Calculation of Thermodynamic Equilibrium Compositions for Various Petrochemical Reactions

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Abstract

The calculation methods for thermodynamic equilibrium compositions of the reaction system, where the isomerization of product isomers takes place, have been demonstrated. The types of reaction employed are,

(1) $A \rightleftarrows X_i$, (2) $2A \rightleftarrows X_i$, (3) $A+B \rightleftarrows X_i$, (4) $A \rightleftarrows X_i+Q$, (5) $2A \rightleftarrows X_i+Q$,
(6) $A+B \rightleftarrows X_i+Q$,

where the isomerization of product, X_i, takes place; $X_1 \rightleftarrows X_2 \rightleftarrows X_3 \rightleftarrows \cdots$. Corresponding to these types, the equilibrium compositions of some reaction systems have been calculated and shown in the figures or tables.

A thermodynamic analysis of the reaction system often provide considerable information on the proper conditions for obtaining the desired products. In planning petrochemical research, it is customary first to survey the literature and then, before attempting experimental work, to make a thermodynamic analysis of the system, in order to determine the feasibility of the reaction. Reactions which cannot occur may definitely be eliminated.

In the petrochemical reactions, certain products are often obtained as the mixture of isomers, and the thermodynamic equilibrium should be calculated for the system including the product isomers. Such calculation, however, is not very familier task for the inexperienced chemist. In this article, the methods for calculation as well as the examples of thermodynamic equilibrium compositions of such systems are shown, which are helpful for the petrochemical research.

Methods for Calculation

Nomenclature

P Total pressure of the reaction system

K_i $(i=1, 2,...)$ Equilibrium constant

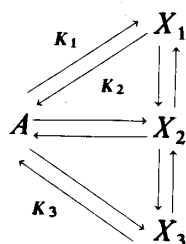b Content of component B at initial

x_i Content of component X_i at equilibrium

r_e $(r=a, b, x_i$ and $q)$ Concentration of component R at equilibrium

Type 1. Monomolecular reaction shown as scheme 1. One component reactant,

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A, produces the mixture of isomers, x_i ($i = 1$, 2, and 3) without changing the amounts of substance.

Scheme 1.

The method for calculation of this type has been already shown elsewhere[1]. The equilibrium composition can be calculated by the following equations.
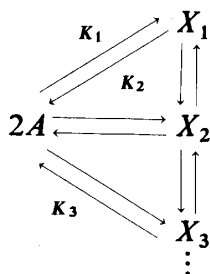
$$a_e = 1/K \tag{1.1}$$

$$x_{ie} = K_i/K \tag{1.2}$$

where
$$K = 1 + K_1 + K_2 + K_3 \tag{1.3}$$

When the number of product isomers increases, Eq. (1.3) should be amended as,

$$K = 1 + K_1 + K_2 + K_3 + \cdots \tag{1.4}$$

Type 2. Bimolecular reaction shown as scheme 2. Two mol of the reactant, A, react to form one mol of the mixture of isomers, X_i, with decreasing the amounts of substance.

Scheme 2.

The mol fractions of each components at equilibrium are as follows:

$$A: \quad a_e = (1 - 2X)/(1 - X) \tag{2.1}$$

$$X_i: \quad x_{ie} = x_i/(1 - X) \tag{2.2}$$

where
$$X = x_1 + x_2 + x_3 + \cdots \tag{2.3}$$

Since the reaction proceeds under the reaction pressure, P, the equilibrium constants are,

$$K_i = x_i(1 - X)/(1 - 2X)^2 P \tag{2.4}$$

By definition,

$$4(K_1 + K_2 + K_3 + \cdots) + 1/P = K \tag{2.5}$$

Hence,

$$1/(1 - 2X)^2 P = K \tag{2.6}$$

By proper substitution,

$$x_i = 2K_i P/(PK + \sqrt{PK}) \tag{2.7}$$

Then, one arrives at following equations, by which the equilibrium compositions can be calculated

$$a_e = 2/(\sqrt{PK} + 1) \tag{2.8}$$

$$x_{ie} = 4PK_i/(\sqrt{PK} + 1)^2 \tag{2.9}$$

Type 3.   Bimolecular reaction shown as scheme 3.   One mol of reactant, A, reacts with one mol of the other reactant, B, to form one mol of the mixture of isomers, X_i, under the reaction pressure, P, with decreasing the amounts of substance.
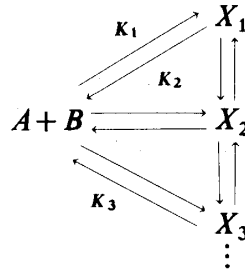
Scheme 3.

The mol fractions of each components at equilibrium are as follows:

$$A: \quad a_e = (1 - X)/(1 + b - X) \tag{3.1}$$

$$B: \quad b_e = (b - X)/(1 + b - X) \tag{3.2}$$

$$X_i: \quad x_{ie} = x_i/(1 + b - X) \tag{3.3}$$

where $\qquad X = x_1 + x_2 + x_3 + \cdots$ $\qquad\qquad$ (3.4)

The equilibrium constants are,

$$K_i = x_i(1 + b - X)/(1 - X)(b - X)P \tag{3.5}$$

Then,

$$K_i/K_1 = x_i/x_1 \tag{3.6}$$

By definition,

$$(K_1 + K_2 + K_3 + \cdots)/K_1 = K \tag{3.7}$$

Hence,

$$X = x_1 K \tag{3.8}$$

Then,

$$K_1 = x_1(1 + b - Kx_1)/(1 - Kx_1)(b - Kx_1)P \tag{3.9}$$

Solving the Eq. (3.9),

$$x_1 = \{(1 + b)(KK_1P + 1) - \sqrt{KK_1P + 1}\sqrt{(1 - b)^2(KK_1P + 1) + 4b}\}/2K(KK_1P + 1) \tag{3.10}$$
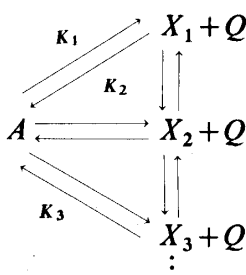
One can accordingly calculate the equilibrium compositions by the following equations.

$$A: \quad a_e = (1 - Kx_1)/(1 + b - Kx_1) \tag{3.11}$$

$$B: \quad b_e = (b - Kx_1)/(1 + b - Kx_1) \tag{3.12}$$

$$X_i: \quad x_{ie} = K_i x_1/K_1(1 + b - Kx_1) \tag{3.13}$$

Type 4.   Monomolecular reaction shown as scheme 4.   One mol of the reactant, A, splits into one mol of Q and one mol of the mixture of isomers, X_i, under the reaction pressure, P, with increasing the amounts of substance.

Scheme 4.

The method for calculation of this type has also been demonstrated elsewhere[2]. The equilibrium composition can be calculated by the following equations.

$$A: \quad a_e = (K - K_m)/(K + K_m) \tag{4.1}$$

$$X_i: \quad x_{ie} = K_i/(K + K_m) \tag{4.2}$$
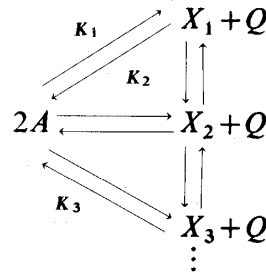
$$Q: \quad q_e = K_m/(K + K_m) \tag{4.3}$$

where

$$K_m = K_1 + K_2 + K_3 \tag{4.4}$$

$$K = \sqrt{K_m(K_m + P)} \tag{4.5}$$

When the number of product isomers increases, Eq. (4.4) should be modified as,

$$K_m = K_1 + K_2 + K_3 + \cdots \tag{4.6}$$

Type 5.   Bimolecular reaction shown as scheme 5.   Two mol of reactant, A, react to form one mol of product, Q, and one mol of the mixture of isomers, X_i, without changing the amounts of substance.

$$
\begin{array}{c}
\xrightarrow{K_1}\ X_1+Q \\
\xrightarrow{\ K_2\ } \\
2A \rightleftarrows X_2+Q \\
\xrightarrow{K_3}\ X_3+Q \\
\vdots
\end{array}
$$

Scheme 5.

The mol fractions of each components at equilibrium are as follows:

$$A: \quad a_e = 1 - X \tag{5.1}$$

$$X_i: \quad x_{ie} = x_i/2 \tag{5.2}$$

$$Q: \quad q_e = X/2 \tag{5.3}$$

where $\qquad X = x_1 + x_2 + x_3 + \cdots$ (5.4)

The equilibrium constants are

$$K_i = x_i X/4(1-X)^2 \tag{5.5}$$

By definition,

$$\sqrt{K_1 + K_2 + K_3 + \cdots} = K \tag{5.6}$$

Then,

$$X = 2K/(2K+1) \tag{5.7}$$

By proper substitution,

$$x_i = 2K_i/K(2K+1) \tag{5.8}$$

Then the equilibrium compositions can be calculated by the following equations.

$$A: \quad a_e = 1/(2K+1) \tag{5.9}$$

$$X_i: \quad x_{ie} = K_i/K(2K+1) \tag{5.10}$$

$$Q: \quad q_e = K/(2K+1) \tag{5.11}$$

Type 6.   Bimolecular reaction shown as scheme 6.   One mol of reactant, A, reacts with one mol of the other reactant, B, to form the mixture of isomers, X_i, without changing the amounts of substance.

$$A + B \rightleftharpoons \begin{cases} X_1 + Q \\ X_2 + Q \\ X_3 + Q \\ \vdots \end{cases}$$
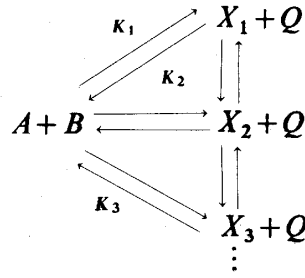
K_1 K_2 K_3

Scheme 6.

The mol fractions of each components at equilibrium are as follows:

$$A: \quad a_e = (1-X)/(1+b) \tag{6.1}$$

$$B: \quad b_e = (b-X)/(1+b) \tag{6.2}$$

$$X_i: \quad x_{ie} = x_i/(1+b) \tag{6.3}$$

$$Q: \quad q_e = X/(1+b) \tag{6.4}$$

where

$$X = x_1 + x_2 + x_3 + \cdots \tag{6.5}$$

The equilibrium constants are

$$K_i = x_i X/(1-X)(b-X) \tag{6.6}$$

Then,

$$K_i/K_1 = x_i/x_1 \tag{6.7}$$

By definition,

$$(K_1 + K_2 + K_3 + \cdots)/K_1 = K \tag{6.8}$$

Hence

$$X/x_1 = K \tag{6.9}$$

Then,

$$K_1 = Kx_1^2/(1-Kx_1)(b-Kx_1) \tag{6.10}$$

Solving the Eq. (6.10)

$$x_1 = \{(1+b)KK_1 - \sqrt{KK_1}\sqrt{(b-1)^2KK_1 + 4b}\}/2K(KK_1 - 1) \tag{6.11}$$

One can accordingly calculated the equilibrium compositions by the following equations:

$$A: \quad a_e = (1-Kx_1)/(1+b) \tag{6.12}$$

$$B: \quad b_e = (b-Kx_1)/(1+b) \tag{6.13}$$

$$X_i: \quad x_{ie} = K_i x_1/K_1(1+b) \tag{6.14}$$

$$Q: \quad q_e = Kx_1/(1+b) \tag{6.15}$$

Applications and Discussion

The thermodynamic values given by the American Petroleum Institute Research Project 44[3] have been used for the calculation.

Type 1. The isomerization of C_6 and C_8 paraffines, and C_9 aromatics have been employed as the examples. Fig. 1 shows the equilibrium composition diagram consisting of hexane, 2-methylpentane, 3-methylpentane, 2, 2-dimethylbutane and 2, 3-dimethylbutane. The one-dotted-broken lines are drawn on the basis of Ridgway's data experimentally obtained in the isomerization of hexanes[4]. The two-dotted-broken lines are drawn according to Lawrance and Rawlings[5]. The discrepancies observed between the solid and broken lines may be due to the accuracy of API data. Since small Gibbs energy difference of isomerization is obtained as the difference between the large Gibbs energies of formation, any errors involved may be magnified.

Table 1 shows the equilibrium compositions of octane, 2-methylheptane, 3-methylheptane, 4-methylheptane, 3-ethylhexane, 2, 2-dimethylhexane, 2, 3-dimethylhexane, 3, 4-dimethylhexane, 2, 2, 3-trimethylpentane, 2, 2, 4-trimethylpentane, 2, 3, 3-trimethylpentane, 2, 3, 4-trimethylpentane, 3-ethyl-2-methylpentane, 3-ethyl-3-methylpentane, and 2, 2, 3, 3-tetramethylbutane. The thermodynamic values of 3-methylheptane and 2, 2, 3-trimethylpentane used are those of (3RS)-methylheptane and of 2, 2, (3RS)-trimethylpentane, respectively. The values of equilibrium mixtures are employed for 3, 4-dimethylhexane. The contents of trimethylpentanes and of tetramethlybutane are quite small.

Table 1. Equilibrium compositions of C_8 paraffins.

Temp. T/K	n-Octane	Methylheptane 2-	3-	4-	Dimethylhexane 2,2-	2,3-	2,4-	2,5-	3,3-	3,4-	3-Ethyl-hexane	Pentane 3-Ethyl-2-methyl	3-Ethyl-3-methyl	Trimethylpentane 2,2,3-	2,2,4-	2,3,3-	2,3,4-	2,2,3,3-Tetramethyl-butane
200	0.18	3.61	1.29	0.36	37.51	0.53	9.16	32.29	4.53	0.25	0.19	0.12	0.04	0.74	8.09	0.44	0.28	0.38
298	2.06	11.54	7.44	2.25	18.81	2.45	12.98	25.96	5.68	1.47	1.42	0.61	0.14	1.00	4.64	0.80	0.59	0.16
300	2.14	11.65	7.52	2.29	18.63	2.48	13.10	25.60	5.76	1.50	1.45	0.62	0.14	1.01	4.55	0.79	0.60	0.16
400	5.54	15.73	13.70	4.41	10.13	3.90	12.38	16.97	5.01	2.64	3.18	1.12	0.20	0.86	2.64	0.81	0.69	0.08
500	8.68	16.90	17.05	5.80	6.36	4.57	11.06	11.88	4.29	3.27	4.57	1.43	0.23	0.71	1.72	0.73	0.69	0.05
600	11.07	17.11	18.46	6.86	4.51	4.74	10.36	8.67	3.81	3.79	5.39	1.72	0.24	0.60	1.28	0.68	0.68	0.03
700	12.57	17.00	19.52	7.24	3.53	4.90	9.58	7.14	3.53	3.76	6.30	1.78	0.25	0.54	1.04	0.65	0.65	0.02
800	14.22	16.33	20.89	7.73	2.82	4.85	8.71	5.93	3.41	3.85	6.44	1.97	0.26	0.49	0.85	0.60	0.64	0.02
900	14.97	15.15	21.10	8.25	2.55	5.16	8.66	5.20	3.37	3.97	7.00	1.87	0.27	0.47	0.74	0.61	0.65	0.02
1000	16.06	15.44	20.78	8.07	2.29	5.03	8.45	4.59	3.26	3.97	7.34	1.92	0.28	0.46	0.78	0.60	0.67	0.02

Concentrations /mol%

Table 2 shows the equilibrium compositions of propylbenzene, cumene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene, 1, 2, 3-trimethylbenzene, 1, 2, 4-trimethylbenzene and 1, 3, 5-trimethylbenzene. The concentration (mol%) of 1, 2, 3-trimethylbenzene shows a maximum at around 600°C, and that of cumene is quite small.

Type 2. The dimerization of ethylene to form n-butenes has been employed as an example. Fig. 2 and Table 3 show the equilibrium compositions of the system con-
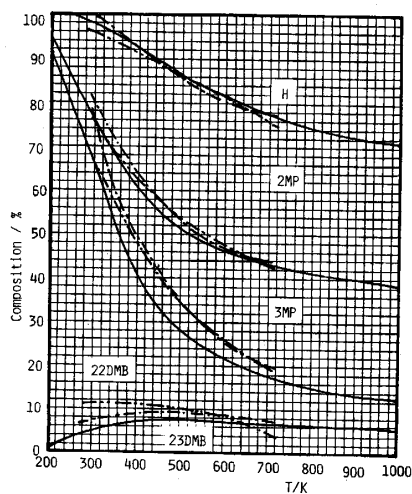
Fig. 1 Calculated thermodynamic equilibria of C_6 paraffins.

H: n-hexane, 2MP: 2-methylpentane, 3MP: 3-methylpentane,
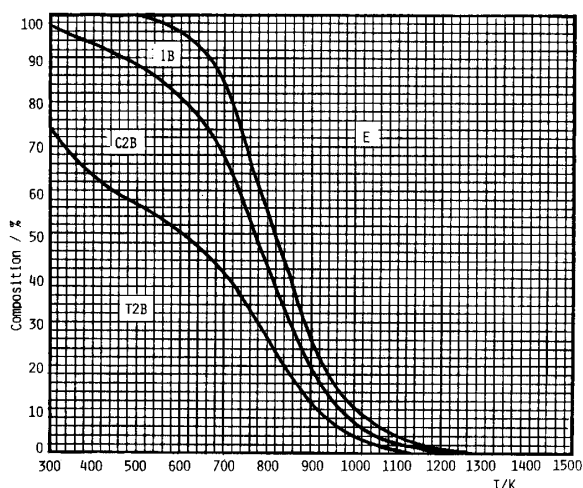22DMB: 2, 2-dimethylbutane, 23DMB: 2, 3-dimethylbutane.

Fig. 2 Calculated thermodynamic equilibria at 1 atm for the
dimerization of ethylene.

E: ethylene, 1B: 1-butene, C2B: cis-2-butene, T2B:
trans-2-butene.

sisting of ethylene, 1-butene, cis-2-butene, trans-2-butene under 1 atm and 10 atm, re-
spectively. Since the n-butenes are also in the equilibrium, the mol ratios of individual
n-butene isomer to total n-butenes are respectively equal to those calculated by Eqs.
(1.1–4).

Type 3. The ethylation of ethylbenzene to form diethylbenzenes has been
employed as an example, the isomerization of ethylbenzene not being assumed. Table
4 shows the equilibrium composition of the system consisting of ethylene, ethylbenzene,
o-diethylbenzene, m-diethylbenzene and p-diethylbenzene under 1 atm, the reactants of
stoichiometric ratio being used. Fig. 3 shows the equilibrium compositions of the

Table 2. Equilibrium compositions of C_9 aromatics.

Temp.	Concentrations /mol%						
T/K	Propyl-benzene	Cumene	Ethyltoluene			Trimethylbenzene		
			o-	m-	p-	1,2,3-	1,2,4-	1,3,5-
298	0.01	0.02	0.18	1.15	1.03	5.23	56.17	36.21
300	0.02	0.02	0.18	1.18	1.06	5.28	56.24	36.01
400	0.15	0.11	0.93	4.29	3 34	7.97	55.17	28.03
500	0.53	0.31	2.27	8.27	5.88	9.54	51.10	22.10
600	1.17	0.59	3.98	12.29	8.18	10.11	45.88	17.79
700	2.04	0.92	5.80	15.87	10.10	10.06	40.70	14.57
800	3.07	1.28	7.57	18.84	11.41	9.71	35.99	12.12
900	4.13	1.62	9.21	21.20	12.40	9.23	31.94	10.26
1000	5.24	1.94	10.65	23.04	13.07	8.70	28.54	8.83
1100	6.30	2.22	11.89	24.40	13.56	8.19	25.72	7.72
1200	7.22	2.49	12.96	25.51	13.86	7.70	23.42	6.84
1300	8.09	2.74	13.90	26.36	14.09	7.24	21.43	6.14
1400	8.90	2.98	14.67	27.07	14.21	6.85	19.75	5.78
1500	9.76	3.20	15.33	27.52	14.21	6.51	18.35	5.11

Table 3. Equilibrium compositions of dimerization of ethylene to form n-butenes under 10 atm.

Temp.	Concentrations	/mol%		
T/K	Ethylene	Butene		
		1-	cis-2-	trans-2-
298	0.00	2.38	23.22	74.40
300	0.00	2.42	23.33	74.24
400	0.00	5.75	29.88	64.36
500	0.11	10.23	31.90	57.76
600	1.08	14.74	31.88	52.30
700	5.29	18.47	29.89	46.35
800	16.45	20.14	25.41	38.01
900	36.19	18.08	18.69	27.04
1000	59.64	13.03	11.32	16.01
1100	78.53	7.69	5.77	8.01
1200	89.45	4.12	2.70	3.73
1300	94.74	2.21	1.28	1.76
1400	97.21	1.25	0.65	0.89
1500	98.41	0.75	0.35	0.48

system under 5 atm, in the case that the mol ratio of ethylene to ethylbenzene at initial is 1.5.   In these cases, the compositions among diethylbenzenes are naturally equal to those calculated by Eqs. (1.1–4).
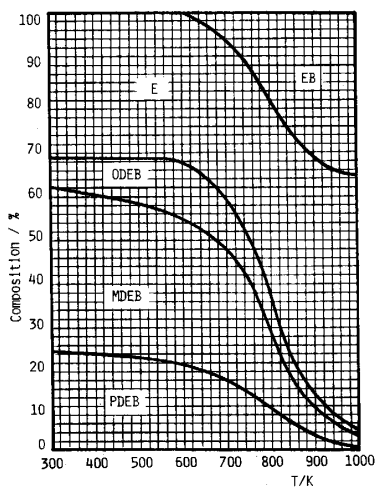

Fig. 3   Calculated thermodynamic equilibria at 5 atm for the ethylation of ethylbenzene.   Ethylene/ethylbenzene, at initial is 1.5.

EB: ethylbenzene, E: ethylene,
ODEB: o-diethylbenzene,
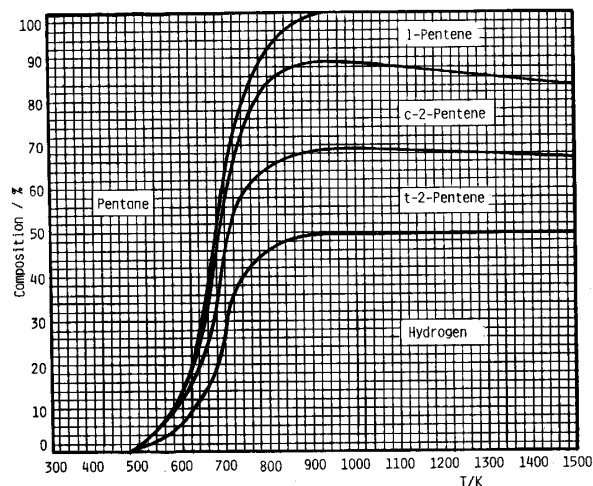MDEB: m-diethylbenzene,
PDEB: p-diethylbenzene.

Fig. 4   Calculated thermodynamic equilibria at 0.1 atm for the dehydrogenation of n-pentane.

Type 4.   The dehydrogenation of n-pentane to form 1-pentene, cis-2-pentene, trans-2-pentene and hydrogen has been employed as an example.   Table 5 and Fig. 4 show the equilibrium compositions of the reaction under 1 atm and under 0.1 atm, respectively.

The compositions among n-pentenes are equal to those calculated by Eqs. (1.1-4).

Table 4. Equilibrium compositions of ethyl-
ation of ethylbenzene to form diethyl-
benzenes. Reaction pressure is 1 atm
and reactant ratio, ethylene/ethyl-
benzene, at initial is 1.0.

Temp.	Concentrations	/mol%			
T/K	Ethyl-benzene	Ethylene	Diethylbenzenes		
			o-	m-	p-
298	0.00	0.00	9.57	55.59	34.83
300	0.00	0.00	9.63	55.56	34.81
400	0.06	0.06	12.92	54.36	32.60
500	1.22	1.22	15.34	52.10	30.12
600	8.68	8.68	14.92	43.42	24.31
700	27.40	27.40	9.02	23.41	12.78
800	43.41	43.41	2.84	6.73	3.60
900	48.44	48.44	0.71	1.57	0.82
1000	49.56	49.56	0.21	0.44	0.22

Tabe 5. Equilibrium compositions of dehydro-
genation of n-pentane to form n-pentenes
and hydrogen under 1 atm.

Temp.	Concentrations	/mol%			
T/K	Pentane	Pentene			Hydrogen
		1-	cis-2-	trans-2-	
298	100.00	0.00	0.00	0.00	0.00
300	100.00	0.00	0.00	0.00	0.00
400	99.99	0.00	0.00	0.00	0.01
500	99.54	0.02	0.10	0.11	0.23
600	95.01	0.26	1.10	1.13	2.49
700	74.88	1.70	5.49	5.37	12.56
800	35.60	5 37	13.56	13.28	32.20
900	9.04	8.88	18.63	17.97	45.48
1000	2.01	10.87	19.32	18.81	49.00
1100	0.54	12.21	19.00	18.52	49.73
1200	0.18	13.53	18.22	18.15	49.91
1300	0.07	14.53	17.60	17.84	49.97
1400	0.03	15.45	17.02	17.52	49.99
1500	0.01	16.42	16.52	17.04	49.99

Type 5. Two kinds of disproportionation reaction have been employed as ex-
amples. One is the case that two mol of toluene react to produce benzene, o-xylene,
m-xylene, and p-xylene. Table 6 shows the equilibrium compositions of the system.
The compositions among xylenes are equal to those calculated by Eqs. (1.1-4).

Table 6. Equilibrium composition of dispro-
portionation of toluene to form
benzene and xylenes

Temp.	Concentrations	/mol%			
T/K	Toluene	Benzene	Xylene		
			o-	m-	p-
298	46.06	26.97	4.39	16.16	6.42
300	46.04	26.98	4.41	16.15	6.42
400	45.09	27.45	5.20	15.62	6.64
500	44.37	27.82	5.88	15.24	6.69
600	43.78	28.11	6.45	14.97	6.69
700	43.36	28.32	6.91	14.77	6.64
800	43.02	28.49	7.30	14.61	6.58
900	42.77	28.61	7.62	14.48	6.51
1000	42.54	28.73	7.91	14.37	6.46
1100	42.37	28.81	8.14	14.27	6.40
1200	42.22	28.89	8.35	14.19	6.35
1300	42.09	28.95	8.52	14.13	6.30
1400	41.98	29.01	8.66	14.08	6.26
1500	41.86	29.07	8.81	14.03	6.22

Table 7. Equilibrium compositions of toluene
with ethylbenzene to form ethyl-
toluenes and benzene. Reactant ratio,
toluene/ethylbenzene, at initial is 1.0.

Temp.	Concentrations	/mol%				
T/K	Toluene	Ethyl-benzene	Ethyltoluene			Benzene
			o-	m-	p-	
298	28.60	28.60	1.61	10.42	9.37	21.40
300	28.58	28.58	1.62	10.44	9.35	21.40
400	27.95	27.95	2.40	11.05	8.59	22.05
500	27.48	27.48	3.12	11.34	8.07	22.52
600	27.08	27.08	3.73	11.52	7.67	22.92
700	26.78	26.78	4.25	11.63	7.34	23.22
800	26.55	26.55	4.69	11.68	7.07	23.45
900	26.36	26.36	5.09	11.71	6.84	23.64
1000	26.19	26.19	5.42	11.73	6.66	23.81
1100	26.06	26.06	5.71	11.72	6.51	23.94
1200	25.95	25.95	5.96	11.72	6.37	24.05
1300	25.86	25.86	6.17	11.71	6.26	24.14
1400	25.76	25.76	6.36	11.73	6.15	24.24
1500	25.67	25.67	6.54	11.73	6.06	24.32

The other is the case that two mol of propylene react to form ethylene, 1-butene,
cis-2-butene and trans-2-butene. Fig. 5 shows the equilibrium compositions of the

system.   The compositions among n-butenes reasonably agree with those shown in Fig. 2 and Table 3.
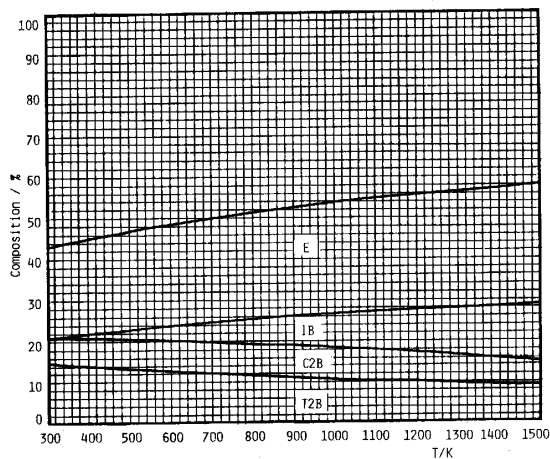

Fig. 5   Calculated thermodynamic equilibria for disproportionation of propylene.

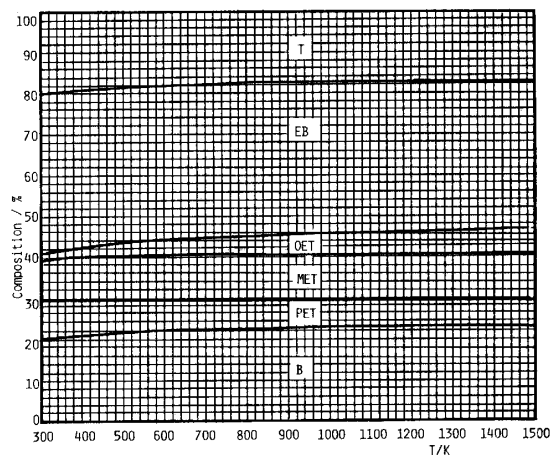P: propylene,   E: ethylene,   1B: 1-butene, C2B: cis-2-butene,   T2B: trans-2-butene.

Fig. 6   Calculated thermodynamic equilibria for the reaction, toluene + ethylbenzene = benzene + ethyltoluene.   Toluene/ethylbenzene at initial is 1/1.5.

T: toluene,   EB: ethylbenzene,   OET: o-ethyltoluene,   MET: m-ethyltoluene, PET: p-ethyltoluene,   B: benzene.

Type 6.   A transalkylation reaction has been employed as an example; toluene reacts with ethylbenzene to form benzene and ethyltoluenes.   It is assumed in this case that the isomerization of ethylbenzene does not take place, but that ethyltoluenes are isomerized.   Table 7 shows the equilibrium compositions of the system consisting of toluene, ethylbenzene, o-ethyltoluene, m-ethyltoluene, p-ethyltoluene and benzene, the mol ratio of toluene to ethylbenzene at initial being unity.   Fig. 6 shows the case that the mol ratio is 1/1.5.   The compositions among ethyltoluenes in these cases also agree with those shown in Table 2.

Conclusion

The calculation methods for thermodynamic equilibrium compositions of the following types of reaction system, where the isomerization of product isomers, X_i, takes place, have been demonstrated;   (1) $A \rightleftarrows X_i$,   (2) $2A \rightleftarrows X_i$,   (3) $A + B \rightleftarrows X_i$,   (4) $A \rightleftarrows X_i + Q$,   (5) $2A \rightleftarrows X_i + Q$,   (6) $A + B \rightleftarrows X_i + Q$.   The equilibrium compositions calculated are consistent with each other, and shown in the figures or tables in the text.

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