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Use of the fundamental equation to derive expressions for the transformed Gibbs energy, entropy, and enthalpy of a gaseous reaction system at a specified partial pressure of a reactant

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When the chemical potentials or partial pressures of some reactants are externally fixed, a Legendre transform can be used to define a new thermodynamic potential that provides the criterion of equilibrium and leads to a new fundamental equation that provides the means for computing the equilibrium composition and deriving equations for the transformed thermodynamic properties of the equilibrium system. This method is applied to a simple system and to the polymerization of the alkylbenzenes in the presence of ethylene, which involves an infinite number of isomer groups.

I. INTRODUCTION

Chemical equilibrium is generally considered at a specified temperature and pressure, and so the Gibbs energy is the criterion of equilibrium; $(dG)_{T,P} \leq 0$. However, there are many situations in which it is of interest to choose temperature, pressure, and the partial pressure (or concentration) of a reactant as independent variables. Alberty and Oppenheim¹ considered the alkylation of benzene by ethylene in the ideal-gas phase and showed how a Legendre transform can be used to define a new thermodynamic potential G' that is at a minimum at equilibrium: $(dG')_{T,P,P_e} \leq 0$, where P_e is the specified partial pressure of ethylene. Then they² treated the statistical mechanics of this system by use of a semigrand ensemble and continued the thermodynamic treatment by showing how the fundamental equation of thermodynamics in terms of the transformed Gibbs energy G' can be used to derive the expressions for the other transformed thermodynamic properties of the system in terms of molar thermodynamic properties or molecular partition functions of the various species. This more recent work was all done by specifying the chemical potential of a reactant at equilibrium. However, the chemical potential of a reactant is not a very convenient variable from an experimental point of view since it is a function of temperature and the specified partial pressure of the reactant, even for systems of ideal gases. When the partial pressure of a reactant is chosen as an independent variable, rather than its chemical potential, the fundamental equation for G' and the expressions for the transformed thermodynamic properties of the system are all changed. This article is concerned with these changes. A simple reaction system is considered before going on to the alkylation of benzene by ethylene.

II. FUNDAMENTAL EQUATION FOR A SIMPLE REACTION SYSTEM AT A SPECIFIED CHEMICAL POTENTIAL OF A REACTANT

The simplest illustration is the following reaction:



The fundamental equation for the Gibbs energy G of an open one-phase system containing species A , B , and C is

$$dG = -SdT + VdP + \mu_A dn_A + \mu_B dn_B + \mu_C dn_C, \quad (2)$$

if only pressure-volume work is involved. For a closed system, $dn_A = dn_B = -dn_C$ so that Eq. (2) can be written as

$$dG = -SdT + VdP + (\mu_A + \mu_B - \mu_C)dn_A. \quad (3)$$

If the system is closed, the criterion of equilibrium is $(dG)_{T,P} \leq 0$. This leads to the well-known criterion for chemical equilibrium,

$$\mu_A + \mu_B = \mu_C. \quad (4)$$

This equation, of course, leads to the equilibrium expression for reaction (1), but we will pursue a different course here, which is applicable to much more complicated systems.

Equation (4) can be substituted into Eq. (2) to obtain the fundamental equation for the system at chemical equilibrium. If we eliminate the chemical potential of C we obtain

$$\begin{aligned} dG &= -SdT + VdP + \mu_A dn_A \\ &\quad + \mu_B dn_B + (\mu_A + \mu_B)dn_C \\ &= -SdT + VdP + \mu_A (dn_A + dn_C) \\ &\quad + \mu_B (dn_B + dn_C). \end{aligned} \quad (5)$$

This is an example of a fundamental equation written in terms of components. The number of components C is given by $N - R$, where N is the number of species and R is the number of independent reactions, provided there are no constraints beyond the element balances. There are three species and one reaction, and so there are two components. They can be considered as the A and B components because the chemical potentials of A and B are involved in the two μdn terms. Equation (5) is an example of the statement by Beattie and Oppenheim³ that the chemical potential of a constituent of a phase when considered to be a species is equal to its chemical potential when considered to be a component. The reduction in the number of terms in the fundamental equation when it

is written in terms of components can be very large; this is of interest for simplifying the thermodynamic treatment of complex systems. If, in addition to reaction (1), there are the reactions $A + 2B = AB_2$, $A + 3B = AB_3$, ..., the number of μdn terms in the fundamental equation in terms of components is still two.

Equation (5) can be integrated at constant T , P , and mole fractions to obtain

$$G = \mu_A(n_A + n_C) + \mu_B(n_B + n_C). \quad (6)$$

This equation indicates that the Gibbs energy of the system at chemical equilibrium at T, P is a function of $(n_A + n_C)$ and $(n_B + n_C)$. Thus, we might as well define two new variables

$$\tilde{n}_I \equiv n_A + n_C, \quad (7)$$

$$\tilde{n}_B \equiv n_B + n_C. \quad (8)$$

At specified μ_B , A and C become pseudoisomers in the sense that the ratio of their partial pressures is a function of temperature only, and so A and C will be referred to as a pseudoisomer group with amount \tilde{n}_I . \tilde{n}_B is the total amount of B in the system, bound and unbound. Equations (5) and (6) can be written for an open system at equilibrium as

$$dG = -SdT + VdP + \mu_A d\tilde{n}_I + \mu_B d\tilde{n}_B, \quad (9)$$

$$G = \tilde{n}_I \mu_A + \tilde{n}_B \mu_B. \quad (10)$$

Now we use the Legendre transform introduced earlier¹ to obtain a new thermodynamic potential, the transformed Gibbs energy G' ,

$$G' \equiv G - (n_B + n_C)\mu_B = G - \tilde{n}_B \mu_B. \quad (11)$$

Taking the differential of Eq. (11) and substituting Eq. (2) yields

$$dG' = -SdT + VdP + \mu_A dn_A + (\mu_C - \mu_B)dn_C - (n_C + n_B)d\mu_B. \quad (12)$$

If the system is closed with respect to A and C , $dn_A = -dn_C$ and

$$dG' = -SdT + VdP + (\mu_A + \mu_B - \mu_C)dn_A - (n_C + n_B)d\mu_B \quad (13)$$

so that the criterion for chemical equilibrium is $(dG')_{T,P,\mu_B} \leq 0$.

We can see from Eq. (4) that at chemical equilibrium the transformed chemical potentials of A and C , that is μ_A and $\mu_C - \mu_B$, respectively, are equal. This is the reason for referring to A and C as pseudoisomers at specified μ_B . The transformed chemical potential of the pseudoisomer group is represented by $\tilde{\mu}_I$,

$$\mu_A = \mu_C - \mu_B = \tilde{\mu}_I. \quad (14)$$

Since A and C have the same transformed chemical potential $\tilde{\mu}_I$ at equilibrium, two of the terms in Eq. (12) can be combined, and, by using definitions (7) and (8), the fundamental equation for the transformed Gibbs energy G' for reaction system (1) can be written for an open system at chemical equilibrium as

$$dG' = -SdT + VdP + \tilde{\mu}_I d\tilde{n}_I - \tilde{n}_B d\mu_B. \quad (15)$$

This equation was derived earlier,² but the symbols used here are slightly different. Thus at specified T, P , and μ_B , the thermodynamic behavior of the reaction system is that of a one-component system.

Beattie and Oppenheim³ have discussed the seven forms of the fundamental equation when nonexpansion work is involved in addition to expansion work. They obtained the various forms by subtracting TS , $-PV$, and $-yX$ one at a time, two at a time, and three at a time from the internal energy. Since $\mu_B \tilde{n}_B$ is a chemical work term, the same pattern is followed here. Since our notation is a little different, the internal energy and its seven transformations, together with their total differentials, are as follows:

$$U, \quad dU = TdS - PdV + \mu_B d\tilde{n}_B + \mu_A d\tilde{n}_I \quad (16)$$

$$U' = U - \tilde{n}_B \mu_B, \quad dU' = TdS - PdV - \tilde{n}_B d\mu_B + \tilde{\mu}_I d\tilde{n}_I \quad (17)$$

$$H = U + PV, \quad dH = TdS + VdP + \mu_B d\tilde{n}_B + \mu_A d\tilde{n}_I \quad (18)$$

$$\dot{H}' = U + PV - \tilde{n}_B \mu_B, \quad dH' = TdS + VdP - \tilde{n}_B d\mu_B + \tilde{\mu}_I d\tilde{n}_I \quad (19)$$

$$A = U - TS, \quad dA = -SdT - PdV + \mu_B d\tilde{n}_B + \mu_A d\tilde{n}_I \quad (20)$$

$$A' = U - TS - \tilde{n}_B \mu_B, \quad dA' = -SdT - PdV - \tilde{n}_B d\mu_B + \tilde{\mu}_I d\tilde{n}_I \quad (21)$$

$$G = U - TS + PV, \quad dG = -SdT + VdP + \mu_B d\tilde{n}_B + \mu_A d\tilde{n}_I \quad (22)$$

$$G' = U - TS + PV - \tilde{n}_B \mu_B, \quad dG' = -SdT + VdP - \tilde{n}_B d\mu_B + \tilde{\mu}_I d\tilde{n}_I. \quad (23)$$

The last two equations are the same as Eqs. (9) and (15).

III. FUNDAMENTAL EQUATION FOR A SIMPLE REACTION SYSTEM AT A SPECIFIED PARTIAL PRESSURE OF A REACTANT

So far, the equations have been completely general, but now we assume the gases are ideal so that there is an explicit relation between μ_i and P_i ,

$$\mu_i = \mu_i^0 + RT \ln P_i. \quad (24)$$

In order to use P_B as an independent variable in the fundamental equation for the transformed Gibbs energy G' , $d\mu_B$ in Eq. (12) is replaced with

$$d\mu_B = \left(\frac{\partial \mu_B}{\partial T} \right)_{P_B} dT + \left(\frac{\partial \mu_B}{\partial P_B} \right)_T dP_B. \quad (25)$$

When the derivatives are taken, this equation becomes

$$d\mu_B = -(\bar{S}_B^0 - R \ln P_B) dT + (RT/P_B) dP_B. \quad (26)$$

When this is substituted in Eq. (12), and some rearrangements are made to eliminate the total pressure P in favor of P_I using

$$P = P_I + P_B \quad (27)$$

and relations between these three pressures and the amounts n_A , n_B , n_C , and \tilde{n}_I , we obtain

$$dG' = -S'dT + VdP_I + \mu_A dn_A + (\mu_C - \mu_B)dn_C - (n_C RT/P_B)dP_B, \quad (28)$$

where S' is the extensive transformed entropy of the system given by

$$S' = S - \bar{n}_B(\bar{S}_B^0 - R \ln P_B). \quad (29)$$

If the system is closed with respect to A and C , $dn_A = -dn_C$ and

$$dG' = -S'dT + VdP_I + (\mu_A + \mu_B - \mu_C)dn_C - (n_C RT/P_B)dP_B, \quad (30)$$

so that the criterion for chemical equilibrium is $(dG')_{T,P_I,P_B} \leq 0$.

At chemical equilibrium in a system that is open, the coefficients of dn_A and dn_C in Eq. (28) are equal to $\tilde{\mu}_I$ so that Eq. (28) can be written as

$$dG' = -S'dT + VdP_I + \tilde{\mu}_I d\bar{n}_I - (n_C RT/P_B)dP_B. \quad (31)$$

Since $\tilde{\mu}_I d\bar{n}_I = \mu_A dn_A + (\mu_C - \mu_B)dn_C$ [see Eqs. (12) and (15)], Eq. (31) can be integrated at constant T , P_I , and P_B to

$$G' = \mu_A n_A + (\mu_C - \mu_B)n_C = \bar{n}_I \{r_A \mu_A^0 + r_C [\mu_C^0 - (\mu_B^0 + RT \ln P_B)] + RT(r_A \ln r_A + r_C \ln r_C) + RT \ln P_I\}, \quad (32)$$

where r_A is the equilibrium mole fraction of A in the A,C pseudoisomer group.

The fundamental equation for G' [Eq. (31)] shows us how to calculate S' , V , and $\tilde{\mu}_I$, by taking derivatives of G' ,

$$S' = -\left(\frac{\partial G'}{\partial T}\right)_{P_I, \bar{n}_I, P_B}, \quad (33)$$

$$V = \left(\frac{\partial G'}{\partial P_I}\right)_{T, \bar{n}_I, P_B}, \quad (34)$$

$$\tilde{\mu}_I = \left(\frac{\partial G'}{\partial \bar{n}_I}\right)_{T, P_I, P_B}. \quad (35)$$

Equation (33) yields the transformed entropy S' ,

$$S' = \bar{n}_I(\bar{S}_I'^0 - R \ln P_I), \quad (36)$$

where the standard transformed molar entropy of the isomer group is given by

$$\bar{S}_I'^0 = r_A \bar{S}_A^0 + r_C [\bar{S}_C^0 - (\bar{S}_B^0 - R \ln P_B)] - R(r_A \ln r_A + r_C \ln r_C), \quad (37)$$

and \bar{S}_I^0 is the standard molar entropy of i . The use of Eq. (34) yields

$$V = \bar{n}_I RT/P_I. \quad (38)$$

The transformed chemical potential of the isomer group is obtained by use of Eq. (35),

$$\tilde{\mu}_I = \tilde{\mu}_I^0 + RT \ln P_I. \quad (39)$$

The standard transformed chemical potential of the isomer group is given by

$$\tilde{\mu}_I^0 = r_A \mu_A^0 + r_C [\mu_C^0 - (\mu_B^0 + RT \ln P_B)] + RT(r_A \ln r_A + r_C \ln r_C). \quad (40)$$

The standard transformed molar enthalpy of the isomer group at chemical equilibrium can be calculated using

$$\bar{H}_I'^0 = \tilde{\mu}_I^0 + T\bar{S}_I'^0, \quad (41)$$

which yields

$$\bar{H}_I'^0 = r_A \bar{H}_A^0 + r_C (\bar{H}_C^0 - \bar{H}_B^0). \quad (42)$$

Equation (40) is of the same form as the equation for the standard chemical potential for an A,C isomer group^{4,5} at a specified temperature; the difference is that the standard transformed chemical potential of isomer C in the equation for an ordinary isomer group is replaced by $[\mu_C^0 - (\mu_B^0 + RT \ln P_B)]$. The standard transformed chemical potential $\tilde{\mu}_I^0$ for a pseudoisomer group at equilibrium at P_B can be calculated from the standard transformed chemical potentials of the two pseudoisomers A and C by use of

$$\tilde{\mu}_I^0 = -RT \ln \{\exp[-(\mu_A^0/RT)] + \exp\{-(\mu_C^0 - (\mu_B^0 + RT \ln P_B))/RT\}\}. \quad (43)$$

The equilibrium mole fractions of A and C are given by

$$r_A = \exp[(\tilde{\mu}_I^0 - \mu_A^0)/RT], \quad (44)$$

$$r_C = \exp[(\tilde{\mu}_I^0 - \mu_C^0 + (\mu_B^0 + RT \ln P_B))/RT]. \quad (45)$$

Equations (40), (37), and (42) can be written in terms of the transformed formation properties $\Delta_f G_i'^0$, $\Delta_f S_i'^0$, and $\Delta_f H_i'^0$ for the pseudoisomer group at P_B and the usual formation properties $\Delta_f G_i^0$, $\Delta_f S_i^0$, and $\Delta_f H_i^0$ for A , B , and C . Thus, if the standard formation properties of the reactants are known, the equilibrium composition and the standard transformed formation properties of the pseudoisomer group can be calculated.

In Eqs. (15) and (35), we have seen two definitions of the chemical potential of an isomer group,

$$\tilde{\mu}_I = \left(\frac{\partial G'}{\partial \bar{n}_I}\right)_{T, P_I, P_B} = \left(\frac{\partial G'}{\partial \bar{n}_I}\right)_{T, P_I, P_B}. \quad (46)$$

IV. FUNDAMENTAL EQUATION FOR A MULTIREACTION SYSTEM AT A SPECIFIED PARTIAL PRESSURE OF A REACTANT

This use of a Legendre transformed Gibbs energy G' to treat a chemically reacting system from the viewpoint of an isothermal-isobaric semigrand ensemble is readily extended to the treatment of equilibrium in a whole homologous series. Alberty and Oppenheim¹ considered the alkylbenzene homologous series $\phi_j = C_j H_{2j-6}$, where $j = 6, 7, 8, \dots$, and ϕ_6 is benzene, ϕ_7 is toluene, ϕ_8 is the xylene isomer group, etc. The reactions are

$$\phi_j + \frac{1}{2}e = \phi_{j+1}, \quad j = 6, 7, 8, \dots, \infty, \quad (47)$$

where e is ethylene. When ethylene is admitted to the system at a specified chemical potential μ_e , the transformed Gibbs energy of the system is defined by

$$G' \equiv G - \bar{n}_e \mu_e, \quad (48)$$

where \bar{n}_e is the total amount of ethylene (free ethylene plus ethylene required to form the alkylbenzenes present) in the system,

$$\bar{n}_e = n_e + \sum_{j=6}^{\infty} (j/2)n_j. \quad (49)$$

The carbon number of the alkylbenzene isomer group is represented by j . When the chemical potential of ethylene is fixed, the successive isomer groups in the alkylbenzene homologous series become pseudoisomers, and it is possible to calculate thermodynamic properties of the alkylbenzene homologous series as a whole under these conditions.

It is convenient to write the fundamental equation for the transformed Gibbs energy using the transformed chemical potential for the alkylbenzene isomer group j defined by

$$\bar{\mu}_j \equiv \mu_j - (j/2)\mu_e, \quad (50)$$

where the $j/2$ comes in because half an ethylene molecule is required to produce the next-higher isomer group. The fundamental equation for the transformed Gibbs energy G' of the alkylbenzene system is given by¹

$$dG' = -SdT + VdP + \sum_{j=6}^{\infty} \bar{\mu}_j dn_j - \bar{n}_e d\mu_e. \quad (51)$$

Integration of this equation at constant T, P, μ_e yields

$$G' = (\mu_6 - 3\mu_e)n_6 + (\mu_7 - \frac{7}{2}\mu_e)n_7 + \cdots. \quad (52)$$

Since the transformed chemical potentials of the successive isomer groups in the homologous series are equal, this equation can be rewritten by incorporating

$$\bar{\mu}_{\text{HSG}} = \bar{\mu}_6 = \bar{\mu}_7 = \cdots, \quad (53)$$

$$\bar{n}_{\text{HSG}} = n_6 + n_7 + \cdots, \quad (54)$$

to obtain for an open system at chemical equilibrium

$$dG' = -SdT + VdP + \bar{\mu}_{\text{HSG}} d\bar{n}_{\text{HSG}} - \bar{n}_e d\mu_e, \quad (55)$$

where HSG is the abbreviation for homologous series group. Equation (55) is equivalent to Eq. (15). When the gases are ideal and the equivalent of Eq. (25) is used, Eq. (55) becomes

$$dG' = -SdT + VdP_{\text{HSG}} + \bar{\mu}_{\text{HSG}} d\bar{n}_{\text{HSG}} - (\bar{n}_{\text{HSG}} \bar{n}/2)(RT/P_e)dP_e, \quad (56)$$

where $\sum j r_j = \bar{n}$ is the average number of carbon atoms in an isomer group of alkylbenzenes. Equation (56) is equivalent to Eq. (28), but HSG replaces I , since the whole homologous series is involved.

Equation (52) can be written in the following form by expressing the chemical potentials in terms of partial pressures:

$$G' = \bar{n}_{\text{HSG}} \left\{ \sum_j r_j [\mu_j^0 - (j/2)(\mu_e^0 + RT \ln P_e)] + RT \sum_j r_j \ln r_j + RT \ln P_{\text{HSG}} \right\}. \quad (57)$$

The standard transformed molar properties of the homologous series group can be calculated by taking the appropriate derivatives of G' . The expressions corresponding with Eqs. (40), (37), and (42) are

$$(\bar{G}'^0)_{\text{HSG}} = \sum r_j [\mu_j^0 - (j/2)(\mu_e^0 + RT \ln P_e)] + RT \sum r_j \ln r_j, \quad (58)$$

$$(\bar{S}'^0)_{\text{HSG}} = \sum r_j [\bar{S}_j^0 - (j/2)(\bar{S}_e^0 - R \ln P_e)] - R \sum r_j \ln r_j, \quad (59)$$

$$(\bar{H}'^0)_{\text{HSG}} = \sum r_j [\bar{H}_j^0 - (j/2)\bar{H}_e^0]. \quad (60)$$

The equilibrium mole fractions r_i can be calculated using extensions of Eqs. (43)–(45). Equations (58)–(60) can be written in terms of standard formation quantities.

V. DISCUSSION

When the equilibrium partial pressure or concentration of a reactant in a reaction system is specified, a new set of standard thermodynamic properties comes into play. These standard transformed properties at specified pressure or concentration of a reactant can be calculated from the usual thermodynamic properties. When a single reaction is at equilibrium at a specified partial pressure of one of the reactants, the system behaves as if it contains a single component. Thus this component (a pseudoisomer group) has a standard transformed molar Gibbs energy $\bar{\mu}_I^0$, standard transformed molar entropy \bar{S}_I^0 , and standard transformed molar enthalpy \bar{H}_I^0 . When the ethylene partial pressure is held constant and a whole homologous series can be formed, the I is replaced by HSG because the successive isomer groups in the homologous series group are pseudoisomers. Thus an equilibrium system with an infinite number of species can be treated thermodynamically as if it was a single component. In applications, $\bar{\mu}_I^0$, \bar{S}_I^0 , and \bar{H}_I^0 are replaced with $\Delta_f G_I^0$, $\Delta_f S_I^0$, or $\Delta_f H_I^0$ or $\Delta_f G_{\text{HSG}}^0$, $\Delta_f S_{\text{HSG}}^0$, and $\Delta_f H_{\text{HSG}}^0$ because the properties of the elements cancel when these quantities are used in a calculation. In fact, chemical reactions can be written in terms of homologous series at a specified partial pressure of ethylene.⁶

These calculations illustrate the usefulness of the fundamental equation of thermodynamics and Legendre transforms in finding equilibrium conditions for choices of independent variables involving the chemical potentials or partial pressures of one or more species. They also show how the number of terms in the fundamental equation of a complex system can be greatly reduced. The fundamental equation for a system at chemical equilibrium can be written in a number of ways. (1) It can be written in terms of species. The number of species may be very large, as, for example, in equilibrium calculations on an organic system at a high temperature. (2) When a system contains isomers, the terms for isomers can be added together because isomers have the same chemical potential at chemical equilibrium. The isomer groups can then be considered to be pseudospecies. (3) The number of terms in the fundamental equation can also be reduced by writing it in terms of the extent of reaction of a set of independent reactions, but this reduction is generally

small. (4) The fundamental equation can also be written in terms of components when the chemical potential or partial pressure of a reactant is specified, and this can cause a very large reduction in the number of terms because the number of components is much smaller, as shown here. (5) The fundamental equation can be written in terms of the specified chemical potentials or partial pressures of certain reactants.

This method has also been applied in calculating the equilibrium distribution of benzene series benzenoid polycyclic aromatic hydrocarbons under flame conditions;⁷ in this case, the equilibrium partial pressures of acetylene and molecular hydrogen are fixed.

Norval *et al.*⁸ have given equilibrium calculations in which the partial pressure of SO₂ or H₂ is specified and have discussed the theory. They refer to the specification of partial pressures of reactants at equilibrium as "equilibrium constraints."

The same considerations apply to solution reactions. For example,⁹ adenosine triphosphate (ATP) exists in a number of ionic forms in aqueous solution at a specified pH and pMg. However, a transformed Gibbs energy G' can be defined and the properties $\Delta_f G'^{\circ}(\text{ATP})$, $\Delta_f S'^{\circ}(\text{ATP})$, and

$\Delta_f H'^{\circ}(\text{ATP})$ can be calculated and used in equilibrium calculations on solutions containing ATP at a specified pH and pMg.

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