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Standards in biothermodynamics [☆], [☆] [☆]



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Abstract

The field of biothermodynamics encompasses physical property measurements on biochemical and biological systems. This chapter reviews the status of standards documents that are pertinent to biothermodynamics as well as recommendations that have been made for the reporting of experimental results. The importance of standards in nomenclature, symbols, units, and uncertainties is discussed and a summary of sources of data for biochemical substances and reactions is given. © 2014 The Authors. Published by Elsevier GmbH. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/3.0/>).

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Introduction

Thermodynamic measurements on biochemical and biological systems are of fundamental scientific importance. Since the aim of these measurements is to obtain reliable values of physical properties, it is important for workers in this area to be aware of documents that provide guidance for the performance of these measurements and for the reporting of results. When documents of this sort carry the imprimatur of a well-known scientific or standards organization, these documents serve as *de facto* standards for this community of researchers. It is the aim of this chapter to summarize briefly the status of the standards documents that are pertinent to biothermodynamics as well as recommendations that have been made for the reporting of experimental results. In its broadest sense, the field of biothermodynamics encompasses all physical property measurements on biochemical and biological systems. However, since equilibrium and calorimetric measurements have been of primary interest in this field, properties that fall into these two categories have received the most attention in the literature and in the standards documents.

Nomenclature, symbols, units, and uncertainties

The effective communication of scientific information is enhanced by the use of a standard set of nomenclature, symbols, and units. For example, it would be difficult and confusing to read a publication in which the symbol S was used for equilibrium constant and the symbol K was used for entropy or if the symbol Z was used for pH. The problem would be compounded if the aforementioned properties were referred to by names that are not commonly used. Additionally, while several historical units such as British Thermal Units, pounds, and miles have their place, they have generally been replaced in the scientific literature and in most countries by the International System of units (SI) ([Bureau International des Poids et Mesures, 2006](#)).¹ Just as writers should rely on a dictionary, thesaurus, and style guide, researchers should rely upon a “language of science” ([Mills, 1997](#)) for effective communication. The need for standards in scientific communication has grown even more pressing as values of physical properties, i.e. data, are now being incorporated in large-scale efforts such as the Brenda ([Schomburg et al., 2000](#)) and Sabio-RK ([Wittig et al., 2012](#)) databases. Additionally, the entries in these databases are often used for calculations of other properties and for further applications which impact progress in science, health, and the economy. Thus, standards are needed in essentially all areas of science.

¹The thermochemical calorie, which is defined by the relation $1 \text{ cal} = 4.184 \text{ J}$ ([Cohen et al., 2007](#)), is a unit that still persists in the literature. The reasons for this are its long history and the fact that some scientific software uses the calorie rather than the joule. However, most calorimeters are calibrated by means of electrical energy, which implicitly has units of joules. Then, if one chooses to use calories, one must change the result of the calibration, already done in terms of joules, to calories. Thus one must perform an extra computational step in order to use a unit that has been obsolete for many years.

The most useful and definitive source of information on nomenclature for quantities, symbols, and units pertinent to physical chemistry is *Quantities, Units and Symbols in Physical Chemistry* ([Cohen et al., 2007](#)). This publication, which was prepared under the auspices of the Union of Pure and Applied Chemistry (IUPAC), traces its origin to the *Manual of Symbols and Terminology for Physicochemical Quantities and Units*, which was prepared in 1970. There have been several editions published between the 1970 Manual ([McGlashan, 1970](#)) and the most recent edition of *Quantities, Units and Symbols in Physical Chemistry* ([Cohen et al., 2007](#)). Since all of these editions have been published with a green cover, the publication is often referred to as the *Green Book*. The current edition of the *Green Book* ([Cohen et al., 2007](#)) is broad in scope and covers a wide variety of topics such as mechanics (classical and quantum), electricity and magnetism, spectroscopy, electromagnetic radiation, general chemistry, thermodynamics, kinetics, and transport properties.

Of fundamental importance to science and to the system of units are the concept of measurement and the use of quantity calculus. The system of SI units is based on seven base quantities: length, mass, time, electric current, thermodynamic temperature, amount of substance, and luminous intensity. All other physical quantities are derived from these base quantities. Physical quantities are represented as the product of a number and a unit and they follow the rules of mathematics. Thus, if the concentration of a solute is $c = 0.0010 \text{ mol dm}^{-3}$, one can write $c/(\text{mol dm}^{-3}) = 0.0010$ or $10^3 c/(\text{mol dm}^{-3}) = 1.0$. In the last two representations, the right side of the equation is a number. This emphasizes the fact that the result of an experiment is a ratio of the measured quantity to the value of some standard quantity, which, in this case is 1.0 mol dm^{-3} . In some usage, one sees $c (\text{mol dm}^{-3}) = 0.001$. However, it is formally incorrect. While there is little chance of confusion in this case, confusion arises often in regards to powers of 10 in table headings. For example, using the previously used value of c , if one were to write $10^{-3}c = 1.0$, one formally has $c = 1000 \text{ mol dm}^{-3}$. The author has seen this type of confusion many times in the literature and it is not always easy to determine the intent of the author(s) of the publication.

Clearly, the result of a measurement is significantly enhanced by a statement of its reliability or uncertainty. The uncertainty can be evaluated by the use of statistical methods and by a consideration of the possible systematic errors that might be associated with the measurement(s). Guidance on the estimation of uncertainties can be found in the *Guide to the expression of uncertainty in measurement* (1995) and in *Guidelines for evaluating and expressing the uncertainty of NIST measurement results* ([Taylor and Kuyatt, 1994](#)). When assigning uncertainties to measurement results in a publication, it is critical to also give the basis for these uncertainties.

Standards documents in biothermodynamics

Several standards documents that are specifically intended for the field of biothermodynamics have been published. Included in these documents are discussions of the fine points of experiments such as useful test reactions as well as guidance and recommendations regarding nomenclature,

symbols, and the reporting of results. Specific topics that have been covered are: isothermal titration calorimetry (ITC) (Schwarz et al., 2008), differential scanning calorimetry (Hinze and Schwarz, 2001), isothermal microcalorimetry and solution calorimetry (Wadsö and Goldberg, 2001), and cellular systems (Belaich et al., 1982). Additionally, general recommendations regarding terminology, symbols, and units in biothermodynamics have been dealt with in several publications dating back to 1976 (Alberty et al., 1994; Alberty et al., 2011; Wadsö, 1985; Wadsö et al., 1976). The most recent publication by Alberty et al. (2011) contains a thorough discussion of most of the quantities commonly dealt with in biothermodynamics and, as done by its predecessors in the series, gives recommendations regarding terminology, symbols, and units. Particular attention is given in this document to the apparent equilibrium constant K' , the calorimetrically determined enthalpy of reaction $\Delta_r H(\text{cal})$, the standard transformed Gibbs energy of reaction $\Delta_r G'^{\circ}$, the standard transformed enthalpy of reaction $\Delta_r H'^{\circ}$, changes in binding of a ligand $\Delta_r N(X)$, and the standard apparent electrode potential of a cell E'° - quantities that are of primary importance in biothermodynamics.

Recommendations for reporting experimental results

Recommendations for Terminology and Databases for Biochemical Thermodynamics (Alberty et al., 2011) also gives explicit recommendations for the reporting of experimental results in biothermodynamics. These recommendations are important and provide useful guidance to researchers in this field. The recommendations follow. "The usefulness and lasting value of an experimental investigation are made possible and enhanced by a careful reporting of the results of the investigation. In this regard, there are several matters that require attention:

- The identity of the principal substances used in the investigation must be stated. This can be accomplished by use of standard (e.g. IUPAC) and commonly accepted names, CAS registry numbers, and by presenting the structures of the reactants and products. The last method is, by far, the most definitive method and avoids making the reader check the literature to obtain the structure(s). A combination of these methods is recommended. If substances have chiral centers, attention to which chiral forms are present is also required. If enzymes are used in a study they should be identified by EC numbers (Enzyme Nomenclature, 2013) and origin (e.g., species, tissue).
- The estimated purities of the materials and the methods of analysis used in the study should be reported.
- A description of the apparatus and procedures used in the investigation should be given.
- A clear reporting of the actual numerical values of the properties measured in the study is essential. While graphical presentation is very useful to illustrate a point, it is essential that the actual results be presented in numerical form. This saves the reader the difficulty and possible errors associated with having to extract numerical values from a graph.
- The reaction under investigation and its stoichiometry must be specified. For binding studies, one must state the basis for the assumed binding stoichiometry. If CO_2 , N_2 , NH_3 , or other possible gaseous substances are involved in a reaction, it should be specified if their state in the reaction pertains to the gas phase or to the solution phase. If a reactant is bound to a surface or on a membrane, this should be clearly specified.
- A chemical reaction involves specific chemical (often ionic) species. It must balance both atoms and charges. A biochemical reaction involves sums of species and should not show charged species (Alberty et al., 1994). Also, a biochemical reaction does not indicate that hydrogen atoms or magnesium atoms are conserved. However, C, N, O, and P, etc. are conserved. Thus, chemical and biochemical reactions have distinctly different physical and chemical bases. Therefore, they must not be confused. Nor should they be intermingled or combined. As stated in the 1994 Recommendations (Alberty et al., 1994), one must be able to distinguish between these two types of reactions on sight.
- The equilibrium constant or apparent equilibrium constant must be clearly defined. This sometimes requires care in how one deals with water as a reactant. For reactions in aqueous media, the usual convention is to take the activity (or concentration) of water equal to unity. However, this is not the case for reactions carried out in non-aqueous media such as organic solvents. In this case, one must know the concentration of water in order to have a thermodynamically meaningful equilibrium constant as distinct from a ratio of concentrations for some of the reactants.
- When reporting the value of an equilibrium constant, particularly for an unsymmetrical reaction, one should specify the units of concentration used to calculate the equilibrium constant. It is recommended that the standard state either be 1 mol L^{-1} or 1 mol kg^{-1} . There must be no ambiguity in the direction of the reaction to which the equilibrium constant pertains.
- Concentration, units of mol L^{-1} , is an accepted measure of the amount of a substance in a given volume of solution and molality (mol kg^{-1}) is appropriate for the amount in a given mass of solvent. Molality is little used in biochemistry, but it has the advantage that its value does not change with temperature and it is easily calculated from laboratory determinations of mass.
- It is essential that both the actual reaction and the conditions of measurement be specified. The conditions of measurement include, but are not limited to, the temperature, the pressure, pH, and the concentrations of the substances in solution. These quantities are measured directly. Other important quantities are pMg and ionic strength. However, these are not measured directly and must be calculated. To perform these calculations, one needs information on the total concentrations of the reactants in the solution as well as the dissociation constants for all of the pertinent weak acids and magnesium complex ions. One also must make some assumption(s) about the activity coefficients used in these calculations. It is recommended that the experimental quantities, i.e. the temperature, the pressure, pH, and the concentrations of the substances in solution, be fully reported. If possible, one should also calculate the pMg and the ionic strength and report these values. A somewhat more extensive calculation can be performed that will lead to values of the equilibrium

constant K and the standard molar enthalpy change $\Delta_r H^\circ$ for a chemical reference reaction that corresponds to the (overall) biochemical reaction. If possible, it is also recommended that this calculation of K and $\Delta_r H^\circ$ be performed. The choice of the chemical reference reaction is arbitrary. The method of calculation should be described and any auxiliary data used in these calculations should be included in the publication.

- For the study of biochemical reactions under 'near physiological conditions,' the following set of conditions have been widely used as a *de facto* standard: $T=310.15$ K, $pH=7.0$, $pMg=3.0$, and $I=0.25$ mol L⁻¹. It is recognized that there is no unique set of physiological conditions and that for many purposes it will be necessary and desirable to study biochemical reactions under different sets of conditions. For example, specific recommendations have been agreed to for the study of enzymes of yeast (Van Eunen et al., 2010).
- For calorimetric measurements, it is important to measure the extent of reaction.
- For equilibrium measurements, it is important to establish that the reaction under investigation has reached equilibrium. Product inhibition and a loss of enzyme activity are common phenomena that can lead to large systematic errors.
- The result of a measurement is also enhanced by a statement of its reliability or uncertainty. The uncertainty can be evaluated by the use of statistical methods and by a consideration of the possible systematic errors that might be associated with the measurement. Guidance on the estimation of uncertainties can be found in the [Guide to the Expression of Uncertainty in Measurement \(1995\)](#).
- IUPAC has published a *Guide to the Procedures for the Publication of Thermodynamic Data* (Kolesov et al., 1972) and CODATA has published a [Guide for the presentation in the primary literature of numerical data derived from experiments \(1974\)](#). Both of these "Guides" provide useful information on the reporting of physical property data."

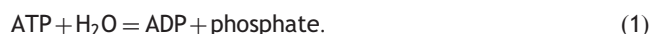
The importance of reporting essential information and results was emphasized in the IUPAC Recommendations published in 1972 by Kolesov et al., 1972: "The highly interdependent nature of thermodynamic data imposes special obligations upon the author of papers reporting the results of thermodynamic investigations. He must give enough information about his experiment to allow readers to appraise the precision and accuracy of his results so that they may be properly consolidated within the existing body of data in the literature. Further, as accepted values of physical constants change or as new thermodynamic data for related systems become available, subsequent investigators often can recalculate results if it is clear that they are based on good experiments for which adequate information is presented, however old they may be. For these reasons, an author's prime responsibility is to report his results in a form related as closely to experimentally observed quantities as is practical, with enough experimental details and auxiliary information to characterize the results adequately and to allow critical assessment of the accuracy claimed. For the convenience of the reader, the author may interpret and correlate the primary results as appropriate and present derived results in a form easy to utilize. However, such

derived (or secondary) results never should be published at the cost of omitting the primary results on which they are based. Reference may be made to accessible earlier publications for some details".

It is appreciated that a complete and unambiguous description may not be possible for complex biological systems. Nevertheless, it is essential that a "best" effort be made in such cases. Also, it is expected that as science advances, standards, nomenclature, and the symbols used will also evolve. However, a carefully done experiment will continue to be of lasting value provided that it has been properly documented.

The apparent equilibrium constant

As mentioned above, it is critical to distinguish between the apparent equilibrium constant which pertains to overall biochemical reactions and the (standard) equilibrium constant which pertains to chemical reactions. The basis of this difference arises from the fact that, for overall biochemical reactions, thermodynamic quantities are, in general, functions of temperature T , pH, pX, and ionic strength I . Here, $pX = -\log_{10}[X]$, where $[X]$ is the concentration of a species X , typically an ion, that binds to one or more of the reactants. This dependency on pH and pX arises because of the multiple states of ionization and metal ion binding in which the reactant molecules can exist. This point is illustrated by means of a generic reaction - the hydrolysis of adenosine 5'-triphosphate (ATP) to adenosine 5'-diphosphate (ADP) and phosphate (all reactions discussed in this chapter pertain to aqueous media),



The apparent equilibrium constant K' for this reaction is

$$K' = [\text{ADP}][\text{phosphate}]/[\text{ATP}]. \quad (2)$$

By convention the concentration of water has been omitted in the expression for K' . The concentrations used in Eq. (2) are *total* concentrations of the various ionic and metal bound forms of the reactants and products. For example

$$[\text{ATP}] = [\text{ATP}^{4-}] + [\text{HATP}^{3-}] + [\text{H}_2\text{ATP}^{2-}] + [\text{H}_3\text{ATP}^{-}] \\ + [\text{MgATP}^{2-}] + [\text{MgHATP}^{-}] + [\text{MgH}_2\text{ATP}] + [\text{Mg}_2\text{ATP}], \quad (3)$$

$$[\text{ADP}] = [\text{ADP}^{3-}] + [\text{HADP}^{2-}] + [\text{H}_2\text{ADP}^{-}] + [\text{MgADP}^{-}] + [\text{MgHADP}], \quad (4)$$

$$[\text{phosphate}] = [\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^{-}] + [\text{H}_3\text{PO}_4] \quad (5)$$

If calcium or other metal ions are present, one must also consider additional, analogous species such as CaATP^{2-} . The essential point is that, because biochemical reactants such as ATP, ADP, and phosphate exist in several different ionic and metal bound forms, there is a multiplicity of species that make up each of these reactants. This, in turn, leads to the aforementioned dependencies of thermodynamic quantities on pH and pX. Illustrations of these dependencies are shown in [Figure 1](#). These surface plots were calculated

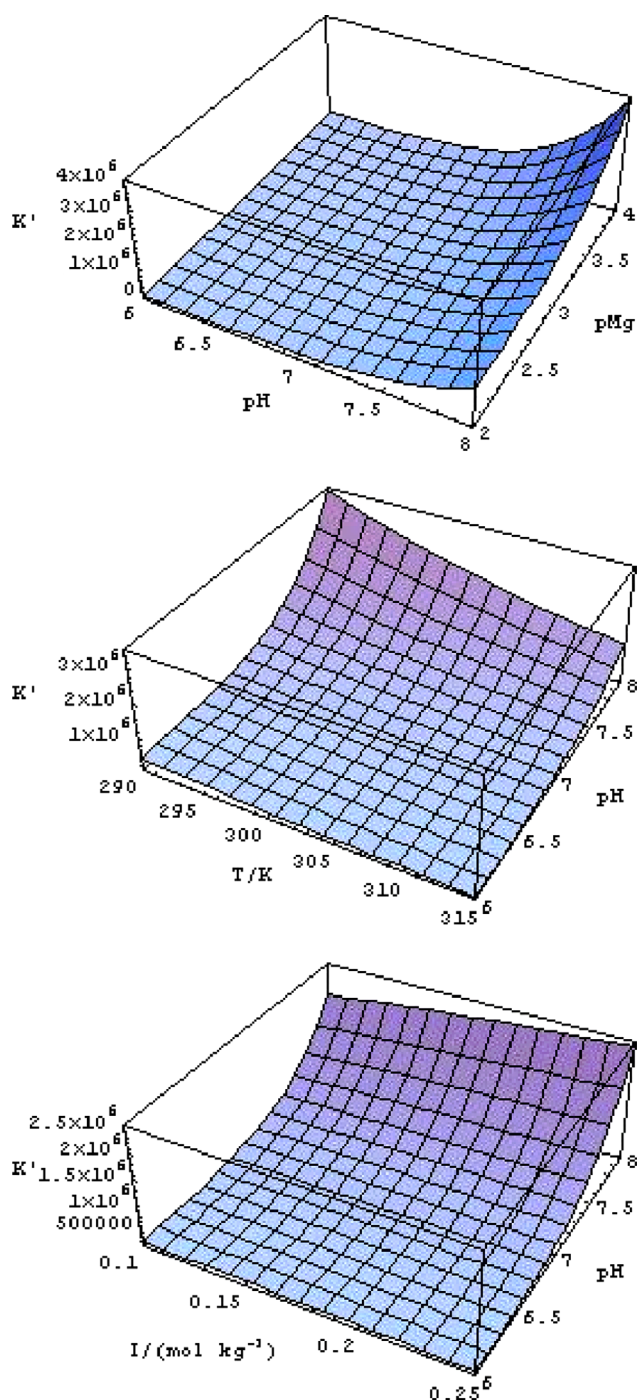
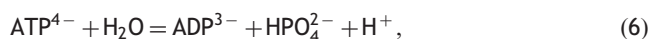
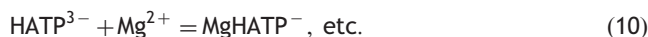


Figure 1 The apparent equilibrium constant K' for the hydrolysis reaction ($\text{ATP} + \text{H}_2\text{O} = \text{ADP} + \text{phosphate}$) as a function of temperature T , pH, pMg, and ionic strength I . Since it is not possible to represent a five dimensional surface in two dimensions, three 3-D projections with appropriate constraints are shown. These constraints are: $T=298.15 \text{ K}$ and $I=0.25 \text{ mol dm}^{-3}$ (A); $I=0.25 \text{ mol dm}^{-3}$ and $\text{pMg}=3.0$ (B); and $T=298.15 \text{ K}$ and $\text{pMg}=3.0$ (C).

by using the equilibrium constant for the chemical reference reaction



and equilibrium constants for the pertinent H^+ and Mg^{2+} binding constants:



It is important to recognize that the equilibrium constants K for reactions (6)-(10) pertain to specific chemical species. Clearly, these chemical reactions *must* balance both the number of atoms and the charges. While equilibrium constants K depend on temperature and ionic strength they do not depend on pH or pX as do apparent equilibrium constants K' . Thus, it is important to maintain a clear distinction between K and K' (Alberty et al., 2011). The book *Thermodynamics of Biochemical Reactions* (Alberty, 2003) contains a definitive treatment of transformed thermodynamic properties and many examples involving biochemical reactions.

Standards for data transfer

In 2002 IUPAC established a project to create standardized mechanisms for thermodynamic data communications using XML (Extensible Markup Language) technology. The aim is to enhance efficient information transfer all the way from measurement to publication to data-management systems and to scientific and engineering applications. In addition to numerical data, the related metadata must also be incorporated into the data structure. ThermoML covers a wide variety of properties (≈ 125) and deals with pure chemical compounds, multicomponent mixtures, and chemical reactions. Biochemical substances and reactions are explicitly covered in ThermoML (Chirico et al., 2010). The intent is that the developed dictionary and corresponding XML schema will become an internationally accepted standard for thermodynamic data storage and exchange (Frenkel et al., 2011).

Sources of data for biochemical substances and reactions

Thermodynamics provides a formal structure or *framework* by which one can calculate values for many properties of substances and reactions. However, to be made useful, this framework must be filled with values of properties that can be obtained either by direct measurement or which can be calculated from other measured property values by means of thermodynamic relations. A recent publication (Goldberg, 2009) contains a brief description of how thermodynamic networks can be used to calculate values of standard molar Gibbs energies of formation $\Delta_f G^\circ$, standard molar enthalpies of formation $\Delta_f H^\circ$, and standard molar entropies S° . Once one has a table of these property values, one can calculate values of equilibrium constants K and standard molar enthalpies of reaction $\Delta_r H^\circ$ for any reaction in which the appropriate values of the properties of the reactants and products are listed in the table. It is important to appreciate that serious errors can result if values of standard formation properties from different tables are combined to calculate property values for a given reaction.

Table 1 Sources of thermodynamic data for biochemical substances and reactions.^a

Publication	Content
Krebs et al. (1957)	Values of $\Delta_f G^\circ$ for ~130 biochemical species; values of $\Delta_r G'^\circ$ and E'° for ~100 biochemical reactions
Wilhoit (1969)	Values of $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , and C_p° for ~246 biochemical species
Domalski (1972)	Values of $\Delta_c H^\circ$ and $\Delta_f H^\circ$ for 719 organic compounds
Thauer et al. (1977)	Values of $\Delta_f G^\circ$ for ~165 biochemical species. Many of the values of $\Delta_f G^\circ$ were taken from other tables
Pedley et al. (1986)	Extensive tabulation and evaluation of values of $\Delta_c H^\circ$ and $\Delta_f H^\circ$ for organic compounds
Goldberg and Tewari (1989)	Values of $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , and C_p° for carbohydrates (pentoses and hexoses) and their monophosphates
Miller and Smith-Magowan (1990)	Values of $\Delta_f G^\circ$ for compounds in the Kreb's cycle
Goldberg et al. (1993, 2004, 2007), Goldberg and Tewari (1994a, 1994b, 1995a, 1995b), Goldberg (1999)	Extensive tabulations of values of K' and $\Delta_r H(\text{cal})$ for enzyme-catalyzed reactions
Caffrey (1993)	LIPIDAT is a database of thermodynamic (T_{trs} and $\Delta_{trs}H$) and associated information on lipid mesophase and crystal polymorphic transitions
Domalski and Hearing (1996)	Extensive tabulations and evaluation of values of S° , and C_p° for organic compounds
Pettit and Powell (2000)	Extensive tabulation of values of pK and $\Delta_r H^\circ$ for proton ionization and metal ligand binding reactions
Ould-Moulaye et al. (2001, 2002)	Values of $\Delta_f G^\circ$, $\Delta_f H^\circ$, S° , and C_p° for purines, pyrimidines, nucleosides, nucleotides, and nucleotide phosphates
Goldberg et al. (2002)	Evaluated values of pK , $\Delta_r G^\circ$, $\Delta_r H^\circ$, $\Delta_r S^\circ$, and $\Delta_r C_p^\circ$ for biochemical buffers
Martell et al. (2003)	Extensive tabulation of values of pK and $\Delta_r H^\circ$ for proton ionization and metal ligand binding reactions

Table 1 (continued)

Publication	Content
Alberty (2006, 2007)	Values of $\Delta_f G^\circ$ and $\Delta_f H^\circ$ for ~199 biochemical species
Li et al. (2010)	Values of $\Delta_f G^\circ$ and $\Delta_r G^\circ$ pertinent to glycolysis and to the tricarboxylic acid cycle

^aThe symbols used in this table are [Cohen et al., 2007; Alberty et al., 2011]: C_p° , the standard molar heat capacity; $\Delta_r C_p$, the standard molar heat capacity change for a reaction; E'° , the standard apparent electrode potential of a cell; $\Delta_f G^\circ$, the standard Gibbs energy of formation of a substance at specified temperature T , pressure P , and ionic strength I ; $\Delta_r G'^\circ$, the standard transformed Gibbs energy of formation of a reactant at specified T , P , pH , pMg and I ; $\Delta_r G^\circ$, the standard molar Gibbs free energy of a reaction; $\Delta_r G'^\circ$, the transformed Gibbs energy of a biochemical reaction at specified T , P , pH , pMg , and I ; $\Delta_c H^\circ$, the standard molar enthalpy of combustion; $\Delta_f H^\circ$, the standard enthalpy of formation of a substance; $\Delta_r H^\circ$, the standard molar enthalpy of a reaction; $\Delta_r H(\text{cal})$, the calorimetrically determined enthalpy of reaction that includes the enthalpies of reaction of H^+ and Mg^{2+} (consumed or produced) with any buffer in solution; $\Delta_{trs}H$, the molar enthalpy change associated with a transition; K , the equilibrium constant; K' , the apparent equilibrium constant; pK , $-\log_{10}K$; $\Delta_r S^\circ$, the standard molar entropy change for a reaction; S° , the standard molar entropy; and T_{trs} , the temperature of a transition.

Also, pertinent to the construction of such tables are values of associated properties such as standard molar enthalpies of combustion $\Delta_c H^\circ$, standard molar entropies S° , standard molar heat capacities C_p° , solubilities s , and standard molar enthalpies of solution $\Delta_{sol}H^\circ$. Table 1 provides references to several tables of standard formation properties that are relevant to biochemical substances and reactions and to several other sources that contain tabulations of the aforementioned properties. However, if the desired property values are not found in these sources, one must either search for the desired property values in the literature or determine if the desired values can be calculated by using thermodynamic relations. In the absence of any directly measured values or values that can be obtained by means of a thermodynamic calculation, one can turn to estimation methods (Goldberg, 2009) to obtain possibly the desired property value(s).

Conflict of interest statement

The author has no conflict of interest.

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