The Calculation of Formation Curves of Metal Complexes from pH *Titration Curves in Mixed Solvents.*

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The formation curve of a system of metal–ligand complexes can be calculated directly from pH-meter readings during a titration, without knowlege of the hydrogen-ion concentration or activity. Simple general equations, which can be used for all ligands which are conjugate bases to weak acids, are derived, and their application to specific systems illustrated. The method, which is valid both in water and in mixed solvents, gives stoicheiometric stability constants of the metal complexes. Stoicheiometric stability constants of the ligand–proton complexes can also be obtained. The possibility of converting stoicheiometric constants into thermodynamic constants is discussed.

CALVIN and WILSON (*J. Amer. Chem. Soc.*, 1945, **67**, 2003) have shown that pH measurements made during titration with alkali of a solution of a chelating agent, in the presence and in the absence of metal ions, could be used to calculate the free ligand exponent, pL, the degree of formation of the system, $\bar{n}$, and thence the stability constants, K_n, of the metal–ligand complexes present (J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941). Explicit equations have since been deduced at length by Maley and Mellor for acetylacetone, salicylaldehyde, 8-hydroxyquinoline and its 5-sulphonic acid, histidine, and glycine and its analogues (*Austral. J. Sci. Res.*, 1949, *A*, **2**, 92, 579). Albert has dealt with amino-acids with two or more ionising groups (*Biochem. J.*, 1950, **47**, 531; 1952, **50**, 690), Vickery with ethylenediaminetetra-acetic acid (*J.*, 1952, 1895), and other authors have treated, *e.g.*, diamines (J. Bjerrum, *Kgl. Danske Videnskab.*, 1945, **22**, 1773; Carlson, McReynolds, and Verhoek, *J. Amer. Chem. Soc.*, 1945, **67**, 1334), polyamines (Jonassen, LeBlanc, Meibohm, and Rogan, *ibid.*, 1950, **72**, 4968; *J. Phys. Chem.*, 1952, **56**, 16), and complex polyamino-acids (Charabek and Martell, *J. Amer. Chem. Soc.*, 1952, **74**, 5052, 5057, 6021, 6228).

Owing to the variety of symbols employed, the equivalence of the different equations relating $\bar{n}$ and pL with experimentally determinable quantities is not immediately obvious. The following treatment is simpler, shorter, and quite generally applicable.

Charges being omitted for the sake of clarity, the stoicheiometric stability constant of the metal–ligand complex, ML_n, is defined by ${}^{C}K_n = [ML_n]/[ML_{n-1}][L]$, and that of the ligand–proton complex, LH_j, is defined by ${}^{C}K_j^{H} = [LH_j]/[LH_{j-1}][H]$. The overall stability constants are respectively defined as ${}^{C}\beta_n = {}^{C}K_1{}^{C}K_2{}^{C}K_3 \ldots {}^{C}K_n$ and ${}^{C}\beta_j^{H} = {}^{C}K_1^{H}.{}^{C}K_2^{H}. \ldots {}^{C}K_j^{H}$.

Let the total concentration of ligand, metal, and dissociable hydrogen in the system be T_{L}, T_{M}, and T_{H}, respectively. Then for the degree of formation of metal–ligand complexes

$$\bar{n}_{\mathrm{A}} = \frac{\text{total concentration of ligand bound to metal}}{\text{total concentration of metal}}$$

$$= \{T_{\mathrm{L}} - (\text{concentration of ligand not bound to metal})\}/T_{\mathrm{M}} \quad . \quad . \quad (1)$$

Similarily, for ligand–proton complexes,

$$\bar{n}_{\mathrm{A}} = \frac{\text{total concentration of proton bound to ligand}}{\text{total concentration of ligand not bound to metal}}$$

$$= (T_{\mathrm{H}} - [\mathrm{H}])/(T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Whence, from (1),
$$\bar{n} = \{T_{\mathrm{L}} - (T_{\mathrm{H}} - [\mathrm{H}])/\bar{n}_{\mathrm{A}}\}/T_{\mathrm{M}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

But
$$\bar{n}_{\mathrm{A}} = \sum_{j=1}^{j=J} j[\mathrm{LH}_j] \Big/ \sum_{j=0}^{j=J} [\mathrm{LH}_j] = \sum_{j=0}^{j=J} j\,{}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}[\mathrm{H}]^j \Big/ \sum_{j=0}^{j=J} {}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}[\mathrm{H}]^j \quad . \quad . \quad . \quad (4)$$

Finally, $T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}}$ = concentration of ligand not bound to metal

$$= [\mathrm{L}] \sum_{j=0}^{j=J} {}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}[\mathrm{H}]^j \text{ (where } \beta_0 = 1\text{)}$$

and
$$\mathrm{pL} = \log_{10}\left\{ \sum_{j=0}^{j=J} {}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}[\mathrm{H}]^j \Big/ (T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}}) \right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Consider now the value of T_{H} in the general case. If to a concentration of mineral acid E is added sufficient ligand carrying dissociable hydrogen in the form $\mathrm{H}_y\mathrm{L}$ to give a total ligand concentration T_{L}, then the total initial concentration of dissociable proton will be $E + yT_{\mathrm{L}}$. Thus for ligands such as ammonia or ethylenediamine, $y = 0$; for glycine, oxine, acetylacetone, or salicylaldehyde, $y = 1$; for oxalic acid, or the disodium salt of ethylenediaminetetra-acetic acid, $y = 2$. Addition of alkali as sodium hydroxide, to give a sodium-ion concentration, Na (in excess of any due to neutral salt initially present), will reduce the total acidity to a value

$$T_{\mathrm{H}} = E + yT_{\mathrm{L}} - \mathrm{Na} + [\mathrm{OH}] \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where the last term, usually negligible in comparison with the others, appears on account of hydrolysis.

Calculation of $\bar{n}_{\mathrm{A}}$, $\bar{n}$, and pL from equations (2), (3), and (5) requires an accurate knowledge of [H], and two difficulties may arise. (i) If data are taken from a single pH titration curve for mineral acid and ligand, with or without metal present, then in the more acid solutions where Na and [OH] are negligible and where $E \gg T_{\mathrm{L}}$, we have $[\mathrm{H}] \sim E$. The calculated value of $T_{\mathrm{H}} - [\mathrm{H}]$ will then be very sensitive to small errors in [H]. The following procedure largely overcomes this difficulty. Fig. 1, curve 1, shows the titration curve for mineral acid alone, and curve 2 shows that for a mixture of mineral acid and ligand. Points on curve 1 are given by

$$[\mathrm{H}]' = E' + [\mathrm{OH}]' - \mathrm{Na}' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and from equation (2), points on curve 2 are given by

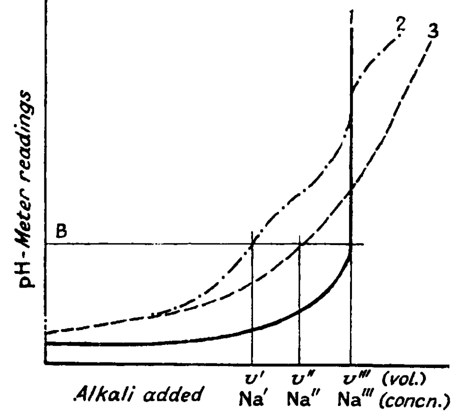
$$[\mathrm{H}]'' = E'' + [\mathrm{OH}]'' - \mathrm{Na}'' + yT_{\mathrm{L}}'' - \bar{n}_{\mathrm{A}}''T_{\mathrm{L}}'' \quad . \quad . \quad . \quad (8)$$

When pH-meter readings are identical for both solutions (ordinate B) $\{\text{H}\}' = \{\text{H}\}''$ and $\{\text{OH}\}' = \{\text{OH}\}''$, and if, further, the solutions have the same ionic strength, $[\text{H}]' = [\text{H}]''$, and $[\text{OH}]' = [\text{OH}]''$. It then follows that

$$\bar{n}_{\text{A}}'' = \{(E'' - E') - (\text{Na}'' - \text{Na}') + yT_{\text{L}}''\}/T_{\text{L}}'' \quad . \quad . \quad . \quad (9)$$

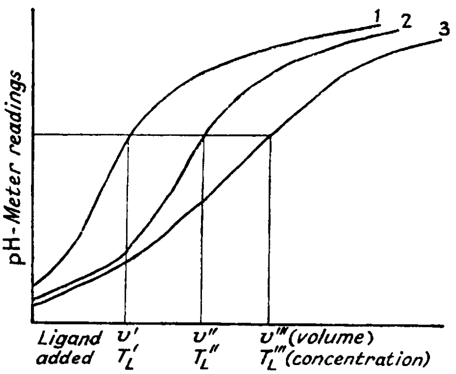
Suppose the initial volumes, V^0, the mineral acid concentrations, E^0, and the total ligand concentrations, $T_{\text{L}}{}^0$, were the same in each titration, and that volumes v', v'' of alkali, concentration N, were added to reach points Na′, Na″.

FIG. 1. *Typical titration curves.*



Curve 1 : *Mineral acid alone. Curve* 2 : *mineral acid and ligand. Curve* 3 : *mineral acid, ligand, and metal. Curves* 2 *and* 3 *are typical for ligands such as oxine. Although the relative disposition of the three curves depends on the nature of the ligands the argument in the text remains unchanged.*

FIG. 2. *Titrations with a solution of the ligand.*



Curves 1 *and* 2 : *mineral acid at two different concentrations. Curve* 3 : *mineral acid and metal ions.*

Then $E'' = V^0E^0/(V^0 + v'')$, $\text{Na}'' = v''N/(V^0 + v'')$, and $T_{\text{L}}'' = V^0T_{\text{L}}{}^0/(V^0 + v'')$. Similar equations can be obtained for E' and Na′. Then from (9),

$$\bar{n}_{\text{A}} = \left\{yT_{\text{L}}{}^0 + \frac{(v' - v'')(N + E^0)}{(V^0 + v')}\right\}\Big/T_{\text{L}}{}^0 \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If, as in the work described in the following paper, $N \gg E^0$, and $V^0 \gg v'$, then,

$$\bar{n}_{\text{A}} = \left\{yT_{\text{L}}{}^0 + \frac{(v' - v'')N}{V^0}\right\}\Big/T_{\text{L}}{}^0 \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

Values of $\bar{n}_{\text{A}}$ may thus be readily obtained from (10) or (10*a*). Although they are calculated from and correspond to particular pH-meter readings rather than to known hydrogen-ion concentrations or activities, such values of $\bar{n}_{\text{A}}$ may be used directly for calculating values of $\bar{n}$ for metal–complex formation as described later (p. 2907).

(ii) A second difficulty which arises is the calculation of values of the ligand–proton stability constants, $K_j{}^{\text{H}}$, from equation (4). To obtain j such constants, at least j widely separated values of $\bar{n}_{\text{A}}$ must be known (Irving and Rossotti, *J.*, 1953, 3397), but in every case the corresponding value of [H] is required. Now in aqueous solution we assume $-\log_{10}\{\text{H}\} = \text{p}\{\text{H}\} = B$, the reading of the pH-meter, since its readings have been correlated with known p{H} values of the buffer solutions used in " standardising " the instrument. Van Uitert and Haas (*J. Amer. Chem. Soc.*, 1953, **75**, 451) have recently shown that the more general relation

$$-\log_{10}[\text{H}] = B + \log f + \log U_{\text{H}}{}^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

between hydrogen-ion concentration and pH-meter readings, B, is equally valid for water and for water–dioxan mixtures. Its use can be extended even to pure ethanol (van Uitert and Fernelius, *ibid.*, 1953, **75**, 3862). Here f is the activity coefficient of hydrogen ions in the solvent mixture under consideration at the same temperature and ionic strength, and U_{H}^0 corresponds to the correction at zero ionic strength. For water, $U_{\mathrm{H}}^0 = 1$, and at unit activity coefficient $[\mathrm{H}] = 1/\mathrm{antilog}\, B$. If then values of $1/\mathrm{antilog}\, B = [\mathrm{H}]f \,.\, U_{\mathrm{H}}^0$ (in the general case) are substituted in equation (4) in place of the less easily determinable values of [H], there will result values for the proton–ligand stability constants which will be termed *practical constants*, denoted by ${}^{\mathrm{P}}K_j^{\mathrm{H}}$. These are related to the desired stoicheiometric constants by the expression

$$ {}^{\mathrm{C}}K_j^{\mathrm{H}} = fU_{\mathrm{H}}^0\, {}^{\mathrm{P}}K_j^{\mathrm{H}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11a) $$

further

$$ {}^{\mathrm{C}}\beta_j^{\mathrm{H}} = (fU_{\mathrm{H}}^0)^j\, {}^{\mathrm{P}}K_j^{\mathrm{H}} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (11b) $$

$\log fU_{\mathrm{H}}^0$ may be obtained as the intercept of the linear plot of p[H] against B, using solutions of known hydrogen-ion concentration, and used to convert *practical* constants into stoicheiometric constants. It will be shown later (p. 2908) that these refinements are not, in fact, necessary for calculating the stability constants of metal–ligand complexes.

Fig. 1, curve 3, shows a typical titration curve for a mixture of mineral acid, ligand, and metal ions. For any point on the curve,

$$ [\mathrm{H}]''' = E''' + yT_{\mathrm{L}}''' + \mathrm{OH}''' - \mathrm{Na}''' - \bar{n}_{\mathrm{A}}'''T_{\mathrm{L}}''' + \bar{n}_{\mathrm{A}}'''\bar{n}'''T_{\mathrm{M}}''' \qquad (12) $$

If the pH-meter reading, B, and the ionic strength of this solution are the same as those given by equation (8) for a point on curve 2 (*i.e.*, the same ordinate, B), then $[\mathrm{H}]'' = [\mathrm{H}]'''$, $[\mathrm{OH}]'' = [\mathrm{OH}]'''$, and $\bar{n}_{\mathrm{A}}'' = \bar{n}_{\mathrm{A}}'''$, so that

$$ \bar{n} = \{(E'' - E''') + (T_{\mathrm{L}}'' - T_{\mathrm{L}}''')(y - \bar{n}_{\mathrm{A}}) - (\mathrm{Na}'' - \mathrm{Na}''')\}/\bar{n}_{\mathrm{A}}'''T_{\mathrm{M}}''' \qquad (13) $$

If the initial volumes, V^0, and concentrations of acid, E^0, and of ligand, T_{L}^0, were the same in each solution, and volumes v'' and v''' of alkali of concentration N were added to reach the points Na″ and Na‴, then from (13)

$$ \bar{n}''' = (v''' - v'')\{N + E^0 + T_{\mathrm{L}}^0(y - \bar{n}_{\mathrm{A}})\}/(V^0 + v'')\bar{n}_{\mathrm{A}}'''T_{\mathrm{M}} \quad . \; . \quad (14) $$

Now if $N \gg E^0$, and $V^0 \gg v''$, then

$$ \bar{n}''' = (v''' - v'')N/V^0\, \bar{n}_{\mathrm{A}}'''T_{\mathrm{M}} \quad . \; . \; . \; . \; . \; . \; . \quad (14a) $$

Some computations illustrating the agreement between results obtained by using the approximate equations (10*a*) and (14*a*), and the rigorous equations (10) and (14) are shown in the accompanying table. It is seen that values of $\bar{n}_{\mathrm{A}}$ and $\bar{n}$ obtained by using

B	4·00	4·00	5·25	6·25	9·50	11·00	11·50
$10^2v'$, ml.	1·667	1·667	1·683	1·683	1·693	1·707	1·721
$10^2v''$, ml.	1·197	1·197	1·450	1·643	1·721	1·898	2·100
$10^3v'''$, ml.	1·647	1·279	1·643	2·066	1·813	—	—
Metal ion	$\mathrm{Cu^{++}}$	$\mathrm{UO_2^{++}}$	$\mathrm{Ni^{++}}$	$\mathrm{Ni^{++}}$	$\mathrm{Mg^{++}}$	—	—
$\bar{n}$ (i)	1·935	1·935	1·463	1·077	0·944	0·620	0·248
(ii)	1·921	1·921	1·456	1·076	0·943	0·625	0·262
Diff..................	0·014	0·014	0·007	0·001	0·001	0·005	0·014
$\bar{n}$ (i)	0·930	0·169	0·527	0·560	0·503	—	—
(ii)	0·918	0·167	0·520	1·538	0·496	—	—
Diff..................	0·012	0·002	0·007	0·022	0·007	—	—

Values in the rows preceded by (i) and (ii) are those calculated by equations (10), (14), and (10*a*), (14*a*) respectively; v''' refers to points on curves of the type 3 (Fig. 1) for the titration of 50% v/v aqueous dioxan containing 0·0200N-perchloric acid, 0·3M-sodium perchlorate, 0·006091M-8-hydroxy-2-methylquinoline, and 0·003045M-metal ions, with 1·175N-sodium hydroxide. In curve 2 (points v''), the metal is omitted, and in curve 1 (points v'), both metal and reagent are omitted. $V^{\circ} = 9{\cdot}85$ ml. in each case, and $y = 1$.

the approximate equations seldom differ significantly from those obtained with the rigorous equations, unless the volume of alkali added is a considerable fraction of V^0.

Values of $\bar{n}_A$ appropriate to each pH-meter reading, B, have previously been obtained from equation (10), so that $\bar{n}$ can be calculated directly from pH-meter readings without any exact knowledge of the corresponding hydrogen-ion activities or concentrations. The calculation of pL from equation (5) would again appear to require a knowledge of [H], but, by a simple transformation,

$$\mathrm{pL} = \log_{10}\left\{\sum_{j=0}^{j=J} \frac{{}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}}{(f\mathrm{U_H}{}^0)^j} \cdot ([\mathrm{H}]fU_{\mathrm{H}}{}^0)^j \Big/ (T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}})\right\}$$

$$= \log_{10}\left\{\sum_{j=0}^{j=J} {}^{\mathrm{P}}\beta_j{}^{\mathrm{H}}(1/\mathrm{antilog}\ B)^j \Big/ (T_{\mathrm{L}} - \bar{n}T_{\mathrm{M}})\right\} \quad . \quad . \quad . \quad . \quad (5a)$$

Hence equation (5) remains of the same form provided that (i) values of 1/antilog B are again used in place of [H], and (ii) the practical overall stability constants ${}^{\mathrm{P}}\beta_j{}^{\mathrm{H}}$, previously obtained for the ligand–proton complexes (cf. p.   ), are used in place of the stoicheiometric values ${}^{\mathrm{C}}\beta_j{}^{\mathrm{H}}$.

Having thus obtained corresponding values of $\bar{n}$ and pL, the formation curve of the metal–ligand system can be drawn, and values of ${}^{\mathrm{C}}K_n$ calculated by the methods previously described (cf. Irving and Rossotti, *loc. cit.*, and references therein).

Titrations in which the Total Concentration of Ligand is varied.—In early studies of the stability of metal ammines, Bjerrum (*op. cit.*) obtained variations in pL by varying the total concentration of ligand in the system by discrete steps. Later workers (*e.g.*, Irving and Griffiths, *J.*, 1954, 213) carried out pH titrations with the amine as titrant. Here a solution containing metal ion and mineral acid is titrated with a solution of the ligand and, as in the method described above, $\bar{n}_A$ and $\bar{n}$ may be obtained directly from the horizontal displacement of titration curves.

In Fig. 2, curves 1 and 2 represent those in which solutions of mineral acid of initial concentration $E^{0\prime}$ and $E^{0\prime\prime}$ are titrated severally with a solution of ligand $\mathrm{H}_y\mathrm{L}$ of molar concentration L. When the ligand is added as the free base, *e.g.*, as ammonia or ethylenediamine, $y = 0$. Points on the two curves are given by

$$\text{Curve 1, } [\mathrm{H}]' = E' - [\mathrm{OH}]' - (\bar{n}_A{}' - y)T_{\mathrm{L}}{}' \quad . \quad . \quad . \quad . \quad (15a)$$

$$\text{Curve 2, } [\mathrm{H}]'' = E'' - [\mathrm{OH}]'' - (\bar{n}_A{}'' - y)T_{\mathrm{L}}{}'' \quad . \quad . \quad . \quad (15b)$$

Now for the same values of the ordinate B, if the solutions have the same ionic strength, $[\mathrm{H}]' = [\mathrm{H}]''$, and $[\mathrm{OH}]' = [\mathrm{OH}]''$, and

$$\bar{n}_A{}' = \bar{n}_A{}'' = (E'' - E')/(T_{\mathrm{L}}{}'' - T_{\mathrm{L}}{}') + y \quad . \quad . \quad . \quad . \quad (16)$$

If now the initial volume of both solutions was V^0, and if volumes v' and v'' of ligand solution were required to give the same pH-meter reading B on curves 1 and 2 respectively, then

$$\bar{n}_A = \frac{E^{0\prime\prime}(V^0 + v') - E^{0\prime}(V^0 + v'')}{L(v'' - v')} + y \quad . \quad . \quad . \quad . \quad . \quad (17)$$

and if $V^0 \gg v', v''$,

$$\bar{n}_A = y + (E^{0\prime\prime} - E^{0\prime})V^0/L(v'' - v') \quad . \quad . \quad . \quad . \quad . \quad (17a)$$

Fig. 2, curve 3, represents the titration curve of a volume V^0 of a solution containing metal ions and acid of initial concentrations $T_{\mathrm{M}}{}^0$ and $E^{0\prime\prime}$, with a ligand solution of molar concentration L. For any point on curve 3,

$$[\mathrm{H}]''' = E'' + [\mathrm{OH}]''' - (\bar{n}_A{}''' - y)T_{\mathrm{L}}{}''' + \bar{n}'''n_A{}'''T_{\mathrm{M}}{}''' \quad . \quad . \quad . \quad (18)$$

If a volume v''' of ligand solution is required to give a pH-meter reading of B, then from (15*b*) and (18)

$$\bar{n}''' = (v''' - v'')\{E^{0''} + (\bar{n}_{\mathrm{A}}'' - y)L\}/(V^0 + v'')\bar{n}_{\mathrm{A}}''\, T_{\mathrm{M}}^0 \quad . \quad . \quad . \quad (19)$$

and if $V^0 \gg v''$, and $(\bar{n}_{\mathrm{A}}'' - y)L \gg E^{0''}$, then

$$\bar{n}''' = (v''' - v'')(\bar{n}_{\mathrm{A}}'' - y)L/V^0\bar{n}_{\mathrm{A}}''T_{\mathrm{M}}^0 \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

which reduces to

$$\bar{n}''' = (v''' - v'')L/V^0T_{\mathrm{M}}^0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (19b)$$

when the ligand is added as free base. Thus the use of equations (17) and (19) to give corresponding values of $\bar{n}_{\mathrm{A}}$ and $\bar{n}$ for a series of pH-meter readings resembles that using equations (10) and (14) of p. 2907. In practice, however, it is often more convenient to obtained values of $\bar{n}_{\mathrm{A}}$ from titrations of an acidic solution of the ligand with alkali [using equation (10)], and then to obtain values of $\bar{n}$ at the same pH-meter reading by the method just described using equation (19). All solutions must have the same ionic strength. In order to construct the formation curve, values of pL are calculated from equation (5*a*).

The Relationship between Values of ${}^{\mathrm{C}}K_j^{\mathrm{H}}$ *and Conventional Acid Dissociation Constants.*—The stability constants ${}^{\mathrm{C}}K_j^{\mathrm{H}}$ for ligand–proton complexes as defined above (p. 2904) are not,of course, identical with the conventionally defined classical dissociation constants of the various acids derived from L. It is customary to use the subscript 1 to designate the dissociation constant of the most acidic species, LH_J, so that

$${}^{\mathrm{C}}K_1 = [\mathrm{H}][\mathrm{LH}]_{J-1}/[\mathrm{LH}_J] = 1/{}^{\mathrm{C}}K_j^{\mathrm{H}}$$

For the next strongest acid

$${}^{\mathrm{C}}K_2 = [\mathrm{H}][\mathrm{LH}_{J-2}]/[\mathrm{LH}_{J-1}] = 1/{}^{\mathrm{C}}K^{\mathrm{H}}{}_{J-1}$$

For the dissociation of the final acid species, ${}^{\mathrm{C}}K_J = [\mathrm{H}][\mathrm{L}]/[\mathrm{LH}]$. In general, then, ${}^{\mathrm{C}}K_j^{\mathrm{H}} = 1/{}^{\mathrm{C}}K_{J+1-j}$.

Thermodynamic Stability Constants.—The above procedures have given stoicheiometric stability constants which could be converted into thermodynamic constants were the appropriate activity coefficients available. For the uncharged complex, ML_2, of a univalent ligand and a bivalent cation, M^{++}, the second thermodynamic stability constant is given by ${}^{\mathrm{T}}K_2 = \{\mathrm{ML}_2\}/\{\mathrm{ML}^+\}\{\mathrm{L}^-\} = {}^{\mathrm{C}}K_2 \,.\, f_{\mathrm{ML}_2}/f_{\mathrm{ML}^+}f_{\mathrm{L}^-} = {}^{\mathrm{C}}K_2/f_{\pm}{}^2$ if it is assumed that the activity coefficient of the uncharged complex, ML_2, is unity, and independent of salt concentration, and that the product $f_{\mathrm{ML}^+}f_{\mathrm{L}^-}$ may be replaced by the square of the mean activity coefficient for hydrochloric acid in the same medium at the same ionic strength. Measurements by Van Uitert and Haas (*loc. cit.*) justify this assumption that the species ML^+ behaves as the cation of a strong electrolyte in aqueous dioxan, at least when M is a transition metal and HL is a 1 : 3-diketone. For the first stability constant

$${}^{\mathrm{T}}K_1 = \{\mathrm{ML}^+\}/\{\mathrm{M}^{++}\}\{\mathrm{L}^-\} = {}^{\mathrm{C}}K_1 \,.\, f_{\mathrm{ML}^+}/f_{\mathrm{M}^{++}}f_{\mathrm{L}^-} = {}^{\mathrm{C}}K_1/f^4$$

if we assume that the ratio $f_{\mathrm{ML}^+}/f_{\mathrm{L}^-}$ is unity and unaffected by change of ionic strength, and that the activity coefficient $f_{\mathrm{M}^{++}}$ for the doubly-charged ion equals the fourth power of the value for a singly-charged ion under the same conditions. Hence

$$\log {}^{\mathrm{T}}K_1 = \log {}^{\mathrm{C}}K_1 - 4 \log f_{\pm 1-1}$$

and, since measurements are made in the presence of a large concentration of neutral salt providing an excess of univalent anions, an equivalent expression can be shown to be

$$\log {}^{\mathrm{T}}K_1 = \log {}^{\mathrm{C}}K_1 + \log f^2_{\pm 1-1}/f^3_{\pm 2-1}$$

where the subscripts refer to 1–1- and 2–1-electrolytes respectively. In a basically similar treatment of thermodynamic stability constants Van Uitert and Haas (*loc. cit.*) deduce that

$$\log {}^{\mathrm{T}}K_1 = -\log {}^{\mathrm{T}}K_1^{\mathrm{H}} + \log [\mathrm{ML}^+]/[\mathrm{M}^{++}] + \log [\mathrm{H}^+]/[\mathrm{HL}] + \log f^2_{\pm 1-1}/f_{\pm 2-1}$$

(in the nomenclature of the present paper) and note that the last term becomes zero and thus independent of ionic strength when the limiting case of the Debye–Hückel law can be applied. Of the two assumptions made in this derivation, *viz.*, (i) $f_{ML^+} = f_{H^+} = f_{L^-} = f_{\pm 1-1}$ and (ii) $f_{M^{++}} = f_{\pm 2-1}$, the latter is incorrect, and the last term of their equation should read $\log f^4_{\pm 1-1}/f^3_{\pm 2-1}$ and will be a function of ionic strength.

Similar calculations may be used to obtain thermodynamic stability constants for ligand–proton complexes and for metal–ligand complexes of different charge type. The assumptions can only be logically justified in dilute solutions, and, especially where ions of multiple charge are involved, it seems desirable always to report the values of stoicheiometric stability constants calculated from the experimental data together with the concentration and nature of the salt background used. Derived values of thermodynamic constants may then be corrected if and when more exact knowledge becomes available concerning the relevant activity coefficients.

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