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Citation: *The Journal of Chemical Physics* **91**, 1824 (1989); doi: 10.1063/1.457087

View online: <http://dx.doi.org/10.1063/1.457087>

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# Use of semigrand ensembles in chemical equilibrium calculations on complex organic systems

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(Received 3 April 1989; accepted 20 April 1989)

When chemical potentials of some reactants are externally fixed, the equilibrium pressures of other reactants can be calculated thermodynamically using Legendre transforms of the usual thermodynamic potentials and statistical mechanically using semigrand ensembles. The use of the semigrand isobaric partition function for complex organic systems involving chemical reactions is discussed. This partition function provides a simplified, but comprehensive, view of chemical equilibrium within homologous and related series, which involve infinite numbers of species. The transformed thermodynamic properties for equilibrium systems of this type are expressed in terms of the molecular partition functions of the various species.

## I. INTRODUCTION

If one or more reactants in a complex organic system at equilibrium have externally fixed chemical potentials, their terms can be removed from the fundamental equation of thermodynamics by use of a Legendre transform to obtain a new thermodynamic potential that is at a minimum at equilibrium. This makes it possible to define homologous series groups and other groups that can be used as single terms in the fundamental equation for the purpose of equilibrium calculations.<sup>1</sup> It is therefore of interest to examine the corresponding semigrand ensembles of statistical mechanics for this purpose. Semigrand ensembles have been used in statistical mechanical theories of solutions,<sup>2</sup> the study of the relation between light scattering and composition fluctuations,<sup>3</sup> constant pressure solution theory,<sup>4-7</sup> studying molecular changes in hemoglobin,<sup>8,9</sup> cooperativity theory in biochemistry,<sup>10</sup> linear aggregation theory in cell biology,<sup>11</sup> solubility in monolayers,<sup>12</sup> calculating the equilibrium distribution of hydrocarbons in homologous series,<sup>13</sup> and predicting the thermodynamic properties of solutions.<sup>14</sup> Statistical mechanics provides the same option as thermodynamics to treat isomers in equilibrium as a single component; the molecular partition functions of the individual isomers are simply added to obtain the molecular partition function of the isomer group.<sup>5,15,16</sup>

In the next section we shall discuss a simple chemical reaction from the thermodynamic point of view. Then, we shall introduce semigrand ensembles to obtain the properties of this system. We shall then extend these considerations to an infinite number of reactions. Then, we shall use the results of the statistical mechanical calculations to rewrite the thermodynamic quantities in a novel form.

## II. THERMODYNAMICS OF A SIMPLE CHEMICAL REACTION

As a simple example, we consider a system containing the species  $A$ ,  $B$ , and  $C$ , all of which are ideal gases. The system is in contact with a reservoir of  $B$  molecules at fixed chemical potential  $\mu_B$  through a semipermeable membrane, permeable to  $B$  only. The chemical reaction



takes place in the system which is open with respect to  $B$  and closed with respect to  $A$  and  $C$ .

The Gibbs energy for this system is

$$G = N_A \mu_A + N_B \mu_B + N_C \mu_C, \quad (2.2)$$

where  $N_A$  is the number of molecules of species  $A$ ,  $\mu_A$  is the chemical potential per molecule of  $A$ , etc. The total differential of  $G$  is given by

$$dG = -S dT + V dP + \mu_A dN_A + \mu_B dN_B + \mu_C dN_C. \quad (2.3)$$

If the reaction is not at equilibrium, the extensive variable  $G$  is determined by specifying one extensive quantity and four intensive variables, viz.  $T$ ,  $P$ , and two intensive composition variables. In order to make this dependence explicit, it is convenient to rewrite Eq. (2.2) as

$$G = (N_A + N_C) \mu_A + N_B \mu_B + N_C (\mu_C - \mu_A) \quad (2.4)$$

and to define the Legendre transformed quantity

$$G_2(T, P, N_I, \mu_B, \mu_C - \mu_A) \\ = G - N_B \mu_B - N_C (\mu_C - \mu_A) = N_I \mu_A. \quad (2.5)$$

The total differential of  $G_2$  is

$$dG_2 = -S dT + V dP + \mu_A dN_I \\ - N_B d\mu_B - N_C d(\mu_C - \mu_A). \quad (2.6)$$

Here,

$$N_I \equiv N_A + N_C \quad (2.7)$$

is the number of molecules in the homologous series consisting of  $A$  and  $C$ . This terminology is used because, when  $B$  is half an ethylene molecule, successive isomer groups in a homologous series can be obtained by adding successive molecules of  $B$ . For example, the successive isomer groups in the alkylbenzene homologous series can be formed from benzene by adding ethylene; in this case  $C$  is toluene. The quantity  $G_2$  is useful whether or not the chemical reaction, Eq. (2.1), is at equilibrium.

At chemical equilibrium,

$$\mu_C = \mu_A + \mu_B, \quad (2.8)$$

and  $G$  is determined by specifying one extensive variable and

three intensive variables consisting of  $T$ ,  $P$ , and one intensive composition variable. We use Eq. (2.4) to obtain

$$G = N_I \mu_A + (N_B + N_C) \mu_B \quad (2.9)$$

and introduce the Legendre transformed quantity

$$G_1 \equiv G - (N_B + N_C) \mu_B \equiv N_I \mu_A \quad (2.10)$$

with differential

$$dG_1 = -S dT + V dP + \mu_A dN_I - (N_B + N_C) d\mu_B. \quad (2.11)$$

Note that  $G_2$  reduces to  $G_1$  at chemical equilibrium. The quantity  $G_1$  has been introduced previously<sup>1</sup> to describe equilibrium properties of homologous series groups from the thermodynamic point of view.

### III. SEMIGRAND PARTITION FUNCTIONS

The system that we discussed in Sec. II, which is open to  $B$  and closed with respect to  $A$  and  $C$ , with chemical reaction Eq. (2.1), can be considered from a statistical mechanical point of view. Initially there are  $N_A^0$  molecules of  $A$  and  $N_C^0$  molecules of  $C$ . As the chemical reaction proceeds, the number of molecules of  $A$ ,  $N_A$ , becomes  $N_A^0 - \xi$  and the number of molecules of  $C$ ,  $N_C$ , becomes  $N_C^0 + \xi$  where  $\xi$  is the extent of reaction expressed in number of molecules. The extent of reaction  $\xi$  is limited by

$$-N_C^0 \leq \xi \leq N_A^0 \quad (3.1)$$

and, of course

$$N_A + N_C = N_A^0 + N_C^0 = N_I. \quad (3.2)$$

A more convenient measure of the extent of reaction is

$$Z = \xi + N_C^0 = N_C, \quad (3.3)$$

where

$$0 \leq Z \leq N_I. \quad (3.4)$$

The system can then be considered open to  $B$ , with no restrictions on  $N_B$ , and open with respect to  $A$  and  $C$ , with the restrictions  $0 \leq N_C \leq N_I$  and that for every molecule of  $C$  which enters the system one molecule of  $A$  must leave.

The appropriate ensemble for describing this system in which the chemical reaction proceeds at constant  $T$  and  $P$  is the isobaric, isothermal ensemble with partition function

$$\begin{aligned} \Gamma(T, P, N_I, \mu_B, \mu_C - \mu_A) \\ = \sum_{V=0}^{\infty} \sum_{N_B=0}^{\infty} \sum_{Z=0}^{N_I} Q(T, V, N_I - Z, N_B, Z) \\ \times e^{-\beta PV} e^{\beta N_B \mu_B} e^{\beta (N_I - Z) (\mu_C - \mu_A)}, \end{aligned} \quad (3.5)$$

where  $Q(T, V, N_I - Z, N_B, Z)$  is the canonical partition function for the system containing  $N_B$  molecules of  $B$ ,  $N_I - Z$  molecules of  $A$ , and  $Z$  molecules of  $C$ .

The thermodynamic quantities of interest can be obtained by taking appropriate derivatives of  $\ln \Gamma$ . Thus,

$$U = -(\partial \ln \Gamma / \partial \beta)_{\beta P, N_I, \beta \mu_B, \beta (\mu_C - \mu_A)}, \quad (3.6a)$$

$$\langle V \rangle = -(\partial \ln \Gamma / \partial \beta P)_{\beta, N_I, \beta \mu_B, \beta (\mu_C - \mu_A)}, \quad (3.6b)$$

$$\mu_A = -(1/\beta) (\partial \ln \Gamma / \partial N_I)_{\beta, \beta P, \beta \mu_B, \beta (\mu_C - \mu_A)}, \quad (3.6c)$$

$$\langle N_B \rangle = (\partial \ln \Gamma / \partial \beta \mu_B)_{\beta, \beta P, N_I, \beta (\mu_C - \mu_A)}, \quad (3.6d)$$

$$\langle N_C \rangle = [\partial \ln \Gamma / \partial \beta (\mu_C - \mu_A)]_{\beta, \beta P, N_I, \beta \mu_B}, \quad (3.6e)$$

$$\langle N_A \rangle = N_I - \langle N_C \rangle, \quad (3.6f)$$

where  $U$  is the internal energy of the system, and the definitions of the other quantities are obvious. We define the thermodynamic quantity  $F$  by

$$\Gamma = e^{-\beta F} \quad (3.7)$$

and find that the total differential of  $F$  can be written

$$\begin{aligned} dF = (1/\beta) \{ (U - F) d\beta + \langle V \rangle d(\beta P) + \beta \mu_A dN_I \\ - \langle N_B \rangle d(\beta \mu_B) - \langle N_C \rangle d[\beta (\mu_C - \mu_A)] \} \\ = [U - F + P \langle V \rangle - \langle N_B \rangle \mu_B \\ - \langle N_C \rangle (\mu_C - \mu_A)] d\beta / \beta \\ + \langle V \rangle dP + \mu_A dN_I - \langle N_B \rangle d\mu_B \\ - \langle N_C \rangle d(\mu_C - \mu_A), \end{aligned} \quad (3.8)$$

which is identical to Eq. (2.6). Therefore,

$$F = G_2 \quad (3.9)$$

and

$$\Gamma = e^{-\beta G_2}. \quad (3.10)$$

The values of the thermodynamic quantities at chemical equilibrium are obtained from Eqs. (3.6a)–(3.6f) by setting  $\mu_C - \mu_A = \mu_B$  after the derivatives are taken. Stockmayer<sup>3</sup> introduced the semigrand partition function  $\Gamma(T, P, N_I, \mu_B)$  to study the relation between light scattering and composition fluctuations of solutions.

The explicit form of  $\Gamma$  for an ideal gas mixture is readily obtained. In this case

$$Q(T, V, N_I - Z, N_B, Z) = \frac{q_A^{N_I - Z}}{(N_I - Z)!} \frac{q_B^{N_B}}{N_B!} \frac{q_C^Z}{Z!}, \quad (3.11)$$

where  $q_A(T, V)$  is the one-particle partition function for species  $A$ . The sums over  $N_B$  and  $Z$  in Eq. (3.5) yield

$$\begin{aligned} \sum_{N_B=0}^{\infty} \sum_{Z=0}^{N_I} Q e^{\beta \mu_B N_B} e^{\beta (\mu_C - \mu_A) Z} \\ = \frac{q_A^{N_I}}{N_I!} \left[ 1 + \frac{q_C}{q_A} e^{\beta (\mu_C - \mu_A)} \right]^{N_I} \exp(q_B e^{\beta \mu_B}). \end{aligned} \quad (3.12)$$

The sum over  $V$  in Eq. (3.5) is facilitated by writing

$$q_A(T, V) = q'_A(T) V \quad (3.13)$$

and similarly for  $q_B$  and  $q_C$ . The sum over  $V$  is replaced by an integral and the result is

$$\Gamma = \left[ \frac{q'_A + q'_C e^{\beta (\mu_C - \mu_A)}}{\beta P - e^{\beta \mu_B} q'_B} \right]^{N_I} \equiv (a/b)^{N_I}, \quad (3.14)$$

where

$$a[\beta, \beta (\mu_C - \mu_A)] \equiv q'_A + q'_C e^{\beta (\mu_C - \mu_A)} \quad (3.15)$$

and

$$b(\beta, \beta P, \beta \mu_B) \equiv \beta P - e^{\beta \mu_B} q'_B. \quad (3.16)$$

Thus

$$\ln \Gamma = N_I \ln(a/b) \quad (3.17)$$

and the derivatives in Eqs. (3.6a)–(3.6f) yield

$$U = -N_I \left[ \frac{(d \ln q'_A/d\beta) q'_A + (d \ln q'_C/d\beta) q'_C e^{\beta(\mu_C - \mu_A)}}{a} + \frac{(d \ln q'_B/d\beta) q'_B e^{\beta\mu_B}}{b} \right], \quad (3.18a)$$

$$\langle V \rangle = N_I/b, \quad (3.18b)$$

$$\mu_A = -(1/\beta) \ln(a/b), \quad (3.18c)$$

$$\langle N_B \rangle = N_I e^{\beta\mu_B} q'_B/b, \quad (3.18d)$$

$$\langle N_C \rangle = N_I q'_C e^{\beta(\mu_C - \mu_A)}/a, \quad (3.18e)$$

$$\langle N_A \rangle = N_I q'_A/a. \quad (3.18f)$$

Substitution of Eqs. (3.18d)–(3.18f) into Eq. (3.18a) yields

$$U = \langle N_A \rangle \langle u_A \rangle + \langle N_B \rangle \langle u_B \rangle + \langle N_C \rangle \langle u_C \rangle, \quad (3.19)$$

where

$$\langle u_A \rangle = -d \ln q'_A/d\beta \quad (3.20)$$

is the average internal energy per molecule of *A*, and similarly for  $\langle u_B \rangle$  and  $\langle u_C \rangle$ . Substitution of Eq. (3.18d) into Eq. (3.16) for *b* yields

$$b = \beta P - (b/N_I) \langle N_B \rangle, \quad (3.21)$$

which when substituted into Eq. (3.18b) yields

$$\beta P \langle V \rangle = N_I + \langle N_B \rangle. \quad (3.22)$$

This is the ideal gas law since the total number of particles in the system is  $N_I + \langle N_B \rangle$ . At chemical equilibrium  $\mu_C - \mu_A = \mu_B$  and Eqs. (3.18e) and (3.18f) become

$$r_C = \langle N_C \rangle / N_I = q'_C e^{\beta\mu_B} / (q'_A + q'_C e^{\beta\mu_B}) \quad (3.23)$$

and

$$r_A = \langle N_A \rangle / N_I = q'_A / (q'_A + q'_C e^{\beta\mu_B}). \quad (3.24)$$

Here,  $r_C$  and  $r_A$  are the equilibrium mole fractions of *C* and *A*, respectively, within the homologous series group. These expressions are the statistical mechanical equivalent of the equations derived from thermodynamics.<sup>1</sup> Finally substitution of Eqs. (3.18b) and (3.18f) into Eq. (3.18c) and use of Eq. (3.22) yields

$$\mu_A = -kT \ln(q'_A kT / y_A P), \quad (3.25)$$

where

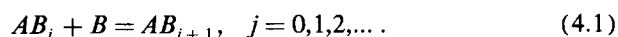
$$y_A = \langle N_A \rangle / (N_I + \langle N_B \rangle) \quad (3.26)$$

is the equilibrium mole fraction of *A* in the system. Equation (3.25) is clearly the correct expression for  $\mu_A$  in this system.

#### IV. MULTISTEP REACTIONS AND SEMIGRAND ENSEMBLES

The extension of the results of Secs. II and III to multistep reactions is straightforward. We consider a system consisting of the species  $AB_j$ ,  $j = 0, 1, 2, \dots$ , and *B*. The system is open for *B* and closed for all  $AB_j$ .

The chemical reactions that take place in the system at constant *T* and *P* are



The Gibbs energy for this system is

$$G = \sum_{j=0} N_j \mu_j + N_B \mu_B, \quad (4.2)$$

where  $N_j$  is the number of molecules of  $AB_j$  and  $\mu_j$  is the chemical potential per molecule of species  $AB_j$ . In particular,  $N_0$  is the number of molecules of *A*, and  $\mu_0$  is its chemical potential. Equation (4.2) can be rewritten

$$G = N_I \mu_0 + \sum_{j=1} N_j (\mu_j - \mu_0) + N_B \mu_B, \quad (4.3)$$

where

$$N_I = \sum_{j=0} N_j \quad (4.4)$$

is the total number of molecules in the homologous series group  $AB_j$ . The appropriate Legendre transformed Gibbs energy is

$$G_2 = G - \sum_{j=1} N_j (\mu_j - \mu_0) - N_B \mu_B = N_I \mu_0 \quad (4.5)$$

with total differential

$$dG_2 = -S dT + V dP + \mu_0 dN_I - \sum_{j=1} N_j d(\mu_j - \mu_0) - N_B d\mu_B. \quad (4.6)$$

The same symbol is used here for the transformed Gibbs energy as in Eqs. (2.5) and (2.6) because this is a generalization to multistep reactions. At chemical equilibrium,

$$\mu_{j+1} = \mu_j + \mu_B \quad (4.7)$$

and

$$\mu_j - \mu_0 = j\mu_B. \quad (4.8)$$

Under these circumstances,  $G_2$  becomes

$$G_1 = G - \left( N_B + \sum_{j=1} j N_j \right) \mu_B = N_I \mu_0 \quad (4.9)$$

with total differential

$$dG_1 = -S dT + V dP + \mu_0 dN_I - \left( N_B + \sum_{j=1} j N_j \right) d\mu_B, \quad (4.10)$$

a form that has been used before<sup>1</sup>; also see Eq. (2.11).

The appropriate semigrand ensemble to treat this problem has the partition function

$$\begin{aligned} \Gamma(T, P, N_I, \mu_B, \mu_1 - \mu_0, \dots, \mu_j - \mu_0, \dots) \\ = \sum_{V=0}^{\infty} \sum_{N_B=0}^{\infty} \sum_{\{N_j\}} \mathcal{Q}(T, V, N_I - \sum_{j=1} N_j, N_B, \{N_j\}) \\ \times e^{-\beta P V} e^{\beta N_B \mu_B} \prod_{j=1} e^{\beta(\mu_j - \mu_0) N_j}, \end{aligned} \quad (4.11)$$

where the notation  $\{N_j\}$  implies the set  $N_1, N_2, \dots$ , etc., and the restriction on the sum over  $\{N_j\}$  is that

$$0 \leq \sum_{j=1} N_j \leq N_I. \quad (4.12)$$

It follows that

$$\Gamma(T, P, N_I, \mu_B, \{\mu_j - \mu_0\}) = e^{-\beta G_2}. \quad (4.13)$$

Again the thermodynamic variables can be obtained by taking appropriate derivatives of  $\ln \Gamma$ . Equations (3.6a)–(3.6d) apply here as in Sec. III, with  $\beta(\mu_C - \mu_A)$  replaced

by  $\{\beta(\mu_j - \mu_0)\}$ . The equations for the averages of  $\{\langle N_j \rangle\}$  become

$$\langle N_j \rangle = [\partial \ln \Gamma / \partial \beta(\mu_j - \mu_0)]_{\beta, \beta_P, N_I, \mu_B, \{\beta(\mu_l - \mu_0)\}^j}, \quad j = 1, 2, \dots, \quad (4.14)$$

where the notation  $\{\beta(\mu_l - \mu_0)\}^j$  implies that all  $\beta(\mu_l - \mu_0)$  are held fixed except for  $l = j$ . Finally, in analogy to Eq. (3.6f),

$$\langle N_0 \rangle = N_I - \sum_{j=1} \langle N_j \rangle. \quad (4.15)$$

The explicit form of Eq. (4.11) for a mixture of ideal gases follows from the form of the canonical partition function:

$$\begin{aligned} Q(T, V, N_I - \sum_{j=1} N_j, N_B, \{N_j\}) \\ = \frac{q_0^{N_I - \sum_{j=1} N_j}}{(N_I - \sum_{j=1} N_j)!} \left( \prod_{j=1} \frac{q_j^{N_j}}{N_j!} \right) \frac{q_B^{N_B}}{N_B!}, \end{aligned} \quad (4.16)$$

where  $q_j$  is the one-particle partition function for species  $AB_j$ .

The sums over  $N_B$  and  $\{N_j\}$  in Eq. (4.11) are easily carried out using the multinomial theorem to obtain

$$\begin{aligned} \sum_{N_B=0}^{\infty} \sum_{\{N_j\}} Q e^{\beta N_B \mu_B} \prod_{j=1} e^{\beta(\mu_j - \mu_0) N_j} \\ = (q_0^{N_I} / N_I!) \left[ 1 + \sum_{j=1} (q_j / q_0) e^{\beta(\mu_j - \mu_0)} \right]^{N_I} \exp\{q_B e^{\beta \mu_B}\}. \end{aligned} \quad (4.17)$$

The sum over  $V$  results in

$$\Gamma(T, P, N_I, \mu_B, \{\mu_j - \mu_0\}) = \left[ \frac{(\sum_{j=0} q'_j e^{\beta(\mu_j - \mu_0)})}{(\beta P - e^{\beta \mu_B} q'_B)} \right]^{N_I}, \quad (4.18)$$

where  $q'$  is defined in Eq. (3.13).

The results for the thermodynamic quantities are

$$U = \sum_{j=1} \langle N_j \rangle \langle u_j \rangle + \langle N_B \rangle \langle u_B \rangle, \quad (4.19)$$

$$\beta P \langle V \rangle = N_I + \langle N_B \rangle, \quad (4.20)$$

$$\mu_0 = -kT \ln(q'_0 kT / y_0 P), \quad (4.21)$$

and

$$r_j = \langle N_j \rangle / N_I = \frac{q'_j e^{j\beta \mu_B}}{\sum_{l=0} q'_l e^{l\beta \mu_B}}, \quad (4.22)$$

where we have set

$$\mu_j - \mu_0 = j\mu_B \quad (4.23)$$

for chemical equilibrium. The expressions for the mole fractions,  $r_j$ , within the homologous series group are the most important result. The partition function in the denominator of Eq. (4.22) is important for the calculation of mole fractions. The corresponding thermodynamic equations have been discussed earlier.<sup>1</sup> The extensions of this treatment to more complicated reactions are straightforward.

## V. RETURN TO THERMODYNAMICS

Since the pertinent Legendre transformed Gibbs energy involves the properties of the homologous series group only, it is sometimes useful to write thermodynamic expressions involving properties of the group alone. We shall illustrate the procedure by considering the system in Sec. II at chemical equilibrium.

We write

$$G_1 = N_A \mu_A + N_C (\mu_C - \mu_B), \quad (5.1)$$

which follows from Eq. (2.10). The explicit form of  $G_1$  for ideal gases is

$$\begin{aligned} G_1 &= N_I [r_A \mu_A + r_C (\mu_C - \mu_B)] \\ &= N_I \{r_A \mu_A^0(T) + r_C [\mu_C^0(T) - \mu_B] \\ &\quad + kT(r_A \ln y_A P + r_C \ln y_C P)\}, \end{aligned} \quad (5.2)$$

where  $r_{A,B}$  are defined in Eqs. (3.23) and (3.24), and we have used the ideal gas chemical potentials

$$\mu_i(T, P, y_i) = \mu_i^0(T) + kT \ln y_i P. \quad (5.3)$$

When  $G_1$  is considered to be a function of  $T$ ,  $P$ ,  $N_I$ , and  $\mu_B$ , its total differential is

$$dG_1 = -S dT + V dP + \mu_A dN_I - (N_B + N_C) d\mu_B, \quad (5.4)$$

which is the same as Eq. (2.11).

It is also possible to look on  $G_1$  as a function of  $T$ ,  $N_I$ ,  $\mu_B$ , and  $P_I$ , where

$$P_I = [N_I / (N_I + N_B)] P, \quad (5.5)$$

and  $P_I$  is the partial pressure exerted by the homologous series group. Equation (5.2) can be written

$$\begin{aligned} G_1 &= N_I \{r_A \mu_A^0(T) + r_C [\mu_C^0(T) - \mu_B] \\ &\quad + kT(r_A \ln r_A P_I + r_C \ln r_C P_I)\}. \end{aligned} \quad (5.6)$$

The total differential of  $G_1$  becomes

$$\begin{aligned} dG_1 &= (\partial G_1 / \partial T)_{P_I, N_I, \mu_B} dT + (\partial G_1 / \partial P_I)_{T, N_I, \mu_B} dP_I \\ &\quad + (\partial G_1 / \partial N_I)_{T, P_I, \mu_B} dN_I \\ &\quad + (\partial G_1 / \partial \mu_B)_{T, P_I, N_I} d\mu_B. \end{aligned} \quad (5.7)$$

The derivatives are easily evaluated from Eq. (5.6) to obtain

$$dG_1 = -S_I dT + V dP_I + \mu_A dN_I - N_C d\mu_B, \quad (5.8)$$

where

$$\begin{aligned} S_I &= -N_I [r_A (d\mu_A^0 / dT) + r_C (d\mu_C^0 / dT) \\ &\quad + k(r_A \ln r_A P_I + r_C \ln r_C P_I)] \\ &= N_I (\bar{S}_I^0 - k \ln P_I). \end{aligned} \quad (5.9)$$

Here

$$\begin{aligned} \bar{S}_I^0 &= -[r_A (d\mu_A^0 / dT) + r_C (d\mu_C^0 / dT) \\ &\quad + k(r_A \ln r_A + r_C \ln r_C)]. \end{aligned} \quad (5.10)$$

The expression for  $\bar{S}_I^0$  has been derived previously.<sup>17</sup>

At constant  $\mu_B$ , the expression for  $dG_1$  contains terms which would appear if the members of the homologous series ( $A$  and  $C$ ) occupied the volume without the presence of  $B$ . At chemical equilibrium, the semigrand partition function for the multistep reaction reduces to

$$\Gamma(T, P, N_I, \mu_B) = \left( \frac{\sum_{j=0} q_j e^{j\beta\mu_B}}{N_I} \right)^{N_I} \quad (5.11)$$

Since  $G_I$  is the characteristic thermodynamic function for  $\Gamma$ ,

$$G_I = -N_I kT \ln \left( \frac{\sum_{j=0} q_j e^{j\beta\mu_B}}{N_I} \right) \quad (5.12)$$

It is important to notice that this has the same form as the expression for the Gibbs energy for a one-component system, where the molecular partition function is replaced by

$$q_I = \sum_{j=0} q_j e^{j\beta\mu_B} \quad (5.13)$$

The fundamental equation yields the following additional relations:

$$S_I = N_I k [T(\partial \ln q_I / \partial T)_{P_I, N_I, \mu_B} + \ln(q_I / N_I)], \quad (5.14)$$

$$\langle V \rangle = N_I kT / P_I, \quad (5.15)$$

$$\mu_I = -kT \ln(q_I / N_I), \quad (5.16)$$

$$r_j = \langle N_j \rangle / N_I = \frac{q_j e^{j\beta\mu_B}}{\sum_{l=0} q_l e^{l\beta\mu_B}}, \quad (5.17)$$

from which the remaining thermodynamic properties can be calculated.

## VI. DISCUSSION

Equilibrium calculations on complex organic systems can be simplified when the chemical potentials of some reactants are known. If enough chemical potentials are specified so that the only remaining intensive variables in the phase-rule sense are temperature and pressure, the remaining reactants become pseudoisomers and the equilibrium distribution is given by an exponential function. The semigrand isobaric partition function yields explicit expressions for the equilibrium mole fractions of the homologous series group in terms of molecular partition functions.

At constant temperature, the equilibrium mole fractions of the pseudoisomer groups are proportional to  $\exp[-\Delta_f G^*(j)/RT]$ . The transformed Gibbs energies of formation,  $\Delta_f G^*(j)$ , are calculated by adjusting the standard Gibbs energies of formation,  $\Delta_f G^\circ(j)$ , of the successive isomer groups to the fixed partial pressure of one of the reactants. After the first couple of isomer groups in a homologous series, it has been found that for the dozen homologous series studied,<sup>18</sup> the  $\Delta_f G^\circ(j)$  component of this exponential function is a linear function of carbon number, as indicated by

$$\Delta_f G^\circ(j) = a + bn_j, \quad (6.1)$$

where  $n_j$  is the carbon number. This indicates that the molecular partition function  $q$  for an isomer group at a particular temperature is multiplied by a constant factor in going from one isomer group to the next higher isomer group. This is one of the advantages in considering isomer groups in a homologous series. Although the successive isomer groups have decreasing equilibrium mole fractions, the mass fraction may go through a maximum.<sup>19</sup>

Hill<sup>10</sup> has shown that the grand canonical ensemble can be applied to a single protein molecule  $P$ , immobile or freely moving in solution, that binds a ligand  $L$ . For this case the  $N_2$  in the grand canonical ensemble can only have the values  $N_2 = 0$  (site empty) or  $N_2 = 1$  (site occupied by  $L$ ). When  $N_2 = 0$ , the canonical ensemble partition function is  $q_P$ , the molecular partition function for the protein. When  $N_2 = 1$ , the canonical ensemble partition function is  $q_{LP}$ , the molecular partition function for the  $LP$  complex. Thus the grand canonical partition function becomes  $\xi = q_P + q_{LP} \times \exp(\mu_L/kT)$ , where  $\xi$  is used as a reminder that this is a small system. This method may also be used to derive the equations given here.

## ACKNOWLEDGMENT

This research was supported by a grant from Basic Energy Sciences of the Department of Energy (Grant No. DE-FG02-85ER13454).

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