# Chapter II

# Standards, Conventions and Contents of the Tables

This chapter outlines and lists the symbols, terminology and nomenclature, the units and conversion factors, the order of formulae, the standard conditions, and the fundamental physical constants used in this volume. They are derived from international standards and have been specially adjusted for the TDB publications.

## II.1  Symbols, terminology and nomenclature

### II.1.1  Abbreviations

Abbreviations are mainly used in tables where space is limited. Abbreviations for methods of measurement are listed in Table II-1.

Table II-1: Abbreviations for experimental methods.

| | |
|---|---|
| aix | Anion exchange |
| AES | Atomic Emission Spectroscopy |
| cal | Calorimetry |
| chr | Chromatography |
| cix | Cation exchange |
| col | Colorimetry |
| con | Conductivity |
| cou | Coulometry |
| cry | Cryoscopy |
| dis | Distribution between two phases |
| DSC | Differential Scanning Calorimetry |
| DTA | Differential Thermal Analysis |
| EDS | Energy Dispersive Spectroscopy |
| em | Electromigration |
| emf | Electromotive force, not specified |

Table II-1 (continued)

| | |
|---|---|
| EPMA | Electron Probe Micro Analysis |
| EXAFS | Extended X–ray Absorption Fine Structure |
| FTIR | Fourier Transform Infra Red |
| IDMS | Isotope Dilution Mass–Spectroscopy |
| ir | Infrared |
| gl | Glass electrode |
| ise–x | Ion selective electrode with ion X stated |
| ix | Ion exchange |
| kin | Rate of reaction |
| LIBD | Laser Induced Breakdown Detection |
| MVD | Molar Volume Determination |
| NMR | Nuclear Magnetic Resonance |
| PAS | Photo Acoustic Spectroscopy |
| pol | Polarography |
| pot | Potentiometry |
| prx | Proton relaxation |
| qh | Quinhydrone electrode |
| red | Emf with redox electrode |
| SEM | Scanning Electron Microscopy |
| sp | Spectrophotometry |
| sol | Solubility |
| TC | Transient Conductivity |
| TEM | Transmission Electron Microscopy |
| TGA | Thermo Gravimetric Analysis |
| TLS | Thermal Lensing Spectrophotometry |
| TRLFS | Time Resolved Laser Fluorescence Spectroscopy |
| UV | Ultraviolet |
| vlt | Voltammetry |
| XANES | X–ray Absorption Near Edge Structure |
| XRD | X–ray Diffraction |
| ? | Method unknown to the reviewers |

Other abbreviations may also be used in tables, such as SHE for the standard hydrogen electrode or SCE for the saturated calomel electrode. The abbreviation NHE has been widely used for the "normal hydrogen electrode", which is by definition identical to the SHE. It should nevertheless be noted that NHE customarily refers to a standard state pressure of 1 atm, whereas SHE always refers to a standard state pressure of 0.1 MPa (1 bar) in this review.

## II.1.2  Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [1979WHI], [1993MIL/CVI]. They are summarised in Table II-2.

Table II-2: Symbols and terminology.

| Symbols and terminology | |
|---|---|
| length | $l$ |
| height | $h$ |
| radius | $r$ |
| diameter | $d$ |
| volume | $V$ |
| mass | $m$ |
| density (mass divided by volume) | $\rho$ |
| molar surface area | $\mathcal{A}$ |
| time | $t$ |
| frequency | $\nu$ |
| wavelength | $\lambda$ |
| internal transmittance (transmittance of the medium itself, disregarding boundary or container influence) | $T$ |
| internal transmission density, (decadic absorbance): $\log_{10}(1/T_i)$ | $A$ |
| molar (decadic) absorption coefficient: $A / c_B l$ | $\varepsilon$ |
| relaxation time | $\tau$ |
| Avogadro constant | $N_A$ |
| relative molecular mass of a substance[a] | $M_r$ |
| thermodynamic temperature, absolute temperature | $T$ |
| Celsius temperature | $t$ |
| (molar) gas constant | $R$ |
| Boltzmann constant | $k$ |
| Faraday constant | $F$ |
| (molar) entropy | $S_m$ |
| (molar) heat capacity at constant pressure | $C_{p,m}$ |
| (molar) enthalpy | $H_m$ |
| (molar) Gibbs energy | $G_m$ |
| chemical potential of substance B | $\mu_B$ |
| pressure | $p$ |
| partial pressure of substance B: $x_B p$ | $p_B$ |
| fugacity of substance B | $f_B$ |

(Continued next page)

Table II-2 (continued)

| Symbols and terminology | |
| --- | --- |
| fugacity coefficient: $f_B/p_B$ | $\gamma_{f,B}$ |
| amount of substance[b] | $n$ |
| mole fraction of substance B: | $x_B$ |
| molarity or concentration of a solute substance B (amount of B divided by the volume of the solution) [c] | $c_B$, [B] |
| molality of a solute substance B (amount of B divided by the mass of the solvent) [d] | $m_B$ |
| factor for the conversion of molarity to molality of a solution: $m_B/c_B$ | $\xi$ |
| mean ionic molality [e], $m_\pm^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$ | $m_\pm$ |
| activity of substance B | $a_B$ |
| activity coefficient, molality basis: $a_B/m_B$ | $\gamma_B$ |
| activity coefficient, concentration basis: $a_B/c_B$ | $y_B$ |
| mean ionic activity [e], $a_\pm^{(\nu_+ + \nu_-)} = a_B = a_+^{\nu_+} a_-^{\nu_-}$ | $a_\pm$ |
| mean ionic activity coefficient [e], $\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$ | $y_\pm$ |
| osmotic coefficient, molality basis | $\phi$ |
| ionic strength: $I_m = \frac{1}{2}\sum_i m_i z_i^2$ or $I_c = \frac{1}{2}\sum_i c_i z_i^2$ | $I$ |
| SIT ion interaction coefficient between substance $B_1$ and substance $B_2$) | $\varepsilon(B_1, B_2)$ |
| stoichiometric coefficient of substance B (negative for reactants, positive for products | $\nu_B$ |
| general equation for a chemical reaction | $0 = \sum_B \nu_B B$ |
| equilibrium constant [f] | $K$ |
| charge number of an ion B (positive for cations, negative for anions) | $z_B$ |
| charge number of a cell reaction | $n$ |
| electromotive force | $E$ |
| $pH = -\log_{10}[a_{H^+}/(mol \cdot kg^{-1})]$ | pH |
| electrolytic conductivity | $\kappa$ |
| superscript for standard state [g] | $\circ$ |

a:   ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ of the mass of an atom of nuclide $^{12}C$.

b:   *cf.* sections 1.2 and 3.6 of the IUPAC manual [1979WHI].

c:   This quantity is called "amount–of–substance concentration" in the IUPAC manual [1979WHI]. A solution with a concentration equal to 0.1 $mol \cdot dm^{-3}$ is called a 0.1 molar solution or a 0.1 M solution.

d:   A solution having a molality equal to 0.1 $mol \cdot kg^{-1}$ is called a 0.1 molal solution or a 0.1 m solution.

e:   For an electrolyte $N_{\nu_+} X_{\nu_-}$ which dissociates into $\nu_\pm \, (= \nu_+ + \nu_-)$ ions, in an aqueous solution with molality $m$, the individual cationic molality and activity coefficient are $m_+ \, (= \nu_+ m)$ and $\gamma_+ \, (= a_+ / m_+)$. A similar definition is used for the anionic symbols. Electrical neutrality requires that $\nu_+ z_+ = \nu_- z_-$.

f:   Special notations for equilibrium constants are outlined in Section II.1.7. In some cases, $K_c$ is used to indicate a concentration constant in molar units, and $K_m$ a constant in molal units.

g:   See Section II.3.1.

## II.1.3   Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [1971JEN], [1977FER], [1990LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

- The formulae of co-ordination compounds and complexes are not enclosed in square brackets [1971JEN] (Rule 7.21). Exceptions are made in cases where square brackets are required to distinguish between co-ordinated and unco-ordinated ligands.

- The prefixes "oxy–" and "hydroxy–" are retained if used in a general way, *e.g.*, "gaseous uranium oxyfluorides". For specific formula names, however, the IUPAC recommended citation [1971JEN] (Rule 6.42) is used, *e.g.*, "uranium(IV) difluoride oxide" for $UF_2O$(cr).

An IUPAC rule that is often not followed by many authors [1971JEN] (Rules 2.163 and 7.21) is recalled here: the order of arranging ligands in co-ordination compounds and complexes is the following: central atom first, followed by ionic ligands and then by the neutral ligands. If there is more than one ionic or neutral ligand, the alphabetical order of the symbols of the ligands determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is not recommended.

It is convenient to have a shorthand method of referring to an a ionic medium where the anion concentration is kept constant, but the cation concentrations vary, since such solutions are often used to minimise changes in interionic attractions. For this we enclose the major cation in parentheses. For example, a solution described as "3.00 M (Na)ClO$_4$" could be a mixture of 0.01 M Th(ClO$_4$)$_4$ and 2.96 M NaClO$_4$ with a total perchlorate concentration of 3.00 M.
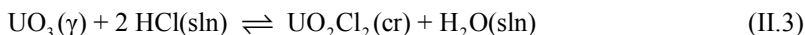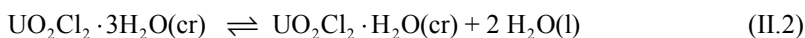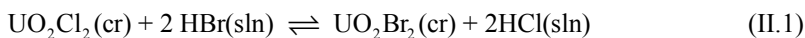
Abbreviations of names for organic ligands appear sometimes in formulae. Following the recommendations by IUPAC, lower case letters are used, and if necessary, the ligand abbreviation is enclosed within parentheses. Hydrogen atoms that can be replaced by the metal atom are shown in the abbreviation with an upper case "H", for example: $H_3edta^-$, Am(Hedta)(s) (where edta stands for ethylenediaminetetraacetate).

## II.1.4   Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example, $UF_4$ occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that are not provided with a phase designator are aqueous ions. They are the only charged species in this review since charged gases are not considered. The use of the phase designators is described below.

- The designator (l) is used for pure liquid substances, *e.g.*, $H_2O(l)$.

- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $U(OH)_4(aq)$, $CO_2(aq)$. Since ionic gases are not considered in this review, all ions may be assumed to be aqueous and are not designed with (aq). If a chemical reaction refers to a medium other than $H_2O$ (*e.g.*, $D_2O$, 90% ethanol/10% $H_2O$), then (aq) is replaced by a more explicit designator, *e.g.*, "(in $D_2O$)" or "(sln)". In the case of (sln), the composition of the solution is described in the text.

- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the difference in the designation of $H_2O$ in Eqs.(II.2) and (II.3). $H_2O(l)$ in Reaction (II.2) indicates that $H_2O$ is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (II.3) involves an HCl solution, in which the thermodynamic properties of $H_2O(sln)$ may not be the same as those of the pure liquid $H_2O(l)$. In dilute solutions, however, this difference in the thermodynamic properties of $H_2O$ can be neglected, and $H_2O(sln)$ may be regarded as pure $H_2O(l)$.

    Example:

$$UO_2Cl_2(cr) + 2\,HBr(sln) \rightleftharpoons UO_2Br_2(cr) + 2HCl(sln) \tag{II.1}$$

$$UO_2Cl_2 \cdot 3H_2O(cr) \rightleftharpoons UO_2Cl_2 \cdot H_2O(cr) + 2\,H_2O(l) \tag{II.2}$$

$$UO_3(\gamma) + 2\,HCl(sln) \rightleftharpoons UO_2Cl_2(cr) + H_2O(sln) \tag{II.3}$$

- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.

- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses, *e.g.*, $SiO_2(quar)$ for quartz and $SiO_2(chal)$ for chalcedony. If there is no mineral name, the designator (cr) is replaced by a Greek letter preceding the formula and indicating the structural phase, *e.g.*, $\alpha$-$UF_5$, $\beta$-$UF_5$.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound to which a thermodynamic quantity refers. The notation is in this case the same as outlined above. In an extended notation (*cf.* [1982LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G_m^o (Na^+, 298.15\ K)$      standard molar Gibbs energy of formation of aqueous $Na^+$ at 298.15 K

$S_m^o (UO_2(SO_4) \cdot 2.5H_2O,\ cr,\ 298.15\ K)$      standard molar entropy of $UO_2(SO_4) \cdot 2.5H_2O(cr)$ at 298.15 K

$C_{p,m}^o (UO_3,\ \alpha,\ 298.15\ K)$      standard molar heat capacity of $\alpha - UO_3$ at 298.15 K

$\Delta_f H_m (HF,\ sln,\ HF \cdot 7.8H_2O)$      enthalpy of formation of HF diluted 1:7.8 with water.

## II.1.5 Processes

Chemical processes are denoted by the operator $\Delta$, written before the symbol for a property, as recommended by IUPAC [1982LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.7. The nature of the process is denoted by annotation of the $\Delta$, *e.g.*, the Gibbs energy of formation, $\Delta_f G_m$, the enthalpy of sublimation, $\Delta_{sub} H_m$, *etc*. The abbreviations of chemical processes are summarised in Table II-3.

Table II-3: Abbreviations used as subscripts of $\Delta$ to denote the type of chemical process.

| Subscript of $\Delta$ | Chemical process |
|---|---|
| at | separation of a substance into its constituent gaseous atoms (atomisation) |
| dehyd | elimination of water of hydration (dehydration) |
| dil | dilution of a solution |
| f | formation of a compound from its constituent elements |
| fus | melting (fusion) of a solid |
| hyd | addition of water of hydration to an unhydrated compound |
| mix | mixing of fluids |
| r | chemical reaction (general) |
| sol | process of dissolution |
| sub | sublimation (evaporation) of a solid |
| tr | transfer from one solution or liquid phase to another |
| trs | transition of one solid phase to another |
| vap | vaporisation (evaporation) of a liquid |

The most frequently used symbols for processes are $\Delta_f G$ and $\Delta_f H$, the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (*cf.* Table II-6).

## II.1.6 Spectroscopic constants and statistical mechanics calculations for gaseous species

In most cases, the thermal functions for gaseous species have been calculated by well-known statistical-mechanical relations (see for example Chapter 27 of [1961LEW/RAN]). The required molecular parameters are given in Appendix E.

The parameters defining the vibrational and rotational energy levels of the molecule in terms of the rotational ($J$) and vibrational ($v$) quantum numbers, and thus many of its thermodynamic properties, are:

- for diatomic molecules (non–rigid rotator, anharmonic oscillator approximation): $\omega$ (vibrational frequency in wavenumber units), $x$ (anharmonicity constant), $B$ (rotational constant for equilibrium position), $D$ (centrifugal distortion constant), $\alpha$ (rotational constant correction for excited vibrational states), and $\sigma$ (symmetry number), where the energy levels with quantum numbers $v$ and $J$ are given by:

$$
\begin{aligned}
E_{(v,J)}/hc =\ & \omega\,(v+1/2) - \omega\,x(v+1/2)^2 + B\,J(J+1) \\
& - D\,J^2\,(J+1)^2 - \alpha\,(v+1/2)\,J\,(J+1)
\end{aligned}
\tag{II.4}
$$

- for linear polyatomic molecules, the parameters are the same as those for diatomic molecules, except that the contributions for anharmonicity are usually neglected.

- for non-linear polyatomic molecules (rigid rotator, harmonic oscillator approximation): $I_x\,I_y\,I_z$, the product of the principal moments of inertia (readily calculated from the geometrical structure of the molecule), $v(i)$, the vibration frequencies and $\sigma$, the symmetry number. While the vibrational energy levels for polyatomic molecules are given approximately by the first term of equation (II.4) for each of the normal vibrations, the rotational energy levels cannot be expressed as a simple general formula. However, the required rotational partition function can be expressed with sufficient accuracy simply in terms of the product of the principal moments of inertia. As for linear polyatomic molecules, anharmonic contributions are usually neglected.

In each case, the symmetry number $\sigma$, the number of indistinguishable positions into which the molecule can be turned by simple rotations, is required to calculate the correct entropy.

The relations for calculating the thermal functions from the partition function defined by the energy levels are well-known – again, see Chapter 27 of [1961LEW/RAN], for a simple description. In each case, the relevant translational and electronic contributions (calculated from the molar mass and the electronic energy levels and degeneracies) must be added. Except where accurate spectroscopic data exist, the geometry and parameters of the excited states are assumed to be the same as those for the ground state.

## II.1.7  Nomenclature in log terms

It is of course clear that the arguments used in log functions must be dimensionless, and this practice had been used in writing pressures, usually as $\log_{10} p/\text{bar}$. However, since the units of the equilibrium constants are frequently quite cumbersome, they have been omitted in the log terms of these constants to facilitate reading of the text.
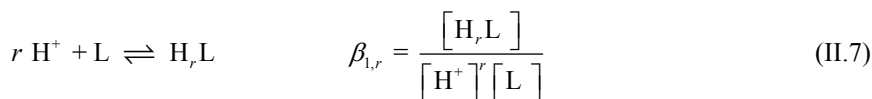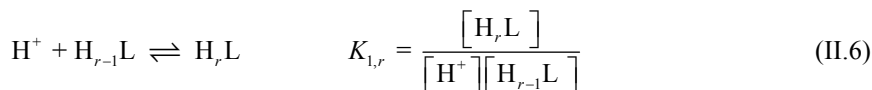
## II.1.8  Equilibrium constants

The IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA has therefore adopted the conventions that have been used in the work *Stability Constants of Metal Ion Complexes* by Sillén and Martell [1964SIL/MAR], [1971SIL/MAR]. An outline is given in the paragraphs below. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It may sometimes be preferable to indicate the number of the reaction to which the data refer, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium:
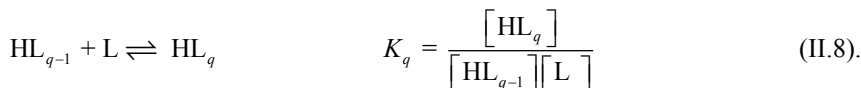
$$m\ \text{M} + q\ \text{L} \rightleftharpoons \text{M}_m\text{L}_q \tag{II.5}$$

both $\beta_{q,m}$ and $\beta$ (II.5) would be appropriate, and $\beta_{q,m}$ (II.5) is accepted, too. Note that, in general, $K$ is used for the consecutive or stepwise formation constant, and $\beta$ is used for the cumulative or overall formation constant. In the following outline, charges are only given for actual chemical species, but are omitted for species containing general symbols (M, L).

### II.1.8.1    Protonation of a ligand

$$\text{H}^+ + \text{H}_{r-1}\text{L} \rightleftharpoons \text{H}_r\text{L} \qquad K_{1,r} = \frac{\left[\text{H}_r\text{L}\right]}{\left[\text{H}^+\right]\left[\text{H}_{r-1}\text{L}\right]} \tag{II.6}$$

$$r\ \text{H}^+ + \text{L} \rightleftharpoons \text{H}_r\text{L} \qquad \beta_{1,r} = \frac{\left[\text{H}_r\text{L}\right]}{\left[\text{H}^+\right]^r\left[\text{L}\right]} \tag{II.7}$$
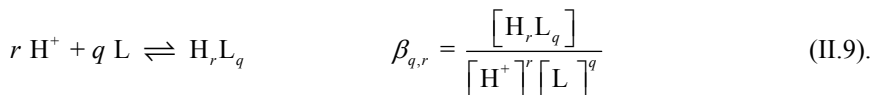
This notation has been proposed and used by Sillén and Martell [1964SIL/MAR], but it has been simplified later by the same authors [1971SIL/MAR] from $K_{1,r}$ to $K_r$.

For the addition of a ligand, the notation shown in Eq.(II.8) is used.

$$\text{HL}_{q-1} + \text{L} \rightleftharpoons \text{HL}_q \qquad K_q = \frac{\left[\text{HL}_q\right]}{\left[\text{HL}_{q-1}\right]\left[\text{L}\right]} \tag{II.8}.$$

Eq.(II.9) refers to the overall formation constant of the species $\text{H}_r\text{L}_q$.

$$r \, H^+ + q \, L \; \rightleftharpoons \; H_r L_q \qquad\qquad \beta_{q,r} = \frac{\left[ H_r L_q \right]}{\left[ H^+ \right]^r \left[ L \right]^q} \qquad\qquad \text{(II.9)}.$$
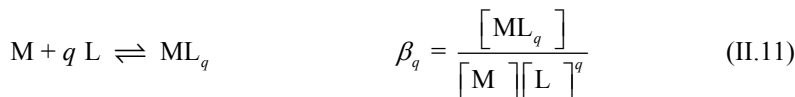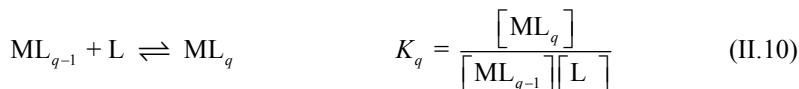
In Eqs.(II.6), (II.7) and (II.9), the second subscript $r$ can be omitted if $r = 1$, as shown in Eq.(II.8).

Example:

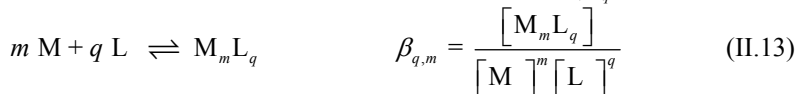$$H^+ + PO_4^{3-} \; \rightleftharpoons \; HPO_4^{2-} \qquad\qquad \beta_{1,1} = \beta_1 = \frac{\left[ HPO_4^{2-} \right]}{\left[ H^+ \right]\left[ PO_4^{3-} \right]}$$

$$2 \, H^+ + PO_4^{3-} \; \rightleftharpoons \; H_2 PO_4^- \qquad\qquad \beta_{1,2} = \frac{\left[ H_2 PO_4^- \right]}{\left[ H^+ \right]^2 \left[ PO_4^{3-} \right]}$$

## II.1.8.2  Formation of metal complexes

$$ML_{q-1} + L \; \rightleftharpoons \; ML_q \qquad\qquad K_q = \frac{\left[ ML_q \right]}{\left[ ML_{q-1} \right]\left[ L \right]} \qquad\qquad \text{(II.10)}$$

$$M + q \, L \; \rightleftharpoons \; ML_q \qquad\qquad \beta_q = \frac{\left[ ML_q \right]}{\left[ M \right]\left[ L \right]^q} \qquad\qquad \text{(II.11)}$$

For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq.(II.6):

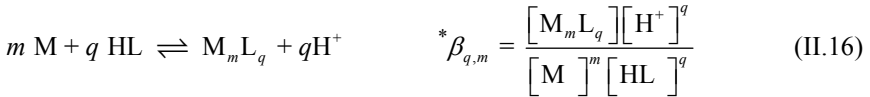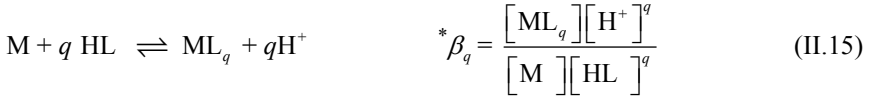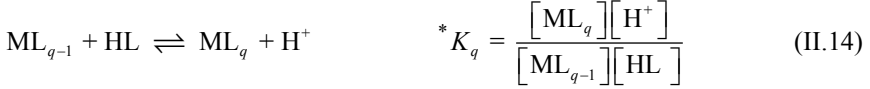$$M + M_{m-1} L \; \rightleftharpoons \; M_m L \qquad\qquad K_{1,m} = \frac{\left[ M_m L \right]}{\left[ M \right]\left[ M_{m-1} L \right]} \qquad\qquad \text{(II.12)}$$
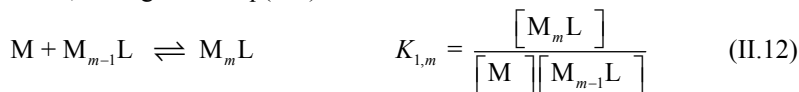
Eq.(II.13) refers to the overall formation constant of a complex $M_m L_q$.

$$m \, M + q \, L \; \rightleftharpoons \; M_m L_q \qquad\qquad \beta_{q,m} = \frac{\left[ M_m L_q \right]}{\left[ M \right]^m \left[ L \right]^q} \qquad\qquad \text{(II.13)}$$
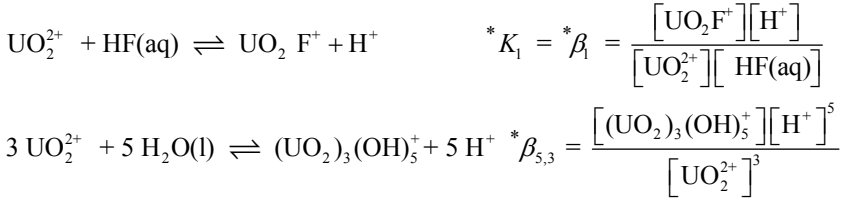
The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes $\beta_q$ if $m = 1$. The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

It has sometimes been customary to use negative values for the indices of the protons to indicate complexation with hydroxide ions, $OH^-$. This practice is not adopted in this review. If $OH^-$ occurs as a reactant in the notation of the equilibrium, it is treated like a normal ligand L, but in general formulae the index variable $n$ is used instead of $q$. If $H_2O$ occurs as a reactant to form hydroxide complexes, $H_2O$ is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs.(II.14) to (II.16) using $n$ as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $M_m L_q H_r$. In many

experiments, the formation constants of metal ion complexes are determined by adding a ligand in its protonated form to a metal ion solution. The complex formation reactions thus involve a deprotonation reaction of the ligand. If this is the case, the equilibrium constant is supplied with an asterisk, as shown in Eqs.(II.14) and (II.15) for mononuclear and in Eq.(II.16) for polynuclear complexes.
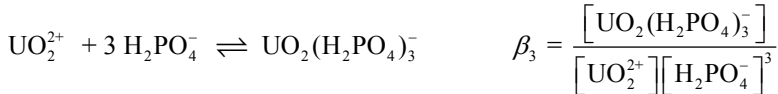
$$ML_{q-1} + HL \rightleftharpoons ML_q + H^+ \qquad {}^*K_q = \frac{[ML_q][H^+]}{[ML_{q-1}][HL]} \qquad (II.14)$$

$$M + q\,HL \rightleftharpoons ML_q + qH^+ \qquad {}^*\beta_q = \frac{[ML_q][H^+]^q}{[M][HL]^q} \qquad (II.15)$$

$$m\,M + q\,HL \rightleftharpoons M_mL_q + qH^+ \qquad {}^*\beta_{q,m} = \frac{[M_mL_q][H^+]^q}{[M]^m[HL]^q} \qquad (II.16)$$

Example:

$$UO_2^{2+} + HF(aq) \rightleftharpoons UO_2F^+ + H^+ \qquad {}^*K_1 = {}^*\beta_1 = \frac{[UO_2F^+][H^+]}{[UO_2^{2+}][HF(aq)]}$$

$$3\,UO_2^{2+} + 5\,H_2O(l) \rightleftharpoons (UO_2)_3(OH)_5^+ + 5\,H^+ \quad {}^*\beta_{5,3} = \frac{[(UO_2)_3(OH)_5^+][H^+]^5}{[UO_2^{2+}]^3}$$

Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added and co-ordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq.(II.17).

$$M + q\,H_rL \rightleftharpoons M(H_rL)_q \qquad \beta_q = \frac{[M(H_rL)_q]}{[M][H_rL]^q} \qquad (II.17)$$

Example:

$$UO_2^{2+} + 3\,H_2PO_4^- \rightleftharpoons UO_2(H_2PO_4)_3^- \qquad \beta_3 = \frac{[UO_2(H_2PO_4)_3^-]}{[UO_2^{2+}][H_2PO_4^-]^3}$$
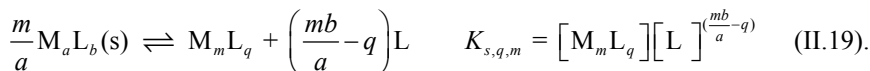
### II.1.8.3 Solubility constants

Conventionally, equilibrium constants involving a solid compound are denoted as "solubility constants" rather than as formation constants of the solid. An index "s" to the equilibrium constant indicates that the constant refers to a solubility process, as shown in Eqs.(II.18) to (II.20).

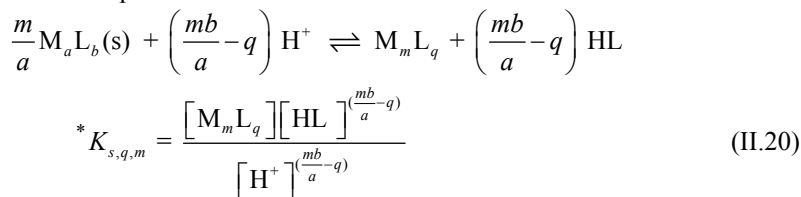$$M_aL_b(s) \rightleftharpoons a\,M + b\,L \qquad K_{s,0} = [M]^a[L]^b \qquad (II.18).$$
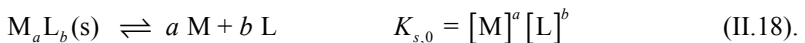
$K_{s,0}$ is the conventional solubility product, and the subscript "0" indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq.(II.13) is used:
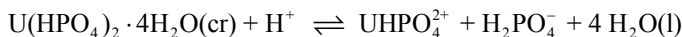
$$\frac{m}{a}M_aL_b(s) \rightleftharpoons M_mL_q + \left(\frac{mb}{a}-q\right)L \qquad K_{s,q,m} = \left[M_mL_q\right]\left[L\right]^{\left(\frac{mb}{a}-q\right)} \qquad (II.19).$$

Example:

$$UO_2F_2(cr) \rightleftharpoons UO_2F^+ + F^- \qquad\qquad K_{s,1,1} = K_{s,1} = \left[UO_2F^+\right]\left[F^-\right] .$$

Similarly, an asterisk is added to the solubility constant if it simultaneously involves a protonation equilibrium:

$$\frac{m}{a}M_aL_b(s) + \left(\frac{mb}{a}-q\right)H^+ \rightleftharpoons M_mL_q + \left(\frac{mb}{a}-q\right)HL$$

$$^*K_{s,q,m} = \frac{\left[M_mL_q\right]\left[HL\right]^{\left(\frac{mb}{a}-q\right)}}{\left[H^+\right]^{\left(\frac{mb}{a}-q\right)}} \qquad (II.20)$$

Example:

$$U(HPO_4)_2 \cdot 4H_2O(cr) + H^+ \rightleftharpoons UHPO_4^{2+} + H_2PO_4^- + 4\,H_2O(l)$$

$$^*K_{s,1,1} = {}^*K_{s,1} = \frac{\left[UHPO_4^{2+}\right]\left[H_2PO_4^-\right]}{\left[H^+\right]} .$$
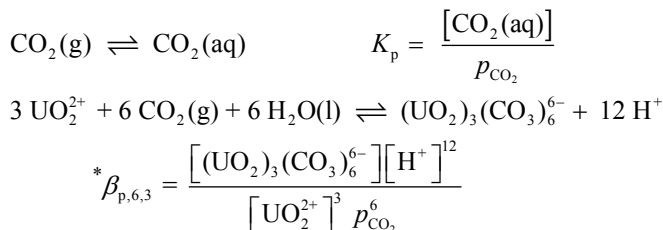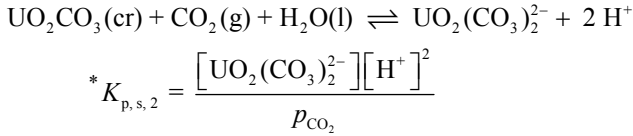
### II.1.8.4  Equilibria involving the addition of a gaseous ligand

A special notation is used for constants describing equilibria that involve the addition of a gaseous ligand, as outlined in Eq.(II.21).

$$ML_{q-1} + L(g) \rightleftharpoons ML_q \qquad K_{p,q} = \frac{\left[ML_q\right]}{\left[ML_{q-1}\right]p_L} \qquad (II.21)$$
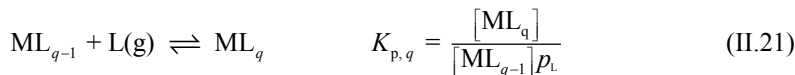
The subscript "p" can be combined with any other notations given above.

Example:

$$CO_2(g) \rightleftharpoons CO_2(aq) \qquad\qquad K_p = \frac{\left[CO_2(aq)\right]}{p_{CO_2}}$$

$$3\,UO_2^{2+} + 6\,CO_2(g) + 6\,H_2O(l) \rightleftharpoons (UO_2)_3(CO_3)_6^{6-} + 12\,H^+$$

$$^*\beta_{p,6,3} = \frac{\left[(UO_2)_3(CO_3)_6^{6-}\right]\left[H^+\right]^{12}}{\left[UO_2^{2+}\right]^3 p_{CO_2}^6}$$

$$UO_2CO_3(cr) + CO_2(g) + H_2O(l) \rightleftharpoons UO_2(CO_3)_2^{2-} + 2\,H^+$$

$$^*K_{p,s,2} = \frac{\left[UO_2(CO_3)_2^{2-}\right]\left[H^+\right]^2}{p_{CO_2}}$$

In cases where the subscripts become complicated, it is recommended that $K$ or $\beta$ be used with or without subscripts, but always followed by the equation number of the equilibrium to which it refers.
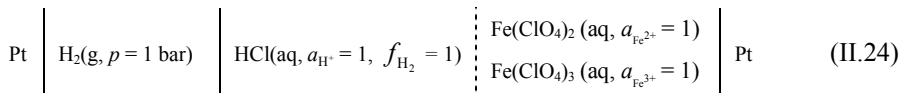
## II.1.8.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, $E$, which is identical to the electromotive force (emf) of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE[1], in accordance with the "1953 Stockholm Convention" [1993MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, $H_2(g)$ is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and $H^+$ is at unit activity. The sign of the electrode potential, $E$, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The standard electrode potential, $E°$, *i.e.*, the potential of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section II.3.1, and with no liquid junction potential) is related to the standard Gibbs energy change $\Delta_r G_m^\circ$ and the standard (or thermodynamic) equilibrium constant $K°$ as outlined in Eq.(II.22):

$$E° = -\frac{1}{n\mathrm{F}}\Delta_r G_m^\circ = \frac{RT}{n\mathrm{F}}\ln K° \tag{II.22}$$

and the potential, $E$, is related to $E°$ by:

$$E = E° - (RT/n\mathrm{F})\sum \nu_i \ln a_i. \tag{II.23}$$

For example, for the hypothetical galvanic cell:

$$\mathrm{Pt}\ \left|\ H_2(g, p=1\ \mathrm{bar})\ \right|\left|\ HCl(aq, a_{H^+}=1,\ f_{H_2}=1)\ \right\vdots\ \begin{array}{l} Fe(ClO_4)_2\ (aq,\ a_{Fe^{2+}}=1) \\ Fe(ClO_4)_3\ (aq,\ a_{Fe^{3+}}=1) \end{array}\ \left|\ \mathrm{Pt}\right. \tag{II.24}$$

where ⁝ denotes a liquid junction and | a phase boundary, the reaction is:

$$Fe^{3+} + \frac{1}{2}H_2(g) \rightleftharpoons Fe^{2+} + H^+ \tag{II.25}$$

Formally Reaction (II.25) can be represented by two half cell reactions, each involving an equal number of electrons, (designated "$e^-$"), as shown in the following equations:

---

[1] The definitions of SHE and NHE are given in Section II.1.1.

$$\text{Fe}^{3+} + \text{e}^- \rightleftharpoons \text{Fe}^{2+} \tag{II.26}$$

$$\frac{1}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{H}^+ + \text{e}^- . \tag{II.27}$$

The terminology is useful, although it must be emphasised "$\text{e}^-$" here does not represent the hydrated electron.

Equilibrium (II.27) and Nernst law can be used to introduce $a_{\text{e}^-}$ :

$$E = E^\circ(\text{II.27}) + \frac{RT}{F}\ln(\sqrt{f_{\text{H}_2}}/(a_{\text{H}^+}a_{\text{e}^-})) \tag{II.28}$$

According to the SHE convention $E^\circ(\text{II.27}) = 0$, $f_{\text{H}_2} = 1$, $a_{\text{H}^+} = 1$, hence

$$E = -\frac{RT}{F}\ln a_{\text{e}^-} \tag{II.29}$$

This equation is used to calculate a numerical value of $a_{\text{e}^-}$ from emf measurements *vs.* the SHE; hence, as for the value of $E$ (V *vs.* the SHE), the numerical value of $a_{\text{e}^-}$ depends on the SHE convention. Equilibrium constants may be written for these half cell reactions in the following way:

$$K^\circ(\text{II.26}) = \frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}} \cdot a_{\text{e}^-}} \tag{II.30}$$

$$K^\circ(\text{II.27}) = \frac{a_{\text{H}^+} \cdot a_{\text{e}^-}}{\sqrt{f_{\text{H}_2}}} = 1 \quad \text{(by definition)} \tag{II.31}$$

In addition, $\Delta_r G_m^\circ(\text{II.27}) = 0$, $\Delta_r H_m^\circ(\text{II.27}) = 0$, $\Delta_r S_m^\circ(\text{II.27}) = 0$ by definition, at all temperatures, and therefore $\Delta_r G_m^\circ(\text{II.26}) = \Delta_r G_m^\circ(\text{II.25})$. From $\Delta_r G_m^\circ(\text{II.27})$ and the values given at 298.15 K in selected auxiliary data for $\text{H}_2(\text{g})$ and $\text{H}^+$, the corresponding values for $\text{e}^-$ can be calculated to be used in thermodynamic cycles involving half cell reactions. The following equations describe the change in the redox potential of Reaction (II.25), if $p_{\text{H}_2}$ and $a_{\text{H}^+}$ are equal to unity *(cf.* Eq.(II.23)):

$$E(\text{II.25}) = E^\circ(\text{II.25}) - RT\ln\left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}\right) \tag{II.32}$$

For the standard hydrogen electrode $a_{\text{e}^-} = 1$ (by the convention expressed in Eq.(II.31)), while rearrangement of Eq.(II.30) for the half cell containing the iron perchlorates in cell (II.24) gives:

$$-\log_{10} a_{\text{e}^-} = \log_{10} K^\circ(\text{II.26}) - \log_{10}\left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}\right)$$

and from Eq.(II.28):

$$-\log_{10} a_{\text{e}^-} = \log_{10} K^\circ(\text{II.25}) - \log_{10}\left(\frac{a_{\text{Fe}^{2+}}}{a_{\text{Fe}^{3+}}}\right) \tag{II.33}$$

and
$$-\log_{10} a_{e^-} \;=\; \frac{F}{RT\ln(10)} E \;(II.25) \qquad\qquad (II.34)$$

which is a specific case of the general equation (II.29).

The splitting of redox reactions into two half cell reactions by introducing the symbol "e⁻", which according to Eq.(II.28) is related to the standard electrode potential, is arbitrary, but useful (this e⁻ notation does not in any way refer to solvated electrons). When calculating the equilibrium composition of a chemical system, both "e⁻", and $H^+$ can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc.* may be defined for both. However, while $H^+$ represents the hydrated proton in aqueous solution, the above equations use only the activity of "e⁻", and never the concentration of "e⁻". Concentration to activity con–versions (or activity coefficients) are never needed for the electron (*cf.* Appendix B, Example B.3).

In the literature on geochemical modelling of natural waters, it is customary to represent the "electron activity" of an aqueous solution with the symbol "pe" or "pε"($= -\log_{10} a_{e^-}$) by analogy with pH ($= -\log_{10} a_{H^+}$), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either "Eh" or "$E_H$" (see for example [1981STU/MOR], [1982DRE], [1984HOS], [1986NOR/MUN]).

In this review, the symbol $E'^{\circ}$ is used to denote the so called "formal poten-tial" [1974PAR]. The formal (or "conditional") potential can be regarded as a standard potential for a particular medium in which the activity coefficients are independent (or approximately so) of the reactant concentrations [1985BAR/PAR] (the definition of $E'^{\circ}$ parallels that of "concentration quotients" for equilibria). Therefore, from

$$E = E'^{\circ} - \frac{RT}{nF}\sum \nu_i \ln c_i \qquad\qquad (II.35)$$

$E'^{\circ}$ is the potential $E$ for a cell when the ratio of the *concentrations* (not the activities) on the right–hand side and the left–hand side of the cell reaction is equal to unity, and

$$E'^{\circ} = E^{\circ} - \frac{RT}{nF}\sum \nu_i \ln \xi \, \gamma_i = -\frac{\Delta_r G_m}{nF} \qquad\qquad (II.36)$$

where the $\gamma_i$ are the molality activity coefficients and $\xi$ is $\left(\frac{m_i}{c_i}\right)$, the ratio of molality to molarity (*cf.* Section II.2). The medium must be specified.
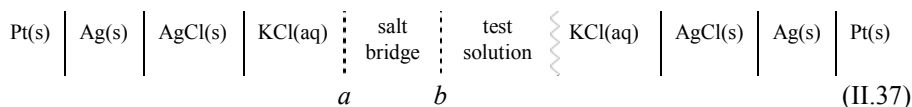
## II.1.9 pH

Because of the importance that potentiometric methods have in the determination of equilibrium constants in aqueous solutions, a short discussion on the definition of "pH" and a simplified description of the experimental techniques used to measure pH will be given here.

The acidity of aqueous solutions is often expressed in a logarithmic scale of the hydrogen ion activity. The definition of pH as:

$$pH = -\log_{10} a_{H^+} = -\log_{10}(m_{H^+} \gamma_{H^+})$$

can only be strictly used in the range of the limiting Debye–Hückel equation (that is, in extremely dilute solutions). In practice the use of pH values requires extra assumptions as to the values for single ion activities. In this review values of pH are used to describe qualitatively the ranges of acidity of experimental studies, and the assumptions described in Appendix B are used to calculate single ion activity coefficients.

The determination of pH is often performed by emf measurements of galvanic cells involving liquid junctions [1969ROS], [1973BAT]. A common setup is a cell made up of a reference half cell (*e.g.*, Ag(s)|AgCl(s) in a solution of constant chloride concentration), a salt bridge, the test solution, and a glass electrode (which encloses a solution of constant acidity and an internal reference half cell):

| Pt(s) | Ag(s) | AgCl(s) | KCl(aq) | salt bridge | test solution | KCl(aq) | AgCl(s) | Ag(s) | Pt(s) |
|-------|-------|---------|---------|-------------|---------------|---------|---------|-------|-------|
|       |       |         |         | *a*         | *b*           |         |         |       | (II.37) |

where ⟩ stands for a glass membrane (permeable to hydrogen ions).

The emf of such a cell is given by:

$$E = E^* - \frac{RT}{nF}\ln a_{H^+} + E_j$$

where $E^*$ is a constant, and $E_j$ is the liquid junction potential. The purpose of the salt bridge is to minimise the junction potential in junction "*b*", while keeping constant the junction potential for junction "*a*". Two methods are most often used to reduce and control the value of $E_j$. An electrolyte solution of *high* concentration (the "salt bridge") is a requirement of both methods. In the first method, the salt bridge is a saturated (or nearly saturated) solution of potassium chloride. A problem with a bridge of high potassium concentration is that potassium perchlorate might precipitate[1] inside the liquid junction when the test solution contains a high concentration of perchlorate ions.

In the other method the salt bridge contains the same *high* concentration of the same inert electrolyte as the test solution (for example, 3 M NaClO$_4$). However, if the concentration of the background electrolyte in the salt bridge and test solutions is reduced, the values of $E_j$ are dramatically increased. For example, if both the bridge and the test solution have $[ClO_4^-] = 0.1$ M as background electrolyte, the dependence of the liquid junction at "*b*" on acidity is $E_j \approx -440 \times [H^+]$ mV·dm$^3$·mol$^{-1}$ at 25°C [1969ROS] (p.110), which corresponds to an error at pH = 2 of ≥ 0.07 pH units.

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[1] KClO$_4$(cr) has a solubility of ≈ 0.15 M in pure water at 25°C

Because of the problems in eliminating the liquid junction potentials and in defining individual ionic activity coefficients, an "operational" definition of pH is given by IUPAC [1993MIL/CVI]. This definition involves the measurement of pH differences between the test solution and standard solutions of known pH and similar ionic strength (in this way similar values of $\gamma_{H^+}$ and $E_j$ cancel each other when emf values are substracted).

Another method of determining the molal $H^+$ concentration, $\log_{10} m_{H^+}$, in chloride solutions up to high ionic strength was proposed by Knauss *et al.* [1990KNA/WOL]. The activity of HCl ($a_{HCl}$) can be measured with a liquid junction free cell consisting of a $H^+$ sensitive glass electrode and a chloride sensitive electrode from the relation:

$$\log_{10} a_{HCl} = 1/2 \,(\log_{10} m_{H^+} + \log_{10} m_{Cl^-} + \log_{10} \gamma_{H^+} + \log_{10} \gamma_{Cl^-}) \qquad (II.38)$$

The value of $\log_{10} m_{H^+}$ in the test solution can then be derived from the measured value of $\log_{10} a_{HCl}$, the given chloride concentration $\log_{10} m_{Cl^-}$ and the activity coefficients $\log_{10} \gamma_{H^+}$ and $\log_{10} \gamma_{Cl^-}$ which can be calculated either with the SIT or, for higher chloride concentrations, with the Pitzer equations as proposed by [1990KNA/WOL].

The measurement and use of pH in equilibrium analytical investigations creates many problems that have not always been taken into account by the investigators, as discussed in many reviews in Appendix A. In order to deduce the stoichiometry and equilibrium constants of complex formation reactions and other equilibria, it is necessary to vary the concentrations of reactants and products over fairly large concentration ranges under conditions where the activity coefficients of the species are either known, or constant. Only in this manner is it possible to use the mass balance equations for the various components together with the measurement of one or more free concentrations to obtain the information desired [1961ROS/ROS], [1990BEC/NAG], [1997ALL/BAN], pp. 326–327. For equilibria involving hydrogen ions, it is necessary to use concentration units, rather than hydrogen ion activity. For experiments in an ionic medium, where the concentration of an "inert" electrolyte is much larger than the concentration of reactants and products we can ensure that, as a first approximation, their trace activity coefficients remain constant even for moderate variations of the corresponding total concentrations. Under these conditions of fixed ionic strength the free proton concentration may be measured directly, thereby defining it in terms of $-\log_{10}[H^+]$ (also often referred to as pcH) rather than on the activity scale as pH, and the value of $-\log_{10}[H^+]$ and pH will differ by a constant term, *i.e.*, $\log_{10}\gamma_{H^+}$. Equilibrium constants deduced from measurements in such ionic media are therefore *conditional* constants, because they refer to the given medium, not to the standard state. In order to compare the magnitude of equilibrium constants obtained in different ionic media it is necessary to have a method for estimating activity coefficients of ionic species in mixed

electrolyte systems to a *common* standard state. Such procedures are discussed in Appendix B.

Note that the precision of the measurement of $-\log_{10}[H^+]$ and pH is virtually the same, in very good experiments, $\pm 0.001$. However, the accuracy is generally considerably poorer, depending in the case of glass electrodes largely on the response of the electrode (linearity, age, pH range, *etc.*), and to a lesser extent on the calibration method employed, although the stoichiometric $-\log_{10}[H^+]$ calibration standards can be prepared far more accurately than the commercial pH standards.

## II.1.10 Order of formulae

To be consistent with CODATA, the data tables are given in "*Standard Order of Arrangement*" [1982WAG/EVA]. This scheme is presented in Figure II-1 below, and shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

Figure II-1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from [1982WAG/EVA]).
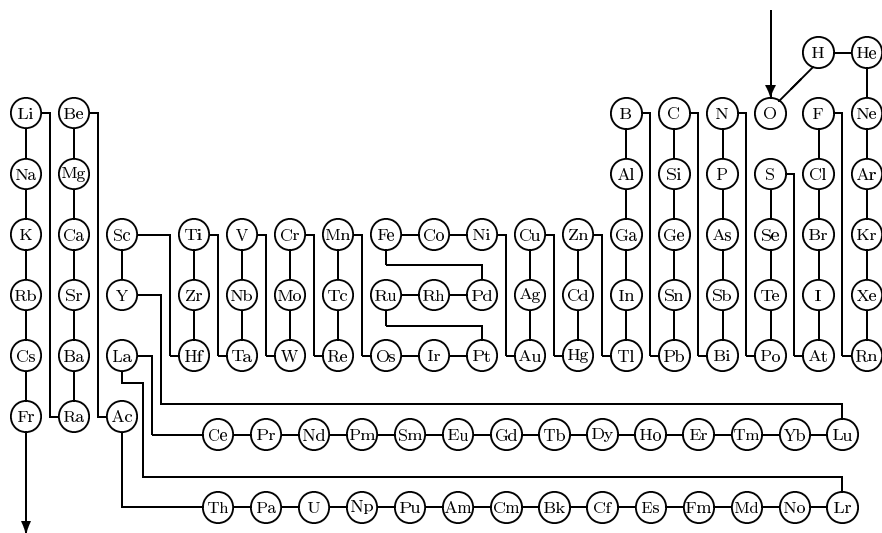
For example, for uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, $U^{4+}$), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing coefficients of the lower rank elements. For example, in the U–O–F class of compounds and complexes, a typical sequence would be $UOF_2(cr)$, $UOF_4(cr)$, $UOF_4(g)$, $UO_2F(aq)$, $UO_2F^+$, $UO_2F_2(aq)$, $UO_2F_2(cr)$, $UO_2F_2(g)$, $UO_2F_3^-$, $UO_2F_4^{2-}$, $U_2O_3F_6(cr)$, *etc*. [1992GRE/FUG]. Formulae with identical stoichiometry are in alphabetical order of their designators.

## II.1.11 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [1987GAR/PAR]. A reference code is made up of the four digits of the year of appearance, followed by the first three letters of the surnames of the first two authors, separated by a slash.

If there are multiple reference codes, a "2" will be added to the second one, a "3" to the third one, and so forth. Reference codes are always enclosed in square brackets.

## II.2  Units and conversion factors

Thermodynamic data are given according to the *Système International d'unités* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non–thermodynamic units, are given in Table II-4.

Table II-4: Unit conversion factors.

| To convert from (non–SI unit symbol) | to (SI unit symbol) | multiply by |
|---|---|---|
| ångström (Å) | metre (m) | $1\times10^{-10}$ (exactly) |
| standard atmosphere (atm) | pascal (Pa) | $1.01325\times10^5$ (exactly) |
| bar (bar) | pascal (Pa) | $1\times10^5$ (exactly) |
| thermochemical calorie (cal) | joule (J) | 4.184 (exactly) |
| entropy unit  e.u. $\triangleq cal \cdot K^{-1} \cdot mol^{-1}$ | $J \cdot K^{-1} \cdot mol^{-1}$ | 4.184 (exactly) |

Since a large part of the NEA-TDB Project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses "M" as an abbreviation of "$mol \cdot dm^{-3}$" for molarity, *c*, and, in Appendices B and C, "m" as an abbreviation of "$mol \cdot kg^{-1}$" for molality, *m*. It is often necessary to convert concentration data from molarity to molality and vice versa. This conversion is used for the correction and extrapolation of equilib-

rium data to zero ionic strength by the specific ion interaction theory, which works in molality units (*cf.* Appendix B). This conversion is made in the following way. Molality is defined as $m_B$ moles of substance B dissolved in 1 kilogram of pure water. Molarity is defined as $c_B$ moles of substance B dissolved in $(\rho - c_B M)$ kilogram of pure water, where $\rho$ is the density of the solution in kg·dm$^{-3}$ and $M$ the molar weight of the solute in kg·mol$^{-1}$. From this it follows that:

$$m_B = \frac{c_B}{\rho - c_B M} .$$

Baes and Mesmer [1976BAE/MES], (*p.*439) give a table with conversion factors (from molarity to molality) for nine electrolytes and various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnel and Novotný [1985SOH/NOV], are reported in Table II-5.

Example:

$$1.00 \text{ M NaClO}_4 \triangleq 1.05 \text{ m NaClO}_4$$
$$1.00 \text{ M NaCl} \triangleq 1.02 \text{ m NaCl}$$
$$4.00 \text{ M NaClO}_4 \triangleq 4.95 \text{ m NaClO}_4$$
$$6.00 \text{ M NaNO}_3 \triangleq 7.55 \text{ m NaNO}_3$$

It should be noted that equilibrium constants need also to be converted if the concentration scale is changed from molarity to molality or vice versa. For a general equilibrium reaction, $0 = \sum_B v_B B$, the equilibrium constants can be expressed either in molarity or molality units, $K_c$ or $K_m$, respectively:

$$\log_{10} K_c = \sum_B v_B \log_{10} c_B$$
$$\log_{10} K_m = \sum_B v_B \log_{10} m_B$$

With $(m_B / c_B) = \xi$, or $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \xi$, the relationship between $K_c$ and $K_m$ becomes very simple, as shown in Eq.(II.39).

$$\log_{10} K_m = \log_{10} K_c + \sum_B v_B \log_{10} \xi \qquad (II.39)$$

$\sum_B v_B$ is the sum of the stoichiometric coefficients of the solutes, *cf.* Eq. (II.55) and the values of $\xi$ are the factors for the conversion of molarity to molality as tabulated in Table II-5 for several electrolyte media at 298.15 K. The differences between the values in Table II-5 and the values listed in the uranium NEA-TDB review [1992GRE/FUG] (*p.*23) are found at the highest concentrations, and are no larger than $\pm 0.003$ dm$^3$·kg$^{-1}$, reflecting the accuracy expected in this type of conversion. The uncertainty introduced by the use of Eq.(II.39) in the values of $\log_{10} K_m$ will be no larger than $\pm 0.001 \sum_B v_B$.

Table II-5: Factors ξ for the conversion of molarity, $c_B$, to molality, $m_B$, of a substance B, in various media at 298.15 K (calculated from densities in [1985SOH/NOV]).

| | $\xi = m_B / c_B$ (dm$^3$ of solution per kg of H$_2$O) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| $c$ (M) | HClO$_4$ | NaClO$_4$ | LiClO$_4$ | NH$_4$ClO$_4$ | Ba(ClO$_4$)$_2$ | HCl | NaCl | LiCl |
| 0.10 | 1.0077 | 1.0075 | 1.0074 | 1.0091 | 1.0108 | 1.0048 | 1.0046 | 1.0049 |
| 0.25 | 1.0147 | 1.0145 | 1.0141 | 1.0186 | 1.0231 | 1.0076 | 1.0072 | 1.0078 |
| 0.50 | 1.0266 | 1.0265 | 1.0256 | 1.0351 | 1.0450 | 1.0123 | 1.0118 | 1.0127 |
| 0.75 | 1.0386 | 1.0388 | 1.0374 | 1.0523 | 1.0685 | 1.0172 | 1.0165 | 1.0177 |
| 1.00 | 1.0508 | 1.0515 | 1.0496 | 1.0703 | 1.0936 | 1.0222 | 1.0215 | 1.0228 |
| 1.50 | 1.0759 | 1.0780 | 1.0750 | 1.1086 | 1.1491 | 1.0324 | 1.0319 | 1.0333 |
| 2.00 | 1.1019 | 1.1062 | 1.1019 | | 1.2125 | 1.0430 | 1.0429 | 1.0441 |
| 3.00 | 1.1571 | 1.1678 | 1.1605 | | 1.3689 | 1.0654 | 1.0668 | 1.0666 |
| 4.00 | 1.2171 | 1.2374 | 1.2264 | | | 1.0893 | 1.0930 | 1.0904 |
| 5.00 | 1.2826 | 1.3167 | | | | 1.1147 | 1.1218 | 1.1156 |
| 6.00 | 1.3547 | 1.4077 | | | | 1.1418 | | 1.1423 |
| $c$ (M) | KCl | NH$_4$Cl | MgCl$_2$ | CaCl$_2$ | NaBr | HNO$_3$ | NaNO$_3$ | LiNO$_3$ |
| 0.10 | 1.0057 | 1.0066 | 1.0049 | 1.0044 | 1.0054 | 1.0056 | 1.0058 | 1.0059 |
| 0.25 | 1.0099 | 1.0123 | 1.0080 | 1.0069 | 1.0090 | 1.0097 | 1.0102 | 1.0103 |
| 0.50 | 1.0172 | 1.0219 | 1.0135 | 1.0119 | 1.0154 | 1.0169 | 1.0177 | 1.0178 |
| 0.75 | 1.0248 | 1.0318 | 1.0195 | 1.0176 | 1.0220 | 1.0242 | 1.0256 | 1.0256 |
| 1.00 | 1.0326 | 1.0420 | 1.0258 | 1.0239 | 1.0287 | 1.0319 | 1.0338 | 1.0335 |
| 1.50 | 1.0489 | 1.0632 | 1.0393 | 1.0382 | 1.0428 | 1.0478 | 1.0510 | 1.0497 |
| 2.00 | 1.0662 | 1.0855 | 1.0540 | 1.0546 | 1.0576 | 1.0647 | 1.0692 | 1.0667 |
| 3.00 | 1.1037 | 1.1339 | 1.0867 | 1.0934 | 1.0893 | 1.1012 | 1.1090 | 1.1028 |
| 4.00 | 1.1453 | 1.1877 | 1.1241 | 1.1406 | 1.1240 | 1.1417 | 1.1534 | 1.1420 |
| 5.00 | | 1.2477 | | 1.1974 | 1.1619 | 1.1865 | 1.2030 | 1.1846 |
| 6.00 | | | | | 1.2033 | 1.2361 | 1.2585 | 1.2309 |
| $c$ (M) | NH$_4$NO$_3$ | H$_2$SO$_4$ | Na$_2$SO$_4$ | (NH$_4$)$_2$SO$_4$ | H$_3$PO$_4$ | Na$_2$CO$_3$ | K$_2$CO$_3$ | NaSCN |
| 0.10 | 1.0077 | 1.0064 | 1.0044 | 1.0082 | 1.0074 | 1.0027 | 1.0042 | 1.0069 |
| 0.25 | 1.0151 | 1.0116 | 1.0071 | 1.0166 | 1.0143 | 1.0030 | 1.0068 | 1.0130 |
| 0.50 | 1.0276 | 1.0209 | 1.0127 | 1.0319 | 1.0261 | 1.0043 | 1.0121 | 1.0234 |
| 0.75 | 1.0405 | 1.0305 | 1.0194 | 1.0486 | 1.0383 | 1.0065 | 1.0185 | 1.0342 |
| 1.00 | 1.0539 | 1.0406 | 1.0268 | 1.0665 | 1.0509 | 1.0094 | 1.0259 | 1.0453 |
| 1.50 | 1.0818 | 1.0619 | 1.0441 | 1.1062 | 1.0773 | 1.0170 | 1.0430 | 1.0686 |
| 2.00 | 1.1116 | 1.0848 | | 1.1514 | 1.1055 | 1.0268 | 1.0632 | 1.0934 |
| 3.00 | 1.1769 | 1.1355 | | 1.2610 | 1.1675 | | 1.1130 | 1.1474 |
| 4.00 | 1.2512 | 1.1935 | | 1.4037 | 1.2383 | | 1.1764 | 1.2083 |
| 5.00 | 1.3365 | 1.2600 | | | 1.3194 | | 1.2560 | 1.2773 |
| 6.00 | 1.4351 | 1.3365 | | | 1.4131 | | | 1.3557 |

## II.3  Standard and reference conditions

### II.3.1  Standard state

A precise definition of the term "standard state" has been given by IUPAC [1982LAF]. The fact that only changes in thermodynamic parameters, but not their absolute values, can be determined experimentally, makes it important to have a well–defined standard state that forms a base line to which the effect of variations can be referred. The IUPAC [1982LAF] definition of the standard state has been adopted in the NEA-TDB Project. The standard state pressure, $p^\circ = 0.1$ MPa (1 bar), has therefore also been adopted, *cf.* Section II.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section II.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.

- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.

- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.

- The standard state for a solute B in a solution is a hypothetical liquid solution, at the standard state pressure, in which $m_B = m^\circ = 1$ mol·kg$^{-1}$, and in which the activity coefficient $\gamma_B$ is unity.

It should be emphasised that the use of superscript, $^\circ$, *e.g.*, in $\Delta_f H_m^\circ$, implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section II.3.3) are listed in Table II-6.

Table II-6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [1982WAG/EVA], [1989COX/WAG], [1991DIN], [2005GAM/BUG], [2005OLI/NOL].

| | | | |
|---|---|---|---|
| $O_2$ | gaseous | Zn | crystalline, hexagonal |
| $H_2$ | gaseous | Cd | crystalline, hexagonal |
| He | gaseous | Hg | liquid |
| Ne | gaseous | Cu | crystalline, cubic |
| Ar | gaseous | Ag | crystalline, cubic |
| Kr | gaseous | Ni | crystalline, fcc |
| Xe | gaseous | Fe | crystalline, cubic, bcc |
| $F_2$ | gaseous | Tc | crystalline, hexagonal |
| $Cl_2$ | gaseous | V | crystalline, cubic |
| $Br_2$ | liquid | Ti | crystalline, hexagonal |
| $I_2$ | crystalline, orthorhombic | Am | crystalline, dhcp |
| S | crystalline, orthorhombic | Pu | crystalline, monoclinic |
| Se | crystalline, trigonal | Np | crystalline, orthorhombic |
| Te | crystalline, hexagonal | U | crystalline, orthorhombic |
| $N_2$ | gaseous | Th | crystalline, cubic |
| P | crystalline, cubic ("white") | Be | crystalline, hexagonal |
| As | crystalline, rhombohedral ("grey") | Mg | crystalline, hexagonal |
| Sb | crystalline, rhombohedral | Ca | crystalline, cubic, fcc |
| Bi | crystalline, rhombohedral | Sr | crystalline, cubic, fcc |
| C | crystalline, hexagonal (graphite) | Ba | crystalline, cubic |
| Si | crystalline, cubic | Li | crystalline, cubic |
| Ge | crystalline, cubic | Na | crystalline, cubic |
| Sn | crystalline, tetragonal ("white") | K | crystalline, cubic |
| Pb | crystalline, cubic | Rb | crystalline, cubic |
| B | crystalline, rhombohedral | Cs | crystalline, cubic |
| Al | crystalline, cubic | | |

## II.3.2  Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by the International Union of Pure and Applied Chemistry IUPAC [1982LAF].

However, the majority of the thermodynamic data published in the scientific literature and used for the evaluations in this review, refer to the old standard state pressure of 1 "standard atmosphere" (= 0.101325 MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propagation of errors. In practice the parameters affected by the change between these two standard

state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [1982WAG/EVA], see also Freeman [1984FRE].

The following expressions define the effect of pressure on the properties of all substances:

$$\left(\frac{\partial H}{\partial p}\right)_T \;=\; V - T\left(\frac{\partial V}{\partial T}\right)_p \;=\; V(1 - \alpha T) \tag{II.40}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T \;=\; -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{II.41}$$

$$\left(\frac{\partial S}{\partial p}\right)_T \;=\; -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{II.42}$$

$$\left(\frac{\partial G}{\partial p}\right)_T \;=\; V \tag{II.43}$$

$$\text{where} \quad \alpha \;\equiv\; \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{II.44}$$

For ideal gases, $V = \mathrm{R}T/p$ and $\alpha = \mathrm{R}/pV = 1/T$. The conversion equations listed below (Eqs. (II.45) to (II.52)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript $^{(atm)}$, and those that refer to the new standard state pressure of 1 bar are assigned the superscript $^{(bar)}$.

For all substances the changes in the enthalpy of formation and heat capacity are much smaller than the experimental accuracy and can be disregarded. This is exactly true for ideal gases.

$$\Delta_f H^{(bar)}(T) \;-\; \Delta_f H^{(atm)}(T) = 0 \tag{II.45}$$

$$C_p^{(bar)}(T) \;-\; C_p^{(atm)}(T) = 0 \tag{II.46}$$

For gaseous substances, the entropy difference is:

$$S^{(bar)}(T) \;-\; S^{(atm)}(T) = \mathrm{R}\,\ln\left(\frac{p^{(atm)}}{p^{(bar)}}\right) = \mathrm{R}\,\ln\,1.01325$$

$$= 0.1094\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \tag{II.47}$$

This is exactly true for ideal gases, as follows from Eq.(II.42) with $\alpha = \mathrm{R}/pV$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\Delta_r S^{(bar)} - \Delta_r S^{(atm)} = \delta \cdot R \ln \left( \frac{p^{(atm)}}{p^{(bar)}} \right)$$

$$= \delta \times 0.1094 \text{ J·K}^{-1} \cdot \text{mol}^{-1} \qquad \text{(II.48)}$$

where $\delta$ is the net increase in moles of gas in the process.

Similarly, the change in the Gibbs energy of a process between the two standard state pressures is:

$$\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = -\delta \cdot RT \ln \left( \frac{p^{(atm)}}{p^{(bar)}} \right)$$

$$= -\delta \times 0.03263 \text{ kJ·mol}^{-1} \text{ at } 298.15 \text{ K}. \qquad \text{(II.49)}$$

Eq.(II.49) applies also to $\Delta_f G^{(bar)} - \Delta_f G^{(atm)}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_f G^{(bar)} - \Delta_f G^{(atm)} = -\delta \times 0.03263 \text{ kJ·mol}^{-1} \text{ at } 298.15 \text{ K}. \qquad \text{(II.50)}.$$

The changes in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq.(II.49),

$$\log_{10} K^{(bar)} - \log_{10} K^{(atm)} = -\frac{\Delta_r G^{(bar)} - \Delta_r G^{(atm)}}{RT \ln 10}$$

$$= \delta \cdot \frac{\ln \left( \frac{p^{(atm)}}{p^{(bar)}} \right)}{\ln 10} = \delta \cdot \log_{10} \left( \frac{p^{(atm)}}{p^{(bar)}} \right)$$

$$= \delta \times 0.005717 \qquad \text{(II.51)}$$

$$E^{(bar)} - E^{(atm)} = -\frac{\Delta_r G^{(bar)} - \Delta_r G^{(atm)}}{n\text{F}}$$

$$= \delta \cdot \frac{RT \ln \left( \frac{p^{(atm)}}{p^{(bar)}} \right)}{n\text{F}}$$

$$= \delta \cdot \frac{0.0003382}{n} \text{V} \quad \text{at } 298.15 \text{ K} \qquad \text{(II.52)}$$

It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.

$$H^+ + e^- \rightleftharpoons \frac{1}{2} H_2(g) \qquad E^\circ \stackrel{\text{def}}{=} 0.00 V \qquad \text{(II.53)}.$$
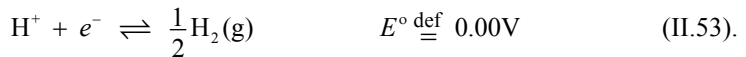
This definition will not be changed, although a gaseous substance, $H_2(g)$, is involved in the process. The change in the potential with pressure for an electrode potential conventionally written as:
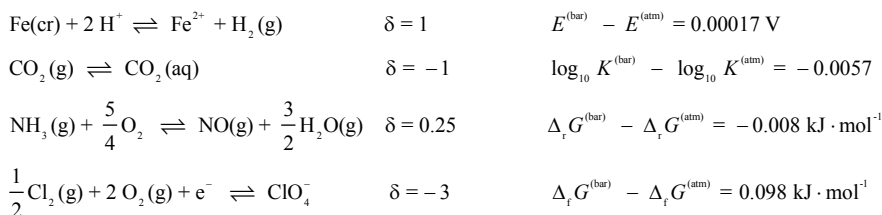
$$Ag^+ + e^- \rightleftharpoons Ag\,(cr)$$
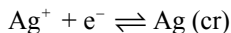
should thus be calculated from the balanced reaction that includes the hydrogen electrode,

$$Ag^+ + \frac{1}{2}H_2\,(g) \rightleftharpoons Ag\,(cr) + H^+$$
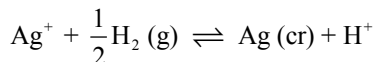
Here $\delta = -0.5$. Hence, the contribution to $\delta$ from an electron in a half cell reaction is the same as the contribution of a gas molecule with the stoichiometric coefficient of 0.5. This leads to the same value of $\delta$ as the combination with the hydrogen half cell.

Example:

| | | |
|---|---|---|
| $Fe(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2\,(g)$ | $\delta = 1$ | $E^{(bar)} - E^{(atm)} = 0.00017\ V$ |
| $CO_2\,(g) \rightleftharpoons CO_2\,(aq)$ | $\delta = -1$ | $\log_{10} K^{(bar)} - \log_{10} K^{(atm)} = -0.0057$ |
| $NH_3(g) + \frac{5}{4}O_2 \rightleftharpoons NO(g) + \frac{3}{2}H_2O(g)$ | $\delta = 0.25$ | $\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = -0.008\ kJ \cdot mol^{-1}$ |
| $\frac{1}{2}Cl_2\,(g) + 2\,O_2\,(g) + e^- \rightleftharpoons ClO_4^-$ | $\delta = -3$ | $\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = 0.098\ kJ \cdot mol^{-1}$ |

### II.3.3   Reference temperature

The definitions of standard states given in Section I.4 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [1982LAF], the reference temperature chosen in the NEA-TDB Project is $T = 298.15$ K or $t = 25.00°C$. Where necessary for the discussion, values of experimentally measured temperatures are reported after conversion to the IPTS–68 [1969COM]. The relation between the absolute temperature $T$ (K, kelvin) and the Celsius temperature $t$ (°C) is defined by $t = (T - T_o)$ where $T_o = 273.15$ K.

## II.4   Fundamental physical constants

To ensure the consistency with other NEA-TDB Reviews, the fundamental physical constants are taken from a publication by CODATA [1986COD]. Those relevant to this review are listed in Table II-7. Note that updated values of the fundamental constants can be obtained from CODATA, notably through its Internet site. In most cases, recalculation of the NEA-TDB database entries with the updated values of the fundamental constants will not introduce significant (with respect to their quoted uncertainties) excursions from the current NEA-TDB selections.

Table II-7: Fundamental physical constants. These values have been taken from CODATA [1986COD]. The digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

| Quantity | Symbol | Value | Units |
|---|---|---|---|
| speed of light in vacuum | c | 299 792 458 | $m \cdot s^{-1}$ |
| permeability of vacuum | $\mu_0$ | $4\pi \times 10^{-7} = 12.566\ 370\ 614\ldots$ | $10^{-7}\ N \cdot A^{-2}$ |
| permittivity of vacuum | $\epsilon_o$ | $1/\mu_0 c^2 = 8.854\ 187\ 817\ldots$ | $10^{-12}\ C^2 \cdot J^{-1} \cdot m^{-1}$ |
| Planck constant | h | 6.626 0755(40) | $10^{-34}\ J \cdot s$ |
| elementary charge | e | 1.602 177 33(49) | $10^{-19}\ C$ |
| Avogadro constant | $N_A$ | 6.022 1367(36) | $10^{23}\ mol^{-1}$ |
| Faraday constant | F | 96 485.309(29) | $C \cdot mol^{-1}$ |
| molar gas constant | R | 8.314 510(70) | $J \cdot K^{-1} \cdot mol^{-1}$ |
| Boltzmann constant, $R/N_A$ | k | 1.380 658(12) | $10^{-23}\ J \cdot K^{-1}$ |
| Non–SI units used with SI: | | | |
| electron volt, $(e/C)$ J | eV | 1.602 177 33(49) | $10^{-19}\ J$ |
| atomic mass unit, | u | 1.660 5402(10) | $10^{-27}\ kg$ |
| $1u = m_u = \dfrac{1}{12} m\ (^{12}C)$ | | | |

# II.5  Uncertainty estimates

One of the principal objectives of the NEA-TDB development effort is to provide an idea of the uncertainties associated with the data selected in the reviews. In general the uncertainties should define the range within which the corresponding data can be reproduced with a probability of 95%. In many cases, a full statistical treatment is limited or impossible due to the availability of only one or a few data points. Appendix C describes in detail the procedures used for the assignment and treatment of uncertainties, as well as the propagation of errors and the standard rules for rounding.

# II.6  The NEA-TDB system

A database system has been developed at the NEA Data Bank that allows the storage of thermodynamic parameters for individual species as well as for reactions. The structure of the database system allows consistent derivation of thermodynamic data for individual species from reaction data at standard conditions, as well as internal recalculations of data at standard conditions. If a selected value is changed, all the dependent values will be recalculated consistently. The maintenance of consistency of all the selected data, including their uncertainties (*cf*. Appendix C), is ensured by the software developed for this purpose at the NEA Data Bank. The literature sources of the data are also stored in the database.

The following thermodynamic parameters, valid at the reference temperature of 298.15 K and at the standard pressure of 1 bar, are stored in the database:

$\Delta_f G_m^o$     the standard molar Gibbs energy of formation from the elements in their reference state (kJ·mol$^{-1}$)

$\Delta_f H_m^o$     the standard molar enthalpy of formation from the elements in their reference state (kJ·mol$^{-1}$)

$S_m^o$     the standard molar entropy (J·K$^{-1}$·mol$^{-1}$)

$C_{p,m}^o$     the standard molar heat capacity (J·K$^{-1}$·mol$^{-1}$).

For aqueous neutral species and ions, the values of $\Delta_f G_m^o$, $\Delta_f H_m^o$, $S_m^o$ and $C_{p,m}^o$ correspond to the standard partial molar quantities, and for individual aqueous ions they are relative quantities, defined with respect to the aqueous hydrogen ion, according to the convention [1989COX/WAG] that $\Delta_f H_m^o(H^+, T) = 0$ and that $S_m^o(H^+, T) = 0$. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

$$\Delta_f H_m^o(B_\pm, aq) = \sum_+ \nu_+ \, \Delta_f H_m^o(\text{cation, aq}) + \sum_- \nu_- \, \Delta_f H_m^o(\text{anion, aq})$$

$$S_m^o(B_\pm, aq) = \sum_+ \nu_+ \, S_m^o(\text{cation, aq}) + \sum_- \nu_- \, S_m^o(\text{anion, aq})$$

As the thermodynamic parameters vary as a function of temperature, provision is made for including the compilation of the coefficients of empirical temperature functions for these data, as well as the temperature ranges over which they are valid. In many cases the thermodynamic data measured or calculated at several temperatures were published for a particular species, rather than the deduced temperature functions. In these cases, a linear regression method is used in this review to obtain the most significant coefficients of the following empirical function for a thermodynamic parameter, $X$:

$$X(T) = a_X + b_X \cdot T + c_X \cdot T^2 + d_X \cdot T^{-1} + e_X \cdot T^{-2} + f_X \cdot \ln T + g_X \cdot T \ln T$$
$$+ h_X \cdot \sqrt{T} + \frac{i_X}{\sqrt{T}} + j_X \cdot T^3 + k_X \cdot T^{-3}. \tag{II.54}$$

Most temperature variations can be described with three or four parameters. In the present series, only $C_{p,m}(T)$, *i.e.*, the thermal functions of the heat capacities of individual species are considered and stored in the database. They refer to the relation:

$$C_{p,m}(T) = a + b \cdot T + c \cdot T^2 + d \cdot T^{-1} + e \cdot T^{-2}$$

(where the subindices for the coefficients have been dropped) and are listed in the selected value tables.

The pressure dependence of thermodynamic data has not been the subject of critical analysis in the present compilation. The reader interested in higher temperatures and pressures, or the pressure dependency of thermodynamic functions for geochemical applications, is referred to the specialised literature in this area, *e.g.*, [1982HAM],

[1984MAR/MES], [1988SHO/HEL], [1988TAN/HEL], [1989SHO/HEL], [1989SHO/HEL2], [1990MON], [1991AND/CAS].

Selected standard thermodynamic data referring to chemical reactions are also compiled in the database. A chemical reaction "*r*", involving reactants and products 'B', can be abbreviated as:

$$0 = \sum_B \nu_B^r \ B \qquad\qquad (II.55)$$

where the stoichiometric coefficients $\nu_B^r$ are positive for products, and negative for reactants. The reaction parameters considered in the NEA-TDB system include:

$\log_{10} K_r^\circ$        the equilibrium constant of the reaction, logarithmic

$\Delta_r G_m^\circ$        the molar Gibbs energy of reaction (kJ·mol$^{-1}$)

$\Delta_r H_m^\circ$        the molar enthalpy of reaction (kJ·mol$^{-1}$)

$\Delta_r S_m^\circ$        the molar entropy of reaction (J·K$^{-1}$·mol$^{-1}$)

$\Delta_r C_{p,m}^\circ$        the molar heat capacity of reaction (J·K$^{-1}$·mol$^{-1}$).

The temperature functions of these data, if available, are stored according to Eq.(II.54).

The equilibrium constant, $K_r^\circ$, is related to $\Delta_r G_m^\circ$ according to the following relation:

$$\log_{10} K_r^\circ \ = \ -\frac{\Delta_r G_m^\circ}{RT \ln(10)}$$

and can be calculated from the individual values of $\Delta_f G_m^\circ(B)$ (for example, those given in selected values tables), according to:

$$\log_{10} K_r^\circ \ = \ -\frac{1}{RT \ln(10)} \sum_B \nu_B^r \ \Delta_f G_m^\circ(B) \qquad\qquad (II.56)$$

## II.7  Presentation of the selected data

The selected data are presented in Chapters III and IV. Unless otherwise indicated, they refer to standard conditions (*cf*. Section I.4) and 298.15K (25°C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix C).

Chapters III contains a table of selected thermodynamic data for individual compounds and complexes of thorium (Table III-1), a table of selected reaction data (Table III-2) for reactions concerning thorium species and a table containing the heat capacities of individual species of thorium (Table III-3) that have been used in the evaluations. The selection of all these data is discussed in Chapters V to XII. For the gaseous species, in particular, only the more important of the heat capacity equations have been given explicitly in the relevant sections of these chapters.

Chapter IV contains, for auxiliary compounds and complexes that do not contain thorium, a table of the thermodynamic data for individual species (Table IV-1) and a table of reaction data (Table IV-2). Most of these values are the CODATA Key Values [1989COX/WAG]. The selection of the remaining auxiliary data is discussed in [1992GRE/FUG], [1999RAR/RAN], [2001LEM/FUG], [2005GAM/BUG] and [2005OLI/NOL].

All the selected data presented in Table III-1, Table III-2, Table III-3 and Table IV-2 are internally consistent. This consistency is maintained by the internal consistency verification and recalculation software developed at the NEA Data Bank in conjunction with the NEA–TDB data base system, *cf.* Section I.7. Therefore, when using the selected data for organic species, the auxiliary data of Chapter IV must be used together with the data in Chapter III to ensure internal consistency of the data set.

It is important to note that Table III-2 and Table IV-2 include only those species for which the primary selected data are reaction data. The formation data derived there from and listed in Table III-1 are obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in that Table III-2 and Table IV-2, rather than taking the derived values in Table III-1 and Table IV-1 to calculate the reaction data with Eq.(II.56). The later approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00°C), but they can be recalculated to other temperatures if the corresponding data (enthalpies, entropies, heat capacities) are available [1997PUI/RAR]. For example, the temperature dependence of the standard reaction Gibbs energy as a function of the standard reaction entropy at the reference temperature ($T_0 = 298.15$ K), and of the heat capacity function is:

$$\Delta_r G_m^\circ(T) = \Delta_r H_m^\circ(T_0) + \int_{T_0}^T \Delta_r C_{p,m}^\circ(T)\, dT - T \left( \Delta_r S_m^\circ(T_0) + \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ(T)}{T} dT \right),$$

and the temperature dependence of the standard equilibrium constant as a function of the standard reaction enthalpy and heat capacity is:

$$\log_{10} K^\circ(T) = \log_{10} K^\circ(T_0) - \frac{\Delta_r H_m^\circ(T_0)}{R \ln(10)} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

$$- \frac{1}{RT \ln(10)} \int_{T_0}^T \Delta_r C_{p,m}^\circ(T)\, dT + \frac{1}{R \ln(10)} \int_{T_0}^T \frac{\Delta_r C_{p,m}^\circ(T)}{T} dT,$$

where R is the gas constant (*cf.* Table II-7).

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150°C, with an additional uncertainty of perhaps about 1 to 2 logarithmic units, due to neglecting the heat capacity contributions to the temperature correction. For isocoulombic / isoelectric reactions the uncertainty may be smaller; for a detailed discussion see [1997PUI/RAR]. However, it is important to observe that "new" aqueous species, *i.e.*, species not present in significant amounts at 25°C and therefore not detected, may be significant at higher temperatures, see for example the work by Ciavatta *et al.* [1987CIA/IUL]. Additional high–temperature experiments may therefore be needed in order to ascertain that proper chemical models are used in the modelling of hydrothermal systems. For many species, experimental thermodynamic data are not available to allow a selection of parameters describing the temperature dependence of equilibrium constants and Gibbs energies of formation. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [1997PUI/RAR]. The thermodynamic data in the selected set refer to infinite dilution for soluble species. Extrapolation of an equilibrium constant $K$, usually measured at high ionic strength, to $K°$ at $I = 0$ using activity coefficients $\gamma$, is explained in Appendix B. The corresponding Gibbs energy of dilution is:

$$\Delta_{dil}G_m = \Delta_r G_m^o - \Delta_r G_m \tag{II.57}$$
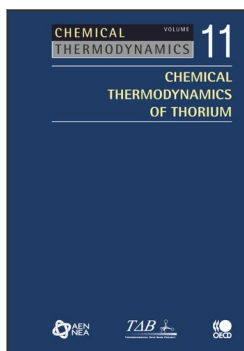
$$= - RT \Delta_r \ln \gamma_{\pm} \tag{II.58}$$

Similarly $\Delta_{dil}S_m$ can be calculated from $\ln \gamma_{\pm}$ and its variations with *T*, while:

$$\Delta_{dil}H_m = RT^2 \frac{\partial}{\partial T}(\Delta_r \ln \gamma_{\pm})_p \tag{II.59}$$

depends only on the variation of $\gamma$ with *T*, which is neglected in this review, when no data on the temperature dependence of $\gamma$'s are available. In this case the Gibbs energy of dilution $\Delta_{dil}G_m$ is entirely assigned to the entropy difference. This entropy of reaction is calculated using $\Delta_r G_m^o = \Delta_r H_m^o - T\Delta_r S_m^o$, the above assumption $\Delta_{dil}H_m = 0$, and $\Delta_{dil}G_m$.

# Part 2

# Tables of selected data