The Gibbs Function Versus Degree of Advancement

The Gibbs valley

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Introductory physical chemistry texts occasionally discuss the thermodynamics of chemical reactions with reference to a graph of the Gibbs function, $G$, of a reacting system versus the degree of advancement, $\xi$ (1–4). As the system approaches equilibrium from either side, the decrease of $G$ which at constant temperature and pressure indicates spontaneity is clearly shown graphically and can be related to the “ballin-a-bowl” analogy of objects seeking minimum gravitational potential. $G$ versus $\xi$ graphs also illustrate the distinctions between $G$, $\Delta G$, and $(\partial G/\partial \xi)$, concepts often obscure to beginning students of physical chemistry.

Most textbook treatments we have seen discuss $G$ as a function of $\xi$ for a specific reaction type, for example gas phase isomerization (1), or simply show the general concave graph with little attempt to relate this to a specific reaction type or to actual chemical data. (One exception we have found is reference (5) where the dissociation of nitrogen tetroxide is treated in detail including a $G$ versus $\xi$ graph.) Our purpose here is to present a completely general expression for $G$ as a function of $\xi$ and to apply this to a few specific chemical reactions.

Consider the general chemical reaction

$$p_{R_1}R_1 + p_{R_2}R_2 + \cdots = p_{P_1}P_1 + p_{P_2}P_2 + \cdots$$

where $R_i$ and $P_j$ are reactant and product species, respectively, and $p_{R_i}$ and $p_{P_j}$ are the stoichiometric coefficients. The Gibbs function, $G$, for any mixture of these species is given by

$$G = \sum n_i \mu_i$$  \hspace{1cm} (1)

where $n_i$ is the moles of species $i$ and $\mu_i$ its chemical potential.

$$\mu_i = \mu_i^0 + RT \ln \xi_i$$  \hspace{1cm} (2)

If initially one has only reactants in stoichiometric amounts, the amounts of all species present during the reaction are

$$n_{R_i} = n_{R_i}(1 - \xi) \quad \text{and} \quad n_{P_j} = n_{P_j}\xi$$  \hspace{1cm} (3)

Substituting eqns. 2 and 3 into eqn. 1 and using the expression for the standard Gibbs function change below,

$$\Delta G^0 = \sum p_{R_i} \mu_{R_i}^0 - \sum p_{P_j} \mu_{P_j}^0$$

give the general expression for $G$ as a function of $\xi$.

$$G = \sum p_{R_i} \mu_{R_i}^0 + [\Delta G^0 + RT(1 - \xi) \sum n_{R_i} \ln \xi_i + \xi \sum n_{P_j} \ln \xi_j]$$  \hspace{1cm} (4)

For a specific reaction the chemical potentials of reactants in standard states, $\mu_{R_i}^0$, the standard Gibbs function change, $\Delta G^0$, and expressions for the activities of all species as functions of $\xi$ are needed. We have chosen three reactions below which under normal conditions are “equilibrium” reactions in the sense that the equilibrium position is far enough removed from pure reactants and products to show the minimum in $G$ when plotted versus $\xi$ at constant temperature and pressure. We have termed such graphs Gibbs valley graphs.

Isomerization of Butane

Stoichiometrically the simplest type of chemical reaction is an isomerization, $A \rightleftharpoons B$, which has been treated in the general case for ideal gases at 1 atm (1, 6). Assuming ideal gas behavior, one has

$$a_i = \rho_i/\rho^0 \quad \rho^0 = 1 \text{ atm (standard state)}$$  \hspace{1cm} (5)

$$p_i = \sum X_i p = \text{partial pressures} \quad p = \text{total pressure}$$  \hspace{1cm} (6)

$$X_i = \text{mole fractions} \quad N = \text{total moles}$$  \hspace{1cm} (7)

For one mole of butane ($N = 1$), these relations with eqns. (3) and (4) give for this reaction type,

$$G = \mu_k^0 + [\Delta G^0 + RT(1 - \xi) \ln(1 - \xi) + \xi \ln \xi] + RT \ln(p/p^0)$$  \hspace{1cm} (8)

The Gibbs valley graph of this function for the $n$-butane (A), isobutane (B) isomerization at 298 K and 1 atm is in Figure 1 (top). The chemical potential of $n$-butane, $\mu_k^0$, is taken as $\Delta G^0(298)$ for $n$-butane. This defines the reference state, i.e., $G = 0$, as the pure standard state (1 atm) elements of butane at 298 K. The $\Delta G^0$ for the isomerization can be calculated from the data in the table. The first and last terms of eqn. (8) are independent and the second linear with respect to $\xi$; thus, it is the third term which results in the concave shape of the

Figure 1. (top) The Gibbs valley graph of $G$ versus $\xi$ for butane isomerization at 298 K and 1 atm. The reference state for $G$, i.e., $G = 0$, is the pure standard state elements of butane. (bottom) $\partial G/\partial \xi_{298}$ versus $\xi$. The equilibrium position ($\xi_{eq} = 0.714$) is shown by the dotted line.

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The reaction at the stoichiometric limit is easy to visualize. Complex than the "dirigible" path, it is the mixing, given in the general case for ideal solutions by,

$$\Delta G_{mix} = NRT \sum X_i \ln X_i$$  \hspace{1cm} (9)

The valley (minimum) in $G$ versus $\xi$ graphs is due to mixing of reacting species, a physical process, rather than from purely chemical effects which, in the absence of mixing, would lead to total conversion to the isomer of lowest chemical potential ($1, 4, 5$).

The expression for the slope of the curve in Figure 1 (top) is obtained by differentiating eqn. (8) with respect to $\xi$.

$$\frac{dG}{d\xi} |_{T,P} = \Delta G^0 + RT \ln \frac{\xi}{(1 - \xi)}$$  \hspace{1cm} (10)

This is plotted in Figure 1 (bottom) for the butane isomerization. The curve approaches the edges of the graph asymptotically. From eqns. (3) and (6) it can be shown that $\Delta G^0/(1 - \xi)$ is equal to $p_{B}/p_A$, and as has been well discussed ($6, 7, eqn. (10)$ is equivalent to a common textbook expression,

$$\Delta G = \Delta G^0 + RT \ln Q$$  \hspace{1cm} (11)

where in this case $Q$, the pressure quotient, is $p_B/p_A$. Thus $\Delta G/\xi |_{T,P}$ and the $AG$ of eqn. 11 refer to the same physical quantity. Although we agree with Bent's (7) suggestion that this quantity is best viewed as a rate, i.e., a derivative, rather than a difference implied by the "A" symbol, the significance of eqn. (11) need not be obscure to students if in addition to the initial and final states, an easily visualized path between them is described. This is simply a pedagogical aid, not a thermodynamic necessity, as $\Delta G$ is path independent. One approach is to consider the isomerization of one mole of $n$-butane in a system sufficiently large (a dirigible full of an isomer mixture, for example) that the initial partial pressures of both isomers are insensitive to the relatively small reacting amount and remain constant throughout. $2$ Viewed as the derivative, $\Delta G/\xi |_{T,P}$ one need not imagine a large system since the infinitesimal change implied by the derivative has a vanishing effect on the partial pressures. A derivative is unambiguous, in contrast to $\Delta G$; no initial or final states need definition, nor is any path implied.

At equilibrium $G$ will be a minimum and $\Delta G/\xi |_{T,P}$ will be zero. Both the equilibrium constant, $K_p$, which is equal to $Q_{eq}$, and $\xi_{eq}$ can be obtained in the standard manner from eqn. (10). The equilibrium position is shown by the dotted line in Figure 1. For a measurable reaction rate, higher temperatures and catalysts are required, thus under the conditions of Figure 1 the equilibrium is not reached in practice.

The Equilibration of BF$_3$ and BC1$_3$

Mixtures of boron trifluoride and boron trichloride equilibrate relatively quickly (~30 min) at ambient temperatures (8).

$$BF_3(g) + BC1_3(g) \rightleftharpoons BF_2Cl(g) + BFCl_2(g)$$  \hspace{1cm} (12)

If one mole each of $BF_3$ and $BC1_3$ is initially present, one has from eqns. 3-7,

$$G = \mu_{BF_3} + \mu_{BC1_3} + \xi \Delta G^0 + 2RT \ln \frac{(1 - \xi)}{(1 + \xi)} + \ln p_{BF_3} \text{ and } \ln p_{BC1_3}.$$  \hspace{1cm} (13)

The equilibrium constant at room temperature has been measured (8) from which $\Delta G^0$ is obtained. The chemical potentials of $BF_3$ and $BC1_3$ were taken as the $\Delta G^0$ for each reactant (see table). The Gibbs valley graph from this data at 298 K and 1 atm using eqn. (12) is shown in Figure 2. The first three terms in eqn. (12) represent the $G$ dependence on the reaction species in their standard (1 atm) and unmixed state. The last (pressure dependent) term corrects for conditions other than standard state. The fourth term is $\Delta G_{mix}$ (eqn. (9)), which, unlike the isomerization, does not vanish at $\xi$ equals 0 and 1 since at each extreme more than one species is present and their mixing occurs.

The expression for the slope of Figure 2 is obtained by differentiation.

$$\frac{dG}{d\xi} |_{T,P} = \Delta G^0 + 2RT \ln \frac{\xi}{(1 - \xi)}$$  \hspace{1cm} (14)

This is equivalent to eqn. (11) with $Q = \xi/(1 - \xi)$, the equilibrium position can be obtained by equating eqn. (13) to zero and solving for $\xi_{eq}$.

Synthesis of Ammonia

The formation of ammonia from its elements is a common textbook example of chemical equilibrium as well as an important industrial process (Haber process) for ammonia production.

$$1/2 N_2(g) + 3/2 H_2(g) \rightleftharpoons NH_3(g)$$  \hspace{1cm} (15)

At 298 K and 1 atm an equilibrium mixture originating from either pure ammonia or a 3:1 hydrogen-nitrogen mixture is about 97% ammonia, although it is not achieved in practice because of unfavorable kinetics. High pressures (200-400 atm) and temperatures (600-800 K), as well as catalysts are used industrially; however, quantitative thermodynamic treatment under such extreme conditions is complicated by the need for (1) standard Gibbs function data at temperatures above 298 K and (2) fugacity coefficients of all species in a wide variety of reaction mixtures.

If one initially has stoichiometric amounts of reactants, eqns. (3)-7 $(N = 2 - \xi)$ give

$$G = \frac{1}{2} \mu N_2 + \frac{3}{2} \mu H_2 + \xi \Delta G^0 + 2RT \ln \frac{\theta}{(1 - \xi)} + \ln p_{N_2} \text{ and } \ln p_{H_2}.$$  \hspace{1cm} (16)

The fourth term is $\Delta G_{mix}$ which vanishes only at $\xi = 1$ since only one product species is formed. The Gibbs valley graph at 298 K and 1 atm is in Figure 3. The chemical potentials of reactants were taken as zero, $\Delta G^0$ as that of formation for ammonia (see table). The expression for the slope in Figure 3 can be obtained either by differentiating eqn. (14) or by expressing the pressure quotient, $Q$ (eqn. (11)) as a function of $\xi$ using eqns. (3), (6), and (7).

$$\frac{dG}{d\xi} |_{T,P} = \Delta G^0 + 2RT \ln \frac{(2 - \xi)}{(2 + \xi)}$$  \hspace{1cm} (17)

The Haber process uses high pressure which favors ammonia yield and high temperature which increases reaction rate but decreases ammonia yield. For temperatures above 298 K the Gibbs-Helmholtz equation

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2 Another easily visualized path consistent with eqn. (11) is the "reaction box" path in reference (6), p. 578. Although slightly more complex than the "dirigible" path, it is a reversible path simply stopping the reaction at the stoichiometric limit is easy to visualize.

3 This assumes ideal gas behavior. If fugacities are used in eqn. (5) becomes $a_i = \gamma_i p/p_i$ and an additional term involving fugacity coefficients, $\gamma_i$, appears.
The Gibbs valley graph for ammonia synthesis at 298 K and 1 atm. The reference state for G is the pure standard state reactants, nitrogen and hydrogen. The equilibrium position, ξ_{eq}, is at 0.97.

\[ \left( \frac{\partial G}{\partial T} \right)_p = \frac{-H(T)}{T^2} \]

and Kirchoff's law

\[ H(T) = H(T') + \int_{T'}^T C_p(T') dT \]

can be used to calculate \( \mu_{N_2}^0, \mu_{H_2}^0, \mu_{NH_3}^0 \), and \( \Delta G^0 \). If heat capacities are available in the form

\[ C_p = a + bT + cT^{-2} \]

the above considerations lead to the following expression for the standard chemical potential of each pure species as a function of temperature and heat capacity constants (\( T' = 298 \) K).

\[ \mu^0(T) = \mu^0(T') + \left[ \frac{H^0(T') - aT' - \frac{bT'^2}{2} + e}{T'} \left[ \frac{1}{T^2} - \frac{1}{T'}^2 \right] - aT' \ln(T/T') + \frac{cT'}{2} \frac{1}{T^2} - \frac{1}{T'} \right] \frac{bT'}{2} (T - T') \]  

(15)

For nitrogen and hydrogen, \( H^0(T') \) was taken as zero, for ammonia, \( \Delta H^0 \) (see table) was used. Heat capacity constants were taken from reference (3), p. 108. From eqns. (14) and (15) Gibbs valley graphs were obtained for reacting mixtures at 1 atm over a temperature range (300–500 K). These graphs are combined in a computer drawn perspective in Figure 4. The effect of temperature on the equilibrium yield of ammonia is shown by the reduced equilibrium position, \( \xi_{eq} \), as temperature increases. The shape of the surface in Figure 4 is determined by the partial derivatives of G with respect to \( \xi \) and with respect to temperature. The former has been discussed, the latter is given by the following,

\[ \left( \frac{\partial G}{\partial T} \right)_{P, \xi} = -S \]

The expression for this derivative can be obtained from eqn. (14) and gives the entropy, S, of the reacting system referenced, as is G, to stoichiometric amounts of pure reactants in standard state at 298 K. The relatively large positive slope, \( \left( \frac{\partial G}{\partial T} \right)_{P, \xi} \), around \( \xi = 1 \) in Figure 4 results primarily from the lower (thus negative) entropy of ammonia as compared to stoichiometric amounts of hydrogen and nitrogen. At the left side of Figure 4 (around \( \xi = 0 \)) the slope is less steep and

| \( \Delta G^0 (298) \) | \( n-C_6H_{14} \) | -15.71 kJ |
| \( \Delta G^0 (298) \) | \( iso-C_6H_{14} \) | -17.98 kJ |
| \( \Delta G^0 (301) \) | BF_3 + BCls \rightarrow BF_2Cl + BFCl \ | 1.59 |
| \( \Delta G^0 (298) \) | BF_2Cl \ | -1093.3 kJ |
| \( \Delta G^0 (298) \) | BCls \ | -360.3 kJ |
| \( \Delta G^0 (298) \) | NH_3 \ | -16.63 kJ |
| \( \Delta G^0 (298) \) | NH_3Cl \ | -48.11 kJ |

Selected Thermodynamic Data

Figure 4. Gibbs valley graphs (G versus ξ) for ammonia synthesis at 1 atm and a 300-500 K range. The equilibrium position, \( \xi_{eq} \), varies from 0.97 to 0.17. A Calcomp 563 plotting computer was used.

Figure 5. Gibbs valley graphs (G versus ξ) for ammonia synthesis at 500 K and a 1–20 atm range. The equilibrium position, \( \xi_{eq} \), varies from 0.17 to 0.68.
negative reflecting primarily the positive entropy of mixing of the two reactants.

As can be seen from the stoichiometry, increasing pressure at constant temperature increases the ammonia equilibrium yield. Computer drawn Gibbs valley graphs over a total pressure range (1–20 atm) at 500 K are shown in Figure 5 and the effect of pressure on the equilibrium position is clearly seen. In addition to \((\partial G / \partial \xi)_T P\), the shape of the surface in Figure 5 is determined by

\[
(\partial G / \partial P)_T P = V
\]

which can be verified in this case by noting that the derivative of eqn. (14) results in an expression for the volume.

\[
(\partial G / \partial P)_T P = (2 - \xi) \frac{RT}{P}
\]

At high pressures accurate Gibbs function calculations for gases require fugacity coefficients which are not obtained easily for gas mixtures. Their magnitude, however, can be estimated from critical constants (9). This estimate was done for the three reacting species at the highest pressure (20 atm) in Figure 5, and all fugacity coefficients were estimated to be in the range 0.98–1.02. Thus, under these conditions no serious error is incurred by assuming ideal gas behavior.

**Summary**

The relation between the Gibbs function and chemical equilibrium is often obscure to beginning students, and Gibbs valley graphs can help to clarify these concepts. It is our opinion that they are most useful when the analytical expressions for the Gibbs function and their derivatives are developed in conjunction with the graphs and the role of mixing in determining the equilibrium position emphasized. Reactions commonly termed “equilibrium” reactions are those for which the mixing term, \(\Delta G_{\text{mix}}\), makes a significant contribution to the \(\xi\) dependent terms of \(G\) (eqn. 4) because \(\Delta G^0\) is small, whereas reactions that “go to completion” are those for which it makes only a minor contribution because \(\Delta G^0\) is relatively large.

It should be kept in mind that a downward slope of a Gibbs valley graph, although indicating thermodynamic spontaneity at constant temperature and pressure, does not guarantee reaction since the kinetics may be unfavorable; however, no system at constant temperature and pressure will spontaneously climb such a slope. This is illustrated by comparing Figures 2 and 3. Under normal conditions the boron halide reaction equilibrates quickly, whereas the ammonia synthesis does not. A steeper slope does not necessarily imply a faster reaction rate, contrary to what might be predicted if the “ball-in-a-bowl” analogy is carried too far.

Finally, although the examples given here are gas phase equilibria, the approach is not limited to such. Gibbs valley graphs for solution or heterogeneous equilibria could be constructed from eqn. (4) if expressions for the activities as functions of \(\xi\) are available. The gas phase is particularly amenable to quantitative treatment since such expressions, obtained from partial pressures, are both simple and reasonably valid over a wide range of conditions. Neither is the approach limited to chemical equilibria. Recently, Perona (10) has applied these same concepts to the vaporization of a liquid.

**Literature Cited**