# Spontaneity and Equilibrium: Why "$\Delta G < 0$ Denotes a Spontaneous Process" and "$\Delta G = 0$ Means the System Is at Equilibrium" Are Incorrect

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ABSTRACT: The fundamental criteria for chemical reactions to be spontaneous in a given direction are generally incorrectly stated as $\Delta G < 0$ or $\Delta A < 0$ in most introductory chemistry textbooks and even in some more advanced texts. Similarly, the criteria for equilibrium are also misstated as being $\Delta G = 0$ or $\Delta A = 0$. Following a brief review of the thermodynamic equations related to reaction spontaneity and equilibrium in systems involving a single reaction, this paper addresses the nature of these errors by first discussing the conceptual problems thereby introduced. This qualitative discussion is followed by a quantitative treatment of the $2NO_2(g) \rightarrow N_2O_4(g)$ reaction conducted both under constant temperature and volume and under constant temperature and pressure conditions. The results provide clear examples of the conceptual problems introduced by using $\Delta G < 0$ or $\Delta A < 0$ as criteria for reaction spontaneity and $\Delta G = 0$ or $\Delta A = 0$ as the corresponding criteria for equilibrium. It is shown that $\Delta G < 0$ or $\Delta A < 0$ are necessary conditions for a transformation from state A to state B to be spontaneous, but they are not sufficient conditions. If ξ denotes the reaction coordinate, the correct criteria for a spontaneous forward reaction are $(\partial G/\partial \xi)_{T,p} < 0$ or $(\partial A/\partial \xi)_{T,V} < 0$ when the process can be characterized by a single reaction coordinate. The correct criterion for equilibrium is either $dG = 0$ or $dA = 0$. The paper concludes with some briefly stated recommendations as to the manner in which textbooks should be altered. The pedagogical problem of presenting the correct criteria for spontaneity and equilibrium to beginning students not versed in calculus and thermodynamics is also addressed, and some recommendations are made.

KEYWORDS: First-Year Undergraduate/General, Upper-Division Undergraduate, Graduate Education/Research, Physical Chemistry, Misconceptions/Discrepant Events, Thermodynamics
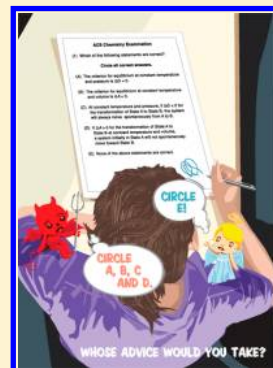
Spontaneity of chemical processes and equilibria are important topics that are covered in detail in every introductory chemistry textbook. These concepts, which are first presented in introductory courses, are often reiterated in more advanced courses covering analytical, organic, and inorganic chemistry. Every modern textbook of physical chemistry considers spontaneity and equilibrium in extensive, quantitative detail.

In spite of the attention devoted to these topics, the criteria for a chemical reaction to be spontaneous in a given direction are generally incorrectly stated in most introductory chemistry textbooks[1−7] and even in some textbooks[8,10,11] for more advanced courses. Example problems and exercises are often included that direct the student to execute calculations that purport to address the topic of spontaneity but which, in fact, are unrelated to whether a process is spontaneous or not under the conditions stated in the examples. Similarly, the criteria for equilibrium are frequently misstated.

In the next section of this paper, we review the basic concepts and equations that determine spontaneity and equilibrium in systems involving only a single reaction. Because these topics are covered in extensive detail in most physical chemistry texts, this review is abbreviated and covers only those points that are needed for the discussion and examples that follow. Following this review, a qualitative discussion of common errors in the statements concerning the criteria for

spontaneity and equilibrium is presented. The simple gas-phase reaction $2NO_2(g) \rightarrow N_2O_4(g)$ conducted under both conditions of constant T and V and constant T and p is treated in quantitative detail as illustrations of these points. Finally, recommendations are made as to how the presentations usually seen in introductory textbooks might be altered to reach students not familiar with calculus and thermodynamics but still present the material clearly and accurately.

■ BRIEF REVIEW OF SPONTANEITY AND EQUILIBRIUM

All principles of spontaneity and equilibrium derive from a combination of the first and second laws of thermodynamics. One of the most important of these is the Clausius inequality that states

$$dS - \frac{\delta q}{T} > 0 \quad \text{for spontaneity} \tag{1}$$

$$dS - \frac{\delta q}{T} = 0 \quad \text{at equilibrium} \tag{2}$$

In eqs 1 and 2, the symbol "δ" is employed to denote an inexact differential whose integral depends upon path.

If the process occurs at constant T and V, the first law tells us that $\delta q = dU - \delta w_n$, where δw_n is the differential nonpressure·volume work done on the system by the surroundings in the process. A common example of such work is the electrical work done during the operation of an electrochemical cell. If, however, T and p are constant, then $\delta q = dH - \delta w_n$. In these equations, U is the internal energy, and H is the enthalpy defined by $H = U + pV$. Hence, the criteria for spontaneity and equilibrium for the process are

$$dS - \frac{dU - \delta w_n}{T} \geq 0 \quad \text{for constant } T \text{ and } V \tag{3}$$

$$dS - \frac{dH - \delta w_n}{T} \geq 0 \quad \text{for constant } T \text{ and } p \tag{4}$$

where the inequality holds if the process is spontaneous and the equality if the process occurs reversibly at equilibrium. If we multiply these equations by $-T$, we obtain

$$dU - \delta w_n - TdS \leq 0 \quad \text{for constant } T \text{ and } V \tag{5}$$

$$dH - \delta w_n - TdS \leq 0 \quad \text{for constant } T \text{ and } p \tag{6}$$

Equations 5 and 6 suggest that it will be convenient to define two new thermodynamic potentials, the Helmholtz free energy (A) and the Gibbs free energy (G)

$$A \equiv U - TS \tag{7}$$

$$G \equiv H - TS. \tag{8}$$

With these definitions, the criteria for spontaneity and equilibrium in eqs 5 and 6 become

$$dA - \delta w_n \leq 0 \quad \text{for spontaneity and equilibrium at}$$
$$dT = 0 \text{ and } dV = 0 \tag{9a}$$

$$dG - \delta w_n \leq 0$$
$$\text{for spontaneity and equilibrium at } dT = 0 \text{ and } dp = 0 \tag{9b}$$

Rearrangement of eq 9b in the form $-\delta w_n \leq -dG$ provides a useful expression for the maximum differential work obtainable in a galvanic cell at constant T and p. As dG will be negative for the spontaneous reaction occurring in a galvanic cell, the maximum differential work obtainable from the system is $(\delta w_n)_{max} = -dG$. Therefore, $(w_n)_{max} = -\int_i^f dG$, where i and f denote the initial and final states of the electrochemical process.

In processes for which $\delta w_n = 0$, eqs 9a and 9b become

$$dA \leq 0 \quad \text{for spontaneity and equilibrium at } dT = 0 \text{ and}$$
$$dV = 0 \tag{10a}$$

$$dG \leq 0 \quad \text{for spontaneity and equilibrium at}$$
$$dT = 0 \text{ and } dp = 0 \tag{10b}$$

which are the usual equations seen in most textbooks covering chemical thermodynamics.

Equations 10a and 10b make it clear that if we wish to address spontaneity and equilibrium, we need to have general expressions that permit us to compute dA and dG. The derivation of the appropriate equations for closed systems with well-defined T, p, and chemical potentials in which there are no changes in the composition of the system due to external factors is straightforward but space consuming. We will,

therefore, simply present these equations and refer the reader to virtually any textbook covering physical chemistry.[9−12] The results are

$$dA = -SdT - pdV + \sum_i \mu_i dn_i \tag{11}$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i \tag{12}$$

where μ_i is the partial molar Gibbs free energy of component i, $(\partial G/\partial n_i)_{T,P,n_j}$. The summations in eqs 11 and 12 range over all the components of the system. The quantity μ_i is commonly termed the chemical potential for component i.

To determine the dependence of μ_i on the pressure for a pure gas, we need $(\partial \mu_i/\partial p)_{T,n}$. This is easily obtained by reversing the order of differentiation and using eq 12. That is

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n} = \left\{ \partial \left[\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}\right] \Big/ \partial p \right\}_{T,n}$$
$$= \left\{ \partial \left[\left(\frac{\partial G}{\partial p}\right)T, n\right] \Big/ \partial n_i \right\}_{T,p,n_j}$$
$$= \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j}$$
$$= V_i, \tag{13}$$

where V_i is the partial molar volume of component i in the system. Integration of both sides of eq 13 yields

$$\mu_i = \int d\mu_i = \int V_i dp = RT \int \frac{dp}{p} = F(T) + RT \ln p \tag{14}$$

provided we are dealing with a gas-phase system at sufficiently low pressure that it may be regarded as being ideal. At higher pressures, p is replaced with the fugacity. In condensed systems, the activity is used in place of pressure. For purposes of the discussion in this paper, we shall assume that we are treating an ideal, gas-phase system.

It should be noted that the pressure appearing in eq 14 is the magnitude only as the pressure units canceled in the ratio dp/p. When using SI units, the pressure magnitude is expressed in pascals (Pa). The bar is defined to be 10^5 Pa with p_s being taken as the standard pressure expressed in bars. The constant function of integration in eq 14, $F(T)$, depends upon temperature as the differential in eq 13 applies only at constant temperature. This function is obtained by evaluation of μ_i at the standard pressure. The result is $F(T) = \mu_i^\circ - RT \ln p_s$, where μ_i° is called the standard chemical potential. In the majority of cases, p_s is taken to be 1 bar so that $F(T) = \mu_i^\circ$.

To treat chemical reactions, the chemical potentials given by eq 14 for pure compounds must be modified by inclusion of the changes produced by the entropy of mixing. Consider a mixture of N ideal gases whose composition is specified by the mole fractions X_i for $i = 1, 2, 3, ..., N$. If a chemical reaction produces molar changes dn_i at constant temperature and pressure, the corresponding change in G is given by

$$dG = dG^{\text{pure}} + dG^{\text{mix}} = \sum_i [\mu_i^{\circ} + RT\ln p]dn_i$$
$$+ RT \sum_i \ln X_i\, dn_i$$
$$= \sum_i [\mu_i^{\circ} + RT\ln(X_i p)]dn_i = \sum_i [\mu_i^{\circ} + RT\ln p_i]dn_i$$

$$(15)$$

where $p_i = X_i p$ is the partial pressure of gas i in the mixture.[9−12] Equation 15 shows that the chemical potential of gas i in the mixture with the entropy of mixing included is given by

$$\mu_i = \mu_i^{\circ} + RT\ln p_i \qquad (16)$$

provided p_s is taken to be 1 bar.

Equations 10a−16 provide the mathematical apparatus that permits questions of reaction spontaneity and equilibrium to be quantitatively addressed for simple, one-reaction systems. Consider a system in which a single gas-phase reaction, aA + bB → cC + dD, occurs. The lower case letters are the unitless stoichiometric coefficients and A, B, C, and D represent reactants and products. Let us assume that this reaction is conducted at constant T and V at a pressure sufficiently low to permit the gases to be treated as being ideal. From eq 11, we have $dA = \mu_A\, dn_A + \mu_B\, dn_B + \mu_C\, dn_C + \mu_D\, dn_D$ because $dT = 0$ and $dV = 0$. Using the stoichiometry of the reaction, we can always express all the dn_i in terms of any one of them. For example, $dn_A = -(a/c)\,dn_C$, $dn_B = -(b/c)\,dn_C$, and $dn_D = (d/c)\,dn_C$. Making these substitutions into eq 11 gives

$$dA = \frac{dn_C}{c}[c\mu_C + d\mu_D - a\mu_A - b\mu_B]. \qquad (17)$$

Insertion of eq 16 into 17 gives, after rearrangement,

$$dA = \frac{dn_C}{c}\left[\Delta\mu^{\circ} + RT\ln\left\{\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}\right\}\right], \qquad (18)$$

where $\Delta\mu^{\circ} = c\mu_C^{\circ} + d\mu_D^{\circ} - a\mu_A^{\circ} - b\mu_B^{\circ}$.

The quantity dn_C/c appearing in eqs 17 and 18 is often written as $d\xi$ where ξ is called the "process coordinate" or, because the process of interest here is a chemical reaction, the "reaction coordinate". In principle, a reaction coordinate is any variable whose value measures the progress of the reaction. For the chemical reaction being discussed, the change in the number of moles of product C is clearly such a variable. It should be noted that the terms appearing inside the square braces in eqs 17 and 18 are intensive quantities with units of energy mol^{-1}. The multiplicative factor outside the braces is an extensive quantity with units of moles. Consequently, dA is an extensive quantity with units of energy. As previously noted, the stoichiometric coefficients are unitless, a fact which is obvious as these coefficients appear as exponents in the argument of the logarithm term.

Equations 10a and 18 provide a quantitative means of determining reaction spontaneity and equilibrium at constant T and V. If we have either $dA < 0$ or $(\partial A/\partial\xi)_{T,V} = c\mu_C < 0$ at a specific composition, the reaction will be spontaneous at that point in the direction of the products, that is in the direction for which $dn_C/c = d\xi > 0$. If, on the other hand, we have either $dA = 0$ or $(\partial A/\partial\xi)_{T,V} = c\mu_C = 0$ at a specific composition, that composition will be one of equilibrium for which we will have

$$\Delta\mu^{\circ} = -RT\ln\left\{\frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}\right\}_{\text{eq}} = -RT\ln K_p$$

$$(19)$$

where K_p is the thermodynamic equilibrium constant, which is a function of temperature only because $\Delta\mu^{\circ}$ depends only upon T. In some textbooks, the notation $\Delta_r G^{\circ}$ is used instead of $\Delta\mu^{\circ}$. Note, if the subscript r is omitted when using the notation $\Delta_r G^{\circ}$, the resulting equation $\Delta G^{\circ} = -RT\ln K_p$ is incorrect. This is clear from the fact that the units on ΔG° are not the same as the units on RT because ΔG° is an extensive quantity with units of energy, whereas RT is intensive with units of energy mol^{-1}. This point has previously been made by several authors in this *Journal*.[13]

As noted in the previous paragraph, $(\partial A/\partial\xi)_{T,V}$ is proportional to the chemical potential of the compound that defines the reaction coordinate, that is, $(\partial A/\partial\xi)_{T,V} = c\mu_C$. Consequently, the chemical potential, μ_C, plays the central role in questions involving spontaneity and equilibrium.

The requirement that $(\partial A/\partial\xi)_{T,V}$ be negative to ensure that a reaction will be spontaneous in the direction of increasing ξ is a specific example of a general principle that extends far beyond the thermodynamics of a chemical reaction to many areas of chemistry, physics, and engineering. If Φ is the potential energy describing any chemical or physical process, and ξ is a process coordinate for some process of interest, then the force acting in the direction of increasing ξ, F_ξ, is always given by

$$F_\xi = -\left(\frac{\partial\Phi}{\partial\xi}\right) \qquad (20)$$

Whenever F_ξ is positive, the process will be spontaneous in the direction of increasing ξ. If $F_\xi < 0$, the process will be spontaneous in the direction of decreasing ξ, and when $F_\xi = 0$, the process is at equilibrium. For chemical reactions, A functions as the thermodynamic potential if temperature and volume are constant. If the reaction is conducted with temperature and pressure constant, G functions as the thermodynamic potential. Therefore, it is not surprising to find that $(\partial A/\partial\xi)_{T,V} < 0$ or $dA < 0$ is the criterion for reaction spontaneity at a specific composition if $dT = 0$ and $dV = 0$, and $(\partial G/\partial\xi)_{T,p} < 0$ or $dG < 0$ is the criterion for reaction spontaneity if $dT = 0$ and $dp = 0$. The correct criteria for equilibrium are that these quantities are equal to zero.

It is important to note that all the criteria for reaction spontaneity and equilibrium, regardless of how stated, always involve differential changes dA or dG. They do not involve changes in the thermodynamic potentials over a finite range. That is, they do not involve ΔA or ΔG. Stated in different terms, the determination of reaction spontaneity and equilibrium at a given temperature requires the evaluation of dA or dG or their derivatives with respect to a reaction coordinate at a specific point in the $(V, p, \text{composition})$ space of the system. In addition to reaction spontaneity, it is meaningful to address the question of spontaneity or nonspontaneity for the transformation a system over a final interval from state A to state B. The criteria for transformation spontaneity and nonspontaneity are also examined in the following sections.

The above criteria for reaction spontaneity apply only in the case of a system involving a single reaction so that the Gibbs and Helmholtz free energies are functions of a single reaction coordinate, ξ. If N different, coupled reactions are occurring, A

and G will be functions of N reaction coordinates. Consequently, $G(\xi_1, \xi_2, \xi_3, ..., \xi_N)$ and $A(\xi_1, \xi_2, \xi_3, ..., \xi_N)$ will be $N +1$-dimensional hypersurfaces and both dG and dA will contain contributions from N partial derivatives of the form $(\partial G/\partial \xi_i)_{T,p,\xi_j}$. In such cases, the criteria for spontaneity and equilibrium are much more complex.

■ COMMON PRACTICE

Although the equations and concepts reviewed previously are discussed in quantitative detail in virtually every recent textbook of physical chemistry, they are still misstated in almost all introductory textbooks. Instead of eqs 10a and 10b, almost all such textbooks assert that the criteria for reaction spontaneity, nonspontaneity, and equilibrium are

at constant temperature and pressure

$\Delta G < 0$ (spontaneous)

$\Delta G > 0$ (nonspontaneous)

$\Delta G = 0$ (equilibrium)   (21a)

at constant temperature and volume

$\Delta A < 0$ (spontaneous)

$\Delta A > 0$ (nonspontaneous)

$\Delta A = 0$ (equilibrium)   (21b)

Frequently, a table is presented with these statements. In some cases, eqs 21a and 21b are enclosed within a box for emphasis. I have made such statements in my own classes many times, which is not surprising as this is what I was taught as an undergraduate.

Even some physical chemistry texts make such statements. After carefully and correctly deriving the criteria for equilibrium and spontaneity in terms of dS_{tot}, dA, and dG, one such text asserts

> The criteria for finite processes are completely analogous to those for infinitesimal processes. For example, for a simple system at constant pressure and temperature, a spontaneous process must obey $\Delta G \leq 0$.

The next sentence claims that this equation is the most useful criterion for determining the spontaneity and equilibrium of chemical reactions. In another textbook, we find,

> For macroscopic changes at constant p and T in which no nonexpansion work is possible, the condition for spontaneity is $\Delta G < 0$...

and then one paragraph later

> Similarly, for macroscopic changes at constant V and T in which no nonexpansion work is possible, the condition for spontaneity is $\Delta A < 0$, ...

The next section presents two quantitative examples showing why such claims are fallacious. However, it is not hard to see that something is wrong by considering the logical difficulties such criteria raise. For example, let us represent the value of ΔG computed at constant T and p for some finite interval of integration over the reaction coordinate ξ by $\Delta G = \int_I^F dG$, where I and F denote the initial and final values of ξ for the finite interval, respectively. If we find that $\Delta G < 0$ for some arbitrary choice of I and F, does this result mean the reaction is spontaneous at all points in the interval I to F? Does it mean the reaction is spontaneous at the initial point I? Is it spontaneous at the final point F or at some intermediate point,

that is, the center of the I−F interval? Alternatively, what is the significance or meaning of the result that $\Delta G = 0$? Does this mean that the system is in equilibrium at every point in the interval from I to F? Is it at equilibrium at point I, or at point F, or at the midpoint of the I−F interval? The very existence of such questions is a result the fallacious nature of the criteria expressed by eqs 21a and 21b. The answers to these questions are clearly shown by the following examples, which demonstrate that the spontaneity criteria given in eqs 21a and 21b are necessary conditions for a transformation from state I to F to be spontaneous, but they do not constitute sufficient conditions. With respect to reaction spontaneity at given points, the criteria in eqs 21a and 21b provide only partial information. The examples also show that the result $\Delta G = 0$ or $\Delta A = 0$ does not denote equilibrium nor does such a result give any information about the point at which equilibrium does exist.

■ QUANTITATIVE EXAMPLE USING A SIMPLE GAS-PHASE REACTION

Constant Temperature and Volume

As a first quantitative example of the qualitative points made previously, let us consider the simple gas-phase reaction $2NO_2(g) \rightarrow N_2O_4(g)$. The usual method of studying this reaction would be inside a closed, thermostatted container to maintain constant temperature and volume. Therefore, the criterion for spontaneity and equilibrium is dA as expressed in eq 10a. We shall assume that $T = 298.15$ K and that both gases behave ideally so that the chemical potential is given by eq 16. To simplify the notation, we will represent $NO_2(g)$ by A and $N_2O_4(g)$ by B so that the reaction in question is $2A \rightarrow B$. The absolute values of the standard chemical potentials cannot be obtained, but as we are concerned only with slopes and differences of A and G, values of these quantities relative to some reference point are sufficient. If the standard chemical potentials for the elements at 298.15 K and 1 bar pressure are taken to be zero, the measured standard molar Gibbs free energies of formation at 298.15 K and 1 bar pressure, $\Delta_f G°$, provides such relative values. These values can be found in almost any table of thermodynamic data. The required relative values are $\Delta_f G°(A) = \mu_A° = 51,310$ J mol^{-1} and $\Delta_f G°(B) = \mu_B° = 97,890$ J mol^{-1}. The reaction coordinate will be taken to be $\xi = n_B =$ number of moles of $N_2O_4(g)$ formed. We define the initial n_A value to be n_o moles and initially take n_B to be zero moles. Therefore, in this example $\xi = 0$ corresponds to n_o moles of pure $NO_2(g)$ and $\xi = n_o/2$ to complete reaction to pure $N_2O_4(g)$ gas.
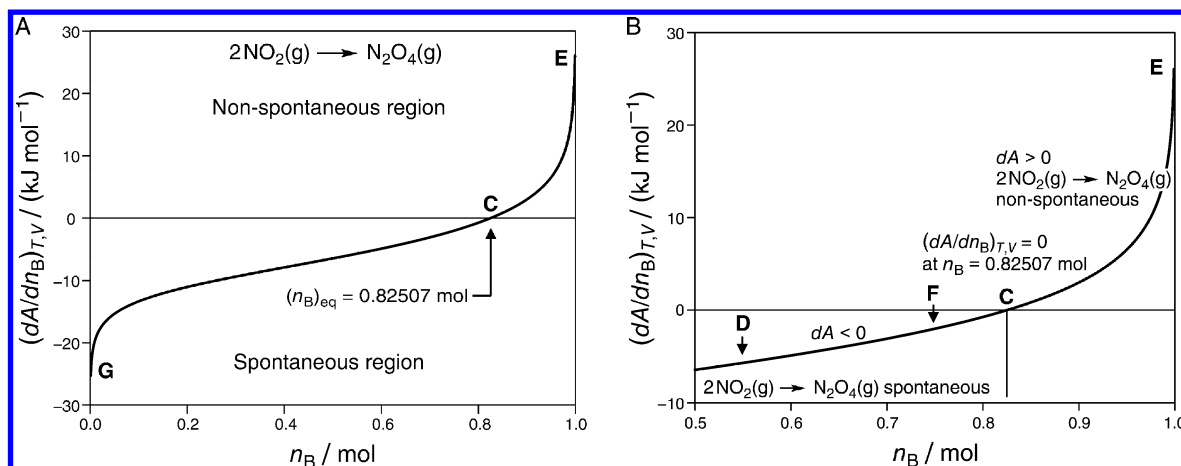
Using eq 11, we have

$$dA = -SdT - pdV + \Sigma_i \mu_i dn_i$$
$$= \Sigma_i \mu_i dn_i$$
$$= \mu_A dn_A + \mu_B dn_B \qquad (22)$$

because both dT and dV are zero. The stoichiometry of the reaction requires that $dn_A = -2dn_B$ so that eq 22 may be written as

$$dA = dn_B[\mu_B - 2\mu_A] = d\xi[\mu_B - 2\mu_A] \qquad (23)$$

Insertion of eq 16 for the chemical potentials yields

Figure 1. (A) Variation of $(\partial A/\partial n_B)_{T,V}$ or $\mu(N_2O_4(g))$ with n_B where n_B is the number of moles of $N_2O_4(g)$ formed in the reaction $2NO_2(g) \rightarrow N_2O_4(g)$ at 298.15 K in a closed container of volume 24.788 L and $n_o = 2$ mol. The points C, G, and E are defined in Table 1. Point C is the equilibrium point for the reaction at this temperature. (B) An enlargement of the data shown in Figure 1A for the range $0.5 \leq n_B \leq 1$. The points C, D, E, and F are defined in Table 1.

$$dA = dn_B[(\mu_B^o - 2\mu_A^o) + RT \ln p_B - 2RT \ln p_A]$$
$$= dn_B[\Delta\mu^o + RT \ln p_B - 2RT \ln p_A] \quad (24)$$

where $\Delta\mu^o = \mu_B^o - 2\mu_A^o$.

Using the ideal gas law, the partial pressures of A and B appearing in eq 24 may be written as

$$p_A = \frac{n_A RT}{V} = \alpha n_A \quad \text{and} \quad p_B = \frac{n_B RT}{V} = \alpha n_B \quad (25)$$

where we have written α for RT/V to simplify the notation. Combination of eqs 24 and 25 and insertion of the stoichiometric condition that $n_A = n_o - 2n_B$ gives

$$dA = dn_B[\Delta\mu^o + RT \ln(\alpha n_B) - 2RT \ln(\alpha n_A)]$$
$$= dn_B[\Delta\mu^o + RT \ln(\alpha n_B) - 2RT \ln(\alpha(n_o - 2n_B))] \quad (26)$$

with $\Delta\mu^o = 97{,}890 - 2(51{,}310) = -4730$ J mol^{-1}. Equation 26 is the correct expression to determine spontaneity and equilibrium. Note that an evaluation of $\Delta\mu^o$ alone is insufficient to determine whether a chemical reaction is spontaneous at given point. All quantities within the square brace of eq 26 are intensive with units of joules per mole, and dn_B and dA are extensive with units of moles.

To obtain an appropriate expression for the Helmholtz free energy of the reaction, we need to execute an indefinite integral of eq 26 to obtain

$$A = n_B\Delta\mu^o + RT[n_B\ln(\alpha n_B) - n_B]$$
$$+ RT[(n_o - 2n_B)\ln(\alpha(n_o - 2n_B)) - (n_o - 2n_B)]$$
$$+ C(T) \quad (27)$$

where $C(T)$ is a constant function of integration that depends upon temperature. This function may be determined by evaluation of A at the point where $\xi = n_B = 0$. At this point, we have n_o moles of pure $NO_2(g)$ for which the Helmholtz free energy is $A(n_B = 0) = G(n_B = 0) - n_o RT = n_o\mu_A^o + n_o RT \ln(n_o\alpha) - n_o RT$. This evaluation yields

$$C(T) = n_o\mu A^o. \quad (28)$$

Therefore, the final result is

$$A = n_o\mu_A^o + n_B\Delta\mu^o + RT[n_B\ln(\alpha n_B)$$
$$+ (n_o - 2n_B)\ln(\alpha(n_o - 2n_B)) + n_B - n_o] \quad (29)$$

To provide a numerical example of these results, we need to choose the values of α, which depends upon the volume of our reaction vessel, and n_o. To simplify the arithmetic, we take $V = 24.788$ L, which makes $\alpha = 1$, and $n_o = 2$ mol so that initially $NO_2(g)$ is at a pressure of 2 bar and the final product $N_2O_4(g)$ when $\xi = n_B = 1$ will be at the standard pressure of 1 bar. This choice gives

$$A = 2\mu_A^o + n_B\Delta\mu^o + RT[n_B\ln(n_B)$$
$$+ (2 - 2n_B)\ln(2 - 2n_B) + n_B - 2] \quad (30)$$

$$(\partial A/\partial n_B)_{T,V} = [\Delta\mu^o + RT\ln(n_B) - 2RT\ln(2 - 2n_B)] \quad (31)$$

Equations 30 and (31 allow A and $(\partial A/\partial n_B)_{T,V}$ to be computed and plotted versus n_B. It should be remembered that these equations are valid only for the choices $n_o = 2$ mol and $V = 24.788$ L. For other cases, eqs 26 and 29 must be used to fit the new conditions for n_o and V.

Figure 1A shows the variation of $(\partial A/\partial n_B)_{T,V} = \mu(N_2O_4(g))$ for the reaction as a function of n_B or ξ as given by eq 31. Figure 1B shows an enlargement of the equilibrium region of Figure 1A The points denoted C, D, E, F, G, and E in Figures 1A and 1B are defined in Table 1. They are employed to facilitate the discussion of these results. Figure 2A shows the variation of A predicted by eq 30 as a function of n_B. Figure 2B is an enlargement of the equilibrium region of Figure 2A. The labeled points in these figures are also defined in Table 1.

Figures 1A and 1B provide a proper analysis of the spontaneity and equilibrium characteristics of the 2 $NO_2(g) \rightarrow N_2O_4(g)$ reaction when conducted in the manner described in the initial portion of this section. As seen in Figure 1A, $(\partial A/\partial n_B)_{T,V} = \mu(N_2O_4(g))$ is negative throughout the region from $0 \leq n_B < 0.82507$ mol. This range is denoted by points G and C in Figure 1A. The driving, chemical force for the reaction is the negative slope of the thermodynamic potential A as stated in eq 18. Over this range, this force is in the direction of the reaction coordinate. Therefore, the reaction will proceed spontaneously toward $N_2O_4(g)$ at every point in the range. For the range

Table 1. Helmholtz Free Energies and Derivative Values at the Labeled Points in Figures 1A,B and 2A,B for the Case V = 24.788 L, n_o = 2 Moles, and T = 298.15 K[a]

point	n_B (mol)	A (J), eq 30	$(\partial A/\partial n_B)_{T,V}$ (J mol^{-1}), eq 31
	1	95,411.4	∞
	0	101,098.4	$-\infty$
C	0.82507	94,500.9	-0.023
D	0.54894	95,380.2	$-5,706.0$
E	0.99900	95,380.2	$26,077.3$
F	0.74900	94,582.1	$-2,029.8$
G	0.00100	101,070.9	$-25,284.5$
H	0.82507	95,380.2	
I	0.82507	95,109.4	
J	0.60000	95,109.4	$-4,890.0$
K	0.98187	95,109.4	$11,669.3$

[a]All values of A are relative to those of the chemical potentials of the elements, which are assigned the value of zero at 298.15 K and 1 bar of pressure.

0.82507 < $n_B \leq 1$ mol, $(\partial A/\partial n_B)_{T,V}$ is positive. Therefore, the chemical driving force for the reaction moves it in the direction of NO_2(g). Hence, the reaction 2 NO_2(g) → N_2O_4(g) is nonspontaneous over this range.

At the single point of equilibrium, point C, we have $(\partial A/\partial n_B)_{T,V} = 0$. The concentrations of NO_2(g) and N_2O_4(g) at this point can be easily determined using eq 30. At the point of equilibrium, we have $n_B = \xi = 0.82507$ mol, which is correct to five significant digits. The corresponding equilibrium constant at 298.15 K can be obtained using eq 19. This yields $K_P = \exp[-\Delta\mu°/RT] = 6.7407$. Using eq 25, we find that the partial pressures of NO_2(g) and N_2O_4(g) at equilibrium are 0.34987 and 0.82507 bar, respectively. If K_P is computed from these data, we obtain $K_P = (0.82507/(0.34987)^2) = 6.7403$. The excellent agreement between these values for K_p serves as partial verification that the integrated form for A, eq 30, is correct.

Now let us examine the problems that arise when reaction spontaneity and equilibrium are addressed using eq 21b. We first address questions of spontaneity.

The usual manner in which introductory textbooks approach the question of spontaneity is to direct the student to compute ΔA for the complete reaction in which the initial state ($\xi = 0$) is transformed into the final state ($\xi = 1$). This calculation is easily executed using eq 30 and the data given in Table 1

$$\Delta A(\xi = 0 \rightarrow \xi = 1) = \int_0^1 dA = A(1) - A(0)$$

where the notation $A(i)$ denotes the value of the Helmholtz free energy at the value of the reaction coordinate corresponding to $\xi = n_B = i$. Using the data in Table 1, we obtain $\Delta A(\xi = 0 \rightarrow \xi = 1) = 95,411.4 - 101098.4 = -5,687$ J. Because $\Delta A < 0$, virtually all introductory textbooks would proclaim the reaction to be spontaneous.

What does such a proclamation mean? Does it mean that a reaction system at $\xi = 0$ will proceed spontaneously to a point where $\xi = 1$? That is, does it mean that the transformation of the system from state $\xi = 0$ to state $\xi = 1$ is spontaneous? In point of fact, this will be the interpretation made by many students and even some more senior scientists. Such an interpretation is erroneous. The reaction will proceed spontaneously from $\xi = 0$ to $\xi = 0.82507$ (point C) and no further. The $\xi = 0 \rightarrow \xi = 1$ transformation is nonspontaneous. The interpretation that the system will move spontaneously from $\xi = 0$ to $\xi = 1$ implicitly assumes that dA is negative at every point in the $\xi = 0 \rightarrow \xi = 1$ interval simply because the integral $\int_0^1 dA < 0$. A glance at the results shown in Figure 1A shows that this implicit assumption is incorrect. The determination that $\Delta A < 0$ at constant T and V for the transformation of a system from state A to state B is not a sufficient condition to ensure that the transformation will be spontaneous.

Having dispensed with the notion that the result $\Delta A(\xi = 0 \rightarrow \xi = 1) < 0$ implies that dA is negative over the entire finite interval, let us ask if such a result means that the reaction will be spontaneous near the end of the interval, or near the center of the interval, or in any other arbitrary segment of the interval. The answer to all of these questions is "no". The only thing that can be safely inferred is that the reaction will be spontaneous
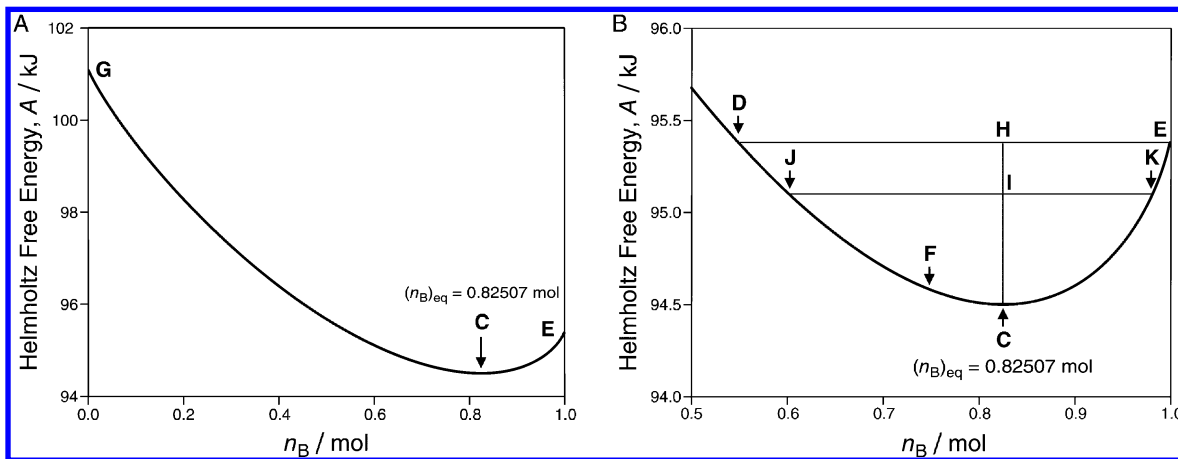
Figure 2. (A) Variation of the Helmholtz free energy, A, with n_B where n_B is the number of moles of N_2O_4(g) formed in the reaction 2NO_2(g) → N_2O_4(g) at 298.15 K in a closed container of volume 24.788 L and n_o = 2 mol. The points C, G, and E are defined in Table 1. Point C is the equilibrium point for the reaction at this temperature. All values of A are relative to those of the chemical potentials of the elements, which are assigned the value of zero at 298.15 K and 1 bar of pressure. (B) An enlargement of the data shown in Figure 2A for the range 0.5 ≤ n_B ≤ 1. The points C, D, E, F, H, I, J, and K are defined in Table 1.

throughout some undetermined region that includes the initial point $\xi = 0$.

Let us now consider the question of spontaneity for a reaction moving the system from point G to point C of Figure 2A. If by means of some laboratory measurement, we know that the reaction will proceed spontaneously from G → C, this information ensures that $dA < 0$ at every point in the path leading from G to C as shown in Figure 1A. With dA known to be negative at every point along the path, we can be certain that $\Delta A = \int_G^C dA < 0$. In other words, $\Delta A < 0$ is a necessary condition for a finite transformation to be spontaneous, but as shown above, it is not a sufficient condition. That is, it is not possible to predict with certainty that a process moving a system from state A to state B will be spontaneous simply because we find that $\Delta A < 0$ for the transformation at constant T and V. The derivation of the spontaneity conditions expressed by eqs 21a 21b that appear in many textbooks show only that these are necessary conditions for spontaneity. They do not show that they are sufficient conditions.

Let us now examine another interesting question concerning spontaneity. Assume a student is told that 0.749 mol of $N_2O_4(g)$ are mixed with 0.502 mol of $NO_2(g)$ at 298.15 K in a closed vessel whose volume is 24.788 L. This mixture corresponds to point F in Figure 2B. He or she is asked to determine if the reaction will proceed spontaneously to form more $N_2O_4(g)$. To assist in the determination, the student is given the values of the Helmholtz free energy for his initial system and that corresponding to complete reaction to form one mole of $N_2O_4(g)$, which is the point at which $\xi = 1$ in Figure 2B. Following eq 21b, the student computes the value of ΔA for the transformation from point F to the point where $\xi = 1$. The result is $\Delta A(F \to \xi = 1) = A(\xi = 1) - A(F) = 829.3$ J. Because $\Delta A > 0$, the student confidently states that the reaction is nonspontaneous and will, therefore, not proceed in the direction of $N_2O_4(g)$. However, reference to Figure 1B shows that $(\partial A/\partial n_B)_{T,V}$ at point F is negative. Therefore, reaction in the direction of $N_2O_4(g)$ is spontaneous.

The foregoing example shows that the result $\Delta A > 0$ over some finite interval cannot be interpreted to mean the reaction in question is nonspontaneous at the initial point of the interval or, for that matter, at any other arbitrary point in the finite interval. The result $\Delta A > 0$ at constant T and V is not a sufficient condition to ensure reaction nonspontaneity at some arbitrary point in the finite interval. The only thing that can be safely inferred is that the reaction is nonspontaneous throughout an undetermined region near the end of the interval. Because we know that the reaction must be nonspontaneous near the end of the interval, we can also be certain that the transformation over the interval is non-spontaneous. . Thus, $\Delta A > 0$ is a sufficient condition to ensure nonspontaneity of a finite transformation from State I to State F, but it is not a necessary condition.

Let us now turn our attention to the statement that the criterion for a system to be at equilibrium for a reaction conducted under constant volume and temperature conditions is $\Delta A = 0$.

Assume that we have a $NO_2(g)$–$N_2O_4(g)$ mixture containing 0.54894 mol of $N_2O_4(g)$ and 0.90212 mol of $NO_2(g)$ at 298.15 K in a closed 24.788 L container. This is point D in Figure 2B. Using the data given in Table 1, a student computes ΔA for the transformation of his initial system to one containing 0.999 mol of $N_2O_4(g)$ and 0.002 mol $NO_2(g)$. The result is $\Delta A(D \to E) = 95,380.2 - 95,380.2$ J = 0. Equation 21b tells us that the system

must be in equilibrium because $\Delta A = 0$. Such a conclusion is obviously nonsense. First, the system is far from its equilibrium point, C. More importantly, the concept that any system can be in equilibrium over any finite range is incorrect. When the temperature is constant, equilibrium exists at a single point, not over a finite range.

It should not be assumed that the above result is unusual. Such a result exists for an infinite number of ranges. This is clearly shown in Figure 2B. There are an infinite number of points on the line segment from point C to point H. One such point is point I. If a tieline is drawn through point I parallel to the reaction coordinate, the intersection points with the Helmholtz free energy curve, points J and K, will define initial and final states for which the integral $\Delta A(J \to K) = \int_J^K dA = 0$. Hence, ΔA can be zero for an infinitude of different finite ranges, none of which serve to identify the equilibrium point. In fact, the result that $\Delta A = 0$ for some finite range has nothing to do with equilibrium.

Constant Temperature and Pressure

All of the conclusions related to the relationships between dA, $(\partial A/\partial \xi)_{T,V}$, $\mu(N_2O_4(g))$, and ΔA with respect to spontaneity and equilibrium for a single reaction conducted at constant temperature and volume are also valid for dG, $(\partial G/\partial \xi)_{T,p}$, $\mu(N_2O_4(g))$, and ΔG when the reaction is carried out at constant temperature and pressure. As an illustrative example, we consider the same reaction previously treated, but this time the reaction occurs at a constant pressure, p_o. This requires that we perform the reaction inside a cylinder and piston apparatus and continuously depress the piston as $N_2O_4(g)$ forms to maintain the pressure constant at p_o. As before, we take $T = 298.15$ K with the initial state being n_o moles of pure $NO_2(g)$.

The criteria for spontaneity and equilibrium is now eq 12, which at $dT = 0$ and $dp = 0$ gives

$$dG = \mu_A dn_A + \mu_B dn_B \tag{32}$$

Using the same procedure as in the constant volume example, this leads to

$$dG = dn_B[\Delta\mu^o + RT \ln p_B - 2RT \ln p_A] \tag{33}$$

where p_B and p_A are the partial pressures of $N_2O_4(g)$ and $NO_2(g)$, respectively, given by eq 25. Now, however, the volume is not constant. It is given by

$$V = \frac{n_{total}RT}{p_o} = \frac{(n_o - 2n_B + n_B)}{p_o} = \frac{(n_o - n_B)RT}{p_o} \tag{34}$$

Substitution of eqs 25 and 34 into eq 33, insertion of the stoichiometric requirement that $n_A = n_o - 2n_B$, and separation of the logarithm terms yields the required expression for dG. It is

$$dG = dn_B[\Delta\mu^o + RT \ln(p_o n_B) - 2RT \ln(p_o(n_o - 2n_B)) \\ + RT\ln(n_o - n_B)] \tag{35}$$

To obtain the Gibbs free energy, we now take the indefinite integral of both sides of eq 35. After evaluation of the function of integration $C(T)$, the final result is

$$G = n_o\mu_A^o + n_B\Delta\mu^o + RT[n_B\ln(p_o n_B) \\ + (n_o - 2n_B)\ln(p_o(n_o - 2n_B)) \\ + (n_B - n_o)\ln(n_o - n_B)] \tag{36}$$

To obtain a numerical example, we take $n_o = 2$ moles as before, and we choose $p_o = 1$ bar so that the constant pressure in the example corresponds to the final pressure of $N_2O_4(g)$ in the constant volume example. Figure 3 shows the computed
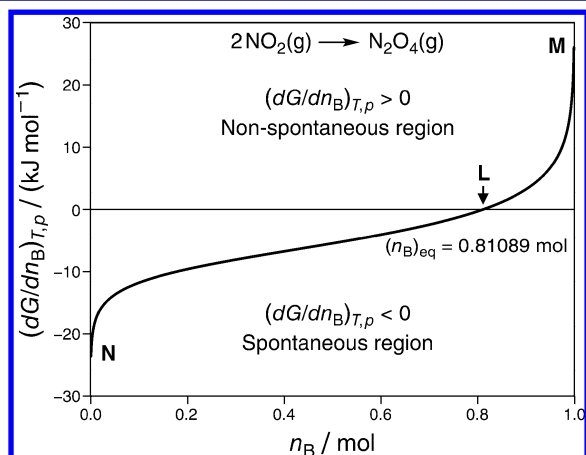
Figure 3. The variation of $(\partial G/\partial n_B)_{T,p} = \mu_B$ with n_B where n_B is the number of moles of $N_2O_4(g)$ formed in the reaction $2NO_2(g) \rightarrow N_2O_4(g)$ at 298.15 K at a constant pressure of 1 bar with $n_o = 2$ mol. The points M, L, and M are defined in Table 2. Point L is the equilibrium point for the reaction at this temperature.

values of $\mu_B = (\partial G/\partial n_B)_{T,p}$ as a function of n_B for the entire reaction. Figure 4 shows the corresponding values of the Gibbs free energy over the same range. The labeled points in the Figures 3 and 4 are defined in Table 2.
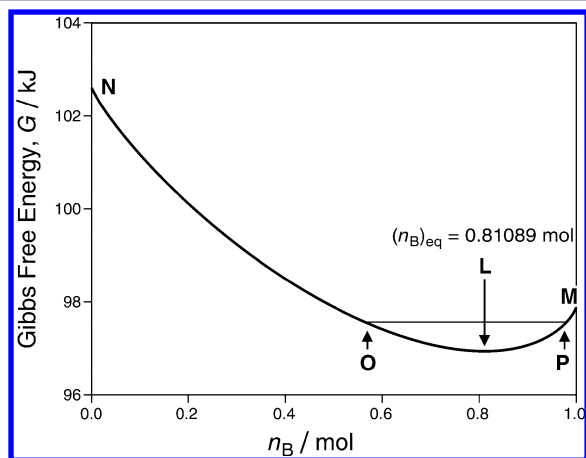
Figure 4. The variation of G with n_B, where n_B is the number of moles of $N_2O_4(g)$ formed in the reaction $2NO_2(g) \rightarrow N_2O_4(g)$ at 298.15 K at a constant pressure of 1 bar with $n_o = 2$ mol. The points L, M, N, O, and P are defined in Table 2. Point L is the equilibrium point for the reaction at this temperature. All values of G are relative to those of the chemical potentials of the elements, which are assigned the value of zero at 298.15 K and 1 bar of pressure.

For the constant pressure reaction, we see that the equilibrium point occurs at point L where the slope of the G versus n_B plot goes to zero. In this case, at equilibrium we have $(\xi)_{eq} = (n_B)_{eq} = 0.81089$ mol. Note that the equilibrium point is now shifted toward $NO_2(g)$ relative to its position for the constant volume reaction where we obtained $(\xi)_{eq} = (n_B)_{eq} = 0.82507$ mol. This shift is a quantitative example of Le Chatelier's principle. The pressure in the constant volume

Table 2. Gibbs Free Energies and Derivative Values at the Labeled Points in Figures 3 and 4 for the Case $p_o = 1$ Bar, $n_o = 2$ Moles, and $T = 298.15$ K[a]

point	n_B (mol)	G (J), eq 36	$(\partial G/\partial n_B)_{T,p}$ (J mol^{-1}), eq 35
N	0	102,620.	$-\infty$
L	0.81089	96,941.	0.000
M	1.00000	97,890.	∞
O	0.57515	97,517.36	
P	0.97543	97,517.36	

[a]All values of G are relative to those of the chemical potentials of the elements, which are assigned the value of zero at 298.15 K and 1 bar of pressure.

process is higher than in this constant pressure example. Consequently, the equilibrium amount of $N_2O_4(g)$ is greater when $dV = 0$. The equilibrium partial pressures of $N_2O_4(g)$ and $NO_2(g)$ are easily computed using eqs 25 and (34. The results are 0.68193 and 0.31807 bar for $N_2O_4(g)$ and $NO_2(g)$, respectively. This gives $K_p = 6.7405$. Because $\Delta\mu°$ depends only upon temperature, K_p is the same in both the constant pressure and constant volume processes, as expected.

Comparison of Figures 4 and 2A shows that the same type of errors present when $\Delta A < 0$ is used as the criterion for spontaneity when temperature and volume are constant occur when $\Delta G < 0$ is used as the criterion for spontaneity in a constant temperature and pressure reaction. For example, suppose a student in an introductory course were asked to determine if the reaction $N_2O_4(g) \rightarrow 2\,NO_2(g)$ is spontaneous at 298.15 K when one mole of $N_2O_4(g)$ is placed in a cylinder and piston apparatus and allowed to react at a constant pressure of 1 bar while the temperature is held constant. Using eq 21a, the student would employ the data in Table 2 to compute $\Delta G = \int_M^N dG = G(N) - G(M) = 102,620 - 97890 = +4730$ J. Because $\Delta G > 0$, the student would erroneously conclude that the reaction is nonspontaneous. However, Figure 3 clearly shows that $(\partial G/\partial n_B)_{T,p} > 0$ at point M. Therefore, the reaction is spontaneous in the negative direction of the reaction coordinate, that is, toward $NO_2(g)$. This case provides another example that demonstrates that the criterion $\Delta G > 0$ at constant temperature and pressure is not a sufficient condition to ensure reaction nonspontaneity at the initial point of the interval or any other arbitrary point. The only thing that may be safely inferred is that the reaction is nonspontaneous in an undetermined region that includes the end of the interval. Again, because the reaction is nonspontaneous at the end of the interval, the transformation process between initial and final states of the interval must be nonspontaneous.

It should be noted that if eq 9b is employed to obtain the maximum non-PV work available for some reaction using $(w_n)_{max} = -\int_i^f dG$, i and f must define a range over which $dG < 0$ at every point in the interval. In the present example, if i is taken to be point N where we have two moles of $NO_2(g)$ at 1 bar pressure, f should be the equilibrium point, L. This choice yields $(w_n)_{max} = -\int_N^L dG = -[G(L) - G(N)] = 5679$ J. If $(w_n)_{max}$ is computed for the complete reaction by taking f to be point M where we have one mole of $N_2O_4(g)$ at 1 bar, the result is $(w_n)_{max} = -\int_N^M dG = -[G(M) - G(N)] = 4730$ J, which is incorrect. The reason is that we are now summing over regions where $\xi = n_B > 0.81089$ for which $dG > 0$, and the reaction is nonspontaneous.

The same type of difficulties associated with using $\Delta A = 0$ as the criterion for equilibrium in a constant temperature—

constant volume reaction occur in the same manner when $\Delta G = 0$ is used as the criterion for equilibrium in a reaction occurring at constant temperature and pressure. There are an infinitude of different ranges for which $\Delta G = 0$. A tieline through any point on the line shown in Figure 4 going through point L that intersects the Gibbs free energy curve both on the left and right of the line, for example, the one shown that intersects the curve at points O and P, will provide lower and upper limits for which we will have $\Delta G = \int_O^P dG = 0$. None of these results have anything to do with identifying the equilibrium point L.

Recommendations

It seems very clear that existing textbooks should be modified in future editions to remove all erroneous statements concerning the criteria for spontaneity and equilibrium. New textbooks should not contain such statements. However, this does present a significant pedagogical problem. Students taking introductory courses usually are not sufficiently well versed in calculus and thermodynamics to be able to follow and understand the points made in the review section of this paper. Many have never encountered the concept of differentials or derivatives. How then should the material be presented so as to be understood but at the same time be accurate? No claim is made that following recommendations are the best method. They are presented only as suggestions and as evidence that such a presentation in introductory courses is possible.

The topics of reaction spontaneity and equilibrium can be approached from the point of view of slopes of a potential and forces using eq 20. Every college student knows what the slope of a curve or a line is. In this context, the slope need not be written in derivative notation. The English word itself can be used. The gravitational potential close to the earth, $\Phi = mgh$, might be used as an introductory example. The process of interest could be moving an object of mass m from a position where the height above the ground is $h = 0$ to a point where it is some value h^*. An illustrative plot of Φ versus h would be a straight line with slope mg. The height h could be identified as a process coordinate that measures the progress of raising the mass. Finally, students who have completed a high school course in physics know that the gravitation force is $-mg$. Using this fact, the instructor can point out that the gravitational force is the negative of the slope of the gravitational potential. That is,

$$\text{gravitational force} = -(\text{slope of the gravitational potential})$$
$$= -mg \tag{37}$$

It can also be noted that because the gravitational force is negative, it operates in a direction opposite to an increase of the process coordinate, h. That is, the spontaneous direction for the process is for h to decrease.

From this point, the instructor can now assert that this type of result holds in many areas of chemistry and physics. For example,

$$\text{gravitational force} = -(\text{slope of the gravitational potential}) \tag{38a}$$

$$\text{electrostatic force} = -(\text{slope of the electrostatic potential}) \tag{38b}$$

$$\text{intramolecular force} = -(\text{slope of the intramolecular potential}) \tag{38c}$$

$$\text{intermolecular force} = -(\text{slope of the intermolecular potential}) \tag{38d}$$

It might be useful to mention that eqs 38c and 38d are the basis of all molecular dynamics calculations wherein the motion of atoms in a potential field are determined. Such a general concept will serve the students well not only in chemistry but in many more-advanced courses in physics and engineering.

The stage is now set for the introduction of the thermodynamic potential, G, the Gibbs free energy. The instructor can assert that the thermodynamic potential has two parts, one dealing with the reaction exo- or endothermicity, called the enthalpy H, and a second part dealing with order-to-chaos transformations. Such transformations are measured by the quantity $-TS$, where S is called the entropy. The Gibbs free energy is the sum of these two parts, that is, $G = H - TS$. Most introductory textbooks contain excellent qualitative discussions of these two effects. There is no need to modify any of this discussion.

Finally, a qualitative curve of G versus a reaction coordinate can be shown. It would have a form similar to Figure 4. Alternatively, Figure 4 itself might employed. With G already introduced as the thermodynamic potential, the chemical driving force for spontaneity easily becomes the negative slope of the G versus ξ curve, and the point of equilibrium is the point of zero force or zero slope. Some introductory textbooks already include such a qualitative illustration. Unfortunately, such clear illustrations always follow assertions that the criteria for spontaneity and equilibrium are those given in eqs 21a and 21b. All that needs be done is remove those statements and replace them with a discussion of forces and slopes.

Clearly, the students will not yet be prepared to execute the type of calculations performed in the examples presented here. However, the instructor can provide the class with a modified form of eq 18, that is,

$$\text{chemical force} = -(\text{slope of the thermodynamic potential}, \ G \text{ or } A)$$
$$= -RT[\ln Q - \ln K_P] \tag{39}$$

where Q is the usual ratio of partial pressures or concentrations at a given point at which we wish to predict spontaneity or equilibrium. That is

$$Q = \frac{(p_C)^c (p_D)^d}{(p_A)^a (p_B)^b} \tag{40}$$

for gases. Approximate calculations can be executed for solutions by replacing K_P with K_C and pressures with concentrations. The use of eqs 39 and 40 requires only basic arithmetic. Most importantly, the predictions the student makes using these equations will be conceptually correct.

■ SUMMARY

For a system involving only a single chemical reaction, the appropriate criteria for reaction spontaneity and equilibrium at a specific point along the reaction coordinate are

$$dA < 0 \quad \text{or} \quad (\partial A / \partial \xi)_{T,V} < 0 \quad \text{for reaction spontaneity}$$

$$dA = 0 \quad \text{or} \quad (\partial A / \partial \xi)_{T,V} = 0$$

$$\text{for equilibrium when } dT = 0 \text{ and } dV = 0$$

or

$$dG < 0 \quad \text{or} \quad (\partial G/\partial \xi)_{T,p} < 0 \quad \text{for reaction spontaneity}$$

$$dG = 0 \quad \text{or} \quad (\partial G/\partial \xi)_{T,p} = 0$$

$$\text{for equilibrium when } dT = 0 \text{ and } dp = 0$$

Because $(\partial A/\partial \xi)_{T,V} = (\partial G/\partial \xi)_{T,p} = c\mu_C$, where compound C with stoichiometric coefficient c defines the reaction coordinate ξ, it is seen that the chemical potential μ_C plays the central role in determining spontaneity and equilibrium.

The quantities ΔA and ΔG for a finite interval yield very little information concerning reaction spontaneity at specific points along the interval and no information about the equilibrium point. The following information about reaction spontaneity is available from knowledge about ΔA and ΔG for a given finite interval:

- If $\Delta A < 0$ (constant T and V) or $\Delta G < 0$ (constant T and p), no information about reaction spontaneity at the final point or at any other arbitrary point in the interval is available. The reaction is known to be spontaneous in an underdetermined region that includes the initial point of the interval.

- If $\Delta A > 0$ (constant T and V) or $\Delta G > 0$ (constant T and p), no information about reaction spontaneity at the initial point or at any other arbitrary point in the interval is available. The reaction is known to be nonspontaneous in an underdetermined region that includes the end point of the interval.

- With respect to the spontaneity of the transformation of a system from state A to state B, the result that $\Delta A < 0$ (constant T and V) or $\Delta G < 0$ (constant T and p) for the transformation yields no information about the spontaneity or nonspontaneity of the process. The result $\Delta A > 0$ (constant T and V) or $\Delta G > 0$ (constant T and p) guarantees that the transformation is nonspontaneous.

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Notes

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