NEA
NUCLEAR ENERGY AGENCY

$T\Delta B$
THERMOCHEMICAL DATA BASE PROJECT

TDB-5

STANDARDS AND CONVENTIONS FOR TDB PUBLICATIONS

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May 2000

(Updated in May 2015)

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Standards and Conventions for TDB Publications

The results from the review of the chemical thermodynamics of each key element are published in separate volumes under the authorship of the respective specialist teams. The drafts are edited and prepared for publication at the OECD Nuclear Energy Agency.

This document defines the symbols and terminology, the standard conditions, the standard order of arrangement of the formulae, and the standard outline of the chapters in the TDB publications. These rules are to be followed in each volume. They are derived from international standards and have been specially adjusted for the TDB publications.

1 Symbols, terminology and nomenclature

1.1 Abbreviations

Abbreviations are mainly used in tables where space is limited. Abbreviations for methods of measurement are kept to a maximum of three characters (except for composed symbols) and are listed in Table 2.

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.

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 [79WHI]. They are summarized in Table 1.

Table 1: Symbols and terminology.

Symbols and terminology	
length	*l*
height	*h*
radius	*r*
diameter	*d*

(Continued on next page)

Table 1: (continued)

Symbols and terminology	
volume	V
mass	m
density (mass divided by volume)	ρ
time	t
frequency	ν
wavelength	λ
internal transmittance (transmittance of the medium itself, disregarding boundary or container influence)	T
internal transmission density, (decadic absorbance): $\log_{10}(1/T)$	A
molar (decadic) absorption coefficient: $A/c_B l$	ϵ
relaxation time	τ
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) heat capacity at constant pressure of a solute	$C_{p,m,2}$
(molar) enthalpy	H_m
(molar) Gibbs energy	G_m
chemical potential of substance B	μ_B
pressure	p
partial pressure of substance B: $x_B p$	p_B
fugacity of substance B	f_B
fugacity coefficient: f_B/p_B	$\gamma_{f,B}$
amount of substance[b]	n
mole fraction of substance B: $n_B/\sum_i n_i$	x_B
molarity or concentration of a solute substance B (amount of B divided by the volume of the solution)[c]	c_B, [B]

(Continued on next page)

Table 1: (continued)

Symbols and terminology	
molality of a solute substance B (amount of B divided by the mass of the solvent)[(d)]	m_B
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	γ_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)], $\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	$\gamma_\pm$
osmotic coefficient, molality basis	ϕ
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)	ν_B
general equation for a chemical reaction	$0 = \sum_B \nu_B B$
equilibrium constant[(f)]	K
rate constant	k
Faraday constant	F
charge number of an ion B (positive for cations, negative for anions)	z_B
charge number of a cell reaction	n
electromotive force	E
$pH = -\log_{10}[a_{H^+}/(mol \cdot kg^{-1})]$	
electrolytic conductivity	κ
superscript for standard state[(g)]	$\circ$

[(a)] The 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 [79WHI].

[(c)] This quantity is called "amount-of-substance concentration" in the IUPAC manual [79WHI]. 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 concentration 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 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 3.1.

1.3   Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [71JEN, 77FER] on the nomenclature of inorganic compounds and complexes, except for the following items:

i. The formulae of coordination compounds and complexes are not enclosed in square brackets [71JEN, Rule 7.21]. However, in cases where the absence of brackets may cause ambiguities or make presentations unclear, exceptions may be made.

ii. 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 [71JEN, Rule 6.42] is used, *e.g.*, "uranium(IV) difluoride oxide" for $UF_2O(cr)$.

An IUPAC rule that is often not followed [71JEN, Rules 2.163 and 7.21] is the following: The order of arranging ligands in coordination 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 ligating atoms determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is non-standard and should not be used.

The treatment of organic ligands poses certain problems due to the complicated composition of most of them. A notation in conformity with the structural features of the molecule may take too much space and is difficult to read, whereas the summation over the atoms of the molecule often leads to ambiguous formulae. It has therefore been decided to accept abbreviations for all organic ligands except for the very simple ones, such as formate, HCO_2^-, or oxalate, $C_2O_4^{2-}$. The abbreviations are enclosed in parentheses when this is necessary to distinguish the organic ligand from the other atoms in the complex, or otherwise without any parentheses according to the IUPAC recommendations [71JEN, Rule 7.35], writing

Table 2: Abbreviations for experimental methods

aix	anion exchange
cal	calorimetry
chr	chromatography
cix	cation exchange
col	colorimetry
con	conductivity
cor	corrected
cou	coulometry
cry	cryoscopy
dis	distribution between two phases
em	electromigration
emf	electromotive force, not specified
gl	glass electrode
ise-X	ion selective electrode with ion X stated
ix	ion exchange
kin	rate of reaction
mvd	mole volume determination
nmr	nuclear magnetic resonance
pol	polarography
pot	potentiometry
prx	proton relaxation
qh	quinhydrone electrode
red	emf with redox electrode
rev	review
sp	spectrophotometry
sol	solubility
tc	transient conductivity
tls	thermal lensing spectrophotometry
vlt	voltammetry
?	method unknown to the reviewers

e. g. H_4edta, H_3edta$^-$, but Co(en)$_3^{3+}$. Abbreviations used for organic ligands are listed in Table 3.

When mentioned in general as a substance in running text, organic substances should still be mentioned using all lower-case letters, such as in "the complexation behaviour of edta has long been...".

Table 3: List of abbreviations for organic compounds

Abbreviation	Chemical formula	Trivial name
ac	CH_3COO^-	acetate
acac	$CH_3COCHCOCH_3^-$	acetylacetonate
ala	$CH_3CHNHCOO^{2-}$	alaninate
altu	$CH_2CHCH_2NHCSNH_2(aq)$	allyl-thiourea
arg	$NH_2NHCNH(CH_2)_3CHNH_2COO^-$	argininate
asp	$COOCH_2CHNH_2COO^{2-}$	asparaginate
aspa	$COOCH_2CHNH_2COO^{2-}$	aspartate
bal	$NH_2CH_2CH_2COO^-$	$\beta-$ alaninate
bipy	$(C_5H_4N)_2(aq)$	2,2'-bipyridine
bz	$C_6H_5COO^-$	benzoate
cat	$C_6H_4O_2^{2-}$	catecholate
chel	$COOC_5H_2NOCOO^{3-}$	chelidamate
cit	$COOCH_2COHCOOCH_2COO^{3-}$	citrate
cy	$SCH_2CHNHCOO^{3-}$	cysteinate
cys	$(SCH_2CHNH_2COO)_2^{2-}$	cystinate
dcac	Cl_2CHCOO^-	dichoroacetate
dcta	$(CH_2COO)_4NC_6H_{10}N^{4-}$	1,2-diaminocyclohexanetetraacetate
ddta	$(CH_2COO)_4N(CH_2)_{12}N^{4-}$	dodecamethylenediaminetetraacetate
deta	$(CH_2COO)_4N(CH_2)_2O(CH_2)_2N^{4-}$	diaminodiethylethertetraacetate
dien	$NH_2(CH_2)_2NH(CH_2)_2NH_2(aq)$	diethylenetriamine
dipic	$COOC_5H_3NCOO^{2-}$	dipicolinate
dpa	$(C_5H_4NCH_2)_2NH(aq)$	bis(2-pyridylmethyl)amine
dtpa	$(CH_2COO)_5N(CH_2)_2N(CH_2)_2N^{5-}$	diethylenetriaminepentaacetate
dtta	$(CH_2COO)_4N(CH_2)_2S(CH_2)_2N^{4-}$	diaminodiethylthioethertetraacetate
edta	$(CH_2COO)_4N(CH_2)_2N^{4-}$	ethylenediaminetetraacetate
en	$NH_2(CH_2)_2NH_2(aq)$	ethylenediamine
entu	$CH_2CHNHCSNH_2(aq)$	ethylen-thiourea
etu	$CH_3CH_2NHCSNH_2(aq)$	N-ethyl-thiourea
e2tu	$CH_3CH_2NHCSNHCH_2CH_3(aq)$	N,N'-diethyl-thiourea
fum	$CO_2(CH)_2CO_2^{2-}$	fumarate
glu	$COO(CH_2)_2CHNH_2COO^{2-}$	glutaminate
gly	$CH_2NH_2COO^-$	glycinate
glyc	CH_2OHCOO^-	glycolate
hdta	$(CH_2COO)_4N(CH_2)_6N^{4-}$	hexamethylenediaminetetraacetate

Table 3: (continued)

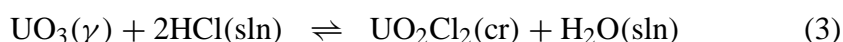| Abbreviation	Chemical formula	Trivial name
his	$C_3H_3N_2CH_2CHNH_2COO^-$	histidinate
hypro	$OHC_4H_7NCOO^-$	hydroxyprolinate
ida	$NH(CH_2COO)_2^{2-}$	iminodiacetate
ileu	$CH_3CH_2CHCH_3CHNH_2COO^-$	isoleucinate
lac	$CH_3CHOHCOO^-$	lactate
leu	$(CH_3)_2CHCH_2CHNH_2COO^-$	leucinate
lys	$NH_2(CH_2)_4CHNH_2COO^-$	lysinate
mal	$NH_2COCHCHCOO^-$	maleate
mcac	$ClCH_2COO^-$	monochloroacetate
men	$CH_3NH(CH_2)_2NH_2$	N-methylethylenediamine
met	$CH_3S(CH_2)_2CHNH_2COO^-$	methionate
mida	$CH_3N(CH_2COO)_2^{2-}$	methyliminodiacetate
mpmida	$CH_3C_5H_3CH_2N(CH_2COO)_2^{2-}$	N-(6-methyl-2-pyridylmethyl)iminodiacetate
mpo	$CH_3CHSCOO^{2-}$	2-mercaptopropenaoate
mtu	$CH_3NHCSNH_2(aq)$	N-methyl-thiouea
m2tu	$CH_3NHCSNHCH_3(aq)$	N,N'-dimethyl-thiouea
m4tu	$(CH_3)_2NCSN(CH_3)_2(aq)$	N,N,N',N'-tetramethyl-thiouea
nta	$N(CH_2COO)_3^{3-}$	nitrilotriacetate
obut	$CH_3CH_2CHOHCOO^-$	alpha-hydroxybutyrate
orn	$NH_2(CH_2)_3CHNH_2COO^-$	ornithate
hoq	$NC_9H_6O^-$	8-hydroxyquinolinate
pdta	$(CH_2COO)_4N(CH_2)_2CH_2N^{4-}$	propylenediaminetetraacetate
penten	$(NH_2(CH_2)_2)_4N(CH_2)_2N(aq)$	tetrakis(2-aminoethyl)ethylenediamine
peta	$(CH_2COO)_4N(CH_2)_5N^{4-}$	pentamethylenediaminetetraacetate
ph	$C_6H_5O^-$	phenolate
phe	$(C_6H_5)CH_2CHNH_2COO^-$	
phen	$(C_5H_3N)_2C_2H_2(aq)$	1,10-phenanthroline
phth	$C_6H_4(COO)_2^{2-}$	phthalate
pic	$C_5H_4NCOO^-$	picolinate
pmida	$C_5H_4CH_2N(CH_2COO)_2^{2-}$	N-(2-pyridylmethyl)iminodiacetate
pro	$C_4H_8NCOO^-$	prolinate
prop	$CH_3CHOHCOO^-$	2-hydroxy propionate
py	$C_5H_5N(aq)$	pyridine
sal	$C_6H_4OHCOO^-$	salicilate
ser	$CH_2OHCHNH_2COO^-$	serinate
tart	$COOCHOHCHOHCOO^{2-}$	tartrate
tcac	CCl_3COO^-	trichloroacetate
3tet	$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2(aq)$	
4tet	$NH_2(CH_2)_2NH(CH_2)_4NH(CH_2)_2NH_2(aq)$	
5tet	$NH_2(CH_2)_2NH(CH_2)_5NH(CH_2)_2NH_2(aq)$	

Table 3: (continued)

Abbreviation	Chemical formula	Trivial name
6tet	$NH_2(CH_2)_2NH(CH_2)_6NH(CH_2)_2NH_2(aq)$	
8tet	$NH_2(CH_2)_2NH(CH_2)_8NH(CH_2)_2NH_2(aq)$	
teta	$(CH_2COO)_4N(CH_2)_4N^{4-}$	tetramethylenediaminetetraacetate
tglyc	CH_2SHCOO^-	thioglycolate
tmal	$CHCOSHCHCONH_2^-$	thiomaleate
thr	$CH_3CHOHCHNH_2COO^-$	threoninate
tla	$(CH_3C_5H_3NCH_2)_3N(aq)$	tris(6-methyl-2-pyridylmethyl)amine
tmta	$(CH_2COO)_4N(CH_2)_3N^{4-}$	trimethylenediaminetetraacetate
tog	$COO(CH)_3(OH)_3COO^{2-}$	trihydroxyglutarate
tpa	$(C_5H_4NCH_2)_3N(aq)$	tris(2-pyridylmethyl)amine
tpen	$(C_5H_4NCH_2)_4N(CH_2)_2N(aq)$	tetrakis(2-pyridylmethyl)amine
tren	$(NH_2(CH_2)_2)_3N(aq)$	2,2',2''-triaminotriethylamine
trien	$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2(aq)$	triethylenetetraamine
try	$C_8H_6NCH_2CHNH_2COO^-$	tryptophanate
tta	$C_4H_3SCOCH_2COCF_3(aq)$	
tu	$NH_2CSNH_2(aq)$	thiourea
tyr	$OC_6H_4CH_2CHNH_2COO^{2-}$	thyrosinate
val	$(CH_3)_2(CH_2)_2NH_2COO^-$	valinate

1.4 Phase designators

The same chemical formula may refer to different chemical species and must often 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. 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. (2) and (3). H_2O(l) in Reaction (2) indicates that H_2O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (3) involves a 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).

$$UOCl_2(cr) + 2HBr(sln) \;\rightleftharpoons\; UOBr_2(cr) + 2HCl(sln) \tag{1}$$

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

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

- 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.*, α-UF_5, β-UF_5.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound a thermodynamic quantity refers to. The notation is in this case the same as outlined above. In an extended notation (*cf.* [82LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G_m^\circ$ (Na^+, aq, 298.15 K)	standard molar Gibbs energy of formation of aqueous Na^+ at 298.15 K
S_m° ($UO_2SO_4 \cdot 2.5H_2O$, cr, 298.15 K)	standard molar entropy at 298.15 K of $UO_2SO_4 \cdot 2.5H_2O$(cr)
$C_{p,m}^\circ$ (UO_3, α, 298.15 K)	standard molar heat capacity at 298.15 K of α-UO_3 at
$\Delta_f H_m$(HF, sln, HF $\cdot$ 7.8H_2O)	enthalpy of formation of HF diluted 1:7.8 with water

1.5 Processes

Chemical processes are denoted by the operator Δ, written before the symbol for a property, as recommended by IUPAC [93MIL/CVI]. An exception to this rule is the equilibrium constant, *cf*. Section 1.7. The nature of the process is denoted by annotation of the Δ, *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 summar-ized in Table 4. The most frequently used symbols for processes are $\Delta_f G$ and

Table 4: Abbreviations used as subscripts of Δ to denote the type of chemical processes.

Subscript to Δ	Chemical process
at	separation of a substance into its constituent gaseous atoms (atomization)
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	vaporization (evaporation) of a liquid

$\Delta_f H$, the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (*cf*. Table 7).

1.6 Thermodynamic data

The following parameters, valid at the reference temperature of 298.15 K and at the standard pressure of 1 bar, are the ultimately selected values in the TDB data base:

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

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

S_m° the standard molar entropy $(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

$C_{p,m}^\circ$ the standard molar heat capacity at constant
pressure $(\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$

For aqueous neutral species and ions, the values of $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° and $C_{p,m}^\circ$ 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 [89COX/WAG] that $\Delta_f H_m^\circ(\text{H}^+, \text{aq}, T) = 0$, and that $S_m^\circ(\text{H}^+, \text{aq}, T) = 0$. Furthermore, for an *ionized solute* B containing any number of different cations and anions:

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

$$S_m^\circ(\text{B}_\pm, \text{aq}) = \sum_+ \nu_+ S_m^\circ(\text{cation}, \text{aq}) + \sum_- \nu_- S_m^\circ(\text{anion}, \text{aq}).$$

A chemical reaction "r", involving reactants and products "B", can be abbreviated as

$$0 = \sum_\text{B} \nu_{r,\text{B}} \, \text{B} \tag{4}$$

where the stoichiometric coefficients $\nu_{r,\text{B}}$ are positive for products, and negative for reactants. The reaction parameters that can be stored in the NEA/TDB data base are:

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

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

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

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

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

The equilibrium constant, K_r°, 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) according to,

$$\log_{10} K_r^\circ = -\frac{1}{RT \ln(10)} \sum_B \nu_{r,B} \, \Delta_f G_m^\circ(B).$$

Often, reaction parameters are measured in terms of concentrations rather than activities. In these cases, it is convenient to specify

$$\Delta_r G_m = \Delta_r G_m^{\circ\prime} + RT \ln(10) \sum_B \nu_{r,B} \log c_B$$

such that

$$\Delta_r G_m^{\circ\prime} = \Delta_r G_m^\circ + RT \ln(10) \sum_B \nu_{r,B} \log_{10} \gamma_B \varrho$$

where ϱ is the molality/molarity conversion factor (see Section 2), and γ is the activity coefficient (on the molality scale).

When using $\Delta_r G_m^{\circ\prime}$, the medium in which the energy was measured must be specified (e. g. "$\Delta_r G_m^{\circ\prime}$(V.87, 1 M NaClO$_4$)").
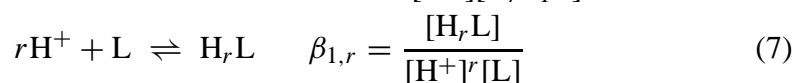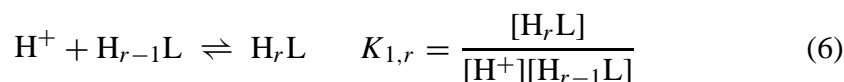
1.7 Equilibrium constants

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 [64SIL/MAR, 71SIL/MAR]. An outline is given below in Paragraphs 1.7.a-1.7.e. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It is often preferable to indicate the number of the reaction the data refer to, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium

$$mM + qL \;\rightleftharpoons\; M_m L_q \tag{5}$$

both $\beta_{q,m}$ and $\beta(5)$ would be correct, but $\beta_{q,m}(5)$ is the least ambiguous and should be used in most cases. Note that, in general, K is used for the consecutive or stepwise formation constant, and β 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).

1.7.a Protonation of a ligand

$$H^+ + H_{r-1}L \;\rightleftharpoons\; H_r L \qquad K_{1,r} = \frac{[H_r L]}{[H^+][H_{r-1}L]} \tag{6}$$

$$rH^+ + L \;\rightleftharpoons\; H_r L \qquad \beta_{1,r} = \frac{[H_r L]}{[H^+]^r [L]} \tag{7}$$

This notation has been proposed and used by Sillén and Martell [64SIL/MAR], but it has been simplified later by the same authors [71SIL/MAR] from $K_{1,r}$ to K_r. The TDB review retains, for the sake of consistency, *cf.* Eqs. (8) and (9), the older formulation of $K_{1,r}$.

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

$$\text{HL}_{q-1} + \text{L} \; \rightleftharpoons \; \text{HL}_q \qquad K_q = \frac{[\text{HL}_q]}{[\text{HL}_{q-1}][\text{L}]} \tag{8}$$
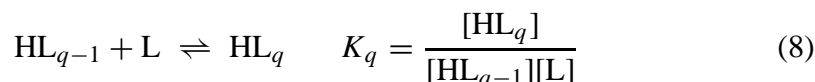
Eq. (9) refers to the overall formation constant of the species H_rL_q.

$$r\text{H}^+ + q\text{L} \; \rightleftharpoons \; \text{H}_r\text{L}_q \qquad \beta_{q,r} = \frac{[\text{H}_r\text{L}_q]}{[\text{H}^+]^r[\text{L}]^q} \tag{9}$$

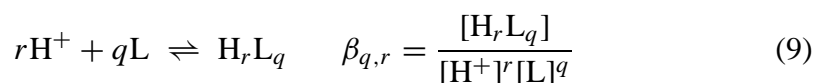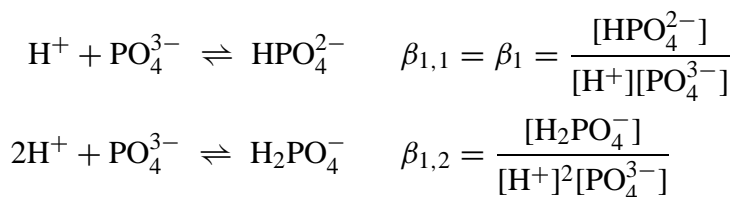In Eqs. (6), (7) and (9), the second subscript r can be omitted if $r = 1$, as shown in Eq. (8).

Example:

$$\text{H}^+ + \text{PO}_4^{3-} \; \rightleftharpoons \; \text{HPO}_4^{2-} \qquad \beta_{1,1} = \beta_1 = \frac{[\text{HPO}_4^{2-}]}{[\text{H}^+][\text{PO}_4^{3-}]}$$

$$2\text{H}^+ + \text{PO}_4^{3-} \; \rightleftharpoons \; \text{H}_2\text{PO}_4^- \qquad \beta_{1,2} = \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}^+]^2[\text{PO}_4^{3-}]}$$

1.7.b   Formation of metal ion complexes

$$\text{ML}_{q-1} + \text{L} \; \rightleftharpoons \; \text{ML}_q \qquad K_q = \frac{[\text{ML}_q]}{[\text{ML}_{q-1}][\text{L}]} \tag{10}$$

$$\text{M} + q\text{L} \; \rightleftharpoons \; \text{ML}_q \qquad \beta_q = \frac{[\text{ML}_q]}{[\text{M}][\text{L}]^q} \tag{11}$$
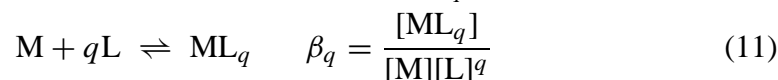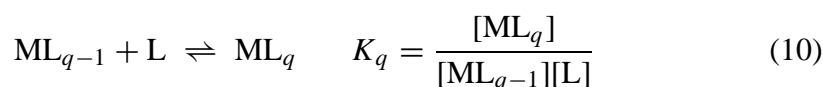
For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq.(6):

$$\text{M} + \text{M}_{m-1}\text{L} \; \rightleftharpoons \; \text{M}_m\text{L} \qquad K_{1,m} = \frac{[\text{M}_m\text{L}]}{[\text{M}][\text{M}_{m-1}\text{L}]} \tag{12}$$
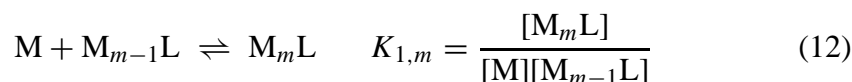
Eq. (13) refers to the overall formation constant of a complex M_mL_q.

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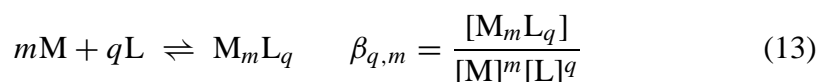
The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes β_q if $m = 1$. The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

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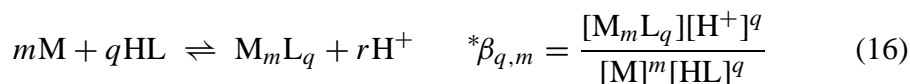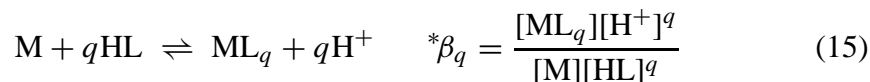, so that the reaction is treated as described below in Eqs. (14) to (16) using n as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $M_mL_qH_r$. In many experiments, the formation constants of metal ion complexes are determined by adding to a metal ion solution a ligand in its protonated form. 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. (14) and (15) for mononuclear and in Eq. (16) for polynuclear complexes.

$$ML_{q-1} + HL \; \rightleftharpoons \; ML_q + H^+ \qquad {}^*K_q = \frac{[ML_q][H^+]}{[ML_{q-1}][HL]} \tag{14}$$
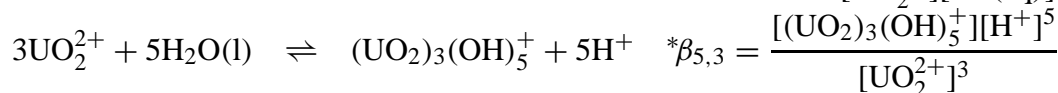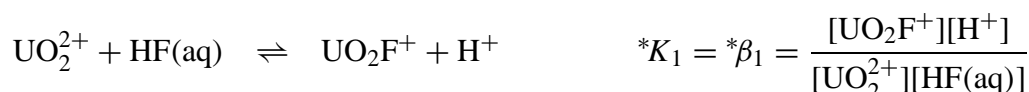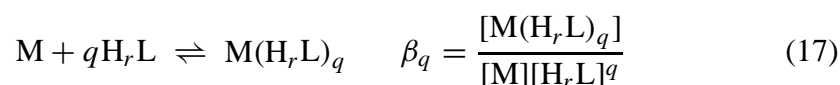
$$M + qHL \; \rightleftharpoons \; ML_q + qH^+ \qquad {}^*\beta_q = \frac{[ML_q][H^+]^q}{[M][HL]^q} \tag{15}$$

$$mM + qHL \; \rightleftharpoons \; M_mL_q + rH^+ \qquad {}^*\beta_{q,m} = \frac{[M_mL_q][H^+]^q}{[M]^m[HL]^q} \tag{16}$$

Example:

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

$$3UO_2^{2+} + 5H_2O(l) \quad \rightleftharpoons \quad (UO_2)_3(OH)_5^+ + 5H^+ \qquad {}^*\beta_{5,3} = \frac{[(UO_2)_3(OH)_5^+][H^+]^5}{[UO_2^{2+}]^3}$$
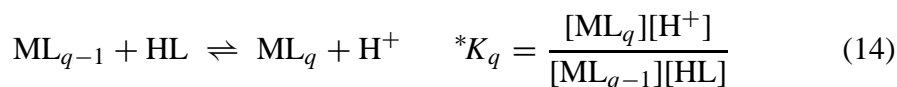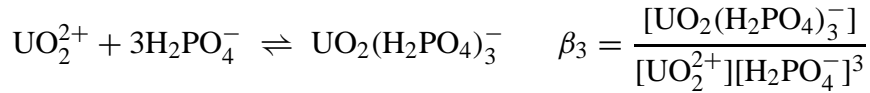
Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added and coordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (17).

$$M + qH_rL \; \rightleftharpoons \; M(H_rL)_q \qquad \beta_q = \frac{[M(H_rL)_q]}{[M][H_rL]^q} \tag{17}$$

Example:

$$\text{UO}_2^{2+} + 3\text{H}_2\text{PO}_4^- \;\rightleftharpoons\; \text{UO}_2(\text{H}_2\text{PO}_4)_3^- \qquad \beta_3 = \frac{[\text{UO}_2(\text{H}_2\text{PO}_4)_3^-]}{[\text{UO}_2^{2+}][\text{H}_2\text{PO}_4^-]^3}$$
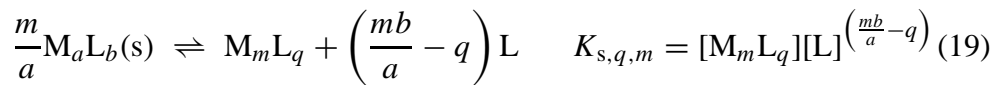
1.7.c Solubility constants

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. (18) to (20).

$$\text{M}_a\text{L}_b(\text{s}) \;\rightleftharpoons\; a\text{M} + b\text{L} \qquad K_{\text{s},0} = [\text{M}]^a[\text{L}]^b \qquad (18)$$
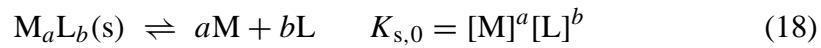
$K_{\text{s},0}$ is the conventional solubility product, and the subscript "0" indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq. (13) is used:

$$\frac{m}{a}\text{M}_a\text{L}_b(\text{s}) \;\rightleftharpoons\; \text{M}_m\text{L}_q + \left(\frac{mb}{a} - q\right)\text{L} \qquad K_{\text{s},q,m} = [\text{M}_m\text{L}_q][\text{L}]^{\left(\frac{mb}{a}-q\right)} \; (19)$$

Example:

$$\text{UO}_2\text{F}_2(\text{cr}) \;\rightleftharpoons\; \text{UO}_2\text{F}^+ + \text{F}^- \qquad K_{\text{s},1,1} = K_{\text{s},1} = [\text{UO}_2\text{F}^+][\text{F}^-]$$

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

$$\frac{m}{a}\text{M}_a\text{L}_b(\text{s}) + \left(\frac{mb}{a} - q\right)\text{H}^+ \;\rightleftharpoons\; \text{M}_m\text{L}_q + \left(\frac{mb}{a} - q\right)\text{HL}$$

$$^*K_{\text{s},q,m} = \frac{[\text{M}_m\text{L}_q][\text{HL}]^{\left(\frac{mb}{a}-q\right)}}{[\text{H}^+]^{\left(\frac{mb}{a}-q\right)}} \quad (20)$$

Example:

$$\text{U}(\text{HPO}_4)_2 \cdot 4\text{H}_2\text{O}(\text{cr}) + \text{H}^+ \;\rightleftharpoons\; \text{UHPO}_4^{2+} + \text{H}_2\text{PO}_4^- + 4\text{H}_2\text{O}(\text{l})$$

$$^*K_{\text{s},1,1} = {}^*K_{\text{s},1} = \frac{[\text{UHPO}_4^{2+}][\text{H}_2\text{PO}_4^-]}{[\text{H}^+]}$$
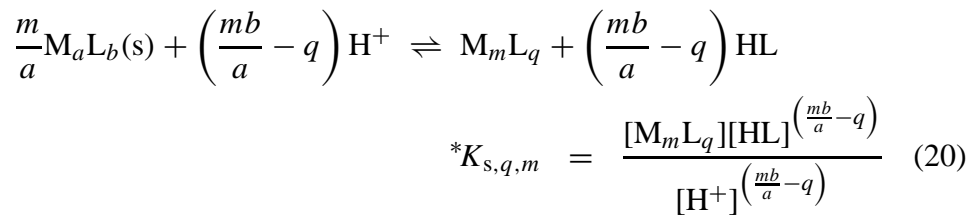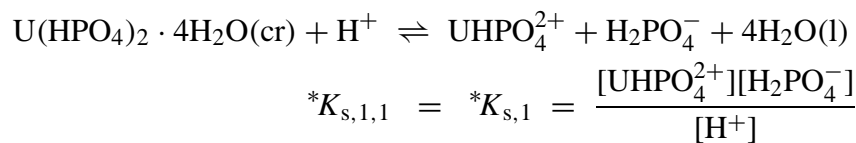
1.7.d Equilibria involving the addition of a gaseous ligand

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

$$ML_{q-1} + L(g) \; \rightleftharpoons \; ML_q \qquad K_{p,q} = \frac{[ML_q]}{[ML_{q-1}]p_L} \qquad (21)$$

The subscript "p" can be combined with any other notations given above.

Example:

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

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

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

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

$$^*K_{p,s,2} = \frac{[UO_2(CO_3)_2^{2-}][H^+]^2}{p_{CO_2}}$$
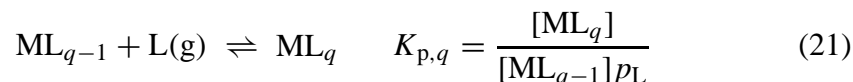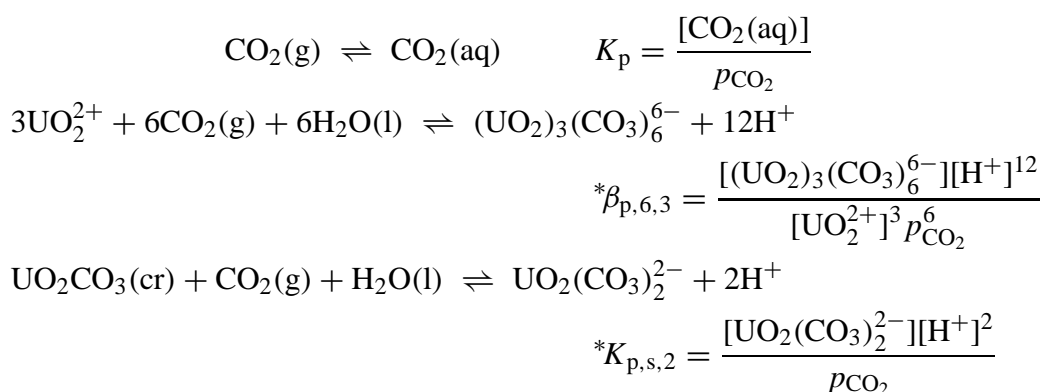
In cases where the subscripts become complicated, it is recommended that K or β be used with or without subscripts, but always followed by the equation number of the equilibrium to which it refers.

1.7.e Redox equilibria

Thermodynamic data for redox reactions are presented in different ways:

- as *normal*, or *standard* potentials

- as standard Gibbs energies of reaction, $\Delta_r G_m^\circ$

- as equilibrium constants

- as pe° values

In the following section we will make a brief review of these concepts.

It is not possible to study the formation of free electrons, *e.g.*, in reactions such as:

$$U^{4+} + 2H_2O \; \rightleftharpoons \; UO_2^{2+} + 4H^+ + 2e^- \qquad (22)$$
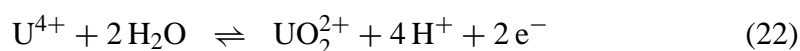
because they cannot occur in ordinary aqueous chemical systems. This is in complete analogy with the previous example on acid/base equilibria where H^+ is a fictive species. However, the reaction may take place as a *half-cell reaction* in an electrochemical cell. The electrons released in one half-cell are taken up by the reactant(s) in a second half-cell. The zero point is defined by the choice of the second half-cell. By international definition the half-cell reaction between the aqueous hydrogen ion and hydrogen gas is used as a reference:
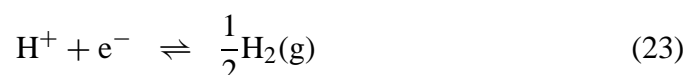
$$H^+ + e^- \quad \rightleftharpoons \quad \frac{1}{2}H_2(g) \tag{23}$$

The equilibrium constant for this half-cell reaction is defined as unity:

$$K^\circ(23) \quad = \quad \frac{a_{H^+} \, a_{e^-}}{\sqrt{f_{H_2}}} = 1 \qquad \text{(by definition)} \tag{24}$$

In addition, $\Delta_r G_m^\circ$ (23) $= E^\circ$(23) $= \Delta_r H_m^\circ$ (23) $= \Delta_r S_m^\circ$ (23) $= 0$ by definition, at all temperatures.

By combining Reactions (22) and (23) we obtain:

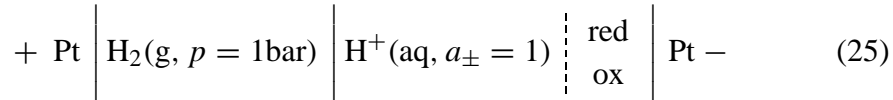$$U^{4+} + 2H_2O(l) \quad \rightleftharpoons \quad UO_2^{2+} + 2H^+ + H_2(g)$$

In contrast to Reaction (22), the equilibrium constant of the last equation can be measured. In the same way as for acid–base reactions it can be considered as the product of two equilibrium reactions but in this case involving free electrons rather than free protons.

Redox reactions like (22) are usually quantified in terms of their standard electrode (half-cell) potential, E° (see below), which is identical to the electromotive force (emf) of a standard galvanic cell in which the reference electrode is the standard hydrogen electrode, SHE (see Section 1.1), in accordance with the "1953 Stockholm Convention" [88MIL/CVI]. This means that electrode potentials are given as *reduction potentials* relative to the standard hydrogen electrode, which acts as an electron donor (Reaction (23)). The sign of the standard electrode potential, E°, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. Several compilations of E° values may be found in the literature [71CHA/COL, 85BAR/PAR, 89BRA, *etc.*]. It must be noted that some older compilations of redox data report *oxidation* potentials instead (notably that of Latimer: *Oxidation Potentials of the Elements* [52LAT]).

In the standard hydrogen electrode (Reaction (23)), $H_2(g)$ is at unit fugacity (an ideal gas at unit pressure, 1 bar); H^+ is at unit activity (*cf.* Section 3.1); and the galvanic cell where the SHE is used has a negligible liquid junction potential. In general one does not use the standard hydrogen electrode in experimental studies, but secondary standards (*e.g.*, the Ag/AgCl electrode, or the calomel electrode)

which are easy to work with, and whose electrode potentials are accurately known on the standard hydrogen electrode scale.

Consider the hypothetical galvanic cell

$$+ \ \text{Pt} \ \left| \ \text{H}_2(\text{g}, \, p = 1\text{bar}) \ \right| \ \text{H}^+(\text{aq}, \, a_\pm = 1) \ \vdots \ \begin{array}{c} \text{red} \\ \text{ox} \end{array} \ \right| \ \text{Pt} \ - \quad (25)$$

where "ox" is the oxidised form of some chemical species and "red" is the reduced form. The overall chemical reaction for this cell is

$$\text{ox} + \frac{n}{2}\text{H}_2(\text{g}) \quad \rightleftharpoons \quad \text{red} + n\text{H}^+ \quad (26)$$
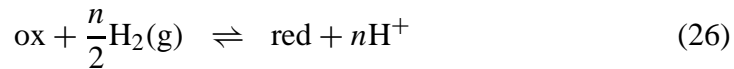
The change in the Gibbs energy for this reaction is:

$$\Delta_\text{r} G_\text{m}(26) \quad = \quad \Delta_\text{r} G_\text{m}^\circ(26) + RT \ln \left(\frac{a_\text{red} \, a_{\text{H}^+}^n}{a_\text{ox} \, f_{\text{H}_2}^{n/2}} \right)$$

The electrode potential is related to the Gibbs energy change, $\Delta_\text{r} G_\text{m}$ as shown in Eq. (27–28).

$$E(26) \quad = \quad -\frac{1}{nF} \Delta_\text{r} G_\text{m}(26) \quad (27)$$

$$E^\circ(26) \quad = \quad -\frac{1}{nF} \Delta_\text{r} G_\text{m}^\circ(26) \quad (28)$$

At equilibrium, this gives

$$E^\circ(26) \quad = \quad -\frac{1}{nF} \Delta_\text{r} G_\text{m}^\circ(26) = \frac{RT \ln(10)}{nF} \log_{10} K^\circ(26) \quad (29)$$

Setting f_{H_2} and a_{H^+} equal to unity, one obtains

$$\Delta_\text{r} G_\text{m}(26) \quad = \quad \Delta_\text{r} G_\text{m}^\circ(26) - RT \ln \left(\frac{a_\text{ox}}{a_\text{red}} \right)$$

$$E(26) \quad = \quad E^\circ(26) - \frac{RT}{nF} \ln \left(\frac{a_\text{red}}{a_\text{ox}} \right) \quad (30)$$

where the last equation is the familiar Nernst equation.

As described above, Reaction (26) may formally be written as two half-cell reactions:

$$\text{ox} + n\,\text{e}^- \quad \rightleftharpoons \quad \text{red} \quad (31)$$

$$\text{H}^+ + \text{e}^- \quad \rightleftharpoons \quad \frac{1}{2}\text{H}_2(\text{g})$$
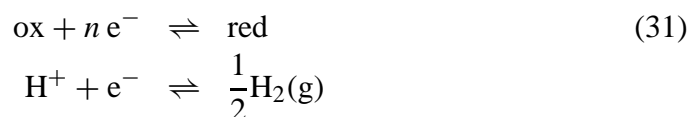
The equilibrium constants for these reactions are denoted $K°(31)$ and $K°(23)$, respectively.

The equilibrium constant for Eq. (26) isrelated to the equilibrium constants for the two half-cell reactions:

$$K°(26) \; = \; \left(K°(23) \right)^n \times K°(31)$$

Introducing Eq. (24):

$$K°(26) \; = \; K°(31) \; = \; \frac{a_{\text{red}}}{a_{\text{ox}}\, a_{e^-}^n} \tag{32}$$

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" (*defined* as: $\text{pe} = -\log_{10} a_{e^-}$) by analogy with pH ($= -\log_{10} a_{H^+}$), while 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 [81STU/MOR, 82DRE, 84HOS, 94NOR/MUN]). The variable "pe" may be introduced in Eq. (32):

$$-\log_{10} a_{e^-} \; = \; \text{pe} \; = \; \frac{1}{n} \left(\log_{10} K° + \log_{10} \frac{a_{\text{ox}}}{a_{\text{red}}} \right) \tag{33}$$

At standard conditions the activities of reactants and products are unity ($a_{\text{red}} = a_{\text{ox}} = 1$), and the relation between pe° and E° is obtained:

$$\text{pe}° \; = \; \frac{1}{n} \log_{10} K° \; = \; \frac{F E°}{R T \ln(10)} \tag{34}$$

pe° may be introduced into Eq. (33):

$$\text{pe} \; = \; \text{pe}° + \frac{1}{n} \log_{10} \frac{a_{\text{ox}}}{a_{\text{red}}} \tag{35}$$

Finally, the relation between a_{e^-} and the redox potential against the standard hydrogen electrode, Eh, may be obtained from Eqs. (30), (33), and (34):

$$-\log_{10} a_{e^-} \; = \; \frac{F Eh}{R T \ln(10)} \tag{36}$$

In analogy with $\Delta_r G_m^{°\prime}$ (see Section 1.6), the symbol $E^{°\prime}$ is used to denote the so-called "formal potential" [74PAR]. 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 [85BAR/PAR] Again using reaction (26) as an example, we have

$$E(26) = E^{°\prime}(26) - \frac{R T \ln(10)}{n F} \log_{10} \frac{c_{\text{red}}}{c_{\text{ox}}} \tag{37}$$

$E^{\circ\prime}$ 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

$$E^{\circ\prime}(26) = E^{\circ}(26) - \frac{RT \ln (10)}{nF} \log_{10} \frac{\varrho \gamma_{\mathrm{red}}}{\varrho \gamma_{\mathrm{ox}}} \tag{38}$$

where the γ is the molality activity coefficient and ϱ is (m_i/c_i), the ratio of molality to molarity (*cf.* Section 2). For these cases, the medium in which the potential was measured must be specified.

In chemical equilibrium modelling, 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, "e^-" is not an aqueous species, and it is necessary to set its concentration to *zero* during the calculations (arbitrary values, however, may be assigned to a_{e^-} which are then related to E by Eq. (36)).

The "activity of electrons" in Eqs. (24) and (32), (33) may be interpreted to represent the relative tendency for a dissolved oxidant to accept electrons, or for electrons to "leave" the half-cell electrode. Alternatively, the symbol "a_{e^-}" might just be considered to be a mathematical representation of the function "$\sqrt{f_{H_2}}/a_{H^+}$" (*cf.* Eq. (24)), and may therefore also be seen as equivalent to the standard electrode potential of the half-cell (*cf.* Eq. (36)).

1.8 pH

Because of the importance of potentiometric methods in the determination of the acidity of 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 is

$$\mathrm{pH} = -\log_{10} a_{H^+} = -\log_{10}(m_{H^+} \gamma_{H^+}) \tag{39}$$

The activity can only be estimated from the known concentration of H^+ in the limited range of the Debye-Hückel equation (that is, in extremely diluted solutions). In practice the use of pH values requires extra assumptions on the values for single ion activities.

The determination of pH is often performed by emf measurements of galvanic cells involving liquid junctions [69ROS, 73BAT]. 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) corresponding to the following galvanic cell:

$$
\text{glass electrode}
$$

$$
- \;\text{Ag(s)} \;\Big|\; \text{AgCl(s)} \;\Big|\; \text{HCl(aq)} \;\vdots\; \underset{a}{\overset{\text{salt}}{\text{bridge}}} \;\vdots\; \underset{b}{\overset{\text{test}}{\text{solution}}} \;\vdots\; \text{HCl(aq)} \;\Big|\; \text{AgCl(s)} \;\Big|\; \text{Ag(s)} \;+
$$

$$
\underbrace{\phantom{\text{Ag(s) AgCl(s) HCl(aq)}}}_{E_{\text{ref.}}} \qquad \underbrace{\phantom{\text{test solution HCl(aq) AgCl(s) Ag(s)}}}_{E_{\text{glass}}}
$$

(40)
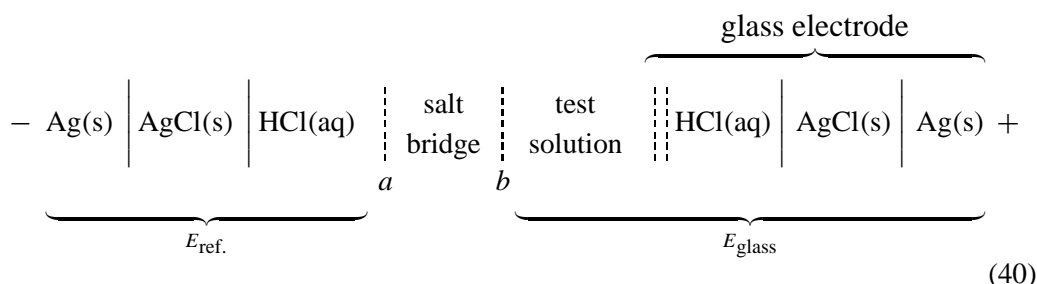
where "$\vdots$" denotes a liquid junction, and "$\vdots$" stands for a glass membrane (permeable to hydrogen ions). The emf of such a cell is given by

$$
E(40) \;=\; E_{\text{glass}} - E_{\text{ref.}} + E_{\text{j}} \;=\; E^{*} + \frac{RT}{nF}\ln a_{\text{H}^{+}} + E_{\text{j}}
$$

where $E_{\text{ref.}}$ and E_{glass} are the half cell potentials of the reference cell and the test solution half-cell, respectively, E^{*} is a constant, and E_{j} is the junction potential. Precise determinations of the E* constant are easily performed with Gran plots [65ROS/ROS].

Two methods are often used to reduce and control the value of E_{j} [93AND, 73BAT], electrolyte solution of high concentration (the "salt bridge") being a requirement of both methods:

1. 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 inside the liquid junction when the test solution contains a high concentraction of perchlorate ions ($KClO_4$(cr) has a solubility of about 0.15 M in pure water at 25° C).

2. 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 [80BIE/DOU]. 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 junction b, *cf.* Eq. (40), on acidity is $E_{\text{j}} = 440[\text{H}^{+}]\text{mV·dm}^{3}\text{·mol}^{-1}$ at 25° C [69ROS, p. 110], which corresponds to an error at pH = 2 of $\geq$ 0.07 pH units.

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 [88MIL/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 γ_{H^+} and E_j cancel each other when emf values are subtracted).

Most of the experimental studies on the determination of equilibrium constants are performed at a constant ionic strength in order to eliminate the variation of the single ion activity coefficients among the experimental data [61ROS/ROS, 72BJE, 80HAR/BUR]. In the presence of a large background electrolyte concentration, emf measurements give values for the concentration of H^+ rather than its activity, and Eq.(39) shows that in this case pH and "pH$_c$" (= -$\log_{10}[H^+]$) differ by a constant amount, $\log_{10}\gamma_{H^+}$, which depends on I. Another advantage of the "constant background electrolyte" method is that, as described in point 2 above, it also reduces considerably the uncertainty in the value of the junction potential [73BAT, 93AND].

1.9 Presenting numeric values of chemical quantities

When presenting a value for a chemical quantity, such as *e. g.*, $\Delta_r G_m^\circ$, in the text, the following should be observed:

- Values with uncertainties, whether negative or positive, should be enclosed in parentheses, as in

$$\Delta_r G_m^\circ(\text{V.89, 298.15 K}) = -(245.6 \pm 3.4)\,\text{kJ·mol}^{-1}$$
$$\Delta_r H_m^\circ(\text{V.89, 298.15 K}) = -(333.2 \pm 1.6)\,\text{kJ·mol}^{-1}$$

- Values referring to a chemical reaction should have the reference number of the reaction attached, as in $\Delta_r G_m^\circ(\text{VI.89, 298.15 K})$, which also implies that the each such value should have a corresponding chemical reaction presented in the review. This may not be necessary for equilibrium constants, for the cases where the notation of the constant gives unambiguous information on the reaction it refers to (see Section 1.7).

- Selected values of thermodynamic parameters should always be presented on separate lines in the text. Also, preferably the numerical values should be presented only once, with other referrals using the number of the equation for the reaction or referring to the appropriate section. This is in order to avoid having selected values spread throughout the report, and to make selected values easier to find, both for the reader and for the authors when proof-reading. In this way, selected values, which may change during the production of a report, are defined unambiguously in one place only, and

one avoids the risk of having different values in different sections of the report.

1.10   Order of formulae

To be consistent with CODATA, the data tables are given in "Standard Order of Arrangement" [82WAG/EVA, p. 2-25]. This scheme is presented in Figure 1 showing the sequence of the "ranks" of the elements in this convention. The elements which come first in the sequence, starting with O, are said to have lower rank than the following elements.

The basic order follows the ranks of the elements, with O first, then H *etc.* For compounds with more than one element, the element of highest rank determines the order, then the element with the second highest rank, the third highest rank and so on. Example: $O_2(g)$, H^+, Na, NaO, NaH, NaOH, NaI, $NaIO_3$, Na_2SO_4, $NaHSO_4$, NaN_3, $NaI \cdot 4.5NH_3$, $NaHCO_3$.

For compounds and complexes with the same set of elements, increasing coefficients of the lower rank elements go before increasing coefficients of the higher rank elements, independently of the way the formula is written.

For compounds with the same stoichiometry, the order is determined by the state of aggregation as follows:

1. crystalline solid (cr)

2. amorphous

3. liquid

4. vitreous (glassy)

5. gas

6. aqueous solution

For aqueous species, uncharged species are listed first, then positive ions in order of increasing charge, and finally negative ions in order of decreasing charge.

For example, in the U-O-F class of compounds and complexes (where U has the highest rank, then F, then O), a typical sequence would be: $UO_2F(aq)$, UO_2F^+, $UOF_2(cr)$, $UO_2F_2(cr)$, $UO_2F_2(g)$, $UO_2F_2(aq)$, $UO_2F_3^-$, $UOF_4(cr)$, $UOF_4(g)$, $UO_2F_4^{2-}$, $U_2O_3F_6(cr)$, *etc*.

Figure 1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (reproduced by permission from Ref.[82WAG/EVA]).
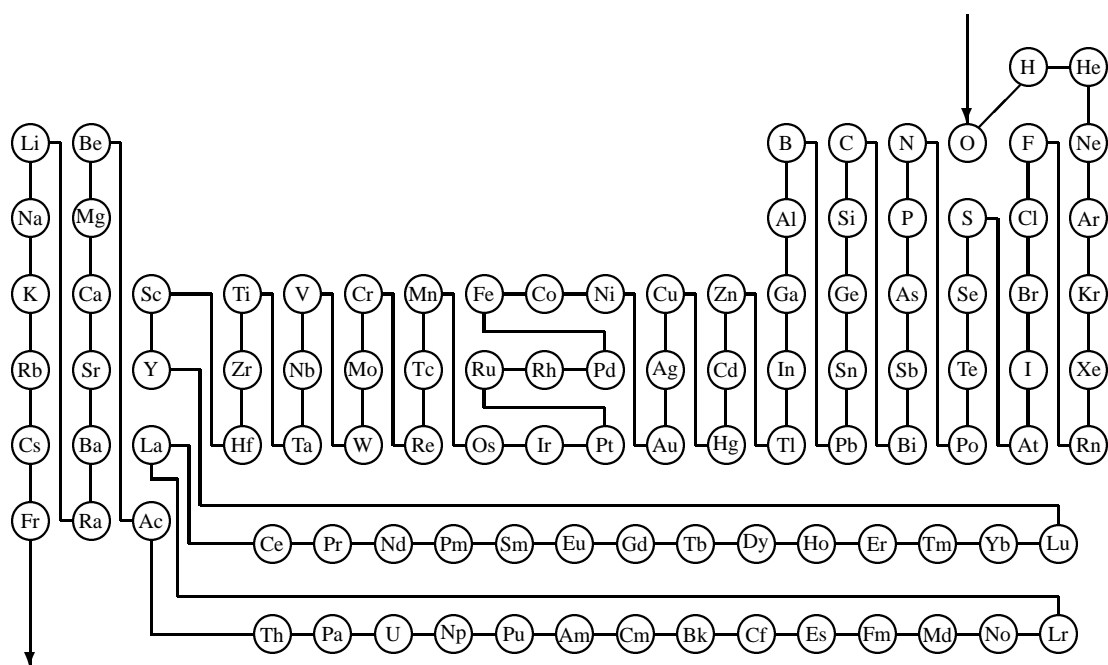
1.11 Referenced publications

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [87GAR/PAR]. A reference code is made up of the final two digits of the year of appearance (if the publication is not from the 20th century, the year will be put in full). The year is 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. In the bibliography entries, for the sake of brevity, several standard abbreviations may be used: Proc., Conf., Symp., Vol., Inc., Ltd., Co., Dept., Jr., No., *ed., eds.*. Further, use US for U.S., USA for U.S.A., and UK for U.K.

1.11.1 Titles

– Capitalize only the first word of the title or subtitle.

– Transcribe the title exactly as it appears on the title page of the document. Do not standardize spelling.

– Separate the title from a subtitle with a colon, even if the colon does not appear on the title page. Use only one space after the colon.

1.11.2 Publication Information

The following information must always be included for the publications cited in the NEA/TDB reviews:

• The full names of all the authors.

• The full title of the publication cited, including any booktitles and titles of chapters or sections where applicable.

• The full name of the journal, if applicable.

• The publishing year.

• The volume number for journals.

• The page numbers (first and last) of the article or chapter, section *etc.* in a book.

• For books, the name and address of the publisher and the total number of pages.

- For reports, the name and address of the publishing institution and the number of the report, if any.

- For a book in a series, the name of the series and the volume or number in the series of the book quoted.

The purpose of citing publications in a review report is to give the reader the possibility to look up the original work and check the facts (or at least what was reported as facts). For this reason, references that are not publicly available and hence impossible to obtain for the reader should be avoided as far as humanly possible. Please *avoid* citing the following:

- Personal communications. If such communications have to be cited, try to get them in a letter and deposit (a copy of) the letter with the NEA.

- Secondary references, i. e. a reference to a publication that is referenced in another publication (not to mention secondary references to personal communications!). Always try to obtain the original publication.

- Abstracts for conference papers or talks. These abstracts are usually only made available to the people participating in the conference, and cannot be found at libraries etc. after the conference.

2 Units and conversion factors

Thermodynamic data are given according to the *Système International d'unité* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non-thermodynamic units, are given in Table 5.

Table 5: Unit conversion factors

To convert from (non-SI unit symbol)	to (SI unit symbol)	multiply by
ångström (Å)	metre (m)	1×10^{-10} (exactly)
standard atmosphere (atm)	pascal (Pa)	1.01325×10^5 (exactly)
bar (bar)	pascal (Pa)	1×10^5 (exactly)
thermochemical calorie (cal)	joule (J)	4.184 (exactly)
entropy unit (e.u. $\stackrel{\triangle}{=} \text{cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)	$\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	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, the reviews use the unit "M" as an abbreviation

of "mol $\cdot$ dm^{-3}" for molarity, c, and sometimes "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 equilibrium data to zero ionic strength by the SIT method which works in molality units (*cf.* the TDB-2 Guideline). This conversion is possible in the following way. Molality is defined as m_B moles of substance B dissolved in 1000 grams of pure water. Molarity is defined as c_B moles of substance B dissolved in $(1000\rho - c_B M)$ grams of pure water, where ρ is the density of the solution and M the molar weight of the solute. From this it follows that

$$m_B = \frac{1000 c_B}{1000\rho - c_B M} \tag{41}$$

Baes and Mesmer [76BAE/MES, *p.* 439], give a table with these conversion factors for nine electrolytes and various ionic strengths. Conversion factors at 298.15 K calculated using the density equations reported by Söhnel and Novotný [85SÖH/NOV] are reported in Table 6.

Example:

$$
\begin{array}{lcl}
1.00 \text{ M NaCl} & \mathrel{\hat{=}} & 1.02 \text{ m NaCl} \\
1.00 \text{ M NaClO}_4 & \mathrel{\hat{=}} & 1.05 \text{ m NaClO}_4 \\
2.00 \text{ M KNO}_3 & \mathrel{\hat{=}} & 2.19 \text{ m KNO}_3 \\
4.00 \text{ M NaClO}_4 & \mathrel{\hat{=}} & 4.95 \text{ m NaClO}_4 \\
6.00 \text{ M NaNO}_3 & \mathrel{\hat{=}} & 7.54 \text{ m NaNO}_3
\end{array}
$$

Equilibrium constants, unless they are dimensionless, need also to be converted if the concentration scale is changed from molarity to molality or vice versa. For a general equilibrium reaction, $0 = \sum_B \nu_B B$, the equilibrium constants can be expressed either in molarity or molality units, K_c or K_m, respectively:

$$\log_{10} K_c = \sum_B \nu_B \log_{10} c_B$$

$$\log_{10} K_m = \sum_B \nu_B \log_{10} m_B$$

With $(m_B/c_B) = \varrho$, or $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \varrho$, the relationship between K_c and K_m becomes very simple, as shown in Eq. (42).

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \varrho \tag{42}$$

$\sum_B \nu_B$ is the sum of the stoichiometric coefficients of the reaction, and the values of ϱ are the factors for the conversion of molarity to molality as tabulated

Table 6: Factors ϱ 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 [85SÖH/NOV]).

	$\varrho = m_B/c_B$ (dm³ of solution per kg of H₂O)							
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_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_4Cl	$MgCl_2$	$CaCl_2$	$NaBr$	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_4NO_3	H_2SO_4	Na_2SO_4	$(NH_4)_2SO_4$	H_3PO_4	Na_2CO_3	K_2CO_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

in Table 6 for several electrolyte media at 298.15 K. The differences between the values in Table 6 and the values listed in the uranium NEA-TDB review [92GRE/FUG, *p*.23] are found at the highest concentrations, and are $\leq \pm0.003$ dm^3/kg, reflecting the accuracy expected in this type of conversions. The uncertainty introduced by the use of Eq. (42) in the values of $\log_{10} K_m$ will then be $\leq \pm0.001 \sum_B \nu_B$.

From the values in Table 6 it can be seen that when dealing with very dilute solutions, molarity and molality may be used interchangeably, and $K_m \approx K_c$.

3   Standard and reference conditions

3.1   Standard state

A precise definition of the term "standard state" has been given by IUPAC [93MIL/CVI]. 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 [93MIL/CVI] 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 3.2. The application of the standard state principle to pure substances and solutions is summarized below. The standard state is always linked to a reference temperature, cf. Section 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 in a liquid or solid solution is referenced to the ideal dilute behaviour of the solute. It is the (hypothetical) state of solute B at the standard molality $m\circ$, standard pressure $p\circ$ and exhibiting infinitely dilute solution behaviour.

It should be emphasized that the use of °, *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 are listed in Table 7.

Table 7: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [82WAG/EVA, 89COX/WAG, 91DIN].

O_2	gaseous	Al	crystalline, cubic
H_2	gaseous	Zn	crystalline, hexagonal
He	gaseous	Cd	crystalline, hexagonal
Ne	gaseous	Hg	liquid
Ar	gaseous	Cu	crystalline, cubic
Kr	gaseous	Ag	crystalline, cubic
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, hexagonal ("black")	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	β, crystalline, rhombohedral	Cs	crystalline, cubic

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

[93MIL/CVI]. However, the majority of the thermodynamic data published in the sci-entific literature and used for the evaluations in this review, refer to the old stand-ard 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 these corrections in order to avoid inconsistencies and propagation of er-rors. 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 in-volve 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 parameters are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [82WAG/EVA], see also Freeman [84FRE].

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

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1 - \alpha T) \tag{43}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right) \tag{44}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{45}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V, \tag{46}$$

$$\text{where} \qquad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p. \tag{47}$$

For ideal gases, $V = \frac{RT}{p}$ and $\alpha = \frac{R}{pV} = \frac{1}{T}$. The conversion equations listed below (Eqs. (48) to (55)) 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 $^{(\text{atm})}$ here, the ones that refer to the new standard state pressure of 1 bar the superscript $^{(\text{bar})}$.

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

$$\Delta_{\text{f}} H^{(\text{bar})}(T) - \Delta_{\text{f}} H^{(\text{atm})}(T) = 0 \tag{48}$$

$$C_p^{(\text{bar})}(T) - C_p^{(\text{atm})}(T) = 0 \tag{49}$$

For gaseous substances, the entropy difference is

$$
\begin{aligned}
S^{\text{(bar)}}(T) - S^{\text{(atm)}}(T) &= R \ln\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right) \\
&= R \ln 1.01325 \\
&= 0.1094 \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}.
\end{aligned} \tag{50}
$$

This is exactly true for ideal gases, as follows from Eq. (45) with $\alpha = \frac{R}{pV}$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$
\begin{aligned}
\Delta_{\text{r}}S^{\text{(bar)}} - \Delta_{\text{r}}S^{\text{(atm)}} &= \delta \times R \ln\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right) \\
&= \delta \times 0.1094 \, \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1},
\end{aligned} \tag{51}
$$

where δ 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

$$
\begin{aligned}
\Delta_{\text{r}}G^{\text{(bar)}} - \Delta_{\text{r}}G^{\text{(atm)}} &= -\delta \times RT \ln\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right) \\
&= -\delta \times 0.03263 \, \text{kJ} \cdot \text{mol}^{-1} \quad \text{at 298.15 K.}
\end{aligned} \tag{52}
$$

Eq. (52) applies also to $\Delta_{\text{f}}G^{\text{(bar)}} - \Delta_{\text{f}}G^{\text{(atm)}}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$
\Delta_{\text{r}}G^{\text{(bar)}} - \Delta_{\text{r}}G^{\text{(atm)}} = -\delta \times 0.03263 \, \text{kJ} \cdot \text{mol}^{-1} \quad \text{at 298.15 K.} \tag{53}
$$

The change in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq. (52):

$$
\begin{aligned}
\log_{10} K^{\text{(bar)}} - \log_{10} K^{\text{(atm)}} &= -\frac{\Delta_{\text{r}}G^{\text{(bar)}} - \Delta_{\text{r}}G^{\text{(atm)}}}{RT \ln 10} \\
&= \delta \times \frac{\ln\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right)}{\ln 10} = \delta \times \log_{10}\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right) \\
&= \delta \times 0.005717 \\
E^{\text{(bar)}} - E^{\text{(atm)}} &= -\frac{\Delta_{\text{r}}G^{\text{(bar)}} - \Delta_{\text{r}}G^{\text{(atm)}}}{nF} \\
&= \delta \times \frac{RT \ln\left(\frac{p^{\text{(atm)}}}{p^{\text{(bar)}}}\right)}{nF} \\
&= \delta \times \frac{0.0003382}{n} \, \text{V} \quad \text{at 298.15 K.}
\end{aligned} \tag{54, 55}
$$

The standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.

$$H^+ + e^- \; \rightleftharpoons \; \tfrac{1}{2}H_2(g) \qquad E^\circ \stackrel{\text{def}}{=} 0.00 \, V \qquad (56)$$

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
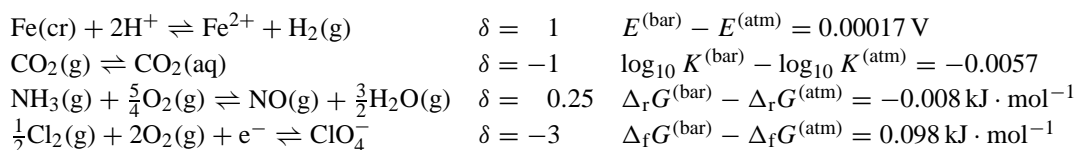
$$Ag^+ + e^- \; \rightleftharpoons \; Ag(cr)$$
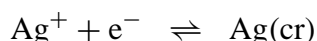
should thus be calculated from the balanced reaction that includes the hydrogen electrode,

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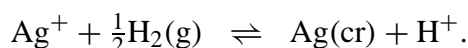
Here $\delta = -0.5$. Hence, the contribution to δ from an electron in a half cell reaction is the same as the contribution of a gas molecule with the stoichiometric coefficient of 0.5. This leads to the same value of δ as the combination with the hydrogen half cell.

Example:

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

3.3 Reference temperature

The definitions of standard states given in Section 3.1 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 [93MIL/CVI], the reference tem-perature chosen in the NEA-TDB project is $T = 298.15$ K or $t = 25°C$. Where necessary for the discussion, values of experimentally measured temperatures are reported after conversion to the IPTS-68 [69COM]. The relation between the ab-solute temperature T (K, kelvin) and the Celsius temperature t (°C) is defined by $t = (T - T_0)$ where $T_0 = 273.15$ K.

4 Fundamental physical constants

The fundamental physical constants are taken from a publication by CODATA [86COD]. Those relevant to this review are listed in Table 8.

Table 8: Fundamental physical constants. These values have been taken from CODATA [86COD]. 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	$\mathrm{m \cdot s^{-1}}$
permeability of vacuum	$\mu_\circ$	$4\pi \times 10^{-7}$	
		$= 12.566\,370\,614\ldots$	$10^{-7}\,\mathrm{N \cdot A^{-2}}$
permittivity of vacuum	$\epsilon_\circ$	$1/\mu_\circ c^2$	
		$= 8.854\,187\,817\ldots$	$10^{-12}\,\mathrm{C^2 \cdot J^{-1} \cdot m^{-1}}$
Planck constant	h	6.626 0755(40)	$10^{-34}\,\mathrm{J \cdot s}$
elementary charge	e	1.602 177 33(49)	$10^{-19}\,\mathrm{C}$
Avogadro constant	N_A	6.022 1367(36)	$10^{23}\,\mathrm{mol^{-1}}$
Faraday constant, $N_\mathrm{A} \times e$	F	96 485.309(29)	$\mathrm{C \cdot mol^{-1}}$
molar gas constant	R	8.314 510(70)	$\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23}\,\mathrm{J \cdot K^{-1}}$
Non-SI units used with SI:			
electron volt, $(e/\mathrm{C})\,\mathrm{J}$	eV	1.602 177 33(49)	$10^{-19}\,\mathrm{J}$
atomic mass unit, $1\mathrm{u} = m_\mathrm{u} = \frac{1}{12}m(^{12}\mathrm{C})$	u	1.660 5402(10)	$10^{-27}\,\mathrm{kg}$

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