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MANUAL OF SYMBOLS AND TERMINOLOGY FOR PHYSICOCHEMICAL QUANTITIES AND UNITS. APPENDIX IV: NOTATION FOR STATES AND PROCESSES, SIGNIFICANCE OF THE WORD *STANDARD* IN CHEMICAL THERMODYNAMICS, AND REMARKS ON FUNCTIONS USED IN THERMODYNAMIC TABLES

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Comments from the viewpoint of languages other than English are encouraged. These may have
special significance regarding the eventual publication in various countries of translations of
the nomenclature finally approved by IUPAC.

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MANUAL OF SYMBOLS AND TERMINOLOGY FOR PHYSICOCHEMICAL QUANTITIES AND
UNITS - APPENDIX IV.   NOTATION FOR STATES AND PROCESSES, SIGNIFICANCE OF
THE WORD *STANDARD* IN CHEMICAL THERMODYNAMICS, AND REMARKS ON FUNCTIONS
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SECTION 1. INTRODUCTION

The main IUPAC Manual of symbols and terminology for physicochemical quantities and units[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 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*
>   functions used in thermodynamic tables.

The treatment which follows is compatible with that given in the IUPAC Manual[1] and its
Appendix I[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 unnecessary complexity
should be given: whilst symbols should be rigorous, they need not be more complex than the
given context requires. Thus the symbol $f(\text{NH}_3,\ \text{g},\ 500\ \text{K},\ 200\ \text{MPa})$, quoted in paragraph 2.3
as the symbol for the fugacity of gaseous ammonia at a temperature of 500 K and a pressure
of 200 MPa, would be abbreviated to $f(500\ \text{K},\ 200\ \text{MPa})$ 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 standardised 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[1]) should be used, as explained in paragraph 2.3.

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 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 solution (see Appendix I, paragraph A.I.9) is sln; in
> many contexts it will be clear whether a liquid solution or a solid
> solution is meant, but where this is unclear the compounded symbols lsln
> and ssln may be used
>
> 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 footnote 3).

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 gas state;
$\alpha(l)$	cubic expansion coefficient of a liquid;
$KBr(s)$	potassium bromide in the solid state;
$C_V(fl)$	constant-volume heat capacity of a fluid;
$V_m(lc)$	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;
$\phi(vit)$	fluidity of a vitreous substance;
$\rho(ads)$	density of an adsorbed species;
$\beta(sln)$	pressure coefficient of volume of a solution.

Chemical equation

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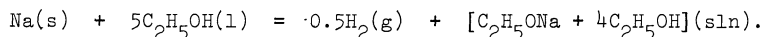
2.2 Use of simple subscripts and superscripts

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[1]), or by use of extended
notation, as described in paragraph 2.3. The significance of the superscript $^\circ$ is
explained in more detail in paragraph 4.1.

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

Examples:

symbols	meaning
$S_m^{\circ}(g)$	standard molar entropy of a gas;
$C_{p,2}^{*}$	(molar) heat capacity[2] at constant pressure of pure species 2;
$\underline{\sigma}_B^{*}(l)$	surface tension of pure liquid B;
H_B^{∞}	partial molar enthalpy of species B in solution at infinite dilution[3];
$\gamma^{id}(g)$	the ratio C_p/C_V for an ideal gas;
$G^{\ddagger}$	Gibbs energy of an activated complex.

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 than one chemical species is 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[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
$\underline{\rho}^{*}(l, sat(g), 410\ K)$	density of a pure liquid in equilibrium with its own vapour at a temperature of 410 K;

symbols	meaning
$T_c(0.8N_2 + 0.2O_2)$	gas—liquid critical temperature (absolute) of a mixture of nitrogen and oxygen in which the mole fraction of nitrogen is 0.8;
$\underline{\eta}$(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;
$\underline{\lambda}$(ssln, w_{Cu} = 0.9, w_{Ag} = 0.1)	thermal conductivity of a solid copper + silver alloy containing a mass fraction, w, of copper equal to 0.9;
$f(NH_3$, g, 500 K, 2 MPa)	fugacity of gaseous ammonia at a temperature 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, as precursor to a 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 imply *the magnitude of the property* X *for a final condition* β *less the magnitude of the property* X *for an initial condition* α. Hence $\Delta_\alpha^\beta X$ corresponds to the change in X for the process $\alpha \rightarrow \beta$, where α and β 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[2] when a substance changes from the crystalline to the gas 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 gas state, i.e. the standard energy of vaporization of a liquid (evaporation);
$\Delta_s^l H^\circ$ $= H^\circ(l) - H^\circ(s)$	the change in (molar) standard enthalpy[2] when a substance changes from the solid to the liquid state, i.e. the standard enthalpy of melting of a solid (fusion).

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 (six of these are recommended below, but these

do not cover all possible situations), whereas for indicating chemical changes it is advantageously neat:

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 a chemical reaction in general is r

the symbol for a combustion reaction[4] is c

the symbol for a reaction in which a compound is formed from its elements
(formation) is f

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 is now recommended. 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
$\Delta_{vap} U_m^{\ominus}$ $= U_m^{\ominus}(g) - U_m^{\ominus}(l)$	the change in molar standard energy due to vaporization of a liquid;
$\Delta_{sub} S_m^{\ominus}$ $= S_m^{\ominus}(g) - S_m^{\ominus}(s)$	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;
$\Delta_{trs} C_V(cr\ II \to cr\ III)$ $= C_V(cr\ III) - C_V(cr\ II)$	the change in (molar) constant-volume heat capacity[2] due to the transition of crystal form II to crystal form III;
$\Delta_{mix} V_m(313.15\ K)$ $= [V_m - \Sigma_B x_B V_B^*]\ (313.15\ K)$	the change in volume due to the operation of preparing unit amount of mixture at a temperature of 313.15 K;
$\Delta_{sol} H_{B,m}(x_B = 0.1)$	the change in enthalpy due to the dissolution of unit amount of solute B in a solvent to form a solution having mole fraction of B equal to 0.1;
$\Delta_r G^{\ominus}(1000\ K)$	the change in (molar) standard Gibbs energy[2] due to a chemical reaction at a temperature of 1000 K;
$\Delta_c H^{\ominus}(n\text{-}C_4H_{10},\ g,\ 298.15\ K)$	the change in (molar) standard enthalpy[2] at 298.15 K due to combustion of n-butane gas, i.e. the reaction $C_4H_{10}(g) + 6.5O_2(g) = 4CO_2(g) + 5H_2O(l)$;
$\Delta_f S^{\ominus}(HgCl_2,\ cr,\ 298.15\ K)$	the change in (molar) standard entropy[2] due to the formation of crystalline mercuric chloride from its elements at a temperature of 298.15 K, i.e. the reaction $Hg(l) + Cl_2(g) = HgCl_2(cr)$.

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[1] (where the alternative
symbols o and ⊖ 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*.

Since the absolute values of some thermodynamic quantities are unknown, but only the change
in the values as, say, temperature and pressure change, it is important to define a base-
line for substances, to which the effect of changes 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 defined pressure, and historically the defined *standard-
state pressure* was 1 standard atmosphere. In view of the obsolescence of the latter unit,
IUPAC has considered whether to recommend a change in the standard-state pressure, but has
concluded that no change should be made, save in the expression to be used, namely
101 325 Pa, rather than 1 standard atmosphere. The standard state pressure in general is
symbolized as p^o, so p^o is customarily taken as 101 325 Pa; instances may occur where
it is desirable to adopt another value for p^o, but authors doing so must clearly state the
value adopted.

Definitions of the standard states of substances in various states of aggregation are best
developed[5] from the following defining equation for the chemical potential of a *gaseous*
substance B, whose mole fraction in a gas mixture is y_B:

$$\mu_B(T, p, y_B) - \mu_B^o(T) \;=\; RT \ln(y_B p/p^o) + \int_0^p (V_B/RT - 1/p)\,dp.$$

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

> Hence, the standard state for a pure gaseous substance is that of the
> substance as a (hypothetical) ideal gas at the standard-state pressure,
> customarily 101 325 Pa.

> Similarly, the standard state for a pure liquid substance is that of
> the pure liquid under the standard-state pressure, customarily 101 325 Pa.

> Also, the standard state for a pure solid substance is that of the pure
> crystalline substance under the standard-state pressure, customarily
> 101 325 Pa.

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. For
solutions, the standard-state molality, written as $\underline{m}^o$ for the general case, is to be
defined; customarily $\underline{m}^o$ is taken as 1 mol kg^{-1}. The following defining equation for the
chemical potential of a *solute* B is the best starting point[5] for further discussion of
solutions:

$$\mu_B^o(T) \;=\; \{\underline{\mu}_B - RT \ln(\underline{m}_B/\underline{m}^o)\}^{\infty} + \int_p^{p^o} V_B^{\infty}\,dp,$$

where $\mu_B = \mu_B$ (solute, T, p, m). It follows that $\mu_B^\infty(T) = \mu_B^O(T)$ for the particular case that $(\underline{m}/\underline{m}^O)^\infty = 1$ and $p = p^O$.

> Hence the standard state for a substance in solution is the hypothetical
> one of an ideal solution (infinitely dilute) of standard-state molality,
> customarily 1 mol kg^{-1}, and at the standard-state pressure, customarily
> 101 325 Pa.

> Similarly the standard state for a substance in a mixture is the
> hypothetical one of an ideal mixture (infinitely dilute) at unit mole
> fraction, and at the standard-state pressure, customarily 101 325 Pa.

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 utilise a relatively small number of *reference temperatures* to complete the definition of the standard state in particular contexts, e.g. zero, 273.15 K, 293.15 K, 298.15 K. The most favoured of these in modern thermodynamics is 298.15 K. Thus one might speak of "a gas in its standard state at the usual reference temperature, meaning the (hypothetical) ideal gas at p^O = 101 325 Pa, and T = 298.15 K. It must be stressed, however, that there is no reason why another reference temperature (say 427.9 K) should not be adopted by a given author in a given context, so long as this is clearly stated.

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, like enthalpy, entropy and heat capacity, can be derived by established equations[5]. Examples of the use of ^{O} with symbols for a thermodynamic quantity of a substance and for the change in thermodynamic 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 described 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 experimental 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 know the activity of the main component; in the case of a real gas it will be necessary to know the equation of state; in the case of a chemical reaction it may be necessary to allow for several effects, as treated in detail for combustion reactions[6].

The use of subscript f was discussed in paragraph 3.3. When ^{O} is additionally used, as in $\Delta_f H^O$, 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*; the reference states of the elements will normally be those that are stable at the chosen

reference temperature[7]. A resulting feature of tabulations of $\Delta_f H^O$ and $\Delta_f S^O$ 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 $\Delta_f H^O(SOBr_2,g)$ would show discontinuous changes at ca. 59 °C, 95 °C and 119 °C, corresponding to $Br_2(l) \to Br_2(g)$, S (cr,I) $\to$ S (cr,II), and S (cr,II) $\to$ 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 standard equilibrium constant K^O, defined by:

$$K^O = \exp(- \textstyle\sum_B \nu_B \mu_B^O(z)/RT) ,$$

where ν_B is the stoichiometric coefficient of substance B and z symbolizes the state of aggregation in general, whence

$$\Delta_r G^O = - RT \ln K^O .$$

It should be noted that K^O as defined above must be a pure number. In this respect it may differ from equilibrium constants differently defined. In gas-phase equilibria, for instance, the "fugacity" equilibrium constant, K_f, which has the dimension of [fugacity]$^{\sum_{B'} \nu_{B'}}$, is only a pure number when $\sum_{B'} \nu_{B'}$ happens to be zero. (Here B' refers to all the species present that are gaseous). In solution chemistry, "concentration" equilibrium constants are much used; a discussion of these quantities in relation to the practical problems occurring in biochemistry has been published by the Interunion Commission on Biothermodynamics[8]. Standard equilibrium constants for reactions in solution often remain unknown for lack of knowledge of the activity coefficients of the species concerned. "Concentration" equilibrium constants measured for very dilute solutions will approximate to standard equilibrium constants in magnitude, though the two quantities may be dimensionally different, for reasons similar to those mentioned above for gas-phase equilibria.

SECTION 5. FUNCTIONS USED IN THERMODYNAMIC TABLES

5.1 Functions related to Gibbs energy

The quantities $- \{G^O(T) - H^O(0)\}/T$ and $- \{G^O(T) - H^O(298.15 \text{ K})\}/T$ have become widely used in tabulations of thermodynamic data for wide temperature ranges, following their introduction by Giauque[9]. 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 of the unwieldy nature of the defining algebraic expression it is convenient to utilize a compact symbol, defined as follows:

$$\Phi = - \{G(T) - H^O(0)\}/T$$

$$\text{and } \Phi' = - \{G(T) - H^O(298.15 \text{ K})\}/T.$$

In the great majority of cases, the corresponding *standard phi functions* will be used:

$$\Phi^O = - \{G^O(T) - H^O(0)\}/T$$

$$\Phi',^{\mathrm{o}} = -\{G^{\mathrm{o}}(T) - H^{\mathrm{o}}(298.15\ \mathrm{K})\}/T.$$

The name recommended for Φ^{o} is the *standard tempered Gibbs energy, relative to zero temperature*, and for $\Phi',^{\mathrm{o}}$ is the *standard tempered Gibbs energy, relative to 298.15 K*. The word *tempered* in the above names is intended to have the exact meaning conveyed by the above algebraic definitions, as well as the normal English-language meaning of *modified*.

5.2 Tabular presentation of thermodynamic data in dimensionless form

Many existing tabulations of thermodynamic quantities as functions of temperature employ the calorie as the energy unit. Whereas the joule will become more widely used as the energy unit, there are advantages in expressing many molar thermodynamic quantities in *dimensionless* form, by dividing the values by the universal gas constant R, in the appropriate unit. Hence it is recommended that values of C_p^{o}/R, S^{o}/R, $\{H(T) - H^{\mathrm{o}}(0)\}/RT$, Φ^{o}/R and $\Phi',^{\mathrm{o}}/R$ should be tabulated. Not only would the calorie—joule controversy be avoided thereby, so also would physicochemical calculations using statistical-mechanical and calorimetric data be facilitated. Numbers obtained by dividing appropriate thermodynamic quantities by R may be called *rational*, e.g. C_p^{o}/R may be called the *rational standard heat capacity at constant pressure*. In derivation of tables, by division by R, the value of R employed should be stated.

Footnotes

1. Manual of symbols and terminology for physicochemical quantities and units. (Edited by M L McGlashan, revised by M A Paul) Pergamon Press, Oxford (1975).

2. As explained in paragraph 1.4 of the IUPAC Manual[1] it is permissible to omit subscript m for *molar* when the text makes it obvious that a molar quantity is meant.

3. Parenthetic addition of sln to the main symbol is unnecessary, as ∞ is used only for solutions.

4. The text should make clear the form of combustion under discussion; the term is most commonly used to imply complete oxidative degradation.

5. M L McGlashan, Chemical Thermodynamics, Volume 1, p.1, The Chemical Society, London (1973).

6. M Månsson and W N Hubbard, Experimental Chemical Thermodynamics, Volume 1, (S Sunner and M Månsson, eds.), chapter 5, Pergamon Press, Oxford (1978).

7. If a metastable form is chosen as the reference state, it is encumbent on the author(s) to make this clear.

8. CODATA Bulletin No. 20 (1976).

9. W F Giauque, J. Amer. Chem. Soc. 52, 4808 (1930).