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Analytic expressions for equilibrium distributions of isomer groups in homologous series of alkanes, alkenes, and alkynes at a specified partial pressure of molecular hydrogen

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The chemical equilibrium distributions of isomer groups in a homologous series of hydrocarbons can be calculated at a specified temperature, total pressure, and partial pressure of molecular hydrogen. If 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, the equilibrium distribution is given by an analytic function that depends only on A for ideal gases. The analytic functions for the equilibrium mole fraction distributions y_n and equilibrium mass fraction distributions w_n are derived for the alkanes, alkenes, and alkynes. Equations for the mean carbon number \bar{n} , standard deviation σ , the carbon number n_{\max} at which w_n is a maximum, and the mass-average carbon number \bar{n}_m are also derived.

INTRODUCTION

The intensive state of a gas-phase system containing hydrocarbons in chemical equilibrium with molecular hydrogen can be fixed by specifying T , P , and P_{H_2} , and this has been used for calculations on catalytic naphtha reforming¹ and other complex organic systems.² When the equilibrium partial pressure of molecular hydrogen, or other reactant in the system, is specified, a Legendre transform can be used to define a new thermodynamic potential that is at a minimum at equilibrium.³ However, since molecular hydrogen is an element, it is convenient to fix its partial pressure in an equilibrium calculation by simply changing its standard state pressure to the desired value and adjusting the standard Gibbs energies of formation of the hydrocarbons accordingly. That procedure is followed here and all calculations are restricted to ideal gases. This article is concerned with systems in which the infinite number of species in a single homologous series are in principle present. Such calculations are greatly simplified by using isomer groups that are made up of all of the isomers with a given carbon number in equilibrium with each other. An isomer group can be treated as a single species in an equilibrium calculation and standard thermodynamic properties can be calculated for the isomer group.⁴

In general, the standard chemical thermodynamic properties of isomer groups in a homologous series in the gas phase are linear functions of the carbon number after the first member or two.⁵ Thus the standard Gibbs energies of formation $\Delta_f G_n^0$ of the successive isomer groups in a homologous series are represented pretty well by

$$\Delta_f G_n^0 = A + Bn, \quad (1)$$

where n is the carbon number and A and B are functions of temperature only. Alberty and Oppenheim⁶ showed that when the partial pressure of ethylene is fixed and Eq. (1) is followed, the transformed Gibbs energies of formation of the successive isomer groups in an homologous series at a specified partial pressure of ethylene are given by

$$\Delta_f G_n^* = a + bn, \quad (2)$$

where a and b are now functions of the temperature and the specified partial pressure of ethylene. They showed that in this case the equilibrium mole fractions of the successive isomer groups in the alkane and alkene homologous series at a certain temperature can be represented by analytic functions that depend only on b .

When the partial pressure of molecular hydrogen at equilibrium is specified and equations of the form of Eqs. (1) and (2) are followed, the equilibrium mole fractions of the successive isomer groups in the alkane homologous series are represented by an analytic function⁷ that depends only on a . The purpose of this article is to describe the properties of this distribution and to derive the equilibrium distributions for the alkenes and alkynes.

EQUILIBRIUM MOLE FRACTIONS OF ISOMER GROUPS IN THE ALKANE HOMOLOGOUS SERIES AT A SPECIFIED PARTIAL PRESSURE OF MOLECULAR HYDROGEN

When the partial pressure of hydrogen is fixed for an equilibrium system containing alkanes, the alkanes constitute a single component and so, according to the phase rule, there are just two degrees of freedom T and P . In this case, the calculation of the equilibrium composition becomes the same as the calculation of the equilibrium composition for the polymerization of an element in the gas phase, since molecular hydrogen is supplied to the extent needed. Smith and Missen⁸ have treated the equilibrium polymerization of an element for a finite number of polymers and have shown that at equilibrium

$$\mu_n = n\lambda, \quad (3)$$

where λ is a Lagrange multiplier. Thus the equilibrium chemical potentials of the n mers are integer multiples of a constant at a given temperature.

When the partial pressure of hydrogen is fixed, the formation reaction for an alkane isomer group can be written

$$nC(\text{graphite}) + (n+1)H_2(g, P_{H_2}) \\ = C_n H_{2n+2}(g, P_{hc}), \quad n \geq 1, \quad (4)$$

where g indicates gas. The equilibrium distribution of the isomer groups in the alkane homologous series is dependent on the pressure, and so it is necessary to correct the Gibbs energies of formation to the pressure that the homologous series has at equilibrium; P_{hc} is the sum of the partial pressures of the alkane isomer groups at equilibrium. The "standard" Gibbs energy of formation $\Delta_f G_n^*$ of the n th isomer group under these conditions is

$$\Delta_f G_n^* = \Delta_f G_n^0 + RT \ln(P_{hc}/P^0) \\ - (n+1)RT \ln(P_{H_2}/P^0), \quad (5)$$

where P^0 is the reference pressure (1 bar). Assuming that Eq. (1) is followed, the transformed Gibbs energies of formation are given by an equation of the form of Eq. (2) with

$$a = A + RT \ln[(P - P_{H_2})/P^0] - RT \ln(P_{H_2}/P^0), \quad (6)$$

$$b = B - RT \ln(P_{H_2}/P^0), \quad (7)$$

where $P = P_{H_2} + P_{hc}$. Note that a is a function of the chosen independent variables T , P , and P_{H_2} .

It has been shown⁷ that the equilibrium mole fractions of the successive isomer groups in the alkane homologous series are given by

$$y_n = [\exp(-a/RT)][1 + \exp(-a/RT)]^{-n} \\ = \frac{\exp(-a/RT)}{1 + \exp(-a/RT)} \left[\frac{1}{1 + \exp(-a/RT)} \right]^{n-1}, \\ n = 1, 2, 3, \dots \quad (8)$$

The expression for the equilibrium mole fraction has been written in the second form because this is a geometric distribution,⁹ which is generally written in the form

$$y_n = pq^{n-1}, \quad n = 1, 2, 3, \dots \quad (q = 1 - p). \quad (9)$$

The geometric distribution arises when there are independent trials, each having a probability p of being a success and a probability $q = 1 - p$ of being a failure. The function y_n is the probability that the first success occurs on the n th-independent trial. Thus

$$p = [\exp(-a/RT)]/[1 + \exp(-a/RT)], \quad (10)$$

$$q = 1/[1 + \exp(-a/RT)]. \quad (11)$$

The concept of a sequence of independent trials can be applied to cutting an idealized infinite linear chain of carbon atoms as follows: Starting at the end, we attempt to cut successive bonds. If the first bond is cut, we obtain a molecule with one atom ($n = 1$); $y_1 = p$. If the first bond is not cut, but the second is, we obtain a molecule with two atoms ($n = 2$); $y_2 = p(1 - p)$. If the first two bonds are not cut, but the third is, we obtain a molecule with three atoms ($n = 3$); $y_3 = p(1 - p)^2$. This process is continued and, of course,

$$\sum_{n=1}^{\infty} y_n = 1. \quad (12)$$

Although this simple model yields the same distribution as

Eq. (8), it is important to remember that Eq. (8) is based on an equilibrium calculation that includes all possible isomers of alkanes. Flory¹⁰ has shown that a geometric distribution is obtained for condensation polymers on the basis of the principle of equal reactivity of all functional groups.

If $a = 0$, the probabilities of success and failure are each equal to $1/2$ and $y_n = (1/2)^n$. As a increases from zero, the probability p of a cut decreases and the average carbon number increases. Equation (6) shows that a increases as A increases (when the temperature is changed), the partial pressure P_{hc} of the alkanes is increased, or the partial pressure P_{H_2} of molecular hydrogen is decreased. The effects of the partial pressure of the alkanes and the partial pressure of molecular hydrogen on the distribution are understandable in terms of this oversimplified model, because raising the partial pressure of alkanes reduces the probability that a bond will be cut and reducing the partial pressure of molecular hydrogen reduces the probability that a bond will be cut, since hydrogen is required to react with the dangling bonds after cutting.

The equations for the mean \bar{n} and variance σ^2 of the geometric distribution are well known:⁹

$$\bar{n} = 1/p, \quad (13)$$

$$\sigma^2 = (1 - p)/p^2, \quad (14)$$

where σ is the standard deviation. Thus, the mean carbon number \bar{n} of the alkanes at equilibrium at a specified T, P, P_{H_2} is given by

$$\bar{n} = 1 + \exp(a/RT). \quad (15)$$

The standard deviation σ in the carbon number is given by

$$\sigma = [1 + \exp(-a/RT)]^{1/2} / \exp(-a/RT). \quad (16)$$

At a given T and P , a will be equal to zero for some specified P_{H_2} and then $y_n = (1/2)^n$, as mentioned above. At higher P_{H_2} , a is negative and the higher alkanes cannot exist at equilibrium at significant mole fractions. When P_{H_2} is decreased below that required for $a = 0$, a is positive and the equilibrium mole fractions of the higher isomer groups increase. The distributions of equilibrium mole fractions y_n for the alkanes are shown in Fig. 1 (a) for three values of a/RT . This distribution has the same shape as the distribution at a specified ethylene partial pressure and the values of a/RT in Fig. 1 were chosen to give the same plots as those published earlier⁶ for the distributions at specified ethylene partial pressures. The mean carbon numbers \bar{n} for the three distributions shown in Fig. 1 (a) are 2.54, 3.85, and 10.05. These numbers are analogous to mean molar masses for polydisperse high polymers. The standard deviations for the plots in Fig. 1 (a) are 1.98, 3.32, and 9.98.

Table I shows the partial pressures of molecular hydrogen required to obtain these equilibrium distributions at 500, 1000, and 1500 K at $P = 1$ bar. The parameters A and B in Eq. (1) have been calculated from values in Ref. 5 with the omission of methane since it does not fall on the line. Table I applies to the problem of converting methane directly to higher hydrocarbons in the sense that partial pressures of molecular hydrogen have to be maintained in this range so that it is thermodynamically "downhill" to higher hydrocarbons.

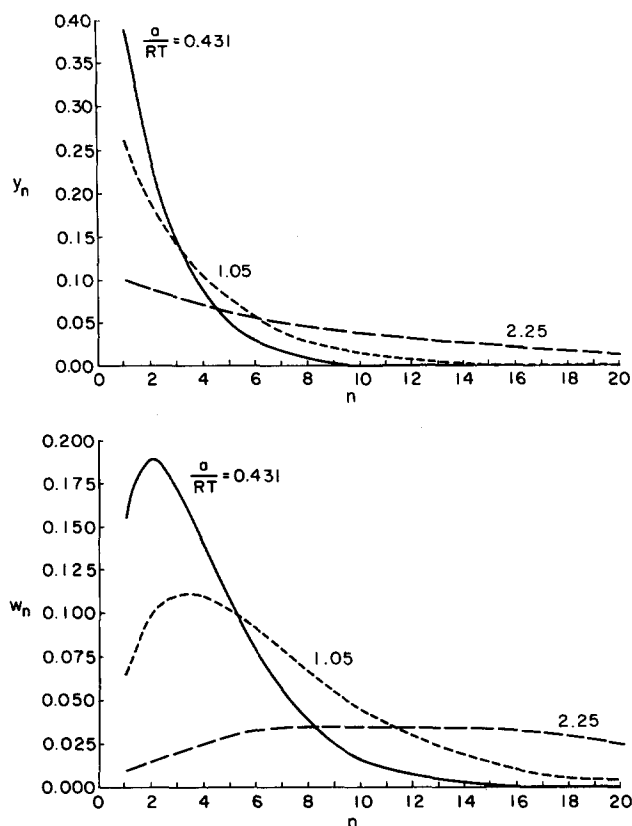


FIG. 1. (a) Distributions of equilibrium mole fractions y_n of alkanes as a function of carbon number n . (b) Distributions of equilibrium mass fractions w_n of alkanes as a function of carbon number n .

EQUILIBRIUM MASS FRACTIONS OF ISOMER GROUPS IN THE ALKANE HOMOLOGOUS SERIES AT A SPECIFIED PARTIAL PRESSURE OF MOLECULAR HYDROGEN

The equilibrium mass fractions w_n of the successive isomer groups of the alkanes are defined by

$$w_n = ny_n / \sum_{n=1}^{\infty} ny_n = ny_n / \bar{n}, \quad (17)$$

TABLE I. Properties of the equilibrium distributions in Fig. 1 and the partial pressures of molecular hydrogen required to give these distributions at a total pressure of 1 bar.

a/RT	0.431	1.05	2.25
Properties of y_n			
\bar{n}	2.54	3.85	10.05
σ	1.98	3.32	9.98
Properties of w_n			
n_{\max}	2	3	10
\bar{n}_m	4.08	6.70	19.10
Partial pressures of molecular hydrogen in bars			
500 K	8.01×10^{-6}	4.31×10^{-6}	1.30×10^{-6}
1000 K	2.28×10^{-3}	1.23×10^{-3}	0.37×10^{-3}
1500 K	16.10×10^{-3}	8.65×10^{-3}	2.61×10^{-3}

if the masses of the hydrogen atoms in the molecules are ignored. Substituting Eqs. (8) and (16) yields

$$w_n = [\exp(-2a/RT)]n[1 + \exp(-a/RT)]^{-(n+1)}. \quad (18)$$

The equilibrium mass fraction distributions for the alkanes are plotted in Fig. 1 (b) for three values of a/RT .

The carbon number n_{\max} at which w_n is a maximum can be obtained by taking ratios:

$$w_{n+1}/w_n = (n+1)q/n < 1 \quad (19)$$

if and only if $n > q/p$. Thus w_n is maximized when n is the smallest integer $\geq q/p = \exp(a/RT)$ and, if $n = q/p$ (an integer), $w_n = w_{n+1}$ are the two maxima. The values of n_{\max} for the distributions in Fig. 1 (b) are 2, 3, and 10.

The quantity that corresponds with the mass-average molar mass, which is used by polymer chemists, is the mass-average carbon number \bar{n}_m for the equilibrium mixture of alkanes, which is defined by

$$\bar{n}_m = \sum_{n=1}^{\infty} nw_n, \quad (20)$$

if the masses of the hydrogen atoms in the molecules are ignored. Substituting Eq. (18) and using

$$\sum_{n=1}^{\infty} n^2 x^n = x(1+x)/(1-x)^3, \quad x < 1 \quad (21)$$

yields

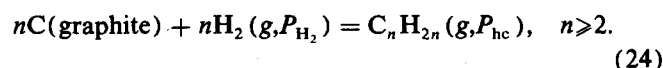
$$\bar{n}_m = 1 + 2 \exp(a/RT). \quad (22)$$

If $a = 0$, $\bar{n}_m = 3$. The mass-average carbon numbers \bar{n}_m for the distributions shown in Fig. 1 (b) are 4.08, 6.70, and 19.10. Note that $\bar{n}_m = 2\bar{n} - 1$. Alternatively, the expression for the mass-average carbon number can be derived by using Eqs. (13) and (14) to find the expectation of the square of the geometric random variable as $\sigma^2 + \bar{n}^2$,

$$\bar{n}_m = (1/\bar{n}) \sum_{n=1}^{\infty} n^2 y_n = (\sigma^2 + \bar{n}^2)/\bar{n}. \quad (23)$$

EQUILIBRIUM DISTRIBUTION OF ISOMER GROUPS IN THE ALKENE HOMOLOGOUS SERIES

The equilibrium distribution of alkene isomer groups is independent of the partial pressure of molecular hydrogen because the isomer groups all have the same H/C ratio, but the equilibrium distribution can be derived in the same way as for the alkanes. The formation of an alkene isomer group at a specified partial pressure of molecular hydrogen can be written as



The transformed Gibbs energies of formation of the successive isomer groups are given by an equation of the form of Eq. (2) with

$$a = A + RT \ln(P_{\text{hc}}/P^0), \quad (25)$$

$$b = B - RT \ln(P_{\text{H}_2}/P^0). \quad (26)$$

Note that a is now a function only of the sum of the partial pressures of the alkenes and is not a function of the specified

partial pressure of molecular hydrogen. In terms of the phase rule, the alkenes constitute a single component if they are in chemical equilibrium, and so there are just two degrees of freedom T and P .

The equilibrium mole fractions are obtained by following the procedure published earlier in the note,⁷ which yields

$$y_n = [\exp(-a/RT)]x^n, \quad n \geq 2, \quad (27)$$

so that

$$\sum_{n=2}^{\infty} y_n = 1 = [\exp(-a/RT)] \sum_{n=2}^{\infty} x^n. \quad (28)$$

Since x is positive and less than unity, the use of

$$\sum_{n=2}^{\infty} x^n = x^2/(1-x), \quad x < 1 \quad (29)$$

yields

$$x = \frac{-1 + \sqrt{1 + 4 \exp(-a/RT)}}{2 \exp(-a/RT)}. \quad (30)$$

Equation (27) can also be written in the form of a geometric distribution starting at 2,

$$y_n = pq^{n-2}, \quad n = 2, 3, \dots \quad (31)$$

with the probability of success given by

$$p = x^2 \exp(-a/RT) = \frac{[-1 + \sqrt{1 + 4 \exp(-a/RT)}]^2}{4 \exp(-a/RT)} = 1 - x, \quad (32)$$

and the probability of failure given by

$$q = 1 - p = \frac{-1 + \sqrt{1 + 4 \exp(-a/RT)}}{2 \exp(-a/RT)} = x. \quad (33)$$

Thus we can also think about the result of an equilibrium polymerization of alkenes as being obtained from the simple model described for the alkanes after Eq. (11). If we start with an infinitely long alkene with the double bond between the first and second carbon atoms and attempt to cut bonds after the first, the probability of getting C_2H_4 is $y_2 = p$, the probability of getting C_3H_6 is $y_3 = p(1-p)$, the probability of getting C_4H_8 is $y_4 = p(1-p)^2$, etc. The thermodynamic calculation is concerned with isomer groups and not just linear alkenes. The probability of cutting a bond in this model is dependent only on T and P_{hc} [Eq. (25)], since A is a function of temperature.

The distributions of equilibrium mole fractions y_n for the alkenes are shown in Fig. 2 (a) for $a/RT = 1$ and $a/RT = 2$. The partial pressures of alkenes corresponding with these values of a/RT at 500, 600, and 700 K are given in Table II. These values have been calculated from standard Gibbs energies of formation of the alkenes isomer groups¹¹ using only the values for C_4H_8 to C_8H_{16} , since ethylene and propylene do not follow the linear relationship. The probabilities p of cutting bonds in the model are 0.222 for $a = 1$ and 0.108 for $a = 2$.

The mean carbon number \bar{n} of the alkenes, defined by Eq. (10), except that the lower limit is now $n = 2$, can be calculated by using

$$\sum_{n=2}^{\infty} nx^n = x^2(2-x)/(1-x)^2, \quad x < 1 \quad (34)$$

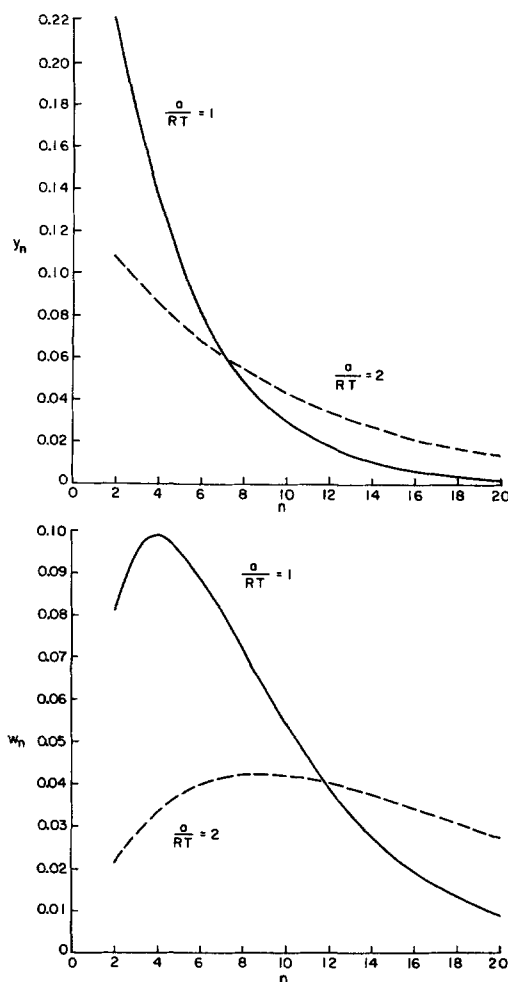


FIG. 2. (a) Distributions of equilibrium mole fractions y_n of alkenes or alkynes as a function of carbon number n . (b) Distributions of equilibrium mass fractions w_n of alkenes or alkynes as a function of carbon number n .

to obtain

$$\bar{n} = (2-x)/(1-x). \quad (35)$$

The mean carbon numbers for the two distributions in Fig. 2 are 5.49 and 10.28. The standard deviation σ is given by

$$\sigma = x^{1/2}/(1-x). \quad (36)$$

TABLE II. Properties of the equilibrium distributions in Fig. 2 and the partial pressures of alkenes required to give these distributions.

a/RT	1	2
Properties of y_n		
\bar{n}	5.49	10.28
σ	3.96	8.77
Properties of w_n		
n_{max}	4	9
\bar{n}_m	8.35	17.75
Partial pressures of alkenes in bars		
500 K	3.58×10^{-3}	9.73×10^{-3}
600 K	0.16	0.44
700 K	2.29	6.24

The equilibrium mass fraction, defined by $w_n = ny_n/\bar{n}$, is given by

$$w_n = nx^{n-2}(1-x)^2/(2-x). \quad (37)$$

The distribution of equilibrium mass fractions for the alkenes are shown in Fig. 2 (b) for two values of a/RT .

The carbon number n_{\max} at which w_n is a maximum can be obtained by the same procedure used with the alkanes [Eq. (19)]. Thus w_n is maximized when n is the smallest integer $\geq q/p$:

$$q/p = 2/[-1 + \sqrt{1 + 4 \exp(-a/RT)}] = x/(1-x). \quad (38)$$

The mass-average carbon number \bar{n}_m , defined by Eq. (20) with a lower limit of $n = 2$, for the equilibrium mixture of alkenes is given by

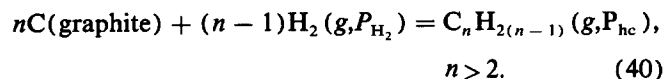
$$\bar{n}_m = \frac{4 - 3x + x^2}{(2-x)(1-x)}. \quad (39)$$

These equations for the equilibrium distributions of the alkenes have the same general form as the equation derived earlier⁶ for equilibrium at a specified partial pressure of ethylene. Thus a certain P_{hc} corresponds to a certain $P_{\text{C}_2\text{H}_4}$.

Earlier, equilibrium mass fractions for the alkenes have been calculated by Krambeck,¹² Tabac *et al.*,¹³ and Alberty¹⁴ using known isomer group Gibbs energies of formation for the first several isomer groups and linearly extrapolated values for higher isomer groups. These earlier calculations were all made using EQUALC, a general equilibrium program written by Krambeck.¹⁵ The present calculations assuming that ethylene and propylene follow Eq. (1) yield too high values for these species, but the effect of this error in the calculation becomes smaller as the mean carbon number rises.

EQUILIBRIUM DISTRIBUTION OF ISOMER GROUPS IN THE ALKYNE HOMOLOGOUS SERIES AT A SPECIFIED PARTIAL PRESSURE OF MOLECULAR HYDROGEN

The formation of acetylene and higher isomer groups in the alkyne homologous series at a constant partial pressure of molecular hydrogen is represented by



The transformed Gibbs energies of formation are given by an equation of the form of Eq. (2) with

$$a = A + RT \ln[(P - P_{\text{H}_2})/P^0] + RT \ln(P_{\text{H}_2}/P^0), \quad (41)$$

$$b = B - RT \ln(P_{\text{H}_2}/P^0). \quad (42)$$

Note that for the alkynes, a is again a function of T , P , and P_{H_2} , but the sign of the term in P_{H_2} is the opposite of that in Eq. (6). Thus raising P_{H_2} favors polymerization in the alkyne homologous series.

The equilibrium mole fractions of the successive isomer groups are given by Eq. (27) since the homologous series starts with $n = 2$, as in the case of the alkenes. Equation (30) also applies, but of course a is calculated using Eq. (39). The

TABLE III. Partial pressures of molecular hydrogen in bars required to give the distributions in Fig. 2 of alkynes at a total pressure of 1 bar.

a/RT	1	2
900 K	6.32×10^{-4}	17.2×10^{-4}
1000 K	4.20×10^{-4}	11.4×10^{-4}

equilibrium mass fractions are given by Eq. (35), if the masses of the hydrogen atoms in the molecules are ignored. Thus the equilibrium distribution of the alkynes at specified partial pressures of molecular hydrogen are given in Fig. 2. Table III gives the partial pressures of molecular hydrogen to give the equilibrium distributions in Fig. 2 of alkynes at a total pressure of 1 bar. The standard Gibbs energies of formation of the alkyne isomer groups¹⁶ C_3H_4 to C_8H_{14} were used. The properties of the plots are, of course, the same as those given in Table II.

DISCUSSION

Although the first one or two members of a homologous series do not follow Eq. (1), it is useful to consider the distribution of isomer groups in a homologous series that does follow Eq. (1) because analytic functions are obtained and they happen to be discrete geometric distributions. Thus the properties of the equilibrium distributions are readily calculated. The errors resulting from the use of Eq. (1) decrease as the mean carbon number \bar{n} at equilibrium increases.

The alkane homologous series is unusual in that the H/C ratio of the successive isomer groups decreases with carbon number, so that reducing P_{H_2} favors high carbon numbers. This is of interest in connection with attempts to produce higher hydrocarbons from methane in a one-step process. The equations derived here for the alkanes are useful for calculating distributions that are thermodynamically stable provided that the effective partial pressure of molecular hydrogen can be reduced by an oxidant. The alkene homologous series is unusual in that the equilibrium distribution depends only on P_{hc} . In contrast, raising the partial pressure of molecular hydrogen favors high carbon numbers in the alkyne homologous series.

This article has not dealt with the competition between homologous series when several homologous series are in equilibrium at a specified partial pressure of molecular hydrogen.

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¹ M. P. Ramage, K. R. Graziani, and F. J. Krambeck, *J. Chem. Eng. Sci.* **35**, 41 (1980).

² R. A. Alberty, *J. Phys. Chem.* **89**, 880 (1985).

³ R. A. Alberty and I. Oppenheim, *J. Chem. Phys.* **89**, 3689 (1988).

⁴ R. A. Alberty, *I&EC Fund.* **22**, 318 (1983).

- ⁵R. A. Alberty and C. A. Gehrig, *J. Phys. Chem. Ref. Data* **13**, 1173 (1984).
- ⁶R. A. Alberty and I. Oppenheim, *J. Chem. Phys.* **84**, 917 (1986).
- ⁷R. A. Alberty, *J. Chem. Phys.* **91**, 7999 (1989).
- ⁸W. R. Smith and R. W. Missen, *Chemical Reactions Equilibrium Analysis* (Wiley, New York, 1982).
- ⁹S. Ross, *A First Course in Probability* (MacMillan, New York, 1988).
- ¹⁰P. J. Flory, *Principles of Polymer Chemistry* (Cornell University, Ithaca, New York, 1953).
- ¹¹R. A. Alberty and C. A. Gehrig, *J. Phys. Chem. Ref. Data* **14**, 803 (1985).
- ¹²F. J. Krambeck, *Inst. Chem. Eng. Symp. Ser.* **87**, 733 (1984).
- ¹³S. A. Tabak, F. J. Krambeck, and W. E. Garwood, *AIChE J.* **32**, 1526 (1986).
- ¹⁴R. A. Alberty, *Chem. Eng. Sci.* **42**, 2325 (1987).
- ¹⁵F. J. Krambeck, *AIChE Meeting* (Miami Beach, FL, 1978).
- ¹⁶R. A. Alberty and E. Burmenko, *J. Phys. Chem. Ref. Data* **15**, 1339 (1986).