

STABILITY CONSTANTS OF METAL-ION COMPLEXES

SECTION I: INORGANIC LIGANDS

Compiled by LARS GUNNAR SILLEN

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The second edition of "Stability Constants of Metal-Ion Complexes, with Solubility Products of Inorganic Substances", which was originally compiled under the auspices of the International Union of Pure and Applied Chemistry by Jannik Bjerrum, Gerold Schwarzenbach, and Lars Gunnar Sillén, and was published by the Chemical Society as Part I, Organic Ligands, Special Publication No. 6, 1957 and Part II, Inorganic Ligands, Special Publication No. 7, 1958.

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PREFACE

SINCE the first edition which appeared as Part I in 1957 and Part II in 1958 has been widely used by chemists working in many different fields, we felt encouraged to prepare a second edition. After completion of the first edition, Professor G. Schwarzenbach handed over responsibility for the tables on organic ligands to Professor A. E. Martell. The inorganic tables, as before, are the responsibility of Professor L. G. Sillén.

We have been happy to agree to the Chemical Society's suggestion that the tables for inorganic and organic ligands should now be bound as one volume, which we hope will prove more convenient for users. Both sections have been brought up to date by the inclusion of all data published up to the end of 1960 and of some which have appeared in 1961-63; some older data which were omitted from the first edition have also been added, especially in the organic section. The scope of the inorganic section has been extended to cover redox equilibria and the extraction of inorganic ligands into non-aqueous solvents. The arrangement of material is now more uniform than in the two parts of the first edition, but there remain minor differences of presentation between the inorganic and the organic section which are described under the heading "How to Use the Tables". The introductory text by Professor G. Schwarzenbach on the determination of stability constants has been omitted since good monographs on this topic are now available.

As before, it has been the policy of the compilers to attempt to read each paper in the original: abstracting journals are quoted only if there was no opportunity to check the original paper. We have tried to record faithfully what the authors of the original paper considered their results to be, although it has been hard to be completely consistent in presentation. The equilibrium constants quoted are usually those given by the authors. Very occasionally we have used the sign "(?)", denoting doubt by the compiler; in a critical compilation it could have been used more frequently. The absence of a question mark should not be interpreted as a recommendation of the value given, nor should its presence be thought a reproach.

Thanks for valuable aid in the preparation of the tables are expressed to Mrs. Ingegerd Nordsjö, Mrs. Ingrid Ollas, and Mrs. Marie-Luise von Gersdorff in Stockholm (inorganic section) and to Mrs. Mary Budrys, Miss Eleanora Clarke, and Mr. George Lenz in Chicago (organic section). We are greatly indebted to many chemists from all over the world who have informed us about recent or forthcoming publications, pointed out errors, and suggested additions. Especially helpful comments have come from Professors D. Dyrssen and I. Leden (inorganic section) and from Professor Dr. G. Schwarzenbach, Dr. G. Anderegg, and Dr. H. Freiser and his co-workers (organic section). Communications about errors that remain in the new edition, data omitted, and data published subsequently would be appreciated. Comments about the tables of inorganic ligands should be sent to Professor L. G. Sillén, Department of Inorganic Chemistry, KTH, Stockholm 70, Sweden. Comments about the tables of organic ligands should be sent to Professor A. E. Martell, Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago, 16, Ill., U.S.A.

We also thank Professor K. W. Sykes of Queen Mary College, University of London, who, although no longer Specialist Editor, has again arranged the introductory material and written the section entitled "How to Use the Tables".

ARTHUR MARTELL, Illinois Institute of Technology, Chicago.

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HOW TO USE THE TABLES

1. **GENERAL ARRANGEMENT.** Each table summarises the data up to 1960 for the association of one particular ligand with all the metallic ions which have been studied in conjunction with it, as far as the compilers located them. Some data published in 1961—1963 have also been included. Method of measurement, composition, and temperature of the media to which the data refer, appropriate stability constants for the various complexes formed, and references to the original papers are given for each ligand-metal pair. Acid dissociation constants of the ligands are recorded by including the hydrogen ion among the metals as one of the cations with which the ligands associate. Redox equilibria are represented by including the electron as a ligand, and hydrolysis of the metallic ions is described by regarding the hydroxyl ion as one of the ligands. The tables are divided into two sections, the first dealing with inorganic ligands and the second with organic ligands. In the following description of the arrangement and presentation of the data, all statements refer to both inorganic and organic sections unless the contrary is specifically stated.

2. **ORDER OF LIGANDS AND METAL IONS—INORGANIC SECTION.** The inorganic ligands are placed in the following order, which is based on the Periodic System and differs only slightly from that used in Part II of the first edition :

electron :	redox equilibria.
hydroxide :	
a-groups :	vanadate, niobates and tantalates, chromate, molybdate, wolframate (tungstate), manganates, rhenates, cyanoferrate (II), cyanoferrate (III), cyanocobaltate (III), other ligands with a-group elements.
group 3b :	borate.
group 4b :	cyanide, cyanate, thiocyanate, selenocyanate, other ligands with CN and b group elements, carbon monoxide, carbonate, other ligands with C, silicate, germanate, stannate, other ligands with 4b elements.
group 5b :	ammonia ; amide, imide and nitride ; hydrazine, hydroxylamine, azide, nitric oxide, nitrite, nitrate, other ligands with N, hypophosphite, phosphite, phosphate, diphosphate, trimetaphosphate, triphosphate, tetrametaphosphate, polyphosphates, amidophosphates, other ligands with P, arsenite, arsenate, other ligands with As, ligands with Sb or Bi.
group 6b :	water, peroxide, sulphide, thiosulphate, sulphite, sulphate, amidosulphate, other ligands with S, selenide, selenite, selenate, telluride, tellurite, tellurate.
group 7b :	fluoride, chloride, hypochlorite, chlorite, chlorate, perchlorate, bromide, hypobromite, bromate, iodide, hypoiodite, iodate, periodate, other ligands with 7b elements, halides : mixed and comparative.

Metal ions are placed down the first column of each inorganic ligand table in the order of the following form of the Periodic System. Where an element has several valencies, a lower oxidation state precedes a higher one. This arrangement is the same as that in Part II of the first edition.

group 1a :	H, Li, Na, K, Rb, Cs, Fr.
group 2a :	Be, Mg, Ca, Sr, Ba, Ra.
group 3a + 4f :	Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ac.
group 4a :	Ti, Zr, Hf, Th.
group 5a :	V, Nb, Ta, Pa.
group 6a + 5f :	Cr, Mo, W, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lw.
group 7a :	Mn, Tc, Re.
group 8 :	Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt.
group 1b :	Cu, Ag, Au.
group 2b :	Zn, Cd, Hg.
group 3b :	B, Al, Ga, In, Tl.
group 4b :	C, Si, Ge, Sn, Pb.
group 5b :	N, P, As, Sb, Bi.
group 6b :	O, S, Se, Te, Po.
group 7b :	F, Cl, Br, I, At.

3. ORDER OF LIGANDS AND METALLIC IONS—ORGANIC SECTION. In the organic section the ligands and metals are arranged in the same way as in Part I of the first edition : *i.e.*, the ligands in order of their empirical formulæ according to Beilstein's system, a brief description of which is given immediately below, and the metallic ions in the alphabetical order of their international symbols. The hydrogen ion is now included, as in the inorganic section, as one of the cations with which the ligands associate ; it is placed first in each table before the metallic cations.

Beilstein's system

(a) The formulæ are written with the elements in the order :

C H O N Cl Br I F S P

followed by the other elements in the alphabetical order of their symbols.

(b) All formulæ containing p carbon atoms precede those containing $(p + 1)$ carbon atoms where p is any integer.

(c) For a given value of p , all formulæ containing q different elements other than carbon precede those containing $(q + 1)$ other elements, where q is any integer.

(d) For given values of p and q , formulæ containing different combinations of elements are arranged as follows :

(i) the first element is always carbon ;

(ii) the second element is chosen in turn from the elements after carbon given in the list in (a) ;

(iii) for a given choice of the second element (X), the third is selected in turn from those after X in the list given in (a) ;

(iv) in general, for a given choice of the first r elements, the r th, of which is Z, the $(r + 1)$ th is selected in turn from those after Z in the list given in (a).

(e) The above rules may be illustrated by compounds containing only C, H, O, N, and Cl. Provided the number of carbon atoms is constant, the following order holds irrespective of how many atoms of H, O, N, or Cl the molecule contains :

$q = 1$: CH, CO, CN, CCl

$q = 2$: CHO, CHN, CHCl, CON, COCl, CNCl

$q = 3$: CHON, CHOCl, CHNCl, CONCl

(f) Formulæ with the same combination of elements are ordered by reference to the numbers of the various atoms in the molecule. Let X and Y be any pair of successive elements in a molecule $C_p \dots X_i Y_j \dots$, composed of a given combination of elements ; i and j are any integers other than zero ; then :

(i) all formulæ containing i atoms of X precede those containing $(i + 1)$ atoms of X, irrespective of j (the number of atoms of Y) ;

(ii) for a given value of i , all formulæ containing j atoms of Y precede those containing $(j + 1)$ atoms of Y.

(g) The rules in (f) may be illustrated by the order of the eight formulæ of the type CHON which can be constructed from 1C, 2H, 2O, and 2N :

CHON CHON₂ CHO₂N CHO₂N₂ CH₂ON CH₂ON₂ CH₂O₂N CH₂O₂N₂

(h) The rules that determine the order of isomers will not be discussed here. Since the Tables contain relatively few isomers of any given formula, readers should be able to find isomeric ligands by trial and error without much difficulty.

4. METHOD OF MEASUREMENT. The method by which the stability constants were measured is shown in the second column of each Table by the following abbreviations :

act	activity coefficient, not specified.
aix	anion exchange.
ana	chemical analysis.
bp	boiling point.
cal	calorimetry.
cfu	centrifuge or ultracentrifuge.
cix	cation exchange.

col	colorimetry (often for measuring pH).
con	conductivity.
dis	distribution between two phases.
<i>E</i>	electromotive force, not specified.
est	estimated.
fp	freezing point.
gl	glass electrode.
hyp	from some hypothesis.
<i>iE</i>	current-voltage studies.
ir	infrared spectra.
ix	ion exchange.
kin	rate of reaction.
lit	from critical survey of literature data.
mag	magnetic susceptibility.
MHg	e.m.f. with amalgam electrode.
nmr	nuclear magnetic resonance.
oth	other methods, specified in " results " column.
$p\text{H}_2\text{O}$, $p\text{L}$	partial pressure of substance indicated.
pH	pH method, not specified.
pol	polarography.
pre	preparative work.
qh	quinhydrone electrode.
Ram	Raman spectra.
red	e.m.f. with redox electrode.
sol	solubility.
sp	spectrophotometry.
tp	electrical migration or transference number.
tyn	tyndallometry, nephelometry.
X	X-ray diffraction.
var	several methods, specified in " results " column.
ΔG	combination of thermodynamic data.
Ag, Cd, etc.	e.m.f. with electrode of metal stated.
H, O, etc.	e.m.f. with electrode of gas stated.
conJ, spJ, etc.	conductimetry, spectrophotometry, etc., by " Job's method " of continuous variation.
gl Δ , H Δ , etc.	e.m.f. by differential method (minimum buffer capacity).
?	method not known to compilers.

5. TEMPERATURE. The third column of each table gives the temperature in °C. " rt " denotes room temperature, and " ? " is used if the value was not found by the compilers. When results for several temperatures are available, only the upper and the lower limit of the range are stated in the third column. The fifth column then gives either the individual temperatures in parentheses after the corresponding values of the equilibrium constant, or an empirical expression for the variation of the equilibrium constant with temperature. In such expressions, " *t* " denotes °C and " *T* " °K.

6. MEDIUM. The nature of the medium to which the equilibrium constants refer is specified in the fourth column of each table, as indicated by the examples below. In general, concentrations are expressed in mole litre⁻¹ (M), but the relatively few which are reported in mole kg.⁻¹ (m) are not distinguished; consequently neither the symbol M nor m is used in this column. Unless otherwise stated, the solvent is water.

→0	constants extrapolated to zero ionic strength.
0 corr	constants corrected to zero ionic strength by the application of some theoretical or empirical formula; this procedure is not always sharply distinguished from extrapolation.

0.06	an ionic strength of 0.06 mole litre ⁻¹ .
3 NaClO ₄	constant concentration of the substance stated (3 mole litre ⁻¹ NaClO ₄).
2(NaClO ₄)	ionic strength held constant at the value stated (2 mole litre ⁻¹) by addition of the inert salt shown in parentheses.
<i>I</i> (NaClO ₄)	measurements made at a series of ionic strengths (<i>I</i>) with sodium perchlorate as the inert salt; the individual values are given in the fifth column in parentheses placed after the corresponding equilibrium constants.
2(Na)ClO ₄	concentration of the anion (ClO ₄ ⁻) held constant at the value stated (2 mole litre ⁻¹) with the ion shown in parentheses as the inert cation.
<i>I</i> (NO ₃ ⁻)	measurements made at a series of nitrate-ion concentrations, the individual values of which are given in the fifth column in parentheses placed after the corresponding equilibrium constants.
dil	dilute solution, concentration usually not more than 0.01 mole litre ⁻¹ .
var	ionic medium varied, and in some cases no special attempt was made to control the ionic strength.
KCl var	the medium was mainly aqueous KCl at various concentrations.
EtOH	ethanol as solvent.
org	various organic solvents.
50% MeOH	the solvent consists of the stated percentage of the component specified, water being the other component. In the organic section percentage compositions are given by weight unless otherwise stated. In the inorganic section they are usually expressed by weight, but occasionally by volume or by moles; if the difference is important, the original paper should be consulted.

7. RESULTS. The fifth column of the tables records the logarithm to base 10 ($\log K$) of the equilibrium constants with the convention that "log" and "=" are always omitted; *e.g.*, " K_2 2.35" means " $\log K_2 = 2.35$ " and " $K_4 < 0.3$ " means " $\log K_4 < 0.3$ ". Concentrations ($[]$) are mostly expressed in mole litre⁻¹, though the occasional mole kg.⁻¹ is not distinguished if the solvent is water; if mole fractions (x) are used, this is stated explicitly. All pressures (p) are in atmospheres.

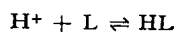
A formula of the type H_nL or L is given in the heading of each ligand table, in order to define the entity L in terms of which the equilibrium constants are expressed. In the organic section, most of the data are represented by means of a few standard types of equilibrium constant which are explained in paragraph 8, and all other equilibria are defined by giving the chemical equation after each constant. The inorganic section, however, contains a much wider variety of equilibrium constants, which are defined in paragraph 9 in terms of a systematic notation of subscripts and superscripts.

Some other comments apply to both the inorganic and organic sections. Ligand formulae such as BO_2^- , $H_2BO_3^-$, and $B(OH)_4^-$, which differ only in the number of molecules of solvent they contain, or complex formulae which differ only in the number of medium ions associated with them, cannot be distinguished by equilibrium methods. Particular formulae for which there is good structural evidence are usually given, but otherwise an arbitrary formula is used in the conventional manner. No attempt is made to show structural features of complex formation which cannot strictly be deduced from equilibrium considerations, but in many cases the reader can easily select the appropriate structure. Thus lysine (2,6-diaminohexanoic acid, HL) may acquire an extra proton to become H_2L^+ which then reacts with a metal ion M^{n+} to give the complex MHL^{n+} . The equilibrium formulation does not indicate which of the two amino-groups has lost its proton, but it is very probably the one in the 2-position. Throughout the tables, as a rule, only the minimum number of constants required to represent the authors's results are given. Constants for many other equilibria can be calculated by combining the tabulated values.

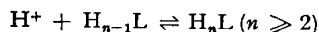
In defining the activity scale for hydrogen ions, it is usual to make the activity equal to the concentration in infinitely dilute aqueous solution. When other media are used, it would be logical to refer the activity scale to an infinitely dilute solution of hydrogen ions in that medium, but all workers have not been consistent in this respect. If it is important to know which convention has been used, reference should be made to the original literature.

8. EQUILIBRIUM CONSTANTS—ORGANIC SECTION.

(a) Protonation of ligands



$$K_1 = \frac{[\text{HL}]}{[\text{H}^+][\text{L}]}$$



$$K_{1n} = \frac{[\text{H}_n\text{L}]}{[\text{H}^+][\text{H}_{n-1}\text{L}]}$$

Example: $\text{C}_3\text{H}_7\text{O}_2\text{N}$ α -aminopropionic acid $\text{HL} \rightleftharpoons \text{H}^+$ (table 170) K_1 9.870 (25°), K_{12} 2.340 (25°)

$$K_1 = \frac{[\text{CH}_3\cdot\text{CH}(\text{NH}_3^+)\cdot\text{CO}_2^-]}{[\text{H}^+][\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2^-]} = 10^{9.870} \text{ mole}^{-1} \text{ litre at } 25^\circ\text{C}$$

$$K_{12} = \frac{[\text{CH}_3\cdot\text{CH}(\text{NH}_3^+)\cdot\text{CO}_2\text{H}]}{[\text{H}^+][\text{CH}_3\cdot\text{CH}(\text{NH}_3^+)\cdot\text{CO}_2^-]} = 10^{2.340} \text{ mole}^{-1} \text{ litre at } 25^\circ\text{C}$$

This example illustrates data from an original investigation of acidity constants by the method listed in the second column of the table, and details of the investigation will be found directly in the reference cited. Also listed at the beginning of each table are the values of the acidity constants which were used in the determination of various metal-ion–ligand stability constants; in such cases the reference is to the paper in which the metal-ion results are given, and sometimes a second reference is added to indicate the source of the acid dissociation data. If the reader wishes to find whether the authors themselves measured the acidity constants, or whether they took the values from the literature, then the original paper should be consulted. In any calculations on the equilibria, inconsistencies may be avoided in part by combining the proton–ligand and metal-ion–ligand stability constants reported by the same authors.

(b) Combination of ligands with metal ions

(i) Consecutive or stepwise constants, K , are used as follows whenever possible:



Example: $\text{C}_3\text{H}_7\text{O}_2\text{N}$ α -aminopropionic acid $\text{HL} \rightleftharpoons \text{Cu}^{2+}$ (table 170) K_1 8.18, K_2 6.65

$$K_1 = \frac{[\text{Cu}(\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2^+)]}{[\text{Cu}^{2+}][\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2^-]} = 10^{8.18} \text{ mole}^{-1} \text{ litre}$$

$$K_2 = \frac{[\text{Cu}(\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2)_2]}{[\text{Cu}(\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2^+)] [\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2^-]} = 10^{6.65} \text{ mole}^{-1} \text{ litre}$$

(ii) Cumulative or gross constants, β_n , are used if they are the only quantities which are determined or if the sequence of stepwise constants is incomplete.



Example: $\text{C}_3\text{H}_4\text{N}_2$ imidazole $\text{L} \rightleftharpoons \text{Cu}^{2+}$ (table 144) β_4 12.6

$$\beta_4 = \frac{[\text{Cu}(\text{C}_3\text{H}_4\text{N}_2)_4^{2+}]}{[\text{Cu}^{2+}][\text{C}_3\text{H}_4\text{N}_2]^4} = 10^{12.6} \text{ mole}^{-4} \text{ litre}^4$$

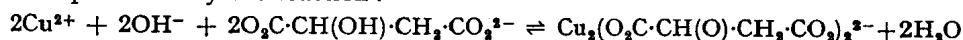
(iii) If the authors report their data in the form of free-energy changes and give no equilibrium constants, only free-energy changes are listed in the tables. ΔG_n° is the standard Gibbs free-energy change for the reaction of equilibrium constant K_n , and is related to the latter by the equation $\Delta G_n^\circ = -RT \ln K_n$, where R is the gas constant (1.987 cal. deg.⁻¹ mole⁻¹) and T is the temperature in °K. Alternatively the chemical equation to which the free-energy change refers may be given in parentheses.

(iv) All equilibria other than those detailed in (i), (ii), and (iii) above are dealt with by writing the chemical equation in parentheses after the symbol K .

Example: $\text{C}_4\text{H}_6\text{O}_5$ DL-malic acid $\text{H}_2\text{L} \rightleftharpoons \text{Cu}^{2+}$ (table 204) $K(2\text{Cu}^{2+} + 2\text{OH}^- + 2\text{L}^{2-} \rightleftharpoons \text{Cu}_2\text{L}_2(\text{OH})_2^{2-})$ 28.9

$$K = \frac{[\text{Cu}_2(\text{O}_2\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2)_2(\text{OH})_2^{2-}]}{[\text{Cu}^{2+}]^2[\text{OH}^-]^2[\text{O}_2\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2^-]^2} = 10^{28.9} \text{ mole}^{-5} \text{ litre}^5$$

This example also illustrates the inability of equilibrium data to distinguish between formulæ which differ only in the elements of the solvent. In aqueous solution, the addition of a hydroxyl ion is equivalent to the removal of a proton. Thus the data can equally well be represented by the reaction :



in which each of the two hydroxyl ions, instead of being added to the complex by substitution for water molecules in the hydration shells of the cupric ions, removes a proton from the hydroxyl group of the malic acid.

9. EQUILIBRIUM CONSTANTS—INORGANIC SECTION.

(a) Consecutive or stepwise constants : K

(i) Addition of ligand (L)

K_n is used for the stepwise addition of ligands to metallic ions as explained in the section 8(b)(i), where an example is given.

(ii) Addition of protonated ligand (HL) with elimination of proton



Example : $\text{F}^- - \text{Fe}^{3+}$ (table 66) *K_1 2.26, *K_2 0.99, *K_3 -0.10, $[K_1(\text{H}^+)$ 2.94]

$${}^*K_1 = \frac{[\text{FeF}^{2+}][\text{H}^+]}{[\text{Fe}^{3+}][\text{HF}]} = 10^{2.26}$$

$${}^*K_2 = \frac{[\text{FeF}_2^+][\text{H}^+]}{[\text{FeF}^{2+}][\text{HF}]} = 10^{0.99}$$

$${}^*K_3 = \frac{[\text{FeF}_3][\text{H}^+]}{[\text{FeF}_2^+][\text{HF}]} = 10^{-0.10}$$

In deriving these results, it was assumed that

$$K_1(\text{F}^- - \text{H}^+) = \frac{[\text{HF}]}{[\text{H}^+][\text{F}^-]} = 10^{2.94} \text{ mole}^{-1} \text{ litre}$$

(iii) Addition of protonated ligand (H_pL)



Example : $\text{PO}_4^{3-} - \text{Ca}^{2+}$ (table 38) $\text{HL}^{2-} : K_1$ 2.70, $\text{H}_2\text{L}^- : K_1$ 1.08

$$\text{HL}^{2-} : K_1 = \frac{[\text{CaHPO}_4]}{[\text{Ca}^{2+}][\text{HPO}_4^{2-}]} = 10^{2.70} \text{ mole}^{-1} \text{ litre}$$

$$\text{H}_2\text{L}^- : K_1 = \frac{[\text{CaH}_2\text{PO}_4^+]}{[\text{Ca}^{2+}][\text{H}_2\text{PO}_4^-]} = 10^{1.08} \text{ mole}^{-1} \text{ litre}$$

(iv) Addition of gaseous ligand $[\text{L}(\text{g})]$



Example : $\text{NO} - \text{Fe}^{2+}$ (table 32), K_{p1} 0.61

$$K_{p1} = \frac{[\text{FeNO}^{2+}]}{[\text{Fe}^{2+}]\rho_{\text{NO}}} = 10^{0.61} \text{ atmosphere}^{-1}$$

(v) Inner-sphere and outer-sphere complexes

If the ligand displaces only solvent molecules outside the inner co-ordination sphere of the central atom, the constant is denoted by K_n^{out} ; its relation to the corresponding constant for the inner-sphere complex (K_n) is expressed by $K_n^{\text{is}} = K_n^{\text{out}}/K_n$. This notation is only used if the authors distinguish between the two types of complex.

Example : $\text{SO}_4^{2-}-\text{Co}(\text{NH}_3)_6^{3+}$ (table 56), $K_{15} = 0.05$

$$K_{15} = \frac{K_1^{\text{out}}}{K_1} = \frac{[\{\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}\}^{3+}\text{SO}_4^{2-}]}{[\text{Co}(\text{NH}_3)_6\text{SO}_4^{2+}]} = 10^{-0.05}$$

(vi) Addition of central atom (M)

K_1 and K_{1n} as defined in the organic section 8(a) are used for the addition of either protons or metal ions to a ligand.

(b) Cumulative or gross constants : β

In β_{nm} and $^*\beta_{nm}$ the subscripts n and m denote the composition of the complex M_mL_n formed ; when $m = 1$, the second subscript ($= 1$) is omitted.

(i) addition of central atoms (M) and ligands (L)

$$m\text{M} + n\text{L} \rightleftharpoons \text{M}_m\text{L}_n \quad \beta_{nm} = \frac{[\text{M}_m\text{L}_n]}{[\text{M}]^m[\text{L}]^n}$$

Examples : $\text{NH}_3-\text{Cu}^{2+}$ (table 27), $\beta_4 = 12.67$

$$\beta_4 = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 10^{12.67} \text{ mole}^{-4} \text{ litre}^4$$

$\text{I}^- - \text{Ag}$ (table 75), $\beta_{61} = 30.0$

$$\beta_{61} = \frac{[\text{Ag}_6\text{I}_6^{4-}]}{[\text{Ag}^+]^6[\text{I}^-]^6} = 10^{30.0} \text{ mole}^{-7} \text{ litre}^7$$

(ii) addition of central atoms (M) and protonated ligands (HL) with elimination of protons

$$m\text{M} + n\text{HL} \rightleftharpoons \text{M}_m\text{L}_n + n\text{H}^+ \quad ^*\beta_{nm} = \frac{[\text{M}_m\text{L}_n][\text{H}^+]^n}{[\text{M}]^m[\text{HL}]^n}$$

Examples : $\text{OH}^- - \text{U}^{4+}$ (table 2), $^*\beta_2 = 2.30$

$$^*\beta_2 = \frac{[\text{U}(\text{OH})_2^{2+}][\text{H}^+]^2}{[\text{U}^{4+}]} = 10^{-2.30} \text{ mole}^2 \text{ litre}^{-2}$$

$\text{OH}^- - \text{Bi}^{3+}$ (table 2), $^*\beta_{12,6} = 0.33$

$$^*\beta_{12,6} = \frac{[\text{Bi}_6(\text{OH})_{12}^{3+}][\text{H}^+]^{12}}{[\text{Bi}^{3+}]^6} = 10^{0.33} \text{ mole}^7 \text{ litre}^{-7}$$

Note that if $\text{L} = \text{OH}^-$, $\text{HL} = \text{H}_2\text{O}$

(c) Solubility constants : K_s

(i) Solid M_aL_b in equilibrium with free ions in solution



Examples : $\text{I}^- - \text{Ag}^+$ (table 75), $K_{s0} = 16.03$

$$K_{s0} = [\text{Ag}^+][\text{I}^-] = 10^{-16.03} \text{ mole}^2 \text{ litre}^{-2} \text{ (solid} = \text{AgI)}$$

$\text{S}^{2-} - \text{Bi}^{3+}$ (table 53), $K_{s0} = 97$

$$K_{s0} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3 = 10^{-97} \text{ mole}^5 \text{ litre}^{-5} \text{ (solid} = \text{Bi}_2\text{S}_3)$$

K_{s0} is the conventional solubility product and the subscript zero indicates that the equilibrium of the solid with the simple (uncomplexed) species M and L is considered. Unless otherwise stated, the solid M_aL_b is the stable substance normally formed from the central atom M and the ligand L e.g., AgI and Bi_2S_3 in the above illustrations.

(ii) Solid M_aL_b in equilibrium with complex M_mL_n and ligand L in solution.

$$\frac{m}{a}\text{M}_a\text{L}_b(\text{s}) \rightleftharpoons \text{M}_m\text{L}_n + \left(\frac{mb}{a} - n\right)\text{L} \quad K_{snm} = [\text{M}_m\text{L}_n][\text{L}]^{(mb/a-n)}$$

In K_{snm} the subscripts n and m denote the composition of the complex M_mL_n formed in solution. When $m = 1$, the second subscript ($= 1$) is omitted. The ligand L may occur on either the right- or the left-hand side of the chemical equation, depending on whether $\left(\frac{mb}{a} - n\right)$ is positive or negative.

Examples : $\text{I}^- - \text{Ag}^+$ (table 75), $K_{s3} = 2.52$, $K_{s62} = 3.0$

$$K_{s3} = \frac{[\text{AgI}_3^{2-}]}{[\text{I}^-]^3} = 10^{-2.52} \text{ mole}^{-1} \text{ litre} [\text{AgI}(s) + 2\text{I}^- \rightleftharpoons \text{AgI}_3^{2-}]$$

$$K_{s62} = \frac{[\text{Ag}_2\text{I}_6^{4-}]}{[\text{I}^-]^4} = 10^{-3.0} \text{ mole}^{-3} \text{ litre}^3 [2\text{AgI}(s) + 4\text{I}^- \rightleftharpoons \text{Ag}_2\text{I}_6^{4-}]$$

(iii) Protonated ligand reacts with elimination of proton

$$\frac{m}{a} \text{M}_a\text{L}_b(s) + \left(\frac{mb}{a} - n\right) \text{H}^+ \rightleftharpoons \text{M}_m\text{L}_n + \left(\frac{mb}{a} - n\right) \text{HL}, *K_{sm} = \frac{[\text{M}_m\text{L}_n][\text{HL}]^{(mb/a-n)}}{[\text{H}^+]^{(mb/a-n)}}$$

Examples : $\text{OH}^- - \text{Be}^{2+}$ (table 2), $*K_{s0} = 6.86$, $*K_{s33} = 11.67$

$$*K_{s0} = \frac{[\text{Be}^{2+}]}{[\text{H}^+]^2} = 10^{6.86} \text{ mole}^{-1} \text{ litre} [\text{Be}(\text{OH})_2(s) + 2\text{H}^+ \rightleftharpoons \text{Be}^{2+} + 2\text{H}_2\text{O}]$$

$$*K_{s33} = \frac{[\text{Be}_3(\text{OH})_3^{3+}]}{[\text{H}^+]^3} = 10^{11.67} \text{ mole}^{-2} \text{ litre}^2 [3\text{Be}(\text{OH})_2(s) + 3\text{H}^+ \rightleftharpoons \text{Be}_3(\text{OH})_3^{3+} + 3\text{H}_2\text{O}]$$

(d) Acidic and basic constants

(i) When L is hydroxide (OH^-), HL is water (H_2O) and $*K_n$ is the n th acid dissociation constant for the hydrolysis of a metal ion.

Example : $\text{OH}^- - \text{Fe}^{3+}$ (table 2) $*K_1 = 2.17$

$$*K_1 = \frac{[\text{FeOH}^{2+}][\text{H}^+]}{[\text{Fe}^{3+}]} = 10^{-2.17} \text{ mole litre}^{-1}$$

(ii) See 9(a)(vi) for the use of H^+ as the central atom to represent protolytic constants.

(iii) Other acidic constants are denoted by K_a , followed by parentheses enclosing the formula of the species donating the proton.

Example : $K_a(\text{H}_2\text{FeL}_4) = 4.4$, $K_a(\text{HFeL}_4^-) = 13.4$ (table 20, $\text{L} = \text{CO}$)

$$K_a(\text{H}_2\text{FeL}_4) = \frac{[\text{H}^+][\text{HFe}(\text{CO})_4^-]}{[\text{H}_2\text{Fe}(\text{CO})_4]} = 10^{-4.4} \text{ mole litre}^{-1}$$

$$K_a(\text{HFeL}_4^-) = \frac{[\text{H}^+][\text{Fe}(\text{CO})_4^{2-}]}{[\text{HFe}(\text{CO})_4^-]} = 10^{-13.4} \text{ mole litre}^{-1}$$

(iv) Basic constants for the transfer of a proton from the solvent to the ligand are denoted by K_b followed, if necessary, by parentheses enclosing the formula of the species accepting the proton.

Example : $\text{NH}_3 - \text{H}^+$ (table 27) $K_b = 4.79$

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 10^{-4.79} \text{ mole litre}^{-1}$$

(e) Special constants

(i) K (equation)

The equation defines the reaction to which K refers, as in 8 (b) (iv).

(ii) $\dagger K_{nm}$, $\dagger K_{snm}$

The corresponding reaction is given as a footnote to the table, or in parentheses after the constant when the latter is first used in the same table.

(iii) β (formula)

The formula gives the composition of the complex in terms of the species from which it is formed. Species with negative subscripts are eliminated in the formation of the complex.

Examples : $\text{SO}_4^{2-} - \text{Fe}^{3+}$ (table 56), $\beta(\text{Fe}^{3+}\text{L}_2^{2-}\text{SCN}^-) = 5.69$

$$\beta(\text{Fe}^{3+}\text{L}_2^{2-}\text{SCN}^-) = \frac{[\text{Fe}(\text{SO}_4)_2\text{SCN}^{2-}]}{[\text{Fe}^{3+}][\text{SO}_4^{2-}]^2[\text{SCN}^-]} = 10^{5.69} \text{ mole}^{-3} \text{ litre}^3$$

$\text{PO}_4^{3-}-\text{Th}^{4+}$ (table 38), $\beta(\text{Th}^{4+}\text{H}_3\text{L})$ 1.89, $\beta(\text{Th}^{4+}\text{H}_{-1}+\text{H}_3\text{L})$ 2.18

$$\beta(\text{Th}^{4+}\text{H}_3\text{L}) = \frac{[\text{ThH}_3\text{PO}_4^{4+}]}{[\text{Th}^{4+}][\text{H}_3\text{PO}_4]} = 10^{1.89} \text{ mole}^{-1} \text{ litre}$$

$$\beta(\text{Th}^{4+}\text{H}_{-1}+\text{H}_3\text{L}) = \frac{[\text{ThH}_2\text{PO}_4^{3+}][\text{H}^+]}{[\text{Th}^{4+}][\text{H}_3\text{PO}_4]} = 10^{2.18}$$

(iv) K_s (formula)

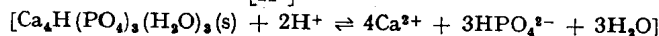
The formula gives the composition of the solid phase in terms of the species with which it is in equilibrium in solution. Species with negative subscripts are eliminated in the formation of the solid.

Examples: $\text{PO}_4^{3-}-\text{Ca}^{2+}$ (table 38), $K_s(\text{Ca}^{2+}\text{HL}^{2-})$ -6.25

$$K_s[\text{Ca}^{2+}_4(\text{HL}^{2-})_3\text{H}^{+}_{-2}(\text{H}_2\text{O})_3] 9.3$$

$$K_s(\text{Ca}^{2+}\text{HL}^{2-}) = [\text{Ca}^{2+}][\text{HPO}_4^{2-}] = 10^{-6.25} \text{ mole}^2 \text{ litre}^{-2} [\text{CaHPO}_4(\text{s}) \rightleftharpoons \text{Ca}^{2+} + \text{HPO}_4^{2-}]$$

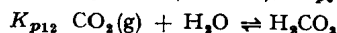
$$K_s[\text{Ca}_4^{2+}(\text{HL}^{2-})_3\text{H}^{+}_{-2}(\text{H}_2\text{O})_3] = \frac{[\text{Ca}^{2+}]^4[\text{HPO}_4^{2-}]^3}{[\text{H}^+]^2} = 10^{9.3} \text{ mole}^5 \text{ litre}^{-5}$$



(v) K_{pnm} , $\dagger K_{pnm}$

Equilibria involving a gas are in general denoted by K_p , and the composition of the complex formed is indicated by the figures given after p in the subscript. For consecutive addition of gaseous ligands, see 9(a)(iv); otherwise the corresponding reactions are given at the beginning of the ligand table under H^+ .

Examples: $\text{CO}_3^{2-}-\text{H}^+$ (table 21), $K_{p0} \text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$;



(f) *Redox equilibria*

Results are given in table 1 of the inorganic section in two forms: as standard electrode potentials, and as equilibrium constants for the addition of the electron as a ligand.

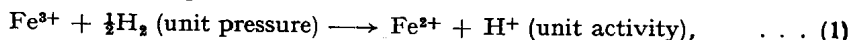
According to the I.U.P.A.C. 1953 convention,* the electrode potential (E_1) of, say, the $\text{Fe}^{2+}-\text{Fe}^{3+}$ system on the hydrogen scale is the potential of the right-hand electrode less that of the left-hand electrode in the cell



when hydrogen gas is at unit pressure and hydrogen ions are at unit activity. The electrode potential has its standard value E° when the ratio of the activities of Fe^{2+} and Fe^{3+} is unity. The electrode potential is also related by the equation

$$-\Delta G_1 = zFE_1$$

to the Gibbs free-energy change (ΔG_1) of the reaction



which takes place when one faraday (F) of positive charge ($z = 1$) passes through the cell from left to right. The standard electrode potential E_1° is similarly related to the standard free-energy change ΔG_1° . Thus

$$\Delta G_1 = \Delta G_1^\circ + \frac{RT}{F} \ln \frac{\{\text{Fe}^{2+}\}}{\{\text{Fe}^{3+}\}}$$

$$E_1 = E_1^\circ + \frac{RT}{F} \ln \frac{\{\text{Fe}^{3+}\}}{\{\text{Fe}^{2+}\}},$$

where $\{ \}$ denotes activity.

The overall chemical reaction (1) may be represented formally by two stages in which electrons take part:



*I.U.P.A.C. Manual of Physico-Chemical Symbols and Terminology, Butterworths Scientific Publications, London, 1959, p. 4.

An electron-activity scale may be established by taking the equilibrium constant of the second stage to be unity for all temperatures and all ionic media :

$$\text{i.e., } K_2 = \frac{\{H^+\}\{e^-\}}{p_{H_2}^{1/2}} = 1 \text{ (activities and fugacity are equilibrium values)}$$

$$\text{and } \Delta G_2^\circ = \Delta H_2^\circ = \Delta S_2^\circ = 0.$$

With the electron activity defined, an equilibrium constant may be written for reaction (2), which may be regarded as the addition of the electron as a ligand :

$$K_2 = \frac{\{Fe^{2+}\}}{\{Fe^{3+}\}\{e^-\}} \quad (\text{activities are equilibrium values}).$$

$$\text{But } K_2 = K_1/K_3 = K_1,$$

$$-\Delta G_1^\circ = zFE_1^\circ = RT \ln K_1,$$

and thus

$$\log_{10} K_2 = zE_1^\circ \left(\frac{RT}{F} \ln 10 \right)^{-1}$$

The fifth column of table 1 gives the chemical equation written as a reduction with z electrons on the left-hand side, the logarithm to base 10 of the corresponding equilibrium constant (analogous to K_2), and then in parentheses the standard electrode potential.

Potentials reported before 1948 are given in international volts (1 international volt = 1.00034 absolute volt), and subsequent ones in absolute volts. If in the original paper E° was calculated from ΔG° , the equilibrium constant has often been calculated directly from the free-energy change rather than from the potential. The factor $RTF^{-1} \ln 10$ has the following values in millivolts (absolute) : 54.195 (0°C), 59.155 (25°C), 64.115 (50°C), 74.035 (100°C).

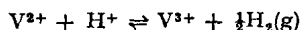
It is hoped that the equilibrium constants will prove more useful than the potentials, since concentrations can be calculated from them more readily.

Examples (25°C, zero ionic strength) :

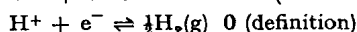
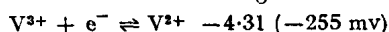
The equilibrium constant

$$K = \frac{[V^{3+}]p_{H_2}^{1/2}}{[V^{2+}][H^+]}$$

for the reaction



can be calculated from the data given in table 1 for the constituent reactions :



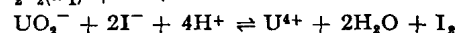
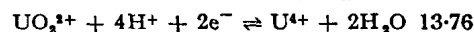
In terms of the equilibrium constants :

$$K = 10^{-(-4.31) + 0} = 10^{4.31} \text{ atm}^{1/2} \text{ mole}^{-1} \text{ litre},$$

and in terms of the potentials :

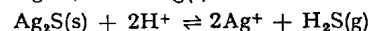
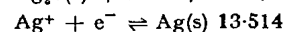
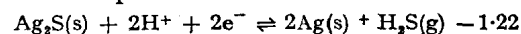
$$\log_{10} K = \left(\frac{zFE^\circ}{2.303 RT} \right) = \frac{-(-255) + 0}{59.155} = 4.31 \text{ (} K \text{ in atm}^{1/2} \text{ mole}^{-1} \text{ litre)}$$

The following further examples are worked only in terms of the equilibrium constants which avoid the introduction of the factor $RTF^{-1} \ln 10$.



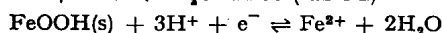
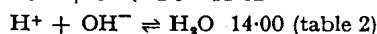
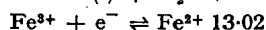
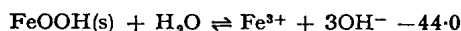
$$K = \frac{[U^{4+}][I_2]}{[UO_2^{2+}][I^-]^2[H^+]^4} = 10^{13.76-2} + 10^{10.52} = 10^{-7.28} \text{ mole}^{-5} \text{ litre}^5.$$

The reaction required need not be a redox one :



$$K = \frac{[Ag^+]^2 p_{H_2S}}{[H^+]^2} = 10^{-1.22 - 2 \times 13.514} = 10^{-28.25} \text{ atm}$$

One may also calculate the equilibrium concentrations in a solution of known electron activity, *e.g.*, the concentration of Fe^{2+} in a solution of known pH and known electron activity in contact with solid FeOOH :



$$K = \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3 \{ \text{e}^- \}} = 10^{-44.0 + 13.02 + 3 \times 14.00} = 10^{11.0} \text{ mole}^{-3} \text{ litre}^3$$

It is interesting to compare the customary treatment of redox equilibria in terms of potentials with the treatment of acid-base equilibria. In the early days it was proposed that acidities should be expressed by "acidity" potentials in volts, but the choice of $\{ \text{H} \}$ and pH has proved to be convenient. For any redox system, either homogeneous or heterogeneous, one may define the quantity pE , analogous to pH, by the equation

$$pE = -\log_{10} \{ \text{e}^- \}.$$

From the equations given above, it can be seen that the pE of any system is related to its electrode potential by the relation

$$pE = \left(\frac{RT}{F} \ln 10 \right)^{-1} E,$$

and that for a system in which the activities of the chemical substances are unity

$$pE^\circ = \left(\frac{RT}{F} \ln 10 \right)^{-1} E^\circ = \frac{1}{z} \log_{10} K,$$

where K is the equilibrium constant for the chemical reaction written as a reduction with z electrons on the left-hand side. The concept of pE is thus closely related to the type of equilibrium constant given in table 1 and so may be found to be useful.

10. **ENTHALPY AND ENTROPY CHANGES.** These are included in the fifth column and, unless otherwise stated, ΔH is in kilocalories and ΔS in calories degree⁻¹, each for the numbers of moles in the corresponding chemical equation. Where the symbol K is used for the equilibrium constant, H or S is given the same superscript or subscript as the corresponding K : *e.g.*, $K_n \Delta H_n$; $K_{so} \Delta H_{so}$; $\dagger K_{nm} \Delta \dagger H_{nm}$; etc. For inorganic equilibria which are represented by a cumulative constant, β , the following notation is used: $\beta_n \Delta H_{\beta n}$; $\beta_{nm} \Delta H_{\beta nm}$; $*\beta_{nm} \Delta *H_{\beta nm}$; etc.

Readers making rough estimates of heat-content changes from temperature coefficients of equilibrium constants, or *vice versa*, may find the following numerical values useful. In the equation

$$\frac{d \log K}{dT} = \frac{\Delta H}{2.303RT^2} = \text{constant} \times \Delta H$$

the constant is 0.00293 (0°C), 0.00246 (25°C), and 0.00209 (50°C) if ΔH is expressed in kcal.

11. **REMARKS.** The following abbreviations are also used in the fifth column, chiefly in the inorganic section:

ev $M_m L_n$	evidence for the existence of the complex $M_m L_n$.
cpx	complex.
cat	cationic (positive).
ani	anionic (negative).
unch	uncharged.
polyn	polynuclear.
?	author's doubt expressed in the reference given.
(?)	compiler's doubt.
(K_1 3.71)	the value $\log K_1 = 3.71$ was assumed (<i>e.g.</i> , from earlier work).

For a convention used in the organic section for references to acidity constant determinations, see Section 8(a).

12. REFERENCES. The symbols in the last column of each table relate to the references which are listed at the end of each table. Each reference is characterised by two figures denoting the year of publication followed by a capital letter denoting the name of the author, or of the first author when there are several. All years up to and including 1900 are given as 00, and to distinguish between references with the same year and capital letter, a lower-case letter is added as in 57M, 57Ma, 57Mb, etc.

In the inorganic section, the plus sign (+), the oblique stroke (/), and the signs for equality (=) and approximate equality (\simeq) are used to give additional information by means of the conventions illustrated by the examples below. References placed after the oblique stroke used mainly, or exclusively, the data of other workers, and the plus sign denotes that additional data were taken from the references following it.

55M	conclusions of 55M from data in 55M.
55M + 47S	conclusions of 55M from data in 55M and in 47S.
55M +	conclusions of 55M from data in 55M and in numerous or unspecified other references.
57A \simeq 55M	conclusions and data of 57A are substantially the same as those of 55M.
57A = 55M	conclusions and data of 57A are identical with those of 55M.
55M/62S	conclusions of 62S from data in 55M.
55M/	conclusions of compiler from data in 55M.
/32S	conclusions of 32S from data in numerous or unspecified other references.

If a critical survey is claimed, "lit" is used.

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