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Thermodynamics of chemical reactions written in terms of homologous series

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In calculating equilibrium compositions of complicated organic systems it is advantageous to aggregate whole homologous series; in fact, chemical reactions can be written in terms of homologous series at a specified partial pressure of ethylene. The standard Gibbs energies of formation, enthalpies of formation, entropies, and heat capacities of homologous series may be calculated as a function of ethylene pressure. The change in standard Gibbs energy of formation at a specified partial pressure of ethylene may, for a reaction written in terms of homologous series groups, be used to calculate an equilibrium constant that can be used to calculate the equilibrium composition. The interpretation of the effect of temperature and pressure on the equilibrium is more complicated because the stoichiometric coefficients are functions of the ethylene partial pressure and temperature.

INTRODUCTION

In making chemical equilibrium calculations on complicated systems it is desirable to aggregate species so that the number of components can be reduced. De Donder¹ introduced the idea of using probability density functions when the variation in thermodynamic properties is nearly continuous. He discussed this approach to chemical equilibria in a general way, and so have Aris and Gavalas,² but no one has shown how to ensure atom balances in treating chemical reactions using continuous thermodynamics. Isomer groups can be aggregated in chemical thermodynamic calculations since all the molecules have the same atomic composition. Equilibrium constant expressions can be written in terms of isomer groups.³ Homologous series can be aggregated because the atomic compositions of successive isomer groups can be represented by a formula. For example, since the number of hydrogen atoms in a molecule of alkylbenzene is given by $2n - 6$, where n is the number of carbon atoms, the number of hydrogen atoms in an average molecule in a mixture of alkylbenzenes is $2N - 6$, where N is the average number of carbon atoms per molecule. Equilibrium constant expressions can be written in terms of homologous series groups.⁴ For example, the conversion of the alkene homologous series to the alkane and alkylbenzene homologous series is represented by

$$\frac{1}{Q} C_Q H_{2Q} = \frac{3}{3M + N} C_M H_{2M+2} + \frac{1}{3M + N} C_N H_{2N-6}. \quad (1)$$

This reaction is important in the conversion of methanol to gasoline using a zeolite catalyst.⁵ In this chemical equation the molecular formulas represent average compositions of equilibrium mixtures at a specified partial pressure of ethylene. This article is concerned with calculations of equilibrium compositions and heat effects of reactions written in terms of homologous series groups.

The general equilibrium problem has been solved earlier in the sense that the equilibrium composition may be calculated for any list of isomer groups specified by formula and Gibbs energy of formation at a specified temperature, total

pressure, and H/C ratio.^{6,7} The method described in this article is different in that it involves the specification of the partial pressure of one component, rather than the total pressure.

THEORY

The standard Gibbs energy of formation of an isomer group is calculated using

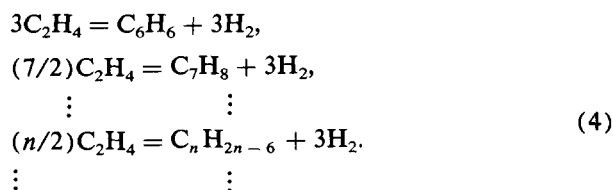
$$\Delta_f G^\circ(I) = -RT \ln \sum_{i=1}^{N_I} e^{-\Delta_f G_i^\circ/RT}, \quad (2)$$

where $\Delta_f G_i^\circ$ is the standard Gibbs energy of formation of isomer i . The other standard thermodynamic properties of an isomer group may be calculated using the usual derivatives.⁸ The equilibrium mole fraction of a particular species within an isomer group is calculated using

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

Ideal mixtures of perfect gases are assumed in all calculations in this article.

The concept of a homologous series group is based on the fact that if the partial pressure of ethylene is fixed, the equilibrium ratios of successive isomer groups in a homologous series are a function only of temperature. Thus the methods for calculating thermodynamic properties of isomer groups can be used for whole homologous series under these conditions.⁹ This really amounts to using ethylene at a specified partial pressure as the reference state for the thermodynamic properties of the successive isomer groups in the homologous series. For example, the formation reactions for the successive alkylbenzene isomer groups can be written as follows:



The standard Gibbs energy of formation of the alkylbenzene

isomer group C_nH_{2n-6} at a specified partial pressure of ethylene and a hydrogen partial pressure of 1 bar is given by

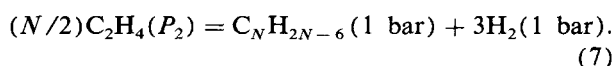
$$\Delta_f G_n^*(I) = \Delta_f G_n^\circ(I) - (n/2)(\Delta_f G_2^\circ + RT \ln P_2), \quad (5)$$

where $\Delta_f G_n^\circ(I)$ is the standard Gibbs energy of formation of the isomer group for the usual reference state, $\Delta_f G_2^\circ$ is the standard Gibbs energy of formation of ethylene for the usual reference state, and P_2 is the specified partial pressure of ethylene. In equations in this paper it is to be understood that P represents P/P° where the standard pressure P° is 1 bar.

Thus the standard Gibbs energy of formation of the alkylbenzene homologous series group (HSG) at a specified partial pressure of ethylene is given by

$$\Delta_f G^*(\text{HSG}) = -RT \ln \sum e^{-\Delta_f G_n^*(I)/RT}. \quad (6)$$

In this paper the limits on summations for homologous series groups will be understood to go from the lowest member to infinity. Equation (6) gives the change in standard Gibbs energy for the formation of the alkylbenzene homologous series from ethylene at a specified partial pressure; that is the Gibbs energy change for the following reaction:



The equilibrium mole fraction r_n of the n th isomer group within the homologous series is given by

$$r_n = \exp\{[\Delta_f G^*(\text{HSG}) - \Delta_f G_n^*(I)]/RT\}. \quad (8)$$

The average number of carbon atoms in a molecule of alkylbenzene at a specified partial pressure of ethylene is readily calculated using

$$N = \sum nr_n. \quad (9)$$

The calculation of equilibrium compositions using Eq. (8) is equivalent to the use of the Stockmayer ensemble, that is intermediate between the isothermal-isobaric ensemble and the generalized ensemble.⁴

Equation (6) can be written in another form that clarifies its significance:

$$\Delta_f G^*(\text{HSG}) = \sum r_n \Delta_f G_n^*(I) + RT \sum r_n \ln r_n. \quad (10)$$

Thus the standard Gibbs energy of formation of a homologous series group is equal to a mole fraction weighted average Gibbs energy of the isomer groups in the homologous series at a specified partial pressure of ethylene plus a term for the Gibbs energy of mixing the isomer groups. One of the advantages of using homologous series groups is that when the standard Gibbs energy of formation of isomer groups is linear in carbon number, as is found at higher carbon numbers, an analytic function may be derived for the distribution of successive isomer groups.¹⁰

Equation (10) can be written in another way that suggests a simplification. When Eq. (5) is substituted in Eq. (10) we obtain the following relation:

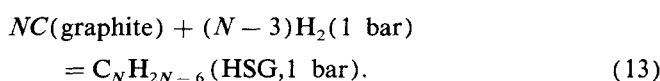
$$\Delta_f G^*(\text{HSG}) = \sum r_n \Delta_f G_n^\circ(I) + RT \sum r_n \ln r_n$$

$$- (N/2)(\Delta_f G_2^\circ + RT \ln P_2). \quad (11)$$

However, it can be shown that the term for ethylene cancels when $\Delta_f G^*(\text{HSG})$ is used to calculate ΔG^* for a chemical reaction. Therefore, in the application of Eq. (10), and its derivatives to calculate changes in thermodynamic properties for reactions, it is convenient to simply use

$$\Delta_f G^{**}(\text{HSG}) = \sum r_n \Delta_f G_n^\circ(I) + RT \sum r_n \ln r_n, \quad (12)$$

where r_n is calculated using Eq. (8). This is the Gibbs energy of formation of a homologous series group from graphite and molecular hydrogen; the mole fractions of the successive isomer groups in the homologous series are determined by the equilibrium with ethylene at a specified partial pressure. Thus, $\Delta_f G^{**}(\text{HSG})$ is the change in Gibbs energy for the following formation reaction:



The change in standard Gibbs energy for reaction (1) at a specified partial pressure of ethylene is given by

$$\begin{aligned} \Delta G^* &= \frac{3}{3M+N} \Delta_f G^*(C_MH_{2M+2}) \\ &+ \frac{1}{3M+N} \Delta_f G^*(C_NH_{2N-6}) \\ &- \frac{1}{Q} \Delta_f G^*(C_2H_4). \end{aligned} \quad (14)$$

As indicated earlier the same change in Gibbs energy is obtained when $\Delta_f G^{**}(\text{HSG})$ is used. The equilibrium constant for reaction (1) calculated using ΔG^* or ΔG^{**} is given by⁴

$$K = \frac{3/(3M+N)}{P_{C_MH_{2M+2}}} \frac{1/(3M+N)}{P_{C_NH_{2N-6}}} \frac{-1/Q}{P_{C_2H_4}}, \quad (15)$$

where the pressures are for the alkane, alkylbenzene, and alkene homologous series groups.

OTHER THERMODYNAMIC PROPERTIES FOR HOMOLOGOUS SERIES GROUPS

The standard enthalpy of formation of a homologous series group at a specified partial pressure of ethylene is obtained by use of

$$\Delta_f H^*(\text{HSG}) = -T^2 \left\{ \frac{\partial [\Delta_f G^*(\text{HSG})/T]}{\partial T} \right\}_{P_2}. \quad (16)$$

Carrying out the differentiation yields

$$\Delta_f H^*(\text{HSG}) = \sum r_n \Delta_f H_n^*(I), \quad (17)$$

where the enthalpy of formation of a particular isomer group at a specified partial pressure of ethylene is given by

$$\Delta_f H_n^*(I) = \Delta_f H_n^\circ(I) - (n/2)\Delta_f H_2^\circ \quad (18)$$

and $\Delta_f H_2^\circ$ is the enthalpy of formation of ethylene. The standard enthalpy of formation of a homologous series group at a particular partial pressure of ethylene is the mole fraction weighted average of the standard enthalpies of formation of

the various isomer groups at that partial pressure of ethylene. Equation (17) can also be written in the form

$$\Delta_f H^*(\text{HSG}) = \sum r_n \Delta_f H_n^\circ(I) - (N/2) \Delta_f H_n^\circ \quad (19)$$

which makes it clearer that it is the enthalpy change for the formation reaction in Eq. (7).

Since the contribution of ethylene in Eq. (19) cancels when $\Delta_f H^*(\text{HSG})$ is used to calculate the change in enthalpy for a chemical reaction, it is more convenient to simply use

$$\Delta_f H^{**}(\text{HSG}) = \sum r_n \Delta_f H_n^\circ(I) \quad (20)$$

following the pattern set by Eq. (12). This enthalpy of formation of a homologous series group is simply the change in enthalpy for formation reaction (13).

The standard entropy of formation of a homologous series group at a specified partial pressure of ethylene is obtained by use of

$$\Delta_f S^*(\text{HSG}) = - \left[\frac{\partial \Delta_f G^*(\text{HSG})}{\partial T} \right]_{P_2} \quad (21)$$

Carrying out the differentiation yields

$$\Delta_f S^*(\text{HSG}) = \sum r_n \Delta_f S_n^\circ(I) - R \sum r_n \ln r_n, \quad (22)$$

where

$$\Delta_f S_n^\circ(I) = \Delta_f S_n^\circ(I) - (n/2)(\Delta_f S_2^\circ - R \ln P_2). \quad (23)$$

Equation (22) can also be written in the form

$$\Delta_f S^*(\text{HSG}) = \sum r_n S_n^\circ(I) - R \sum r_n \ln r_n - (N/2)(\Delta_f S_2^\circ - R \ln P_2) \quad (24)$$

which makes it clearer that it is the change in entropy for the formation reaction in Eq. (7). Since the contribution of ethylene in Eq. (24) cancels in calculating the change in entropy for a chemical reaction, we can follow the pattern set in Eqs. (12) and (20) and write

$$\Delta_f S^{**}(\text{HSG}) = \sum r_n \Delta_f S_n^\circ(I) - R \sum r_n \ln r_n. \quad (25)$$

This is the change in entropy for formation reaction (13). Since the entropies of graphite and hydrogen cancel on the two sides of Eq. (24) when it is written in terms of absolute entropies, it is more convenient to simply use

$$S^{**}(\text{HSG}) = \sum r_n S_n^\circ(I) - R \sum r_n \ln r_n. \quad (26)$$

Thus the standard entropy of a homologous series group at a specified partial pressure of ethylene is simply the mole fraction weighted average of the entropies of the successive isomer groups plus the entropy of mixing the isomer groups.

The heat capacity of formation of a homologous series group at a specified partial pressure of ethylene is obtained from

$$\Delta_f C_P^*(\text{HSG}) = \left[\frac{\partial \Delta_f H^*(\text{HSG})}{\partial T} \right]_{P_2} \quad (27)$$

Carrying out the differentiation yields

$$\Delta_f C_P^*(\text{HSG}) = \sum r_n \Delta_f C_{P_n}^*(I) + \Delta_f C_{P, \text{LeCh}}^*, \quad (28)$$

where $\Delta_f C_{P, \text{LeCh}}^*$, the LeChatelier contribution to the heat capacity, represents the heat absorbed when the equilibria between isomer groups shift as the temperature changes. The heat capacity at constant pressure of the n th isomer group for a specified pressure of ethylene is given by

$$\Delta_f C_{P_n}^*(I) = \Delta_f C_{P_n}^\circ(I) - (n/2) \Delta_f C_{P_2}^\circ. \quad (29)$$

The LeChatelier term is given by

$$\Delta_f C_{P, \text{LeCh}}^* = \frac{1}{RT^2} \left\{ \sum r_n [\Delta_f H_n^*(I)]^2 - [\Delta_f H^*(\text{HSG})]^2 \right\} \quad (30)$$

is always positive because the weighted average of the squares of the enthalpies of formation of the successive isomer groups is always larger than the square of the weighted average.

In applying Eq. (28) to chemical reactions, it is convenient to drop the ethylene term and the heat capacities of the reference state and use

$$\begin{aligned} C_P^{**}(\text{HSG}) &= \sum r_n C_P^\circ(I) + \frac{1}{RT^2} \\ &\times \left\{ \sum r_n [\Delta_f H_n^\circ(I)]^2 - [\Delta_f H^\circ(\text{HSG})]^2 \right\}. \end{aligned} \quad (31)$$

CALCULATION OF EQUILIBRIUM COMPOSITIONS USING REACTION (1)

According to the phase rule, a system of this type has three degrees of freedom. We will only be interested in compositions with a 2:1 ratio of hydrogen to carbon, and that leaves two degrees of freedom that are taken to be temperature and the specified partial pressure of ethylene.

Equilibrium compositions have been calculated using isomer group thermodynamic properties in SI units for a standard state pressure of 1 bar.¹¹⁻¹³ Isomer group thermodynamic properties up to C_{20} were obtained by linear extrapolation. A computer program was written to calculate chemical thermodynamic properties for homologous series groups at a given temperature and partial pressure of ethylene. In making these calculations the specified partial pressure of ethylene must be kept small enough so that the calculated equilibrium mole fraction at the highest carbon number of a homologous series (20 in these calculations) is less than about 0.01; otherwise misleading values will be obtained.

Calculations at three specified pressures of ethylene (10^{-2} , 10^{-4} , and 10^{-6} bar) at 600, 650, and 700 K are summarized in Tables I-III. These calculations show that as the specified partial pressure of ethylene is reduced reaction (1) approaches



These tables give the average numbers of carbon atoms M , N , and Q calculated using analogs of Eq. (9). In contrast with a simple reaction the stoichiometric coefficients ν in reaction

TABLE I. Calculation of equilibrium compositions at a partial pressure of ethylene of 0.01 bar.^a

<i>T</i> /K	600	650	700
Average numbers of carbon atoms			
<i>M</i> (alkanes)	1.098 26	1.029 63	1.015 63
<i>N</i> (alkylbenzenes)	15.585 07	8.707 92	7.595 00
<i>Q</i> (alkenes)	6.676 68	3.968 25	3.082 52
Stoichiometric coefficients			
Alkanes	0.158 90	0.254 31	0.281 90
Alkylbenzenes	0.052 97	0.084 77	0.093 97
Alkenes	0.149 78	0.252 00	0.324 41
$\Delta\nu$	0.062 09	0.087 07	0.051 46
Properties of alkane homologous series groups			
$\Delta_f G^*$	− 55.62	− 51.17	− 47.15
$\Delta_f G^{**}$	− 20.14	− 17.01	− 12.53
$\Delta_f H^{**}$	− 85.09	− 84.87	− 85.63
<i>S</i> ^{**}	224.47	223.47	226.53
Properties of alkylbenzene homologous series groups			
$\Delta_f G^*$	− 50.07	− 25.00	− 14.10
$\Delta_f G^{**}$	453.46	263.90	244.77
$\Delta_f H^{**}$	− 222.36	− 24.40	10.13
<i>S</i> ^{**}	1000.09	571.65	510.41
Properties of alkene homologous series groups			
$\Delta_f G^*$	− 1.01	12.95	19.98
$\Delta_f G^{**}$	214.70	144.61	125.04
$\Delta_f H^{**}$	− 100.26	− 25.01	3.37
<i>S</i> ^{**}	580.07	411.41	358.70
Changes in properties for reaction (1)			
ΔG^* or ΔG^{**}	− 11.34	− 18.40	− 21.10
ΔH^{**}	− 10.28	− 17.35	− 24.28
ΔS^{**}	1.76	1.61	− 4.54
Equilibrium constants			
<i>K</i>	9.71	30.08	37.53
Equilibrium partial pressures			
<i>P</i> (alkanes)	67 570.085 544	5124.555 643	1018.037 411
<i>P</i> (alkylbenzenes)	22 523.361 848	1708.185 214	339.345 804
<i>P</i> (alkenes)	1.181 485	0.092 215	0.031 175
<i>P</i> (total)	90 094.628 877	6832.833 073	1357.414 389

^a Pressures in bars, ΔG and ΔH in kJ/mol, and *S* in J/K mol.

(1) are functions of temperature and pressure of ethylene. Whereas, $\Delta\nu$ for reaction (32) is $-1/18$, this quantity is positive at all three temperatures for an ethylene partial pressure of 0.01 bar.

The standard thermodynamic properties of the alkane, alkylbenzene, and alkene homologous series groups have been calculated using Eqs. (6), (12), (20), and (25). The equilibrium constants for reaction (1) calculated using ΔG^* or ΔG^{**} provide a means for calculating the equilibrium composition in terms of the three homologous series groups.

The equilibrium partial pressure of the alkenes is calculated using

$$P_{C_2H_2} = P_2/r_2, \quad (33)$$

where P_2 is the specified partial pressure of ethylene at equilibrium and r_2 is its equilibrium mole fraction calculated using Eq. (8). The equilibrium partial pressure of the alkane and alkylbenzene homologous series groups are calculated using Eq. (15), the equilibrium constant expression written in terms of homologous series groups. Since we are concerned here only with systems with $H/C = 2$,

$$P_{C_M H_{2M+2}} = 3P_{C_N H_{2N-6}}, \quad (34)$$

Thus Eq. (15) may be used to calculate $P(C_N H_{2N-6})$. If

TABLE II. Calculation of equilibrium compositions at a partial pressure of ethylene of 0.0001 bar.^a

<i>T</i> /K	600	650	700
Average numbers of carbon atoms			
<i>M</i> (alkanes)	1.003 96	1.002 14	1.001 33
<i>N</i> (alkylbenzenes)	6.953 40	6.450 29	6.229 47
<i>Q</i> (alkenes)	2.590 95	2.245 30	2.117 66
Stoichiometric coefficients			
Alkanes	0.301 05	0.317 24	0.324 91
Alkylbenzenes	0.100 35	0.105 75	0.108 30
Alkenes	0.385 96	0.445 38	0.472 22
$\Delta\nu$	0.015 44	− 0.022 39	− 0.039 01
Properties of alkane homologous series groups			
$\Delta_f G^*$	− 43.86	− 38.60	− 33.67
$\Delta_f G^{**}$	− 22.96	− 17.83	− 12.96
$\Delta_f H^{**}$	− 83.35	− 84.44	− 85.42
<i>S</i> ^{**}	216.46	220.72	224.98
Properties of alkylbenzene homologous series groups			
$\Delta_f G^*$	52.13	65.61	76.10
$\Delta_f G^{**}$	196.91	199.34	204.94
$\Delta_f H^{**}$	35.73	52.03	58.68
<i>S</i> ^{**}	429.26	406.02	400.76
Properties of alkene homologous series groups			
$\Delta_f G^*$	42.73	48.51	52.71
$\Delta_f G^{**}$	96.68	95.06	96.51
$\Delta_f H^{**}$	23.08	34.41	38.12
<i>S</i> ^{**}	306.16	287.12	282.43
Changes in properties for reaction (1)			
ΔG^* or ΔG^{**}	− 24.46	− 26.91	− 27.59
ΔH^{**}	− 30.42	− 36.61	− 39.40
ΔS^{**}	− 9.92	− 14.92	− 16.87
Equilibrium constants			
<i>K</i>	134.81	145.50	114.51
Equilibrium partial pressures			
<i>P</i> (alkanes)	68.176 698	13.607 655	3.693 635
<i>P</i> (alkylbenzenes)	22.725 566	4.535 885	1.231 212
<i>P</i> (alkenes)	0.000 184	0.000 128	0.000 113
<i>P</i> (total)	90.902 448	18.143 668	4.924 959

^a Pressures in bars, ΔG and ΔH in kJ/mol, and *S* in J/K mol.

desired, the equilibrium compositions in terms of individual isomer groups may be calculated using Eq. (8). The equilibrium mole fractions of individual species may then be calculated using Eq. (3).

The total pressure *P* of the hydrocarbons is given by the sum of the partial pressures of the alkanes, alkylbenzenes, and alkenes:

$$P = P_{C_M H_{2M+2}} + P_{C_N H_{2N-6}} + P_{C_2 H_2}. \quad (35)$$

The numbers of significant figures in the tables in some cases are excessive, but make it easier to see what is happening.

The fact that ΔH^{**} and ΔS^{**} change as rapidly as they do with temperature shows that ΔC_p^{**} for reaction (1) is considerably larger than ΔC_p^* for reaction (32). This is due to the shifting composition of each homologous series with temperature and the LeChatelier term in Eq. (28).

Although the reaction evolves heat, the equilibrium constant increases when the temperature is raised at an ethylene partial pressure of 0.01 bar. Thus the Gibbs–Helmholtz equation in the form

$$\ln \frac{K_2}{K_1} = \frac{\Delta H(T_2 - T_1)}{RT_1 T_2} \quad (36)$$

is not even approximately correct for reaction (1). The rea-

TABLE III. Calculation of equilibrium compositions at a partial pressure of ethylene of 1E-6 bar.^a

T/K	600	650	700
Average numbers of carbon atoms			
<i>M</i> (alkanes)	1.000 37	1.000 21	1.000 13
<i>N</i> (alkylbenzenes)	6.126 27	6.051 18	6.024 42
<i>Q</i> (alkenes)	2.062 12	2.024 79	2.011 80
Stoichiometric coefficients			
Alkanes	0.328 68	0.331 43	0.332 42
Alkylbenzenes	0.109 56	0.110 48	0.110 81
Alkenes	0.484 94	0.493 88	0.497 07
Δv	-0.046 70	-0.051 98	-0.053 84
Properties of alkane homologous series groups			
$\Delta_f G^*$	-32.36	-26.15	-20.27
$\Delta_f G^{**}$	-23.02	-17.86	-12.98
$\Delta_f H^{**}$	-83.30	-84.42	-85.40
<i>S</i> ^{**}	216.05	220.49	224.82
Properties of alkylbenzene homologous series groups			
$\Delta_f G^*$	125.93	142.61	157.74
$\Delta_f G^{**}$	183.12	192.76	201.61
$\Delta_f H^{**}$	65.33	66.56	66.21
<i>S</i> ^{**}	364.69	370.88	380.85
Properties of alkene homologous series groups			
$\Delta_f G^*$	68.43	74.60	80.13
$\Delta_f G^{**}$	87.68	91.38	94.78
$\Delta_f H^{**}$	42.11	42.46	42.03
<i>S</i> ^{**}	265.33	267.81	272.20
Changes in properties for reaction (1)			
ΔG^* or ΔG^{**}	-30.02	-29.76	-29.09
ΔH^{**}	-40.64	-41.60	-41.95
ΔS^{**}	-17.70	-18.22	-18.37
Equilibrium constants			
<i>K</i>	410.95	246.14	148.12
Equilibrium partial pressures			
<i>P</i> (alkanes)	0.297 910	0.068 663	0.019 654
<i>P</i> (alkylbenzenes)	0.099 303	0.022 888	0.006 551
<i>P</i> (alkenes)	0.000 001	0.000 001	0.000 001
<i>P</i> (total)	0.397 214	0.091 551	0.026 207

^a Pressures in bars, ΔG and ΔH in kJ/mol, and *S* in J/K mol.

son for this is discussed in the next section.

As mentioned in the Introduction the general equilibrium problem can be solved on a computer, and so this is not the only way to calculate the equilibrium composition of such a system. Several calculations given here have been confirmed by use of EQUICALC.⁷ However, it is important to note the difference in specification of the conditions for the two calculations. In using homologous series groups, the equilibrium partial pressure of ethylene is specified and the total pressure results from this. In using EQUICALC, the total pressure is specified and the equilibrium partial pressure of ethylene results from this. The use of Eq. (1) helps us to understand the nature of the chemical equilibrium, but as a calculational method its advantage may be that it allows us to specify the equilibrium partial pressure of any one component.

THE USE OF THE GIBBS-HELMHOLTZ EQUATION FOR REACTIONS OF HOMOLOGOUS SERIES GROUPS

Tables I and II show that Eq. (36) cannot be used for reactions written in terms of homologous series groups. The reason for this is that the stoichiometric coefficients in Eq.

(1) change with temperature. In using the Gibbs-Helmholtz equation the transition between

$$\left[\frac{\partial(G/T)}{\partial(1/T)} \right]_P = H \quad (37)$$

for one component and

$$\left[\frac{\partial(\Delta G/T)}{\partial(1/T)} \right]_P = \Delta H \quad (38)$$

for a reaction with stoichiometric coefficients that are independent of temperature is simple, but for reactions written in terms of homologous series groups

$$\begin{aligned} \left[\frac{\partial(\sum v_i \Delta_f G_i^*/T)}{\partial(1/T)} \right]_{P_2} \\ = \sum v_i \Delta_f H_i^* - T \sum \Delta_f G_i^* \left(\frac{\partial v_i}{\partial T} \right). \end{aligned} \quad (39)$$

Although the left-hand side of this equation is equal to $R [\partial \ln K / \partial(1/T)]_{P_2}$, the integration to another temperature involves a term in addition to the enthalpy of reaction.

Although the equilibrium constant for reaction (1) appears to violate LeChatelier's principle, this is only apparent since there is a heat change with temperature in each homologous series as the degree of alkylation changes with temperature at a constant partial pressure of ethylene.

CONCLUSIONS

These calculations show that equilibrium constants for chemical reactions written in terms of homologous series may be used to calculate equilibrium compositions at a specified temperature and partial pressure of ethylene. Equilibrium compositions at a specified total pressure may be obtained by iteration. In this paper ethylene has been used to define a reference state, but for reactions of hydrocarbons any hydrocarbon could be used rather than ethylene. This provides a method for calculating the composition of the equilibrium state with this particular hydrocarbon at a specified partial pressure.

The calculations in this paper have been carried out using thermodynamic properties of complete isomer groups, but the selectivity of a catalyst may be provided for by using isomer group thermodynamic properties calculated by omitting the isomers excluded by the catalyst. The exclusion of highly branched isomers, for example, has the effect of increasing the slope of the plot of the standard Gibbs energy of formation vs carbon number that is used for the extrapolation to higher carbon numbers.

Chemical thermodynamic properties for homologous series groups may be used in the usual way for calculation of equilibrium compositions, equilibrium constants, and heat effects, but the use of the Gibbs-Helmholtz equation is altered by the fact that the stoichiometric coefficients of reactions written in terms of homologous series groups are functions of temperature.

The process of aggregating species in chemical thermodynamic calculations, first into isomer groups, and second into homologous series groups, can be continued. Fixed-ratio subgroups of species with different molecular formulas can also be included in the calculation of the chemical thermodynamic properties of an isomer group.¹⁴

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