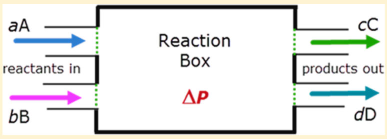
JOURNAL OF CHEMICAL EDUCATION
Communication
pubs.acs.org/jchemeduc

# Correct Use of Helmholtz and Gibbs Function Differences, Δ*A* and Δ*G*: The van't Hoff Reaction Box

Leslie Glasser*

Nanochemistry Research Institute, Department of Chemistry, Curtin University, GPO Box U1987, Perth, Western Australia 6845, Australia

**ABSTRACT:** Helmholtz and Gibbs function (or energy) differences, $\Delta A$ and $\Delta G$, are often invoked by their signs to describe conditions of spontaneity, nonspontaneity, and equilibrium in chemical reactions. While their differences are necessary conditions to establish these behaviors, they are insufficient because they do not apply to local situations where differential values, $dA$ and $dG$, are appropriate. We here show that the differences are fully meaningful quantities, being important in examining overall reaction, such as in chemical synthesis, where $dA$ and $dG$ may be irrelevant. Interpretation of the differences is readily understood in terms of the van't Hoff reaction box in which reactants are converted to products, without reference to kinetics or mechanisms, and products are extracted as independent materials, each under their own specified conditions. This behavior can be attained in practical situations where a product can be extracted in a phase separate from the reactants, such as a single gas, an immiscible liquid, a precipitate, a new pure solid phase, or even in an electrochemical or fuel cell. This is illustrated in the case of the Haber–Bosch industrial process for the production of ammonia.



**KEYWORDS:** *Second-Year Undergraduate, Upper-Division Undergraduate, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics, Reactions, Equilibrium, Synthesis*

## ■ INTRODUCTION

In important contributions to the *Journal* over recent times, a number of authors[1] have discussed the common but incorrect usage of differences of the Helmholtz ($A$) and Gibbs ($G$) functions (or energies[2]) in supposed "predictions" of the spontaneity of chemical reactions in closed systems and of their conditions for equilibrium. In essence, these incorrect procedures use *integral* differences, $\Delta A$ and $\Delta G$, corresponding to *ranges* of states, to make incorrect predictions about *local* state situations which rather require *differential* values, $dA$ and $dG$. However, these publications have left in question the correct and valuable use of the integral values in thermodynamic application, and it is the purpose of the present communication to demonstrate such correct applications.

To place this discussion in context, we first note the following. In a process within a closed system in which no pressure–volume work is performed, at fixed temperature and fixed volume, $dA_{T,V} \leq 0$ are the necessary and sufficient conditions for a spontaneous process under the specified local conditions and at equilibrium, respectively. Similarly, at fixed temperature and fixed pressure, $dG_{T,p} \leq 0$ are the necessary and sufficient conditions for a spontaneous process under the specified local conditions and at equilibrium, respectively. On the other hand, the integral expressions $\Delta A_{T,V} \leq 0$ and $\Delta G_{T,p} \leq 0$ provide no information concerning questions of spontaneity or equilibrium at specific local points (see Figure 1). Similarly, the reverse integral conditions, $\Delta A_{T,V} \geq 0$ or $\Delta G_{T,p} \geq 0$, tell nothing of the nonspontaneity or equilibrium of the local situation. When $\Delta A_{T,V} < 0$ or $\Delta G_{T,p} < 0$, the process can be harnessed to produce useful work, as in an operating electrochemical cell, with the maximum useful work being obtained when the process is performed in a quasi-equilibrium sequence.

## ■ CORRECT USE OF THE INTEGRAL TERMS

In the following discussion, we examine the correct use of the integral terms. We focus on the Gibbs function alone for convenience, but the issues discussed apply equally well to the Helmholtz function. The extensive quantity $\Delta G$ refers to a general process causing a change in Gibbs function, while $\Delta_r G$ refers to change in a balanced chemical reaction, which must be specified for calculation.

The equilibrium constant, $K_a$, in terms of dimensionless activities $a_k$, is expressed in the form

$$\Delta_r\mu^\circ = \sum_k \nu_k\mu_k^\circ = -RT \ln K_a \qquad (1)$$

with the chemical potential (the partial molar Gibbs function) defined by $\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,p,n_j}$.

$\Delta_r\mu^\circ$ is the difference of standard chemical potentials of the reaction components, each in their *standard reference states* (at 1 bar pressure), weighted by their stoichiometric coefficients for a specified reaction. The activity may be replaced by dimensionless ideal gas pressure $(p/p^\circ)$, fugacity $(f/f^\circ)$, mole fraction $(x/x^\circ)$, or concentration $(c/c^\circ)$, to generate equilibrium constants $K_{p/p^\circ}$, $K_{f/f^\circ}$, $K_{x/x^\circ}$, or $K_{c/c^\circ}$ as most

**Received:** November 17, 2015
**Revised:** February 18, 2016

DOI: 10.1021/acs.jchemed.5b00925

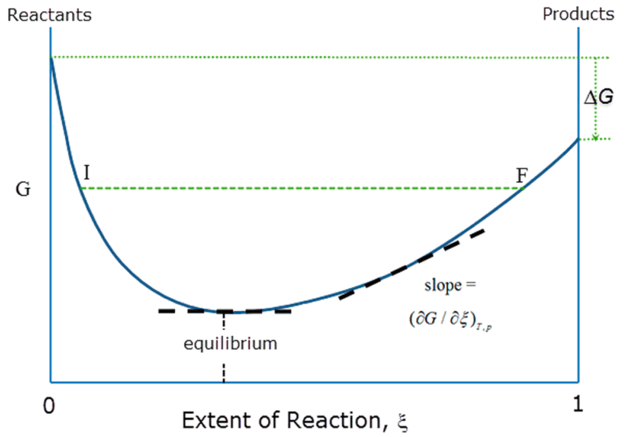


**Figure 1.** Gibbs function, $G$ (an extensive quantity), plotted as a function of the extent of reaction (or degree of advancement), $\xi$, for a reaction at constant temperature, $T$, and pressure, $p$, from Reactants to Products. For example, $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$ has the extensive property change $\Delta_r G \equiv \Delta G = (c\Delta_f G_C + d\Delta_f G_D) - (a\Delta_f G_A + b\Delta_f G_B)$, with $d\xi = -dn_A/a = -dn_B/b = dn_C/c = dn_D/d$, where $n_A$, $n_B$, $n_C$, $n_D$ = number of moles and $a$, $b$, $c$, $d$ = stoichiometric coefficient of component A, B, C, D, respectively, in the reaction equation. The equilibrium condition occurs at the minimum of the Gibbs function, where $(\partial G/\partial \xi)_{T,p} = 0$. This diagram is also invoked in nonequilibrium thermodynamics, where the instantaneous slope relates to the reaction rate.[3] The process I → F depicted involves no change in $G$ but is not at equilibrium; the products simply have the same value of Gibbs function as do the reactants.

appropriate. It should be noted that the right-hand $RT$ term in eq 1 is intensive, with units of energy per mole, so that $\Delta_r \mu°$ is necessarily also intensive.

To establish values for $\Delta_r \mu°$, we note that the chemical potential of a pure material $k$ is simply the Gibbs function per mole, so that

$$\mu_k = \frac{G_k}{n_k} \Rightarrow \frac{\Delta_f G_k}{n_k} \tag{2}$$

where the difference, $\Delta_f G_k$, reflects the fact that the formation Gibbs function is defined relative to the constituent chemical elements of $k$, each in their standard reference states at the temperature of concern.

We note that, when $K_a = 1$, $\Delta_r \mu° = 0$. Similarly, when $K_a > 1$, $\Delta_r \mu° < 0$, while when $K_a < 1$, $\Delta_r \mu° > 0$. How are we to understand these thermodynamic relations when they apply to an overall process? An appropriate way to conceptually model a thermodynamic process is through use of a van't Hoff reaction box (Figure 2).[4] In such a box, reactants are allowed to enter in their defined states through semipermeable membranes and leave, also in their defined states, through other semipermable membranes. We do not enquire what occurs within the reaction box, or the speed of reaction, but note that the reaction box simply provides a mechanism for a change in state, and the thermodynamics of a change in state is independent of the detailed mechanism. For example, $\Delta G = 0$ simply means that the sum of the Gibbs energies of reactants entering the box is equal to the sum of the Gibbs energies of the products leaving the box, without enquiring as to how the Gibbs energies alter at intermediate steps in the process.

It may be thought that the reaction box is simply a convenient conceptual fiction since no real ideal semipermeable membranes can exist; however, it can be closely approached in systems where a product can be extracted in a phase separate from the reactants, such as a single gas developing from a condensed reacting system in an open vessel, an immiscible liquid from a fluid system, formation of a pure solid product such as a precipitate, or even in an electrochemical cell. (A working fuel cell provides an example of such a process in a stationary state, with reactants being continuously introduced and products continuously removed.[6]) Since newly formed phases are continuously removed in their production from such reacting mixtures, the reaction can go essentially to completion, as in the Haber–Bosch industrial process for the production of ammonia discussed below.

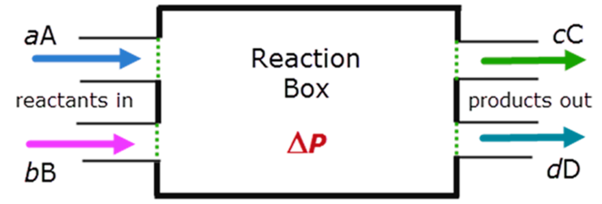


**Figure 2.** A van't Hoff reaction box.[5] Reactants enter through semipermeable membranes independently and under their separate conditions, and products are removed independently through semipermeable membranes and under their separate conditions. We do not enquire into the processes inside the box. $\Delta P$ represents the change in the value of a state function, such as enthalpy, entropy, or Gibbs function, in the reaction.

Even if a pure phase cannot readily be extracted, $\Delta G$ for a real chemical system still has a real meaning, and is of particular significance in synthetic chemistry,[7] when one wishes to establish in advance whether a proposed reaction is thermodynamically suitable for preparing adequate proportions of product: that is, if $\Delta G_{T,p} < 0$. If this condition does not apply, then it is purposeless to attempt the synthesis under the conditions specified, and other conditions need to be selected (such as coupling[8] the desired reaction with one which has $\Delta G_{T,p} < 0$ overall), but note that, if $\Delta G_{T,p}$ has a small positive value (say less than ~20 kJ mol$^{-1}$), then reaction can still proceed to some extent to produce a possibly useful proportion of products. In this way, thermodynamics avoids pointless exercises in preparation, and guides the researcher in more feasible directions.

## THE HABER–BOSCH INDUSTRIAL PROCESS AS A van't HOFF REACTION BOX

The Haber–Bosch industrial process for the manufacture of ammonia from nitrogen and hydrogen gases proceeds by mixing the reactant gases, pressurizing them to about 200 atm, and passing them over an iron-based catalyst at temperatures of about 450 °C. The high temperature increases the rate of reaction but reduces the equilibrium constant of this exothermic process, while the high pressure favors production of ammonia, according to Le Chatelier's Principle (since reaction reduces the number of gas molecules). Under these conditions, with an equilibrium constant, $K$, of about $5 \times 10^{-5}$ and rapid gas flow, only about 15% of the possible ammonia is produced; this is continuously extracted by cooling and the residual gases are recycled. Thus, overall we observe an example of a van't Hoff reaction box, with reactant gases entering and product gas removed.

The Gibbs function change at 450 °C may be calculated according to eq 1, as follows:[9]

$$\begin{aligned}\Delta_r G^\circ/\mathrm{kJ\ mol^{-1}} &= 2\Delta_f G^\circ(\mathrm{NH_3, g}) - \Delta_f G^\circ(\mathrm{N_2, g}) - 3\Delta_f G^\circ(\mathrm{H_2, g}) \\ &= 2(-193.9) - (-144.9) - 3(-100.7) = 59.3\end{aligned}$$

Of course, this large positive value represents only a single step in the overall process. A final cooling process is required to separate ammonia by its liquefaction. For the overall reaction at 25 °C, $\Delta_r G^\circ = -32.8$ kJ mol$^{-1}$, and $K = 5.6 \times 10^5$. Condensation of gaseous ammonia to liquid will further reduce $\Delta_r G^\circ$ and increase $K$.

## AUTHOR INFORMATION

### Corresponding Author

*E-mail: l.glasser@curtin.edu.au.

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

I acknowledge the valuable contributions of my three anonymous reviewers who have corrected my errors and enhanced this presentation.

## REFERENCES

(1) (a) Quílez, J. First-Year University Chemistry Textbooks' Misrepresentation of Gibbs Energy. *J. Chem. Educ.* **2012**, *89* (1), 87−93. (b) Gislason, E. A.; Craig, N. C. Criteria for Spontaneous Processes Derived from the Global Point of View. *J. Chem. Educ.* **2013**, *90* (5), 584−590. (c) Raff, L. M. Spontaneity and Equilibrium: Why "ΔG < 0 Denotes a Spontaneous Process" and "ΔG = 0 Means the System Is at Equilibrium" Are Incorrect. *J. Chem. Educ.* **2014**, *91* (3), 386−395. (d) Raff, L. M. Spontaneity and Equilibrium II: Multireaction Systems. *J. Chem. Educ.* **2014**, *91* (6), 839−847. (e) Raff, L. M. Spontaneity and Equilibrium III: A History of Misinformation. *J. Chem. Educ.* **2014**, *91* (12), 2128−2136. (f) Borge, J. Reviewing Some Crucial Concepts of Gibbs Energy in Chemical Equilibrium Using a Computer-Assisted, Guided-Problem-Solving Approach. *J. Chem. Educ.* **2015**, *92* (2), 296−304.

(2) Cohen, E. R.; Cvitaš, T.; Frey, J. G.; Holmström, B.; Kuchitsu, K.; Marquardt, R.; Mills, I.; Pavese, F.; Quack, M.; Stohner, J.; Strauss, H. L.; Takami, M.; Thor, A. J. *Quantities, Units and Symbols in Physical Chemistry—The IUPAC Green Book*, 3rd ed.; IUPAC: RSC Publishing: Cambridge, U.K., 2007.

(3) Glasser, L. The nonequilibrium thermodynamics of chemical processes. *J. Chem. Educ.* **1965**, *42* (11), 597−600.

(4) (a) Bazhin, N. M.; Parmon, V. N. Conversion of Chemical Reaction Energy into Useful Work in the Van't Hoff Equilibrium Box. *J. Chem. Educ.* **2007**, *84* (6), 1053−1055. (b) Bazhin, N. M. Mechanism of Electric Energy Production in Galvanic and Concentration Cells. *J. Eng. Thermophys.* **2011**, *20* (3), 302−307. (c) Íñiguez, J. Work Degrading and the Reversible to Irreversible Transition in Chemical Reactions. *Int. J. Chem.* **2014**, *6* (3), 1−13. (d) Fermi, E. *Thermodynamics*: Dover (reprint): Minneola, NY, 1956.

(5) van't Hoff, J. H. Die Rolle des osmotischen Druckes in der Analogie zwischen Lösungen und Gasen. *Z. Physik. Chem.* **1887**, *1*, 481−493.

(6) Pilatowsky, I.; Romero, R. J.; Isaza, C. A.; Gamboa, S. A.; Sebastian, P. J.; Rivera, W. *Cogeneration Fuel Cell-Sorption Air Conditioning Systems*; Springer Verlag: London, 2011; (Chapter 2: Thermodynamics of Fuel Cells).

(7) Glasser, L.; Jenkins, H. D. B. Predictive thermodynamics for condensed phases. *Chem. Soc. Rev.* **2005**, *34* (10), 866−874.

(8) IUPAC, Chemical Induction (Coupling). http://goldbook.iupac.org/C01025.html (accessed Jan 2016).

(9) Outotec HSC Chemistry 8. http://www.outotec.com/en/Products--services/HSC-Chemistry/ (accessed Feb 2016).

DOI: 10.1021/acs.jchemed.5b00925
*J. Chem. Educ.* XXXX, XXX, XXX−XXX