

3.2 Solution equilibria

3.2.1 Introduction

It is desirable to recommend standard symbols for equilibrium constants. However, it is hard to predict in which direction research will proceed and, hence, the standards must not be too rigidly fixed to the interests of present-day equilibrium chemists. Even authors following the recommendations below are strongly advised to define the symbols they are using in a prominent place in the beginning of each book or research paper.

The IUPAC-Chemical Society Tables entitled "Stability Constants of Metal-Ion Complexes" (Part A, Inorganic Ligands [1982] and Part B, Organic Ligands [1980], Pergamon Press, Oxford), brought with them, even without any official decision by the IUPAC, a certain *de facto* standardization of symbols for equilibrium constants. The symbols used for stepwise and overall or cumulative constants K_n and β_n appear in practically all papers published by the leading schools of coordination chemistry. Other defined symbols are also used, though less frequently.

More recently the publication of the "Stability Constants Database" [1993] (IUPAC/Academic Software, Otley, UK) has introduced the constraints of a PC database in reporting equilibria (which may have used more extended formulae in a book volume). The 1980, 1982 and earlier book volumes of stability constants were included in the Stability Constants Database by late 1995. This will achieve a uniformity of symbols used to express solution equilibria and will set a format for publication of data.

3.2.2 General rules

The general symbol for an *equilibrium constant* is K . The equilibrium constant for any reaction may be denoted by K , followed by the reaction formula within parentheses.

Thermodynamic definition

Equilibrium constants are strictly thermodynamically defined in terms of activities. The (relative) activity for each species is defined in terms of some measurable quantity, e.g., a concentration, a partial pressure, a mole fraction, so that the activity approaches this quantity as the system approaches a certain limiting state. For dissolved species, the limiting state, the *medium*, is sometimes defined as the pure solvent (H_2O , C_2H_5OH , etc). It may, however, be defined as a mixed solvent or a salt medium such as 3M $NaClO_4$ at 25°C.

For a reaction involving only dissolved species, the equilibrium constant may be defined as the limiting value of the concentration quotient when the concentrations of the reactants and products approach zero.

Examples:

$$K(\text{H}^+ + \text{A}^- \rightleftharpoons \text{HA}) = \lim ([\text{HA}][\text{H}^+]^{-1}[\text{A}^-]^{-1}),$$

as $[\text{H}^+] \rightarrow 0$, $[\text{A}^-] \rightarrow 0$, and $[\text{HA}] \rightarrow 0$ in the pure medium.

$$K(\text{HgBr}_2 + \text{Br}^- \rightleftharpoons \text{HgBr}_3^-) = \lim ([\text{HgBr}_3^-][\text{HgBr}_2]^{-1}[\text{Br}^-]^{-1}),$$

as $[\text{HgBr}_2] \rightarrow 0$, $[\text{Br}^-] \rightarrow 0$, and $[\text{HgBr}_3^-] \rightarrow 0$
in the pure medium.

The medium could, for example, be pure H_2O , 30 wt% $\text{C}_2\text{H}_5\text{OH}$ in water, or 3M LiNO_3 .

It is not often realized that equilibrium constants that refer to an *ionic medium* are as well defined thermodynamically as those referring to pure H_2O . The difference is only that another activity scale is being used, where, for example, $a(\text{Br}^-)/[\text{Br}^-] \rightarrow 1$ as $[\text{Br}^-] \rightarrow 0$ in the pure ionic medium instead of in $\text{H}_2\text{O}(\text{l})$.

Necessary specification

The formula must give the reacting species, and the phases in which they occur. It may be stated in the text that, if nothing is said to the contrary, a species is in one particular phase. The temperature and pressure (if not 1 bar) and the activity scale must be stated explicitly. The pressure unit should be stated for gases. For dissolved substances it should be stated, for instance, whether the activities are defined so that the ratio (activity/concentration) approaches unity on dilution with pure solvent or with some ionic medium. The concentration unit should also be stated (M, mol dm^{-3} , mole/kg solvent, mole fraction).

Special and *ad hoc* symbols

Special symbols are recommended below for a few common types of equilibrium constants. To avoid confusion these symbols must not be used for other purposes. Some of the recommended symbols may be a convenient shorthand notation for use in Tables. Authors will possibly invent convenient symbols such as K' , K'' etc. for their special purpose. Such *ad hoc* symbols must be clearly defined in some conspicuous place in the beginning of the text and provided with the necessary specifications mentioned above. However, this approach should not be used in preference to the symbols defined in 3.3.3. The recommended symbols are discussed in detail in the Manual accompanying "Stability Constants Database" [1993].

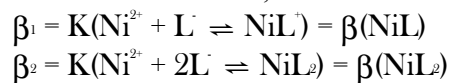
3.2.3 Complex formation equilibria

3.2.3.1 Mononuclear binary complexes

- (i) The *overall formation constant* or *cumulative formation constant* for any complex can be denoted by the symbol β_n , where n indicates the number of ligands L binding to metal M in a single overall (cumulative) process. A clear specification of the species (including their electronic charges) to which L and M refer should always be given.

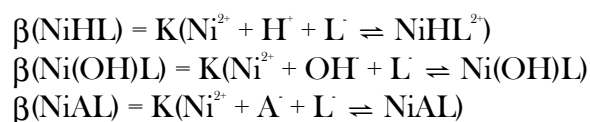
Examples:

For the reaction between Ni^{2+} and L^- ,



- (ii) if two or more metals (including H^+) or ligands are involved in complex formation then the β_n nomenclature is inadequate. To become explicit β must be followed, in parentheses, by the product formula or by the reactant stoichiometries.

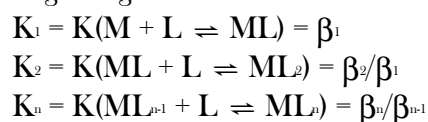
Examples:



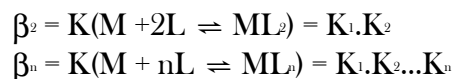
- (iii) Cumulative formation constants β_n (for addition of n ligands to a metal) are related to *stepwise formation constants* K_n (for addition of the nth ligand to a metal):

$$\text{K}_n = \beta_n / \beta_{n-1}$$

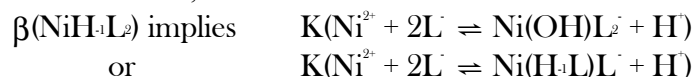
Examples, omitting charges:



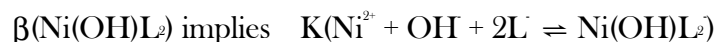
Conversely:



- (iv) When using the β notation the product formula will be based on the reactant stoichiometries. Thus,



whereas

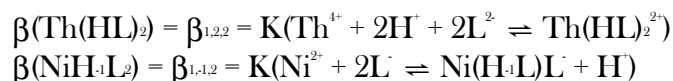


3.2.3.2 General binary or ternary systems

The *overall formation constants* for all equilibria can be represented explicitly by use of the $\beta_{p,q,r}$ notation. The coefficients p, q and r refer to the stoichiometry of components, e.g. M, H and L, in the overall process, and must be defined by an appropriate equation:



Examples:

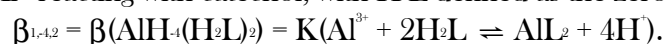


In these examples p, q and r are used to define the stoichiometries of M, H and L. However, this is only one convention to be found in the literature. Others are $\beta_{p,q,r} = \beta(\text{H}_p\text{M}_q\text{L}_r)$ and $\beta_{p,q,r} = \beta(\text{M}_p\text{L}_q\text{H}_r)$. Because there is no standard formalism it is essential that $\beta_{p,q,r}$ be defined explicitly in the text.

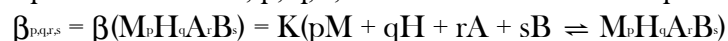
β_n refers to the ligand at zero proton level, which in the above examples is L. Although this is a common convention it is not adopted universally. For example, when a ligand has very weakly acidic protons, which in the absence of a metal ion do not all dissociate in an accessible pH range, it is convenient to write:



Example: for Al^{3+} reacting with catechol, with H_2L defined as the zero proton level,

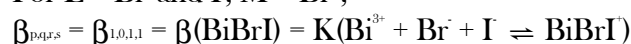


Note: The use of β_n is given preference in cases with simple mono-nuclear metal-ligand complexes. However, in cases where there are several different ligands or several different metal atoms, or protonated or deprotonated complexes, or one does not wish to distinguish between 'metal' and 'ligand' in the reactions, then $\beta_{p,q,r}$ should be used. Additional components, such as A and B and appropriate coefficients, p, q, r, s should be defined as required:

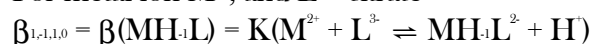


Examples:

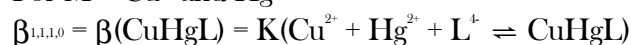
For L = Br⁻ and I⁻; M = Bi³⁺;



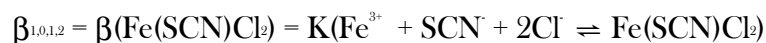
For metal ion M²⁺, and L = citrate³⁻



For M = Cu²⁺ and Hg²⁺



For L = SCN⁻ and Cl⁻



3.2.3.3 Polynuclear complexes

For (homo- or hetero-)polynuclear complexes it may sometimes be practicable to use β with double or multiple subscripts. Their general meaning must be defined very clearly with a full reaction formula. Strict standardization in this field has not yet been achieved. The 'Stability Constants Database' uses the following definitions:

$$\beta_{m,n} = \beta(M_m L_n) = K(mM + nL \rightleftharpoons M_m L_n)$$

By this definition, the first subscript gives the number of 'metal' ions. For mononuclear complexes, $\beta_{1,n} = \beta_n$ so that the first subscript can be dropped.

Example: for $M = \text{Sn}^{2+}$ and $L = \text{OH}$,

$$\beta_{3,4} = \beta(\text{Sn}_3(\text{OH})_4) = K(3\text{Sn}^{2+} + 4\text{OH} \rightleftharpoons \text{Sn}_3(\text{OH})_4^{2-});$$

3.2.3.4 Ligand acidity constant

The *acidity constant*, K_a , is the equilibrium constant for splitting off the n th proton from a charged or uncharged acid, to be defined. One may write K_n for K_{a1} .

Example: for second dissociation step of H_3PO_4 ,

$$K_{a2} = K(\text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+).$$

3.2.3.5 Ligand protonation constant

The *protonation constant*, K_p , is the equilibrium constant for the addition of the n th proton to a charged or uncharged ligand, L . The cumulative protonation constant, β_n is the equilibrium constant for the addition of n H^+ to L .

Examples: For the conjugate base (ligand) PO_4^{3-} .

$$K_1 = K(\text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{HPO}_4^{2-})$$

$$\beta_3 = K(3\text{H}^+ + \text{PO}_4^{3-} \rightleftharpoons \text{H}_3\text{PO}_4)$$

$$K_3 = K(\text{H}_2\text{PO}_4^- + \text{H}^+ \rightleftharpoons \text{H}_3\text{PO}_4),$$

where the reciprocal value $1/K_3 = K(\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+)$ is K_{a1} or $K_a(\text{H}_3\text{PO}_4)$.

A particularly important example is when $L = \text{OH}$, then

$$K_1 = K(\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O})$$

and $1/K_1 = K_w$, the autoprotolysis constant or ionic product of water.

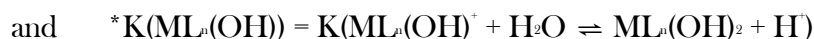
In the case of metal ion hydrolysis to give polynuclear species the symbol $\beta_{m,n}$ is used. For example, for Al^{3+} ,

$$^*\beta_{3,4} = K(3\text{Al}^{3+} + 4\text{H}_2\text{O} \rightleftharpoons \text{Al}_3(\text{OH})_4^{5+} + 4\text{H}^+)$$

3.2.3.6 Proton dissociation from complexes

Equilibrium between a 'metal' M or metal complex ML_n and H_2O , with liberation of H^+ , is so often studied that it is practical to use a special symbol. In "Stability Constants Database", the symbol *K is used.

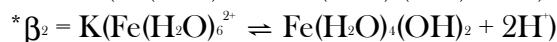
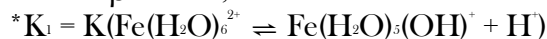
$$^*K(\text{ML}_n) = K(\text{ML}_n^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{ML}_n(\text{OH})^+ + \text{H}^+)$$



For certain ligands, which may deprotonate beyond the zero proton level (e.g. citrate):



For metal aqua ions an hydrolysis reaction to yield a mononuclear hydroxo species is also represented by *K_n or ${}^*\beta_n$. Thus, for Fe^{2+}



3.2.4 Connected quantities (average ligand number etc.)

A barred letter, following the usage in other fields, denotes the average value for the quantity in question among the species considered.

\bar{n} , the average number of ligands (L) bound per metal ion (M), is given by the general expression:

$$\bar{n} = \frac{\sum n[\text{M}_m\text{L}_n]}{\sum m[\text{M}_m\text{L}_n]} = \frac{\sum n\beta_{m,n}[\text{M}]^m[\text{L}]^n}{\sum m\beta_{m,n}[\text{M}]^m[\text{L}]^n}$$

The sums are, in general, taken for all the species M_mL_n , with $n = 0, 1, 2, \dots, n_{\text{max}}$, and $m = 0, 1, 2, \dots, m_{\text{max}}$. If only mononuclear complexes ($m=1$) are formed

$$\bar{n} = \frac{\sum n[\text{ML}_n]}{\sum [\text{ML}_n]} = \frac{\sum n\beta_n[\text{M}][\text{L}]^n}{\sum \beta_n[\text{M}][\text{L}]^n} = \frac{\sum n\beta_n[\text{L}]^n}{\sum (1 + \beta_n[\text{L}]^n)}$$

This implies that theoretical \bar{n} (log [L]) curves are easily calculated if the different β_n values are known. Furthermore, it can be seen that coinciding \bar{n} (log [L]) curves will be obtained (independent of $[\text{M}]_{\text{tot}}$ and $[\text{L}]_{\text{tot}}$) if a series of mononuclear complexes are formed. This will also be the case if homonuclear species are formed provided that the "free" metal ion concentration is negligible.

Experimental \bar{n} values can also be calculated. For example, if $\text{L} = \text{OH}$, \bar{n} is given by the expression:

$$\bar{n} = \frac{([\text{OH}]_{\text{tot}} - K_w[\text{H}^+]^{-1} + [\text{H}^+])}{[\text{M}]_{\text{tot}}}$$

In the presence of a weak base L, \bar{n} can be calculated with the assumption that only a series of complexes M_mL_n are formed:

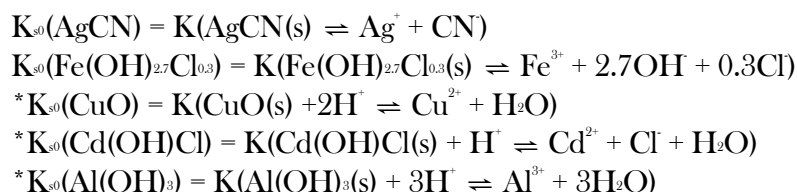
$$\bar{n} = \frac{\{[\text{L}]_{\text{tot}} - ([\text{H}^+]_{\text{tot}} - [\text{H}^+] + K_w[\text{H}^+]^{-1}) / \bar{n}_{\text{H}}\}}{[\text{M}]_{\text{tot}}}$$

Here \bar{n}_{H} denotes the average number of protons bound per ligand L.

3.2.5 Solubility equilibria

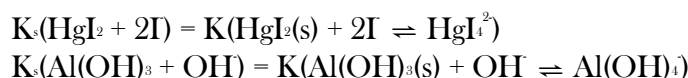
For equilibria in which one solid phase is dissolved to give a number of species in solution, one may use the shorthand notation, K_{s0} , followed, within parentheses, by the formulae for the other participants in the reaction. If the reactant is dissolved in the stoichiometric amount of acid then the symbol ${}^*K_{s0}$ is used.

Examples:



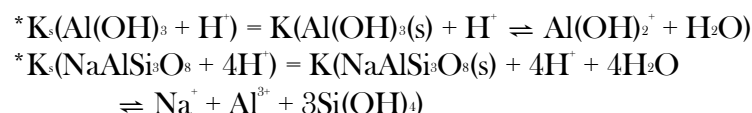
Other dissolution reactions (for example, dissolution in a solution containing a ligand in excess) are specified by (i) the symbol K_s , followed in parentheses by the reactant species and stoichiometries, or (ii) by the symbol K , followed by the equation for the complete reaction.

Examples:



However, if the solution process involves the reaction between a solid phase and protons, then the reaction is specified by (i) the symbol $*K_s$, followed in parentheses by the reactant species and stoichiometries, or (ii) by the symbol K , followed by the equation for the complete reaction.

Examples:



3.2.6 Conditional constants

A *conditional constant* is a concentration quotient that is applicable only when the concentration/activity of one or more reactants or products is fixed at a definite value. For example, when the equilibrium $\text{M} + \{\text{L} + \text{HL} + \text{H}_2\text{L} + \dots + \text{H}_n\text{L}\} \rightleftharpoons \text{ML} + \omega\text{H}^+$ is studied at fixed pH, a conditional (or effective) constant can be defined by (ionic charges are omitted for the sake of simplicity):

$$K_{L,\text{eff}} = [\text{ML}]/[\text{M}][\text{L}]' = [\text{ML}]/[\text{M}]\{\text{L} + \text{HL} + \text{H}_2\text{L} + \dots + \text{H}_n\text{L}\}$$

where $\{\text{L} + \text{HL} + \text{H}_2\text{L} + \dots + \text{H}_n\text{L}\}$ is the total non-complexed ligand. If the β_n protonation constants are known, then

$$K_{L,\text{eff}} = K_L/(1 + \beta_1[\text{H}] + \beta_2[\text{H}]^2 + \dots + \beta_n[\text{H}]^n)$$

Thus, a concentration quotient will also be a conditional constant when the experimental method has not differentiated between the chemical forms of the complex (e.g. ML , MHL , MH_2L) and/or ligand (L , HL , H_2L) in the reaction $\text{M} + \text{Ligand} \rightleftharpoons \text{Complex}$. For example, for the binding of a metal to a protein at pH 7.4:

$$K_{\text{eff}} = ([\text{ML}] + [\text{MHL}] + \dots)/[\text{M}](\text{[L]} + [\text{HL}] + \dots + [\text{H}_n\text{L}])$$

Conditional constants are valid only for the experimental conditions defined.