Simplified Calculation of Chemical Equilibria in Hydrocarbon Systems Containing Isomers

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An improved method is presented for handling isomer groups in the calculation of chemical equilibria in complex hydrocarbon mixtures. The new method reduces the number of simultaneous equations involved and makes practical the rigorous calculation of any hydrocarbon system for which free-energy data are available, no matter how complex.

The constant search for new raw materials for the petrochemical industry has led to the development of elaborate separation processes to recover specific compounds from petroleum fractions. Quite often the particular compound desired is present in such small amounts in the crude that it is impossible to meet the demand by recovery of the virgin material alone. In these cases isomers or homologues of the desired compound may be recovered and converted by some catalytic process to the specific compound desired. In a study of the catalytic conversion processes it is worthwhile to calculate the equilibrium composition of the reaction mixtures. This paper describes a method for simplifying the equilibrium calculations when the system contains isomer groups.

Brinkley (*1, 2*) and Kandiner and Brinkley (*3*) have described a basic method of calculating chemical equilibria in complex mixtures which simplifies the arithmetic considerably. This simplification and the improved method of handling isomer groups which is described in this paper permit the calculation of hitherto neglected systems with only a minimum expenditure of technical manpower.

THERMODYNAMIC EQUATIONS REQUIRED

The chemical equilibrium constant, K_a, for a chemical reaction represented by the following stoichiometric equation

$$bB + cC = mM + nN$$

is defined by

$$K_a = K_f = \frac{(n_M)^m(n_N)^n}{(n_B)^b(n_C)^c} \cdot \frac{(f/p)_M{}^m(f/p)_N{}^n}{(f/p)_B{}^b(f/p)_C{}^c} \left(\frac{p}{n}\right)^{m+n-b-c} \quad (1)$$

for real gases in ideal solutions and by

$$K_a = \frac{(\gamma_M)^m(\gamma_N)^n}{(\gamma_B)^b(\gamma_C)^c} \frac{(x_M)^m(x_N)^n}{(x_B)^b(x_C)^c}$$

for nonideal liquid solutions. The standard states are unit fugacity for gases, and for liquids and solids the pure component at the temperature and pressure of the reaction.

The calculation of K_a is accomplished through the use of free-energy data (*4*) and the equation

$$\Delta F^\circ = RT \ln K_a$$

where

$$\Delta F^\circ = \sum (\Delta F_f^\circ)_{products} - \sum (\Delta F_f^\circ)_{reactants}$$

CHOICE OF INITIAL AND FINAL STATES

The equilibrium composition calculated depends upon the initial and final states (not standard states) specified for the reacting system. The temperature and pressure for both states are of course the temperature and pressure chosen for the reaction. The specification of the initial state is completed by specifying the amounts of each of the chemical elements present in the feed. A change in the feed composition which changes the relative amounts of the elements present will result in a changed equilibrium composition.

Similarly the specification of the final state is completed by specifying which chemical species are to be present in the equilibrium mixture. The equilibrium composition calculated depends upon the chemical constituents which the calculator assumes to be present at equilibrium. Choosing fewer or more constituents results in different equilibrium compositions. In some cases the calculator may purposely omit some of the constituents known to be present; for example, in any reaction system where hydrocracking results in the formation of carbon and light hydrocarbons, the true equilibrium mixture would contain only traces of compounds heavier than methane. This fact can be illustrated by choosing carbon and hydrogen as the independent components and then writing Equation (1) for methane, ethane, and benzene. (Ideal gases and a reaction temperature of 800°K. were assumed.)

$$n_{CH_4} = 1.41\ (p/n)(n_{H_2})^2$$

$$n_{C_2H_6} = 4.49 \times 10^{-5}\ (p/n)^2(n_{H_2})^3$$

$$n_{C_6H_6} = 3.68 \times 10^{-15}\ (p/n)^2(n_{H_2})^3$$

The values for K_f were obtained from reference *4*.

Omission of carbon and the lightest hydrocarbons from the equilibrium system permits the calculation of more useful results. In any case the calculator should realize that the equilibrium composition calculated depends upon the final state assumed.

CHOICE OF INDEPENDENT COMPONENTS

The fact that thermodynamic equilibrium is independent of the reaction paths assumed permits one to assume that the reaction mixture is formed from a certain number of independent components. All the other constituents assumed present are then derived from these independent components. The feed constituents may or may not be chosen as independent components. Kandiner and Brinkley (*3*) describe an analytical method for determining how many independent components are required and list several rules for their selection. For simple hydrocarbon systems containing only carbon and hydrogen the number required is two. The number chosen cannot exceed the number of elements present but must be sufficient to permit the writing of chemical equations in which each of the derived constituents is formed individually from one or more of the independent components. Each chemical equation must contain no more than one derived constituent. Also the independent components must be related by at least one of the chemical equations, and for ease of calculation they should predominate

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TABLE 1. CALCULATION OF THE EQUILIBRIUM CONSTANT K_a FOR EACH OF THE DERIVED CONSTITUENTS

Constituent	Chemical equation	$\Delta F°$	K_a*
1, 2 DMB	1, 3 DMB = 1, 2 DMB	1.004	0.4305
1, 4 DMB	1, 3 DMB = 1, 4 DMB	0.961	0.4470
1, 2, 3 TMB	1, 2, 4 TMB = 1, 2, 3 TMB	2.573	0.1159
1, 3, 5 TMB	1, 2, 4 TMB = 1, 3, 5 TMB	1.158	0.3780
1, 2, 3, 4 TMB	2[1, 2, 4 TMB] − 1, 3 DMB = 1, 2, 3, 4 TMB	2.854	0.0913
1, 2, 3, 5 TMB	2[1, 2, 4 TMB] − 1, 3 DMB = 1, 2, 3, 5 TMB	1.417	0.3045
1, 2, 4, 5 TMB	2[1, 2, 4 TMB] − 1, 3 DMB = 1, 2, 4, 5 TMB	1.893	0.2045
Benzene	3[1, 3 DMB] − 2[1, 2, 4 TMB] = benzene	2.572	0.1159
Toluene	2[1, 3 DMB] − 1, 2, 4 TMB = toluene	0.382	0.7262
Penta MB	3[1, 2, 4 TMB] − 2[1, 3 DMB] = penta MB	3.893	0.03817
Hexa MB	4[1, 2, 4 TMB] − 3[1, 3 DMB] = hexa MB	10.636	0.000134

*K_a = 1.0 for an independent component.

in the equilibrium mixture. If pure carbon is assumed to be present, it must be chosen as an independent component, since because of the choice of standard state its concentration will not appear in any of the equilibria equations.

USE OF K VALUES TO SIMPLIFY ISOMER CALCULATIONS

Rossine (5) has described the importance of K values in calculating the equilibria between isomers. This principle can be expanded to simplify the calculation of equilibrium in complex systems containing one or more isomer groups.

If one considers an isomer group containing constituents R, S, $T\cdots$ formed from independent components B and C, the stoichiometric coefficients for B and C will be the same in all the chemical equations

$$bB + cC = R$$

$$bB + cC = S, \quad \text{etc.}$$

Assuming ideal gases for the sake of simplicity and solving for the moles of each isomer, one can write Equation (1) for each isomer as

$$\left.\begin{aligned} n_R &= K_R\left(\frac{n}{p}\right)^{1-b-c}(n_B)^b(n_C)^c \\ n_S &= K_S\left(\frac{n}{p}\right)^{1-b-c}(n_B)^b(n_C)^c, \text{ etc.} \end{aligned}\right\} \quad (2)$$

Then

$$n_S = \left(\frac{K_S}{K_R}\right)n_R, \quad n_T = \left(\frac{K_T}{K_R}\right)n_R, \quad \text{etc.}$$

Letting n_I be the total moles of isomers present and x_R the mole fraction of R in the isomer group, one can show that

$$x_R = \frac{n_R}{n_I}$$

$$= \frac{K_R}{K_R + K_S + K_T + \cdots} = \frac{K_R}{\sum K's}$$

When one generalizes,

$$x_i = \frac{K_i}{\sum K's} \quad (3)$$

Equation (3) illustrates the fact that for ideal gases the ratio of one isomer to its fellow isomers is independent of what other constituents are present at equilibrium and depends on temperature only. If one is interested in the isomer group alone, the log K_f values tabulated in reference 4 are very convenient.

Inspection of Equation (2) shows that

$$n_I = (K_R + K_S + K_T + \cdots) \cdot\left(\frac{n}{p}\right)^{1-b-c}(n_B)^b(n_C)^c \quad (4)$$

This means that in calculating the equilibrium for the entire system the equilibria equations for the various isomers in the group can be reduced to one equation representing the entire group. The K value in this equation is the summation of the K's of the various isomers. Once n_I is obtained Equation (3) can be used to calculate the breakdown within the group. This method significantly reduces the number of equations required, particularly if any of the higher isomer groups are included in the equilibrium system.

EXAMPLE

The chemical equilibrium existing at 600°K. in a system containing benzene and all the methylbenzenes and originating from a feed of trimethylbenzenes will be calculated as an illustration. Experimental results have indicated that 1, 3 dimethylbenzene and 1, 2, 4 trimethylbenzene will be predominant in the equilibrium mixture, and they will be used as the independent components. Table 1 lists the chemical equations written for each derived constituent and the corresponding free energies of reaction and equilibrium constants. The free-energy data were obtained from reference 4 and from a paper by Hastings and Nicholson (6).

The next step is to write the expressions defining K_a for each chemical equation. This is done by substituting in Equation (1). Ideal gases can be assumed, and since the $(m + n - b - c)$ term is zero for each chemical equation, Equation (1) reduces to

$$n_i = K_i n_1^{\nu_{i,1}} n_2^{\nu_{i,2}}$$

The exponents $\nu_{i,1}$, and $\nu_{i,2}$ may be positive or negative in sign.

Two other equations are necessary before the calculations can be started. These are material-balance equations on the independent components. If q_1 and q_2 represent the amounts of the independent components present initially, then the amounts present at equilibrium must be

$$n_1 = q_1 - \sum_{i=3}^{i=13} \nu_{i,1} n_i$$

$$n_2 = q_2 - \sum_{i=3}^{i=13} \nu_{i,2} n_i$$

TABLE 2. MATERIAL-BALANCE AND EQUILIBRIA EQUATIONS

Constituent or isomer group	i	$\nu_{i,1}$	$\nu_{i,2}$	Material-balance and equilibria equations
1, 3 DMB	1	—	—	$n_1 = 0.0 - \sum_{i=3}^{i=13} \nu_{i,1} n_i$
1, 2, 4 TMB	2	—	—	$n_2 = 1.0 - \sum_{i=3}^{i=13} \nu_{i,2} n_i$
DMB's	1, 3, and 4	1	0	$n_{\text{DMB}} = 1.877\, n_1$
Tri MB's	2, 5, and 6	0	1	$n_{\text{Tri MB}} = 1.494\, n_2$
Tetra MB's	7, 8, and 9	−1	2	$n_{\text{Tetra MB}} = 0.6003 \frac{(n_2)^2}{n_1}$
Benzene	10	3	−2	$n_{\text{Benzene}} = 0.1159 \frac{(n_1)^3}{(n_2)^2}$
Toluene	11	2	−1	$n_{\text{Toluene}} = 0.7262 \frac{(n_1)^2}{n_2}$
Penta MB	12	−2	3	$n_{\text{PMB}} = 0.03817 \frac{(n_2)^3}{(n_1)^2}$
Hexa MB	13	−3	4	$n_{\text{HMB}} = 0.000134 \frac{(n_2)^4}{(n_1)^3}$

The q_1 and q_2 are obtained by transforming the original feed into equivalent amounts of the independent components containing the same number of moles of all the elements as the original feed. In this example, since the feed is all trimethylbenzene, the q for 1, 3 dimethylbenzene must be zero and the q for 1, 2, 4 trimethylbenzene must be 1.0 if 1 mole of original feed is taken as the calculation basis.

Table 2 lists the material-balance equations for the independent components and the equilibria equations for each of the derived constituents. The stoichiometric coefficients are listed also for convenience in making the material balances on the independent components. It must be noted that when an isomer group contains an independent component, the n for the isomer group cannot be used in the material-balance equations without first subtracting the n assumed for the independent component.

The number of equations which must now be solved simultaneously has been reduced from thirteen to nine by representing each isomer group by a single equation. Solution of these equations involves assuming values of n_1 and n_2, calculating the n's for all the derived constituents by means of the equilibria equations, and then checking on the assumed values of n_1 and n_2 by utilizing the material-balance equations. Since two unknowns, n_1 and n_2, must be assumed each time, it is impractical to guess the values to be used for the next trial. Kandiner and Brinkley (*3*) describe three methods which sometimes aid in selecting the values of n_1 and n_2 for the successive trials. However a direct graphical approach is usually the surest and often the quickest way of obtaining a solution. Select a value of n_2 and run through the solution of the equations three times with this assumed n_2 and three evenly spaced values of n_1. Then select another value of n_2 and repeat the calculations with this n_2 and the same three values of n_1. Calculate Δn_1 and Δn_2 by subtracting the assumed from the calculated values. Plot the Δn_1's and Δn_2's vs. n_1 with parameters of constant n_2. The Δn_1 and Δn_2 curves will intersect at zero when the correct values of n_1 and n_2 are assumed. Interpolation or extrapolation on a line drawn through the two intersections obtained will indicate the correct n_1 and n_2 to assume for the final trial.

Figure 1 illustrates the solution of the nine equations. It was known that the concentration of 1, 2, 4 trimethylbenzene would be in the 20 to 30% range, and values for n_2 of 0.26 and 0.23 were therefore selected for the six preliminary trials. Likewise the concentration of 1, 3 dimethylbenzene was expected to be 10 to 15%, and values for n_1 of 0.11, 0.13, and 0.15 were used. Interpolation on the straight line drawn between the two intersections indicates the correct values for n_1 and n_2 to be 0.131 and 0.251, respectively, and these were the values used in the final trial, trial 7. The numerical calculations for trial 7 are shown in Table 3 to illustrate the labor required for each trial and the degree of convergence obtained in this example.

The calculation time required for this example was approximately 4 hr., when a desk calculator was used. This time was about evenly divided between the calculation of the K's from free-energy data and the solution of the nine simultaneous equations.

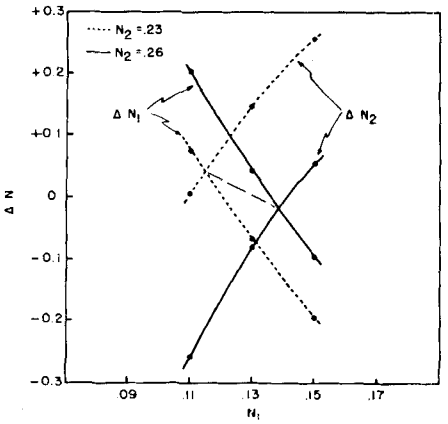

Fig. 1. Estimation of the final answer from the six preliminary trials.

TABLE 3. SOLUTION OF THE EQUILIBRIA AND MATERIAL-BALANCE EQUATIONS

Trial	7
Assumed n_1	0.1310
Assumed n_2	0.2510
Calculated n's	
DMB's	0.2459
Tri MB's	0.3750
Tetra MB's	0.2887
Benzene	0.0041
Toluene	0.0497
Penta MB	0.0352
Hexa MB	0.0002
1, 3 DMB balance	
q_1	0
$-(1.0)\ (n_{\text{DMB}}) + n_1$	−0.1149
$+(1.0)\ (n_{\text{Tetra MB}})$	0.2887
$-(3.0)\ (n_{\text{Benzene}})$	−0.0123
$-(2.0)\ (n_{\text{Toluene}})$	−0.0994
$+(2.0)\ (n_{\text{PMB}})$	0.0704
$+(3.0)\ (n_{\text{HMB}})$	0.0006
Calculated n_1	0.1331
Δn_1 = calculated-assumed	0.0021
1, 2, 4 TMB balance	
q_2	1.0
$-(1.0)\ (n_{\text{Tri MB}}) + n_2$	−0.1240
$-(2.0)\ (n_{\text{Tetra MB}})$	−0.5774
$+(2.0)\ (n_{\text{Benzene}})$	0.0082
$+(1.0)\ (n_{\text{Toluene}})$	0.0497
$-(3.0)\ (n_{\text{PMB}})$	−0.1056
$-(4.0)\ (n_{\text{HMB}})$	−0.0008
calculated n_2	0.2501
Δn_2 = calculated-assumed	−0.0009

Another way of making the material-balance calculation or of checking the calculations made in Table 3 is to calculate the methyl-group-to-benzene-ring ratio. This ratio must be the same in the equilibrium mixture as in the original feed. In this example, since a trimethylbenzene feed was used, the ratio must be 3.0.

CONCLUSIONS

Calculation methods have been developed to the point where the rigorous calculation of chemical equilibrium is practicable for any system for which free-energy data are available. The number of equations which must be solved can be reduced considerably in systems containing isomer groups by representing each isomer group by a single equation. For example, a reformate containing all saturated paraffins, five- and six-ring naphthenes, and aromatics with saturated side chains boiling below 350°F. can be represented by twenty-five equilibria equations and two material-balance equations. The time required for solution would be approximately three times that required for the example problem. The number of components represented by the twenty-five equilibria equations is one hundred and thirty-six. If pentanes and lighter are eliminated from the equilibrium mixture in order to study the relations between the heavier paraffins, naphthenes, and aromatics, the number of equilibria equations is reduced to twenty.

NOTATION

a	= activity, f/f°
f	= fugacity, f° denotes fugacity in the standard state
ΔF_f°	= free energy of formation in the standard state
ΔF°	= free energy of reaction in the standard state
K_a or K_f	= chemical equilibrium constant in terms of activities or fugacities
n	= moles
Δn	= calculated n minus the assumed n for the independent components
p	= total pressure, atm.
q_1 and q_2	= moles of independent components 1 and 2 equivalent to the original feed in terms of the amount of each element contained
$v_{i,1}$ and $v_{i,2}$	= stoichiometric coefficients for independent components 1 and 2 in the chemical equation for derived constituent i
x	= mole fraction
x_i	= mole fraction of ith isomer in isomer group only
(f/p)	= fugacity coefficient
γ	= activity coefficient = a/x

LITERATURE CITED

1. Brinkley, S. R., Jr., *J. Chem. Phys.*, **14**, 9, 563 (1946).
2. *Ibid.*, **15**, 2, 107 (1947).
3. Kandiner, H. J., and S. R. Brinkley, Jr., *Ind. Eng. Chem.*, **42**, 850 (1950).
4. *Am. Petroleum Inst. Project* **44** (1953).
5. Rossini, F. D., "Chemical Thermodynamics," John Wiley and Sons, New York (1950).
6. Hastings, S. H., and D. E. Nicholson, *J. Chem. Phys.*, **61**, 6, 730 (1957).

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