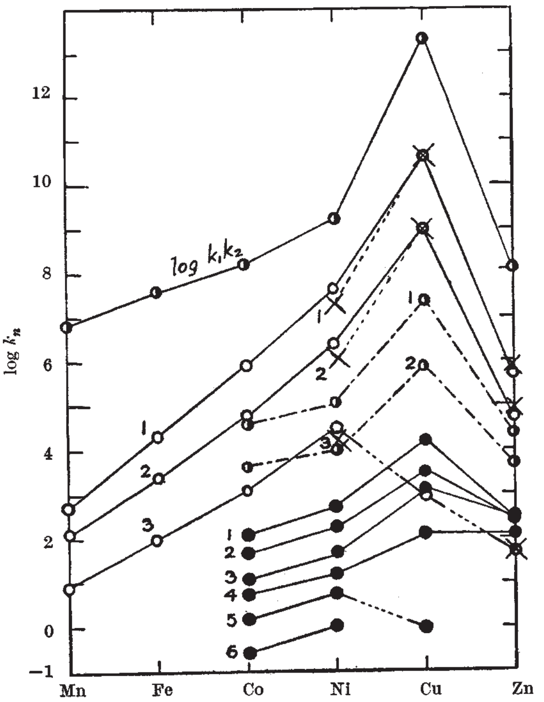
# ORDER OF STABILITY OF METAL COMPLEXES

By Dr. H. IRVING and R. J. P. WILLIAMS
Inorganic Chemistry Department, Oxford

MELLOR and Maley[1,2] have recently pointed out that the stability of complexes of bivalent metal ions follows the order

$$\mathrm{Pd} > \mathrm{Cu} > \mathrm{Ni} > \mathrm{Co} > \mathrm{Zn} > \mathrm{Cd} > \mathrm{Fe} > \mathrm{Mn} > \mathrm{Mg}$$

irrespective of the nature of the ligands involved, and remark that "although it is not clear what determines the order of metals in the series, it is worth noting that metals forming $dsp_2$ bonds ($\mathrm{Cu^{II}}$ and $\mathrm{Pd^{II}}$) head the list". Although our own programme of experimental work is incomplete, it appears desirable to indicate some of our conclusions in this field, since they extend the observations of Mellor and Maley and render to some extent more intelligible the order of decreasing stability found experimentally.



The numbers give the value of $n$ in log $k_n$ for: ●, ammonia; ○, ethylene diammine; ×, propylene diammine; ◑, salicylaldehyde

If published data[2] on the successive stability constants of divalent ions of the first transition series are plotted against their atomic number (see graph), it is seen that the stability of complexes increases steadily to reach a maximum at copper whether the ligands be ammonia, ethylene diammine, propylene diammine or salicylaldehyde. The reluctance of copper to exceed a co-ordination number of 4 is shown by the low value of $k_5$ for the pentammino-, and $k_3$ for the tris-ethylenediammino-complexes. All zinc complexes are markedly less stable than those of $\mathrm{Cu^{II}}$, and it is perhaps significant that the $M$-shell is completely filled in $\mathrm{Zn^{II}}$, whereas the attachment of six groups through $d_2sp_3$ or $dsp_2$ orbitals (involving resonance) is possible throughout the sequence $\mathrm{Ca^{II}}$ to $\mathrm{Cu^{II}}$. A similar trend of stabilities can be noted in the second transition series with $\mathrm{Pd^{II}} > \mathrm{Cd^{II}}$, but the interposition of $\mathrm{Ag^{II}}$ (which forms complexes isomorphous with those of $\mathrm{Cu^{II}}$) can as yet be only inferred. In the third transition series, the order of stability is certainly $\mathrm{Pt^{II}} > \mathrm{Hg^{II}}$ and $\mathrm{Pb^{II}}$.

Published data on the *absolute* stability of complexes are limited so far to those already quoted. Yet it is obvious that the formation of an inner complex represented by the equation

$$M^{n+} + n\,\mathrm{H}R \rightleftharpoons MR_n + n\mathrm{H}^+$$

involves essentially a competition between (hydrated) protons and metal cations for the anion of the reagent forming the complex: the more stable the complex, the lower the $p$H at which it can persist, and *vice versa*. (It is, of course, implicit that any ligand displaces an equivalent number of water molecules from the hydrated cation; for example, ammonia or pyridine displace one; diammine, salicylaldehyde or dithizone displace two, etc.) It can be shown that the $p$H for 50 per cent precipitation (or 50 per cent extraction of metal complexes for a constant excess of reagent) is a measure of their relative stability. Such data, with figures for the $p$H of incipient precipitation of metal quinaldinates and, for comparison, the stability constants of salicylaldehyde complexes are collected in the accompanying table and confirm the sequences of stability already noted.

| Metal | 'Oxine'; $p$H for 50% precipitation[3] | 'Dithizone'; $p$H for 50% extraction with carbon tetrachloride[9] | Quinaldinic acid; $p$H for incipient precipitation[4] | Salicylaldehyde; log $k_1k_2$ in aqueous dioxane[1,2] |
|---|---|---|---|---|
| Mn | 4·8 | ∼9 | — | 6·8 |
| Fe | — | 5·6 | — | 7·6 |
| Co | 3·2 | 4·9 | 3·9 | 8·3 |
| Ni | 3·2 | 3·0 | 3·9 | 9·2 |
| Cu | 2·3 | 1·0 | 0·5 | 13·3 |
| Zn | 3·1 | 3·2 | 1·85 | 8·1 |
| Pd | — | ∼−2·0 | 2·5 | 14·8 |
| Cd | 4·2 | 4·1 | 3·2 | 7·8 |
| Pt | — | ∼−2·0 | — | — |
| Hg | — | ∼−2·0 | 0·2 | 6·8 |
| Pb | 5·2 | 5·5 | 3·6 | 9·1 |

It is worth noting that among the divalent cations of the first transition series, copper alone is precipitated by 5:7-dibrom-8-hydroxyquinoline in normal acid[5], and similar examples of the outstanding stability of cupric complexes are commonplaces of analytical chemistry. H. Fischer[6] noted a similar order of stability for complexes with α-nitroso-β-naphthol, β-nitroso-α-naphthol and diphenyl carbazone, though the positions of cobalt and nickel were sometimes interchanged.

It must be emphasized that the order may be radically changed if the divalency of any of the participants is altered. Thus the selectivity of nitrosonaphthols as reagents for cobalt depends on their capacity to oxidize it and form a complex of trivalent cobalt far stabler than the corresponding complexes of divalent iron and nickel (or cobalt). That divalent copper, palladium (and trivalent iron) interfere with the cobalt test[7] shows that their complexes are comparable in stability even with those of trivalent cobalt. Derangement of the 'natural' order of stability may also arise from steric and other factors. Thus, copper forms normal 1 : 2 complexes with M-methyl- and NN′-diethyl-ethylenediammine but cannot do so with N-methyl (or ethyl)-N′-diethyl-ethylenediammine[8]; and trivalent gallium, indium and thallium, but not aluminium, will give insoluble 1 : 3 complexes with 2-methyl-8-hydroxyquinoline and similar reagents[9]. We shall present elsewhere our observations with sterically hindered ligands such as α-methyl- and α : α′-dimethyl-*o*-phenanthroline.

The stability of complexes formed by any one ligand, for example, ammonia, with a series of metals may be expected to increase with the electronegativity of the metal concerned. Though reliable values for the transition elements are not yet available, it is of interest to record that a plot of instability constants (log $k_n$) against the second ionization potential (corresponding to the change $M \rightarrow M^{++} + 2e$ for the metal concerned) is approximately linear from manganese to copper, points for zinc lying somewhat off the curves. Thence, or less readily from the accompanying graph, it can be seen that the successive increments in stability in passing from manganese to copper complexes are of much the same order whether water is replaced by two molecules of ammonia, or one of salicylaldehyde or a diammine. When any one metal is considered, the gain in configurational entropy consequent upon ring formation is strikingly demonstrated by the high relative stability of the latter complexes.

Whereas it seems reasonably certain that the most stable complexes are always formed by elements terminating the transition series, and probable that the same 'natural' order of stability is preserved throughout each series, the acceptance of a unique order of stability operating throughout the Periodic Table must wait upon more extensive quantitative measurements with more varied types of ligands and upon a wider range of metals. Quantitative studies on chromous complexes should prove of particular interest.

[1] Mellor, D. P., and Maley, L., *Nature*, **159**, 370 (1947).
[2] Mellor, D. P., and Maley, L., *Nature*, **161**, 436 (1948).
[3] Goto, H., *J. Chem. Soc. Japan*, **54**, 725 (1933); **56**, 314 (1935).
[4] Flagg, J. F., and McClure, F. T., *J. Amer. Chem. Soc.*, **65**, 2346 (1943).
[5] Berg, R., "Die analytische Verwendung von Oxin".
[6] Fischer, H., *Mikrochemie*, **30**, 38 (1942).
[7] Feigl, F., "Spot Tests", 110 (3rd Eng. edit., 1947).
[8] Pfeiffer, P., and Glaser, H., *J. Pract. Chem.*, **151**, 134 (1938).
[9] Irving *et al.* (unpublished work).

# FIRST INTERNATIONAL CONGRESS ON RHEOLOGY

SOON after the end of the War, the Committee of the British Rheologists' Club approached rheologists in the Netherlands about the possibility of holding an International Rheological Congress in Holland. Dutch rheologists welcomed the suggestion and set up a Committee to organise the Congress (see *Nature* of January 17, 1948, p. 104).

Shortly afterwards, the International Council of Scientific Unions appointed a Joint Committee on Rheology which held its first meeting in London in September 1947. The honorary secretary, Prof. J. M. Burgers, was taking a leading part in the organisation of the Congress, and it was agreed that the plans for the Congress should be made in close co-operation with the Joint Committee, the second annual meeting of which would also be held at the same date and place as the Congress itself. The Congress was held at Scheveningen during September 20–25.

The technical business of the Congress was divided into two parts: (1) general lectures given by invitation of the Committee; (2) shorter communications submitted by members. The latter part was arranged to run in three concurrent programmes, though the subject-matter was grouped in four categories: (*a*) theoretical problems; (*b*) experimental methods; (*c*) rheological properties of various systems; (*d*) biological systems.

The official languages of the Conference were English and French, the Dutch members showing a remarkable proficiency in the English language.

There was also a general discussion on nomenclature introduced in a general lecture by Prof. J. M. Burgers, who also presented a communication from the International Joint Committee. The Joint Committee had instructed two of its members, Prof. J. M. Burgers and Dr. G. W. Scott Blair, to draw up a report on nomenclature based on the various wartime publications of the British Rheologists' Club and of Dutch rheological organisations. Although developed entirely independently of one another, these reports had been found to have very much in common.

Prof. Burgers also summarized in his address the general scope of the work which the Congress was about to undertake.

The general lectures covered a wide field of rheology. Prof. F. Eirich, of the Polytechnic Institute of Brooklyn, N.Y., dealt with experimental methods in rheology, discussing the relative merits of different types of viscometers and rheometers for industrial and academic problems. Prof. C. Sadron, of the University of Strasbourg, spoke on the viscosity of dilute solutions of macromolecules, with special reference to molecular shape and orientation. This lecture was particularly valuable in drawing together information from Dutch, American, British and French sources, and in presenting a composite picture of the complex problems of viscosity-concentration relations.

Dr. M. Reiner, of the Technical College, Haifa, spoke on rheological relations in complex systems, outlining first the applications of the classical theories of elasticity and hydrodynamics, and then proceeding to discuss how the classical rheological coefficients vary with structural changes in the material and how various groupings of elastic and viscous elements are linked together to account for the behaviour of complex systems. Dr. K. Weissenberg, of the British Rayon Research Association, Manchester, also spoke on rheology of abnormal systems, developing a comprehensive scheme by which all macroscopic aspects of rheological behaviour can be dealt with whether previously regarded as 'normal' (that is, conforming to some established theory or convention) or as 'abnormal'. The scheme is based on a general theory of transformation for defining invariant rheological parameters. The lecture was ably illustrated by experiments.

Dr. G. W. Scott Blair (University of Reading) discussed psychophysical aspects of rheology, and the relationship between physical measurements and subjective judgments of rheological conditions as made by craftsmen in industry, and explored the possibilities of applying multiple factorial analysis to data from batteries of empirical rheological tests. Prof. A. L. Copley (New York University) spoke on biological problems in rheology, dealing especially with rheological problems of protoplasm, of cellular coats and intercellular substances, and on the rheology