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Determination of Gibbs energies of formation in aqueous solution using chemical engineering tools

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HIGHLIGHTS

- The standard Gibbs energy of formation is important in metabolism studies.
- This study enables to reduce the confusion encountered when looking for missing data.
- The differences between pure compound and infinite dilution properties were clarified.
- We provide the thermodynamic relations used to convert these properties consistently.
- Quantum based tools and thermodynamic tables enable to complete existing databanks.

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ABSTRACT

Standard Gibbs energies of formation are of primary importance in the field of biothermodynamics. In the absence of any directly measured values, thermodynamic calculations are required to determine the missing data. For several biochemical species, this study shows that the knowledge of the standard Gibbs energy of formation of the pure compounds (in the gaseous, solid or liquid states) enables to determine the corresponding standard Gibbs energies of formation in aqueous solutions. To do so, using chemical engineering tools (thermodynamic tables and a model enabling to predict activity coefficients, solvation Gibbs energies and pK_a data), it becomes possible to determine the partial chemical potential of neutral and charged components in real metabolic conditions, even in concentrated mixtures.

1. Introduction

For building developmental models of living organisms, it is necessary to describe physical constraints, physiological reactions, their interactions and their responses to the environment. A robust modeling of any living system (microbial metabolism up any evolved living complex organism) must include chemical elements conservation principles, via stoichiometric approaches, and link this mass balance approach to energy conservation laws, *i.e.* to the first principle of thermodynamics and to the constraints imposed by the second law. Most of biochemical transduction processes involves a near-equilibrium reaction which can be assessed with a multi-linear thermodynamic approach. Intuitively, a complete modeling has lots of sub-models since it takes into accounts the compartmentalized structure of organisms and must include metabolic description of the different parts as function of the developmental stages. Here the approach aims at developing a global overview energy metabolism, *i.e.* the total of all reactions that occur in cells (McCarty and Johnson, 2002; Cogne et al., 2011). To do so, physical property measurements are performed on biochemical and biological systems. Among these properties, the transformed Gibbs energy of reaction $\Delta_r G'^{\circ}$ (at a given temperature, pressure, pH and ionic strength I) which permits the evaluation of thermodynamic equilibrium proximity, is of primary importance (Goldberg, 2014). It is common for biologists and biochemists to calculate apparent equilibrium constants (K') of biochemical reactions and/or transformed reduction potentials (E'°) even by performing measurements or from the knowledge of the standard transformed Gibbs energies of formation ($\Delta_f G_i'^{\circ}$) of the different biochemical species involved in such a reaction

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Nomenclature

E°	standard electrode potential of a cell (in V)
E'°	standard transformed electrode potential of a cell (in V)
$\mathcal{F}$	Faraday constant (96,485 C mol^{-1})
I	ionic strength (in mol L^{-1} or M)
i, j	species numbers
K'	apparent reaction equilibrium constant
K	reaction equilibrium constant
M_{H_2O}	molar mass of the water molecule (in kg mol^{-1})
$m^*_{i,sat}$	solubility of the solid i (in mol kg^{-1})
m_{is}	molality of the solution (in mol kg^{-1})
n	number of electrons (involved in the redox reaction)
N_H	number of hydrogen atoms in a given molecule
p	pressure (in Pa), in reference conditions $p = p_r = 10^5$ Pa
pK_a	dissociation constant
P^0_i	vapor pressure of the component i (in Pa)
R	the gas constant (8.31 J mol^{-1} K^{-1})
T	temperature (in K), in reference conditions $T = T_r =$ 298.15 K
$v^{0,liq}_i$	molar volume of the liquid (in m^3 mol^{-1})
x_i	mole fraction of the species i
z_i	charge of the species i
ε	dielectric constant
∞	infinity
$\Delta_r G^\circ$	standard Gibbs energy of reaction (in kJ mol^{-1})
$\Delta_r G'^\circ$	standard transformed Gibbs energy of reaction (in kJ mol^{-1})
$\Delta_f G^\circ_i$	standard Gibbs energy of formation at infinite dilution in water in the molality scale (in kJ mol^{-1})
$\Delta_f G'^\circ_i$	standard transformed Gibbs energy of formation in the molality scale (in kJ mol^{-1})
ΔG^{solv}_i	solvation Gibbs energy of the species i (in kJ mol^{-1})
$\mu^{0,gas}_i$	standard Gibbs energy of formation of the pure gas in the mole fraction scale (in kJ mol^{-1})
$\mu^{0,liq}_i$	standard Gibbs energy of formation of the pure liquid in the mole fraction scale (in kJ mol^{-1})
$\mu^{0,solid}_i$	standard Gibbs energy of formation of the pure solid in the mole fraction scale (in kJ mol^{-1})
$\mu^{0,pure}_i$	standard Gibbs energy of formation of the pure compound in the mole fraction scale (in kJ mol^{-1})
$\mu^{0,\infty}_i$	standard Gibbs energy of formation at infinite dilution in water in the mole fraction scale (in kJ mol^{-1})
μ^L_i	chemical potential of the species i in the liquid mixture (in kJ mol^{-1})
μ^r_i	chemical potential of the species i in reference condition (in kJ mol^{-1})
μ^*_i	pseudo-chemical potential of the species i (in kJ mol^{-1})
γ^∞_i	infinite dilution activity coefficient of the species i
γ_i	activity coefficient of the species i

Superscripts

cal	calculated property
exp	experimental property
lit	literature data

$$\begin{cases} K' = \exp\left(\frac{-\Delta_r G'^o}{RT}\right) = \exp\left(\frac{-\sum \nu'_i \Delta_f G'^o_i}{RT}\right) \\ E'^\circ = \frac{-1}{n\mathcal{F}} \sum \nu'_i \Delta_f G'^o_i \end{cases} \tag{1}$$

The $\Delta_f G'^\circ_i(\mathrm{pH},I)$ value of a species (i) is usually given in physiological conditions at pH 7, in reference conditions (T_r = 298.15 K and $p_r = 10^5$ Pa) at infinite dilution in water, in the molality scale. In particular, Alberty (1998) demonstrated that $\Delta_f G'^\circ_i(\mathrm{pH},I)$ can be calculated using the following relation:

$$\Delta_f G'^\circ_i(\mathrm{pH},I) = \Delta_f G^\circ_i + (N_H RT \ln 10)\mathrm{pH} - RT\left(\frac{2.91482\, I^{1/2}}{1 + 1.6 I^{1/2}}\right) z_i^2 \tag{2}$$

where z_i and N_H are respectively the charge of the species (i) and the number of hydrogen atoms in it, while $\Delta_f G^\circ_i = \Delta_f G^\circ_i(\mathrm{pH} = 0, I = 0)$ denotes the standard Gibbs energy of formation in reference conditions (T_r = 298.15 K and $p_r = 10^5$ Pa) at infinite dilution in water, in the molality scale (Alberty, 1998).

Thus, it becomes mandatory to determine all the $\Delta_f G'^\circ_i$ values involved in the studied metabolism in order to determine their corresponding values in real metabolic conditions using Eq. (2).

In this context, the pioneer works of Thauer et al. (1977) and Alberty (1998, 2003) provide a good databank in this regards. In these works, from the measurement of the $\Delta_r G'^\circ$ of a reaction involving species (j) with known $\Delta_f G'^\circ_j$ values except the last remaining molecule (i) for which the $\Delta_f G'^\circ_i$ value is then calculated and added to the table so that these methods are also classified as reactant contributions (RC) methods (Noor et al., 2013).

Goldberg (2014) has reviewed several other sources of thermodynamic data for biological substances and reactions. For molecules which are not included in these sources, one must either search if the desired property values can be found in the literature or calculated by using thermodynamic relations.

In this context, chemical engineers generally performs thermochemistry calculations from the knowledge of the standard Gibbs energy of formation ($\mu^{0,pure}_i$ also denoted as $\Delta_f G^\circ_i$ by several authors) of the pure compound (which can be gaseous, liquid or solid), in the mole fraction scale. These data are summarized in many thermodynamic tables and databanks (Reid et al., 1977; Lide and Frederikse, 2002; Rowley et al., 2009). However these data are not explicitly related to their corresponding values at infinite dilution in water so that biochemical and thermodynamic tables of $\Delta_f G^\circ_i$ data can be considered as apparently inconsistent with each other and people who are looking for a missing standard transformed Gibbs energy of formation $\Delta_f G'^\circ_i$ data can perform an inappropriate choice of the available literature data.

The primary purpose of this study is to avoid such confusions by clarifying the differences between the chosen reference states and demonstrating that by using the appropriate tools (thermodynamic models and relations), it is possible to consistently conciliate both kinds of Gibbs energy of formation data, meanwhile the performance of the existing tools in chemical engineering can be extended to the investigation of the calculation of standard transformed formation properties, and vice versa.

Furthermore, in the absence of any directly measured values or values that can be obtained by means of thermodynamic calculations, estimation methods are good alternatives to determine the missing $\Delta_f G^\circ_i$ data (Goldberg, 2014).

Group contribution (GC) methods were relatively successful in the estimation of the thermodynamic properties in the gas phase and in a less extend in the liquid and solid states (Benson, 1968; Goldberg, 2014 and references therein). Later, several group contribution methods have been developed to directly provide

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