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Equilibrium distributions of isomer groups in homologous series of hydrocarbons at a specified partial pressure of molecular hydrogen

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The equilibrium distribution of isomer groups within a homologous series at a specified partial pressure of molecular hydrogen is given by a geometric distribution when the standard Gibbs energies of formation of the successive isomer groups in the homologous series are given by $A + Bn$, where n is the carbon number of the isomer group and A and B are functions of temperature only. This distribution depends only on A, the specified partial pressure of molecular hydrogen, and the pressure on the homologous series. This applies to the usual homologous series, where the increment between successive isomer groups is CH_2, and to the benzenoid polycyclic aromatic hydrocarbons, where the increment is C_4H_2. In some homologous series (e.g., alkenes and the coronene series of polycyclic aromatic hydrocarbons) where the successive isomer groups have the same H/C ratio, the equilibrium distribution within the homologous series is, of course, independent of the specified pressure of molecular hydrogen, but the distribution can be calculated in the same way.

INTRODUCTION

For the usual homologous series of hydrocarbons, it has been found[1] that, after the first one or two members, the standard thermodynamic properties of the successive isomer groups are linear functions of the carbon number n. For the benzenoid polycyclic aromatic hydrocarbons, this applies to all members of the homologous series that have been studied. Here, we are especially interested in the standard Gibbs energy of formation of an isomer group $\Delta_f G_n^0$, which is given by

$$\Delta_f G_n^0 = A + Bn, \tag{1}$$

where A and B are functions of temperature only for a given homologous series. When partial pressures of one or more reactants are taken as independent variables for the calculation of the equilibrium distribution within an homologous series, the transformed Gibbs energy[2,3] of formation of an isomer group $\Delta_f G_n^*$ is given by

$$\Delta_f G_n^* = a + bn, \tag{2}$$

where a and b are functions of A and B, respectively, the specified partial pressures of reactants, and the pressure on the homologous series. In all of these calculations, ideal gases are assumed.

When the partial pressure of molecular hydrogen is specified, the calculation of the equilibrium distribution reduces to that for the polymerization of an element.[4,5] Smith and Missen[6] have shown that for the polymerization of an element, the equilibrium chemical potential of an n-mer is proportional to n; thus

$$\mu_n = n\lambda, \tag{3}$$

where λ is a constant. Alberty[4] showed that the equilibrium mole fraction y_n of an n-mer within the alkane homologous series calculated using Eqs. (1)–(3) is a geometric[7] distribution

$$y_n = (1 - q)q^{n-1}, \quad n = 1,2,3,..., \tag{4}$$

where q is equal to $1/[1 + \exp(-a/RT)]$. This is the equilibrium distribution that would be obtained if the alkane homologous series was placed in a reactor with a semipermeable membrane connected to a reservoir of molecular hydrogen at P_{H_2}. The reactor is assumed to contain a catalyst for the formation of all of the isomer groups in the homologous series. The equilibrium composition also depends on P_{hc}, the sum of the partial pressures of the isomer groups, since higher P_{hc} favors polymerization.

For the alkenes and alkynes,[5]

$$y_n = (1 - q)q^{n-2}, \quad n = 2,3,4,..., \tag{5}$$

where q is obtained as a function of a by solving a quadratic equation. The form of Eq. (5) suggests that the ordinal number N of the isomer group in the homologous series should be used since for the alkenes and alkynes $N = n - 1$. Thus, the equilibrium distributions for all three homologous series at specified P_{H_2} and P_{hc} are given by

$$y_N = (1 - q)q^{N-1}, \quad N = 1, 2, 3,.... \tag{6}$$

Of course, the equilibrium distribution of the alkenes does not depend on the partial pressure of molecular hydrogen, but the equilibrium distribution at a specified partial pressure of alkenes can be derived in the same way as the other geometric distributions.

The purpose of this paper is to show how Eq. (6) can be applied to all other homologous series with increments of CH_2 and to all homologous series of benzenoid polycyclic aromatic hydrocarbons, which have increments of C_4H_2 between successive isomer groups. Treatments are given for a generalized homologous series of the usual type and a generalized homologous series of benzenoid polycyclic aromatic hydrocarbons.

EQUILIBRIUM DISTRIBUTIONS OF ISOMER GROUPS IN THE USUAL HOMOLOGOUS SERIES OF HYDROCARBONS AT A SPECIFIED PARTIAL PRESSURE OF MOLECULAR HYDROGEN

As shown in Table I, the molecular formulas of the successive isomer groups in the usual homologous series of hydrocarbons can be represented by $C_n H_{2(n+n')}$, where n is the carbon number and n' is $1, 0, -1, -2, ...$ depending on the homologous series. There is an infinite number of these series.

The generalized formation reaction for the isomer group with n carbons in a particular homologous series at the specified conditions, T, P_{hc}, P_{H_2}, is

$$n C(\text{graphite}) + (n+n') H_2 (P_{H_2}) = C_n H_{2(n+n')} (P_{hc}). \quad (7)$$
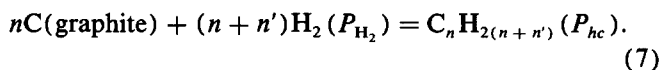
The transformed Gibbs energy of formation is given by

$$\Delta_f G_n^* = \Delta_f G_n^0 + RT \ln P_{hc} - (n+n') RT \ln P_{H_2}. \quad (8)$$

When Eq. (1) is substituted, this equation takes the form of Eq. (2) with

$$a = A + RT \ln P_{hc} - n' RT \ln P_{H_2}, \quad (9)$$

$$b = B - RT \ln P_{H_2}. \quad (10)$$

Following the procedure described earlier,[4] the equilibrium mole fraction y_n for the isomer group with carbon number n within the homologous series is given by

$$y_n = [\exp(a/RT)] x^n, \quad n = n_1, (n_1 + 1), (n_1 + 2), ..., \quad (11)$$

where n_1 is the carbon number of the first member. The sum of the equilibrium mole fractions within a homologous series is given by

$$1 = [\exp(-a/RT)] (x^{n_1} + x^{n_1 + 1} + x^{n_1 + 2} + ...)$$

$$= [\exp(-a/RT)] x^{n_1} (1 + x + x^2 + ...)$$

$$= [\exp(-a/RT)] x^{n_1}/(1-x), \quad (12)$$

where the expression for the sum of the geometric series has been used. The root of

$$[\exp(-a/RT)] x^{n_1} + x - 1 = 0, \quad (13)$$

in the range $0 < x < 1$ can be obtained by an iterative computer program. CENTSECT, an APL program written by Helzer,[8] is convenient for this purpose. Equation (13) has a single root because the first two terms form an increasing function of x with a positive derivative. Eliminating $\exp(-a/RT)$ between Eqs. (11) and (12) yields

$$y_n = (1-x) x^{n-n_1}. \quad (14)$$

Introducing $n = N + n_1 - 1$ yields

$$y_N = (1-x) x^{N-1}, \quad (15)$$

which is equivalent to Eq. (6). Thus Eq. (6) applies to all homologous series of the usual type at a specified partial pressure of molecular hydrogen.

Equation (6) can be interpreted in terms of a very simple model of polymerization in which an increment of CH_2 is added to the first member of a series in successive trials with probability q of addition of a CH_2 group. The probability that the chain ends with $(N-1)$ CH_2 groups added is y_N, independent of the size of the polymer. If the first attempt to add a CH_2 group is unsuccessful, the resulting molecule consists of the first member, which can be represented by C_{n_1}. The probability of this is $y_1 = 1 - q$. Or, if the first trial to add CH_2 is successful, but the second is not, the resulting molecule can be represented by $C_{n_1 + 1}$. This has a probability $y_2 = (1-q)q$. If, in another sequence of trials, the first two attempts are successful and the third is not, which has a probability of $y_3 = (1-q)q^2$, the resulting molecule can be represented by $C_{n_1 + 2}$, and so on. Flory[9] derived this same distribution for condensation polymers on the basis of the principle of equal reactivity of all functional groups; his treatment applies to the kinetics of the polymerization rather than to equilibrium.

Significant polymerization is not obtained when a [see Eq. (9)] is zero or negative, and the degree of polymerization increases with increasingly positive values of a. For the alkene homologous series, the specified partial pressure of molecular hydrogen has no effect on the degree of polymerization.

For the geometric distribution, there are simple expressions for the mean and variance.[7] The mean ordinal number $\bar{N}$ and the variance σ^2 of the ordinal number at equilibrium at the specified partial pressure of molecular hydrogen are given by

$$\bar{N} = 1/(1-q) = 1/(1-x), \quad (16)$$

$$\sigma^2 = q/(1-q)^2 = x/(1-x)^2, \quad (17)$$

where σ is the standard deviation.

EQUILIBRIUM DISTRIBUTION OF ISOMER GROUPS IN HOMOLOGOUS SERIES OF POLYCYCLIC AROMATIC HYDROCARBONS AT A SPECIFIED PARTIAL PRESSURE OF MOLECULAR HYDROGEN

There is an infinite number of series of benzenoid polycyclic aromatic hydrocarbons[10] in which the increment between successive isomer groups is $C_4 H_2$. The molecular formulas of the successive isomer groups for the first six series are given in Table II, where the name of the first member is used to designate the series. Thus the molecular formulas of the successive isomer groups in these homologous series can be represented by $C_n H_{n/2 + n'}$, where n' is a positive or negative integer characteristic of the series. There is an approximate geometric increase in the number of isomers in an isomer group with each addition of $C_4 H_2$. The standard

TABLE I. Molecular formulas of the successive isomer groups of some homologous series of hydrocarbons.

Alkanes	$C_n H_{2(n+1)}$	$n = 1, 2, 3, ...$
Alkenes	$C_n H_{2n}$	$n = 2, 3, 4, ...$
Alkynes	$C_n H_{2(n-1)}$	$n = 2, 3, 4, ...$
Dienes	$C_n H_{2(n-1)}$	$n = 4, 5, 6, ...$
Trienes	$C_n H_{2(n-2)}$	$n = 6, 7, 8, ...$
Alkylbenzenes	$C_n H_{2(n-3)}$	$n = 6, 7, 8, ...$

TABLE II. Molecular formulas of the successive isomer groups for the first six homologous series of benzenoid polycyclic aromatic hydrocarbons.

Benzene	$C_nH_{n/2+3}$	$n = 6,10,14,...$
Pyrene	$C_nH_{n/2+2}$	$n = 16,20,24,...$
Naphthopyrene	$C_nH_{n/2+1}$	$n = 22,26,30,...$
Coronene	$C_nH_{n/2}$	$n = 24,28,32,...$
Naphthocoronene	$C_nH_{n/2-1}$	$n = 30,34,38,...$
Ovalene	$C_nH_{n/2-2}$	$n = 32,36,40,...$

thermodynamic properties of all the isomers in the first several isomer groups of the first six series have been estimated,[1,11,12] for the temperature range 298–3000 K using the Benson[13] group additivity method with parameters of Stein and Fahr.[14] For the twenty isomer groups studied, Eq. (1) is followed, and it has been found that the six series have the same value of A at each temperature.[15]

The generalized formation reaction for the isomer group with n carbon atoms in a particular series at the specified T, P_{hc}, P_{H_2} is

$$nC(\text{graphite}) + (n'/2 + n/4)H_2(P_{H_2})$$
$$= C_nH_{n/2+n'}(P_{hc}). \quad (18)$$
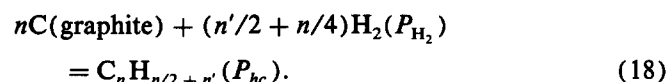
The transformed Gibbs energy of formation $\Delta_f G_n^*$ is given by

$$\Delta_f G_n^* = A + B_i n + RT \ln P_{hc}$$
$$- (n'/2 + n/4)RT \ln P_{H_2}, \quad (19)$$

where B_i is for the ith series. Thus the parameters in Eq. (2) are given by

$$a = A + RT \ln P_{hc} - (n'/2)RT \ln P_{H_2}, \quad (20)$$
$$b = B_i - (1/4)RT \ln P_{H_2}. \quad (21)$$

Equation (20) is different from Eq. (9) because the zeroth member of the series has the composition $H_{n'}$, rather than $H_{2n'}$ for the usual homologous series.

The equilibrium mole fraction y_n for the isomer group with carbon number n is given by

$$y_n = [\exp(-a/RT)]x^n, \quad n = n_1,(n_1 + 4),(n_1 + 8),..., \quad (22)$$

where n_1 is the carbon number of the first member of the homologous series. Following the procedure in the preceding section, the sum of the equilibrium mole fractions within a homologous series is given by

$$1 = [\exp(-a/RT)](x^{n_1} + x^{n_1+4} + x^{n_1+8} + \cdots)$$
$$= [\exp(-a/RT)]x^{n_1}(1 + x^4 + x^8 + \cdots)$$
$$= [\exp(-a/RT)]x^{n_1}/(1 - x^4). \quad (23)$$

The series

$$1/(1 - x^4) = 1 + x^4 + x^8 + \cdots \quad (24)$$

has been used. The root of

$$[\exp(-a/RT)]x^{n_1} + x^4 - 1 = 0, \quad (25)$$

in the range $0 < x < 1$ can be obtained by use of a computer. Eliminating $\exp(-a/RT)$ between Eqs. (22) and (23) and

introducing the ordinal number N of an isomer group in the homologous series with $n = 4N + n_1 - 4$ yields Eq. (6) with

$$q = x^4. \quad (26)$$

Thus the equilibrium distribution of benzenoid polycyclic aromatic hydrocarbons at a specified partial pressure is also given by the geometric distribution, although the increment between successive isomer groups is C_4H_2, the formation reaction is different, and the polynomial equation to be solved for x is different.

For the coronene homologous series, the equilibrium distribution is independent of the specified partial pressure of molecular hydrogen since $n' = 0$ [see Eq. (20)].

The equilibrium distributions of polycyclic aromatic hydrocarbons in the benzene series at various levels in a near-sooting benzene flame have been calculated[16] using both a general equilibrium program, EQUCALC[17] and the geometric distribution.[18]

THE DIFFERENT TENDENCIES OF VARIOUS HOMOLOGOUS SERIES TO POLYMERIZE

The value of a/RT determines the equilibrium extent of polymerization in a homologous series, but the relationship is not simple because a polynomial involving the carbon number of the first member of a series has to be solved and different series start with different carbon numbers. The partial pressure of molecular hydrogen does not affect the equilibrium distributions for the alkenes and for the coronene series since $n' = 0$. The A values for the alkenes at 298, 500, and 1000 K are 55.8, 27.6, and -37.3 kJ mol^{-1}, respectively, so that the degree of polymerization decreases with increasing temperature. The corresponding A values for the benzenoid polycyclic aromatic hydrocarbons are 6.2, 14.7, and 46.1 kJ mol^{-1}, respectively, so that the degree of polymerization of the coronene series increases with increasing temperature. This is illustrated by the remarkable stabilities of the higher benzenoid polycyclic aromatic hydrocarbons in flames.[14,16,18]

DISCUSSION

When the partial pressure of molecular hydrogen is chosen as an independent variable for an equilibrium calculation on hydrocarbons, the equilibrium distribution [Eq. (6)] within a homologous series is given by a geometric distribution when the standard Gibbs energies of formation of the successive isomer groups are given by $A + Bn$, where n is the carbon number. At a given temperature, the distribution depends only on the value of A, P_{H_2}, and the sum of the partial pressures of the isomer groups in the homologous series. Significant polymerization is obtained only for positive a values.

Since specifying the partial pressure of molecular hydrogen reduces the calculation of the equilibrium distribution within an homologous series of hydrocarbons to a pseudo-element polymerization, it is of interest to consider briefly the polymerization of carbon atoms. The standard Gibbs energies of C_1, C_2, C_3, C_4, and C_5 in the gas phase are

given in JANAF.[19] There is an alternation in the stabilities of molecules with even and odd numbers of carbon atoms, but, in a general way, the Gibbs energies increase with carbon number. The approximate A values at 298, 500, and 1000 K are 606, 576, and 505 kJ mol^{-1}, which are very large compared with the A values for the alkenes and for the coronene series. Thus, in the absence of hydrogen, carbon tends to polymerize very strongly.[20]

ACKNOWLEDGMENTS

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