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Fundamental equation for systems in chemical equilibrium

Robert A. Alberty and Irwin Oppenheim

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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At constant temperature and pressure, the differential of the Gibbs energy can be written in terms of species, components, extents of reaction, isomer groups, and homologous series groups under specified conditions. The applicability of each of these options in deriving expressions for equilibrium constants and devising other methods for calculating equilibrium compositions is discussed. If one or more reactants are available to a system at a constant chemical potential, their terms can be removed from the summation by use of a Legendre transform to obtain a new thermodynamic potential that is a minimum at equilibrium. This permits the definition of homologous series and other groups that can be used as single terms in the fundamental equation for the purpose of equilibrium calculations. By use of these techniques, calculations can be made on organic systems with indefinitely large numbers of species.

INTRODUCTION

The fundamental equation for the Gibbs energy of an open system consisting of a single homogeneous phase is

$$dG = -SdT + VdP + \sum_{i=1}^N \mu_i dn_i, \quad (1)$$

provided that volume change is the only form of work. The number of species is represented by N . When there are no chemical reactions, the interpretation of this equation is clear, since the summation includes all substances that are added to the system. Of course, ions cannot be added to the system separately because it must remain electrically neutral. When there are chemical reactions and the system is at equilibrium, the differentials dn_i of the amounts of the various species are not independent. Gibbs¹ wrote "we may also form a fundamental equation of different import and containing a smaller number of independent variables, which has reference solely to the final phases of equilibrium." This reduction in the number of terms by use of components has been discussed by Denbigh,² Beattie and Oppenheim,³ and Franzen and Myers.⁴

OPEN SYSTEM WITH CHEMICAL EQUILIBRIUM

When there are chemical reactions in a system at equilibrium, the number of independent composition variables is equal to the number of components, and so the fundamental equation can be written

$$dG = -SdT + VdP + \sum_{i=1}^c \mu_i dn_i^c, \quad (2)$$

where dn_i^c is the differential of the amount of the i th component. The number c of components is equal to the number N of species reduced by the number R of independent reactions among the species, the number m of independent arbitrary constraints on the composition, and by one for electroneutrality, if ions are involved:

$$c = N - R - m(-1). \quad (3)$$

For a given list of species, the number of independent reactions and a suitable set of independent reactions can be ob-

tained by a Gaussian elimination of the formula matrix for the system⁵ or by the method described by Denbigh.² The reduction in the number of terms in the fundamental equation for a system at equilibrium has been illustrated by Beattie and Oppenheim³ and by Franzen and Myers.⁴ Beattie and Oppenheim³ have given general proofs that (1) the chemical potential of a component of a phase is independent of the choice of components and (2) 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. These are the reasons that a superscript c has been left off of the chemical potential in Eq. (2). This reduction in the number of terms in the fundamental equation can be quite large because the number of components is usually equal to the number of elements involved; the principal exception, that gives a smaller number of components, occurs when two or more elements are present in the species with a fixed ratio, so that the combination of two or more elements can be regarded as a pseudoelement. It is often convenient to use elements as components, but c species can be used if they contain all of the elements.

There is another way in which the number of terms in the fundamental equation at equilibrium can be reduced that is especially striking in organic systems with isomerization. The number of isomers increases geometrically after the first several members of a homologous series, and so the number of species in an equilibrium calculation with organic substances at high temperatures, or in contact with an isomerization catalyst, can be very large. When isomers are in equilibrium with each other, they each have the same chemical potential μ_I , and so the contribution of the isomer group to the differential of the Gibbs energy at constant temperature and pressure is given by

$$(dG)_{T,P} = \mu_I dn_1 + \mu_I dn_2 + \cdots + \mu_I dn_{N'} \\ = \mu_I dn_I, \quad (4)$$

where N' is the number of isomers in the isomer group, and the total amount n_I of the isomer group is given by

$$n_I = n_1 + n_2 + \cdots + n_{N'}. \quad (5)$$

Thus,

$$dn_I = dn_1 + dn_2 + \cdots + dn_{N_I} \quad (6)$$

Equation (4) shows that μ_I is also the chemical potential for the whole isomer group. The following derivation of the relation of the chemical potential μ_I of an isomer group of ideal gases to the standard chemical potentials of the individual isomers has been given by Smith and Missen.⁵ The chemical potentials of the individual isomers and the isomer group are given by

$$\mu_i = \mu_i^0 + RT \ln (n_i P / n_i^0), \quad (7)$$

$$\mu_I = \mu_I^0 + RT \ln (n_I P / n_I^0), \quad (8)$$

where P represents P/P^0 , and P^0 is the standard state pressure. The total amount of gas in the system is represented by n_t . Solving these equations for n_i and n_I yields

$$n_i = (n_i/P) \exp[(\mu_i - \mu_i^0)/RT], \quad (9)$$

$$n_I = (n_I/P) \exp[(\mu_I - \mu_I^0)/RT]. \quad (10)$$

Substituting in Eq. (5) and taking the logarithm yields

$$\mu_I^0 = -RT \ln \sum_{i=1}^{N_I} \exp(-\mu_i^0/RT), \quad (11)$$

since $\mu_i = \mu_I$. The equilibrium mole fraction r_i of isomer i within an isomer group can be calculated using

$$r_i = \exp(-\mu_i^0/RT) / \exp(-\mu_I^0/RT). \quad (12)$$

In practice standard Gibbs energies of formation are used instead of standard chemical potentials, and values for the first several isomer groups in a number of homologous series have been calculated.⁶ Although the above derivation applies to a system containing a single isomer group, the fundamental equation can be written for a system containing several isomer groups, and the terms for each isomer group I_i can be replaced by $\mu(I_i)dn(I_i)$ when the isomers are in equilibrium.

CLOSED SYSTEM WITH CHEMICAL EQUILIBRIUM

When a system is closed and chemical reactions occur, the differentials of the amounts of species in Eq. (1) are not all independent, and a transformation can be made to a smaller set of independent variables, the extents ξ of an independent set of chemical reactions. The usual derivation of the general expression for the equilibrium constant is based on Eq. (1) written in terms of the reactants in a single reaction; the dn 's are expressed in terms of the differential of the extent of reaction ξ , and $(dG/d\xi)_{T,P} = 0$ is invoked. When there is only one reaction,

$$n_i = n_i^0 + \nu_i \xi, \quad (13)$$

where n_i^0 is the initial amount of the i th species and ν_i is its stoichiometric coefficient, so that

$$dn_i = \nu_i d\xi. \quad (14)$$

An isomer group at equilibrium can be counted as a single species. Thus, if the species and isomer groups in the equilibrium system are involved in a single reaction, the fundamental equation at constant temperature and pressure can be written

$$(dG)_{T,P} = d\xi \sum_{i=1}^N \nu_i \mu_i. \quad (15)$$

For example, if a system contains the four isomers of butene, the two isomers of butane, molecular hydrogen, and an isomerization catalyst, the fundamental equation at constant temperature and pressure can be written

$$(dG)_{T,P} = \mu(C_4H_8)dn(C_4H_8) + \mu(C_4H_{10})dn(C_4H_{10}) + \mu(H_2)dn(H_2), \quad (16)$$

where the first two terms are for isomer groups. Now if a hydrogenation catalyst is added, the following reaction occurs:



The differentials of the amounts can now be written in terms of the extent of this reaction, and the expression for the equilibrium constant

$$K = P(C_4H_{10})P^0/P(C_4H_8)P(H_2) \quad (18)$$

can be derived in the usual way.

If there is more than one independent reaction in a system, the fundamental equation at equilibrium will involve differentials of R extents of reaction. Denbigh² illustrated this by considering the fundamental equation for a gaseous system containing CO, H₂, H₂O, CH₃OH, and C₂H₆ at equilibrium. He showed how to write the fundamental equation in terms $dn(CH_3OH)$ and $dn(C_2H_6)$, but these differentials should be written $d\xi_1$ and $d\xi_2$ since with five species and two independent reactions, there are three independent components.

Transforming to extents of reaction does not significantly reduce the number of terms in the fundamental equation for isomer groups, since if there are 100 isomers, there are 99 independent reactions between them. However, we have seen how to handle isomer groups in the preceding section.

When a system containing N species or isomer groups is closed, and there are R independent reactions between these species and isomer groups, the amounts n_i at a later time are given by

$$n_i = n_i^0 + \sum_{j=1}^R \nu_{ij} \xi_j, \quad i = 1, 2, \dots, N. \quad (19)$$

This set of relations can be written more compactly by use of matrix notation. The amount of substance matrix \mathbf{n} ($N \times 1$) is given by

$$\mathbf{n} = \mathbf{n}^0 + \boldsymbol{\nu} \boldsymbol{\xi}, \quad (20)$$

where \mathbf{n}^0 is the initial amount of substance matrix ($N \times 1$), $\boldsymbol{\nu}$ is the stoichiometric coefficient matrix ($N \times R$), and $\boldsymbol{\xi}$ is the extent of reaction matrix ($R \times 1$). Thus,

$$d\mathbf{n} = \boldsymbol{\nu} d\boldsymbol{\xi}. \quad (21)$$

The fundamental equation for the Gibbs energy at constant temperature and pressure can be written

$$(dG)_{T,P} = \boldsymbol{\mu} \boldsymbol{\nu} d\boldsymbol{\xi}, \quad (22)$$

where $\boldsymbol{\mu}$ is the vector ($1 \times N$) of chemical potentials for the system. There are R terms in the fundamental equation when there is equilibrium and the system is closed with respect to the addition of reactants. In order for the system to be in equilibrium, it is necessary for the coefficient of each of these terms to be equal to zero.

In complex systems, quantitative calculations of equi-

librium compositions can be made by minimizing the Gibbs energy by using the Newton-Raphson method with Lagrange multipliers to bring in the element balance equations^{5,7} or solution of the simultaneous set of independent equilibrium expressions.⁵

SYSTEM WITH A FIXED PARTIAL PRESSURE OF A REACTANT AT CHEMICAL EQUILIBRIUM

A reactant can be provided to a system at a specified partial pressure by use of a semipermeable membrane. This type of system is more familiar in the grand canonical ensemble of statistical mechanics than in thermodynamics, but it is useful in thermodynamics as well when a reactant is at constant partial pressure. This reactant does not literally have to be brought into the system through a semipermeable membrane in the experimental situation, but it can be formed by other chemical reactions in the system that are not under consideration.

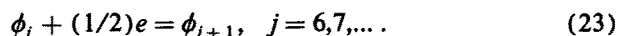
One application of this concept is in calculations on the processing of petroleum. Krambeck^{8,9} has pointed out that when the partial pressure of hydrogen is fixed, adjusted Gibbs energies of formation of hydrocarbons can be used to calculate the equilibrium distribution at that partial pressure of hydrogen. The adjustment is made by changing the standard state pressure of hydrogen in the formation reaction of the hydrocarbon to the specified value, while the standard state pressure of the hydrocarbon is kept at 1 bar. This has been illustrated by calculations on mixtures of alkanes, alkenes, and alkylbenzenes.¹⁰ This technique can be extended to reactants that are not elements. For example, equilibrium compositions within whole homologous series can be calculated by fixing the partial pressure of ethylene. For a calculation of the equilibrium distribution of alkylbenzene isomer groups, the independent variables are usually taken to be T , P , and H/C . However, if the alkylbenzenes are in equilibrium with ethylene, it may be more practical to take the independent variables as T , P , and $P(C_2H_4)$. Equilibrium distributions have been calculated in this way¹¹ for alkylbenzenes, and it has been shown that analytic expressions for the equilibrium distributions of isomer groups in homologous series can be derived when the standard Gibbs energies of successive isomer groups are a linear function of carbon number.¹² Chelugot, Missen, and Smith¹³ have shown how compositional constraints can be applied by developing a compatible stoichiometric coefficient matrix and adjusting standard Gibbs energies of formation for the fixed value of the concentration of the species held constant.

When a substance is available to a system through a semipermeable membrane, it need not be represented by a term in the summation in the fundamental equation. This is accomplished by defining a new thermodynamic potential by using a Legendre transform.^{3,14-17} Wyman^{18,19} has used Legendre transforms to develop thermodynamic potentials especially suited by the treatment of the binding of ligands by a polyfunctional macromolecule. For a total differential expression for a thermodynamic potential with N variables, there are $2^N - 1$ possible Legendre transformations; this is illustrated by the transformations of U to H , A , and G for a closed system with only PV work and by the seven Legendre

transformations of U for a one-component system of variable size with only PV work.¹⁷ For a multicomponent system, N can be very large, and so a very large number of new thermodynamic potentials can be defined, each of which contains all the thermodynamic information on the system.

For a system containing a whole homologous series at equilibrium, the Gibbs energy is a minimum at a given T , P , and H/C ratio. But, for calculation of the equilibrium distribution at a specified chemical potential of ethylene, we need the thermodynamic potential that is a minimum when the variables are T , P , and $\mu(C_2H_4)$. Since there are now three pairs of conjugate variables, there are seven possible Legendre transforms. If $n_1 \mu_1$, where ethylene is considered to be species 1, is subtracted from U , H , A , and G , the new potentials are designated U_1 , H_1 , A_1 , and G_1 , following Beattie and Oppenheim.³

We consider a system containing the ideal gases ethylene(e) and the alkylbenzene homologous series $\phi_j = C_jH_{2j-6}$, where $j = 6, 7, 8, \dots$, and ϕ_6 is benzene, ϕ_7 is toluene, γ_8 is the xylene isomer group, etc. The temperature, total pressure, and partial pressure of ethylene are fixed. The chemical reactions in this system are



The differential of the Gibbs energy at constant temperature and pressure is given by

$$(dG)_{T,P} = \mu_e dn_e + \sum_{j=6}^{\infty} \mu_j dn_j. \quad (24)$$

At equilibrium,

$$\mu_j + (1/2)\mu_e = \mu_{j+1}, \quad (25)$$

and at fixed T, P, μ_e , the values of μ_j and μ_{j+1} differ by a constant. It is convenient to define the quantity $\tilde{\mu}_j$ by

$$\begin{aligned} \tilde{\mu}_j &\equiv \mu_j - (j/2)\mu_e \\ &= \mu_j^0 - (j/2)\mu_e + RT \ln P_j \\ &\equiv \mu_j^* + RT \ln P_j, \end{aligned} \quad (26)$$

where P_j is the partial pressure of ϕ_j and μ_j^* is defined by this equation. The chemical potential $\tilde{\mu}_j$ is independent of j .

Equation (24) can now be rewritten

$$(dG)_{T,P} = \mu_e d\tilde{n}_e + \sum_{j=6}^{\infty} \tilde{\mu}_j dn_j, \quad (27)$$

where

$$d\tilde{n}_e = dn_e + \sum_{j=6}^{\infty} (j/2)dn_j. \quad (28)$$

The desired thermodynamic potential G_1 is obtained by making the following Legendre transform of the Gibbs energy:

$$G_1 \equiv G - \tilde{n}_e \mu_e, \quad (29)$$

which means that

$$(dG_1)_{T,P,\mu_e} = \sum_{j=6}^{\infty} \tilde{\mu}_j dn_j. \quad (30)$$

Thus,

$$\left(\frac{\partial G_1}{\partial n_j} \right)_{T,P,\mu_e,n_{i \neq j}} = \tilde{\mu}_j. \quad (31)$$

Since $\tilde{\mu}_j$ is independent of j , Eq. (27) can be written

$$(dG)_{T,P} = \mu_e d\tilde{n}_e + \mu_{\text{HSG}} d\tilde{n}_{\text{HSG}}, \quad (32)$$

where

$$\mu_{\text{HSG}} = \tilde{\mu}_j \quad (33)$$

and

$$d\tilde{n}_{\text{HSG}} = \sum_j dn_j. \quad (34)$$

Here the subscript HSG refers to the homologous series group of alkylbenzenes. Equation (30) becomes

$$(dG_1)_{T,P,\mu_e} = \mu_{\text{HSG}} d\tilde{n}_{\text{HSG}}. \quad (35)$$

The number of components of this system is two, but when μ_e is specified there is only one component. Following the arguments in connection with Eqs. (4)–(12), we write

$$\begin{aligned} \mu_{\text{HSG}} &= \mu_{\text{HSG}}^* + RT \ln y_{\text{HSG}} P \\ &= \mu_j^* + RT \ln y_j P, \end{aligned} \quad (36)$$

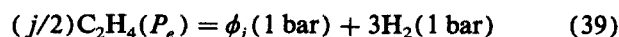
where y_{HSG} is the mole fraction of the homologous series group in the system, and y_j is the mole fraction of ϕ_j . Thus,

$$\mu_{\text{HSG}}^* = -RT \ln \sum_{j=6}^{\infty} \exp(-\mu_j^*/RT), \quad (37)$$

and the mole fraction of isomer group j in the homologous series group is given by

$$r_j = n_j/\tilde{n}_{\text{HSG}} = \exp[(\mu_{\text{HSG}}^* - \mu_j^*)/RT]. \quad (38)$$

μ_j^* can be written in terms of the Gibbs energies of formation, $\Delta_f G^*(j)$, for the reactions



so that

$$\begin{aligned} \Delta_f G^*(j) &= \mu_j^* = \Delta_f G^0(j) - (j/2) \\ &\quad \times [\Delta_f G_e^0 + RT \ln P_e], \end{aligned} \quad (40)$$

where $\Delta_f G_e^0$ is the standard Gibbs energy of formation of ethylene. Equation (37) can then be rewritten

$$\Delta_f G^*(\text{HSG}) = -RT \ln \sum_{j=6}^{\infty} \exp[-\Delta_f G^*(j)/RT]. \quad (41)$$

However, there is an important difference between this equation and Eq. (11). The partition function for an isomer group has a finite number of terms, but the partition function in Eq. (41) has an infinite number of terms, and may blow up. In calculating isomer group thermodynamic properties for a number of homologous series, it has been found that the standard Gibbs energy of formation of isomer groups in the homologous series increases with carbon number and becomes a linear function of carbon number after the first couple of isomer groups. Thus, the series in Eq. (41) converges at ethylene partial pressures below some critical value.¹² At ethylene partial pressures below this critical value, the equilibrium mole fraction of the j th isomer group in the homologous series is given by

$$\begin{aligned} r_j &= \exp[-\Delta_f G^*(j)/RT] / \\ &\quad \exp[-\Delta_f G^*(\text{HSG})/RT]. \end{aligned} \quad (42)$$

The average number of carbon atoms in a molecule of alkyl-

benzene at a specified partial pressure of ethylene is given by

$$N = \sum_{j=6}^{\infty} jr_j. \quad (43)$$

If a system contains alkylbenzenes, alkanes, and alkenes, all in equilibrium with ethylene, the differential of the transformed Gibbs energy at constant temperature and pressure is given by

$$\begin{aligned} (dG_1)_{T,P,\mu_e} &= \mu(\text{alkben}) d\tilde{n}(\text{alkben}) + \mu(\text{alka}) d\tilde{n}(\text{alka}) \\ &\quad + \mu(\text{alke}) d\tilde{n}(\text{alke}). \end{aligned} \quad (44)$$

As shown earlier,²⁰ an equilibrium constant expression can be derived for the reaction

$$\begin{aligned} (1/Q)\text{C}_Q\text{H}_{2Q} &= [3/(3M+N)]\text{C}_M\text{H}_{2M+2} \\ &\quad + [1/(3M+N)]\text{C}_N\text{H}_{2N-6}, \end{aligned} \quad (45)$$

where M , N , and Q are the average numbers of carbon atoms per molecule in the alkane, alkylbenzene, and alkene homologous series. The equilibrium constant expression is obtained by replacing the $d\tilde{n}$'s in Eq. (44) with the corresponding expression in terms of the extent of reaction (45).

SYSTEM WITH FIXED PARTIAL PRESSURES OF MORE THAN ONE REACTANT AT CHEMICAL EQUILIBRIUM

The techniques of the previous section can be applied when more than one reactant is available at a fixed chemical potential. A place where this approach can be used is provided by a near-sooting benzene flame.²¹ In the lower part of the flame where the benzene partial pressure is decreasing slowly with height from the top of the burner, benzenoid polycyclic aromatic hydrocarbons are formed, presumably, by the addition of acetylene and the production of hydrogen. The chemical thermodynamic properties of the first six isomer groups of the benzene series (C_6H_6 , C_{10}H_8 , $\text{C}_{14}\text{H}_{10}$, $\text{C}_{18}\text{H}_{12}$, $\text{C}_{22}\text{H}_{14}$, and $\text{C}_{26}\text{H}_{16}$) have been estimated²² using Benson group values of Stein and Fahr²³ for temperatures from 298.15 to 3000 K. Since the chemical thermodynamic properties are very nearly linear in carbon number, the chemical thermodynamic properties of higher isomer groups may be estimated by linear extrapolation. The benzene series is only a small fraction of the benzenoid polycyclic aromatic hydrocarbons formed in flames, but it is desirable to consider the thermodynamics of subsystems that may be treated in semiisolation from each other.

It is known that polycyclic aromatic hydrocarbons grow in some regions of flames and "crack" in others. The first several isomer groups in the benzene series are of special interest because the synthesis of all larger polycyclic aromatic hydrocarbons must go through these species. Therefore, conditions for growth in the benzene series are especially important for the initiation of polymerization. Since the molecules in the benzene series are closely related, it is of interest to calculate their equilibrium distribution under flame conditions.

According to the phase rule, such a one-phase system has three independent intensive variables. These are normally thought of as temperature, pressure, and H/C ratio, but this is not a practical choice for calculating equilibrium com-

positions of mixtures of benzenoid polycyclic aromatic hydrocarbons in flames. Although temperatures and partial pressures of a number of species have been measured along the axes of several flames, the sum of the pressures of the benzenoid polycyclic aromatic hydrocarbons and the gross H/C ratio of this population are now known. Since data are available on the partial pressures of hydrogen and acetylene in some flames and since these substances are believed to be involved in the polymerization and cracking reactions, a practical choice of the three intensive variables required by the phase rule is temperature, partial pressure of acetylene, and partial pressure of hydrogen. In other words, the system of polycyclic aromatic hydrocarbons is considered to be in material contact with a reservoir containing acetylene and hydrogen.

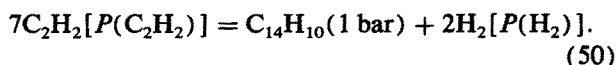
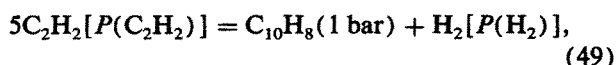
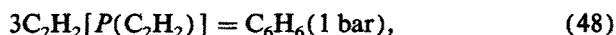
Since the temperature and partial pressures of acetylene and hydrogen have been measured along the axes of certain flames,²¹ they can be taken as given, and the partial pressures of the various isomer groups of polycyclic aromatic hydrocarbons can be calculated on the basis of the assumption that higher isomer groups are in equilibrium with benzene, which is the fuel. This calculation can be made most conveniently by use of a new thermodynamic potential G_{12} that is minimized at constant temperature, pressure, and specified chemical potentials of acetylene and hydrogen. This is accomplished by using the following Legendre transform of the Gibbs energy:

$$G_{12} = G - \tilde{n}(\text{C}_2\text{H}_2)\mu(\text{C}_2\text{H}_2) - \tilde{n}(\text{H}_2)\mu(\text{H}_2). \quad (46)$$

The fundamental equation for this transformed Gibbs energy at constant temperature, pressure, and chemical potentials of acetylene and hydrogen is

$$(dG_{12})_{T,P,\mu(\text{C}_2\text{H}_2),\mu(\text{H}_2)} = \sum_{i=6}^{\infty} \mu_i dn_i, \quad (47)$$

where the summation includes isomer groups of polycyclic aromatic hydrocarbons and excludes acetylene and hydrogen. The standard transformed Gibbs energies of formation of the successive isomer groups in the benzene series under the specified conditions can be calculated from the following formation reactions:



For example, the transformed Gibbs energy of formation of naphthalene is given by

$$\begin{aligned} \Delta_f G_{12}^*(\text{C}_{10}\text{H}_8) &= \Delta_f G^0(\text{C}_{10}\text{H}_8) - 5[\Delta_f G^0(\text{C}_2\text{H}_2) \\ &\quad + RT \ln P(\text{C}_2\text{H}_2)] + RT \ln P(\text{H}_2). \end{aligned} \quad (51)$$

The use of transformed Gibbs energies of formation of this type yields Eqs. (41) and (42) again. It is important to note that the partition function blows up for certain combinations of $P(\text{C}_2\text{H}_2)$ and $P(\text{H}_2)$. If the pressure of acetylene is high enough, successive isomer groups in a homologous series each become more stable, and there is no equilibrium distri-

bution if the whole "homologous" series is included.

Since 4 conjugate pairs are involved in the fundamental equation, the formulas of Beattie and Oppenheim³ indicate 96 reciprocity relations, 4 C_p equations, 4 C_v equations, 8 Gibbs-Helmholtz equations in A , and 8 Gibbs-Helmholtz equations in G .

DISCUSSION

The thermodynamics potentials G_1 and G_{12} are not required for thermodynamic calculations, in the same sense that the enthalpy, Helmholtz energy, and Gibbs energy are not required. All thermodynamic questions can be answered by use of the internal energy and the entropy. However, Legendre transforms are useful for defining thermodynamic potentials that are more convenient under certain circumstances. The new thermodynamic potentials described here are convenient for calculations of equilibrium distributions when one or more reactants are available at constant chemical potentials. These thermodynamic potentials contain all of the thermodynamic information about a system, and so enthalpies, entropies, and heat capacities can be obtained by differentiation of the expressions given for $\Delta_f G_1^0$ and $\Delta_f G_{12}^0$.

ACKNOWLEDGMENT

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