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A continuous thermodynamics approach to chemical equilibrium within an isomer group

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As the number of carbon atoms increases in an homologous series the number of isomers becomes so large that it becomes advantageous to use standard thermodynamic properties for the isomer group and to use probability density functions to represent the distribution of properties within the isomer group. The Pearson type III probability density function is used to represent the distribution of the standard Gibbs energy of formation within an isomer group. The standard Gibbs energy of formation of the isomer group is expressed in terms of the minimum, mean, and standard deviation of this probability density function. The probability density function for the equilibrium mole fraction within the isomer group is expressed in terms of these same properties for the isomer group and the temperature. Two types of equations are derived for the calculation of the other standard thermodynamic properties of an isomer group from the probability density function for the standard Gibbs energy of formation. The use of these equations is illustrated by the calculation of isomer group properties for the decanes at 1000 K in the ideal gas state.

INTRODUCTION

Continuous thermodynamics has been useful in calculating phase distributions for complex organic systems,[1] but it is more difficult to use for chemical equilibria because of the necessity of conserving elements. Chemical reactions within isomer groups, however, do not involve this problem, and so this provides an opportunity to test the use of probability density functions in describing chemical reactions. This is of special importance because of the geometric increase in the number of isomers in organic homologous series at higher carbon numbers. For example, decane ($C_{10}H_{22}$) has 136 isomers, pentadecane ($C_{15}H_{32}$) has 18 127, and icosane ($C_{20}H_{42}$) has 3 396 844.[2] Thus as the carbon number increases, the distribution of thermodynamic properties within an isomer group becomes more nearly continuous. In calculating equilibrium compositions in systems involving isomer groups, it is convenient to use standard thermodynamic properties for isomer groups. The standard Gibbs energy of formation $\Delta_f G°(I)$ for an isomer group may be calculated from the standard Gibbs energies of formation $\Delta_f G_i°$ of the individual species using[3]

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

where N_I is the number of isomers in the isomer group, including stereoisomers. The single most important determinant of the value of $\Delta_f G°(I)$ is the minimum, or most negative, Gibbs energy for any of the isomers $\Delta_f G°_{\min}$, since $\Delta_f G°(I)$ is necessarily more negative than this. The greatest difference between $\Delta_f G°(I)$ and $\Delta_f G°_{\min}$ is obtained when all of the isomers in a group have the same standard Gibbs energy of formation. In this case

$$\Delta_f G°(I) = \Delta_f G_i° - RT \ln N_I. \qquad (2)$$

The equilibrium mole fraction r_i of an isomer within an isomer group is given by

$$r_i = \exp\{ [\Delta_f G°(I) - \Delta_f G_i°]/RT \}. \qquad (3)$$

This relation reflects the fact that the equilibrium mole frac-

tion of an isomer within an isomer group is independent of the arbitrary zero for the standard Gibbs energy of formation. If all the isomers have the same standard Gibbs energy of formation $r_i = 1/N_I$.

Since Eq. (1) gives the standard Gibbs energy of formation of an isomer group as a function of temperature, $\Delta_f H°(I), S°(I)$, and $C_P°(I)$ may be obtained by use of standard thermodynamic derivatives.[4] It is therefore of interest to see whether a probability density function can be used to represent the distribution of Gibbs energies of formation within an isomer group to calculate $\Delta_f G°(I)$, to calculate the equilibrium mole fractions within the isomer group, and to calculate the other thermodynamic properties of the isomer group.

The equations derived in this article will be illustrated with the decane isomer group. Earlier statistical mechanical correlations, started by Pitzer,[5] were extended by Scott,[6] who calculated the standard chemical thermodynamic properties for all of the alkanes through decane. Alberty and Gehrig[7] have used these tables to calculate the corresponding isomer group thermodynamic properties. In addition they calculated the thermodynamic properties of all of the alkanes through the decanes using the Benson group method.[8]

In tabulating standard thermodynamic properties of organic compounds it is convenient to list properties of racemates of chiral substances, rather than putting in separate lines for right- and left-handed forms. The standard Gibbs energy of formation of a racemate $\Delta_f G°(RS)$ is equal to $\Delta_f G°(R) - RT \ln 2$, where $\Delta_f G°(R) = \Delta_f G°(S)$ are the standard Gibbs energies of formation of the R and S forms. The standard entropy of a racemate $S°(RS)$ is equal to $S°(R) + R \ln 2$, where $S°(R) = S°(S)$.

In the remainder of this paper the following abbreviations are used: g = standard Gibbs energy of formation $\Delta_f G°$; $g_{\min}$ = minimum value of $\Delta_f G°$ in an isomer group; $\bar{g}$ = average $\Delta_f G°$ in an isomer group; $\langle g \rangle$ = weighted average standard Gibbs energy of formation for an isomer group at equilibrium; $\Delta g_{\min}$ = Gibbs energy of mixing; $g(I)$ = stan-
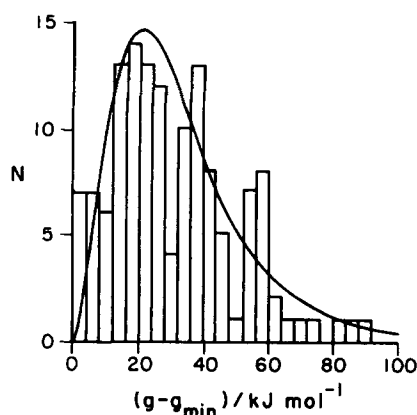
FIG. 1. The bar graph gives numbers of decane isomers with standard Gibbs energies of formation in 4 kJ mol^{-1} intervals at 1000 K. The line has been calculated with Eq. (5) using parameters calculated from the minimum, mean, and standard deviation of the Gibbs energies for the 136 isomers.

dard Gibbs energy of formation of an isomer group $\Delta_f G°(I)$; h = standard enthalpy of formation $\Delta_f H$; $h(I)$ = standard enthalpy of formation of an isomer group $\Delta_f H°(I)$; s = standard entropy $S°$; $s(I)$ = standard entropy of an isomer group $S°(I)$; $\langle s \rangle$ = weighted average standard entropy for an isomer group at equilibrium; Δs_{mix} = entropy of mixing; c_p = standard heat capacity at constant pressure; $c_p(I)$ = standard heat capacity at constant pressure for an isomer group; and $\langle c_p \rangle$ = weighted average standard heat capacity at constant pressure at equilibrium. As a further simplification the modifiers "standard" and "of formation" have been omitted in the text. All calculations are concerned with ideal mixtures of ideal gases.

REPRESENTATION OF THE DISTRIBUTION OF GIBBS ENERGIES IN AN ISOMER GROUP BY A PROBABILITY DENSITY FUNCTION

The distribution of Gibbs energies in an isomer group may be illustrated by a bar graph which gives the numbers of isomers in successive equal intervals, starting with the lowest $\Delta_f G°$ value. Figure 1 shows the distribution for the 136 decane isomers with an interval of 4 kJ mol^{-1}. The tables used[7] are for a standard state pressure of 1 bar. Since the tables list racemates, $RT \ln 2$ was added to each $\Delta_f G°$ for a chiral decane, and then the values for chiral isomers were put in the list twice. If there were more isomers and the interval could be made smaller, the bar graph would, in the limit, approach a continuous curve represented by a probability density function $f(g)$ such that the fraction of isomers having Gibbs

energies between g and $g + dg$ is $f(g)dg$. A suitable probability density function for this purpose must have a value of zero at g_{min} and should decrease to zero at high values of g. The Pearson type III distribution,[9] often referred to as the Schulz distribution, has been widely used in continuous thermodynamics. It is

$$f(x) = \frac{1}{\beta \Gamma(p)} y^{p-1} e^{-y} \quad (x \geqslant \alpha), \tag{4}$$

with $y = (x - \alpha)/\beta$, mean $= \alpha + p\beta$, and variance $= p\beta^2 = \sigma^2$. Taking x as the Gibbs energy g and α as g_{min}, yields the following form for the probability density function for the Gibbs energy:

$$f(g) = \frac{(g - g_{min})^{p-1}}{\beta^p \Gamma(p)} e^{-(g - g_{min})/\beta}. \tag{5}$$

The parameters p and β were calculated for the alkanes at 900, 1000, and 1100 K using

$$p = [(\bar{g} - g_{min})/\sigma]^2, \tag{6}$$

$$\beta = \sigma^2/(\bar{g} - g_{min}) \tag{7}$$

and these values are given in Table I. Figure 1 shows that the curve calculated with Eq. (5) gives a good representation of the decanes at 1000 K.

CALCULATION OF THE GIBBS ENERGY OF AN ISOMER GROUP USING A PROBABILITY DENSITY FUNCTION

The transition to the continuous case is made by introducing the normalized probability density function $f(g)$ into Eq. (1). Since the number of isomers in an isomer group is N_I, the number of isomers with Gibbs energies between g and $g + dg$ is $N_I f(g)dg$. Replacing the summation in Eq. (1) with an integration yields

$$g(I) = -RT \ln \int_{g_{min}}^{\infty} N_I f(g) e^{-g/RT} dg. \tag{8}$$

Substituting Eq. (5) in Eq. (8) yields

$$g(I) = -RT \ln \frac{N_I}{\beta^p \Gamma(p)} \int_{g_{min}}^{\infty} (g - g_{min})^{p-1}$$
$$\times e^{-(g - g_{min})/\beta} e^{-g/RT} dg$$
$$= -RT \ln \frac{N_I e^{-g_{min}/RT}}{\beta^p \Gamma(p)} \int_{g_{min}}^{\infty} (g - g_{min})^{p-1}$$
$$\times \exp\left[-\left(\frac{1}{\beta} + \frac{1}{RT} \right)(g - g_{min}) \right] dg. \tag{9}$$

Now $g - g_{min}$ is replaced with z.

TABLE I. Parameters and standard Gibbs energy of formation for the decane isomer group.[a]

T(K)	900	1000	1100
g_{min}	652.84	760.06	866.86
$\bar{g}$	680.96	790.78	900.50
σ	17.44	18.90	20.22
β	10.816	11.628	12.154
p	2.5998	2.6419	2.7679
$\Delta_f G°(I)$ [Eq. (1)]	633.5	737.0	843.3
$\Delta_f G°(I)$ [Eq. (12)]	632.3	738.4	841.8

[a] All quantities are in kJ mol^{-1} for a standard-state pressure of 1 bar, except for p which is dimensionless.

$$g(I) = -RT \ln \frac{N_I e^{-g_{min}/RT}}{\beta^p \Gamma(p)} \int_0^\infty$$

$$\times z^{p-1} \exp\left[-\left(\frac{1}{\beta} + \frac{1}{RT}\right)z\right]dz. \qquad (10)$$

Next $[(1/\beta) + (1/RT)]z$ is replaced by w to obtain

$$g(I) = -RT \ln \frac{N_I e^{-g_{min}/RT}}{(1 + \beta/RT)^p \Gamma(p)} \int_0^\infty w^{p-1} e^{-w} dw. \qquad (11)$$

The gamma function cancels so that

$$g(I) = g_{min} - RT \ln N_I + pRT \ln\left(1 + \frac{\beta}{RT}\right). \qquad (12)$$

This equation may be written in terms of the mean and standard deviation of the isomer distribution.

$$g(I) = g_{min} - RT \ln N_I + \left(\frac{\bar{g} - g_{min}}{\sigma}\right)^2 RT$$

$$\times \ln\left[1 + \frac{\sigma^2}{RT(\bar{g} - g_{min})}\right]. \qquad (13)$$

Thus if $N_I, g_{min}, \bar{g}$, and σ are known for an isomer group, the Gibbs energy of the isomer group can be calculated on the assumption that the distribution of Gibbs energies follows the Pearson type III distribution. The Gibbs energy of the decane isomer group at 1000 K calculated in this way is in excellent agreement with the value calculated by the discrete method, as shown by Table I.

As the standard deviation decreases for a constant average value, the Pearson type III probability density function approaches a delta function centered at the average value of the Gibbs energy, and so Eq. (12) should reduce to Eq. (2). If $\beta \to 0$, and $p \to \infty$ for fixed βp, $\ln(1 + x)$ can be replaced with x to obtain

$$g(I) = \bar{g} - RT \ln N_I, \qquad (14)$$

as expected.

CALCULATION OF THE PROBABILITY DENSITY FUNCTION FOR THE EQUILIBRIUM MOLE FRACTION

For the discrete case the equilibrium mole fractions are given by Eq. (3). The mole fractions of the decanes calculated in this way have been tabulated by Alberty and Gehrig.[7] In order to produce a bar graph to show the numbers of molecules in the equilibrium mixture as a function of the Gibbs energy, a list of Gibbs energies was prepared using the computer with each value repeated a number of times proportional to its equilibrium mole fraction. To make Fig. 2 a species with an equilibrium mole fraction of 0.001 was put in the list once and the Gibbs energy of a species with an equilibrium mole fraction of 0.100 was put in 100 times. Comparison of the bar graph in Fig. 2 with that in Fig. 1 shows that at equilibrium within the isomer group the isomers with the lowest Gibbs energies tend to predominate. The interval is 4 kJ mol^{-1} for both figures, but the ordinates in Fig. 2 have been reduced.

In the limit of an infinite number of isomers such as bar graph becomes continuous and may be represented by a probability density function $r(g)$, where $r(g)dg$ is the fraction
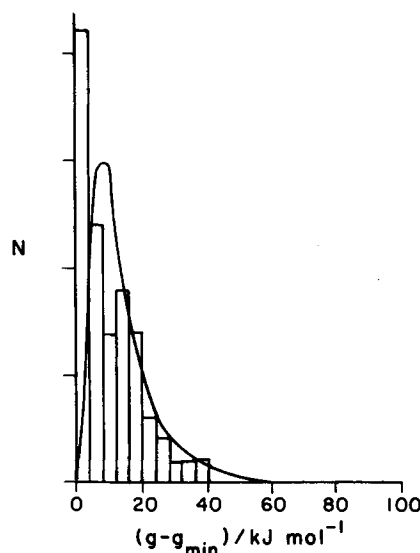

FIG. 2. The bar graph gives numbers of decane molecules with various standard Gibbs energies of formation in 4 kJ mol^{-1} intervals in an equilibrium population of 1005 at 1000 K. The line has been calculated using Eq. (18) with parameters calculated from the minimum, mean, and standard deviation of the Gibbs energies for the 136 isomers.

of the molecules at equilibrium having Gibbs energies between g and $g + dg$.

In transforming Eq. (3) for the equilibrium mole fractions of isomers in the discrete case to the continuous case, the equilibrium mole fractions within the isomer group are represented by the normalized probability density function $r(g)$. Equation (3) becomes

$$r(g) = \frac{N_I f(g) e^{-g/RT}}{\int_{g_{min}}^\infty N_I f(g) e^{-g/RT} dg}. \qquad (15)$$

Using Eq. (8) yields

$$r(g) = N_I f(g) \exp\{[g(I) - g]/RT\}$$

$$= \exp\{[g(I) - (g - RT \ln N_I f(g))]/RT\}. \qquad (16)$$

Using Eq. (12) for $g(I)$ leads to

$$r(g) = \left(1 + \frac{\beta}{RT}\right)^p e^{-(g-g_{min})/RT} f(g). \qquad (17)$$

Thus the probability density function for the equilibrium mole fraction $r(g)$ is obtained from the probability density function $f(g)$ for the isomer group by multiplying by a Boltzmann factor and renormalizing. Substituting Eq. (5) for $f(g)$ yields

$$r(g) = \frac{1}{\Gamma(p)} \left(\frac{1}{\beta} + \frac{1}{RT}\right)^p (g - g_{min})^{p-1}$$

$$\times \exp\left[-\left(\frac{1}{\beta} + \frac{1}{RT}\right)(g - g_{min})\right]. \qquad (18)$$

Thus the effect of the chemical equilibrium is to replace $1/\beta$ with $(1/\beta) + (1/RT)$. In this way the temperature determines the extent to which the species with the lowest Gibbs energies tend to predominate in the equilibrium mixture.

As the standard deviation decreases with the mean held constant $r(g)$ becomes a delta function centered at $\bar{g}$. Thus this equation correctly reduces to the case that the isomers all have the same value of the Gibbs energy.

The solid line in Fig. 2 was calculated using Eq. (18) with parameters from Table I for 1000 K. Thus the probability density function $r(g)$ derived using the Pearson type III distribution adequately represents the equilibrium distribution of the isomers at 1000 K.

CALCULATION OF ISOMER GROUP THERMODYNAMIC PROPERTIES USING THE PROBABILITY DENSITY FUNCTION FOR EQUILIBRIUM MOLE FRACTIONS

For the discrete case the thermodynamic properties of an isomer group can be written in terms of summations involving the equilibrium mole fractions of the various isomers in the isomer group.[4] As will be seen below, the Gibbs energy of an isomer group is the weighted average (weighted according to the equilibrium mole fraction) of the Gibbs energies of the isomers plus the Gibbs energy of mixing the isomers. The enthalpy is the weighted average enthalpy for the isomer group. The entropy is the weighted average entropy plus the entropy of mixing the isomers. The heat capacity is the weighted average heat capacity plus σ_H^2/RT^2, where σ_H is the standard deviation of the equilibrium distribution of enthalpies in the isomer group. The quantity σ_H^2/RT^2 is the heat absorbed per degree rise in temperature by the shift in equilibria within the isomer group.

For the discrete case

$$g(I) = \langle g \rangle + \Delta g_{\text{mix}}, \tag{19}$$

where

$$\langle g \rangle = \sum_{i=1}^{N_I} r_i \, g_i, \tag{20}$$

$$\Delta g_{\text{mix}} = RT \sum_{i=1}^{N_I} r_i \ln r_i. \tag{21}$$

In using Eq. (19) to calculate $g(I)$, r_i and g_i for racemates may be used. However, this puts the entropy of mixing the racemate pairs in the first term. In making the transition to the continuous case there are two ways to look at it. According to the first way the Gibbs energy of mixing the isomers with Gibbs energies between g and $g + dg$ is provided for by using $g - RT \ln N_I f(g)$ in the first term.

$$g(I) = \int_{g_{\text{min}}}^{\infty} r(g)[g - RT \ln N_I f(g)] dg$$

$$+ RT \int_{g_{\text{min}}}^{\infty} r(g) \ln r(g) dg. \tag{22}$$

As in the case of racemates this puts part of the entropy of mixing in the first term. According to the second way no entropy of mixing is put in the first term, but is put in the second term by putting in the degeneracy of the isomers with Gibbs energies in the range g to $g + dg$:

$$g(I) = \int_{g_{\text{min}}}^{\infty} r(g)g \, dg + RT \int_{g_{\text{min}}}^{\infty} r(g) \ln [r(g)/N_I f(g)] dg. \tag{23}$$

Equations (22) and (23) yield the same value for $g(I)$, but Eq. (23) is better in that it provides a complete separation of the entropy of mixing terms from the weighted average Gibbs energy. The weighted average Gibbs energy and the Gibbs

energy of mixing calculated using the two terms of Eq. (23) for the Pearson type III distribution are

$$\langle g \rangle = g_{\text{min}} + \frac{\beta p}{1 + \beta/RT}, \tag{24}$$

$$\Delta g_{\text{mix}} = -RT \ln N_I + pRT \ln(1 + \beta/RT) - \frac{\beta p}{1 + \beta/RT}. \tag{25}$$

For the decanes at 1000 K these equations yield $\langle g \rangle = 772.9$ kJ mol^{-1} and $\Delta g_{\text{mix}} = -34.4$ kJ mol^{-1}, leading to $g(I) = 738.5$ kJ mol^{-1}. For the discrete case, Eqs. (20) and (21) yield $\langle g \rangle = 770.4$ kJ mol^{-1} and $\Delta g_{\text{mix}} = -33.3$ kJ mol^{-1}, leading to $g(I) = 737.1$ kJ mol^{-1}, when r_i and g_i for individual species (not racemates) are used.

For the discrete case,

$$h(I) = \sum_{i=1}^{N_I} r_i h_i. \tag{26}$$

For the continuous case,

$$h(I) = \int_{g_{\text{min}}}^{\infty} r(g)h(g) dg, \tag{27}$$

where $h(g)$ is the enthalpy of formation as a function of the Gibbs energy. The enthalpies of the 136 isomers of decane at 1000 K are given in Fig. 3 as a function of the difference between their Gibbs energy and the minimum Gibbs energy in the isomer group. The relation between Eq. (27) and Fig. 3 is to be understood as follows: In the limit of an infinite number of isomers the species with Gibbs energies between $(g - g_{\text{min}})$ and $(g - g_{\text{min}}) + d(g - g_{\text{min}})$ have the same equilibrium mole fractions, but they have a range of enthalpy values. Since they have equal mole fractions, the appropriate value to use in Eq. (27) for $h(g)$ at this value of g is the average. In the present calculations this is accomplished by least squaring the enthalpy to a power series in $g - g_{\text{min}}$.

$$h(g) = c_0 + c_1(g - g_{\text{min}}) + c_2(g - g_{\text{min}})^2 + c_3(g - g_{\text{min}})^3. \tag{28}$$

Inserting this equation in Eq. (27) yields

$$h(I) = c_0 + c_1 \int_{g_{\text{min}}}^{\infty} r(g)(g - g_{\text{min}}) dg$$

$$+ c_2 \int_{g_{\text{min}}}^{\infty} r(g)(g - g_{\text{min}})^2 dg$$

$$+ c_3 \int_{g_{\text{min}}}^{\infty} r(g)(g - g_{\text{min}})^3 dg \tag{29}$$

$$= c_0 + c_1 m_1 + c_2 m_2 + c_3 m_3, \tag{30}$$

where m_1, m_2, and m_3 are the first, second, and third moments.

$$m_1 = p \left(\frac{1}{\beta} + \frac{1}{RT} \right)^{-1}, \tag{31}$$

$$m_2 = p(p + 1) \left(\frac{1}{\beta} + \frac{1}{RT} \right)^{-2}, \tag{32}$$

$$m_3 = p(p + 1)(p + 2) \left(\frac{1}{\beta} + \frac{1}{RT} \right)^{-3}. \tag{33}$$

The values of c_0, c_1, c_2, and c_3 for the decanes at 1000 K calculated from Fig. 3 are -309.99 kJ mol^{-1}, -0.232,
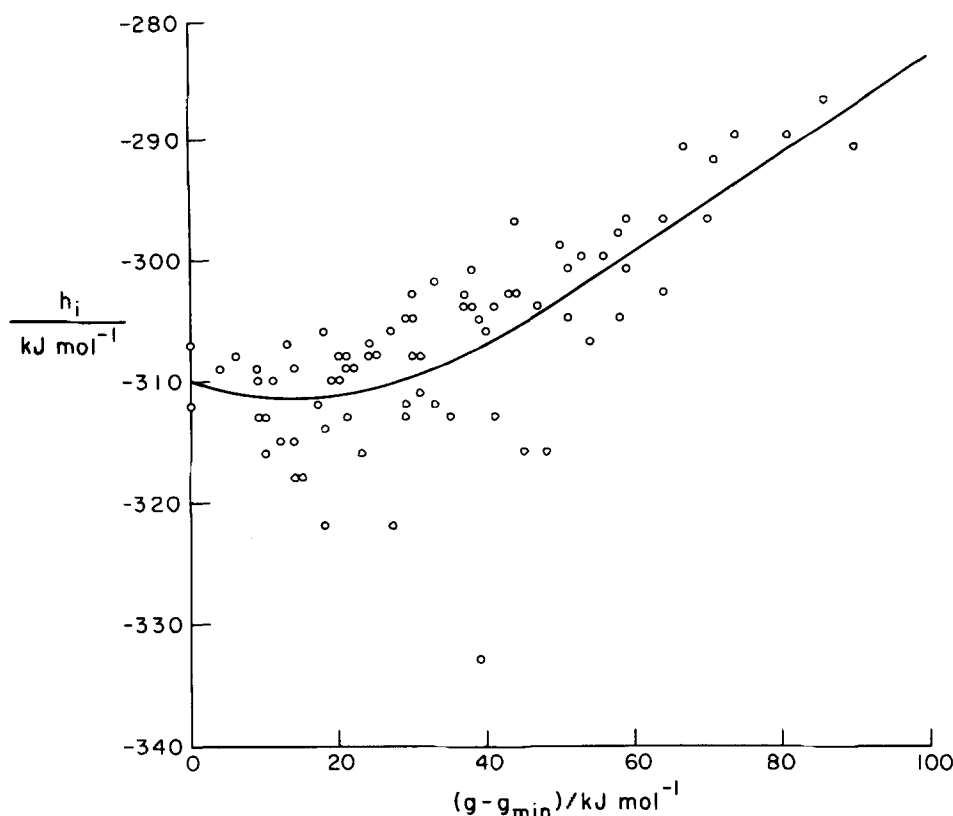
FIG. 3. Standard enthalpy of formation of decane species at 1000 K vs $g - g_{min}$. The line has been calculated using a cubic equation with parameters determined by least squaring.

0.0110 $(kJ \ mol^{-1})^{-1}$, and $- 6.4 \times 10^{-5} \ (kJ \ mol^{-1})^{-2}$. Substitution of these values and the various moments in Eq. (30) yields $h(I) = - 310.8 \ kJ \ mol^{-1}$ compared with the value calculated using Eq. (26) of $- 310.6 \ kJ \ mol^{-1}$.

For the discrete case

$$s(I) = \langle s \rangle + \Delta s_{mix},\tag{34}$$

where

$$\langle s \rangle = \sum_{i=1}^{N_I} r_i s_i,\tag{35}$$

$$\Delta s_{mix} = - R \sum_{i=1}^{N_I} r_i \ln r_i.\tag{36}$$

The continuous version of this equation is

$$s(I) = \int_{g_{min}}^{\infty} r(g)[s(g) + R \ln N_I f(g)] dg$$

$$- R \int_{g_{min}}^{\infty} r(g) \ln r(g) dg$$

$$= \int_{g_{min}}^{\infty} r(g) s(g) dg - R \int_{g_{min}}^{\infty} r(g) \ln [r(g)/N_I f(g)] dg,\tag{37}$$

where $s(g) + R \ln N_I f(g)$ has to be used to provide for the entropy of mixing of species with Gibbs energies between g and $g + dg$. Equation (17) is used to eliminate the $f(g)$ term. Then Eq. (31) is used. The result is

$$s(I) = \int_{g_{min}}^{\infty} r(g) s(g) dg + R \ln N_I$$

$$+ \frac{p}{T}\left(\frac{1}{\beta} + \frac{1}{RT}\right)^{-1} - Rp \ln\left(1 + \frac{\beta}{RT}\right).\tag{38}$$

The entropies of individual decane species are plotted vs $g - g_{min}$ in Fig. 4. As for the enthalpies, the entropy is represented as a function of $g - g_{min}$ with a power series.

$$s(g) = d_0 + d_1(g - g_{min}) + d_2(g - g_{min})^2 + d_3(g - g_{min})^3.\tag{39}$$

The weighted average entropy is therefore given by

$$\int_{g_{min}}^{\infty} r(g) s(g) dg = d_0 + d_1 m_1 + d_2 m_2 + d_3 m_3,\tag{40}$$

where the moments are given in Eqs. (31)–(33). The values of d_0, d_1, d_2, and d_3 for the decanes at 1000 K are 1003.1 $J \ K^{-1} \ mol^{-1}$, $- 1.2502 \ J \ K^{-1} \ mol^{-1} \ (kJ \ mol^{-1})^{-1}$, 0.01147 $J \ K^{-1} \ mol^{-1}(kJ \ mol^{-1})^{-2}$, and $- 6.7 \times 10^{-5}$ $J \ K^{-1} \ mol^{-1} \ (kJ \ mol^{-1})^{-3}$, respectively. When Eq. (40) is used for the first term in Eq. (38), $s(I) = 1023.8 \ J \ K^{-1} \ mol^{-1}$ for the decanes at 1000 K, compared with 1025.4 $J \ K^{-1} \ mol^{-1}$ calculated for the discrete case using Eq. (34).

The point furthest from the line in both Figs. 3 and 4 represents 2,2,5,5-tetramethylhexane. This is an unusually stable molecule with an unusually low entropy which is partially due to its high symmetry number. As pointed out by Pitzer, di-neopentyl does not have much strain because the neopentyl groups are so far apart. Isomer groups containing rather unique molecules of this type can be treated with a mixture of discrete and continuous thermodynamics, often called semicontinuous thermodynamics.[1h] When several discrete components are present with a continuous distribution the normalization equation for the mole fraction y at equilibrium becomes

$$\Sigma y_i + (1 - \Sigma y_i) \int_{g_{min}}^{\infty} r(g) dg = 1.\tag{41}$$
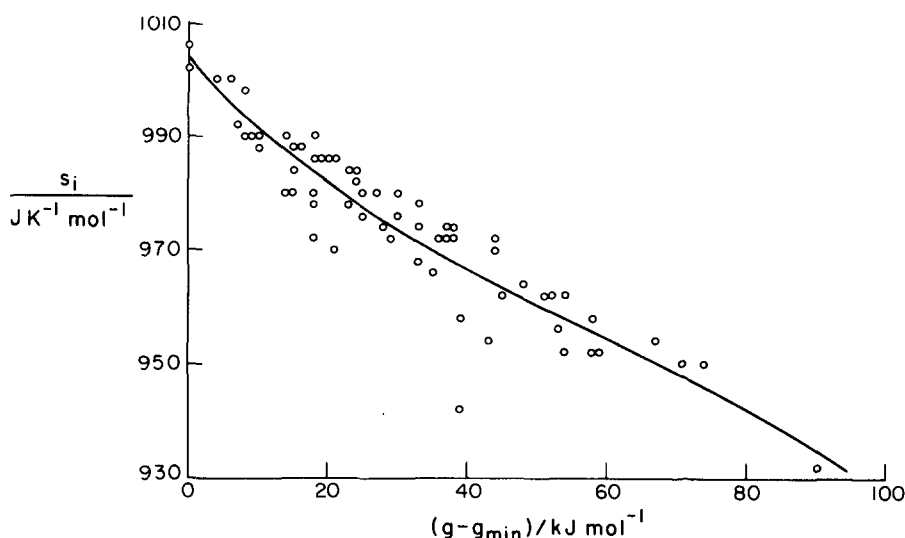
For the discrete case,

FIG. 4. Standard entropy of decane species at 1000 K vs $g - g_{min}$. The line has been calculated using a cubic equation with parameters determined by least squaring.

$$c_P(I) = \langle c_P \rangle + c_{P\,LeC}, \qquad (42)$$

where

$$\langle c_P \rangle = \sum_{i=1}^{N_I} r_i c_{Pi} \qquad (43)$$

and the Le Chatelier term is given by

$$c_{P\,LeC} = \frac{1}{RT^2}\left[\sum_{i=1}^{N_I} r_i h_i^2 - h(I)^2\right]. \qquad (44)$$

The continuous forms of Eqs. (43) and (44) are

$$\langle c_P \rangle = \int_{g_{min}}^{\infty} r(g) c_P(g) dg, \qquad (45)$$

$$c_{P\,LeC} = \frac{1}{RT^2}\left[\int_{g_{min}}^{\infty} r(g) h(g)^2 dg - h(I)^2\right]. \qquad (46)$$

The quantity $c_P(g)$ can be expressed in terms of a power series in $g - g_{min}$ and Eq. (28) may be used for $h(g)$. Thus $c_P(I)$ can also be calculated for an isomer group using the continuous method.

CALCULATION OF THE ENTHALPY AND ENTROPY OF AN ISOMER GROUP USING THE TEMPERATURE DERIVATIVES OF THE PARAMETERS IN THE PROBABILITY DENSITY FUNCTION

The expressions for the other thermodynamic properties of an isomer group may be obtained from Eq. (12) by using the derivatives

$$h(I) = -T^2\left\{\frac{d\,[g(I)/T\,]}{dT}\right\}_P, \qquad (47)$$

$$s(I) = -\left[\frac{dg(I)}{dT}\right]_P, \qquad (48)$$

$$c_P(I) = \left[\frac{dh(I)}{dT}\right]_P. \qquad (49)$$

Since $g(I)$ is not a function of pressure Eq. (47) yields

$$h(I) = g_{min} - T\frac{dg_{min}}{dT} - RT^2\left[\ln\left(1 + \frac{\beta}{RT}\right)\right]$$
$$\times \frac{dp}{dT} + \frac{p}{1 + \beta/RT}\left(\beta - T\frac{d\beta}{dT}\right). \qquad (50)$$

Equation (48) yields

$$s(I) = -\frac{dg_{min}}{dT} + R\ln N_I - R\left[\ln\left(1 + \frac{\beta}{RT}\right)\right]$$
$$\times \left(p + T\frac{dp}{dT}\right) + \frac{p}{T(1 + \beta/RT)}\left(\beta - T\frac{d\beta}{dT}\right). \qquad (51)$$

Since the Gibbs energy of mixing is given by Eq. (25), we can calculate the entropy of mixing:

$$\Delta s_{mix} = -\Delta g_{mix}/T$$
$$= R\ln N_I - pR\ln(1 + \beta/RT) + \frac{\beta p/T}{1 + \beta/RT}. \qquad (52)$$

Subtracting this from Eq. (51) yields the weighted average entropy:

$$\langle s \rangle = -\frac{dg_{min}}{dT} - RT\left[\ln\left(1 + \frac{\beta}{RT}\right)\right]\frac{dp}{dT}$$
$$- \frac{p}{(1 + \beta/RT)}\frac{d\beta}{dT}. \qquad (53)$$

As $\beta \to 0$ and $p \to \infty$ with βp fixed, the weighted average entropy approaches $-d\bar{g}/dT$.

Equation (50) yields

$$c_P(I) = -T\frac{d^2 g_{min}}{dT^2} - 2RT\left[\ln\left(1 + \frac{\beta}{RT}\right)\right]\frac{dp}{dT}$$
$$- RT^2\left[\ln\left(1 + \frac{\beta}{RT}\right)\right]\frac{d^2 p}{dT^2}$$
$$+ \frac{p\beta^2/RT^2}{[1 + (\beta/RT)]^2} + \frac{p}{1 + (\beta/RT)}\frac{d\beta}{dT}. \qquad (54)$$

In order to test Eqs. (50) and (51), the three derivatives were determined by fitting g_{min}, β, and p from Table I to $y = a + bT + cT^2$ and calculating the derivatives at 1000 K using $dg/dT = b + 2cT$. The values of $h(I)$ and $s(I)$ for the decanes at 1000 K calculated using Eqs. (50) and (51) are given in Table II. They are in excellent agreement with the values calculated by the discrete method and the values calculated using the probability density function for equilibrium mole fractions.

TABLE II. Derivatives of parameters and standard thermodynamics properties for decanes at 1000 K.

|	
$dg_{\min}/dT$ (kJ mol^{-1} K^{-1})	1.070 1
$d\beta/dT$ (kJ mol^{-1} K^{-1})	0.006 69
dp/dT (K^{-1})	0.000 841
$\Delta_f H°(I)$ (kJ mol^{-1}) [Eq. (26)]	− 310.6
$\Delta_f H°(I)$ (kJ mol^{-1}) [Eq. (30)]	− 310.9
$\Delta_f H°(I)$ (kJ mol^{-1}) [Eq. (50)]	− 310.8
$S°(I)$ (J K^{-1} mol^{-1}) [Eq. (34)]	1025.4
$S°(I)$ (J K^{-1} mol^{-1}) [Eq. (38)]	1023.8
$S°(I)$ (J K^{-1} mol^{-1}) [Eq. (51)]	1024.9

In calculating $h(I)$ and $s(I)$ over a range of temperature and carbon numbers, Eqs. (50) and (51) are preferred over Eqs. (30) and (38). Values of $g_{\min}$, β, and p can be fit to functions of temperature and carbon number. Then these functions can be differentiated to obtain $dg_{\min}/dT$, $d\beta/dT$, and dp/dT.

DISCUSSION

These calculations show that the Pearson type III probability density function adequately represents the distribution of Gibbs energies for the decanes at 1000 K in the calculation of the Gibbs energy, enthalpy, and entropy for the isomer group and the distribution of equilibrium mole fractions. The enthalpy and entropy of the decane isomer group at 1000 K were calculated by two different methods provided by continuous thermodynamics which give the same result as the discrete method. The continuous thermodynamics approach should become increasingly useful at higher carbon numbers where the numbers of isomers become so large that it is no longer possible to deal with individual molecular species. In order to calculate thermodynamic properties for higher isomer groups using this method it is necessary to estimate $g_{\min}$, $\bar{g}$, and σ. The number of isomers N_I, which is also needed, has already been calculated for some homologous series.[2]

Some calculations have been made using the properties of the distribution of Gibbs energies of the decanes at 1000 K estimated by use of the Benson method.[8] These calculations yield values for the Gibbs energy, enthalpy, and entropy in good agreement with those presented in this paper.

These calculations show that continuous thermodynamics can be used to calculate the equilibrium composition within an isomer group. As a next step it may be used to calculate the equilibrium composition in an organic system in which two different isomer groups are interconverted. For example, the $C_{10}H_{20}$ alkene isomer group may be hydrogenated to the $C_{10}H_{22}$ alkane isomer group.

$$C_{10}H_{20}(\text{isomer group}) + H_2 = C_{10}H_{22}(\text{isomer group}).$$
(55)
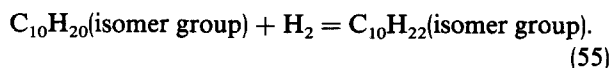
Different values of the parameter $g_{\min}$, β, and p can be used

to represent the Gibbs energies of the C_{10} alkenes and C_{10} alkanes. The standard Gibbs energies of formation for the alkene and alkane isomer groups calculated using the probability density functions can be used to calculate $\Delta G°$ for this reaction. The change in Gibbs energy is given by

$$\Delta g = g(I, C_{10}H_{22}) - g(I, C_{10}H_{20})$$

$$= g_{\min a} - g_{\min e} - RT \ln \frac{N_{Ia}}{N_{Ie}}$$

$$+ RT \ln \left[\frac{(1 + \beta_a/RT)^{p_a}}{(1 + \beta_e/RT)^{p_e}} \right],$$
(56)

where the a and e refer to alkanes and alkenes, respectively. Thus the equilibrium constant for reaction (55) can be interpreted in terms of N_I, $g_{\min}$, β, and p for the two isomer groups involved. More complicated systems can be interpreted in this way through extensions[10] of the concept of an isomer group.

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