

fast counters the positive-ion sheath causes no secondary emission on arrival at the cathode, is, of course, unaffected by the above results.

J. D. CRAGGS
A. A. JAFFE

High-Voltage Laboratory,
Research Department,
Metropolitan-Vickers Electrical Co., Ltd.,
Manchester, 17.
Jan. 6.

- ¹ Trost, A., *Z. Phys.*, **105**, 399 (1937).
² Korff, S. A., and Present, R. D., *Phys. Rev.*, **65**, 274 (1944).
³ May, A. N., *Rep. Prog. Phys.*, **5**, 390 (1938).
⁴ Stever, H. G., *Phys. Rev.*, **61**, 38 (1942).
⁵ Wilkening, M. H., and Kanne, W. R., *Phys. Rev.*, **62**, 534 (1942).
⁶ Ramsey, W. E., *Phys. Rev.*, **61**, 96 (1942).
⁷ Curran, S. C., and Strothers, J. E., *Proc. Camb. Phil. Soc.*, **35**, 654 (1939).
⁸ Hill, J. M., and Dunworth, J. V., *Nature*, **158**, 833 (1946).
⁹ Korff, S. A., "Electron and Nuclear Counters" (Van Nostrand, New York, 1946).

Stability Constants of Internal Complexes

APART from the results of a series of studies dealing with complexes of copper, little is known of the stability of internal complexes. Calvin and his collaborators¹ have found wide variation in the stability of complexes of copper formed from a series of β diketones and *o*-hydroxy-aromatic aldehydes. It is a matter of interest to determine whether a similar wide variation of stability occurs with complexes formed by the co-ordination of a series of metals with one chelating molecule. For this reason and also because stability constants may eventually help to throw some light on the inactivation of essential trace metals in biological systems², we have begun an investigation of complexes formed by a variety of metals.

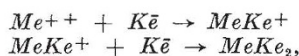
Working in the first instance with 50 per cent water - 50 per cent dioxane solutions and using substantially the method employed by Calvin and Wilson¹, we have obtained the following values (see

TABLE 1

Metal	Radius of metal*	Log K_1	Log K_2	Log K_{av}
Pd	1.32 A.	7.74	7.03	7.39
Cu	1.32	7.40	5.91	6.65
Ni	1.39	5.22	3.97	4.59
Pb	1.46	5.06	4.04	4.55
Co	1.32	4.67	3.63	4.15
Zn	1.31	4.50	3.90	4.05
Cd	1.48	4.62	3.14	3.88
Mg	1.40	3.69	3.11	3.40

* The values quoted in this column are tetrahedral or square equivalent radii taken from "The Nature of the Chemical Bond" by L. Pauling (Cornell Univ. Press, 1939).

Table 1) for the stability constants of complexes formed by a series of bivalent metal ions with salicylaldehyde. The reactions involved are



where $K\bar{e}$ represents the bidentate chelate minus a hydrogen ion. K_1 and K_2 , the equilibrium constants for the two successive steps, are related to K_{av} as follows:

$$(K_{av})^2 = K_1 \cdot K_2 = \frac{[MeKe_2]}{[Me^{++}][K\bar{e}]^2}.$$

Preliminary work with other chelating substances such as glycine and oxine shows that the stability

constants of the metal complexes fall in much the same order as with salicylaldehyde, except that occasionally the position of neighbouring metals is reversed. Not enough types of chelate molecules have yet been studied to say whether this similarity of order is general. Attempts to obtain values of K_{av} for salicylaldehyde complexes in water by a process of extrapolation, using values obtained with water-dioxane mixtures containing progressively less than 50 per cent dioxane, were not satisfactory owing to the fact that even in mixtures containing as little as 10 per cent dioxane the solubility was too low.

However, by using acetylacetone as the chelating substance, it was found practicable to work with water solutions and thus to observe the effect of change of solvent on the magnitude of K_1 , K_2 and K_{av} . The following values were obtained for nickel acetylacetone in different solvents.

TABLE 2

Solvent	K_1	K_2	K_{av}
50% dioxane	6.82	5.24	6.03
20% " "	6.12	4.79	5.46
Water	5.92	4.57	5.25

It is not yet clear what factor or factors determine the order of the metals in Table 1. Electronegativity of the metal might be expected to play some part. If this were so and if electronegativity is accurately defined by the relation recently deduced by Gordy³, we should expect to find a correlation between the covalent radii of bivalent metals and the stability of the complexes formed by them. From Table 1 it can be seen that there is no simple relation between these two constants.

D. P. MELLOR
L. MALEY

Department of Chemistry,
University of Sydney.
Jan. 10.

¹ Calvin, M., and Wilson, K. W., *J. Amer. Chem. Soc.*, **67**, 2003 (1945).
Duffield, R. B., and Calvin, M., *J. Amer. Chem. Soc.*, **68**, 557 (1946).
Calvin, M., and Bailes, R. H., *J. Amer. Chem. Soc.*, **68**, 949 (1946).

² Albert, A., *Med. J. Aust.*, **1**, 245 (1944); other publications in the press.

³ Gordy, W., *Phys. Rev.*, **69**, 604 (1946).

Preparation of Thin Specimen Films

A FILM of cellulose nitrate or a similar material is laid on a water surface and transferred to a specimen holder. A very thin layer of beryllium or aluminium is then deposited on the film from the vapour phase, after which the cellulose nitrate is dissolved away. Only the metal film then remains, and its lack of visible structure can be checked by photographing in the electron microscope. The durability and resistance of the layer to chemical attack are very high. A matter of great importance in the study of specimens in which completely opaque particles occur on the film is that the metal film readily conducts away absorbed energy. With such particles, however, films of cellulose acetate or similar materials are very easily broken. Beryllium and aluminium films of as little as 20 A. thickness (diameter 100 μ), and also aluminium films 12 A. in thickness, have been prepared by this procedure.

Because of the absorption being slight in this film, it is possible to make a closer study of minute