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New fundamental equations of thermodynamics for systems in chemical equilibrium at a specified partial pressure of a reactant and the standard transformed formation properties of reactants

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When temperature, pressure, and the partial pressure of a reactant are fixed, the criterion of chemical equilibrium can be expressed in terms of the transformed Gibbs energy G' that is obtained by using a Legendre transform involving the chemical potential of the reactant that is fixed. For reactions of ideal gases, the most natural variables to use in the fundamental equation are T, P', and P_B, where P' is the partial pressure of the reactants other than the one that is fixed and P_B is the partial pressure of the reactant that is fixed. The fundamental equation for G' yields the expression for the transformed entropy S', and a transformed enthalpy can be defined by the additional Legendre transform $H' = G' + TS'$. This leads to an additional form of the fundamental equation. The calculation of transformed thermodynamic properties and equilibrium compositions is discussed for a simple system and for a general multireaction system. The change, in a reaction, of the binding of the reactant that is at a specified pressure can be calculated using one of the six Maxwell equations of the fundamental equation in G'.

I. INTRODUCTION

When a system involves many thousands of species, calculations of chemical equilibrium compositions are best made using some kind of aggregation. Isomers can always be aggregated because their distribution is a function of temperature only in an ideal gas system. When species are aggregated in a complex system, there are at least two questions. One is whether the aggregation is correct thermodynamically, and the other is how to calculate the various thermodynamic properties for the aggregated pseudospecies. When it is possible, one of the available approaches is to make calculations at specified partial pressures (or concentrations) of one or more reactants. This can lead to a very large reduction in the number of pseudospecies in a calculation. The fundamental equation of thermodynamics for the reaction system has a term for the reactant at the known partial pressure that can be removed by use of a Legendre transform involving the chemical potential of that reactant. Alberty and Oppenheim[1] used this procedure to treat the alkylation of benzene by ethylene at a specified partial pressure of ethylene. They[2] went on to use a semigrand isothermal–isobaric partition function to treat chemical equilibrium in a system consisting of species AB_j, $j = 0, 1, 2,...$, with B at a specified partial pressure. More recently, they[3] have given the four forms of the fundamental equation for a system in which the reaction $A + B = C$ occurs at a specified chemical potential of B. These additional four forms of the fundamental equation are related to the additional four forms given by Beattie and Oppenheim[4] for a system involving nonexpansion work in addition to expansion work. The alkylation of benzene to produce the whole alkylbenzene homologous series was then treated using the fundamental equation for the transformed Gibbs energy G' in terms of T, P', and P_B, where P' is the partial pressure of the reactants other than

B and P_B is the partial pressure of the reactant at known partial pressure. This is a more natural set of variables than T, P, and μ_B. When the partial pressure of a reactant is known at chemical equilibrium, it is as if the reaction system is connected with a reservoir of that reactant through a semipermeable membrane. This treatment is extended here to a general multireaction system and to specifying the equilibrium pressures (concentrations) of more than one reactant.

II. FUNDAMENTAL EQUATIONS FOR THE TRANSFORMED GIBBS ENERGY AND THE TRANSFORMED ENTHALPY OF A SIMPLE REACTION SYSTEM

In order to describe chemical equilibrium for the reaction $A + B = C$ in the ideal gas phase at a specified chemical potential of reactant B, Alberty and Oppenheim[3] used the following Legendre transform to obtain a transformed Gibbs energy G', which can be used to express the criterion of equilibrium under these conditions,

$$G' \equiv G - (n_B + n_C)\mu_B = G - n_B'\mu_B. \tag{1}$$

Here n_B' is the total amount of B in the system (bound and unbound). They showed that the fundamental equation for the transformed Gibbs energy can be written in terms of S, T, P, V, n_B', μ_B, μ_I', and n_I', where I refers to the A, C pseudoisomer group, which has transformed chemical potential μ_I' and amount n_I'. From an experimental point of view, it is more convenient to write the fundamental equation for G' in terms of S', P', and P_B, rather than S, P, and μ_B. The fundamental equation for G' for this simple system is[3]

$$dG' = -S' \, dT + V \, dP' - (n_C RT/P_B)dP_B + \mu_A \, dn_A$$

$$+ (\mu_C - \mu_B)dn_C, \tag{2}$$

where the transformed entropy S' of the system is defined by

$$S' \equiv S - n_B' \bar{S}_B, \tag{3}$$

and $\bar{S}_B$ is the partial molar entropy of B. The partial pressure P' of the reactants other than B is defined by

$$P' = P_A + P_C = P - P_B. \tag{4}$$

The integration of Eq. (2) at constant T, P', P_B, and composition yields

$$G' = n_A \mu_A + n_C(\mu_C - \mu_B), \tag{5}$$

which suggests that the transformed Gibbs energy of the system can be written in terms of transformed chemical potentials μ_A' and μ_C' of the pseudoisomers A and C.

$$G' = n_A \mu_A' + n_C \mu_C', \tag{6}$$

where $\mu_A' = \mu_A$ and $\mu_C' = \mu_C - \mu_B$. Looking ahead to systems that involve more species of the type AB_2, AB_3,..., this equation can be written

$$G' = \sum_{j=1}^{N(\text{iso})} n_j \mu_j', \tag{7}$$

where the pseudoisomer group includes $N(\text{iso})$ species. The transformed chemical potential of a species at a specified chemical potential of B is given by

$$\mu_j' = \mu_j - N_{Bj}\mu_B, \tag{8}$$

where N_{Bj} is the number of molecules of B in species j. This equation is similar to Eq. (1), but it does not involve the amount n_B of unbound B.

Since the single-reaction system contains a single pseudoisomer group, dividing Eq. (6) by $n_A + n_C = n_I$ yields the expression for the transformed chemical potential of the pseudoisomer group,

$$\mu_I' = r_A \mu_A' + r_C \mu_C', \tag{9}$$

where r_A is the mole fraction of A within the A,C pseudoisomer group. For a pseudoisomer group of the type A, AB, AB_2,..., the transformed chemical potential of a pseudoisomer group is given by

$$\mu_I' = \sum_{j=1}^{N(\text{iso})} r_j \mu_j'. \tag{10}$$

Substituting Eq. (7) yields

$$\mu_I' = \sum_{j=1}^{N(\text{iso})} r_j \mu_j - \mu_B \sum_{j=1}^{N(\text{iso})} r_j N_{Bj} = \mu_I - \bar{N}_{BI}\mu_B, \tag{11}$$

where μ_I is the chemical potential of the pseudoisomer group and $\bar{N}_{BI}$ is the average number of B molecules in a molecule of the pseudoisomer group. So far we have not said anything about chemical equilibrium.

When reaction $A + B = C$ is at chemical equilibrium, $\mu_A + \mu_B = \mu_C$, and so the transformed chemical potentials in Eq. (6) are equal and can be referred to as the transformed chemical potential μ_I' of the A,C pseudoisomer group,

$$\mu_A' = \mu_C' = \mu_I'. \tag{12}$$

Thus Eq. (6) can be written

$$G' = (n_A + n_C)\mu_I' = n_I' \mu_I', \tag{13}$$

where the amount of the pseudoisomer group is given by $n_I' = n_A + n_C$. Thus at chemical equilibrium, fundamental Eq. (2) can be written as

$$dG' = -S' \, dT + V \, dP' - (n_C RT/P_B)dP_B + \mu_I' \, dn_I'. \tag{14}$$

The transformed chemical potential μ_I' of a pseudoisomer group is defined by Eq. (12), but for equilibrium calculations it needs to be expressed in terms of the equilibrium mole fractions r_{Aeq} and r_{Ceq} within the A,C pseudoisomer group at P_B. Applying Eq. (9) yields

$$\mu_{Ieq}' = r_{Aeq}\mu_A' + r_{Ceq}\mu_C', \tag{15}$$

where (5,6)

$$r_{Aeq} = \exp[(\mu_I'^0 - \mu_A^0)/RT], \tag{16}$$

and the standard transformed chemical potential of the pseudoisomer group is given by

$$\mu_I'^0 = -RT \ln(\exp[-(\mu_A^0/RT)]$$
$$+ \exp\{-[\mu_C - (\mu_B^0 + RT \ln P_B)]/RT\}). \tag{17}$$

After Eq. (8), we noted that μ_j' does not involve n_B, but the transformed Gibbs energy G' of the system does. When we substitute Eq. (11) in Eq. (13), we obtain

$$G' = n_I'\mu_I - n_I'\bar{N}_{BI}\mu_B, \tag{18}$$

where μ_I is the chemical potential of the pseudoisomer group. The Gibbs energy of the system can be written

$$G = (n_A + n_C)(r_A\mu_A + r_C\mu_C) + n_B\mu_B = n_I'\mu_I + n_B\mu_B. \tag{19}$$

Eliminating the first terms between Eqs. (18) and (19) yields

$$G' = G - (n_B + n_I'\bar{N}_{BI})\mu_B, \tag{20}$$

which is the same as the Legendre transform in Eq. (1).

It is convenient to consider a system with a single isomer group I, but Eq. (13) can be generalized to the consideration of system with N' pseudoisomer groups by writing,

$$G' = \sum_{i=1}^{N'} n_i'\mu_i'. \tag{21}$$

Since the entropy of the simple system is given by

$$S = n_A\bar{S}_A + n_B\bar{S}_B + n_C\bar{S}_C, \tag{22}$$

Eq. (3) shows that the transformed entropy of the system is given by

$$S' = n_A\bar{S}_A + n_C(\bar{S}_C - \bar{S}_B). \tag{23}$$

The form of this equation suggests that the transformed entropy of the system can be written in terms of molar transformed entropies $\bar{S}_A'$ and $\bar{S}_C'$ of reactants A and C,

$$S' = n_A \bar{S}'_A + n_C \bar{S}'_C. \tag{24}$$

In this equation

$$\bar{S}'_A = \bar{S}_A$$

and

$$\bar{S}'_C = \bar{S}_C - \bar{S}_B, \tag{25}$$

as indicated by Eq. (23). Thus the transformed entropy of the system is additive in the transformed entropies of A and C, which are transformed by subtracting the contribution of B that is contained in A and contained in C. This shows that there are transformed entropy equations analogous to Eqs. (7)–(11). The previous paper[3] showed that differentiating G' with respect to T at specified P', P_B, and n'_I also yields Eq. (3).

Since Eq. (14) is a fundamental equation, we can use a further Legendre transform to define the transformed enthalpy H',

$$H' \equiv G' + TS'. \tag{26}$$

The fundamental equation for the transformed enthalpy is obtained by taking the differential of Eq. (26) and substituting Eq. (14) to obtain

$$dH' = T\,dS' + V\,dP' - (n_C RT/P_B)dP_B + \mu'_I\,dn'_I. \tag{27}$$

The expression for the transformed enthalpy H' of the system can be calculated using Eq. (26) since $G' = G - n'_B \mu_B$ [Eq. (1)] and $S' = S - n'_B \bar{S}_B$ [Eq. (3)]. This yields

$$H' = H - n'_B \bar{H}^0_B, \tag{28}$$

where

$$H = n_A \bar{H}^0_A + n_B \bar{H}^0_B + n_C \bar{H}^0_C. \tag{29}$$

The superscripts indicating standard states are used because the enthalpy of an ideal gas is independent of its pressure. Thus the transformed enthalpy of the system is given by

$$H' = n_A \bar{H}^0_A + n_C(\bar{H}^0_C - \bar{H}^0_B) = n_A \bar{H}'^0_A + n_C \bar{H}'^0_C, \tag{30}$$

where an analog of Eqs. (25) is used to define standard transformed molar enthalpies of A and C. This shows that there are enthalpy equations analogous to Eqs. (7)–(11). The expressions for H' can also be obtained by using the Gibbs–Helmholtz equation in G' and H'.

Although thermodynamic derivations are carried out using the molar thermodynamic properties μ_i, $\bar{S}_i$, and $\bar{H}_i$, these quantities can be replaced in actual calculations by the corresponding formation properties $\Delta_f G_i$, $\Delta_f S_i$, and $\Delta_f H_i$, where

$$\Delta_f G_i = \Delta_f G^0_i + RT \ln P_i, \tag{31}$$

$$\Delta_f S_i = \Delta_f S^0_i - R \ln P_i, \tag{32}$$

$$\Delta_f H_i = \Delta_f H^0_i, \tag{33}$$

where the superscripts indicate the standard state properties. The partial pressures are understood to be ratios of the pressure to the standard state pressure P^0 so that they are dimensionless. The standard transformed thermodynamic properties can be calculated from formation reactions written with B at P_B on the left-hand side in place of some of the elements required to form species i. Equations (16) and (17) are then used to calculate the standard transformed properties of the pseudoisomer groups.

III. FUNDAMENTAL EQUATION FOR MULTIREACTION SYSTEMS AT A SPECIFIED PARTIAL PRESSURE OF A REACTANT

Alberty and Oppenheim[3] treated the alkylation of benzene with ethylene and showed that even when there is an infinite number of successive pseudoisomers in the homologous series, the fundamental equation for this system has the same form as Eq. (14); that is, at chemical equilibrium the whole homologous series contributes a single chemical term to the fundamental equation for the transformed Gibbs energy G', and the standard transformed Gibbs energy of the pseudoisomer group can be calculated if the standard Gibbs energies of formation of the species are known or can be estimated. They[3] went on to show how to calculate the standard transformed enthalpy of formation and the standard transformed entropy of formation of the homologous series group. Now we consider a system that may contain a number of homologous series in equilibrium with ethylene or other reactant at a specified partial pressure. As in the previous section, the gases are assumed to be ideal.

Equation (14) can be generalized to apply to a system with an indefinite number of reactants by writing it as follows:

$$dG' = -S'\,dT + V\,dP' - (n_{Bb}RT/P_B)dP_B + \sum_{i=1}^{N'} \mu'_i\,dn'_i, \tag{34}$$

where N' is the number of reactants. Some of these reactants are pseudoisomer groups, but we will see that this equation may include terms for single species. (A species that does not have any pseudoisomers forms a pseudoisomer group of one.) The total amount of B (for example, ethylene) that is bound in the system is represented by n_{Bb}. Note that n_{Bb} is an extensive thermodynamic property of the system on a par with G', S', and V.

The total amount of B bound in the system can be expressed in terms of the amount of pseudoisomer groups,

$$n_{Bb} = \sum_{i=1}^{N'} \bar{N}_{Bi} n'_i, \tag{35}$$

where $\bar{N}_{Bi}$ is the average number of B molecules bound in a molecule in pseudoisomer group i. Note that $\bar{N}_{Bi}$ is a partial molar quantity.

Equation (34) has some other changes from Eq. (14). The definition of S' in Eq. (3) is changed to

$$S' = S - (n_B + n_{Bb})\bar{S}_B, \tag{36}$$

where n_{Bb} is given by Eq. (35). The second term in Eq. (14) is modified by using P' for the sum of the partial pressures of the reactants other than B, so that it is still equal to $P-P_B$.

Now consider a system with two pseudoisomer groups and an additional reactant C,

$$A+B=AB$$
$$+ \qquad +$$
$$C \qquad C$$
$$\| \qquad \|$$
$$AC+B=ABC. \tag{37}$$

When the partial pressure of B is specified, it is convenient to discuss the thermodynamics of this reaction system as the conversion of the A, AB pseudoisomer group into the AC, ABC pseudoisomer group, which can be represented by

$$A, AB+C=AC, ABC. \tag{38}$$

Alternatively, when the partial pressure of C is specified, the system can be discussed as the conversion of the A, AC pseudoisomer group the AB, ABC pseudoisomer group.

The fundamental equation for G' for the system in Eq. (37) at specified P_B can be written as

$$dG'=-S' dT+V dP' -(n_{Bb}RT/P_B)dP_B+\mu'_1 dn'_1$$
$$+\mu'_2 dn'_2+\mu'_3 dn'_3, \tag{39}$$

where the amount of the A, AB pseudoisomer group is represented by $n'_1 = n_A + n_{AB}$, the amount of the AC, ABC pseudoisomer group is represented by $n'_2 = n_{AC} + n_{ABC}$, and the amount of C is represented by $n'_3 = n_C$. The transformed chemical potentials of the three reactants are given by

$$\mu'_i=\mu'^0_i+RT \ln P_i, \tag{40}$$

where $P'=P_1+P_2+P_3$ and μ'^0_1 and μ'^0_2 are given by analogs of Eq. (17) and $\mu'^0_3 = \mu^0_C$. The apparent extent of reaction ξ' is defined in terms of reaction (38), and so Eq. (39) can be written

$$(dG')_{T,P',P_B}=-\mu'_1 d\xi'+\mu'_2 d\xi' -\mu'_3 d\xi'$$
$$=(\mu'_2-\mu'_1-\mu'_3)d\xi'. \tag{41}$$

At chemical equilibrium, $(dG'/d\xi')_{T,P',P_B} = 0$, and so

$$\mu'_1+\mu'_3=\mu'_2. \tag{42}$$

Substituting Eq. (40) yields

$$K'=P_2/P_1P_3=\exp(-\Delta_r G'^0/RT), \tag{43}$$

where the apparent equilibrium constant K' for reaction (38) is a function of T, P', and P_B, and $\Delta_r G'^0 = \mu'^0_2 - \mu'^0_1 - \mu'^0_3$. The temperature coefficient of K' yields $\Delta_r H'^0$, and $\Delta_r G'^0=\Delta_r H'^0-T\Delta_r S'^0$ yields $\Delta_r S'^0$. If the P_C is specified rather than P_B, the equations will have this same general form, but K' will be a function of T, P', and P_C.

Equation (39) can be generalized to cover any single reaction between pseudoisomer groups. When this is the case, the dn'_i can be written as $\nu'_i d\xi'$, where ν'_i is the apparent stoichiometric number of reactant i in the reaction written in terms of pseudoisomer groups [cf., Eq. (38)], and ξ' is the extent of reaction of this reaction. Equation (39) for a one-reaction system can now be written as

$$dG'=-S' dT+V dP' -(n_{Bb}RT/P_B)dP_B+\Delta_r G' d\xi', \tag{44}$$

where the transformed reaction Gibbs energy is given by $\Delta_r G' = (\partial G'/\partial\xi)_{T,P',P_B} = \Sigma\nu'_i\mu'_i$.

Equation (44) leads to six Maxwell equations, of which we will consider two. The first is

$$-\frac{RT}{P_B}\left(\frac{\partial n_{Bb}}{\partial\xi'}\right)_{T,P',P_B} =\left(\frac{\partial\Delta_r G'}{\partial P_B}\right)_{T,P',\xi'}. \tag{45}$$

The change in binding of B in the reaction, that is $(\partial n_{Bb}/\partial\xi')$, can be represented by $\Delta_r n_{Bb}$ in analogy with $\Delta_r G'$. However, a better symbol for this quantity is probably $\Delta_r N_B$ because the change in binding of B in the reaction is dimensionless. The $\Delta_r G'$ on the right-hand side of Eq. (45) can be replaced by $\Delta_r G'^0$ because $\Delta_r G'=\Delta_r G'^0+RT \ln Q$, where Q is the reaction quotient, which can be written in terms of ξ' and is held constant. Thus, Eq. (45) can be written as

$$\Delta_r N_B=-\frac{P_B}{RT}\left(\frac{\partial\Delta_r G'^0}{\partial P_B}\right)_{T,P'} =\left(\frac{\partial \ln K'}{\partial \ln P_B}\right)_{T,P'}, \tag{46}$$

where $\Delta_r G'^0 = -RT \ln K'$ and K' is the apparent equilibrium constant for the reaction written in terms of homologous series. Thus the change in binding of B in the reaction can be determined by measuring K' at a series of P_B. Since $\Delta_r N_B$ is a reaction property, it is given by

$$\Delta_r N_B= \sum_{i=1}^{N'} \nu'_i\bar{N}_{Bi}, \tag{47}$$

where $\bar{N}_{Bi}$, the average binding of B in pseudoisomer group i, is defined by $\Sigma r_j N_{Bj}$. The applicability of this type of equation to any extensive thermodynamic property is discussed by Haase.[7]

The second Maxwell equation from Eq. (44) to be considered involves the transformed entropy S',

$$-\left(\frac{\partial S'}{\partial\xi'}\right)_{T,P',P_B} =\left(\frac{\partial\Delta_r G'}{\partial T}\right)_{P',P_B,\xi'} =-\Delta_r S'. \tag{48}$$

Since the reaction quotient Q is independent of temperature,

$$\Delta_r S'^0=-\left(\frac{\partial\Delta_r G'^0}{\partial T}\right)_{P',P_B} =\Sigma\nu'_i\bar{S}'^0. \tag{49}$$

Using Eq. (26),

$$\Delta_r H'^0=\Delta_r G'^0+\Delta_r S'^0=\Sigma\nu'_i\Delta_f H'^0. \tag{50}$$

For consideration of the thermodynamics of a multireaction system at specified partial pressure of B, the summation in Eq. (34) can be arranged into groups of terms,

with each group of terms corresponding with an independent reaction. If there is a large number of pseudoisomer groups, there will be a large number of possible sets of independent reactions, and any set is suitable for thermodynamic calculations. In order to discuss the arrangement of the terms for reactants in Eq. (34) so that the minimization of G' can be discussed in terms of a set of R' independent reactions, it is convenient to write it in matrix notation.[8,9] Equation (34) can be written in matrix notation as

$$dG' = -S'dT + VdP' - (n_{Bb}RT/P_B)dP_B + \underline{\mu}' d\underline{n}', \quad (51)$$

where $\underline{\mu}'$ is the $1 \times N'$ transformed chemical potential matrix and $\underline{n}'$ is the $N' \times 1$ amount of reactant (sum of species) matrix. The amount of reactant matrix can be written in terms of the apparent extent of reaction matrix $\underline{\xi}'$, which is $R' \times 1$, by use of

$$\underline{n}' = \underline{n}_0' + \underline{v}'\underline{\xi}', \quad (52)$$

where $\underline{n}_0'$ is the initial amount of reactant matrix and $\underline{v}_i'$ is the $N' \times R'$ apparent stoichiometric number matrix. This leads to

$$dG' = -S' \, dT + V \, dP' - (n_{Bb}RT/P_B)dP_B + \underline{\mu}'\underline{v}' \, d\underline{\xi}'. \quad (53)$$

The apparent stoichiometric number matrix $\underline{v}'$ can be obtained from the apparent conservation matrix $\underline{A}'$ by calculating the null space.[5,9] The apparent conservation matrix $\underline{A}'$ can be calculated from the conservation matrix $\underline{A}$ by subtracting from each column an integer times the atomic composition of B that corresponds to the number of B molecules bound in a species. The redundant columns and rows are then deleted to obtain the apparent conservation matrix $\underline{A}'$. Since $\underline{\mu}'$ is $1 \times N'$ and $\underline{v}'$ is $N' \times R'$, $\underline{\mu}'\underline{v}'$ involves R' terms. The condition for chemical equilibrium is that each of these R' terms be equal to zero. Thus reactions can be written in terms of pseudoisomer groups.[10] The apparent conservation matrix may include conditions implicit in the mechanism, as shown, for example, for the polymerization of the polycyclic aromatic hydrocarbons.[11]

IV. DISCUSSION

When the partial pressure of a reactant in a system containing a large number of species is specified, a number of the species become pseudoisomers at chemical equilibrium; that is, their relative mole fractions become functions of temperature only. Terms for pseudoisomers in the fundamental equation can be collected together because the transformed Gibbs energies G' of the pseudoisomers in a group are equal at chemical equilibrium. This may greatly reduce the number of terms in the fundamental equation for a complex system. The number of terms in the fundamental equation can be further reduced to the number R' of independent reactions between pseudoisomer groups by using extents of reactions ξ' of the R' independent reactions in terms of pseudoisomer groups. The apparent number of reactions R' is smaller than the actual number R of reactions because the R' reactions are reactions involving homologous series groups. For a complex system, there are many choices of sets of independent apparent reactions, each of which is suitable for thermodynamic calculations.

The discussions here have been concerned with systems in which the equilibrium partial pressure of one reactant is specified, but a Legendre transform can be used to specify several reactant partial pressures. In considering the polymerization of polycyclic aromatic hydrocarbons in the gas phase, the equilibrium partial pressures of acetylene and molecular hydrogen or acetylene, molecular hydrogen, and atomic hydrogen have been specified.[11]

Wyman and Gill[12] have used Legendre transforms in studying the binding properties of hemoglobin, and Leikin, Rau, and Parsegian[13] have used Legendre transforms in studying DNA in aqueous solution. This device is especially useful in studying equilibria in systems of enzyme-catalyzed reactions because such reactions are generally studied at a specified pH and pMg.[14–16]

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