INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON THERMODYNAMICS*

NOTATION FOR STATES AND PROCESSES, SIGNIFICANCE OF THE WORD *STANDARD* IN CHEMICAL THERMODYNAMICS, AND REMARKS ON COMMONLY TABULATED FORMS OF THERMODYNAMIC FUNCTIONS

(Recommendations 1981)

(Appendix No. IV to *Manual of Symbols and Terminology for Physicochemical Quantities and Units*)

Prepared for publication by
J. D. COX, National Physical Laboratory, Teddington, UK
with the assistance of a Task Group consisting of
S. ANGUS, London; G. T. ARMSTRONG, Washington, DC; R. D. FREEMAN, Stillwater, OK; M. LAFFITTE, Marseille; G. M. SCHNEIDER (Chairman), Bochum; G. SOMSEN, Amsterdam, (from Commission I.2); and C. B. ALCOCK, Toronto; and P. W. GILLES, Lawrence, KS, (from Commission II.3)

NOTATION FOR STATES AND PROCESSES, SIGNIFICANCE OF THE WORD *STANDARD*
IN CHEMICAL THERMODYNAMICS, AND REMARKS ON COMMONLY TABULATED FORMS
OF THERMODYNAMIC FUNCTIONS

SECTION 1. INTRODUCTION

The main IUPAC Manual of symbols and terminology for physicochemical quantities and units
(Ref. 1) presents in its paragraph 2.4 a number of symbols for thermodynamic and related
quantities. These symbols, together with others from chapter 2 of the Manual, provide
the thermodynamicist with the basis for development of the more sophisticated sets of
symbols that are often needed.

It is the purpose of the present Appendix IV (Note a) to supplement the information in
the Manual in respect of the following topics in chemical thermodynamics which are not
treated, or are cursorily treated, in the Manual:

- notation for states of aggregation,
- notation for processes,
- proper usage of the adjective *standard*,
- commonly tabulated forms of thermodynamic functions.

The treatment which follows is compatible with that given in the IUPAC Manual (Ref. 1)
and its Appendix I (Ref. 1). Mostly the symbols given by way of example in this Appendix
are more complex than those given in reference 1, and perhaps a word of warning on un-
necessary complexity should be given: whilst symbols should be rigorous, they need not
be more complex than the given context requires. Thus the symbol $f(NH_3, g, 500\ K, 2\ MPa)$,
quoted in paragraph 2.3 below as the symbol for the fugacity of gaseous ammonia at a
temperature of 500 K and a pressure of 2 MPa, would be abbreviated to $f(500\ K, 2\ MPa)$
if the text in question made clear that the only species under consideration was gaseous
ammonia.

SECTION 2. STATES OF AGGREGATION

2.1 Simple notation for states of aggregation
Symbols for thermodynamic quantities often require annotation to make clear the *state of
aggregation* (also called *state of matter* or just *state*) to which the symbols refer.
Moreover, the symbols for species in chemical equations or in shorthand descriptions
of the species in texts, tables, and figures, often require annotation to make clear
the state of aggregation of the species in question. There is good reason to use a

---

Note a: A provisional form of this Appendix IV was published in 1979 (Ref. 2).

standardized notation for states of aggregation in all contexts, and in many instances this can be achieved by use of the simple notation below. But where the context requires it, a more extended notation (cf. paragraph 2.10 of the IUPAC Manual, reference 1) should be used, as explained in paragraph 2.3 below.

In the following list of symbols, single letters are used to denote the three basic states of aggregation, *gas, liquid,* and *solid,* whilst combinations of letters are used for more subtle descriptions of states:

- the symbol for a gas or a vapour is g
- the symbol for a liquid is l
- the symbol for a solid is s
- the symbol for a condensed phase (i.e., either the solid or the liquid state) is cd
- the symbol for a fluid (i.e., either the gaseous or the liquid state) is fl
- the symbol for a liquid crystal (crystalline liquid) is lc
- the symbol for a crystalline solid is cr; where polymorphism occurs, it may be necessary to augment the symbol cr with a descriptor for the crystal modification under discussion; the preferred descriptors are Roman numerals, with textual definition of the crystallographic significance of the numerals used (see examples given later in this Appendix).
- the symbol for an amorphous solid is am
- the symbol for a vitreous substance (a glass) is vit
- the symbol for a species adsorbed on a substrate (an adsorbate) is ads
- the symbol for a monomeric form is mon
- the symbol for a polymeric form is pol (in many cases the monomeric or polymeric character of the entity will be clear from the context without the symbol, and the symbol should be used only in cases where ambiguity might result)
- the symbol for a solution (see Appendix I, Section A.I.9 in reference 1) is sln; in many contexts it will be clear whether a liquid solution or a solid solution is meant, but where this is unclear it must be made clear by supplemental notation (see e.g. paragraph 2.3 below)
- the symbol for a solution in which water is the solvent (an aqueous solution) is aq; in the past this symbol has sometimes been used to denote an infinitely dilute aqueous solution, but infinite dilution should henceforward be denoted by the extra symbol ∞ (see paragraph 2.2 and Note b).

The above symbols should be printed in roman type without full stops (periods) and should be placed in parentheses after the symbol for a physicochemical quantity or chemical substance to which they relate.

Examples:

| symbols	meaning
HCl(g)	hydrogen chloride in the gaseous state;
α(l)	cubic expansion coefficient of a liquid;

Note b: Parenthetic additon of sln to the main symbol is here unnecessary, as ∞ is used only for solutions.

KBr(s)	potassium bromide in the solid state;
c_V(fl)	constant-volume heat capacity of a fluid;
c_p(cd)	constant-pressure heat capacity of a condensed phase;
V_m(lc)	molar volume of a liquid crystal;
U(cr)	internal energy of a crystalline solid;
MnO_2(am)	manganese dioxide as an amorphous solid;
MnO_2(cr, I)	manganese dioxide as crystal modification I;
$\underline{\phi}$(vit)	fluidity of a vitreous substance;
$\underline{\rho}$(ads)	density of an adsorbed species;
$\underline{\beta}$(sln)	pressure coefficient of volume of a solution;
NaOH(aq)	solution of sodium hydroxide in water;
NaOH(aq, ∞)	solution of sodium hydroxide in water, at infinite dilution.

Chemical equation

$$Na(s) \; + \; 5C_2H_5OH(l) \; = \; 0.5H_2(g) \; + \; \{C_2H_5ONa \; + \; 4C_2H_5OH\}(sln).$$
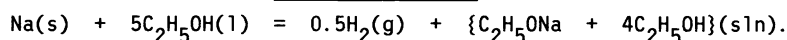
2.2 Use of simple subscripts and superscripts

Extra information on the state of a substance can be imparted either by use of simple subscripts and superscripts (see paragraph 2.11 of the IUPAC Manual (Ref. 1)), or by use of extended notation, as described in paragraph 2.3 below. The significance of the superscript °, which may be substituted by [⊖], is explained in more detail in paragraph 4.1 below.

It is occasionally advantageous to use more than one subscript, or more than one super-script, separated by commas, but subscripts to subscripts etc. should be avoided, by use of extended notation instead.

Examples:

symbols	meaning
S_m°(g)	standard molar entropy of a gas;
$c_{p,2}^\star$	(molar) heat capacity (Note c) at constant pressure of pure species 2;
$\underline{\sigma}_B^\star$(l)	surface tension of pure liquid B;
H_B^∞	partial molar enthalpy of species B in solution at infinite dilution (Note b);
$\underline{\gamma}^{id}$(g)	the ratio c_p/c_V for an ideal gas.

2.3 Extended notation for states of aggregation

In some circumstances the simple notation given in paragraphs 2.1 and 2.2 is inadequate to describe a given state of aggregation, for example when more than one phase or more

Note c: As explained in paragraph 1.4 of the IUPAC Manual (Ref. 1) it is permissible to omit subscript m for *molar* when the text makes it obvious that a molar quantity is meant.

than one chemical species are present. An extended notation is then needed and may require explanation by the author(s) using it. It is impracticable to lay down detailed rules for this purpose, but application of the principles given in paragraph 2.10 of the IUPAC Manual (Ref. 1) should produce a notation that conveys the intended meaning, without loss of information or creation of ambiguity. The following general points are to be noted.

The symbol for the state of equilibrium between phases, whether of a pure substance or a system of more than one component (i.e. the saturated state) is sat, printed in roman type and used either as a subscript or in parentheses.

The symbol for the states occurring at a critical point, whether it involves fluids (e.g. the gas-liquid critical point) or solids (e.g. the superconducting critical point) is c, printed in roman type; c is used as a subscript or superscript to a symbol for a thermodynamic quantity.

The qualitative composition of a mixture or a solvent system is specified by use of chemical formulae or abbreviations placed in parentheses after the symbol to which they refer; the statement can be made quantitative by use of numbers and a statement, abbreviated if desired, specifying mass fraction, mole fraction, volume fraction, molality, or concentration. Extended notation of this sort will require separation of individual symbols by commas or plus signs to make it intelligible -- see the examples below.

Values of temperature and pressure to which the symbol for a thermodynamic quantity refers are specified in parentheses after the symbol.

Examples:

symbols	meaning
$\rho^*(l, sat(g), 410\ K)$	density of a pure liquid in equilibrium with its own vapour at a temperature of 410 K;
$T_c(0.8N_2 + 0.2O_2)$	critical temperature of a mixture of nitrogen and oxygen in which the mole fraction of nitrogen is 0.8. If there is doubt about which phases are under discussion, this should be made clear in the text;
$\underline{\eta}(sln, 0.1\ mol\ kg^{-1}\ of\ NaI$ in acetone, 293.15 K)	viscosity at 293.15 K of a solution of molality 0.1 mol kg^{-1} of sodium iodide in acetone;
$\underline{\lambda}(s, sln, w_{Cu} = 0.9, w_{Ag} = 0.1)$	thermal conductivity of a solid copper + silver solution containing a mass fraction of copper equal to 0.9;

$f(NH_3, g, 500 K, 2 MPa)$ fugacity of gaseous ammonia at a temper-
ature of 500 K and a pressure of 2 MPa.

SECTION 3.   PROCESSES IN THERMODYNAMICS

3.1   Two methods of denoting a process

The word *process* in thermodynamics implies the occurrence of a change in a system,
e.g. a change in the state of aggregation, or a change in the chemical species present.
Thermodynamic change is signified by the operator Δ, written before the symbol for a
property, and the nature of the change is signified by annotation of the Δ. Two methods
of annotation are admissible, (i) use of regular symbols as superscripts and subscripts,
(ii) use of special subscripts to denote the process in question. The two methods are
now described separately.

3.2   Use of regular symbols to denote a process

It is convenient to use the notation $\Delta_\alpha^\beta X$ to indicate *the value of the property X for*
a final condition **b** *less the value of the property X for an initial condition*
a. Hence $\Delta_\alpha^\beta X$ corresponds to the change in X for the process $\underline{\alpha} \to \underline{\beta}$, where $\underline{\alpha}$ and $\underline{\beta}$
are here general symbols for physical states or chemical species. This symbolism tends
to be rather cumbersome for indicating chemical changes, so in practice is most utilized
for changes in the state of aggregation; the regular symbols given in paragraph 2.1 are
employed as superscripts and subscripts to Δ, in the ways exemplified below.

Examples:

symbols	meaning
$\Delta_{cr}^{g} S^\circ = S^\circ(g) - S^\circ(cr)$	the change in (molar) standard entropy (Note c) when a substance changes from the crystalline to the gaseous state, i.e. the standard entropy of sublimation of a crystalline solid;
$\Delta_{l}^{g} U_m^\circ = U_m^\circ(g) - U_m^\circ(l)$	the change in molar standard internal energy when a substance changes from the liquid to the gaseous state, i.e. the standard energy of vaporization (evaporation) of a liquid;
$\Delta_{s}^{l} H^\circ = H^\circ(l) - H^\circ(s)$	the change in (molar) standard enthalpy (Note c) when a substance changes from the solid to the liquid state, i.e. the standard enthalpy of melting (fusion) of a solid.

3.3   Use of special symbols to denote a process

The use of special symbols to denote a process is a more traditional procedure than
that given in paragraph 3.2; for indicating physical changes the traditional method is
disadvantageous in requiring special symbols (twelve of these are recommended below, but

these do not cover all possible situations), whereas for indicating chemical changes it is advantageous.

- the symbol for vaporization (evaporation) of a liquid is vap
- the symbol for sublimation (evaporation) of a solid is sub
- the symbol for melting (fusion) of a solid is fus
- the symbol for transition of one solid phase to another is trs
- the symbol for the mixing of fluids is mix
- the symbol for the process of solution (dissolution) is sol
- the symbol for the dilution of a solution is dil
- the symbol for a chemical reaction in general is r
- the symbol for a combustion reaction (Note d) is c
- the symbol for a process in which an "activated complex" or "transition state" is formed from the reactants (activation) is $\ddagger$
- the symbol for a reaction in which a compound is formed from its elements (formation) is f
- the symbol for a process in which a substance is separated into its constituent gaseous atoms (atomization) is at

All the above symbols should be printed in roman type without full stops (periods).

Four positions for an annotating symbol q are to be found in the literature, namely ΔX_q, $(\Delta X)_q$, $\Delta^q X$, and $\Delta_q X$. The last position is now recommended except that the symbol for activation should be given as a superscript, $\Delta^{\ddagger} X$. Possible confusion between subscript c meaning *critical* and subscript c meaning *combustion* will rarely arise, but if ambiguity exists the author(s) should define c.

Examples:

symbols	meaning
$\Delta_{vap} U_m^\circ = U_m^\circ(g) - U_m^\circ(l)$	the change in molar standard energy due to vaporization of a liquid;
$\Delta_{sub} S_m^\circ = S_m^\circ(g) - S_m^\circ(s)$	the change in molar standard entropy due to sublimation of a solid;
$\Delta_{fus} \underline{\alpha} = \underline{\alpha}(l) - \underline{\alpha}(s)$	the change in coefficient of cubical expansion due to the melting of a solid;
$\Delta_{trs} C_V(\text{cr II} \rightarrow \text{cr III})$ $= C_V(\text{cr III}) - C_V(\text{cr II})$	the change in (molar) constant-volume heat capacity (Note c) due to the transition of crystal form II to crystal form III;
$\Delta_{mix} V_m(313.15 \text{ K}) =$ $[V_m - \Sigma_B x_B V_B^*](313.15 \text{ K})$	the change in volume due to the operation of preparing 1 mole of mixture at a temperature of 313.15 K;

Note d: The text should make clear the form of combustion under discussion; the term is most commonly used to imply complete oxidation of organic substances.

$\Delta_{sol}H_m(B, x_B = 0.1)$ — the change in enthalpy due to the dissolution of 1 mole of solute B in a solvent to form a solution having mole fraction of B equal to 0.1;

$\Delta_{dil}H_m(m_1 \rightarrow m_2)$ — the change in enthalpy per mole of solute for dilution of a solution of molality m_1 in a solvent to a solution of molality m_2 in the same solvent;

$\Delta_r G^\circ(1000 \text{ K})$ — the change in (molar) standard Gibbs energy (Note c) due to a chemical reaction at a temperature of 1000 K;

$\Delta_c H^\circ(\text{n-}C_4H_{10}, \text{ g, } 298.15 \text{ K})$ — the change in (molar) standard enthalpy (Note c) at 298.15 K due to combustion of gaseous butane, i.e. to the reaction $\text{n-}C_4H_{10}(g) + 6.5O_2(g) = 4CO_2(g) + 5H_2O(l)$;

$\Delta_f S^\circ(\text{HgCl}_2, \text{ cr, } 298.15 \text{ K})$ — the change in (molar) standard entropy (Note c) due to the formation of crystalline mercuric chloride from its elements at a temperature of 298.15 K, i.e. to the reaction $Hg(l) + Cl_2(g) = HgCl_2(cr)$;

$\Delta^{\ddagger}H^\circ(298.15 \text{ K})$ — the change in (molar) standard enthalpy (Note c) due to the process of activation at 298.15 K;

$\Delta_{at}H(\text{CH}_4, 298.15 \text{ K})$ — the change in enthalpy due to the process of atomization of CH_4 at 298.15 K, i.e. to the reaction $CH_4(g) = C(g) + 4H(g)$.

SECTION 4. SIGNIFICANCE OF THE WORD *STANDARD* IN CHEMICAL THERMODYNAMICS

4.1 The concept of the standard state

The word *standard* is quoted in paragraph 2.11 of the IUPAC Manual (Ref. 1) (where the alternative symbols $^\circ$ and $^\ominus$ are given for it), but without explanation as to its definition or proper usage. The intention here is to emphasize the proper use of the adjective *standard* as applied to a *thermodynamic quantity* and to the word *state*.

Absolute values of some thermodynamic quantities are unknown. Only changes in values caused by parameters such as temperature and pressure can be determined. It is therefore important to define a base-line for substances, to which the effect of such variations may be referred. The *standard state* is such a base-line.

For a pure substance the concept of standard state applies to the substance in a well-defined state of aggregation at a well-defined but arbitrarily chosen standard pressure.

Historically, the defined pressure for the standard state, i.e., the *standard-state pressure*, has been 1 standard atmosphere (101 325 Pa) and most existing data use this pressure. With the growing use of SI units continued use of the atmosphere is inconvenient and in some countries now illegal. It is recommended that thermodynamic data should be reported for a defined standard-state pressure of 10^5 Pa which is equal to 1 bar. The standard-state pressure in general is symbolized as $p°$. Hitherto $p°$ has customarily been taken as 1 atm. For the future it is recommended that $p°$ should customarily be taken as 10^5 Pa (1 bar). It should be understood that the present recommended change in the standard-state pressure carries no implication for "standard pressures" used in other contexts, e.g. the convention that "normal boiling points" refer to a pressure of 101 325 Pa (1 atm). Instances may occur where it is desirable to adopt yet other values for $p°$ and so all authors must clearly state the value adopted.

The recommendation that the customary value of $p°$ should change from 1 atm (101 325 Pa) to 10^5 Pa will result in small alterations in standard values of some thermodynamic quantities for all substances. For condensed phases the magnitude of these alterations will nearly always be negligible in comparison with the uncertainty of current data. However, the alterations in values of $S°(g)$ for a pure substance and of $\Delta_r G°$ for a reaction involving gaseous species may not be negligible. Thus, one should note that

$$S°(g, p° = 10^5 \text{ Pa}) - S°(g, p° = 101\ 325 \text{ Pa}) = R\ln(101\ 325/10^5)$$

$$\approx 0.11 \text{ J K}^{-1} \text{ mol}^{-1} \quad , \qquad \text{and}$$

$$\Delta_r G°(p° = 10^5 \text{ Pa}) - \Delta_r G°(p° = 101\ 325 \text{ Pa})$$

$$= -RT\{\ln(101\ 325/10^5)\}\Sigma_B \nu_B(g) \quad ,$$

where $\underline{\nu}_B(g)$ is the stoichiometric coefficient of gaseous substance B.

Definitions of the standard states of substances in various states of aggregation are conveniently developed (Ref. 1, 3) from the following defining equation for the chemical potential of a *gaseous substance* B, whose mole fraction in a gaseous mixture is y_B:

$$\mu_B(T, p, y_B) - \mu_B°(T) = RT\ln(y_B p/p°) + \int_0^p (V_B - RT/p)dp \quad .$$

It follows that $\mu_B(T) = \mu_B°(T)$ for the particular case that B is both a pure gas ($y_B = 1$) and an ideal gas ($V_B^{id} = RT/p$) and $p = p°$.

> Hence, 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. [Compare Sections A.I.2, A.I.3, A.I.4, and A.I.5 of Appendix I (Ref. 1).]

> 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 substance at the standard-state pressure.

For application of the concept of standard state to substances in admixture (solutions
and mixtures), the composition of the system, as well as the pressure, must be defined.
As one example for solutions, the standard-state molality, written as m^o for the general
case, is to be defined; customarily m^o is taken as 1 mol kg^{-1}. The following defining
equation for the chemical potential of an undissociated *solute* B, at the standard-
state pressure, is a convenient starting point (Ref. 1, 3) for further discussion of
solutions:

$$\mu_B^o(T) = \{\mu_B - RT\ln(m_B/m^o)\}^\infty + \int_p^{p^o} V_B^\infty dp \quad,$$

where $\mu_B = \mu_B(\text{solute}, T, p, m)$.

> Hence, the customary standard state for a solute B in solution
> is a hypothetical solution, at the standard-state pressure, in
> which $m_B = m^o$, and in which the activity coefficient γ_B has the
> same value (unity) as γ_B^∞. [Compare Sections A.I.11, and A.I.12
> of Appendix I (Ref. 1)].

> The customary standard state for a substance B in a mixture
> is a hypothetical mixture, at the standard-state pressure,
> in which x_B T 1, and in which the activity coefficient f_B
> and the relative activity a_B are unity. [Compare Sections
> A.I.7 and A.I.8 of Appendix I (Ref. 1).]

The above definitions of standard states make no reference to fixed temperature. Hence,
it is possible to have an infinite number of standard states of a substance as the
temperature varies. But generally it is more convenient to complete the definition
of the standard state in a particular context by choosing for the reference temperature
one of a relatively small number of values, e.g., zero, 273.15 K, 293.15 K, 298.15 K.
The most favoured of these, and the one recommended for use is 298.15 K. Because the
quantity "298.15 K" is so frequently used in symbols such as $\Delta_f H^o$(298.15 K) and because
it requires so much space, it is convenient to have a special symbol for this quantity.
Symbols such as T_a, $\mathcal{E}$, T^o etc. are to be found in the literature. Since T^o should mean
a standard temperature in general, the use of T^o to mean exclusively 298.15 K is strongly
discouraged. No recommendation for a special symbol for 298.15 K is made at this time;
any author who prefers to use a special symbol for 298.15 K is urged always to define it.
It must be stressed, however, that there is no reason why another value (say 427.9 K)
should not be adopted for the reference temperature, so long as the author clearly
states what has been done.

4.2   Standard thermodynamic quantities

From defining equations for the standard chemical potential of a substance in a particular
state of aggregation, other standard thermodynamic quantities, such as enthalpy, entropy,
and heat capacity, can be derived by established equations (Ref. 3). Examples of the use
of ^{o} with symbols for a thermodynamic quantity of a substance and for the change in thermo-
dynamic quantity for a process have been given in earlier paragraphs. It is important not
to omit ^{o} when standard-state conditions apply, and not to use ^{o} when standard-state

conditions do not apply, for example when mixed products are formed in a reaction and
no correction for that fact is applied. (Such a correction, when made, is often de-
scribed as a *reduction to standard states*).

Strictly, the above definitions of standard states relate to hypothetical situations,
but there is little difficulty in relating them to the real situations arising in ex-
perimental work, so long as it can be shown that departure from the strict definition
(e.g. use of a slightly impure crystalline solid, or of a non-ideal gas) either causes
a negligible effect on the magnitude in question or can be allowed for, by calculation
of the excess quantity $X^{real} - X^{id}$. Thus in the case of a slightly impure solid it will
be necessary to allow for several effects, as treated in detail for combustion reactions
(Ref. 4).

The use of subscript f was discussed in paragraph 3.3. When ° is additionally used, as
in $\Delta_f H^\circ$, the implication is that both the compound in question and its constituent
elements are in standard states and that the elements, moreover, are in their *reference
states*; for any given temperature the reference states of the elements will normally be
those that are stable at the chosen standard-state pressure and at that temperature
(Note e). A resulting feature of tabulations of $\Delta_f H^\circ$ and $\Delta_f S^\circ$ as functions of temperature
is that discontinuous changes are sometimes to be seen; these correspond to changes in
the stable reference states of the elements, as phase-transition temperatures are passed.
Thus values of $\Delta_f H^\circ(SOBr_2, g)$ would show discontinuous changes at *ca.* 58 °C, 95 °C,
and 119 °C, corresponding to $Br_2(l) \rightarrow Br_2(g)$, $S(cr, I) \rightarrow S(cr, II)$, and $S(cr, II) \rightarrow S(l)$,
respectively, where I refers to rhombic and II to monoclinic crystal forms.

An important standard quantity in the thermodynamics of chemical reactions is the change
in standard Gibbs energy $\Delta_r G^\circ$ due to a chemical reaction, defined by

$$\Delta_r G^\circ = \Sigma_B \underline{\nu}_B \underline{\mu}_B^\circ(z)$$

where $\underline{\nu}_B$ is the stoichiometric coefficient of substance B, and z symbolizes the state
of aggregation in general. From the conditions of chemical reaction equilibrium it
follows that

$$\Delta_r G^\circ = -RT\ln K$$

where K is the thermodynamic equilibrium constant. It should be noted that K is a
dimensionless quantity.

So-called equilibrium constants defined without the use of fugacity coefficients or activity
coefficients are generally not constant over a range of compositions. They are related to
K through proper use of fugacity coefficients or activity coefficients. The thermodynamic
equilibrium constants for reactions in solution often remain imperfectly known for lack of
knowledge of the activity coefficients of the species concerned, and other equilibrium
constants must be used instead. A discussion of these quantities in relation to the practical
problems occurring in biochemistry has been published by the Interunion Commission
on Biothermodynamics (Ref. 5).

Note e: If a metastable form is chosen as the reference state, it is incumbent on the
author(s) to make this clear.

SECTION 5. COMMONLY TABULATED FORMS OF THERMODYNAMIC FUNCTIONS

5.1 Functions related to Gibbs energy

The quantities $- \{G°(T) - H°(0)\}/T$ and $- \{G°(T) - H°(298.15\ K)\}/T$ (or more properly
$- \{G°(T) - H°(0)\}/T - S(\emptyset)$ and $- \{G°(T) - H°(298.15\ K)\}/T - S(\emptyset)$ where $\emptyset$ represents the
state, at $T = 0$, in which the conventional entropy is taken as zero) have become widely
used in tabulations of thermodynamic data for wide temperature ranges. The functions
vary slowly with temperature, permitting easy interpolation and extrapolation, facilitate
the calculation of equilibrium constants as a function of temperature, and are useful in
examining the consistency of thermodynamic data.

Because the algebraic expressions of these quantities are rather long and unwieldy,
various notations for them have been used, e.g. *fef*, *gef*, Φ; and the provisional
text (Ref. 2) of this Appendix proposed one of these (Φ). However, there has recently
appeared a new symbolism (Ref. 6) which bears directly on the choice of an appropriate
symbol for the quantities given above. Unfortunately the timing of the appearance of
the new symbolism was such that full consideration and discussion of it could not be
accomplished without undue delay in publication of this Appendix.

For these reasons no recommendation is made concerning a name or symbol for the quan-
tities discussed above. It is anticipated that recommendation on these matters will
appear in due course.

5.2 Tabular presentation of thermodynamic data in dimensionless form

There are advantages (Ref. 7) in expressing many molar thermodynamic quantities in dimen-
sionless form, by dividing the value by the gas constant R or by RT, as appropriate. Hence
it is recommended that tabulation of values of $C_p°/R$, $S°/R$, $\{H°(T) - H°(0)\}/RT$, etc. should
be considered. In published tables of such quantities the value of R employed should be
stated.

6. REFERENCES

1. *Manual of Symbols and Terminology for Physicochemical Quantities and Units: 1979 edn.*
   pp. 8-15; pp. 37-41 (for Appendix I). Prepared for publication by D.H. Whiffen (1979
   edn.), M.A. Paul (1973 edn.), M.L. McGlashan (1969 edn.). Pergamon Press, Oxford (1979).
2. Appendix IV (Provisional) to *Manual*. Prepared for publication by J.D. Cox. *Pure Appl.
   Chem.* 51, 393-403 (1979).
3. M.L. McGlashan, *Chemical Thermodynamics*, Academic Press, London (1979).
4. M. Månsson and W.N. Hubbard, *Experimental Chemical Thermodynamics*, Volume 1 (S. Sunner
   and M. Månsson, eds.), chapter 5, Pergamon Press, Oxford (1978).
5. *Recommendations for Measurement and Presentation of Biochemical Equilibrium Data.* (Prep-
   ared by the Interunion Commission on Biothermodynamics). *CODATA BULL. 20*, (1976); also
   published in *Q. Rev. Biophys. 9*, 439-456 (1976); *J. Biol. Chem. 251*, 6879-6885 (1976);
   Biochem. Biophys. Acta 461, 1-14 (1976); *Handbook Biochem. Mol. Biol.*, 3rd Ed., *Physical
   and Chemical Data, Vol. 1.*, G.D. Fasman, Editor, CRC Press, Cleveland (1976), pp. 93-106;
   Eur. J. Biochem. 72, 1-7 (1977); *IUPAC Inf. Bull. 61*, 1-17 (1977); *Netsu Sokutei* (Japan)
   4, 172-176 (1977); ibid, *5*, 77-81 (1978); *Biofizika* (USSR) *23*, 739-749 (1978).
6. R.D. Freeman, C.B. Alcock, L. Brewer, S.S. Chang, W.N. Hubbard, C.E. Vanderzee. Report
   of Calorimetry Conf. Committee on Standard States, Symbols, Units, and Nomenclature
   ("COSSSUN Report"). July 1979. *Bull. Chem. Thermodyn. 22*, 475-492 (1979).
7. K.S. Pitzer and L. Brewer, *J. Phys. Chem. Ref. Data 8* (3), 917-919 (1979); *High Temp. Sci.
   11*, 49-54 (1979).