bessemer. Elles ont de plus rendu possible la mise au point d'une série de nouvelles méthodes de production : la fabrication de briques hautement réfractaires sans phases de fusion, de pièces d'appareillage utilisés dans les industries électrotechnique et électronique modernes et possédant des propriétés électriques et magnétiques particulières.

La possibilité de prévoir l'activité des corps solides, au départ de données concernant les perturbations de structure irréversibles, est évidemment de première importance pour l'industrie utilisant la catalyse. On a pu ainsi améliorer la durée et la sélectivité des catalyseurs, empêcher ou ralentir les processus de recristallisation et les échanges indésirables avec la substance de support.

Dans l'industrie de la catalyse, dans la fabrication des pigments, des produits huileux et des vernis, l'attention se porte aujourd'hui sur les influences très diverses de certaines modifications cristallographiques, telles le rutile et l'anatase.

Il va de soi que la connaissance des phénomènes de diffusion à l'état solide est à la base de la préparation des produits métallurgiques et céramiques en poudre des métaux durs et des « Cermets ». Rappelons que l'influence des gaz ambiants dissous, non liés, sur l'activité en surface, joue également un rôle important dans ces préparations.

Pour ce qui est de l'extension des notions de magnéto-, électro-, photo- et phonochimie, ces effets ne sont pas exploités dans la même mesure, du point de vue technique. Certaines réalisations existent cependant. Ainsi, la préparation des ferrites et d'autres substances utilisées en électronique, est facilitée si l'on opère à des températures situées dans l'intervalle de la transformation magnétique. La production de couches minces isolantes, dans les transformateurs, est favorisée par un traitement préalable du métal par les ultrasons.

Depuis longtemps, j'ai attiré l'attention sur le fait qu'il est possible d'influencer la sélectivité d'un catalyseur en utilisant des champs magnétiques ou électriques externes ou d'accélérer la polymérisation de substances organiques, dans les domaines de changement spontané de polarité.

Les réalisations techniques que nous venons de mentionner donnent un aperçu de l'avenir. Les possibilités d'amélioration des méthodes et d'adaptation dans de nouvelles branches de la production sont extrêmement variées. Cela demande toutefois des connaissances encore plus approfondie, des facteurs suivants notamment :

1° Les particularités de la surface en rapport avec la structure; nature et formation des molécules de surface.

2° Effets de polarisation à l'intérieur du réseau par suite de chocs thermiques résultant du chauffage (par exemple, assemblages moléculaires dans les réseaux ioniques).

3° La propagation de certains éléments perturbateurs de l'intérieur vers la surface.

4° La nature réelle des dislocations de toutes formes.

5° Déterminations exactes des défauts irréversibles.

6° Le mécanisme des transformations cristallographiques.

7° Influence de diverses perturbations du réseau sur le mécanisme de transport (diffusion) et détermination de la nature des particules et des modes de transport.

8° Déviations stoechiométriques des formules normales en surface et à l'intérieur et leur influence sur l'activité physico-chimique des surfaces.

9° Les conditions d'échange d'électrons ou de particules de matière à la limite des phases et leur influence sur les effets d'adsorption et de réaction.

10° Recherches approfondies sur les nouveaux effets magnéto-, électro-, photo- et phonochimiques.

Dans la suite de cet exposé, nous donnerons quelques exemples de problèmes actuels en liaison avec ces différents points spécialement en ce qui concerne les applications pratiques.

Les particules situées en surface, aux arêtes et aux angles, sont plus ou moins non saturées. Elles ont tendance, suivant la nature de la substance, à se grouper autrement qu'à l'intérieur du réseau. Il en résulte une structure superficielle spécifique au sein de laquelle les particules ou les groupes possèdent des moments dipolaires propres et produisent des effets de polarisation différents de ceux qui existent à l'intérieur. On sait également que les températures de transformation, observées en surface, sont généralement très inférieures aux températures normales et que l'activité physico-chimique de la surface est influencée par le déroulement général de la transformation. La mobilité des groupes atomiques formés ou adsorbés à la surface est modifiée par les conditions de diffusion à l'intérieur du réseau. Tout ceci est important, non seulement du point de vue théorique, mais aussi du point de vue des applications pratiques dans de nombreux domaines. En effet, les phénomènes dont il vient d'être question agissent aussi bien sur les processus de recristallisation et de frittage que sur l'adsorption et les réactions chimiques. Jusqu'à présent, on a étudié partiellement ces problèmes avec quelques métaux et substances organiques (migration de molécules en surface). Il va de soi que les questions soulevées ne se limitent pas à ces quelques cas, bien que ceux-ci soient d'un intérêt général.

Il arrive souvent, dans la littérature, de voir extrapoler des basses températures à des températures supérieures, lors de l'étude de processus dépendant des propriétés des ions d'un réseau ionique. Ceci suppose que le réseau reste constamment un réseau ionique type. Une telle manière de procéder n'est évidemment pas justifiée. Les chocs thermiques provoquent la formation de groupes moléculaires ou d'autres effets de polarisation. Ceux-ci tendent à perturber ou à faire disparaître le réseau ionique. Lorsqu'on chauffe du CaCO , par exemple, il faut admettre la préformation, dans le réseau, de groupe CO_2. Le mécanisme de décomposition thermique, ainsi que les modifications physiques et chimiques qui l'accompagnent, n'a pas encore été étudié suffisamment. C'est une tâche urgentes et importante de la recherche. On s'occupe beaucoup de ces problèmes maintenant.

En rapport avec ce que nous avons dit et avec ce qui suit, les vues de *W. A. Weyl* méritent un intérêt tout particulier. Elles sont exprimées, par exemple, dans son livre *A New Approach to Surface Chemistry* (1951) et dans sa conférence, présentée à ce Symposium. Il montre la nécessité de considérer de façon différente, d'une part, pour l'état solide et, d'autre part, pour les états liquides et gazeux. les notions de particules élémentaires et leurs rapports d'affinité, dans le cas de formations caractéristiques de ces états.

Il est possible que la théorie de Weyl permettra une compréhension plus profonde et plus concrète des notions de vides et d'espaces inter-réticulaires, de la nature des perturbations et de leur propagation dans les réseaux. Actuellement, ces représentations se limitent en quelque sorte à des formules mathématiques, sans que nous ayons, le plus souvent une image claire de la nature des perturbations du réseau, comme c'est le cas pour le réseau régulier.

Pour une même substance, on peut observer de grandes différences dans la vitesse de certaines transformations cristallographiques, suivant que l'on opère à des températures croissantes ou décroissantes. On a beaucoup écrit à ce propos, sans arriver toutefois à une représentation exacte du mécanisme de ce phénomène.

Comme exemple, on peut citer les transformations de la SiO_2, très importantes du point de vue pratique dans la chimie des silicates et en métallurgie. Les transformations $\alpha \rightleftarrows \beta$ se font rapidement dans les deux sens. La formation de la tridymite et de la cristobalite, bien qu'assez lente, se fait toutefois beaucoup plus vite que le retour au quartz, lorsque la température décroît. Aussi à l'Institut de Göteborg, on s'est attaché depuis longtemps à l'étude de ces processus ainsi qu'au problème de la migration. Ce champ de travail est immense étant donné l'individualité marquante des phénomènes de transport dans les transformation entre phases solides, ou entre phases solides et liquides ou gazeuses.

A Göteborg, nous nous sommes limités à l'étude de systèmes oxygénés, dont l'importance est vitale pour la chimie des silicates et pour la métallurgie. *Jagitsch* a élaboré une méthode radiographique et mis en évidence la migration de groupes lors des « réactions d'échange », dans le cas de nombreux mélanges d'oxydes. En faisant varier la dimension des particules, il a pu déterminer le rapport entre le transport en surface et la diffusion dans le réseau, pour quelques systèmes importants, du point de vue géologique, en particulier.

A Göteborg encore, *Lindner* a élaboré de nouvelles méthodes utilisant les radioisotopes, pour l'étude des phénomènes de diffusion. Ici également, l'importante question du rapport entre la migration de surface et la diffusion interne, a été attaquée avec succès. Les discontinuités, mises en évidence par les courbes de diffusion, ont fait découvrir quelques transformations cristallographiques, inconnues précédemment.

L'étude du mécanisme de la corrosion par oxydation, insuffisamment connu dans la plupart des cas, devrait être entreprise à nouveau. Chez nous, on met au point une méthode d'investigation utilisant l'oxygène lourd.

Il est évident que tous ces problèmes demandent beaucoup de travail et que celui-ci présente un intérêt tant théorique que pratique.

On connaît depuis longtemps les déviations aux formules stoechiométriques caractéristiques seulement pour les composés hétéropolaires typiques. Dans les systèmes métalliques on a défini également les facteurs qui déterminent la composition des alliages.

Les rapports sont différents dans la plupart des composés non métalliques, pour lesquels il existe des écarts déterminés plus ou moins par la température, par exemple, pour les sulfures, les séléniures et les oxydes.

Dans le cas des semi-conducteurs et des substances phosphorescentes ou fluorescentes, ces conditions non stoechiométriques jouent un rôle très important du point de vue technique. Dans beaucoup de cas, cette influence a été justifiée de façon scientifique. La théorie de Weyl, c'est-à-dire « the maximum possible screening » d'un cation, constitue certainement un progrès important pour l'explication de ces faits.

M'étendre sur ce sujet sortirait du cadre de cet exposé. Je m'attacherai plutôt à attirer l'attention sur quelques résultats obtenus dans notre Institut, résultats qui peuvent comme d'autres ouvrir un nouveau champ de travail.

On a démontré, en particulier, que les substances ou les couches superficielles pour lesquelles les conditions stoechiométriques ne sont pas respectées, possèdent des propriétés d'adsorption et de réactions particulières. L'étude approfondie de ces phénomènes est importante pour les processus catalytiques, en particulier. *S. Berger* s'occupe de ces recherches. Ce domaine est toutefois extrêmement vaste; il comprend également l'étude de l'influence des états cristallographiques transitoires. Les vues de Weyl, de même qu'elles précisent les particularités de l'état solide, éclaircissent quelque peu les phénomènes catalytiques, y compris la question importante de la recristallisation des catalyseurs.

Il y a encore d'autres problèmes importants en catalyse qui devraient être étudiés. Ils se rapportent, entre autres, à l'échange électronique entre le catalyseur et le substrat (*Schwab*, *Suhrmann*, *Weyl*) et à la détermination de la phase véritable du catalyseur, à savoir, par exemple, s'il s'agit du métal pur ou d'un oxyde ou d'un carbure formé.

Nous dirons encore quelques mots au sujet de l'extension des notions de magnéto-, électro-, photo- et phonochimie. Les études poursuivies sur les phénomènes de transport à l'aide d'atomes, de groupes d'atomes, et surtout d'électrons, sont communes à ces notions et aux phénomènes envisagés précédemment. Il apparaît que, dans tous les systèmes de substances ferromagnétiques et de substrats très variés étudiés, l'état paramagnétique possède toujours la plus grande activité. *H. Forestier* a non seulement confirmé ces vues, mais il les a développées en démontrant — comme cela a déjà été mentionné — que l'état de transition entre le ferro- et le paramagnétisme détermine, dans le cas des mélanges de poudres également, un maximum relatif de la capacité réactive, suivant le rapport des transformations de structures véritables.

Ces phénomènes « magnétocatalytiques » sont certainement liés aux conditions significatives, déjà mentionnées, de mobilité et d'échange. Ces relations demandent des études physiques approfondies. *E. Justi* a entrepris dernièrement des recherches de ce genre. Il a démontré que des champs magnétiques, placés extérieurement, exercent une influence semblable à celle déjà mentionnée, par exemple, dans le cas de la transformation de l'hydrogène ortho-para.

Les effets « électro-Curie » correspondants constituent également un domaine de recherche attirant. Jusqu'à présent, on a seulement constaté l'apparition des discontinuités dans les propriétés chimiques lors des changements spontanés des propriétés dipolaires. De telles recherches sont à rapprocher des travaux de *Timmermans*.

L'étude approfondie des phénomènes décrits à l'origine comme *photoadsorption*, contribuera certainement à résoudre la question très actuelle de la signification de l'échange électronique dans l'adsorption, et dans les processus chimiques, en général. Il est très important de noter, du point de vue scientifique, que toute substance, et pas seulement celles désignées comme photosubstances, présente des propriétés physico-chimiques différentes, suivant qu'on l'irradie avec des longueurs d'onde susceptibles ou non d'être absorbées ou encore, si elle reste à l'obscurité. Un vaste domaine de travail s'ouvre ici; il faut s'attendre aussi à des applications techniques dans de nombreux domaines.

Les effets chimiques des ultrasons sont un peu mieux connus et plus appliqués. Scientifiquement, il y a ici une certaine difficulté à séparer les effets purs des ultrasons de ceux provenant de l'échauffement local. Cette distinction n'a pas été faite de façon assez précise dans certains travaux. L'activité accrue des surfaces cristallines soumises à l'action des ultrasons suggère, entre autres, une étude détaillée du mécanisme de la formation des germes. C'est d'ailleurs un problème d'un intérêt général : il est étroitement lié à la formation des produits de réaction à la limite des phases.

Pour terminer, il faut souligner que nos connaissances actuelles des facteurs agissant sur l'activité physico-chimique des solides, ont permis de résoudre quelques problèmes sur l'utilisation plus rationnelle et plus économique des matières premières non métalliques et des déchets industriels. Il suffit de citer ici la production des revêtements de fours, des cermets et des produits céramiques en poudre dans le domaine des " alliages " non métalliques.

Nous mentionnerons encore que les éclaircissements apportés au problème de la formation des roches et des minerais ont permis de renouer le lien classique qui existe entre la chimie, la géologie et la minéralogie. On a aussi commencé un travail pour élaborer des méthodes pour la conservation des monuments historiques. Mais ici encore, nous n'en sommes qu'au début.

Discussion des rapports
de J. A. Hedvall et de R. Lindner

M. Barrer. — In self-diffusion in oxides (Table I) and in spinels (Table II) there seems to be a rough correlation between the terms D_o and E in the Arrhenius equation $D = D_o \exp - E/RT$. There are exceptions (e.g. self-diffusion in PbO, according to Table I, and of course some irregularities, but the general trend seems rather clear.

I have previously demonstrated and discussed in several papers a linear relation between $\text{Log}_e D_o$ and E/T for diffusion of gases in rubbers; and also between $\text{Log}_e \theta_o$ and E/T for viscous flow in a large variety of liquids ($\theta = \theta_o \exp - E/RT$) :

$$\text{Log}_e D_o = A + B(E/T)$$

$$\text{Log}_e \theta_o = C + D(E/T)$$

It might be of interest to try similar plots of $\text{Log}_e D_o$ and (E/T) for the systems studied by Dr Lindner. The appropriate value for T is the mean temperature in the range studied.

If one writes the Arrhenius equation in the form :

$$\text{Log}_e D = \text{Log}_e D_o - E/RT$$

then if the ranges in measured values of $\text{Log}_e D$ are always much less than the corresponding ranges in the values of E/RT over a variety of diffusion systems, then to a first approximation these values on $\text{Log}_e D$ can be regarded as constant in comparison with the much greater range in values of E/RT and so :

$$\text{constant} = \text{Log}_e D_o - E/RT$$

giving a function of the observed type. This situation might arise either because of limitations in the accessible range of measurements of D or because of an intrinsic property of these rate processes such that the terms E/RT will always contribute a much larger numerical range than will the values of $\text{Log}_e D$.

The nature of diffusion in crystals may of course be according to several distinct mechanisms whereas that in rubbers, and viscous flow in liquids, is due to the place exchange type of mechanism. There seems therefore less likelihood of uniform behaviour in diffusion in crystals, and so I find the trends shown by Dr Lindner to be very interesting. Evidently the entropy and energy of activation alter together for a very wide variety of rate processes.

M. Lindner. — If the material mentioned in this paper is arranged in the way proposed by Prof. Barrer a general trend of a nearly linear relation between log D_o and E/T becomes obvious (with inclusion of lead oxide). A parallelity between the two constants D_o and E can be demonstrated in different ways :

1. If a common value for the self-diffusion constants at the melting point is valid, the lines representing the temperature function of the self-diffusion constants are intersecting at the melting point and by extrapolation the largest slopes (activation energies) lead to the highest values for log D_o.

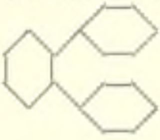
2. A survey of the form suggested by Prof. Barrer has been published for self-diffusion in metals as well as intermetallic diffusion by Dienes (*J. Appl. Phys.*, **21**, 1198, 1950) who stated a nearly linear relation between log $D_o/\nu\,\gamma^2$ as function of E/T_m (T_m : melting temperature). Dienes assumed a sort of a local melting as an elementary activation step for diffusion and identified E/T_m with the activation entropy.

3. The relation between D_o and the entropy of activation has been further developed by Zener (*J. Appl. Phys.*, **22**, 322, 1951), who derived a direct proportionality between the logarithms of D_o and the entropy of activations. The practical consequence of this treatment is that low values of D_o indicate short circuiting paths for diffusion as e.g. grain boundaries, which on the other hand are known to be connected with comparatively low activation energies.

4. Similar relations between log D_o and E have been derived by LeClaire (*Acta Metallurgica*, **1**, 438, 1953).

M. Ubbelohde. — In at least one recent group of studies we have been able to correlate changes of the probality term and the energy term for migration processes, and to interpret this correlation on a structural basis. I refer to the viscosities of melts of various terphenyls measured as a function of temperature, and represented in terms of the entropy of activation $S_\eta^{\pm}$ and the energy of activation $E_\eta^{\pm}$ by means of the absolute reaction rate expression for viscosity $\eta = \frac{hN}{V} \exp(-S_\eta^{\pm}/R) \exp(E_\eta^{\pm}/RT)$, where V is the molar volume.

In these polyphenyls, the force fields between molecules are closely similar in all cases but the degree of interlocking of molecules in the melts is much greater for a molecule such as o-terphenyl



than for a molecule such as *p*-terphenyl 

As a result, *o*-terphenyl molecules require a much greater activation energy (7.9 K cal/mole compared with 3.8 K cal/mole to move in the liquid). This higher activation energy is associated with a larger probability factor. For *o*-terphenyl the entropy of activation is + 5.7 e.u. as compared with — 4.6. e.u. for *p*-terphenyl. One can think of it in this way : to permit *o*-terphenyl to move at all, a larger hole must be produced than in *p*-terphenyl. But this hole can be used in a much less selective way so that the entropy of activation involves an increase of probability over the ground state, instead of a decrease as for *p*-terphenyl.

This interpretation can be confirmed in a rather elegant way from studies of the same flow parameters near the melting points. *p*-Terphenyl shows no appreciable change, but the activation energy to " unlock " neighbouring *o*-terphenyl molecules is dependent in a sensitive way upon the volume. As the volume contracts the activation energy rises, and near the melting point it has more than doubled : $-E_\eta \sim 16$ K cal (mole) .

Presumably a larger hole has to be produced in the melt for flow to become feasible. And the path for flow by means of this larger hole is even less selective than before. The entropy of activation rises to the large positive value of 29 e.u.

A similar interpretation can perhaps be generalised. In structures with similar force fields, large activation energies are associated with less selective reaction paths than small activation energies. Consequently entropies of activation tend to be algebraically more positive, the larger the activation energy, (cf. J. N. Andrews and A. R. Ubbelohde, *Proc. Roy. Soc.*, **228** A, 1955, 435).

M. Bénard. — Les observations du Dr Lindner concernant la comparaison des énergies d'activation de diffusion des deux sortes de cations dans les ferrites, sont extrêmement intéressantes. Elles méritent d'être confrontées avec les résultats des études de l'intensité des spectres de rayon X, qui révèlent dans ces phases une localisation des cations à la température ordinaire. Si nous admettons avec le Dr Lindner que la répartition des cations sur les différentes positions est faite au hasard aux températures élevées, il nous faut conclure que le degré d'ordre observé à basse température doit être une fonction de la vitesse de refroidissement, ce qui ne semble pas avoir été observé. Il paraît en effet difficile d'admettre qu'un ordonnancement des cations puisse se produire d'une manière instantanée. Je voudrais demander au Dr Lindner s'il considère que l'identité des énergies d'activation de diffusion des deux types de cations implique nécessairement l'équivalence des positions au point de vue énergie. Ne serait-il pas possible en effet de concilier l'égalité des énergies d'activation de diffusion des ions avec des énergies différentes pour la localisation des deux types d'ions sur les deux types de position : tétraédrique et octaédrique.

M. Lindner. — En effet, il a été observé et rapporté dans plusieurs conférences du " Colloque international de Ferromagnétisme et d'Antiferromagnétisme " à Grenoble en 1950, que la distribution des ions dans les ferrites à structure de spinelles est une fonction de la vitesse de refroidissement. Par exemple : Pauthenet et Bochirol (*J. Phys. Radium*, **11**, 249, 1951) signalent que l'aimantation des ferrites de cuivre et de magnésium est une fonction de la température de la trempe. Au moyen des rayons X, Bertaut (*J. Phys. Radium*, **12**, 252, 1952) a montré, par exemple dans le ferrite de zinc, qu'une inversion partielle peut être observées après un échauffement à 1000 °C.

Le mécanisme de l'autodiffusion des cations dans les spinelles est, malheureusement, insuffisament connu. Usuellement l'énergie d'activation expérimentale est la somme de l'énergie de formation des lacunes (ou ions interstitiels) et de l'énergie de migration. La structure des spinelles permet de prévoir un grand nombre de lacunes, ce qui a été, d'ailleurs, vérifié grâce aux mesures effectuées par la méthode des rayons X aux basses températures, celles-ci ne sont peut-être pas décisives aux hautes températures; On peut déduire de ces expériences que l'on doit probablement tenir compte d'une énergie de formation des lacunes effectives, et ainsi que l'énergie d'activation expérimentale n'est pas identique à l'énergie d'activation de la migration (c'est-à-dire la hauteur de la barrière d'énergie à franchir pour passer d'une position d'équilibre à l'autre). C'est déjà une des raisons pour lesquelles on ne peut pas répondre à la question du Prof. Bénard au sujet de la relation entre l'énergie d'activation expérimentale et l'énergie nécessaire pour l'échange des cations A et B entre les positions à coordination tétrahédrique et octahédrique. Nous espérons obtenir d'autres évidences expérimentales par des expériences sur des spinelles non stoechiométriques.

M. De Keyser. — Je désire donner un bref aperçu d'expériences récentes, effectuées en collaboration avec M. René Cyprès et qui ont fait l'objet d'une communication au Symposium de la Chimie des Solides à Madrid (avril 1956).

Ces expériences concernent les réactions entre SiO_2/CaO et Al_2O_3/CaO.

Dans l'étude de ces réactions par la mise en contact de pastilles, deux difficultés expérimentales doivent être surmontées :

1° Lors du chauffage, le retrait des deux oxydes en présence n'est pas le même. Il ne se produit pas non plus aux mêmes températures. Il s'ensuit que les briquettes qui sont en contact au début de l'expérience, se séparent très rapidement et que la réaction s'arrête faute d'un contact suffisant.

Cette difficulté a pu être surmontée en utilisant, comme le montre la figure 1, un creuset de marbre très pur ($CaCo_3$) dans lequel on comprime suivant le cas, de la poudre d'$Al(OH)_3$ ou de la silice amorphe. Le retrait de CaO étant supérieur à celui des autres oxydes, le creuset, au cours du chauffage, se contracte sur la pastille intérieure. De plus, un piston en marbre, lesté, maintient un bon contact entre la pastille et le fond du creuset.

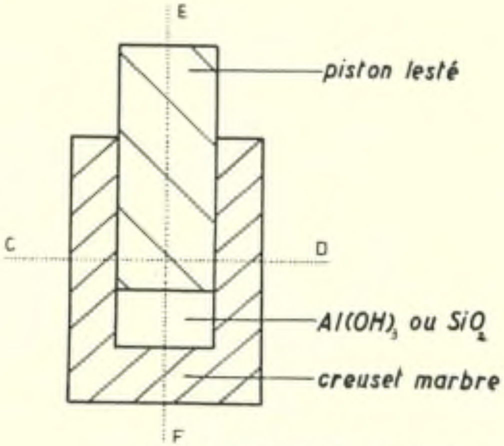


FIG.1 CREUSET DE MARBRE

2° Les pastilles qui ont été soumises aux températures de réaction, sont extrêmement friables. Il est impossible de les manipuler sans les briser et même sans qu'elles ne tombent en poussière. Aucune méthode d'investigation de la surface réagissante n'est applicable sans un traitement préalable de la briquette permettant de figer

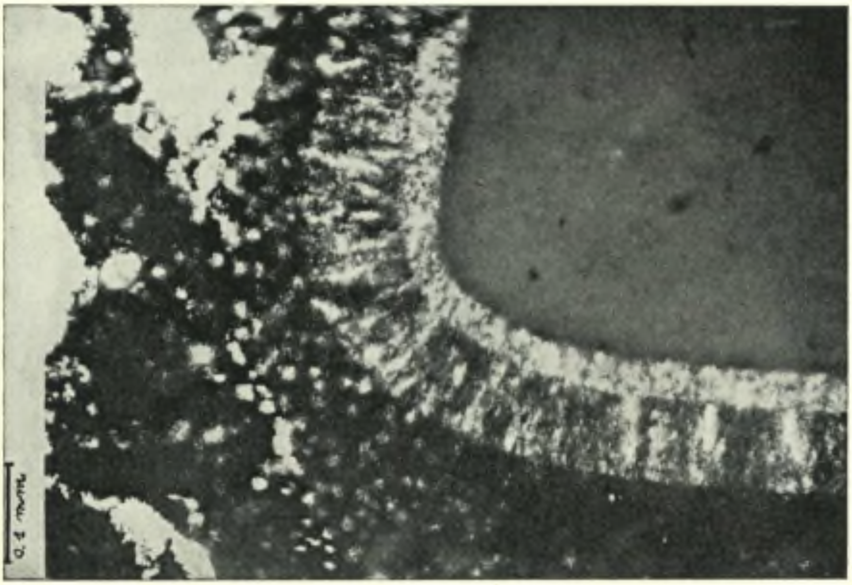


Fig. 2

l'échantillon dans son ensemble après la réaction. Ce résultat peut être obtenu en imprégnant les matières solides de méthyl métacrylate liquide qui est ensuite polymérisé.

Résultats des examens.

1° *Réactions* Al_2O_3/CaO.

La micrographie de la figure 2 montre l'aspect en lumière polarisée d'une lame mince taillée suivant le plan EF (fig. 1) pour un échantillon traité à 1250 °C durant 48 heures.

Pour l'examen de cette lame mince, il faut remarquer que CaO, A_3C_4 et AC_3 sont isotropes et que la biréfringence de l'Al_2O_3 est faible (+). Seul AC orthorhombique présente une biréfringence appréciable.

Le liséré clair situé du côté de l'Al_2O_3 est constitué de AC. Entre cette couche et le CaO, se trouve une zone foncée, dans laquelle on remarque certaines bandes claires.

Les examens par rayons X obtenus en faisant des coupes suivant le plan CD et par usure dans la direction de la flèche (voir fig. 1) confirment que c'est bien de l'AC qui est en contact avec de l'alumine et que la deuxième couche est constituée essentiellement de A_3C_5.

Une étude par la méthode des traceurs radioactifs a d'ailleurs confirmé ces observations.

L'épaisseur de l'ensemble des couches réactionnelles atteint environ 0,2 mm.

La localisation de ces couches a été faite par l'utilisation d'un repère en platine suivant le procédé de Jagitsh. La position de ce repère montre la pénétration de Ca dans Al_2O_3.

(+) Suivant les notions habituelles

AC représente, $Al_2O_3.CaO$

A_3C_5 représente $3(Al_2O_3).5(CaO)$

AC_3 représente $Al_2O_3.3(CaO)$

Sc représente $SiO_2.CaO$

SC_2 représente $SiO_2.2\,CaO$

2° *Réactions* SiO_2/CaO.

La figure 3 reproduit une micrographie (lumière polarisée) d'une lame mince, préparée de la même manière que pour les réactions Al_2O_3/CaO.

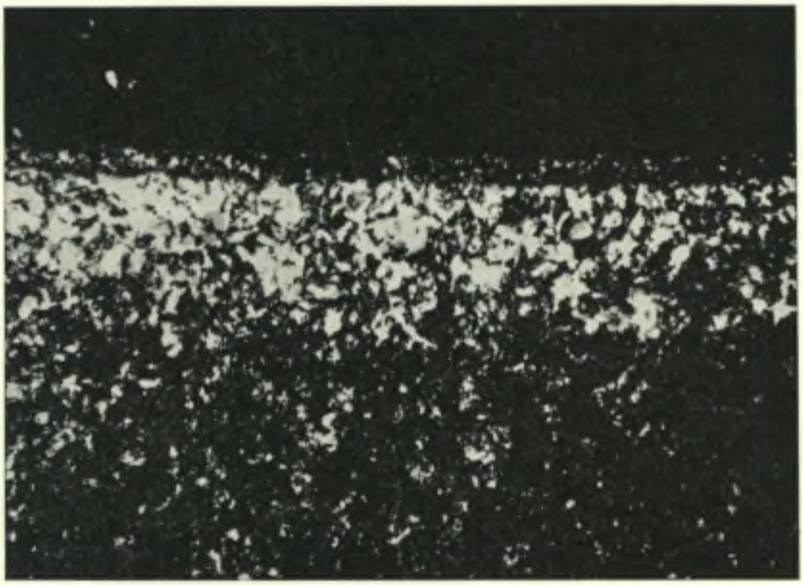


Fig. 3

L'échantillon SiO_2/CaO a été porté à 1250 °C pendant 212 heures. Il a été nécessaire de chauffer très longtemps parce que la vitesse de pénétration de Ca dans CiO_2 est très faible.

Le peu d'épaisseur de la couche réactionnelle rend la détermination exacte de la composition de celle-ci fort difficile. Toutefois, les examens par rayons X y montrent la présence de C_2S, CS et de tridymite.

La tridymite croit au fur et à mesure que l'on pénètre, le α CS persiste. Il faut toutefois remarquer que l'échantillon est fissuré et qu'il est possible que le α CS se forme sur les bords des fissures.

De toute manière, lorsque l'on se trouve à profondeur suffisante (environ 0,86 mm) le α CS disparaît presque complètement, la tridymite persiste tout en diminuant, et il y a apparition graduelle de cristobalite.

Le fait qu'à 1250 °C (température de cuisson de l'échantillon) il n'y a aucune phase liquide CaO-SiO_2, montre nettement que la tridymite s'est formée directement en phase solide, grâce à l'intervention du Ca par un mécanisme du type qui a été proposé par Weyl.

Au sortir de la phase contenant de la tridymite, on constate la présence de cristobalite qui s'est formée directement à partir de SiO_2 amorphe, ce qui est conforme aux observations faites antérieurement par de nombreux chercheurs et par nous-mêmes.

En conclusion de cet examen, on peut dire que la couche réactionnelle située entre CaO et SiO_2 a probablement été obtenue par migration moléculaire de CaO.

La faible vitesse de migration peut expliquer la formation de C_2S.

On sait en effet que dès qu'il y a du Ca en suffisance, ce composé est formé de préférence au CS, ce qui d'ailleurs peut s'expliquer par la théorie de Weyl, les tétraèdres SiO_4 étant mieux couverts par le Ca dans C_2S que dans CS.

Nos examens radiocristallographiques ayant montré qu'au-delà de cette couche, il n'y a que des traces de silicate, mais qu'il y a formation de tridymite, on peut supposer que dans cette région, il y a diffusion de Ca^{++} en faible quantité. Ce Ca^{++} facilite la transformation de cristobalite en tridymite.

M. Collongues. — Nos expériences montrent que la variation de concentration des lacunes à l'intérieur d'une couche de protoxyde de fer formée à la surface du métal n'est pas linéaire. En effet, nous avons étudié la variation de composition en mesurant par la méthode de rayons X en retour le paramètre cristallin des couches successives de protoxyde (1,2). Rappelons que les paramètres des phases protoxyde de fer de différentes compositions varient linéairement depuis $a = 4{,}276$ Å ($Fe_{0,9}O_1$) jusqu'à $a = 4{,}304$ Å (Fe_1O_1).

Nos pellicules étaient préparées par oxydation de fer très pur dans différents mélanges H_2-H_2O. Les résultats sont les suivants :

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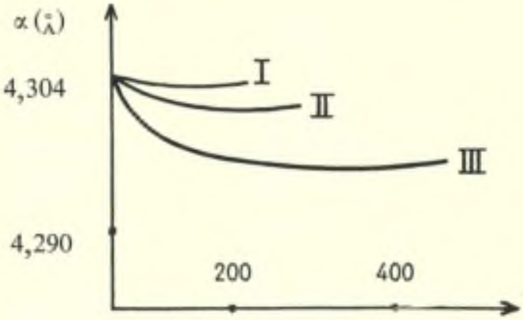
(1) R. Collongues : *Thèse Paris* (1954).

(2) R. Collongues et R. Lifferlen : *Coll. Intern. Réact. Superficielles Paris* (1956).



distance à l'interface en microns

courbe (I) $\frac{pH_2O}{pH_2} = 0{,}7$; phase FeO en équilibre $a = 4{,}303$ Å

courbe (II) $\frac{pH_2O}{pH_2} = 1{,}8$; phase "FeO" en équilibre $a = 4{,}280$ Å

courbe (III) $\frac{pH_2O}{pH_2} = 6{,}4$; phase en équilibre Fe_3O_4.

On constate :

1° que la variation de composition à l'intérieur de la couche d'oxyde n'est pas linéaire. La composition reste sensiblement constante dans la plus grande partie de l'épaisseur de la pellicule et varie très rapidement au voisinage de l'interface métal-oxyde.

2° que la composition de la couche externe à l'interface oxyde-atmosphère ne correspond pas à la composition de la phase " FeO " en équilibre avec le mélange H_2-H_2O utilisé.

Ces conclusions sont valables quelle que soit l'épaisseur de la pellicule à condition qu'une adhérence parfaite soit réalisée à l'interface métal-oxyde.

M. Chaudron. — La diffusion règle généralement la réaction dans l'état solide. Toutefois, il ne faut pas oublier que dans certains cas, la vitesse de diffusion peut devenir très grande et cet obstacle à la réaction devient alors négligeable.

Dans la chimie des phosphates de calcium, Montel, du Laboratoire de Vitry, a mis récemment en évidence des réactions dans l'état solide où la diffusion devient un facteur secondaire (*). Certaines

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(*) G. Montel : Influence de petites quantités de sodium sur la cinétique d'une réaction de synthèse de la fluorapatite. Communication au Troisième Colloque International sur les Réactions dans l'Etat Solide, Madrid, avril 1956 (à paraître).

structures, les apatites par exemple, sont probablement favorables à une diffusion rapide.

Des additions de sels de sodium, dans les expériences de Montel, favorisent également la diffusion. Ce rôle des impuretés peut être expliqué par des mécanismes de Weyl qui ont fait l'objet des précédents rapports.

M. Lindner. — Dans quelques cas, l'accélération de la diffusion par des impuretés peut être expliquée par la théorie de Wagner-Schottky et Frenkel. Dans le cas des ions interstitiels, la concentration peut être augmentée par des impuretés contribuées par des ions de valence inférieure.

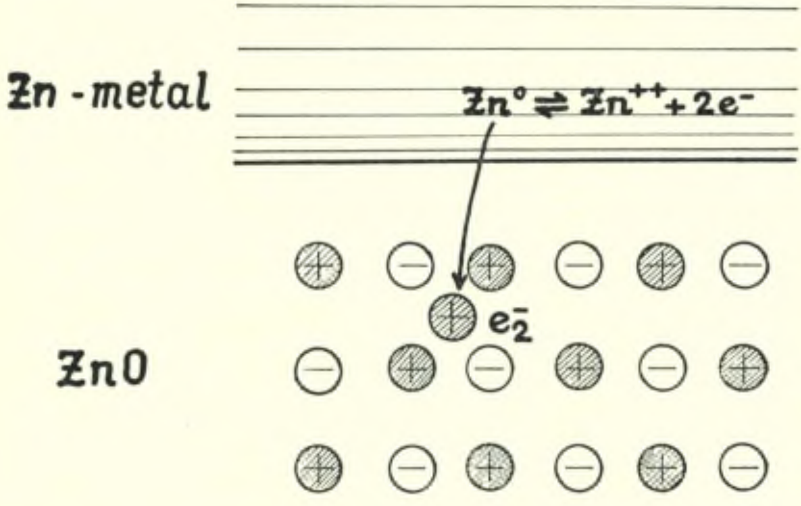
M. Ubbelohde. — It is comparatively easy to understand how certain ionic impurities can increase migration velocities in ionic crystals. For example, when Cd^{++} is dissolved in NaCl, a proportion of the holes practically equal to the concentration of Cd^{++} is generated in order to preserve local electrostatic neutrality. This increased concentration of holes is in mass-action equilibrium with the NaCl lattice also. The increased proportion of holes leads to increased migration probabilities. But how does the addition of impurities decrease the proportion of holes so as to decrease migration velocities?

M. Lindner. — The case treated, i.e. zinc oxide with additions of alumina or gallium oxide does not refer to vacancy disorder but to the occurrence of interstitial zinc ions as responsible for ionic migration and reaction in the solid state (though the alternative possibility of oxygen vacancies, preferred by Prof. Weyl, can be treated in an analogous way). By introducing e.g. alumina into the zinc oxide lattice, two zinc ions are substituted by two aluminium ions. A raise in the positive charge, is, however, prevented by interaction with the three oxygen ions introduced together with the aluminium ions, which may react not only with the two zinc ions formerly belonging to the normal lattice but also with one interstitial zinc ion of higher mobility. With this decrease in mobile carriers the overall diffusion is likewise decreased.

Obviously there is a fundamental difference between the effect of impurities on lattices with cation vacanties on one hand and anion vacancies or interstitial cations on the other. In fact this method of incorporating impurities can be used to determine the character of lattice disorder.

M. Weyl. — It is very difficult to compair the system NaCl + Cd^{++} excess with the system ZnO — Ga^{+++} because NaCl resembles closely an ideal crystal whereas ZnO at temperatures above 600 °C is defective, as can be seen from the fluorescence. Now we assume that such an oxide contains O^{2-} vacancies and as a result we predicted that Ga_2O_3 or Al_2O_3 decreases this rate of sintering a conclusion which could be verified experimentally (Göteborg Proceedings).

The description by Lindner of the interstitial zinc atom-placing, the Zn^{++} between two Zn^{++} ions and the two electrons between the two O^{2-} ions, violates the principle of electroneutrality in this smallest possible volume. The high coulomb repulsion between Zn^{++} — Zn^{++} ions in close proximity or this electron between two O^{2-} ion would raise the energy of such a system to a very high level. I prefer to describe the interstitial Zn atom as a zincous ion, Zn_2^{++} analogous to the mercurous ions Hg_2^{++} and give it the quanticule formula $Zn^{++}(e_2^-)Zn^{++}$.



M. Lindner. — There has been much work and discussion concerning the disorder model of zinc oxide. Many characteristics can be explained by either the occurrence of interstitial zinc ions or oxygen vacancies and a final decision between the two possibilities has not been reached yet. Lately, however, there has been some experimental evidence in favor of the assumption of interstitial zinc ions.

1. Thus Gray (*J. Am. Ceram. Soc.*, **37**, 534, 1954) found a correlation between the colour of preheated zinc oxide crystals and the lattice constant of the oxide, which is larger in the coloured crystals as compared with white zinc oxide. As the colour is assumed to be in some way related to excess zinc, accomodation of this excess in form of interstitial zinc ions looks probable. It must be admitted that such measurements ought to be combined with conventional density measurements and quantitative data for the zinc excess.

2. The lattice constant of cadmium oxide, which oxide is usually supposed to behave very similar to zinc oxide, has been measured — as Prof. Bénard kindly reminded us during the conference — as function of vacua-preheating temperature by Faivre and Michel (*Comptes Rendus*, **207**, 159, 1938), who observe a significant enhancement of the lattice constant with increasing preheating temperature (and subsequent quenching), whereas the constant is not changed if the sample is slowly cooled or preheated in oxygen atmosphere.

3. The self-diffusion of zinc oxidation layers is greatly enhanced as compared with the values in zinc oxide, as mentioned in our paper. Besides, approximate agreement between this rate and the oxidation rate of zinc metal has been obtained. This supports the view that the diffusion of interstitial zinc ions determinated the oxidation rate. The possibilities of a diffusion of oxygen vacancies cannot be completely excluded, but has in no way been experimentally proved.

Summing up the evidence it can be stated that the occurrence of monovalent interstitial zinc ions in zinc oxide looks at the present to be better established than the occurence of oxygen vacancies.

M. Bénard. — Il me paraît intéressant d'attirer l'attention sur un aspect des relations qui existent entre les réactions dans l'état solide et la diffusion, dont il ne semble pas avoir été question jusqu'à maintenant : je pense à l'influence du mode de liaison sur l'énergie d'activation de diffusion. En effet, l'énergie requise pour transporter un atome d'une position d'équilibre du réseau cristallin à une position d'équilibre voisine du même réseau ou d'un réseau différent dépend essentiellement de la nature des liaisons que cet atome échangeait initialement avec ses voisins immédiats. Il semble entre autres que l'existence d'une liaison de covalence forte oppose un obstacle considérable à la diffusion, comme le montre la lenteur de la diffusion dans les réseaux covalents tridimensionnels du type diamant. On pourrait dans ces conditions se demander si les études d'autodiffusion ne constituent pas un moyen commode de comparer les types de liaison dans une série homologue de composés solides. En outre cette méthode d'approche rend compte des phénomènes d'anisotropie de diffusion, dont l'importance est particulièrement marquée dans les réseaux lamellaires, mais qui apparait de façon générale dans tous les solides dans lesquels coexistent des types de liaison différents, suivant une symétrie non cubique.

M. Ubbelohde. — Would Dr Powell like to comment on the expansion of clathrate lattices as various molecules are included therein? We have heard about the importance of this expansion in interstitial compounds of the transitional metals, where there is electronic interaction between the interstitial atoms and the host lattice, and where the concept of expansion pressure has led to some interesting considerations.

In clathrates the expansion pressure is presumably much smaller, since the interactions are mainly of the van der Waals type. But the lattice forces are also smaller and it would be interesting to have information about the magnitude of the lattice expansions.

M. Powell. — The spaces in clathrates vary in size and shape. At least two kinds of behaviour may be distinguished.

In the quinol clathrates the cagework is formed by strong hydrogen bonding of the cage components. If the included molecule is small the cage retains the dimensions of the β-quinol structure with all cavities vacant. Introduction of a large non-spherical molecule such as sulphur dioxide or methyl cyanide has little effect on the lengths of the links-covalencies and hydrogen bonds — which connect the various atoms of the cage. To accommodate these different molecular shapes, the cage alters in a manner analogous to the opening of a piece of trellis work, one of the unit cell dimensions decreasing, the other increasing, while the connected pieces do not alter their lengths.

In a set of tri-*o*-thymotide clathrates, formed for example by the first few members of the *n*-alcohol series, the unit cell dimensions are the same for the empty structure and the first two alcohols. In these there must be still some free space. Further increase in size of the included molecule results in expansion of both lattice dimensions. The molecules forming the cage structure are joined by van der Waals forces only and, within limits, simply move further apart to accommodate the larger molecules.

Influence des gaz adsorbés sur la réactivité et la stabilité du réseau cristallin superficiel

par **H. FORESTIER**

avec la collaboration de A. Clauss

On sait que la réactivité d'un corps solide se manifeste presque toujours par l'intermédiaire de sa surface. La connaissance de celle-ci constitue donc le point fondamental de ce problème. Or, il est bien connu que la structure superficielle d'un solide est nettement différente de sa structure interne, cette différence pouvant d'ailleurs être accentuée par des traitements appropriés. Malheureusement, la connaissance structurale d'un réseau cristallin superficiel sur une épaisseur de quelques dizaines d'Ångström, voire de quelques Ångström, offre de grosses difficultés; par ailleurs, la connaissance de lois gouvernant la réactivité des solides devra tenir compte, essentiellement, de la structure de ces couches, couches dont l'importance est d'autant plus grande que les réactions entre solides s'effectuent généralement, dans la pratique, entre grains fins. A l'heure actuelle, nous avons besoin, avant tout, d'un gros matériel expérimental pour être en mesure de poser convenablement les problèmes concernant cette réactivité.

Tout ce qui peut nous apporter des connaissances nouvelles sur le comportement de cette couche superficielle est donc hautement désirable.

Or, nous avions constaté, il y a une douzaine d'années environ, et non sans surprise, une sensibilité notable de cette couche superficielle à l'action des gaz adsorbés, au cours de réactions entre solides (1). Ce phénomène méritait donc d'être étudié de plus près, et il est devenu le but de nos recherches dans ce domaine depuis un certain nombre d'années.

Ce mémoire résume l'ensemble des travaux effectués par mes collaborateurs, dans l'ordre chronologique, Haasser, Kiehl, Maurer, Stahl, Clauss, Kleine.

Par ailleurs, Hedvall et son école avaient également noté une influence de l'atmosphère sur la réactivité, *à posteriori*, de quelques oxydes (²).

Nous avons donc abordé systématiquement l'étude de l'influence des gaz adsorbés sur les réactions dans l'état solide d'abord, puis, d'une manière plus générale, les problèmes liés à la stabilité du réseau cristallin superficiel. Mais, étant donné la complexité du problème de la surface, il importe essentiellement de bien séparer les facteurs, dans la mesure du possible, et c'est pourquoi, nous avons tenu à limiter tout d'abord ces recherches à certains domaines et à nous imposer certaines conditions ou restrictions : par exemple l'étude de la réactivité des solides au-dessous des températures de diffusion, afin d'éviter que les phénomènes de diffusion ne se superposent à la réaction et commandent pour une large part sa cinétique (*); introduction des gaz rares parmi les autres gaz utilisés, pour être bien certains que nous échappons au phénomène de chimisorption (voir à ce propos les travaux de Hüttig et de Suhrmann) et que nous restons dans le domaine de l'adsorption physique (forces de Van der Waals), et par contre élimination systématique des gaz tels que SO_2, HCl, NH_3, etc. pouvant donner lieu à une réaction chimique; utilisation de métaux nobles dans nos essais mécaniques afin d'éviter toute couche protectrice d'oxyde au cours des différentes opérations.

Comme nous le verrons, l'ensemble de ces précautions nous a permis de dégager une loi générale déduite de l'expérience, loi qui exprime, d'une manière approchée, les variations de stabilité du réseau cristallin superficiel du solide en fonction de la température de liquéfaction des gaz adsorbés, et qui met ainsi en évidence la nécessité de tenir compte de l'atmosphère gazeuse au cours des modifications que peut subir le réseau cristallin superficiel.

⁂

Nous rappellerons d'abord brièvement nos premières études sur la question et nous développerons davantage les résultats les plus récents.

(*) On sait que les températures de début de réaction peuvent être très inférieures aux températures de diffusion perceptibles. Hedvall avait mis ce fait en évidence dès le début de ses travaux; j'ai montré par la suite (H. Forestier et J. Longuet) que la réaction entre Fe^2O^3 et NiO commençait vers 250 °C.

Dans un domaine de températures où la diffusion est faible ou négligeable, nous avions montré que la vitesse de réaction entre corps solides dépendait de la nature et de la quantité des gaz adsorbés par la surface du réseau cristallin, en particulier au cours de l'étude des réactions de formation de ferrites ferromagnétiques à partir de Fe_2O_3 et de monoxydes métalliques, et de la réduction de NiO par W et Cr (³). Nous avons été conduits à énoncer la règle suivante :

« La vitesse de réaction est une fonction croissante de la température de liquéfaction du gaz utilisé, donc du pourcentage de gaz adsorbé (fig. 1, durée de recuit : 15 min.). »

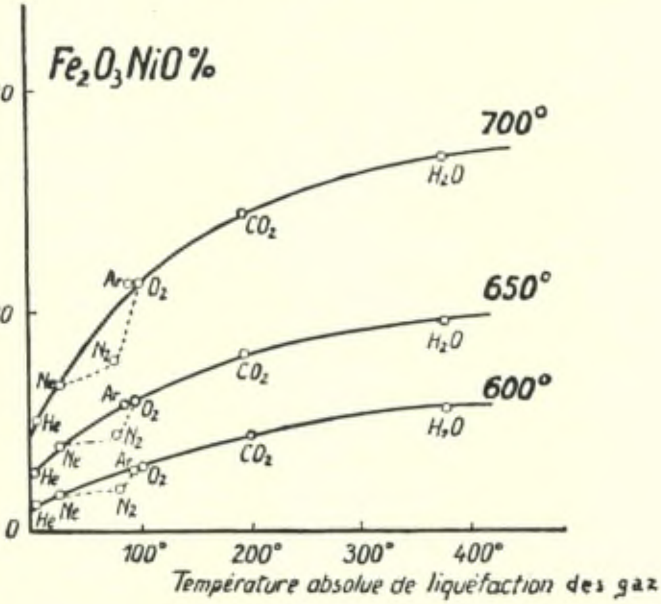


Fig. 1

La faible vitesse de réaction constatée dans le vide nous a incités à étudier l'influence de la pression des gaz. A cet effet, nous avons effectué, avec le même mélange d'oxydes que précédemment, une série de recuits dans la vapeur d'eau sous des pressions variant entre 760 mm Hg et 6.10^{-6} mm Hg (⁴). Les résultats sont résumés dans la fig. 2; ils nous conduisent à une seconde règle :

« Pour un même gaz, la vitesse de réaction paraît être une fonction décroissante approximativement linéaire du logarithme de la

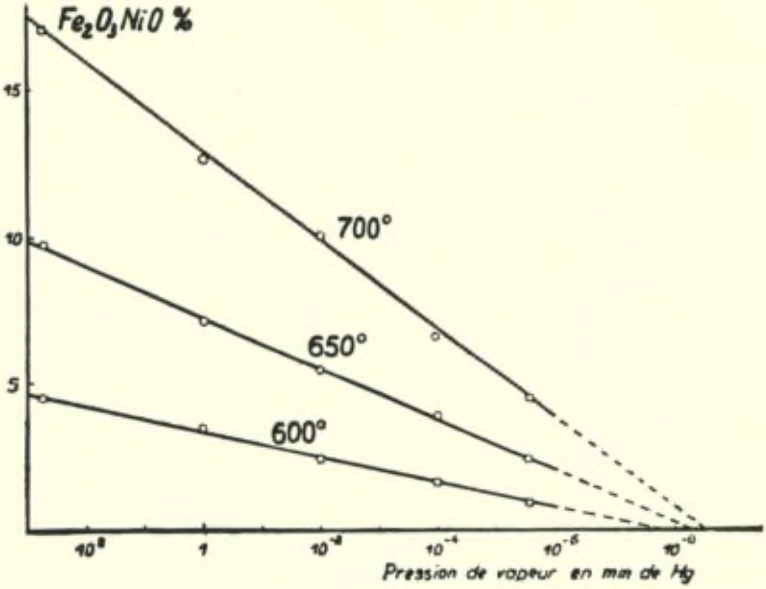


Fig. 2

pression, cette vitesse tendant vers zéro lorsque la pression tend vers zéro. »

Il n'y aurait donc pas de réaction possible entre solides, dans le vide, au-dessous des zones de températures de diffusion. La faible quantité de ferrite qui se forme dans le vide le plus élevé (6.10^{-6} mm Hg) peut être imputée à deux facteurs :

- réaction due à une petite quantité de gaz encore adsorbé à la température du recuit;
- réaction provenant d'une faible diffusion.

Cette seconde règle n'est, toutefois, vérifiée que pour des pressions inférieures à une atmosphère environ. Des mesures faites récemment à des pressions allant jusqu'à 100 atmosphères dans l'argon (recuits de 30 min. à 350 °C), montrent que les courbes logarithmiques s'incurvent aux environs d'une atmosphère et que l'on atteint pratiquement un palier à partir duquel la vitesse de réaction *ne dépend plus de la pression* (fig. 3). Ce résultat est en accord avec l'hypothèse d'une adsorption physique.

Il n'est pas exclu cependant qu'une influence de la pression puisse être mise en évidence pour des valeurs de l'ordre de 500 atmosphères, ou supérieures, ordre de grandeur admis pour la pression

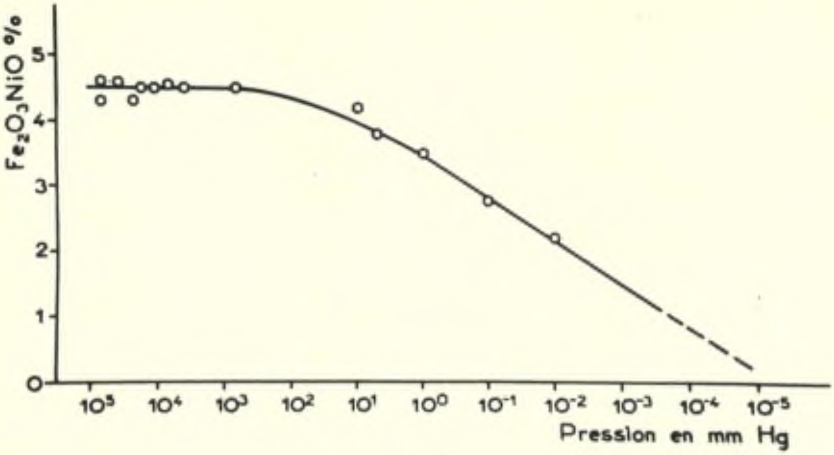


Fig. 3

d'un gaz adsorbé à la surface d'un solide, plongé dans ce gaz à la pression atmosphérique (5).

Par ailleurs, la similitude d'allure des phénomènes, observés aussi bien avec les gaz rares qu'avec des gaz comme l'oxygène ou la vapeur d'eau, montre que le type d'adsorption en cause est bien de nature strictement physique (forces de Van der Waals).

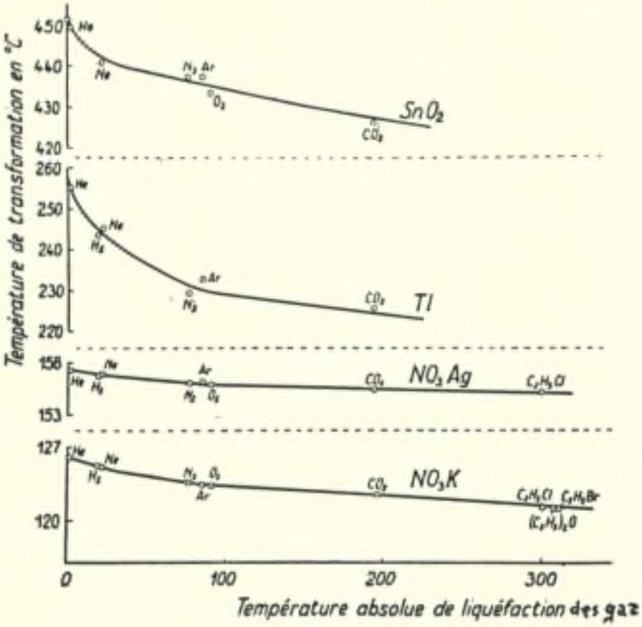


Fig. 4

Nous avons été conduits à admettre, à la suite de ces résultats, un relâchement des liaisons entre atomes à la surface du réseau cristallin, sous l'influence des gaz adsorbés. Si notre hypothèse est exacte, cette diminution de stabilité doit se traduire par une modification des températures auxquelles le réseau subit une transformation de structure (polymorphisme) ou une destruction complète du réseau cristallin (fusion) au voisinage de la surface.

Nous avons donc entrepris, ultérieurement, une étude de l'influence des gaz adsorbés sur les températures de transformation (6) ou de fusion (7) d'une série de corps assez variés. Les résultats obtenus (fig. 4 et 5) peuvent se résumer ainsi :

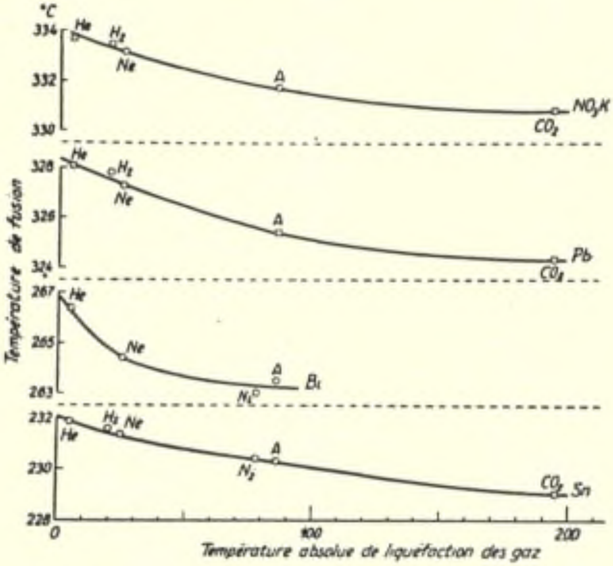


Fig. 5

« Pour un même corps, l'abaissement de la température de transformation, ou de fusion, est une fonction décroissante de la température de liquéfaction du gaz en présence, donc du pourcentage de gaz adsorbé. »

Il est intéressant de noter également que l'amplitude de ces phénomènes varie, d'une manière générale, en sens inverse de la chaleur de transformation ou de fusion : *l'effet constaté est d'autant plus important que la différence du niveau énergétique entre les deux* *formes cristallines est plus faible* (fig. 6), ce qui paraît logique. En effet, lorsque la différence des niveaux énergétiques entre les deux formes est très grande, elle masque l'effet dû aux gaz adsorbés, qui provoquent une variation du niveau énergétique très faible.

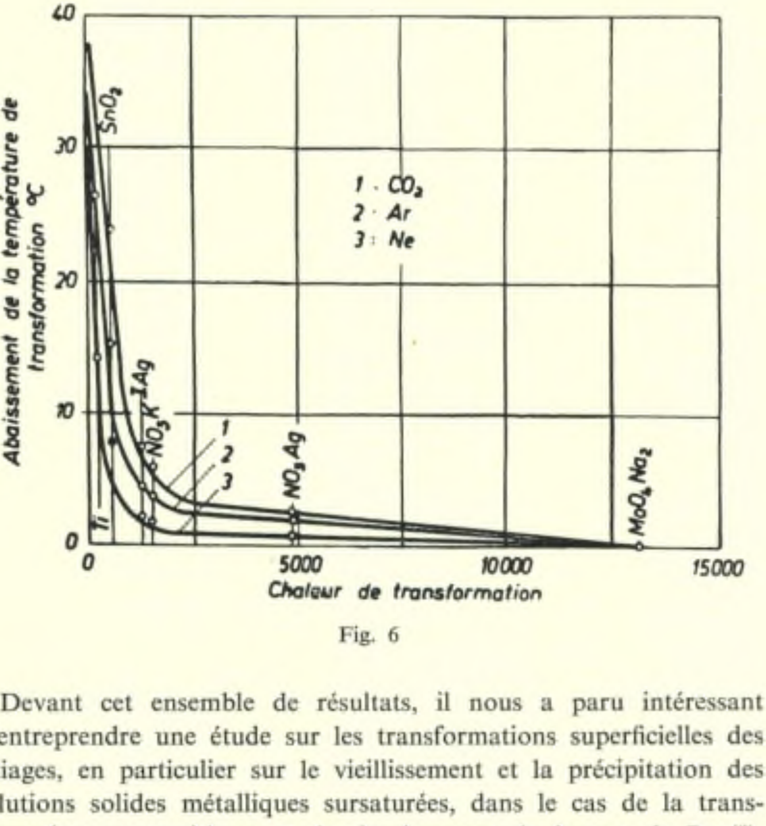


Fig. 6

Devant cet ensemble de résultats, il nous a paru intéressant d'entreprendre une étude sur les transformations superficielles des alliages, en particulier sur le vieillissement et la précipitation des solutions solides métalliques sursaturées, dans le cas de la transformation martensitique, et du durcissement du bronze de Be (8).

La transformation de la martensite en perlite correspond, à la fois, à un changement de structure cristalline et à une précipitation.

Cette étude a été faite sur un acier à 0,8 % de carbone, obtenu à l'état martensitique par trempe à l'eau d'échantillons recuits à 950 °C, sous argon, pendant 30 min. La progression de la transformation martensitique a été suivie par différentes méthodes (examen micrographique des échantillons, variation de la microdureté superficielle au moyen du microduromètre Reichert et variation de la dureté Brinell).

La fig. 7 reproduit les courbes de microdureté, en fonction de la température de liquéfaction des gaz adsorbés, pour une profondeur d'empreinte de l'ordre de 2µ. L'examen de ces courbes, correspondant à différentes températures de revenu, conduit aux conclusions suivantes :

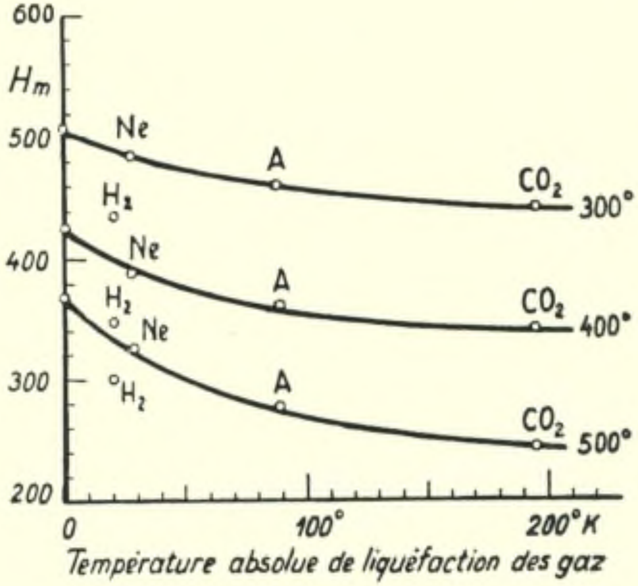


Fig. 7

1° L'allure générale des courbes est analogue aux précédentes. L'anomalie relative à l'hydrogène, qui ne se retrouve d'ailleurs pas dans les mesures de dureté à grande profondeur d'empreinte (Brinell), pourrait être due à un début de décarburation de la surface du métal, en présence de traces de vapeur d'eau provenant de la réduction d'oxydes à l'état d'impuretés dans le métal ;

2° La vitesse de transformation de la martensite varie suivant la nature du gaz adsorbé ;

3° A température et pression constantes, la vitesse de transformation est une fonction croissante, régulière, de la température de liquéfaction du gaz utilisé, donc du pourcentage de gaz adsorbé.

Dans le cas du bronze de beryllium, la transformation correspond uniquement à la cessation de la sursaturation de l'alliage ayant subi une trempe structurale.

Partant de la phase trempée α, en état de sursaturation, la naissance de la phase γ doit se manifester notamment par un durcissement des échantillons, que nous avons mesuré au microduromètre Reichert. D'autre part, la progression du phénomène a été suivie qualitativement par l'analyse aux rayons X.

La fig. 8 donne la température du début de précipitation correspondant au maximum de dureté constatée, en fonction de la température absolue de liquéfaction des gaz. De son examen on peut conclure que :

1° La température du maximum de dureté varie suivant la nature du gaz adsorbé;

2° A température et pression constantes, la vitesse de transformation est une fonction croissante, régulière, de la température de liquéfaction du gaz utilisé, donc du pourcentage de gaz adsorbé.

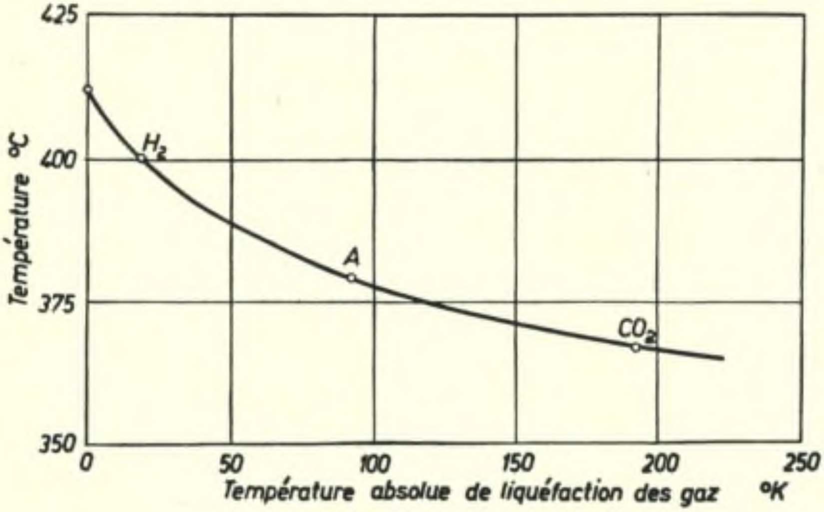


Fig. 8

Ces résultats peuvent être mis en parallèle avec les phénomènes constatés dans l'évolution de la structure martensitique et ceux antérieurement observés dans les transformations polymorphiques. L'effet observé, identique dans ces différents cas, semble bien relié à une variation de stabilité du réseau cristallin superficiel du solide sous l'influence des gaz adsorbés.

Continuant nos investigations dans ce domaine, nous avons abordé l'étude de l'influence des gaz adsorbés sur le phénomène de la recristallisation. Nous verrons successivement la recristallisation superficielle de l'état vitreux (9) et celle de métaux écrouis à froid (10).

L'étude de la recristallisation de l'état vitreux a porté sur les verres suivants :

1° Un verre sodocalcique (verre blanc ordinaire S.C. de St-Gobain);

2° Un verre à 54,5 % B_2O_3, 31,6 % BaO et 13,9 % Li_2O (verre BLB de St-Gobain);

3° Deux verres de composition B_2O_3 — $B_4O_7Na_2$ à 10 % de B_2O_3 (préparés dans des conditions différentes);

4° Le sélénium vitreux.

La recristallisation a été suivie par repérage au microscope en lumière ordinaire et en lumière polarisée, de l'apparition du premier cristal sur les petits fragments de verre. Nous avons appelé température de dévitrification la température d'apparition de ce cristal.

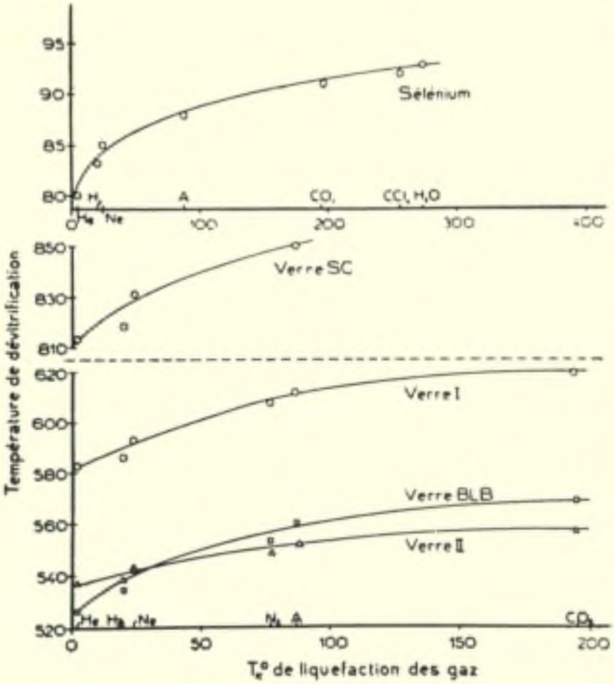


Fig. 9

Les résultats expérimentaux sont donnés par les courbes de la fig. 9 et conduisent aux conclusions suivantes :

1° La température de dévitrification varie selon la nature du gaz en présence;

2° Elle est une fonction croissante régulière de la température absolue de liquéfaction du gaz, donc du pourcentage de gaz adsorbé.

Parallèlement à l'étude de la recristallisation superficielle de l'état vitreux, nous avons étudié l'influence des gaz adsorbés sur le début de la recristallisation superficielle de l'argent écroui à froid.

Deux méthodes ont été employées :

1° Variation de la microdureté de plaques d'argent laminées à froid et recuites à des températures croissantes pour une durée de recuit constante :

Si nous appelons température de recristallisation superficielle la température à laquelle commence la chute de dureté, nous voyons que cette température de recristallisation est une fonction croissante de la température absolue de liquéfaction du gaz (fig. 10), donc de la quantité de gaz adsorbé. Nous observons pour N_2 une anomalie déjà observée antérieurement.

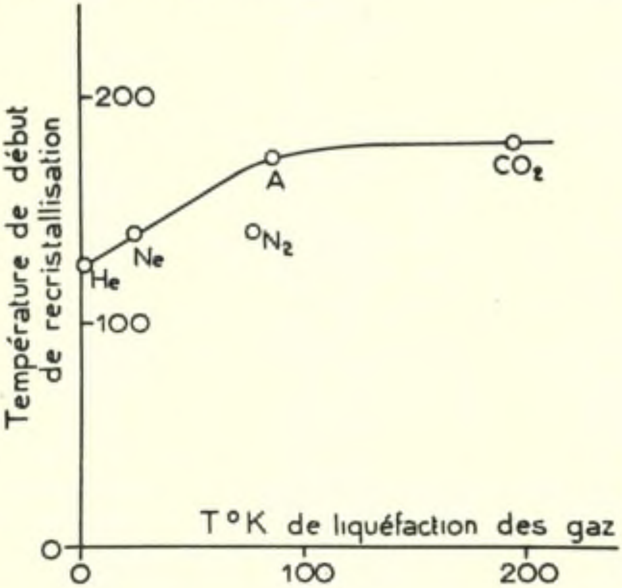


Fig. 10

2° Examen de la structure aux rayons X de plaques d'argent laminées à froid et recuites à température constante pour différentes durées de recuit.

Une première étude aux rayons X ayant paru confirmer ces résultats, nous avons déterminé la durée de recuit nécessaire pour obtenir, à température constante et pour chacun des gaz (He, Ne, A, CO_2) la formation des premiers cristaux décelables par les rayons X, c'est-à-dire à l'apparition de la première tache. La fig. 11 permet d'interpréter les résultats obtenus :

Pour un degré de recristallisation donné (correspondant à l'apparition des premiers cristaux décelés par notre procédé d'analyse aux rayons X), la durée de recuit est une fonction croissante de la température absolue de liquéfaction du gaz, donc de la quantité de gaz adsorbé.

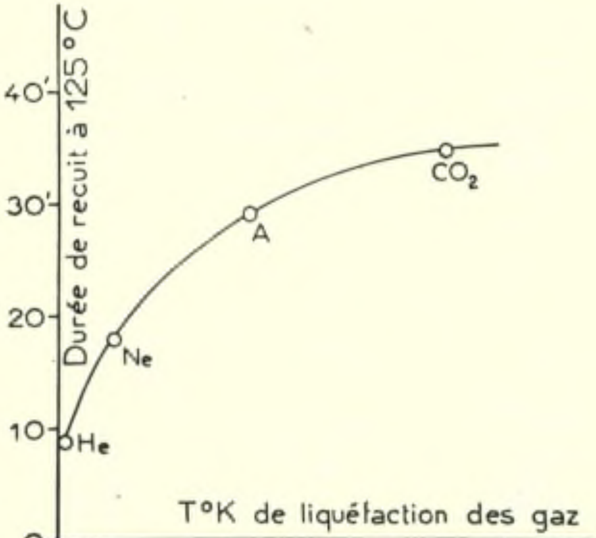


Fig. 11

L'effet dû aux gaz adsorbés, constaté dans cette étude sur la recristallisation, semble être de sens opposé au sens habituel observé jusqu'ici. En effet, les gaz adsorbés auraient plutôt tendance à jouer un rôle d'inhibiteur de recristallisation. Il paraît possible d'interpréter cette apparente inversion de la manière suivante : du point de vue thermodynamique, les phases vitreuse et écrouie sont des phases instables dont le niveau énergétique est légèrement supérieur à celui des phases cristallisées correspondantes. Si l'on augmente cette différence de niveau d'énergie libre, on augmente parallèlement la tendance à la recristallisation et inversement. Or, les gaz adsorbés à la surface d'un solide *diminuent* son énergie libre en relâchant les forces de liaison superficielles. Comme la dévitrification et la recristallisation débutent toujours en surface, où l'énergie libre est la plus élevée, le gaz adsorbé, en diminuant cette énergie, doit donc stabiliser les états vitreux et écroui. Cette action protectrice sera d'autant plus grande que le gaz en présence sera plus fortement adsorbé.

⁂

Cet ensemble de résultats devait manifestement nous entraîner vers l'étude de l'influence des gaz sur la formation de liaisons entre les grains d'une poudre, au cours du phénomène de frittage.

Dans les premières manifestations du frittage, au stade de l'adhésion, l'accroissement d'amplitude de vibration des atomes, causé par l'élévation de température, entraîne des interactions de champ de forces dont résultent, après refroidissement, des liaisons qui se manifestent par une certaine cohésion de la masse. Nous devions pouvoir observer un accroissement de la vitesse de frittage, en présence de gaz adsorbés si l'hypothèse, suggérée par nos résultats antérieurs, d'une mobilité accrue des atomes dans ces conditions, se révélait exacte (le frittage, en effet, est étroitement lié à la diffusion de surface des atomes du solide).

Afin de permettre la mise en évidence de cet effet des gaz adsorbés, il fallait limiter l'étude au seul phénomène d'adhésion; l'examen ne pouvait porter que sur des poudres non comprimées, et chauffées à température relativement basse.

Une poudre de cuivre préparée par réduction de l'oxyde a été utilisée dans cette étude (11).

Pour pouvoir saisir d'une façon précise un accroissement même faible des propriétés mécaniques, nous avons utilisé l'effet global de pénétration d'une aiguille dans une poudre ayant subi le recuit.

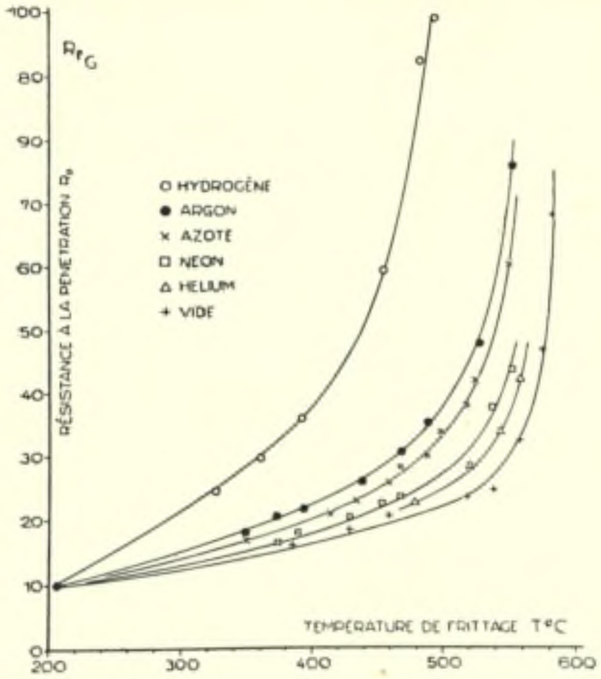

100
80
90
70
60
50
40
30
20
10
0
RfG
RÉSISTANCE À LA PÉNÉTRATION Rp
○ HYDROGÈNE
● ARGON
× AZOTE
□ NEON
△ HELIUM
+ VIDE
TEMPÉRATURE DE FRITTAGE T°C
200
300
400
500
600

Fig. 12

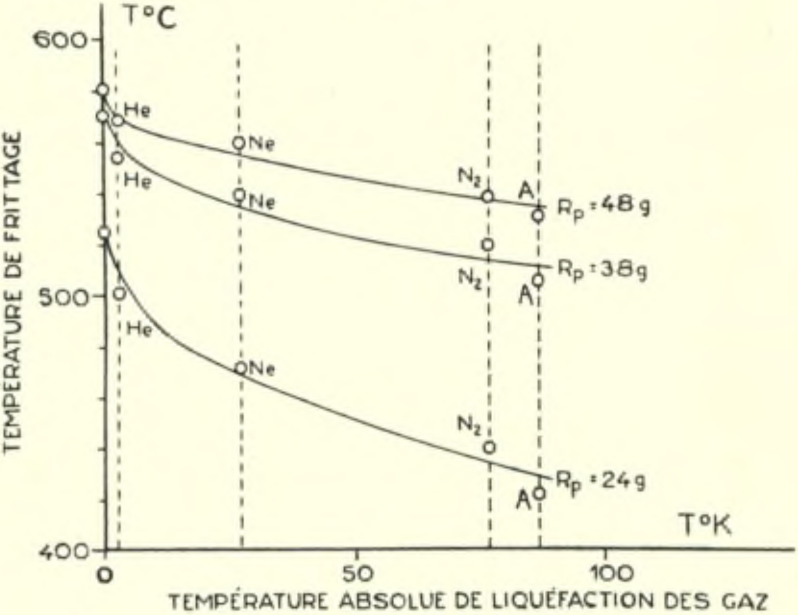

T°C
600
500
400
TEMPÉRATURE DE FRITTAGE
He
Ne
N2
A
Rp = 48 g
He
Ne
N2
A
Rp = 38 g
He
Ne
N2
A
Rp = 24 g
T°K
0
50
100
TEMPÉRATURE ABSOLUE DE LIQUÉFACTION DES GAZ

Fig. 13

La fig. 12 fait ressortir la résistance à la pénétration, en fonction de la température de frittage, des échantillons de poudre, recuits dans différentes atmosphères. L'examen de ces courbes conduit aux conclusions suivantes :

1° L'allure générale des courbes est analogue pour les différents gaz; la charge nécessaire pour un enfoncement constant augmente régulièrement avec la cohésion de la masse, en fonction de la température de frittage;

2° L'adhésion entre les grains varie suivant la nature du gaz en présence;

3° Pour un degré de résistance à la pénétration donné, la température de frittage est une fonction décroissante de la température de liquéfaction du gaz utilisé (fig. 13) ou, ce qui revient au même, l'énergie calorifique nécessaire pour atteindre un degré de frittage déterminé est d'autant plus faible que l'opération est effectuée en présence d'un gaz plus adsorbé;

4° Dans le domaine de température où les propriétés mécaniques augmentent d'une façon considérable, l'influence spécifique des différents gaz semble s'atténuer : une certaine diffusion à l'intérieur du solide interviendrait déjà, et l'effet produit par le gaz adsorbé ne peut plus se manifester.

Nous remarquons une anomalie dans le cas de l'hydrogène. Elle peut être attribuée à la réduction par l'hydrogène dissous, d'oxyde occlus dans la masse métallique, ce qui entraîne, d'après Garner et Ransley, une augmentation de la surface et une désorganisation locale de la structure réticulaire : ces conditions deviennent particulièrement favorables au frittage.

Nous avons, de plus, confirmé ces résultats par des mesures de conductibilité électrique des échantillons.

Des courbes de la fig. 14, nous pouvons déduire que le nombre des contacts entre grains, dont dépend la conductibilité électrique, est d'autant plus élevé que le gaz en présence est plus adsorbé. Nous retrouvons d'ailleurs, là encore, l'anomalie de H_2.

La comparaison, en outre, de la résistance à la pénétration, de la conductibilité électrique et de la densité de produits frittés dans l'argon (fig. 15) fait ressortir qu'avant toute « densification », le

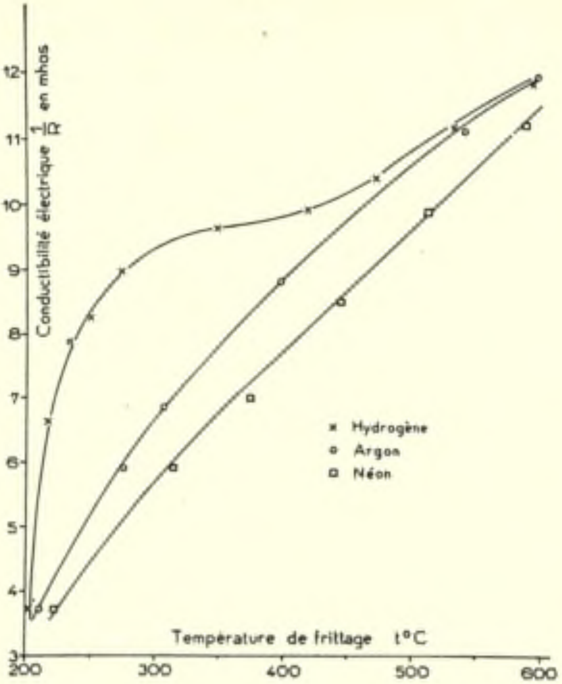

Conductibilité électrique $\frac{1}{R}$ en mhos
3
4
5
6
7
8
9
10
11
12
× Hydrogène
○ Argon
□ Néon
Température de frittage t°C
200
300
400
500
600

Fig. 14

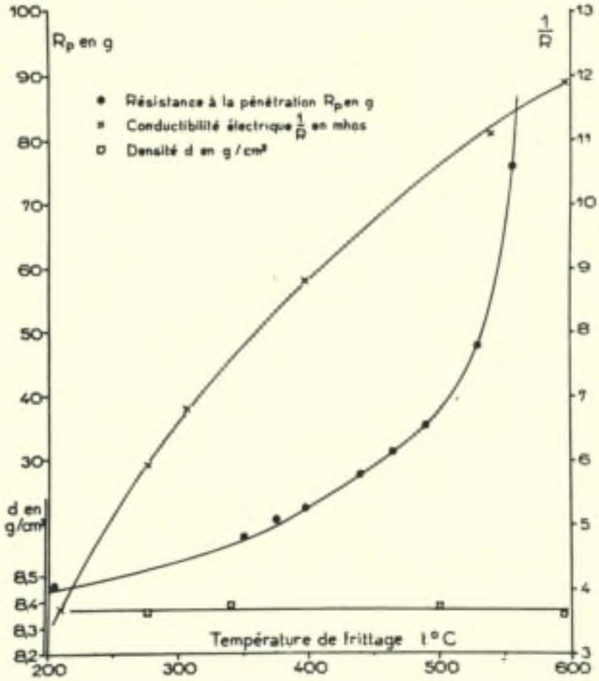

R_p en g
$\frac{1}{R}$
● Résistance à la pénétration R_p en g
× Conductibilité électrique $\frac{1}{R}$ en mhos
□ Densité d en g / cm³
d en g/cm³
100
90
80
70
60
50
40
30
8,5
8,4
8,3
8,2
13
12
11
10
9
8
7
6
5
4
3
Température de frittage t°C
200
300
400
500
600

Fig. 15

nombre des contacts entre grains augmente très rapidement, dès le frittage à basse température, alors que les propriétés mécaniques ne croissent que lentement.

Comme l'observation au microscope, les analyses aux rayons X et par diffraction électronique permettent de préciser qu'aucun changement d'ordre structural n'est intervenu dans les poudres traitées, les variations observées dans les vitesses de frittage semblent donc bien relever du phénomène d'adsorption du gaz en présence.

Des résultats tout à fait comparables ont été obtenus avec une poudre de nickel.

* * *

Les différents phénomènes physiques et physico-chimiques étudiés jusqu'ici, et pour lesquels une influence des gaz adsorbés a pu être mise en évidence, s'étaient toujours manifestés au voisinage de perturbations dans le réseau cristallin dues à un accroissement d'agitation thermique. Il était intéressant d'étendre cette étude à un phénomène permettant *d'atteindre, d'une manière plus directe*, les forces de liaisons entre atomes dans le réseau. Nous nous sommes adressés aux propriétés mécaniques et, plus particulièrement, à la résistance à la traction et au module de torsion de fils métalliques, à la température ambiante ([12]). Les paragraphes suivants exposent les principaux résultats relatifs à cette étude.

L'influence des gaz adsorbés sur la résistance mécanique a été étudiée sur des fils métalliques suffisamment fins pour que cet effet de surface puisse apparaître avec netteté.

Les charges de rupture de ces fils ont été mesurées à l'aide d'un appareil de traction simple, réalisé dans nos laboratoires, permettant, en particulier, d'opérer sous un vide élevé ou dans une atmosphère gazeuse déterminée.

La fig. 16 reproduit les résultats obtenus avec des fils de Pt, Cu, Au de 1/10 mm de diamètre dans différentes atmosphères. De l'examen des courbes, on peut conclure que :

1° La charge de rupture à la traction de fils fins varie selon la nature du gaz adsorbé ;

2° Pour un même métal, la diminution de la charge de rupture est une fonction décroissante régulière de la température de liquéfaction du gaz en présence, donc du pourcentage de gaz adsorbé.

L'anomalie observée pour le platine dans l'hydrogène peut être imputée à un commencement de diffusion de l'hydrogène dans ce métal dont la résistance se trouve anormalement abaissée.

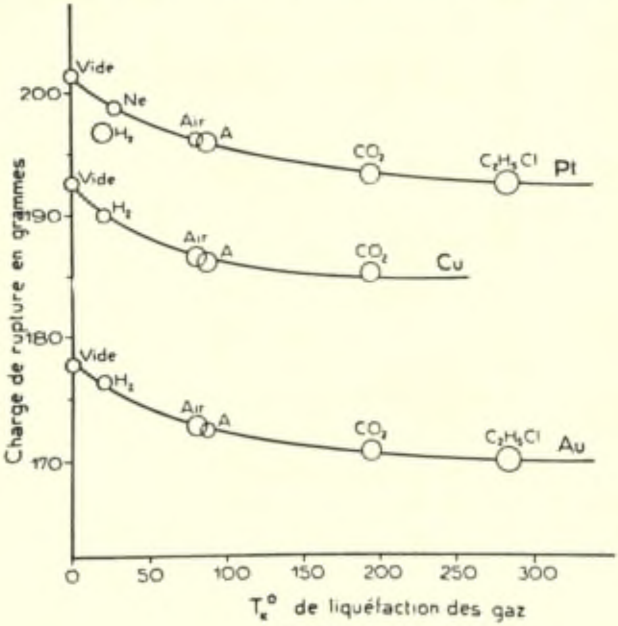


Fig. 16

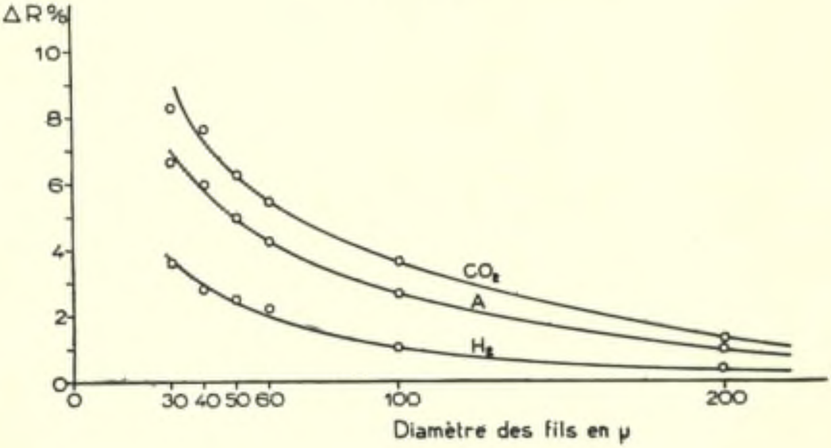


Fig. 17

L'effet observé étant, selon notre hypothèse, lié à un relâchement des liaisons du réseau cristallin superficiel, nous devions nous attendre à une variation de celui-ci suivant l'importance relative de la surface. Ceci nous a conduits à étudier le phénomène en fonction du diamètre des fils, c'est-à-dire, en fonction du rapport de leur surface à leur section.

Les expériences précédentes ont été reprises avec des fils d'argent de 30, 40, 50, 60, 100 et 200 μ de diamètre et des fils de tungstène de 20, 30, 50 et 100 μ de diamètre. Les courbes des fig. 17 et 18 traduisent les résultats obtenus. On a porté en abscisses les diamètres des fils et en ordonnées la diminution relative de la charge de rupture rapportée à la charge de rupture dans le vide :

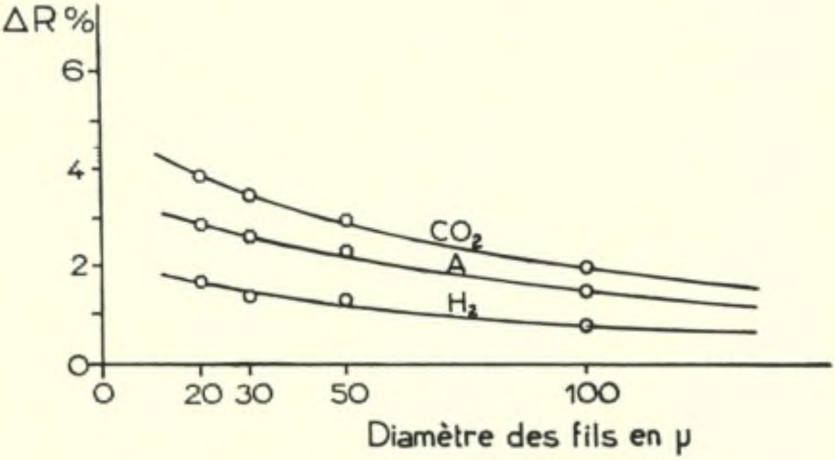


Fig. 18

$$\Delta R\ \% = \frac{R\ \text{vide} - R\ \text{gaz}}{R\ \text{vide}} \cdot 100$$

L'examen de ces courbes confirme notre hypothèse et nous conduit aux conclusions suivantes :

3° La diminution de la charge de rupture dans un gaz donné, par rapport à la charge de rupture dans le vide, varie avec le diamètre du fil ;

4° Pour un même métal et dans un gaz donné, la diminution relative de la charge de rupture est une fonction décroissante régulière du diamètre des fils ;

5° L'allure des deux réseaux de courbes est la même mais, pour un diamètre et dans un gaz donnés, la diminution de la charge semble dépendre de la nature du métal.

Une étude du module de torsion de fils métalliques, faite parallèlement à la précédente, confirme ces résultats.

L'équipage du pendule de torsion utilisé dans cette étude se compose d'un volant portant sur son axe de rotation un miroir qui permet de repérer les oscillations. Cet équipage est suspendu au fil d'argent étudié.

Deux méthodes, l'une dynamique, l'autre statique, ont été utilisées. La première repose sur la détermination de la période d'oscillation du pendule. Le module de torsion est en effet inversement proportionnel au carré de la période. Dans la seconde, on détermine la déviation du pendule de sa position d'équilibre pour un couple de torsion constant. Le module de torsion est également lié au couple par une relation simple. La fig. 19 met en évidence la diminution du module de torsion d'un fil d'argent de 6/100 mm de diamètre. Cette diminution est d'autant plus forte que le gaz est plus adsorbé.

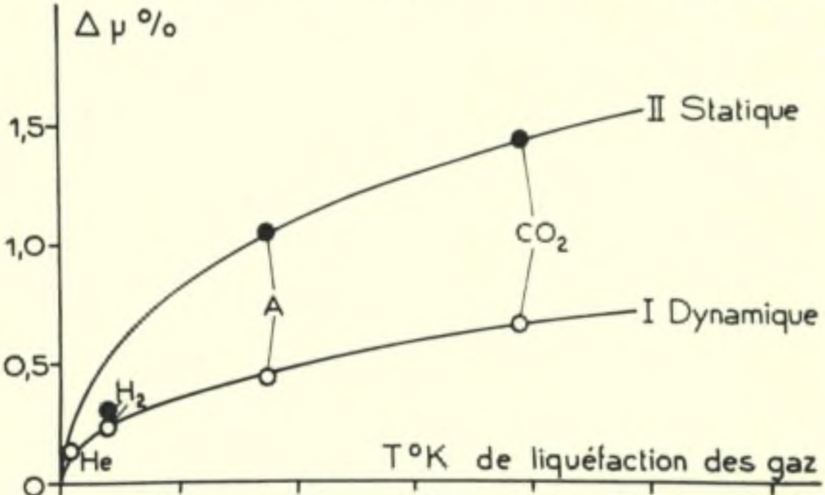


Fig. 19

L'étude des propriétés mécaniques nous a donc permis d'atteindre effectivement les forces de liaisons entre atomes ou grains dans le solide et nous a apporté une confirmation directe de notre hypothèse sur le relâchement des forces de liaisons superficielles du réseau.

Cependant, tous les phénomènes étudiés précédemment, même les propriétés mécaniques, supposent un déplacement d'atomes dans le réseau cristallin. Il était intéressant d'étudier également certaines transformations dans le solide, intervenant uniquement à l'échelle électronique, sans variation de position des atomes; nous avons tenté, dans ce but, l'étude de l'influence des gaz adsorbés sur la transformation magnétique du nickel (transformation du second ordre) d'une part, et sur la conductibilité électrique d'un fil d'or d'autre part.

Nous n'avons pu, dans les deux cas, mettre en évidence aucun effet sensible sur ces deux phénomènes et il semblerait bien que l'effet perturbateur des gaz ne puisse se manifester qu'au voisinage d'une perturbation des liaisons dans le réseau cristallin superficiel.

Certaines expériences de Braunbeck sur des feuilles de Platine en présence d'Hélium et d'Argon, de Suhrmann avec du Xenon, auraient cependant mis en évidence des variations de conductibilité électrique, variations dont le sens correspondrait, dans certains cas, à ce que nous pourrions prévoir (mobilité électronique, croissant de l'Hélium à l'Argon).

Ce point mérite donc d'être réexaminé.

Par ailleurs, il est intéressant de noter également que certaines études sur le coefficient de frottement entre corps solides ont mis en évidence une influence des gaz adsorbés qui correspond à une diminution du frottement en fonction du degré d'adsorption des différents gaz (15, 16); ces résultats paraissent pouvoir se raccorder à nos travaux.

⁂

Si l'on considère l'ensemble des résultas expérimentaux exposés ci-dessus, on ne peut qu'être frappé par la *similitude de l'effet observé dans les différents cas et la régularité de sa variation en fonction de la variable choisie :* la température absolue de liquéfaction du gaz adsorbé. Nous avons utilisé dans nos expériences aussi bien des gaz tels que H_2, O_2, N_2, CO_2, H_2O que des gaz rares, et les différents points expérimentaux obtenus se placent sur une même courbe. Si l'on peut songer, un instant, vu l'ampleur de l'effet observé, à une dissolution des gaz dans le réseau solide, il paraît peu probable que des molécules, si différentes du point de vue de leur structure et de leurs dimensions, suivent une loi de dissolution conforme à nos

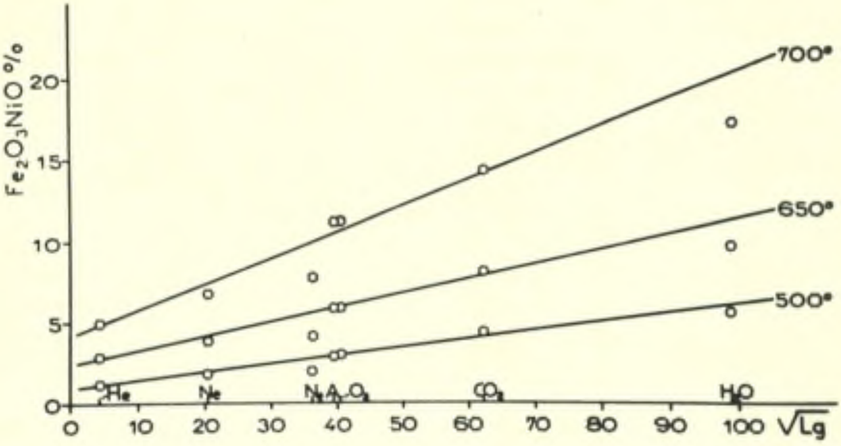


Fig. 20

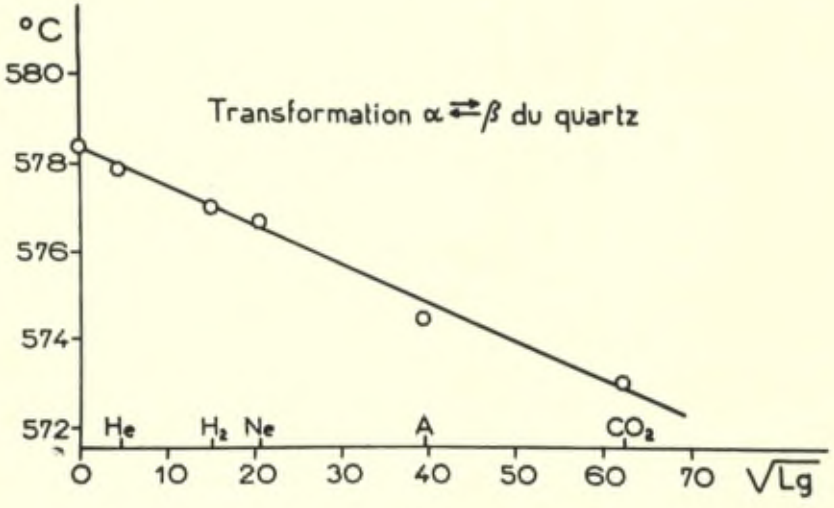


Fig. 21

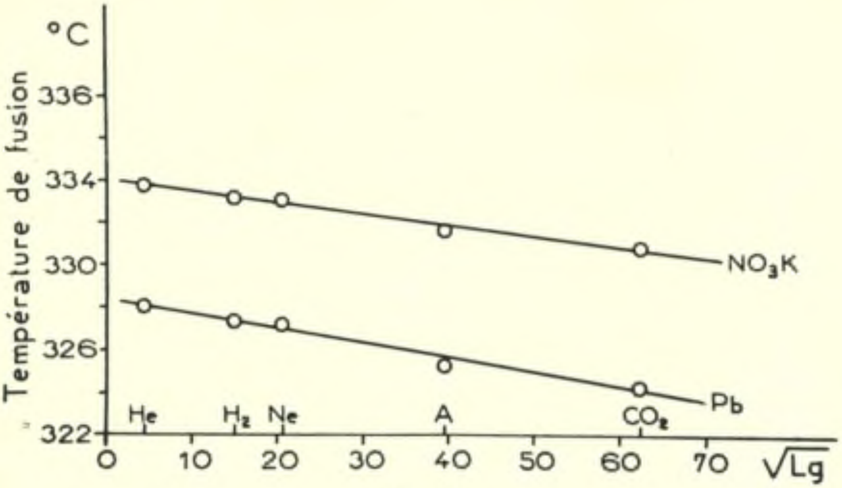


Fig. 22

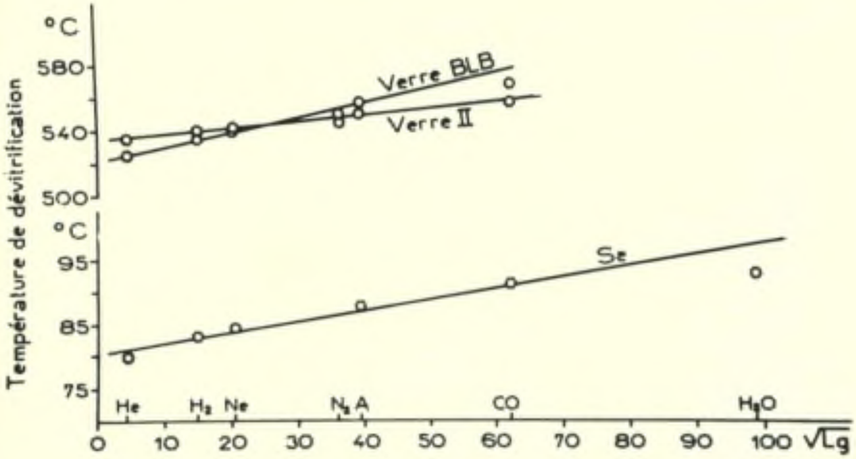


Fig. 23

courbes (*). De plus, les résultats obtenus dans nos expériences sur la résistance mécanique de fils métalliques peuvent difficilement s'expliquer par la diffusion des gaz, phénomène lent qui croît avec la température, mais négligeable à la température ambiante. Par contre, lorsqu'il y a possibilité de dissolution, on observe immédiatement

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(*) D'après l'encombrement, l'ordre devrait être : He, H^2, Ne, H^2O, A, N^2, O^2, CO^2. La dissolution de H^2O et de CO^2 parait peu probable dans un réseau ionique.

une anomalie sur nos courbes (cas de l'hydrogène pour un fil de platine).

Par ailleurs dans notre étude des vitesses de formation du ferrite Fe_2O_3 NiO en fonction de la pression du gaz, le fait d'atteindre un palier aux environs de la pression atmosphérique élimine également l'idée d'une dissolution des gaz dans le solide, car cette dissolution devrait être une fonction croissante de la pression. Cette dissolution est théoriquement possible mais l'effet doit être masqué par l'effet propre dû à l'adsorption.

Enfin, une confirmation supplémentaire nous est donnée par l'application de la règle classique selon laquelle l'énergie d'adsorption d'une substance A sur un adsorbant B est proportionnelle à $\sqrt{L_A.L_B}$, où L_A et L_B sont les chaleurs latentes d'évaporation des deux substances A et B. Cette règle repose, en effet, sur la notion d'interaction de deux molécules selon London et Keesom. Si nous remplaçons, en abscisses, la température absolue de liquéfaction des gaz par la racine carrée de leur chaleur d'évaporation, tout en gardant les mêmes ordonnées sur nos graphiques nous devons obtenir des droites. C'est effectivement ce que nous constatons. Les figures suivantes montrent les variations de : la vitesse de formation des ferrites (fig. 20), de la température de transformation du quartz (fig. 21), de la température de fusion de corps cristallisés (fig. 22), de la température de dévitrification de différents verres (fig. 23), de la charge de rupture d'un fil d'or de 1/10 mm (fig. 24), en fonction

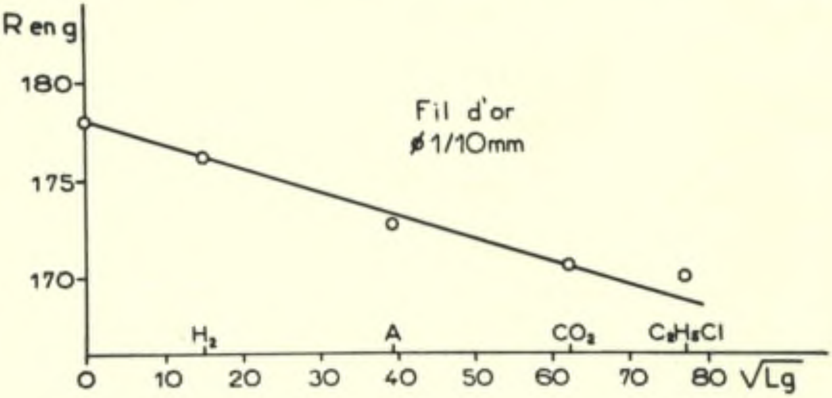

Fig. 24

de la nouvelle variable. On voit que les points expérimentaux s'alignent bien sur une droite, ce qui montre que l'effet observé est lié essentiellement à une adsorption physique réversible par action des forces Van der Waals, sans intervention d'autres types de liaison (adsorption chimique ou dissolution, par exemple).

Nous avions été conduits, récemment, à donner une interprétation de cet effet, fondée sur la considération des fréquences de vibration des atomes dans le solide (13). Cette interprétation ne nous satisfait pas, et nous sommes actuellemnt orientés vers une nouvelle hypothèse explicative, très schématique évidemment, mais qui nous paraît plus simple et plus sûre :

L'approche d'une molécule de gaz à la surface d'un solide provoque, dans le réseau cristallin superficiel de ce dernier, des perturbations engendrées par les forces d'adsorption du type Van der Waals (rappelons que l'énergie des liaisons Van der Waals est notable : quelques centaines à quelques milliers de calories par mol. g). Ces perturbations ont pour origine une distorsion réciproque des couches électroniques de l'ion ou atome adsorbant et de la molécule adsorbée, distorsion qui a pour effet d'augmenter leur polarisation. Or, on sait que toute augmentation de la polarisation d'un ion ou atome entraîne une diminution de sa polarisabilité, c'est-à-dire de sa tendance à une déformation ultérieure par d'autres voisins.

L'approche des atomes ou molécules de gaz adsorbés doit donc provoquer différentes sortes d'interactions avec les atomes du réseau superficiel.

1) L'attraction due aux forces de Van der Waals, entre les molécules de gaz adsorbées et les atomes du réseau superficiel, doit provoquer une attraction de ces derniers vers l'extérieur du réseau du solide et par conséquent augmenter leurs distances par rapport à la couche d'atomes sous-jacents, en diminuant les forces de liaison.

2) L'action des forces de Van der Waals entre le gaz et le solide va provoquer, par définition, une polarisation des atomes de la couche superficielle du solide. Or ces derniers sont déjà polarisés par leurs voisins et cette polarisation réciproque entre les atomes du réseau cristallin apparaît sous la forme de deux termes additifs

dans l'expression qui donne l'énergie de liaison en fonction de la distance (*).

$$\varphi(r) = -\frac{e^2}{r} + \frac{be^2}{r^n} - \frac{(\alpha_1 + \alpha_2)\, e^2}{2r^4} - \frac{2e^2\, \alpha_1\, \alpha_2}{r^7}$$

Les deux derniers termes de cette expression sont dus à la polarisation (**). Ces termes correspondent à des interactions nettement orientées, par exemple, sous forme de dipôles. Or, l'apparition d'une nouvelle action polarisante, due à l'approche des molécules de gaz, dans une direction où il n'en existait pas, va donc modifier la résultante des forces de liaisons dues à la polarisabilité et cette modification s'effectuera, évidemment, dans le sens d'une diminution de l'énergie de liaison entre les atomes du réseau cristallin superficiel.

De plus, il est vraisemblable que cette action polarisante due aux molécules adsorbées n'est pas limitée à la première couche d'atomes du réseau mais se répercute à une certaine distance de la surface. La conception de Fajans sur la polarisation mutuelle des ions nous fournit une image physique de la propagation d'une perturbation de l'état électronique d'un ion à travers le réseau cristallin sous la forme d'induction de dipôles et variation de leurs grandeur et direction.

L'amplitude de cet effet, dû aux gaz adsorbés, paraît toutefois difficilement interprétable par les seules diminutions de la polarisabilité et des interactions entre ions ou atomes superficiels considérés plus haut : la profondeur à laquelle se propage ce phénomène, à partir de la surface, est variable suivant les solides étudiés, mais, après une décroissance assez rapide au début, elle ne disparaît complètement qu'à des distances qui peuvent être supérieures à 0,1 μ. Cette profondeur est considérable à l'échelle atomique, mais elle est explicable si nous considérons que :

1° L'ensemble de nos expériences porte sur des déplacements d'atomes ou des déformations du réseau cristallin (réaction, transformation du premier ordre, recristallisation, précipitation, propriétés mécaniques). Il n'est donc pas surprenant que les imper-

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(*) Rappelons que la participation de la polarisabilité dans le cas des halogénures alcalins, est de 10 à 20 % de l'énergie totale.

(**) Dans cette formule on néglige les interactions dipôle-quadrupôle et quadrupôle-quadrupôle et on ne tient compte ni de l'attraction Van der Waals ni de l'énergie au point zéro.

fections ou fissures superficielles du réseau cristallin se propagent en profondeur, lorsque le réseau commence à se transformer en surface; les gaz adsorbés peuvent ainsi pénétrer profondément et exercer leur action perturbatrice à une certaine distance de la surface;

2° Le champ de force étant plus élevé dans les fissures ou lacunes du réseau qu'à la surface, les gaz adsorbés dans ces fissures le sont plus fortement. On sait, en effet, que l'énergie d'adsorption par forces Van der Waals sur une surface idéale conduit à des valeurs généralement trop faibles par rapport aux valeurs obtenues expérimentalement sur des surfaces réelles. Si l'on tient compte de la structure réelle de la surface et de ses imperfections, on retombe sur l'ordre de grandeur réel. Par exemple, on a pu montrer que l'énergie d'adsorption dans les fissures pouvait atteindre huit fois la valeur calculée pour une surface idéale (14). Cette constatation doit donc entraîner une amplification marquée des perturbations et de l'importance des phénomènes observés.

Il ne nous paraît pas encore possible d'harmoniser les hypothèses explicatives qui précèdent avec le concept du screening de Weyl; cette tentative nous paraît un peu prématurée dans l'état actuel de nos connaissances (et de nos incertitudes!) sur la structure réelle et la répartition des forces de liaison des couches superficielles du réseau cristallin. Cependant, l'état particulier des cations superficiels (effet d'écran plus faible) doit se modifier en fonction du degré d'adsorption des gaz, et le " screening " doit augmenter d'autant plus que le gaz est plus adsorbé; en conséquence, l'accroissement de " screening " pourrait effetivement provoquer un relâchement des forces de liaison entre les ions du réseau superficiel et entraîner l'apparition de l'ensemble des phénomènes observés. Nous nous sommes laissés entraîner assez loin du problème des réactions entre solides, mais l'ampleur et la parfaite régularité de ce phénomène demandait une extension expérimentale aussi large que possible, capable de mettre en évidence toute la généralité de l'effet de relâchement des liaisons du réseau cristallin superficiel, sous l'influence des gaz adsorbés. Cet effet pose, une fois de plus, le problème de la structure d'une surface de solide réel, problème fondamental et malheureusement bien mal élucidé. Nous pensons ne jamais trop attirer l'attention de nos collègues cristallographes et physiciens du solide, sur cette question, qui reste à la base de la chimie de l'état solide.

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Discussion

M. Hedvall. — Je me permets de demander si vous avez trouvé une méthode pour mesurer quantitativement des gaz adsorbés ou bien dissous.

Adsorbés ou dissous, c'est une question d'épaisseur de la couche superficielle du réseau. C'est sans doute une expérience bien difficile à réaliser. Nous nous en occupons depuis quelques années. J'espère que nous publierons quelques résultats prochainement.

Il s'agit également de déterminer la quantité dissoute aux hautes températures et de savoir si le gaz s'évapore ou non en revenant aux températures basses. Ces expériences subissent certainement des transformations d'un système à l'autre.

Il y a peut-être intérêt à mentionner que nous avons effectué également quelques expériences avec du verre. Nous avons chauffé des tubes capillaires préalablement dans différents gaz et nous avons, après ce chauffage préalable, mesuré le coefficient capillaire aux températures ordinaires et constaté une très grande influence de ce traitement. Ces expériences avaient l'avantage d'être indépendantes d'un changement de grandeur de la surface par suite d'un processus de recristallisation.

M. Forestier. — Nous n'avons pas, actuellement, de méthodes suffisamment précises pour déterminer la petite quantité de gaz adsorbé par les solides étudiés dans ce domaine de température.

M. De Keyser. — La présence de la vapeur d'eau semble avoir une importance favorable sur les transformations cristobalite-tridymite (dont les enthalpies sont voisines à la température de formation de la tridymite).

M. Forestier. — Je pense qu'à la température de cuisson des briques de silice, l'effet dû à l'adsorption physique (type van der Waals) ne peut plus se manifester. Cependant, il pourrait avoir une influence lors du passage assez lent de la charge de briques dans le domaine de température dans lequel l'adsorption peut se manifester. Cette influence peut entraîner des effets importants, comme le Prof. De Keyser l'a montré, sur l'apparition d'une variété déterminée de silice.

M. Kuhn. — En ce qui concerne l'influence d'un gaz sur le point de fusion d'un solide, il semble probable qu'il ne s'agit pas d'une action limitée à une couche superficielle du solide. En effet, le processus de fusion s'étend *sur la totalité de la matière solide présente*. Il s'agit d'un changement du point de la température d'équilibre solide-liquide en général. L'observation que le déplacement du point de fusion est d'autant plus grand que la chaleur de fusion est plus petite s'expliquerait par la formule bien connue de Van't Hoff, d'après laquelle l'abaissement moléculaire E du point de fusion est liée à la température absolue T_o du point de fusion et à la chaleur de fusion par gramme L, suivant l'expression :

$$E = \frac{0{,}002\, T_o^2}{L}$$

D'après cette considération l'abaissement du point de fusion par les gaz présents serait dû à une dissolution des gaz dans la phase liquide, correspondant au coefficient de solubilité et à la pression du gaz appliquée et au fait que le point de fusion d'une solution est inférieur à celui du liquide pur.

La remarque ne s'applique pas aux phénomènes superficiels proprement dits.

M. Forestier. — La surface totale des poudres est suffisamment grande par rapport à leur masse pour que le phénomène soit déjà observable et provienne du mécanisme dû à l'adsorption. Mais il n'est pas impossible que le processus se poursuive par une dissolution effective des gaz dans le liquide, dissolution qui continuerait ainsi à mettre en évidence le phénomène observé.

Par ailleurs, la formule de Van 't Hoff ne semble pas devoir s'appliquer au phénomène observé au point de fusion. En effet si les courbes (fig. 6) : " abaissement de la température de transformation en fonction de la chaleur de transformation ", sont bien vérifiées dans le cas des transformations polymorphiques, elles ne le sont pas dans le cas de la fusion.

Je renvoie également aux réponses faites au Prof. Barrer et au Prof. Bénard.

M. Ubbelohde. — I would like to add that I agree with Prof. Kuhn that if true equilibrium points are displaces by the inert gases as reported by Prof. Forestier, this must be due to dissolution of these gases in the phases under discussion. The displacement of an equilibrium temperature in the ideal case is given by the Van't Hoff formula. However, the substances studied by Prof. Forestier may not have been in true equilibrium to start with. Adsorbed gases can in principle affect recrystallisation rates, annealing processes, and the like. Hysteresis loops in a transformation may well be modified by such gases, with a shift of the *apparent* transformation temperatures if the loop has not been detected. Even melting of a partly disordered crystal with the same apparent composition, might be modified for example; but this would not be a strictly reversible process. Has reversibility been completely established in the shifts of transformation and melting temperatures reported by Prof. Forestier?

M. Forestier. — La réversibilité du phénomène est totale en ce qui concerne les transformations polymorphiques. Dans le cas de la fusion, elle ne peut être vérifiée. En effet, nous partons d'une poudre à surface assez grande et, par refroidissement du liquide (sans surface appréciable), nous obtenons une masse compacte : l'effet dû à l'adsorption des gaz sur le phénomène de la solidification ne peut donc être que minime.

Dans les expériences relatées ici, nous ne pouvons envisager, pour expliquer l'effet observé, une action déterminante des gaz par dissolution dans le solide. Des déterminations de température de fusion du ClLi dans différentes atmosphères ne nous ont pas permis d'observer une variation nette de cette température. Nous nous trouvons en présence d'un sel dont le point de fusion (614 °C) est situé dans une zone de température déjà élevée, où les gaz très faiblement adsorbés ne doivent plus avoir une influence notable.

Or la dissolution d'un gaz dans un solide augmente généralement avec la température. L'effet sur ClLi devrait donc être plus important que sur les autres corps étudiés.

Je renvoie également aux réponses faites au Prof. Barrer et au Prof. Bénard.

M. Bénard. — Parmi les différents résultats expérimentaux qui nous sont présentés par le Prof. Forestier, je crois qu'il est utile d'établir une distinction entre ceux qui se rapportent à l'influence des gaz adsorbés sur les transformations irréversibles (recristallisation des verres, restauration des métaux, et dans une certaine mesure, propriétés mécaniques) et les transformations réversibles telles que points de fusion et transformations allotropiques.

Il est assez facile de concevoir que l'adsorption superficielle d'un gaz, fût-il chimiquement inerte, puisse modifier la cinétique d'un processus irréversible. En particulier, si la cinétique est déterminée par un phénomène de nucléation qui s'amorce de préférence dans les régions superficielles ou intercristallines, il n'est pas surprenant qu'une modification même légère de l'état électronique des atomes situés dans ces régions puisse agir d'une façon déterminante sur cette cinétique. Les effets signalés par Rehbinder et par Benedicks sont là pour nous en convaincre.

Il est, par contre, moins aisé de comprendre comment un phénomène d'adsorption, par définition superficiel, peut déplacer la température d'une transformation réversible, essentiellement liée aux propriétés massiques de la substance. A ce point de vue, je crois qu'il est intéressant de rapprocher l'explication qui nous est proposée aujourd'hui par le Prof. Forestier, des très récentes expériences du Prof. Suhrmann et de ses collaborateurs dont je viens d'avoir connaissance. Dans ces expériences, l'accroissement de résistivité du nickel par adsorption de xénon n'est pas instantanée mais présente une certaine période de retard qui témoignerait d'une pénétrations du xénon en profondeur (*Coll. Chim. Phys.*, Paris, 1956, sous presse).

M. Forestier. — Dans le cas des transformations réversibles, il est peut-être possible d'adopter les explications théoriques données par Burton et Cabrera sur l'importance du phénomène d'adsorption superficielle et sa répercussion sur la température de fusion d'un corps. Ces auteurs ont envisagé la possibilité d'une fusion superficielle, c'est-à-dire la formation d'une surface complètement disloquée, comportant une concentration considérable de gradins. Ils ont montré, par le calcul, qu'une couche adsorbée pouvait, en certains cas, faire varier notablement la température de fusion superficielle du cristal sous-jacent.

En considérant un cristal réel, il semble qu'on puisse affirmer que la surface joue un rôle prépondérant dans la rupture du cristal à la fusion, comme étant le siège de dislocations nombreuses, et d'une mobilité particulière. Ces conditions particulières doivent se retrouver pour les transformations polymorphiques : en augmentant considérablement la surface d'un corps, c'est-à-dire en le considérant dans un état très dispersé, ces effets de surface l'emportent sur l'ensemble du corps considéré, et lui confèrent une instabilité telle que la température de fusion ou de transformation peut être abaissée.

M. Defay. — Les expériences du Prof. Forestier trouvent une confirmation dans les expériences de Udin, Shaler et Wulf (*J. Metalls, Trans* 1, 186, 1949), Udin (*ibid.*, **189**, 63, 1951), Buttner, Funk et Udin (*J. Physical. Chem.*, **56**, 657, 1952). Ces auteurs mesurent la tension superficielle de fils solides quelques degrés en dessous du point de fusion, en exerçant sur le fil une traction par des poids variables, et recherchent la charge pour laquelle le fluage cesse d'être un allongement du fil pour commencer à devenir un raccourcissement. Celui-ci a pour cause la tension de la surface extérieure du fil.

Pour l'argent à environ 900 °C en présence d'hélium, la tension superficielle mesurée est de 1140 dynes/cm. Elle s'abaisse à 400 dynes/cm lorsque l'hélium est additionné d'oxygène à la pression partielle de 0,1 atm.

M. Barrer. — One would like to explain in some general way the results reported by Prof. Forestier. Prof. Weyl offers a qualitative suggestion on p 444 in his report. However in the quantitative sense one would ask whether the energy contribution due to interaction of say helium with any group of ions is sufficient to lower significantly the energy of activation for rearrangement of this group of ions into another. It is in any case worth considering other views :

(*a*) reactive gases (H_2, O_2, CO, CO_2) surrounding the solids may modify defect concentrations through the solid. This effect has been well demonstrated by Stone, Gray and others of the Bristol school for gases such as CO, O_2, etc. chemisorbed on Cu_2O films. According to this view, He, Ne and A would have to contain traces of reactive impurities such as oxygen.

(*b*) ambient gases, even He, Ne or A, may blanket the reacting solid and slow down evolution of minute amounts of oxygen, etc. which come from the lattice and so modify defect concentrations. This would involve time as a factor in the observed effects.

Both the above views could be tested for some *n*- and *p*-type semi-conductors, where the defect structures are reasonably well understood. I suspect however that they would be inadequate to account for the rather smooth relations between the boiling points of gases and the effects they produce.

(*c*) a third view is that since physical adsorption increases as the boiling point of the sorbate increases, and so do the effects reported by Prof. Forestier, these effects may be correlated with physical adsorption. A sufficient lowering of surface free energy might well influence the kinetics of some processes, such as sintering.

From the Gibbs adsorption isotherm :

$$\Gamma = -\frac{1}{\mathrm{RT}} \frac{d\sigma}{dlna_s} \qquad (1)$$

where Γ is the surface excess, σ the surface free energy and a_s the activity of the adsorbed molecules, we may obtain :

$$\mathrm{RT}\int_{a_s = o}^{a_s = a_1} \Gamma \; dlna_s = \mathrm{RT}\int_{p = o}^{p = p_1} \Gamma \; dlnp = (\sigma_o - \sigma_1) \qquad (2)$$

where σ_o is the surface free energy of the uncovered surface and where, since $a_s = a_{gas}$ at equilibrium and $a_{gas} = p$, we have replaced $dlna_s$ by $dlnp$; a_1 is the activity of sorbed molecules when the pressure is p_1. Eq.2 may be integrated graphically if the adsorption isotherm is known; which is not the case for the systems Prof. Forestier has studied. However, for pure van der Waals adsorption at temperatures often well above room temperature, Henry's law should be valid ($\Gamma = k_1 p$) and one may make a rough estimate of :

$\sigma_0 - \sigma = \pi =$ surface pressure.

In such dilute films $\pi = \Gamma k\mathrm{T}$ (3)

may be a reasonable eq. of state. If 0.1 % of the surface were covered with the atoms each of 4×10^{-16} cm² cross-section, there would be 2.5×10^{12} atoms/cm². If we identify this number with Γ then at 300 °C

$$\sigma_0 - \sigma = \pi = 2.5 \times 10^{12} \times 300 \times 1.4 \times 10^{-16} \text{ erg/cm}^2$$

Similarly if 1 % of the surface were covered

$$\sigma_0 - \sigma \sim / \text{ erg/cm}^2 \sim 10^{-1} \text{ erg/cm}^2$$

For a physically adsorbed nitrogen film, covering 8 % of the surface (a rather denser film for this more condensable gas), and with a cross sectional area of 16×10^{-16} cm², one has $\sigma_0 - \sigma \sim 2$ erg/cm² The question is wether effects of this magnitude could explain the result on, for example, sintering reactions. It is possible, but rather unlikely. I will leave this point for further comment by Prof. Forestier or others.

(*d*) there is to my mind, a rather greater difficulty in explaining effects of the gases on equilibrium properties than on non-equilibrium ones. Either the gases must alter the melting points by solution, which seems unlikely for He, Ne and A in substances like molten Pb or KNO_3 (see fig. 22 of Prof Forestier's report) or they must alter these melting points by a hydrostatic pressure effect, which again seems unlikely because the influences are too large. Moreover, different gases at the same pressure exercise different influences, which once more, seems to rule out any hydrostatic pressure effect.

Experiments designed to show diffusion of inert gases through mica and through metals have been unsuccessful and so we also should be slow to accept the idea that solid solutions form in such cases.

M. Forestier. — Les mesures de gaz adsorbé dépendent du type de couches superficielles présentées par les solides. J'attire à nouveau l'attention sur le fait que :

1° Une dissolution des gaz ne paraît pas devoir être importante étant donné la nature des résultats obtenus (voir en particulier pp. 525-528.

2° La loi expérimentale obtenue est toujours reliée à l'approche de phénomènes qui perturbent le réseau cristallin en profondeur, multipliant et amplifiant ainsi les défauts ou fissures du réseau à partir de la surface, donc amplifiant beaucoup le phénomène d'adsorption (adsorption rapide, type van der Waals) qui se propage profondément à l'intérieur du réseau en même temps que les perturbations issues de la surface.

Par ailleurs, il est difficile d'admettre que des impuretés puissent intervenir suivant une loi régulière, les gaz ayant été purifiés préalablement dans des conditions identiques.

M. Defay. — Je suis d'accord avec le paragraphe *c)* de l'intervention du Prof. Barrer mais je dois lui demander quelques explications complémentaires en ce qui concerne ses conclusions.
Il me paraît douteux en effet que l'on puisse utiliser pour la couche de gaz adsorbé, l'équation d'état $\pi = \Gamma RT$ qui est une équation de film gazeux. Les expériences de M. Forestier où l'on voit apparaître une proportionnalité avec le logarithme de la pression, si on les compare avec la formule :

$$d\sigma = - \Gamma RT\, dlnp$$

suggèrent que Γ est à peu près constant, c'est-à-dire que la surface est proche de sa saturation. Au lieu de la formule $\pi = \Gamma RT$ il faudrait donc peut-être appliquer une formule de film condensé qui donnerait sans doute un accroissement beaucoup plus considérable de π et donc un effet très sensible sur l'énergie superficielle.

M. Barrer. — It is not correct to say that at temperatures ranging from room temperature up to hundreds of degrees centigrade the surface is satured with respect to physically adsorbed films of He, Ne, or A. On the contrary, these films will be extremely dilute, and Henry's law, according to which amount sorbed is proportional to equilibrium pressure, will be valid. These assumptions are made in my calculations using the equation $\pi = \Gamma RT$.

If, however, the gases are chemisorbed, the film could be concentrated and the above argument and equation of state would not apply, but the film would now be able to contribute to the defect concentration, as shown by Stone, Gray and others for some reactive gases on thin films of Cu_2O.

M. Chaudron. — Je voudrais rappeler des recherches déjà anciennes de Carl Benedicks (*), que l'on peut rapprocher de celles de M. Forestier.

Cet auteur a montré l'influence sur les propriétés mécaniques des métaux des liquides qui provoquent un simple mouillage des surfaces. Il a même mis en évidence que l'essai mécanique dans de nombreux cas ne peut avoir un sens que si l'on définit avec précision le milieu ambiant. Benedicks a également indiqué que certains liquides facilitaient la formation des fissures et d'autres au contraire agissaient contre l'accroissement d'une fissure.

Les métallographes modernes admettent le rôle très important des défauts du réseau, qui sont très sensibles aux atomes étrangers.

On peut mettre en évidence par le microscope électronique, des défauts de surface qui provoqueront, dans l'essai de fatigue par exemple, de véritables fissures. La théorie des dislocations est certainement appelée à jouer un grand rôle dans ce domaine.

M. Weyl. — 1. One cannot exclude the possibility of gases affecting the reactions rate of semiconductors by influencing the number of defects; an influence which is well established since the early days when semiconductors were discovered (CuI in I_2 vapour). However the effect of gases on devitrification cannot be explained on this basis because glasses do not form defective structures of the N- of P-type.

2. The work of Prof. Barrer indicates that the mere presence of Rb-analcite affects the equilibrium of K-analcite with a solution of alkali salts. This effect was explained in terms of strain and stress, a terminology which applies to matter as a continuum. In atomic dimensions stress and strain represent changes of inter-nuclear distances and polarizations of electron clouds. The atomistic interpretation brings those phenomena observed by Prof. Barrer and those observed by Prof. Forestier on the same basis.

M. Barrer. — In the exchange reaction :
$K^+(aq) + Rb^+$ (in analcite lattice) $\rightleftarrows Rb^+(aq) + K^+$ (in analcite lattice), the entry of either ion into the aluminosilicate lattice rich in the other ion involves a measure of misfit.

(*) C. Benedicks : *Rev. Métallurgie*, **46**, 291 (1949).

As Rb, say, accumulates in the K-rich parent phase there comes a time when small parts of the aluminosilicate framework tend to adjust themselves to give the best fit for Rb. A Rb rich phase then nucleates in or on a matrix of the parent K-rich phase. This conception, although it has no doubt been over-simplified above, is all that is needed to explain our results on limited mutual solid solubility of Rb-analcite and K-analcite. Differences in the unit cells of the two forms have been demonstrated by us, by X-ray measurements. The above mechanism need make no reference to screening theory.

As far as the use of the screening theory for an explanation of Prof. Forestier's results is concerned, I have a difficulty when it comes to taking the next step of seeing, for example, where the energy is to come from to lower the energy of activation significantly for a solid state process, in the cases in particular of Ne or He. Their interaction energy with the solids they are influencing is so small. One does need at some stage to test qualitative explanation by moving to a more quantitative approach. Until this approach can be given it will be difficult to prove or disprove the screening theory in this application.

M. D'Or. — Voici quelques observations qu'il est peut-être intéressant d'ajouter à celles que le Prof. Forestier a exposées.

1° *Adsorption des gaz sur les métaux.*

Cette question a été étudiée par différentes méthodes dans mon laboratoire. En particulier, le Dr J. Mignolet a mis au point deux techniques qui permettent la mesure des potentiels de surface créés par les films de gaz adsorbés sur une surface métallique nue.

Parmi les résultats obtenus dans ce domaine, je voudrais mentionner les suivants :

A. L'adsorption physique d'un gaz sur un métal peut-être suivie en fonction du temps par mesure du potentiel de surface. L'expérience montre que l'équilibre entre la phase adsorbée et la phase gazeuse s'établit très rapidement, de telle sorte que les longs temps de relaxation observés par le Prof. Suhrmann lors des mesures de résistance électrique de films de métal en présence de xénon montrent que la variation de la résistance électrique est en relation avec des phénomènes de pénétration des atomes du gaz dans des pores de petites dimensions.

B. L'adsorption physique de molécules non polaires et d'atomes de gaz rares modifie toujours le potentiel de surface du métal,dans le sens d'une diminution du travail d'extraction des électrons du métal. Il se produit donc un transfert électronique des particules adsorbées vers le métal, ce qui peut affecter la tension superficielle du métal soit par effet électrostatique, soit par modification de la structure électronique des couches superficielles du métal et par conséquent modification des forces de cohésion dans ces couches.

2° *Réaction entre sels à l'état solide.*

Mon collaborateur le Dr P. Tarte a suivi par spectrométrie infrarouge l'évolution de différents systèmes binaires formés par des mélanges de cristaux très ténus (diamètre moyen de l'ordre du micron) de deux sels susceptibles de donner lieu à des réactions de double décomposition et préalablement soumis à dessication en présence de P_2O_5. L'expérience montre que la réaction se poursuit de façon tout à fait manifeste lorsqu'elle a pour effet de donner naissance à un sel insoluble dans l'eau; que par contre elle ne se produit pas, dans les cas étudiés jusqu'ici, lorsqu'aucun des produits de la réaction n'est insoluble dans l'eau.

Les choses se passent donc comme s'il subsistait à la surface des cristaux d'un film d'eau et comme si la réaction se produisait par l'intermédiare de ce film jouant le rôle de solvant pour les deux sels.

M. Powell. — The non-stoicheiometric compounds that have been discussed are of two main groups, those, especially the organic inclusion compounds, where a vacant space can occur of itself and those where a lattice defect is not an isolated feature but is tied to some complementary event. This, with the different strengths of the crystals, makes the two groups seem rather loosely related, but in at least one other respect there is a similarity. Inorganic lattice defects may have associated with them some normally unstable chemical entities such as singly charged zinc ions or electrons plus holes. Correspondingly the unusual electronic environment in the space of an inclusion compound may give rise to ordinarily metastable entities. Thus Cramer has found that some nitroso-compounds which are normally colourless dimers give blue inclusion compounds i.e. the included form of molecule is the monomer. Similarly a variety of blue inclusion compounds of iodine do not contain simple iodine molecules but chains in which the iodine-iodine distance is much greater.

TABLE DES MATIÈRES

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