

Some Relationships among the Stabilities of Metal Complexes

HARRY IRVING and HAZEL ROSSOTTI

*Inorganic Chemistry Laboratory, Oxford, England and Department of Inorganic Chemistry,
the Royal Institute of Technology, Stockholm 70, Sweden*

The stability constant, K_{ML} , of a first (1:1) metal-ligand complex, ML, can be related to the stability constant of the corresponding proton-ligand complex, HL, and to the partial molar free energies of the various species in solution. The relationship, (6), which is applicable both in water and in mixed aqueous-organic solvents, forms a basis for discussing the linear relationships which have been observed between the following terms:

(i) $\log K_{ML}$ and $\log K_{HL}$, for complexes of one metal ion with a series of ligands, (8).

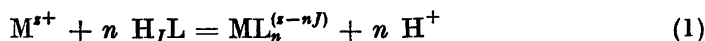
(ii) $\log K_{YL}$ and $\log K_{ZL}$, for complexes of two metal ions, Y and Z, with a series of ligands, (12).

(iii) $\log K_{MP}$ and $\log K_{MQ}$, for complexes of two ligands, P and Q, with a series of metal ions (13).

The relationships are illustrated using a wide variety of experimental data. Special reference is made to the disturbing effects of steric hindrance, and of differences in the co-ordinating power of the donor atoms in a chelating ligand. The variation of $\log K_{HL}$ and $\log K_{ML}$ with the organic content of a mixed solvent is also discussed.

The approach may be of use in analytical chemistry for predicting approximate values of stability constants, and for choosing suitable organic reagents for metal ions.

Many complexes, $ML_n^{(s-n)+}$ derived from a metal ion, M^{s+} , and an organic reagent H_JL , are of analytical importance. Any discussion of problems of theoretical analytical chemistry, such as the sensitivity or specificity of spot-tests, must take into account both the specific properties of the complex $ML_n^{(s-n)+}$ (e. g. its absorption spectrum, solubility in water and in organic solvents, etc.) and the position of equilibrium in the reaction



by which it is produced^{1,2}.

In this connection it is desirable to know how the equilibrium constant of equation (1) is affected by changes in the metal M, *e. g.* by co-ordination of groups other than L, or by replacing M by a different metal. Can such changes be correlated with independently measurable parameters such as ionisation potential, ionic radius, electronic structure or electronegativity, and could they be predicted theoretically? It is also of interest to know how the equilibrium constant is affected when, for the same metal M, changes are made in the structure of the ligand L, and whether these effects can be correlated with concomitant changes in the acid dissociation constants of the reagent H_7L and in the stereochemistry of the complex system. Finally, it is important to consider the effects on equilibrium in each of these cases when an aqueous-organic mixed solvent replaces water as the reaction medium.

In the last ten years, many stability constants of complexes formed between metal ions and organic ligands have been measured, and numerous qualitative and semi-quantitative relationships between the stability of the complex and of the properties of the metal ion and of the ligand have been discussed (*e. g.* ³⁻¹²). A number of authors have, for example, reported empirical relationships between dissociation constants of reagents, and the stability constants of complexes formed by the same metal ion with various ligands ^{3,15-19}. These relationships are by no means generally valid, but are usually only applicable to very limited series of closely related ligands. This paper indicates under what conditions relationships of this type are to be expected from considerations of the free energy changes which occur on complex formation, and suggests other types of relationships that may also exist. These conclusions have been tested on stability constants of metal oxinates and similar complexes (published elsewhere ¹⁹) and on data in the literature; in favourable cases the relationships may be used to predict stability constants of complexes which have not yet been studied experimentally.

GENERAL CONSIDERATIONS

Limiting the discussion in the first instance to the first (1:1) metal-ligand and proton-ligand complexes, ML and HL respectively, the equilibrium constant for reaction (1) can be written in the form

$$K = [ML][H]/[M][HL] = {}^cK_{ML} / {}^cK_{HL} \quad (2)$$

where the stoichiometric stability constants are defined by ${}^cK_{ML} = [ML]/[M][L]$ and ${}^cK_{HL} = [HL]/[L][H]$ and charges are omitted, here and elsewhere, for generality. If ${}^cK_{ML}$ and ${}^cK_{HL}$ are expressed in litres/mole, and if, for each species, S, the partial molar free energy is denoted \bar{G}_S^o , and the activity coefficient referred to the hypothetical one molar standard state is designated y_S , the following relationship is exact

$$\ln {}^cK_{ML} = \ln {}^cK_{HL} + \frac{1}{RT} (\bar{G}_M^o - \bar{G}_{ML}^o - \bar{G}_H^o + \bar{G}_{HL}^o) + \ln (y_M y_{HL} / y_{ML} y_H) \quad (3)$$

Many organic reagents and their metal complexes are very sparingly soluble in water, and stability constants have often been measured in mixed aqueous-

organic solvents. Equation (3), which refers only to aqueous solution, must therefore be extended. Using heavy (*Clarendon*) type to denote factors which refer to a mixed aqueous-organic solvent, the exact equation corresponding to (3) is

$$\ln {}^c K_{ML} = \ln {}^c K_{HL} + \frac{1}{RT} (\bar{G}_M^\circ - \bar{G}_{ML}^\circ - \bar{G}_H^\circ + \bar{G}_{HL}^\circ) + \ln (y_M y_{HL} / y_{ML} y_H) \quad (3a)$$

\bar{G}_S° and \bar{G}_S° are related by the expression

$$\bar{G}_S^\circ - \bar{G}_S^\circ = \bar{G}_{S(\text{transfer})}^\circ = RT \ln y_{S(o)} \quad (4)$$

where $\bar{G}_{S(\text{transfer})}^\circ$ is the partial molar free energy of transfer of the solute species, S, at infinite dilution, from water to the binary mixed solvent, and $y_{S(o)}$ is the activity coefficient of the species S, at infinite dilution in the mixed solvent, referred to infinite dilution in water; thus $\log y_{S(o)}$ represents the "primary medium effect" defined by Owen²⁰, *cf.*²¹. The relationship

$$\bar{G}_{S(\text{transfer})}^\circ = n_x t_s \quad (5)$$

where n_x is the molar fraction of the organic component of the mixed solvent, and t_s is a constant for each combination of solute species and organic solvent, has been shown to hold for a number of solutes in water-methanol and water-ethanol mixtures²²⁻²⁴. If equation (5) is valid for each species in solution, the stoichiometric stability constants ${}^c K_{ML}$ and ${}^c K_{HL}$ measured in a mixed solvent will be related by the following equation

$$\ln {}^c K_{ML} = \ln {}^c K_{HL} + \frac{1}{RT} \left\{ \bar{G}_M^\circ - \bar{G}_{ML}^\circ - \bar{G}_H^\circ + \bar{G}_{HL}^\circ + n_x (t_M - t_{ML} - t_H + t_{HL}) \right\} + \ln (y_M y_{HL} / y_{ML} y_H) \quad (6)$$

Since the activity coefficients y_s are referred to infinite dilution in a particular mixed solvent, the term $(\log y'_s - \log y_s)$ represents Owen's "secondary medium effect"²⁰ *cf.*²¹.

When the solvent is pure water, $n_x = 0$, ${}^c K_{ML} = {}^c K_{ML}$, ${}^c K_{HL} = {}^c K_{HL}$, $y_s = y_s$ and equation (6) reduces to (3). For thermodynamic stability constants ${}^T K_{ML}$ and ${}^T K_{HL}$ measured in water, the equation may be further simplified to

$$\ln {}^T K_{ML} = \ln {}^T K_{HL} + \frac{1}{RT} (\bar{G}_M^\circ - \bar{G}_{ML}^\circ - \bar{G}_H^\circ + \bar{G}_{HL}^\circ) \quad (7)$$

which was given previously by Duncan²⁵.

Since $\bar{G}_H^\circ = 0$, by definition, and values of \bar{G}_M° are tabulated²⁶, equation (7) may be used to calculate values of $(\bar{G}_{HL}^\circ - \bar{G}_{ML}^\circ)$, which will be related to the properties of the metal ion and the ligand. For example, the value of \bar{G}_{ML}° would be decreased by an increase in the ionisation potential of the metal and, unless steric factors are involved, by a decrease in the radius of the metal ion. It would also depend on the co-ordination number and stereochemistry of the metal ion, and the possibility of favourable hybridisation changes accompanying complex formation. Both \bar{G}_{HL}° and \bar{G}_{ML}° would be influenced by the number and nature of the donor atoms in the ligand, by the effective charge on them,

by the size and stereochemistry of the ligand molecule and by changes in entropy and resonance energy accompanying the combination of the ligand with a metal ion or a proton.

As values of ${}^{\tau}K_{ML}$ and ${}^{\tau}K_{HL}$ have only been measured for a few systems, equation (7) must usually be replaced by the more general equation (6). This equation forms a useful basis for discussing the empirical relationships which have been observed among the stabilities of metal complexes. Four types of relationship are discussed below.

Type I. The relationship between the stabilities of metal-ligand, and proton-ligand complexes

Many authors^{3, 15-19} have reported approximately linear relationships between $\log {}^{\circ}K_{ML}$ and $\log {}^{\circ}K_{HL}$ for complexes formed by a given metal ion with a series of closely related ligands. The conditions necessary for a relationship of this type may be deduced from equation (6). By rearrangement

$$\ln {}^{\circ}K_{ML} = \ln {}^{\circ}K_{HL} + A + B \quad (8)$$

where

$$A = \frac{1}{RT} \left\{ -\bar{G}_{ML}^{\circ} + \bar{G}_{HL}^{\circ} + n_x(-t_{ML} + t_{HL}) \right\} - \ln y_{ML} + \ln y_{HL}$$

and

$$B = \frac{1}{RT} \left\{ \bar{G}_M^{\circ} - \bar{G}_H^{\circ} + n_x(t_M - t_H) \right\} - \ln y_H + \ln y_M$$

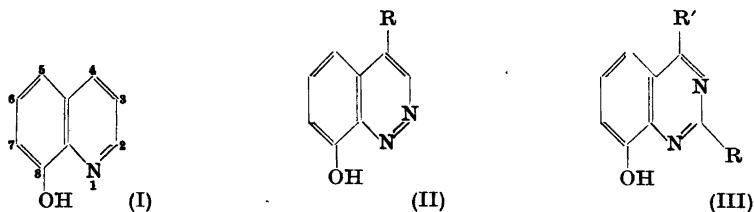
The term B is independent of the nature of the ligand, and is constant for all complexes of a given metal ion, provided that the composition of the solvent, and the ionic strength, are kept constant. Thus, if a plot of $\ln {}^{\circ}K_{ML}$ against $\ln {}^{\circ}K_{HL}$ is found to be a straight line of unit slope, the term A must be constant, (or perhaps negligible compared with the term $\ln {}^{\circ}K_{HL}$). Similarly, if a straight line of non-unit slope is obtained, the term A must itself be a linear function of $\ln {}^{\circ}K_{HL}$. For dilute solutions in pure water ($n_x = 0$), and the value of A will be determined largely by the difference in magnitude of \bar{G}_{ML}° and \bar{G}_{HL}° ; it is unlikely to be negligible in comparison with $\ln {}^{\circ}K_{HL}$, but may possibly vary with change in HL in some comparatively simple manner (*cf.* p. 76).

As would be expected, these conditions only hold for series of reagents of very similar structure. For example, a replot of Calvin and Wilson's data for copper complexes of some derivatives of salicylaldehyde¹⁵ (not reproduced) shows that the relationship

$$\log {}^{\circ}K_{ML} = a \log {}^{\circ}K_{HL} + b \quad (a \text{ and } b \text{ constants}) \quad (9)$$

is approximately applicable only in cases where complex formation would lead to similar changes in resonance energy for each ligand in the series. For these complexes, $a = 1$ and the straight lines are of unit slope. The relationship (9, $a = 1$) is also approximately valid for the iron(III) complexes of some phenol derivatives²⁷. As the substituents in the ligands were either *o*- or *p*- to the hydroxyl group, there was no steric hindrance to complex formation among these reagents. The effect of a substituent adjacent to a donor atom in

the ligand is shown in Fig. 1a, in which $\log {}^cK_{ML}$ is plotted against $\log {}^cK_{HL}$ for magnesium complexes of some derivatives of 8-hydroxyquinoline ("oxine" I) ¹⁹.



There are two types of deviation from the best straight line of unit slope. (i) Major deviations, where $\log {}^cK_{ML}$ is always smaller than predicted. These are invariably associated with reagents having substituents adjacent to the chelating nitrogen atom, and the stabilities of the metal complexes are clearly decreased by steric hindrance. (ii) Minor deviations, in which $\log {}^cK_{ML}$ may be either smaller or larger than predicted from the value of $\log {}^cK_{HL}$. Since each ligand has two donor atoms of differing character, *viz.* oxygen and nitrogen, the magnitude of $\log {}^cK_{HL}$ (which refers only to the dissociation of the O—H group) is not the only factor which influences $\log {}^cK_{ML}$. The observed minor deviations may well be due to differences in the co-ordinating power of the nitrogen atoms in the various ligands (*cf.* ^{2,19,28}).

Plots of $\log {}^cK_{ML}$ against $\log {}^cK_{HL}$ for several other series of complexes are straight lines of non-unit slope, indicating that the term A is an approximately linear function of $\log {}^cK_{HL}$. Data for the copper(II) complexes of some oxine derivatives ¹⁹ are plotted in Fig. 1b, together with the best straight line, which is of slope 2.2. Large deviations from the line are again observed for reagents with substituents adjacent to the chelating nitrogen atom. A similar linear plot ²⁹, of slope 1.3, was obtained for complexes of the uranyl ion, UO_2^{2+} . The importance of steric factors is further emphasised by the fact that plots of $\log {}^cK_{ML}$ against $\log {}^cK_{HL}$, obtained by Van Uitert *et al.* ^{17,30} for complexes of 1,3-diketones with nickel(II) and cerium(III) in 74.5% v/v aqueous dioxan, gave three parallel lines, one for diketones with two terminal aromatic groups, a second for diketones with a single terminal methyl group, and the third for diketones with two terminal methyl groups. The complexes of copper(II) and barium behaved similarly; the slopes were always less than unity, and fell in the order $Cu(II) > Ni(II) > Ba$. The introduction of one or more terminal $-CF_3$ groups had a marked effect in depressing the stability of the copper complexes, somewhat less on the nickel complexes, and very little on the barium complexes. Plots of $\log {}^cK_{ML}$ against $\log {}^cK_{HL}$ for complexes of the silver(I) ion with ammonia and its derivatives also fall on three parallel lines ¹⁶, one for primary (and tertiary heterocyclic) amines and the others for secondary and tertiary aliphatic (or aromatic) amines. An explanation in terms of differences in the degree of hydration of free and co-ordinated amines has been suggested by Trotman-Dickenson ³¹; attention has also been drawn to the possibility of steric hindrance ¹¹.

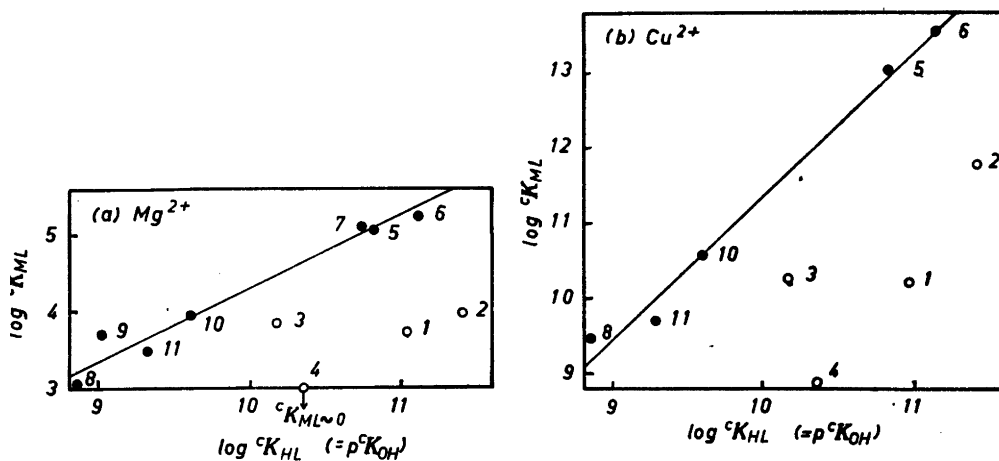


Fig. 1. $\log {}^c K_{ML}$ as a function of $\log {}^c K_{HL}$ for complexes of oxine derivatives¹⁹ in 50 % v/v aqueous dioxan (0.3 M sodium perchlorate) at 20° C. Open points refer to reagents with a substituent adjacent to the chelating nitrogen atom: (1) 2-Methyl-oxine (2) 1,2,3,4-Tetrahydro-10-hydroxyacridine (3) 8-Hydroxy-2,4-dimethylquinazoline (4) 8-Hydroxy-4-methyl-2-phenylquinazoline. Full points refer to other reagents: (5) Oxine (6) 5-Methyl-oxine (7) 6-Methyl-oxine (8) 8-Hydroxycinnoline (9) 8-Hydroxy-4-methylcinnoline (10) 8-Hydroxyquinazoline (11) 5-Hydroxyquinoxaline.

Data for the complexes of magnesium, calcium, strontium, barium and zinc with some aminopolycarboxylic acids indicate that linear plots are only obtained for series of complexes in which the number of rings, and the size of each ring is the same^{18,32}; and different lines are obtained for complexes containing purely aliphatic chelate rings, and those in which a benzenoid system is fused to one of the chelate rings, and those in which a benzenoid system is fused to one of the chelate rings, *cf.*³. For complexes of substituted iminodiacetic acids $X-CH_2-N(CH_2COOH)_2$ ($X = CO_2^-, SO_3^-, PO_3^{3-}$) the slope of each plot is a linear function of the second ionisation potential, I , of the appropriate metal¹⁸. Thus, in this series of complexes ${}^c K_{ML}$ and ${}^c K_{HL}$ are related by the equation

$$\ln {}^c K_{ML} = \ln {}^c K_{HL} (c + dI) + e + B \quad (10)$$

where c , d and e are constants.

It is not difficult to see why the simple relationship (9) is so seldom exactly followed. With monodentate ligands, differences between the size and deformability of the (solvated) proton and the (solvated) metal ion will lead to steric effects (*cf.* the F-strain discussed by Brown and co-workers³³). Superimposed steric effects can arise when the spatial geometry of the free ligand is sufficiently modified by co-ordination to the metal (*cf.* Brown's B-strain³³). With chelating ligands such as the glycinate ion ($L = NH_2CH_2COO^-$), the H—L bond is essentially one between hydrogen and nitrogen, giving the zwitterion $^+NH_3CH_2COO^-$, while in its metal complexes both metal-nitrogen and metal-oxygen bonds are involved. Similar arguments apply to ligands incorporating this basic skeleton within a heterocyclic structure, *e. g.* 8-hydr-

oxyquinoline, 8-hydroxyquinoline (II, R = H), and 8-hydroxyquinazoline (III, R = R' = H). Structural changes in L will change the strength of both metal-oxygen and metal-nitrogen bonds, but not necessarily to the same extent, or even in the same direction^{2,19}. The greatest deviations from equation (9) will be expected with the metals which show the greatest tendency to form strong bonds, and which exhibit the greatest difference in the relative strength of their bonds to different donor atoms.

Type II. The relationship between the stabilities
of complexes of two metal ions with a series
of related ligands

The relationship between metal-ligand, and proton-ligand, complexes of a single metal has been discussed in the previous section, with reference to plots of $\log {}^cK_{ML}$ against $\log {}^cK_{HL}$. The stabilities of complexes formed by two different metal ions, Y and Z, with a series of ligands may be compared in an analogous way by plotting $\log {}^cK_{YL}$ as a function of $\log {}^cK_{ZL}$. Applying equation (6) to each metal ion in turn, and subtracting

$$\ln {}^cK_{YL} = \ln {}^cK_{ZL} + \frac{1}{RT} \{ \bar{G}_Y^\circ - \bar{G}_{YL}^\circ - \bar{G}_Z^\circ + \bar{G}_{ZL}^\circ + n_x(t_Y - t_Z - t_{YL} + t_{ZL}) \} + \ln(y_{ZL}y_Y/y_{YL}y_Z) \quad (11)$$

which can be written in the form

$$\ln {}^cK_{YL} = \ln {}^cK_{ZL} + C + D \quad (12)$$

where
$$C = \frac{1}{RT} \{ -\bar{G}_{YL}^\circ + \bar{G}_{ZL}^\circ + n_x(-t_{YL} + t_{ZL}) \} - \ln y_{YL} + \ln y_{ZL}$$

and
$$D = \frac{1}{RT} \{ \bar{G}_Y^\circ - \bar{G}_Z^\circ + n_x(t_Y - t_Z) \} - \ln y_Z + \ln y_Y$$

Thus equation (12) corresponds to (8), where the symbols Y, Z, C and D now replace M, H, A and B, respectively. Since D is independent of the nature of the ligand, L, the plot of $\ln {}^cK_{YL}$ against $\ln {}^cK_{ZL}$ will be a straight line of unit slope if C is a constant or is negligible compared with $\ln {}^cK_{ZL}$. A straight line of non-unit slope would result if C were a linear function of $\ln {}^cK_{ZL}$. The conditions necessary for a linear relationship between $\log {}^cK_{YL}$ and $\log {}^cK_{ZL}$ are therefore exactly analogous to those necessary for a linear relationship between $\log {}^cK_{ML}$ and $\log {}^cK_{HL}$ (see previous section).

As few stability constants for complexes of two closely related metals with the same group of ligands are available, this relationship cannot be tested thoroughly. However, values of $\log {}^cK_{CuL}$ for fifty six ligands of very varied types are plotted against corresponding values of $\log {}^cK_{NiL}$ in Fig. 2. The predicted behaviour is approximately followed for complexes ranging in stability from ${}^cK_{ML} = 10^{15}$ to $\sim 10^0$. Both monodentate and polydentate ligands have been included and while many of the measurements were made in aqueous

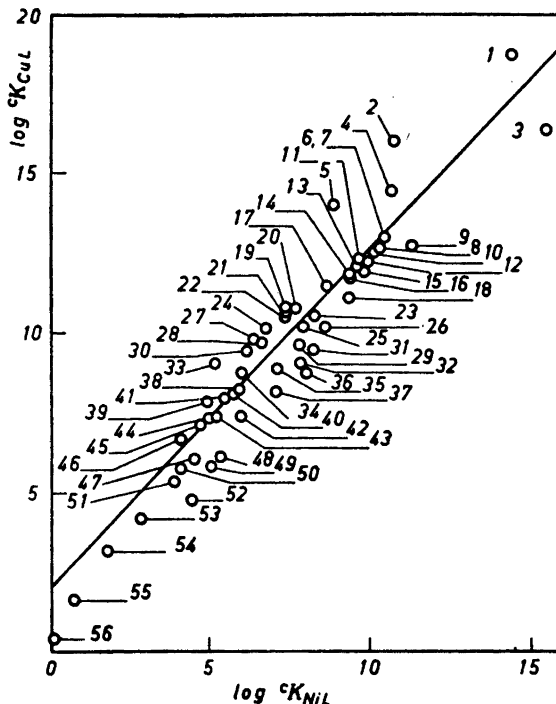


Fig. 2. $\log^{\circ}K_{CuL}$ as a function of $\log^{\circ}K_{NiL}$ for complexes of a wide variety of ligands: (1) β, β', β'' -Triaminotriethylamine, cf.⁴ (2) Diethylenetriamine, cf.⁴ (3) Ethylenediamine-diacetic-dipropionic acid⁵ (4) Tiron (pyrocatechol-3,5-disulphonic acid)²⁴ (5) 1,3-Diaminopropane-2-ammonium ion, cf.⁴ (6) 8-Hydroxyquinoline¹⁹ (7) Dibenzoylmethane²¹ (8) Thenoylbzoylmethane¹⁷ (9) Nitriloacetic acid⁵ (10) Benzoylfuroylmethane¹⁷ (11) $CH_3CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot Si(CH_3)_3$, Ref.¹⁷ (12) Dithenoylmethane¹⁷ (13) Acetylbenzoylmethane¹⁷ (14) Acetylacetone¹⁷ (15) Furoylthenoylmethane¹⁷ (16) Acetylthenoylmethane¹⁷ (17) $(CH_3)_3SiC_2H_4 \cdot CO \cdot CH_2 \cdot CO \cdot C_2H_4 \cdot Si(CH_3)_3$, Ref.¹⁷ (18) 1,2,3-Triaminopropane, cf.⁴ (19) N-Methylethylenediamine²⁸ (20) Ethylenediamine, cf.⁴ (21) 1,2-Diaminopropane, cf.⁴ (22) Iminopropionic acetic acid⁵ (23) Iminodiacetic acid⁵ (24) N-Ethylethylenediamine²⁸ (25) 8-Hydroxy-2,4-dimethylquinazoline¹⁹ (26) 8-Hydroxy-2-methylquinoline¹⁹ (27) 1,3-Diaminopropane, cf.⁴ (28) sym. N,N'-Dimethylethylenediamine²⁸ (29) 5-Hydroxyquinoxaline (30) Iminodipropionic acid⁵ (31) 8-Hydroxycinnoline¹⁹ (32) Folic acid, cf.⁴ (33) N-Propylethylenediamine²⁸ (34) Triethylenetetramine ion, cf.⁴ (35) Aspartic acid, cf.⁴ (36) 1,10-Phenanthroline²⁷ (37) 2,2'-Dipyridyl²⁷ (38) α -Alanine, cf.⁴ (39) Leucine, cf.⁴ (40) Glycine, cf.⁴ (41) Isonicotinic hydrazide²⁵ (42) 2-Methyl-1,10-phenanthroline²⁷ (43) Salicylaldehyde, cf.⁴ (44) Sarcosine, cf.⁴ (45) β -Alanine, cf.⁴ (46) Riboflavin, cf.⁴ (47) Glycyl-glycine, cf.⁴ (48) Oxalate ion, cf.⁴ (49) 2,9-Dimethyl-1,10-phenanthroline²⁷ (50) Malonate ion, cf.⁴ (51) Salicylaldehyde sulphonic acid, cf.⁴ (52) 4-Hydroxypteridine, cf.⁴ (53) Ammonia, cf.⁴ (54) Pyridine, cf.⁴ (55) Acetate ion, cf.⁴ (56) Nitroacetate ion, cf.⁴. The full line is of unit slope.

solution, a number of points refer to water-dioxan mixtures. No attempt has been made to distinguish between points for groups of closely related ligands (e. g. 1,3-diketones or 1,2-diamines), although they generally lie more closely

on linear plots. The line in Fig. 2 has a slope of unity. Divergencies will be due, at least in part, to differences in the preferred geometry of nickel and copper and to the fact that the co-ordination number of (planar) copper does not readily rise above four. That the best straight line through all the points should have a slope greater than unity implies that the difference in stability between the copper and nickel complexes increases with the increasing stability of the complexes.

Closer agreement with the predictions of equation (12) is found for complexes of a pair of metals of greater similarity, *e. g.* strontium and barium, and still better agreement would be expected for a pair of tripositive rare earth ions. At present there are insufficient data to subject equation (12) to really exhaustive tests.

Type III. The relationship between the stabilities of two ligands with a series of metal ions

The stabilities of complexes formed by two ligands, P and Q, with a series of metal ions may conveniently be compared by plotting $\log {}^cK_{MP}$ as a function of $\log {}^cK_{MQ}$. It has previously been found¹⁹ that the experimental points for closely related pairs of ligands sometimes lie approximately on a straight line of unit slope and of intercept ($\log {}^cK_{HP} - \log {}^cK_{HQ}$). The theoretical relationship between $\ln {}^cK_{MP}$ and $\ln {}^cK_{MQ}$ may be derived from equation (6)

$$\begin{aligned} \ln {}^cK_{MP} - \ln {}^cK_{MQ} &= \ln {}^cK_{HP} - \ln {}^cK_{HQ} + \frac{1}{RT} \{-\bar{G}_{MP}^\circ + \bar{G}_{MQ}^\circ + \bar{G}_{HP}^\circ - \bar{G}_{HQ}^\circ + \\ & n_x(-t_{MP} + t_{MQ} + t_{HP} - t_{HQ})\} + \ln (y_{HP}y_{MQ}/y_{MP}y_{HQ}) \quad (13) \\ &= \ln {}^cK_{HP} - \ln {}^cK_{HQ} + E + F + H \end{aligned}$$

where
$$E = \frac{1}{RT} \{(\bar{G}_{MQ}^\circ - \bar{G}_{MP}^\circ) - (\bar{G}_{HQ}^\circ - \bar{G}_{HP}^\circ)\}$$

$$F = \frac{n_x}{RT} \{(t_{MQ} - t_{MP}) - (t_{HQ} - t_{HP})\}$$

and
$$H = \ln y_{MQ}/y_{MP} - \ln y_{HQ}/y_{HP}$$

Thus if the experimental data conform to the linear relationship

$$\log {}^cK_{MP} = \log {}^cK_{MQ} + (\log {}^cK_{HP} - \log {}^cK_{HQ}) \quad (14)$$

the term ($E + F + H$) must be negligible compared with the other terms in equation (13). If $\bar{G}_{MQ}^\circ > \bar{G}_{MP}^\circ$ it is very probable that $\bar{G}_{HP}^\circ > \bar{G}_{HQ}^\circ$; hence the value of E , which depends on the difference between two terms which express the magnitude of these changes, will probably be insignificant in comparison with $\ln {}^cK_{MQ}$ and will tend rapidly to zero as P and Q approach each other in character. The same argument can be applied to the algebraic sum of the transfer coefficients, t_s , which determine the value of F , and to the activity coefficients included in the term H .

It is therefore not surprising that the relationship (14) is often valid for, though restricted to, very similar pairs of ligands. Values of $\log {}^cK_{MP}$ for

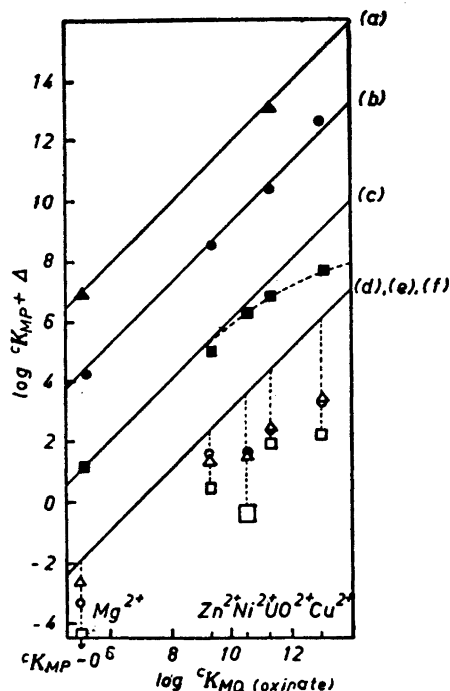


Fig. 3. $\log K_{MP}$ for complexes of oxine derivatives as a function of $\log K_{MQ}$ for the corresponding oxinates. The constants were obtained¹⁹ in 50% v/v aqueous dioxan (0.3 M sodium perchlorate) at 20°C. The ordinates refer to complexes of: (a) 6-Methyl-oxine, $\Delta = 2.0$ (b) 5-Methyl-oxine, $\Delta = -1.0$ (c) 8-Hydroxycinnoline, (II, R = H), $\Delta = -2.0$ (d) 2-Methyl-oxine (open circles), $\Delta = -7.0$ (e) 8-Hydroxy-2,4-dimethylquinazoline (III, R = R' = CH₃, open triangles), $\Delta = -6.3$ (f) 8-Hydroxy-4-methyl-2-phenylquinazoline (III, R = phenyl, R' = CH₃, open squares), $\Delta = -6.5$. The abscissae refer to complexes of oxine. The full lines are of unit slope and of intercept, $(\log K_{HP} - \log K_{HQ})$, predicted by equation (14).

complexes of a number of oxine derivatives¹⁹ are plotted as a function of values of $\log K_{MQ}$ for the corresponding oxinates in Fig. 3. When $\log K_{MP}$ refers to complexes of 5-methyl-oxine (Fig. 3a) or 6-methyl-oxine (Fig. 3b), the experimental points fall closely on the theoretical lines of unit slope and of intercept $(\log K_{HP} - \log K_{HQ})$, as might be expected for reagents which differ only slightly from oxine in their structure and values of pK_{NH} (cf. ¹⁹) and offer no steric hindrance to complex formation. Similar straight lines are also obtained for complexes of magnesium, zinc, nickel(II), copper(II) and uranyl with pairs of reagents chosen from among 5-fluoro-, 5-chloro-, 5-bromo- and 5-methyl-oxine³⁸.

The ordinates of Fig. 3d are values of $\log K_{MP}$ for complexes of 2-methyl-oxine. The experimental points lie from 1 to 3 logarithmic units below the line drawn according to equation (14). This lowering of stability is undoubtedly due to steric hindrance to complex formation. As expected, deviations of the

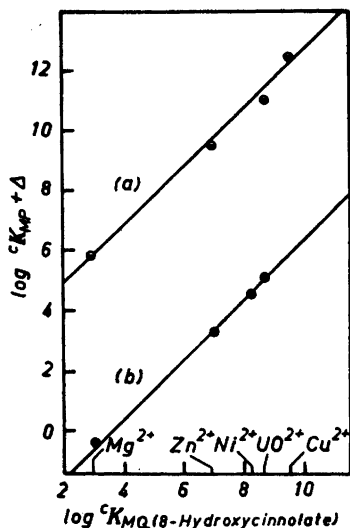


Fig. 4. $\log {}^{\circ}K_{MP}$ for complexes of oxine derivatives as a function of $\log {}^{\circ}K_{MQ}$ for the corresponding complexes of 8-hydroxycinnoline. The constants¹⁹ were obtained in 50 % v/v aqueous dioxan (0.3 M sodium perchlorate) at 20° C. The ordinates refer to complexes of (a) 8-Hydroxyquinazoline (III, R = R' = H), $\Delta = 2.0$ (b) 8-Hydroxy-4-methylcinnoline (II, R = CH₃), $\Delta = -4.0$. The abscissae refer to complexes of 8-hydroxycinnoline (II, R = H). The full lines are of unit slope and of intercept ($\log {}^{\circ}K_{HP} - \log {}^{\circ}K_{HQ}$), predicted by equation (14).

same order of magnitude are obtained for complexes of 8-hydroxy-2,4-dimethylquinazoline (III, R = R' = CH₃; Fig. 3e) and 1,2,3,4-tetrahydro-10-hydroxyacridine (IV; graph²⁹ not reproduced here). When a phenyl group is adjacent to the chelating nitrogen atom (Fig. 3f), there are even greater deviations from the theoretical line, and no complex formation between 8-hydroxy-4-methyl-2-phenylquinazoline (III, R = phenyl, R' = CH₃) and the magnesium ion could be detected.

Values of $\log {}^{\circ}K_{ML}$ for complexes of 8-hydroxycinnoline (II, R = H) form the ordinates in Fig. 3c. The stability constant of the magnesium complex lies on the theoretical line, while that for the copper complex lies well below it. Points for other cations are in intermediate positions. The low value of pK_{NH} of 8-hydroxycinnoline as compared with the value for oxine¹⁹ would be expected to reduce the stability of its copper complex, but to have little effect on the stability of the magnesium complex. Similar plots²⁹ (not reproduced here) are obtained if values of $\log {}^{\circ}K_{MP}$ for complexes of 8-hydroxyquinazoline (III, R = R' = H) and 8-hydroxy-4-methylcinnoline (II, R = CH₃) form the ordinates. Values of $\log {}^{\circ}K_{MP}$ for complexes of both these reagents are plotted against values of $\log {}^{\circ}K_{MQ}$ for the corresponding complexes of 8-hydroxycinnoline in Fig. 4. The experimental points lie much nearer the theoretical line than when the stabilities of the oxinates is made the basis of comparison, doubtless because the variation in pK_{NH} among these reagents is much smaller.

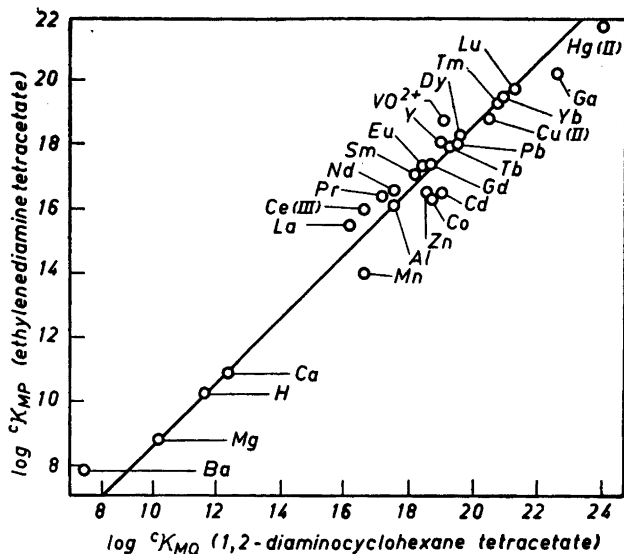
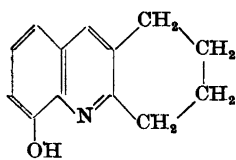
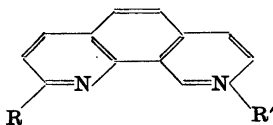


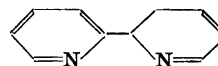
Fig. 5. $\log^{\circ}K_{MP}$ for complexes of ethylenediaminetetraacetic acid as a function of $\log^{\circ}K_{MQ}$ for complexes 1,2-diaminocyclohexanetetraacetic acid. The constants^{39,41} were obtained at 20° C ($\mu = 0.1 M$). All the ions shown are in their usual valency state. The straight line is of unit slope and of intercept, $(\log^{\circ}K_{HP} - \log^{\circ}K_{HQ})$, predicted by equation (14).



(IV)



(V)



(VI)

Recent measurements³⁷ have shown that the 1:1 complexes of the divalent transition metals, manganese, iron, cobalt, nickel, copper and zinc with 1,10-phenanthroline (V, $R = R' = H$; $pK = 4.36$) are consistently stronger than those of the stronger base 2-methyl-1,10-phenanthroline (V, $R = H$, $R' = CH_3$; $pK = 5.42$). On the basis of equation (14) it is possible to calculate the stability constants which would have been expected from the change in basicity, and the instability arising from steric hindrance to complex formation is found to be from 2.5 to 3.5 kcal./mole. For the still less stable complexes of the even more basic reagent 2,9-dimethyl-1,10-phenanthroline (V; $R = R' = CH_3$; $pK = 5.85$) the instability arising from steric factors is 4 to 5.5 kcal./mole. Although 1,10-phenanthroline ("phenan") and 2,2'-dipyridyl (VI; "dipy") are almost identical so far as their mode of chelating is concerned, complexes of the former are always the more stable. A plot of $\log^{\circ}K_{M.dipy}$ against $\log^{\circ}K_{M.phenan}$ (not reproduced) gives a good straight line for the transition metals, but the slope is 0.63

rather than unity; *i. e.* the difference between the stabilities of corresponding complexes of phenanthroline and dipyridyl decreases almost linearly with increasing stability from about 2.2 logarithmic units with manganese to 0.7 with copper. This example shows the limitations of equation (14) and the need for restricting its application to pairs of ligands of the greatest possible similarity.

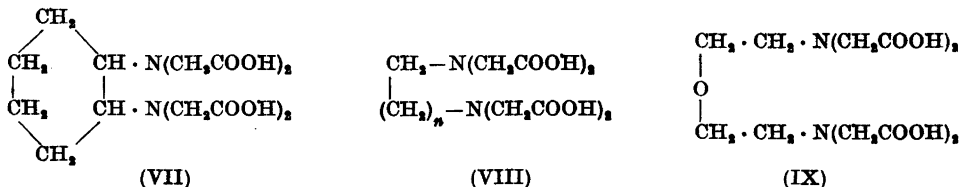


Fig. 5 shows values of $\log {}^c K_{MP}$ for 1:1 complexes of *o*-diaminocyclohexane-tetraacetic acid (VII; $pK = 11.70$) plotted against values of $\log {}^c K_{MQ}$ for the corresponding complexes of ethylenediamine-tetraacetic acid³⁹ (VIII, $n = 1$; "ENTA"; $pK = 10.26$). The straight line shown is of unit slope and of theoretical intercept $\log {}^c K_{HP} - \log {}^c K_{HQ}$. Although the complexes include those of monovalent, divalent and trivalent ions, and ions of both A and B subgroups of the periodic table, the general conformity to equation (14) is quite remarkable considering that the individual complexes differ in stability by as much as a factor of 10^{14} . The fact that values of $\log {}^c K_{ML}$ for ENTA complexes of trivalent rare earth ions do not increase linearly with atomic number has been discussed by Wheelwright *et al.*⁴⁰ who first noted that a break in the curve occurs at gadolinium. From Fig. 5 it would appear that the complexes of VII with lanthanons of atomic number 57 to 62 are less stable than would be predicted from the values of $\log {}^c K_{M.ENTA}$.

For complexes of diaminoethyl ether tetraacetic acid (IX) there is the possibility of co-ordination through the ethereal oxygen atom. Alternatively the 5-atom ring formed by the 1,2-diamine ENTA must be replaced by an 8-membered ring. Now increase of ring-size in the series $A_2N-(CH_2)_n-NA_2$ ($A = -CH_2COOH$) is reflected in a greatly decreasing stability of its alkaline earth complexes⁵. Thus $\log {}^c K_{CaL}$ is 10.59, 7.12, 5.05 and 4.60 for $n = 2, 3, 4$ and 5, respectively. Were the oxygen atom entirely inactive in complex formation, the complexone IX would most closely resemble pentamethylene-tetraacetic acid (VIII, $n = 4$; $pK = 10.58$) for which the stability constant of the calcium complex is only $10^{4.6}$. While this complexone VIII is a very slightly weaker acid than ENTA, the complexone IX ($pK = 9.49$) is a considerably stronger acid, and would therefore be expected to form uniformly weaker complexes. In fact, when values of $\log {}^c K_{MQ}$ for complexes of ENTA are plotted against values for the corresponding complexes of IX (for data *cf.*⁴¹) a straight line of unit slope and of theoretical intercept (not reproduced) passes through or close to points for magnesium, calcium, manganese(II), zinc and copper(II). The large ions barium and cadmium form complexes with IX which are 1.2 and 2.4 logarithmic units more stable than would be expected from the stability of the corresponding ENTA complexes. With these exceptions, all the complexes of IX are, as anticipated, weaker than those with ENTA. The anomalous be-

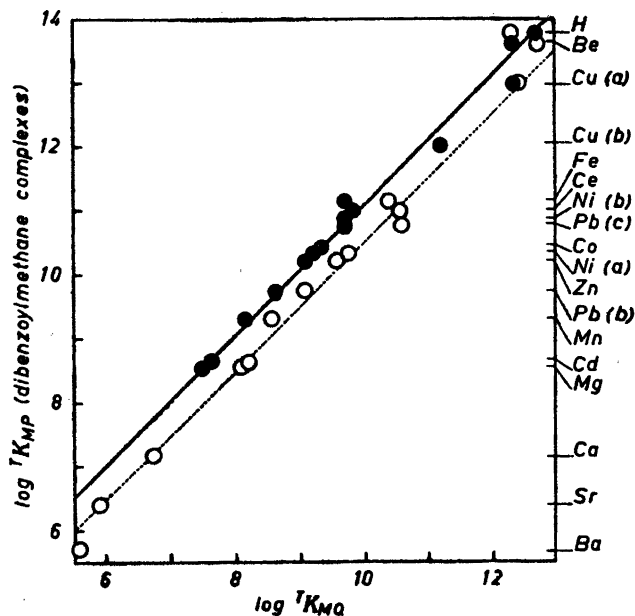


Fig. 6. $\log T K_{MP}$ for complexes of dibenzoylmethane as a function of $\log T K_{MQ}$ for complexes of related 1,3-diketones. The thermodynamic constants were obtained ¹⁷ in 75% v/v aqueous dioxan at 30° C. The ordinates refer to complexes of dibenzoylmethane. The abscissae refer to complexes of acetylacetone (full points and line) and of furoyl-thenoylmethane (open circles and dotted line). The full line is of unit slope and of intercept, $(\log T K_{HP} - \log T K_{HQ})$, predicted by equation (14). The dotted line is the best straight line of unit slope through the open points. The letters (a), (b) and (c) denote chlorides, nitrates and perchlorates respectively; other metals were studied only in the presence of nitrate ions.

haviour of barium can be exploited analytically in a substitution titration of strontium and barium, or in the titration of these alkaline earths and magnesium using Eriochrome Black T as indicator ⁴¹.

Good straight lines are often obtained if values of $\log {}^c K_{MP}$ are plotted against values of $\log {}^c K_{MQ}$ for complexes of pairs of closely related α -diketones. In Fig. 6, complexes of dibenzoylmethane are compared with those of acetylacetone (full circles) and of furoyl-thenoylmethane (open circles). The majority of points for each pair of reagents lie on a straight line of unit slope. However, while the best (full) line for complexes of acetylacetone has the theoretical intercept predicted by equation (14), the best (dotted) line for complexes of furoyl-thenoylmethane has an intercept of 0.6 instead of $\log {}^c K_{MP} - \log {}^c K_{MQ} = 1.45$. Thus all the complexes of the diketone with two heterocyclic end groups are about 0.8 logarithmic unit more stable than expected; similar, but smaller, deviations from predicted behaviour are observed for complexes of other pairs of 1,3-diketones. The effect of different terminal groups of diketones on the stability of their metal complexes has been discussed by Van Uitert *et al.*¹⁷; (cf. p. 76).

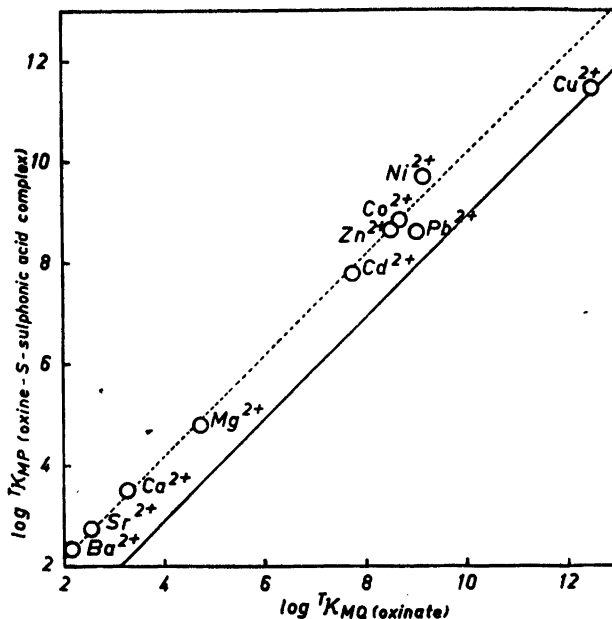


Fig. 7. $\log {}^{\circ}K_{MP}$ for complexes of oxine-5-sulphonic acid as a function of $\log {}^{\circ}K_{MQ}$ for complexes of oxine. The thermodynamic constants were obtained ⁴²⁻⁴⁶ in water at 25° C. The full line is of unit slope and of intercept, $(\log {}^{\circ}K_{HP} - \log {}^{\circ}K_{HQ})$, predicted by equation (14). The dotted line is the best straight line of unit slope through the experimental points.

The relationship (14) is not always valid, even if there is no possibility of steric hindrance and the ligands are very similar (*e. g.* oxine and oxine-5-sulphonic acid). It is well known that the corresponding complexes of these two ligands are of comparable stability, although the values of $\log {}^{\circ}K_{HL}$ ($= pK_{OH}$) for the reagents differ considerably (oxine, $pK_{OH} = 9.81$; oxine-5-sulphonic acid, $pK_{OH} = 8.75$) ^{42,43}. Values of $\log {}^{\circ}K_{MP}$ for complexes of oxine-5-sulphonic acid ⁴⁴ are plotted against values of $\log {}^{\circ}K_{MQ}$ for the corresponding oxinates ^{45,46} in Fig. 7, together with the theoretical (full) line. Although the complexes of oxine-5-sulphonic acid are much more stable than predicted by equation (14), the experimental points for complexes of many of the metal ions lie approximately on a straight line of unit slope (dotted line in Fig. 7). As the terms $(\ln {}^{\circ}K_{HP} - \ln {}^{\circ}K_{HQ})$ and E are constants for a given pair of reagents, this relationship, *viz.*

$$\log {}^{\circ}K_{MP} = \log {}^{\circ}K_{MQ} + \text{constant}$$

will only be obtained if the term

$$F = \frac{1}{RT} \{(\bar{G}_{MQ}^{\circ} - \bar{G}_{MP}^{\circ}) + n_X(t_{MQ} - t_{MP})\} + \ln y_{MQ}/y_{MP}$$

is negligible, or is a constant for complexes of the two ligands with a series of metal ions.

Type IV. The variation of stability with the
composition of the solvent

As many organic reagents and their metal complexes are very sparingly soluble in water, stability constants are often determined in aqueous ethanol or aqueous dioxan and it is of interest to consider how these values would differ from those obtained in water. It has been found^{2,21,47} that values of $\log {}^{\circ}K_{HL}$ for many proton-ligand complexes containing either O—H or N—H groups are approximately linear functions of the molar fraction, n_x , of the organic component of the solvent, at least for low values of n_x . Some plots of this type are shown in Fig. 8.

Now if equation (5) is valid for the species H, L and HL

$$\ln {}^{\circ}K_{HL} - \ln {}^{\circ}K_{HL} = \frac{n_x}{RT} (t_H + t_L - t_{HL}) + \ln \left(\frac{y_H y_L}{y_{HL}} / \frac{y_H y_L}{y_{HL}} \right) \quad (15)$$

and the plot of $\log {}^{\circ}K_{HL}$ against n_x will be a straight line of intercept $\log {}^{\circ}K_{HL}$, provided that the last term in equation (15) is (i) negligible compared with the other terms or (ii) proportional to n_x . The slope of the line is given by

$$d(\log {}^{\circ}K_{HL})/d(n_x) = \frac{1}{2.303RT} (t_H + t_L - t_{HL}) \quad (16i)$$

$$\text{or} \quad d(\log {}^{\circ}K_{HL})/d(n_x) = \frac{1}{2.303RT} (t_H + t_L - t_{HL}) + d_H + d_L - d_{HL} \quad (16ii)$$

for cases (i) and (ii) respectively, where d_s is defined by

$$\ln y_s - \ln y_s = n_x \cdot d_s \quad (17)$$

Fig. 8 shows that the stabilities of complexes containing an O—H link increase with increasing organic content of the solvent, *i. e.* the term $d(\log {}^{\circ}K_{HL})/d(n_x)$ is positive. However, an increase in the organic content of the solvent causes a decrease in the stabilities of proton-ligand complexes containing an N—H link, and for these compounds $d(\log {}^{\circ}K_{HL})/d(n_x)$ is negative. An increase in the organic content of the mixed aqueous-organic solvent results in a decrease in the dielectric constant of the medium. This will increase the ionic interaction between a proton and a negatively charged oxygen atom to a greater extent than the ion-dipole interaction between the proton and the solvent. Thus, as n_x increases, the value of $\ln {}^{\circ}K_{HL}$ should increase for proton-ligand complexes containing O—H bonds. Conversely, an increase in the organic content of the solvent would be expected to increase the ion-dipole forces between a proton and a nitrogen atom in the ligand to a lesser extent than the ion-dipole forces between a proton and the more electronegative donor oxygen atoms of the solvent (*cf.*^{31,52}). A decrease in the value of $\ln {}^{\circ}K_{HL}$ would therefore be expected for complexes containing N—H bonds.

The relationship between n_x and $\ln {}^{\circ}K_{ML}$ for a metal-ligand complex corresponds exactly to equation (16), where M now replaces H. Thus

$$\ln {}^{\circ}K_{ML} - \ln {}^{\circ}K_{ML} = \frac{n_x}{RT} (t_M + t_L - t_{ML}) - \ln \left(\frac{y_M y_L}{y_{ML}} / \frac{y_M y_L}{y_{ML}} \right) \quad (18)$$

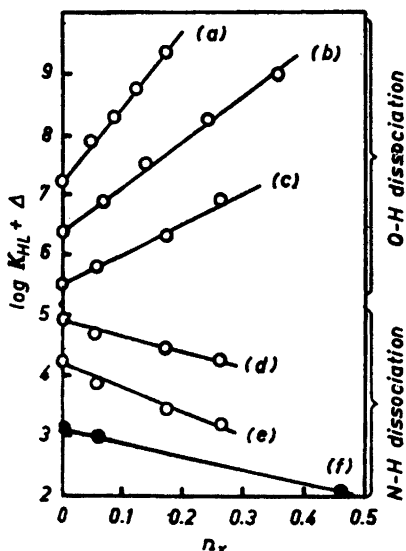


Fig. 8. $\log K_{HL}$ ($= pK$) as a function of the molar fraction, n_x , of the organic content of the solvent. Open and full circles refer to aqueous dioxan and aqueous methanol respectively. (a) to (c); compounds in which an O-H group dissociates: (a) Benzoic acid, $\Delta = 3.0$. Thermodynamic constants⁴⁸ were obtained at 25° C. (b) *m*-Chlorobenzoic acid, $\Delta = 2.5$. Constants were obtained at 25° C and varying ionic strength^{49, 50}. (c) Oxine-5-sulphonic acid, $\Delta = -3.0$. Stoichiometric constants were obtained at 20° C in 0.3 M sodium perchlorate²⁹.

(d) to (f); compounds in which an N-H group dissociates: (d) Oxine-5-sulphonic acid, $\Delta = 1.0$. Stoichiometric constants obtained at 20° C in 0.3 M sodium perchlorate²⁹. (e) Pyridine, $\Delta = -1.0$. Stoichiometric constants obtained at 20° C in 0.3 M sodium perchlorate²⁹. (f) Piperidine, $\Delta = -8.0$. Stoichiometric constants⁵¹ obtained at 25° C and ionic strength 0.1 M.

The conditions, necessary for a linear relationship between $\log {}^c K_{ML}$ and n_x , and the possible values of $d(\log {}^c K_{ML})/d(n_x)$, are analogous to those given above for proton-ligand complexes. Van Uitert *et al.*⁵³ have shown that values of $\log {}^c K_{ML}$ for several acetylacetonates are linear functions of the molar fraction of dioxan in the solvent, and a replot of Maley and Mellor's data⁵⁴ (not reproduced here) shows that a similar relationship exists for the magnesium complex of salicylaldehyde. The stability of these complexes, which all contain O-metal links, is increased by an increase in the organic content of the solvent, i. e. $d(\log {}^c K_{ML})/d(n_x)$ is positive.

Combining equations (15) and (18),

$$\ln {}^c K_{ML} - \ln {}^c K_{ML} = \ln {}^c K_{HL} - \ln {}^c K_{HL} + \frac{n_x}{RT} (t_M - t_{ML} - t_H + t_{HL}) - \ln \left(\frac{y_{ML} y_H}{y_M y_{HL}} \right) \quad (19)$$

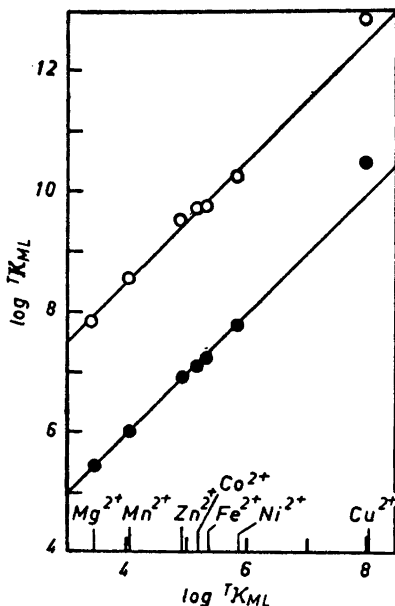


Fig. 9. Thermodynamic stability constants⁵³ of metal acetylacetonates in aqueous dioxan at 30° C. The ordinates refer to values obtained in 75 % (open circles) and 50 % (full circles) v/v aqueous dioxan. The abscissae refer to values obtained in water. The lines are of unit slope and of intercept, $(\log {}^{\circ}K_{HL} - \log {}^{\circ}K_{HL})$, predicted by equation (20).

If the last two terms in equation (19) are negligible compared with the other terms, the equation reduces to

$$\log {}^{\circ}K_{ML} = \log {}^{\circ}K_{ML} + \log {}^{\circ}K_{HL} - \log {}^{\circ}K_{HL} \quad (20)$$

and a plot of $\log {}^{\circ}K_{ML}$ against $\log {}^{\circ}K_{ML}$ for a series of complexes of different metal ions with the same ligand will be a straight line of unit slope and of intercept $(\log {}^{\circ}K_{HL} - \log {}^{\circ}K_{HL})$. This relationship is now found to be applicable to many of the data of Van Uitert *et al.*⁵³ for acetylacetonates in 50 % and 75 % aqueous dioxan, which are shown in Fig. 9. Thus, for acetylacetonate, a change in the composition of the solvent results in parallel changes in $\log {}^{\circ}K_{ML}$ and $\log {}^{\circ}K_{HL}$.

No simple relationship between stability and solvent composition would appear to exist for complexes containing N-metal bonds. An increase in the organic content of the solvent has little influence on the stabilities of certain complexes of ammonia⁵⁵⁻⁵⁹, ethylenediamine⁶⁰⁻⁶², pyridine²⁹ and imidazole⁶³, although the complex $\text{Ag}(\text{en})^+$ is more stable in pure ethanol and *iso*-propyl alcohol than in water⁶⁴.

No one author seems to have investigated the effect of solvent composition on the stabilities of complexes, such as the oxinates, which contain both O-metal and N-metal bonds. By analogy with simpler complexes, an increase in

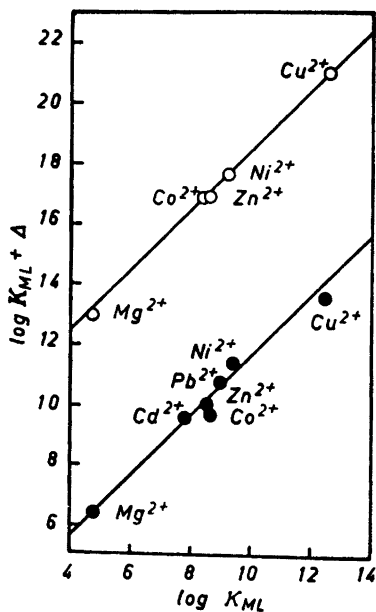


Fig. 10. Stability constants of metal oxinates in aqueous dioxan at 25° C. The ordinates refer to values obtained at varying ionic strengths in 70 % (open circles⁵⁴, $\Delta = 6.0$) and 50 % (full circles⁴⁵, $\Delta = 0$) v/v aqueous dioxan. The abscissae refer to thermodynamic values obtained in water. The straight lines are of unit slope and of intercept, $(\log^{\circ}K_{HL} - \log^{\circ}K_{HL})$, predicted by equation (20).

the organic content of the solvent might be expected to increase the stability of complexes in which the O-metal bond is of predominant importance, but to have less effect on the stability of complexes containing strong N-metal bonds. In Fig. 10, the stabilities of metal oxinates in 50 % and 75 % aqueous dioxan^{54,65} are plotted against the corresponding values obtained in water^{45,46}. Increased dioxan content leads to a marked increase in stability, in approximate agreement with equation (20). Thus for these complexes the last two terms in equation (19) are negligible compared with the other terms, and the variation of $\log^{\circ}K_{ML}$ with the composition of the solvent merely reflects the variation of $\log^{\circ}K_{HL}$. It would be of interest to know if this were also true for other complexes containing both O-metal and N-metal links.

APPLICATIONS

Equation (6) has been used above as a basis for discussing the various empirical linear relationships between the stabilities of related complexes. These plots are of interest from both practical and theoretical considerations.

If the stability constants of some closely related complexes have been measured, the stabilities of other complexes in the same series may be predicted by means of equations (9) and (14). For example, although the stability con-

stants of the zinc, nickel(II) and copper(II) 6-methyl-oxinates could not be measured in 50 % aqueous dioxan, on account of the low solubility of the uncharged complexes¹⁹, approximate values, *viz.* 9.2, 10.4 and 12.9, can be estimated using equation (14) in conjunction with values of the stability constants of the corresponding oxinates, and of $\log {}^{\circ}K_{HL}$ of the two reagents¹⁹ (*cf.* Fig. 3b). The estimation of stability constants of very sparingly soluble complexes is especially important for analytical work involving the separation of metal ions by solvent extraction or selective precipitation².

It has been shown that plots of $\log {}^{\circ}K_{ML}$ against $\log {}^{\circ}K_{HL}$ are often linear for series of very closely related ligands. If divergent lines of different slope are obtained for different metal ions with the same series of ligands (*e. g.* complexes of magnesium, uranyl and copper(II) ions with derivatives of oxine¹⁹) a ligand with a high value of ${}^{\circ}K_{HL}$ will form metal complexes of more varied stability than those formed from a ligand of low ${}^{\circ}K_{HL}$, and will therefore be a more selective reagent for these metal ions. If only very closely related ligands are considered, deviations from linearity in plots of $\log {}^{\circ}K_{ML}$ against $\log {}^{\circ}K_{HL}$, and in plots of the type (14) indicate any tendencies to selective or specific behaviour. Ligands with bulky substituents adjacent to one of the donor atoms form much less stable metal-ligand complexes than would be expected from the stability of the corresponding proton-ligand complexes (*cf.* Fig. 3d, e, f). As this effect depends on the size of the central group, sterically hindered reagents are of use for the analytical separations of certain metal ions (*cf.* the reactions between 2-methyl-oxine and trivalent aluminium, gallium and indium ions,⁶⁶ and refs. therein). Even when no steric hindrance occurs, metal-ligand chelate complexes may deviate appreciably from predicted behaviour (*cf.* Fig. 3c). The formation of a metal chelate involves combination of the metal ion with two or more donor atoms, while the formation of the first proton-ligand complex involves only the atom which has the most basic (donor) character. The observed deviations probably reflect differences in the co-ordinating power of the other donor atoms throughout the series of ligands.

The value of ${}^{\circ}K_{HL}$ for proton-ligand complexes which are very sparingly soluble in water may be estimated by measuring ${}^{\circ}K_{HL}$ in a number of water-ethanol or water-dioxan mixtures; $\log {}^{\circ}K_{HL}$ may then be obtained by linear extrapolation of the plot of $\log {}^{\circ}K_{HL}$ against n_x , to the point $n_x = 0$ (*cf.* equation (15) case (i) or (ii)). The value of ${}^{\circ}K_{ML}$ can be estimated analogously by means of equation (18). If equation (19) is valid, an approximate value of K_{ML} in water may be predicted from the corresponding constant, ${}^{\circ}K_{ML}$, obtained in a mixed solvent, if the proton-ligand stability constants, ${}^{\circ}K_{HL}$ and ${}^{\circ}K_{HL}$, in both solvents are known. Although water has been used as a solvent for most analytical processes in homogeneous systems, a mixed solvent might be of value for absorptiometric work and for certain selective precipitation reactions. Titrations in solvents such as aqueous dioxan, acetic acid, or glycol-isopropyl alcohol mixtures are at present being developed extensively but empirically. Progress would be facilitated if more were known of the effect of change of solvent on the stability of proton-ligand and metal-ligand complexes of all types *cf.*⁶⁷. Equations of the type (15), (18) and (19) might then be used to predict approximate values of stability constants in the appropriate solvent. As O-metal bonds appear to be more influenced by the composition of

the solvent than N-metal bonds, the effect of solvent composition on the stability of chelates containing the O-metal-N link might be an indication of the relative importance of these bonds.

Equation (6) and the foregoing discussion refer to the formation of the first metal-ligand complex, and suggest no correlation of the stabilities of complexes which contain more than one ligand group. Although some authors (*e. g.*¹⁵) have obtained approximate empirical relationships between $\log {}^c K_{HL}$ and $\log K_{av} = \frac{1}{2} \log [ML_2]/[M][L]^2$ it would be expected that in many cases the formation of the complex ML modifies the properties of the metal ion and ligand group to such an extent that any quantitative comparison of equilibrium constants for reactions of the type



would be unjustified.

As so few reliable measurements have been made of the enthalpy and entropy of complex formation, stability constants have been discussed purely in terms of overall changes in free energy. When more precise data become available, a further analysis of heat and entropy changes would be profitable using a similar approach.

Acknowledgements. We would like to thank Dr. James Duncan, University of Melbourne, for stimulating discussion in the early stages of this work, and Professor Lars Gunnar Sillén and Dr. F. J. C. Rossotti, for their helpful comments on the manuscript.

We are also grateful to A. E. R. E., Harwell, and the Swedish Atomic Energy Commission, for financial assistance.

REFERENCES

1. Irving, H. and Williams, R. J. P. *Analyst* **77** (1952) 813.
2. Irving, H. and Rossotti, H. S. *Analyst* **80** (1955) 245.
3. Martell, A. E. and Calvin, M. *Chemistry of the Metal Chelate Compounds*, Prentice Hall Inc. New York 1952.
4. Irving, H. and Williams, R. J. P. *J. Chem. Soc.* **1953** 3192.
5. Irving, H., Williams, R. J. P., Ferrett, D. J. and Williams, A. E. *J. Chem. Soc.* **1954** 3494.
6. Schwarzenbach, G. *Rec. trav. chim. In the press.*
7. Nyholm, R. S. *Rev. Pure Appl. Chem. (Australia)* **4** (1954) 15.
8. Van Uitert, LeG. G. and Fernelius, W. C. *J. Am. Chem. Soc.* **76** (1954) 379.
9. Williams, R. J. P. *J. Chem. Soc.* **1952** 3770.
10. van Eck, C. L. van P. *Rec. trav. chim.* **72** (1953) 50.
11. Bjerrum, J. *Chem. Revs.* **46** (1950) 381.
12. Fyfe, W. S. *J. Chem. Soc.* **1952** 2018.
13. Jørgensen, C. Klixbüll and Bjerrum, J. *Acta Chem. Scand.* **9** (1955) 180.
14. Coulson, C. A. *J. Chem. Soc.* **1955** 2069.
15. Calvin, M. and Wilson, K. W. *J. Am. Chem. Soc.* **67** (1945) 2003.
16. Bruehlman, R. J., and Verhoek, F. H. *J. Am. Chem. Soc.* **70** (1948) 1401.
17. Van Uitert, LeG. G., Fernelius, W. C. and Douglas, B. E. *J. Am. Chem. Soc.* **75** (1953) 457, 2736.
18. Schwarzenbach, G., Ackermann, H. and Ruckstuhl, P. *Helv. Chim. Acta* **32** (1949) 1175.
19. Irving, H. and Rossotti, H. S. *J. Chem. Soc.* **1954** 2910.
20. Owen, B. B. *J. Am. Chem. Soc.* **54** (1932) 1758.
21. Harned, H. S. and Owen, B. B. *Physical Chemistry of Electrolytic Solutions*, Reinhold, 1950.
22. Seatchard, G. *J. Am. Chem. Soc.* **47** (1925) 2098.

23. Åkerlöf, G. *J. Am. Chem. Soc.* **52** (1930) 2353.
24. Butler, J. A. V. and Thomson, D. W. *Proc. Roy. Soc. London A* **141** (1933) 86.
25. Duncan, J. D. *Private communication; cf. discussion to paper by Freiser, H. Analyst* **77** (1952) 830.
26. Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S. and Jaffe, I. *Selected Values of Chemical Thermodynamic Properties*, U. S. Natl. Bur. Standards, 1952.
27. Milburn, R. M. *J. Am. Chem. Soc.* **77** (1955) 2064.
28. Rossotti, H. S. *Rec. trav. chim. In the press.*
29. Rossotti, H. S. *D. Phil. thesis*, Oxford 1954.
30. Van Uitert, LeG. G. and Fernelius, W. C. *J. Am. Chem. Soc.* **75** (1953) 3862.
31. Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949** 1293.
32. Schwarzenbach, G., Willi, A. and Bach, O. *Helv. Chim. Acta.* **30** (1947) 1303.
33. Brown, H. C., Bartholomay, H. and Taylor, M. D. *J. Am. Chem. Soc.* **66** (1944) 441;
34. Brown, H. C. and Taylor, M. D. *J. Am. Chem. Soc.* **66** (1944) 846.
35. Willi, A. and Schwarzenbach, G. *Helv. Chim. Acta* **35** (1952) 2353.
36. Albert, A. *Experimentia* **9** (1953) 370.
37. Irving, H. and Griffiths, J. M. M. *J. Chem. Soc.* **1954** 213.
38. Irving, H. and Mellor, D. M. *J. Chem. Soc. To be published.*
39. Irving, H. and Massy-Beresford, P. *J. Chem. Soc. To be published.*
40. Schwarzenbach, G., Gut, R. and Anderegg, G. *Helv. Chim. Acta* **37** (1954) 937.
41. Wheelwright, E. J., Spedding, F. H. and Schwarzenbach, G. *J. Am. Chem. Soc.* **75** (1953) 4196.
42. Schwarzenbach, G. *Die komplexometrische Titration*, Stuttgart 1955.
43. Näsänen, R., Lumme, P. and Mukula, A.-L. *Acta Chem. Scand.* **5** (1951) 1199.
44. Näsänen, R. and Ekman, A. *Acta Chem. Scand.* **6** (1952) 1384.
45. Näsänen, R. and Uusitalo, E. *Acta Chem. Scand.* **8** (1954) 112.
46. Näsänen, R. *Acta Chem. Scand.* **5** (1951) 1293; **6** (1952) 352; *Suomen Kemistilehti* **32** (1953) 11.
47. Näsänen, R. and Penttinen, U. *Acta Chem. Scand.* **6** (1952) 837.
48. Van Uitert, LeG. G., Haas, C. G., Fernelius, W. C. and Douglas, B. E. *J. Am. Chem. Soc.* **75** (1953) 455.
49. Dunsmore, H. S. and Speakman, J. C. *Trans. Faraday Soc.* **50** (1954) 236.
50. Saxton, B. and Meier, H. F. *J. Am. Chem. Soc.* **56** (1934) 1918.
51. Elliot, J. H. and Kilpatrick, M. *J. Phys. Chem.* **45** (1941) 485.
52. Wynne-Jones, W. F. K. and Salomon, G. *Trans. Faraday Soc.* **34** (1938) 1321.
53. Bell, R. P. and Trotman-Dickenson, A. F. *J. Chem. Soc.* **1949** 1288.
54. Van Uitert, LeG. G., Fernelius, W. C. and Douglas, B. E. *J. Am. Chem. Soc.* **75** (1953) 2739.
55. Maley, M. E. and Mellor, D. P. *Austral. J. Sci. Research A* **2** (1949) 92.
56. Pawelka, F. G. *Z. Electrochem.* **30** (1924) 180.
57. Job, P. *Ann. chim. Paris* **9** (1928) 183.
58. Larrson, E. *Z. physik. Chem. A* **169** (1934) 207.
59. Bjerrum, J. *Diss. Copenhagen* 1941.
60. Van Uitert, LeG. G. and Fernelius, W. C. *J. Am. Chem. Soc.* **76** (1954) 375.
61. Carlson, G. A., McReynolds, J. P. and Verhoek, F. H. *J. Am. Chem. Soc.* **67** (1945) 1334.
62. Bjerrum, J. and Nielsen, E. *Acta Chem. Scand.* **2** (1948) 297.
63. Basolo, F. and Murmann, R. K. *J. Am. Chem. Soc.* **74** (1952) 5243.
64. Li, N. C., White, J. M. and Doody, E. *J. Am. Chem. Soc.* **76** (1954) 6219.
65. Jonassen, H. B., Fagley, T. F., Rolland, C. C. and Yates, P. C. *J. Phys. Chem.* **58** (1954) 286.
66. Johnston, W. B. and Freiser, H. *J. Am. Chem. Soc.* **74** (1952) 5239.
67. Irving, H., Hollinshead, R. G. W. and Harris, G. *Analyst* **80** (1955) 260.
68. Riddick, J. A. *Anal. Chem.* **26** (1954) 77.

Received October 6, 1955.