

INTERNATIONAL UNION OF
PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON EQUILIBRIUM DATA

RECOMMENDED SYMBOLS
FOR SOLUTION EQUILIBRIA

A Report prepared by

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LONDON

BUTTERWORTHS

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RECOMMENDED SYMBOLS FOR SOLUTION
EQUILIBRIA

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INTRODUCTION

The IUPAC–Chemical Society tables of Stability Constants seem to have brought with them, even without any official decision by the IUPAC, a certain *de facto* standardization of symbols for equilibrium constants. Stability constants are increasingly used instead of instability constants, and the symbols K_n and β_n are being used for stepwise and cumulative constants in practically all papers published by the leading schools of coordination chemistry.

The Commission thinks that it is desirable to recommend standard symbols for equilibrium constants. However, it is hard to predict in which direction research will expand in decades to come, and hence the standards must not be too rigidly fixed to the perhaps rather limited interests of the majority of present-day equilibrium chemists.

Even authors following the recommendations below are strongly advised to define the symbols they are using in a conspicuous place in the beginning of each book or research paper.

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 to this quantity as the system approaches a certain limiting state. For dissolved species the limiting

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state—the “medium”—is sometimes defined as the pure solvent (H_2O , $\text{C}_2\text{H}_5\text{OH}$, etc.). It may, however, equally well 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, one may define the equilibrium constant as the limiting value of the concentration quotient when the concentrations of the reactants approach zero.

Examples

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

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

The medium may then for instance be pure H_2O , 30% $\text{C}_2\text{H}_5\text{OH}$, or 3M LiNO_3 .

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

The approximation activity = concentration has usually proved quite good, if the solute concentrations are only a small fraction of the medium ions, and is used by most of those who are determining equilibrium constants in ionic media, without any attempted extrapolation. The error involved in this approximation can as a rule be expected to be no greater than the uncertainty in extrapolation to zero concentration in pure H_2O .

Necessary specification

The formula must give the reacting species, and the phases they occur in. It may be stated in the text that, if nothing is said, a species is in one specific phase; in the examples this is an aqueous solution. When numerical values are given, the temperature and pressure (if not 1 atm) must be stated explicitly, and also the activity scale used. The pressure unit should thus 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, mole/kg solvent, mole fraction).

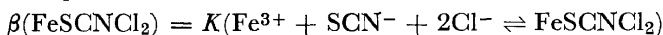
Special and *ad hoc* symbols

Special symbols are recommended below for a few very common types of equilibrium constants. These symbols must not be used for other purposes, if confusion is possible. Some of the recommended symbols may be a convenient shorthand writing in lists and tables but would nevertheless be too unwieldy for use in equations. Each author will surely invent convenient symbols such as K' , K'' , $K_{(8)}$, Q_3 , etc. for his 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.

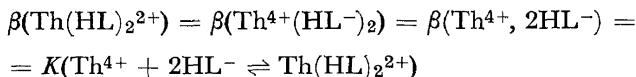
COMPLEX FORMATION EQUILIBRIA

General symbols

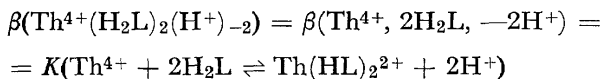
The overall formation constant for any complex can be denoted by β followed, within parentheses, by the formula of the complex or, if there may be ambiguity, by the formulae of the components so that the formula for the complex is obtained by addition.

Examples

This can also be written $\beta(\text{Fe}^{3+}\text{SCN}^-(\text{Cl}^-)_2)$ or

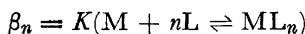
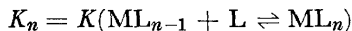
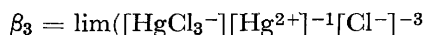
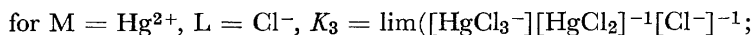


However,

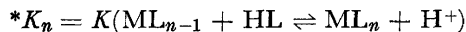


Mononuclear binary complexes

If a central atom (central group) M (the "metal") and a ligand L have been defined, then K_n is the stepwise formation constant, and β_n is the cumulative formation constant for the complex ML_n . They can both be referred to as stability constants (stepwise and cumulative):

*Example*

Equilibria between a "metal" M and a protonated ligand HL, with liberation of H^+ , are so often studied that it may sometimes be practical to use a special symbol. "Stability Constants" uses the symbols $*K_n$ and $*\beta_n$.



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

Note: The use of M, L and n should be given preference in cases with simple mononuclear metal-ligand complexes but other symbols for the reagents, such as A and B, and other symbols for the coefficients, such as p, q, r, s . . . , may be used if needed, e.g. in cases where one has several different ligands or several different metal atoms, or does not wish to distinguish between "metal" and "ligand" in the reactions.

Polynuclear and mixed complexes

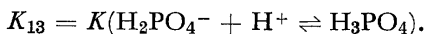
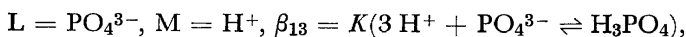
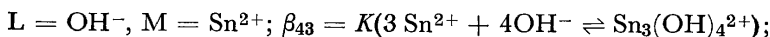
For polynuclear complexes or complexes with several kinds of ligands it may sometimes be practical to use β with double or multiple subscripts. Their general meaning must then be defined very clearly with a full reaction formula. The examples given below of β 's with a double subscript are only illustrations of convenient systems of notation but *the Commission does not find a strict standardization in this field necessary*.

For polynuclear complexes, the classification of one reagent as the "metal" and the other as the "ligand" may sometimes seem arbitrary. "Stability Constants", which had to choose one and be consistent, uses the definition

$$\beta_{nm} = K(nL + mM \rightleftharpoons M_m L_n); K_{1n} = K(M_{n-1} L + M \rightleftharpoons M_n L)$$

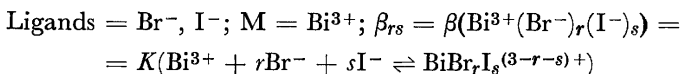
By this definition, the second subscript gives the number of "metal" ions. For mononuclear complexes, $\beta_{n1} = \beta_n$ so that the second index can be dropped.

Examples



For mixed complexes one may use similar notations. The alphabetic order of the ligands is recommended if there is no strong reason for any other order.

Example



If there is no risk that, for instance, β_{22} could be read as " $\beta_{sub 22}$ " then it can be written as here, otherwise a comma should be inserted: $\beta_{2,2}$.

Protonation equilibria

Equilibria with protons may be treated as a special case of complex formation; to make the treatment analogous with that of metal ion complexes, it is usually logical to make $H^+ = M$, the central atom. This is done consistently in the tables of Stability Constants, and is illustrated above for $L = PO_4^{3-}$, $M = H^+$. Some special symbols are convenient, in addition:

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

The *protonation constant*, K_{H_n} is the equilibrium constant for the addition of the n th proton to a charged or uncharged ligand, to be defined. The cumulative protonation constant β_{H_n} is the equilibrium constant for the formation of $H_n L$ from nH^+ and L . For the ionization constant of water, the special symbol K_w may be used, $K_w = K(H_2O \rightleftharpoons H^+ + OH^-)$.

The same equilibrium constant may thus be described in several ways, dependent on how the ligand L , or the acid, has been defined. This may be permissible because of the great importance of protonation equilibria.

Example

$K(\text{H}^+ + \text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}_3\text{PO}_4)$ may be denoted by

K_{13} (if $\text{L} = \text{PO}_4^{3-}$, $\text{M} = \text{H}^+$), by $K_{\text{H}_3}(\text{PO}_4^{3-})$, or $K_{\text{H}}(\text{H}_2\text{PO}_4^-)$

or by the general symbol $\beta(\text{H}^+\text{H}_2\text{PO}_4^-)$. The inverted value,

$K(\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+)$ is $K_a(\text{H}_3\text{PO}_4)$.

Connected quantities (average ligand numbers etc.)

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

Examples

$$\bar{n} = \frac{\sum n[\text{ML}_n]}{\sum [\text{ML}_n]}; \bar{p} = \frac{\sum p[\text{A}_p\text{B}_q]}{\sum [\text{A}_p\text{B}_q]};$$

$$\bar{q} = \frac{\sum q[\text{A}_p\text{B}_q]}{\sum [\text{A}_p\text{B}_q]}$$

The sums are, in general, taken for all species ML_n with $n = 0, 1, 2 \dots n_{\text{max}}$; and for all species A_pB_q except A and B. If some other species should be included or excluded in the sums, this must be stated clearly in the text.

The average number of L bound per M present can often be measured directly. If only mononuclear complexes are present, it is identical with \bar{n} , the average value of n in the formula ML_n .

If, however, polynuclear complexes are present and if their general formula is written as M_mL_n , then the average number of ligands bound per M is not the same as \bar{n} , the average value of n , and must be given another symbol, such as Z .

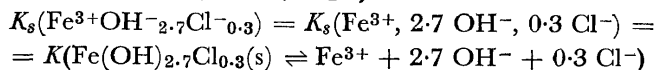
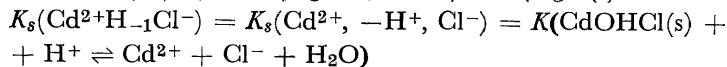
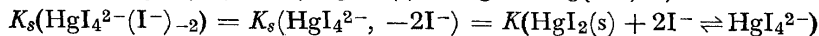
$$Z = \frac{\sum n[\text{M}_m\text{L}_n]}{\sum m[\text{M}_m\text{L}_n]}; \bar{n} = \frac{\sum n[\text{M}_m\text{L}_n]}{\sum [\text{M}_m\text{L}_n]}$$

($[\text{M}]$ is included in the sums for Z , and may be included in those for \bar{n}). For instance, in a solution which contains practically only the complex M_2L_3 , we would have $\bar{n} \approx 3$ (average value of n) but $Z \approx 1.5$ (average number of L bound per M).

What has been called Z might still be called \bar{n} provided the complexes were written as $(\text{ML}_n)_m$ instead of M_mL_n , or another letter than n were used in the general formula. Less confusion would arise, however, if another symbol than \bar{n} were used in systems known to involve polynuclear species.

SOLUBILITY EQUILIBRIA

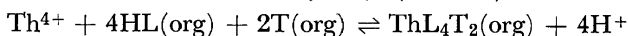
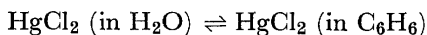
For equilibria in which one solid phase is dissolved to give a number of species in solution, one may use the shorthand notation K_s , followed, within parentheses, by the formulae for the other participants in the reaction.

Examples

LIQUID-LIQUID DISTRIBUTION EQUILIBRIA

Reaction formulae, denotation of phases

Typical distribution equilibria are the following:



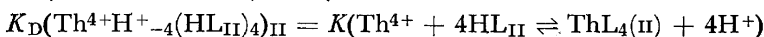
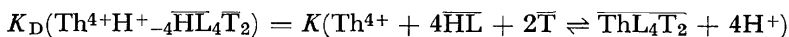
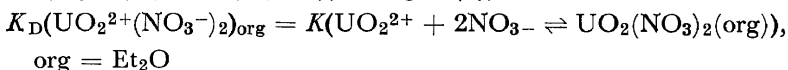
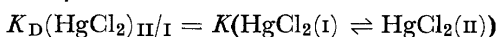
In the last case, one would have to define HL, T, and the solvent, "org".

Most distribution equilibria studied at present involve (like those above) an aqueous phase and an organic phase. In the future, however, other combinations of phases may be studied extensively: $\text{SO}_2(\text{l})$, molten salts and metals, etc., and so it does not seem wise to restrict the symbolism to the organic/aqueous case.

The phases may be denoted by the formula of the solvent, or by "org", (to be defined in the text), or by overlining formulas referring to one phase, usually the less polar phase, or by Roman numerals (also to be defined in the text). One may state (as above) that species without phase notation are in one phase (here aqueous solution). To make typing and printing easier it is recommended that full formulae for solvents be given on the line, and not as a subscript whereas Roman numerals may be used as subscripts, both in reaction formulae and in expressions for concentrations such as $[\text{ThL}_4\text{T}_2]_{\text{II}}$.

Equilibrium constants

The general symbol for an equilibrium constant involving solutes in two liquid phases is K_{D} . The following are examples of a possible notation:

Examples

This way of writing might imply a certain economy of space, especially where it is necessary to write out the formulae for L, T and II.

The first type of equilibrium constant may be called "distribution constant" straight away and the others "overall distribution constants".

Connected quantities

The analytical distribution ratio for any component between two phases will be denoted by D , if necessary with the component and the phases stated, for instance $D(\text{Hg})_{\text{II/I}}$, or D_{Hg} , or D . As a rule, D varies with the composition of the solution, as distinguished from K_{D} , which is a true equilibrium constant.

The symbol K with or without a subscript should be used only for true equilibrium constants, and the occasional misuse of K symbols for variable concentration quotients must be discouraged.