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Citation: [The Journal of Chemical Physics](#) **84**, 917 (1986); doi: 10.1063/1.450537

View online: <http://dx.doi.org/10.1063/1.450537>

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Analytic expressions for the equilibrium distributions of isomer groups in homologous series

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(Received 22 August 1985; accepted 3 October 1985)

The equilibrium distribution of isomer groups in a homologous series is a function of the ratio of the number of hydrogen atoms to the number of carbon atoms at a given temperature and is independent of the pressure, except for homologous series with the molecular formulas $C_n H_{2n}$. Alternatively, the distribution can be taken to be a function of the equilibrium partial pressure of ethylene for all homologous series. An advantage of using the partial pressure of ethylene as the independent variable is that the equilibrium distribution can be expressed as an analytic function of the carbon number at higher carbon numbers. The distribution functions have been derived for the alkanes and alkenes for the case that the standard Gibbs energies of formation of the isomer groups are a linear function of carbon number. Experimentally it is found that a linear relation is approached as the carbon number is increased. Expressions are derived for the mean carbon number and the carbon number contributing the largest weight fraction for given conditions, without calculating the whole distribution using a general equilibrium program.

INTRODUCTION

As a result of catalytic reactions in complicated organic mixtures the isomer groups in a homologous series may be in equilibrium with each other at a given temperature and pressure, especially at high temperatures. When large numbers of species, isomer groups, and homologous series are at equilibrium it is difficult to get an overview and to predict what will happen when conditions are changed. DeDonder¹ pointed out the usefulness of probability density functions in such calculations. This approach has been used a good deal recently in vapor-liquid calculations,² and we³ have shown how this approach, commonly referred to as continuous thermodynamics, may be used to calculate the equilibrium distribution within an isomer group. This type of approach has the advantage of focusing attention on the parameters of the distribution, rather than on the equilibrium mole fractions of individual molecular species. This paper presents the derivation of analytic functions for equilibrium distributions of mole fractions and weight fractions of isomer groups in the alkane and alkene homologous series for the case that the Gibbs energy of formation is a linear function of carbon number. The data on these and other homologous series show that all the thermodynamic properties of isomer groups become a linear function of carbon number as the carbon number increases. These distributions lead to simple relations for the mean carbon number and the carbon number contributing the largest weight fraction at equilibrium under given conditions.

The problem of calculating equilibrium compositions for complex reaction systems has been solved in the sense there are a number of computer programs^{4,5} that will quickly yield the equilibrium mole fractions of the species defined in terms of their atomic compositions and Gibbs energies of formation at the desired pressure and temperature. However, when there are very many components it is desirable to aggregate species in some ways to make it possible to see the nature of the equilibrium. It has been known for some time that isomer groups can be aggregated in such a calcu-

tion.⁶⁻⁸ The equilibrium distribution within an isomer group can then be calculated in a second step since it is a function only of temperature, for ideal gases. The concept of an isomer group can be extended to a homologous series by using the equilibrium partial pressure of ethylene as the independent variable to describe the degree of alkylation in the homologous series.⁹ Equilibrium compositions within homologous series are usually calculated as a function of the ratio of the number of hydrogen atoms to the number of carbon atoms, except for homologous series with the molecular formulas $C_n H_{2n}$. In general, the equilibrium distribution within a homologous series is not a function of the pressure, but it is for the $C_n H_{2n}$ series. There are two advantages in considering the equilibrium distribution to be a function of the partial pressure of ethylene:

(1) The calculations may be made using equations of the form used to calculate the equilibrium mole fractions within an isomer group.

(2) The degree of alkylation, or polymerization for series with the formula $C_n H_{2n}$, of different homologous series in the mixture may be compared through the equilibrium partial pressure of ethylene. Homologous series in equilibrium with the same partial pressure of ethylene are in equilibrium with each other at the same temperature.

In this article we will see that when the standard Gibbs energies of formation of successive isomer groups in the alkane and alkene homologous series are a linear function in carbon number, as they are above C_3 , the equilibrium mole fractions and weight fractions of successive isomer groups at a particular temperature and partial pressure of ethylene can be expressed as analytic functions of the carbon number. All calculations here are for ideal gases.

CALCULATION OF EQUILIBRIUM DISTRIBUTIONS IN HOMOLOGOUS SERIES USING EQUATIONS APPLICABLE TO ISOMER GROUPS

The standard Gibbs energy of formation $\Delta_f G^\circ(I)$ of an isomer group is calculated from

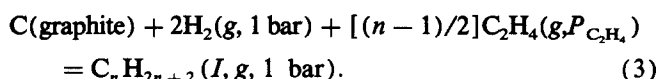
$$\Delta_f G^\circ(I) = -RT \ln \left[\sum_{i=1}^{N_I} \exp(-\Delta_f G_i^\circ/RT) \right], \quad (1)$$

where $\Delta_f G_i^\circ$ is the standard Gibbs energy of formation of isomer i , and N_I is the number of isomers in the isomer group. The equilibrium mole fraction r_i of isomer i in the isomer group is given by

$$r_i = \exp[(\Delta_f G^\circ(I) - \Delta_f G_i^\circ)/RT]. \quad (2)$$

The history of these equations is reviewed by Smith and Missen.⁴

At a fixed partial pressure of ethylene, the successive isomers groups within a homologous series become pseudo-isomers in the sense that their relative mole fractions are a function only of temperature for ideal gases. In order to incorporate the fixed partial pressure of ethylene into the definition of the standard state for an alkane isomer group the formation reaction is written



The Gibbs energy of formation of the isomer group at a fixed partial pressure of ethylene is given by

$$\begin{aligned} \Delta_f G^*[\text{C}_n\text{H}_{2n+2}(\text{I}), P_{\text{C}_2\text{H}_4}] \\ = \Delta_f G^\circ[\text{C}_n\text{H}_{2n+2}(\text{I})] \\ - [(n-1)/2][\Delta_f G^\circ(\text{C}_2\text{H}_4) + RT \ln P_{\text{C}_2\text{H}_4}]. \end{aligned} \quad (4)$$

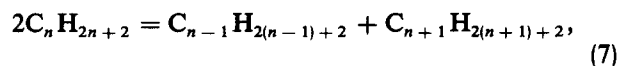
The Gibbs energy of formation of the alkane homologous series group is given by

$$\begin{aligned} \Delta_f G^*(\text{HSG}) = -RT \ln \\ \times \sum_{n=1}^{\infty} \exp\{-\Delta_f G^*[\text{C}_n\text{H}_{2n+2}(\text{I}), P_{\text{C}_2\text{H}_4}]/RT\}. \end{aligned} \quad (5)$$

The equilibrium mole fractions of the successive isomer groups within the homologous series group are given by

$$\begin{aligned} y_n = \exp\{(\Delta_f G^*(\text{HSG}) \\ - \Delta_f G^*[\text{C}_n\text{H}_{2n+2}(\text{I}), P_{\text{C}_2\text{H}_4}])/RT\}. \end{aligned} \quad (6)$$

The equilibrium mole fractions calculated using these equations are independent of the sum of the partial pressures of the members of the homologous series if successive isomer groups have different ratios of the elements, since the equilibria are achieved through disproportionation reactions such as



in which there is no change in the number of molecules.

DISTRIBUTION OF ALKANE ISOMER GROUPS AS AN ANALYTIC FUNCTION OF THE CARBON NUMBER

It is well known that the chemical thermodynamic properties of the *normal* alkanes and alkenes are a linear function of carbon number after the first several members. Although it is less clear that it would necessarily be true, it has been found that the chemical thermodynamic properties of isomer groups become a linear function of carbon number as the carbon number is increased.¹⁰⁻¹² Data on three homologous series are shown in Fig. 1. The points represented by square boxes have been estimated using the Benson meth-

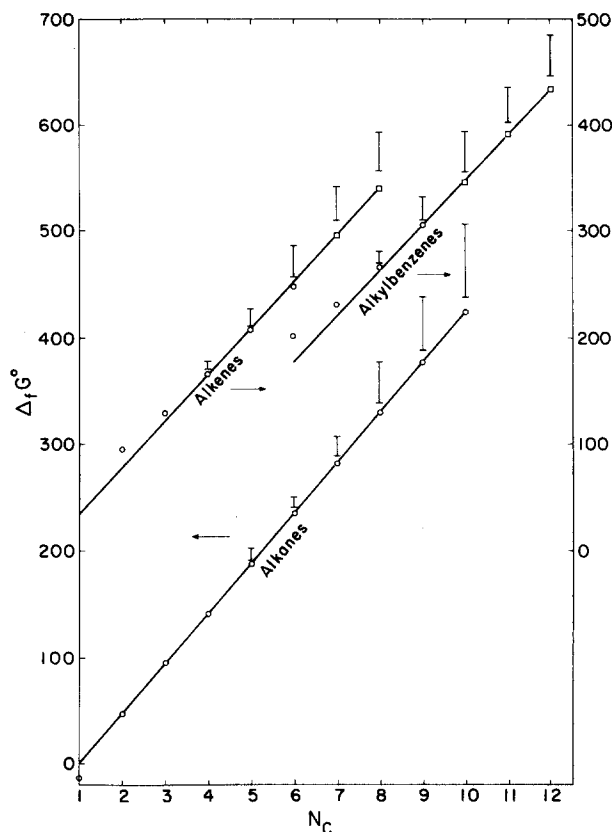


FIG. 1. Standard Gibbs energies of formation of alkane, alkene, and alkylbenzene isomer groups in kJ mol^{-1} for a pressure of 1 bar as a function of carbon number N_c . The ranges show the lowest and highest Gibbs energies for each isomer groups.

od.¹³ When the standard Gibbs energy of formation can be represented by

$$\Delta_f G^\circ(I) = A + Bn, \quad (8)$$

where A and B are empirical constants and n is the carbon number, Eq. (6) can be used to obtain the equilibrium mole fractions of successive isomer groups as an analytic function of carbon number. When this equation applies, the Gibbs energies of formation of the successive isomer groups at a particular partial pressure of ethylene can be written

$$\Delta_f G^*[\text{C}_n\text{H}_{2n+2}(\text{I}), P_{\text{C}_2\text{H}_4}] = a + bn, \quad (9)$$

where

$$a = A + (1/2)\Delta_f G^\circ(\text{C}_2\text{H}_4) + (1/2)RT \ln P_{\text{C}_2\text{H}_4}, \quad (10)$$

$$b = B - (1/2)\Delta_f G^\circ(\text{C}_2\text{H}_4) - (1/2)RT \ln P_{\text{C}_2\text{H}_4}. \quad (11)$$

The Gibbs energy of formation of the homologous series group at this particular partial pressure of ethylene is given by

$$\Delta_f G^*(\text{HSG}) = -RT \ln \sum_{n=1}^{\infty} e^{-(a+bn)/RT}. \quad (12)$$

Fortunately this series can be summed by use of the relation

$$\sum_{n=0}^{\infty} x^n = 1/(1-x) \quad (13)$$

to obtain

$$\Delta_f G^*(\text{HSG}) = a + b + RT \ln(1 - e^{-b/RT}). \quad (14)$$

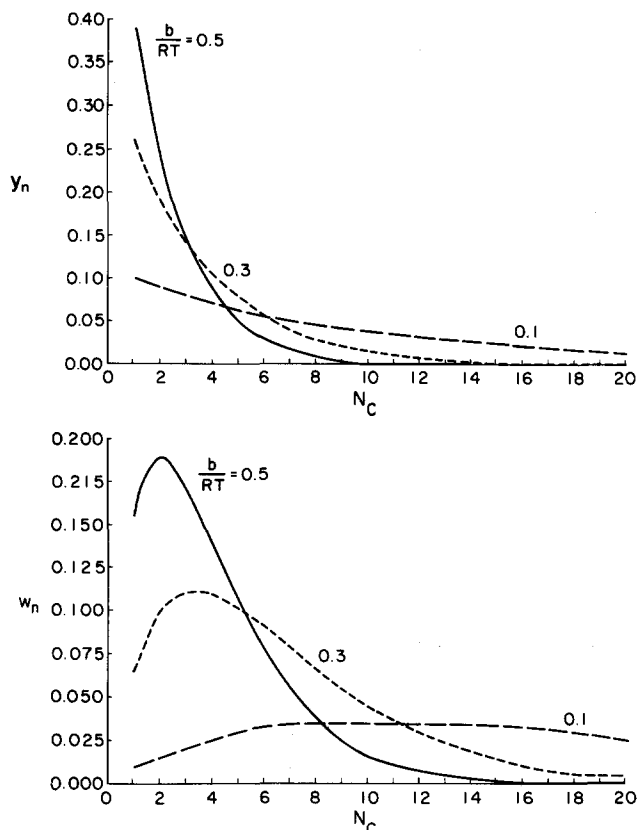


FIG. 2. (a) Distribution of equilibrium mole fractions y_n for the alkanes as a function of carbon number N_C . (b) Distribution of equilibrium weight fractions w_n for the alkanes as a function of carbon number N_C .

Since b must be positive, the Gibbs energy of formation of the homologous series group at a particular partial pressure of ethylene must be less positive than the corresponding Gibbs energy of formation $a + b$ of the first member of the homologous series, in this case methane, at the selected partial pressure of ethylene. The equilibrium mole fraction of the n th isomer group is obtained by substituting Eq. (14) in Eq. (6).

$$y_n = (1 - e^{-b/RT})e^{-(n-1)b/RT}, \quad n \geq 1. \quad (15)$$

Thus the equilibrium mole fractions decrease exponentially with carbon number, according to the value of b , but independent of the value of a . If b is large the equilibrium mole fractions drop off rapidly. As b approaches zero the distributions become flatter, and there is a critical point at $b = 0$.

The mean value \bar{n} of the carbon number of the alkanes at equilibrium at a particular $P_{C_2H_4}$ is given by

$$\bar{n} = \sum_{n=1}^{\infty} n y_n. \quad (16)$$

By use of the relation

$$\sum_{n=1}^{\infty} n x^n = x/(1-x)^2 \quad (17)$$

the series in Eq. (16) may be summed to obtain

$$\bar{n} = (1 - e^{-b/RT})^{-1}. \quad (18)$$

If $b/RT \ll 1$, $\bar{n} = RT/b$. The mean value of the carbon number goes to infinity as b goes to zero. As can be seen from Eq. (11), this occurs when

$$P_{C_2H_4} = \exp\{[2B - \Delta_f G^\circ(C_2H_4)]/RT\}. \quad (19)$$

In view of the wide range of molecular weights involved in a homologous series, the equilibrium weight fraction is often of more interest than the equilibrium mole fraction. Since the analytic expression for the weight fraction in terms of the carbon number is quite complicated, it is more convenient to use the carbon number rather than the mass. This becomes an increasingly good approximation for the weight fraction as the carbon number increases, and so w_n defined as follows will be referred to as the weight fraction.

$$w_n = \frac{n y_n}{\sum_{n=1}^{\infty} n y_n} = \frac{n e^{-bn/RT}}{\sum_{n=1}^{\infty} e^{-bn/RT}}. \quad (20)$$

Using Eq. (17) we obtain

$$w_n = (1 - e^{-b/RT})^2 n e^{-(n-1)b/RT}, \quad n \geq 1. \quad (21)$$

In contrast with the mole fraction, the weight fraction goes through a maximum.

The distribution of equilibrium mole fractions y_n for the alkanes as a function of carbon number is given in Fig. 2(a) for b/RT equal to 0.5, 0.3, and 0.1. The corresponding weight fraction w_n distributions are given in Fig. 2(b).

The carbon number n_{\max} at which w_n is a maximum can be obtained by differentiation, assuming n is a continuous variable.

$$n_{\max} = RT/b = \frac{RT}{B - (1/2)[\Delta_f G^\circ(C_2H_4) + RT \ln P_{C_2H_4}]}. \quad (22)$$

Since methane deviates significantly from the linear relation in Eq. (8), the actual Gibbs energy of formation of methane may be used and the analytic approach can be started with ethane. According to Eq. (4), $\Delta_f G^*(CH_4, P_{C_2H_4}) = \Delta_f G^\circ(CH_4)$. Thus in order to treat methane accurately, Eq. (5) can be written

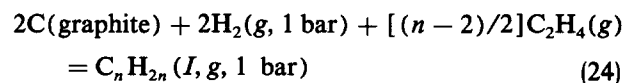
$$\Delta_f G^*(HSG) = -RT \ln \left(e^{-\Delta_f G^\circ(CH_4)/RT} + \sum_{n=2}^{\infty} e^{-(a+bn)/RT} \right). \quad (23)$$

By use of Eq. (13) this equation can be written

$$\Delta_f G^*(HSG) = -RT \ln \left(e^{-\Delta_f G^\circ(CH_4)/RT} + \frac{e^{-(a+2b)/RT}}{1 - e^{-b/RT}} \right).$$

DISTRIBUTION OF ALKENE ISOMER GROUPS AS AN ANALYTIC FUNCTION OF THE CARBON NUMBER

The formation reaction for the alkenes can be written



for $n \geq 2$. The Gibbs energy of formation of the C_nH_{2n} isomer group at a particular partial pressure of ethylene is given by

$$\Delta_f G^*[C_nH_{2n}(I), P_{C_2H_4}] = \Delta_f G^\circ[C_nH_{2n}(I)] - [(n-2)/2][\Delta_f G^\circ(C_2H_4)] + RT \ln P_{C_2H_4}. \quad (25)$$

The Gibbs energy of formation of the alkene homologous

series group at a particular partial pressure of ethylene is given by

$$\Delta_f G^*(\text{HSG}) = -RT \ln \sum_{n=2}^{\infty} \exp\{-\Delta_f G^*[C_n H_{2n}(I), P_{C_2H_4}]/RT\}. \quad (26)$$

In contrast with the alkane homologous series group, the equilibrium distribution in the alkene homologous series group is not independent of the total pressure. The various isomer groups arise in a polymerization reaction



and so the equilibrium composition does depend on the total pressure which may be calculated using

$$P = P_{C_2H_4}/y_2, \quad (28)$$

where y_2 is the equilibrium mole fraction of ethylene calculated using Eq. (6). Thus for the alkene homologous series an iterative calculation is required to obtain the equilibrium mole fractions for the successive isomer groups at a particular total pressure.

If the standard Gibbs energies of the alkene isomer groups are given by Eq. (8) the equilibrium mole fractions of the successive isomer groups and the average number of carbon atoms per molecule are given by

$$y_n = (1 - e^{-b/RT})e^{-(n-2)b/RT}, \quad n \geq 2, \quad (29)$$

$$\bar{n} = \frac{2 - e^{-b/RT}}{1 - e^{-b/RT}}. \quad (30)$$

The equilibrium weight fraction w_n [defined in Eq. (20)] is

$$w_n = \frac{(1 - e^{-b/RT})^2 n e^{-(n-2)b/RT}}{2 - e^{-b/RT}}. \quad (31)$$

The carbon number at which w_n is a maximum is given by Eq. (22). In fact this expression applies to all homologous series. Since ethylene and propylene deviate from the linear relationship, equations can be derived to treat them explicitly and the other isomer groups linearly.

DISCUSSION

In considering chemical equilibrium in complex organic systems containing several homologous series, it is of interest to consider the equilibrium degree of alkylation in various homologous series separately. The equations derived in this article give the equilibrium mole fractions and weight fractions as a function of carbon number when the isomer group Gibbs energies are a linear function of carbon number. This

treatment can be extended to other homologous series and species of lower carbon number can be handled separately, at the cost of complicating the equations. These equations make it possible to calculate the mean carbon number and the carbon number contributing the largest weight fraction at equilibrium.

If the catalyst used does not produce highly branched isomers, for example, the values of A and B in Eq. (10) are affected, and so it is advantageous to have equations such as those derived here which readily show the effects of these changes on the equilibrium distribution within a homologous series.

The use of the partial pressure of ethylene as an independent variable to describe the degree of alkylation in a homologous series has the advantage of indicating the possibility of equilibrium between different homologous series, since homologous series at the same temperature and in equilibrium with the same partial pressure of ethylene are in equilibrium with each other.

ACKNOWLEDGMENTS

This research was supported in part by a grant from Basic Energy Sciences of the Department of Energy and in part by the National Science Foundation under Grant No. CHE 8410682.

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