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Thermodynamic Equilibria among Benzene and the Methylbenzenes from Spectroscopic Data

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PERIODIC interest in the isomerization-disproportionation reactions existing among benzene and the 12 methylbenzenes provided an impetus for calculation of the thermodynamic equilibria involved. The requisite free energy of formation data were calculated previously from infrared and Raman spectroscopic data (2, 4) and calorimetric information.

The actual computation of equilibria in complex mixtures can become involved, unless proper choice of equations is made. The method outlined by Kandiner and Brinkley (3) is particularly valuable in this regard.

In any methylbenzene disproportionation reaction the possibility exists that all of the following components may be present at equilibrium:

Benzene	N_3	1,3,5-Trimethylbenzene	
Methylbenzene	N_4	1,2,3,4-Tetramethylbenzene	
1,2-Dimethylbenzene		1,2,3,5-Tetramethylbenzene	N_5
1,3-Dimethylbenzene	N_1	1,2,4,5-Tetramethylbenzene	
1,4-Dimethylbenzene		Pentamethylbenzene	N_6
1,2,3-Trimethylbenzene		Hexamethylbenzene	N_7
1,2,4-Trimethylbenzene	N_2		

N_i represents the mole fraction of the component present at equilibrium. The total dimethylbenzenes, trimethylbenzenes, and tetramethylbenzenes can be related to the concentration of a single isomer as follows:

1,3-Dimethylbenzene $\underset{\rightleftarrows}{K_x}$ 1,2-Dimethylbenzene

1,3-Dimethylbenzene $\underset{\rightleftarrows}{K_y}$ 1,4-Dimethylbenzene

(1,2-Dimethylbenzene) = K_x(1,3-Dimethylbenzene)
(1,4-Dimethylbenzene) = K_y(1,3-Dimethylbenzene)
(1,3-Dimethylbenzene) = (1,3-Dimethylbenzene)

(Total dimethylbenzenes) = $(1 + K_x + K_y)$(1,3-dimethylbenzene)

This simplification reduces the number of components from 13 to seven for most calculations.

To calculate the seven unknown concentrations, seven independent equations are required. It has not been found possible to write down seven equations explicit in the unknowns. Instead, successive approximations are required, until two criteria are fulfilled—namely, material balances on moles of benzene nuclei and methyl groups. Availability of these two criteria permits selection of two independent components: These are taken to be 1,3-dimethylbenzene and 1,2,4-trimethylbenzene.

The important Kandiner and Brinkley contribution is the choice that is now made for the remaining five equations. Their criterion for this selection is that each equation contain only one of the unknown components in terms of the independent components. Using this criterion, the following equations can be written:

3(1,3-Dimethylbenzene) $\underset{\rightleftarrows}{K_3}$ benzene + 2(1,2,4-trimethylbenzene)

2(1,3-Dimethylbenzene) $\underset{\rightleftarrows}{K_4}$ methylbenzene + 1,2,4-trimethylbenzene

2(1,2,4-Trimethylbenzene) $\underset{\rightleftarrows}{K_5}$

1,2,3,5-tetramethylbenzene + 1,3-dimethylbenzene

3(1,2,4-Trimethylbenzene) $\underset{\rightleftarrows}{K_6}$

pentamethylbenzene + 2(1,3-dimethylbenzene)

4(1,2,4-Trimethylbenzene) $\underset{\rightleftarrows}{K_7}$
N_2

hexamethylbenzene + 3(1,3-dimethylbenzene)
$N_7 N_1$

Accordingly

$$N_7 = \frac{K_7(N_2)^4}{(N_1)^3} \qquad \text{or} \qquad K_7 = \frac{N_7(N_1)^3}{(N_2)^4}$$

Since K_5 can be computed from the data reported previously (2) and N_1 and N_2 are assumed, one can obtain a value for

Table I. Theoretical Equilibrium Concentrations of Methylbenzenes

Compound	300° K.			400° K.			500° K.			600° K.			700° K.			800° K.			900° K.			1000° K.		
	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]	Mole[a]	Wt.[a]	L.V.[a]
Methylbenzene Disproportionation Equilibria																								
Benzene	30.0	25.4	25.2	30.2	25.6	25.3	31.2	26.5	26.2	31.5	26.7	26.5	31.9	27.1	26.8	32.0	27.1	26.9	32.3	27.4	27.1	32.4	27.5	27.2
Methylbenzene	44.0	44.0	44.1	43.1	43.0	43.3	42.2	42.2	42.4	41.7	41.7	41.9	41.1	41.0	41.2	40.6	40.6	40.7	40.6	40.6	40.8	40.3	40.3	40.5
1,2-Dimethylbenzene	3.5	4.0	4.0	4.2	4.7	4.7	4.6	5.3	5.3	5.0	5.7	5.7	5.3	6.2	6.2	5.8	6.6	6.5	5.9	6.8	6.7	6.1	7.0	6.9
1,3-Dimethylbenzene	13.4	15.4	15.5	12.9	15.0	15.1	12.5	14.5	14.6	12.2	14.2	14.2	12.0	13.8	13.9	11.9	13.8	13.9	11.6	13.4	13.5	11.5	13.3	13.5
1,4-Dimethylbenzene	5.3	6.2	6.2	5.6	6.4	6.4	5.5	6.3	6.3	5.5	6.3	6.4	5.4	6.2	6.2	5.4	6.2	6.3	5.2	6.0	6.1	5.2	6.0	6.0
Total dimethylbenzenes	22.2	25.6	25.7	22.7	26.1	26.2	22.6	26.1	26.2	22.7	26.2	26.3	22.7	26.2	26.3	23.1	26.6	26.7	22.7	26.2	26.3	22.8	26.3	26.4
1,2,3-Trimethylbenzene	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.4	0.4	0.4	0.5	0.5	0.4	0.5	0.5	0.5	0.6	0.6	0.5	0.7	0.7
1,2,4-Trimethylbenzene	2.1	2.8	2.8	2.5	3.3	3.2	2.5	3.2	3.2	2.6	3.4	3.3	2.6	3.5	3.5	2.7	3.5	3.5	2.6	3.5	3.5	2.7	3.5	3.5
1,3,5-Trimethylbenzene	1.4	1.8	1.8	1.1	1.5	1.5	1.0	1.3	1.3	0.9	1.2	1.2	0.9	1.1	1.1	0.8	1.1	1.1	0.8	1.0	1.0	0.8	1.0	1.0
Total trimethylbenzenes	3.6	4.7	4.7	3.8	5.0	4.9	3.7	4.8	4.8	3.8	5.0	4.9	3.9	5.1	5.1	3.9	5.1	5.1	3.9	5.1	5.1	4.0	5.2	5.2
Total tetramethylbenzenes	0.2	0.3	0.3	0.2	0.3	0.3	0.3	0.4	0.4	0.3	0.4	0.4	0.4	0.6	0.6	0.4	0.6	0.6	0.5	0.7	0.6	0.5	0.7	0.7
Dimethylbenzenes Disproportionation Equilibria																								
Benzene	4.5	3.3	3.3	4.9	3.6	3.6	5.3	3.9	3.9	5.7	4.2	4.2	6.0	4.4	4.4	6.3	4.6	4.6	6.5	4.8	4.7	6.7	4.9	4.9
Methylbenzene	23.7	20.6	20.7	23.6	20.5	20.5	23.8	20.7	20.7	24.0	20.8	20.9	24.1	21.0	21.0	24.1	21.0	21.1	24.2	20.9	21.1	24.4	21.3	21.5
1,2-Dimethylbenzene	6.7	6.7	6.7	7.8	7.8	7.7	8.7	8.6	8.6	9.1	9.1	9.0	9.7	9.7	9.7	10.3	10.3	10.2	10.4	10.4	10.4	10.8	10.8	10.7
1,3-Dimethylbenzene	25.9	25.9	26.1	24.4	24.4	24.6	23.3	23.3	23.5	22.5	22.5	22.7	21.8	21.8	22.0	21.4	21.4	21.6	20.7	20.7	20.8	20.4	20.4	20.6
1,4-Dimethylbenzene	10.3	10.3	10.3	10.3	10.3	10.4	10.2	10.3	10.3	10.0	10.0	10.1	9.8	9.8	9.8	9.6	9.6	9.8	9.3	9.3	9.4	9.1	9.1	9.3
Total dimethylbenzenes	42.9	42.9	43.1	42.5	42.5	42.7	42.2	42.2	42.4	41.6	41.6	41.8	41.3	41.3	41.5	41.3	41.3	41.6	40.4	40.4	40.6	40.3	40.3	40.6
1,2,3-Trimethylbenzene	0.7	0.8	0.7	1.1	1.2	1.2	1.4	1.6	1.6	1.7	2.0	2.0	2.1	2.3	2.6	2.2	2.5	2.4	2.4	2.8	2.7	2.6	2.9	2.9
1,2,4-Trimethylbenzene	14.8	16.7	16.6	15.9	18.0	17.9	15.5	17.5	17.4	15.2	17.2	17.1	14.7	16.7	16.6	14.3	16.2	16.1	14.2	16.1	16.0	13.8	15.6	15.5
1,3,5-Trimethylbenzene	9.7	11.0	11.1	7.2	8.2	8.2	6.2	7.0	7.0	5.5	6.2	6.2	4.9	5.6	5.3	4.5	5.1	5.2	4.3	4.8	4.9	4.0	4.6	4.6
Total trimethylbenzenes	25.2	28.5	28.4	24.2	27.4	27.3	23.1	26.1	26.0	22.4	25.4	25.3	21.7	24.6	24.5	21.0	23.8	23.7	20.9	23.7	23.6	20.4	23.1	23.0
1,2,3,4-Tetramethylbenzene	0.3	0.4	0.3	0.5	0.6	0.6	0.7	0.9	0.9	0.9	1.2	1.1	1.2	1.5	1.4	1.3	1.6	1.5	1.5	1.9	1.8	1.6	2.1	2.0
1,2,3,5-Tetramethylbenzene	1.9	2.4	2.3	2.4	3.1	3.0	2.8	3.5	3.4	3.0	3.9	3.8	3.3	4.2	4.2	3.4	4.3	4.2	3.7	4.7	4.6	3.8	4.7	4.7
1,2,4,5-Tetramethylbenzene	1.4	1.8	1.8	1.8	2.2	2.2	1.9	2.4	2.4	2.1	2.5	2.5	2.1	2.6	2.6	2.2	2.8	2.8	2.3	2.9	2.9	2.3	2.9	2.8
Total tetramethylbenzenes	3.6	4.6	4.4	4.7	5.9	5.8	5.4	6.8	6.7	6.0	7.6	7.4	6.6	8.3	8.2	6.9	8.7	8.5	7.5	9.5	9.3	7.7	9.7	9.5
Pentamethylbenzene	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.3	0.3	0.3	0.4	0.4	0.3	0.4	0.4	0.4	0.6	0.5	0.5	0.7	0.7	0.5	0.7	0.7
Trimethylbenzene Disproportionation Equilibria																								
Benzene	0.2	0.1	0.1	0.2	0.1	0.1	0.3	0.2	0.2	0.3	0.3	0.3	0.5	0.3	0.3	0.6	0.4	0.4	0.6	0.4	0.4	0.7	0.5	0.5
Methylbenzene	3.2	2.5	2.5	3.9	3.0	3.0	4.5	3.4	3.5	5.2	4.0	4.0	5.4	4.1	4.2	5.5	4.4	4.4	6.0	4.6	4.7	6.4	5.0	5.0
1,2-Dimethylbenzene	3.4	3.0	3.0	4.2	3.7	3.7	4.9	4.3	4.4	5.5	4.9	4.8	5.9	5.2	5.2	6.3	5.6	5.6	6.6	5.8	5.8	6.9	6.1	6.1
1,3-Dimethylbenzene	13.1	11.6	11.7	13.3	11.7	11.9	13.4	11.8	12.0	13.6	12.0	12.2	13.2	11.7	11.9	13.2	11.6	11.9	13.0	11.5	11.7	13.1	11.6	11.8
1,4-Dimethylbenzene	5.2	4.6	4.7	5.6	5.0	5.1	5.8	5.2	5.2	6.0	5.3	5.4	6.0	5.3	5.4	5.9	5.2	5.3	5.8	5.1	5.3	5.9	5.2	5.4
Total dimethylbenzenes	21.7	19.2	19.4	23.1	20.4	20.7	24.1	21.3	21.6	25.1	22.2	22.5	25.1	22.2	22.5	25.4	22.4	22.8	25.4	22.4	22.8	25.9	22.9	23.3
1,2,3-Trimethylbenzene	1.2	1.2	1.2	1.9	1.9	1.9	2.5	2.5	2.5	2.9	2.9	2.9	3.4	3.4	3.3	3.6	3.6	3.5	3.9	3.9	3.8	4.1	4.1	4.0
1,2,4-Trimethylbenzene	28.0	28.0	28.0	28.3	28.3	28.3	26.9	26.9	26.9	25.5	25.6	25.7	24.2	24.2	24.3	23.2	23.2	23.4	22.5	22.5	22.7	21.7	21.7	21.8
1,3,5-Trimethylbenzene	18.4	18.4	18.6	12.9	12.9	13.1	10.7	10.7	10.9	9.2	9.2	9.3	8.1	8.1	8.3	7.4	7.4	7.5	6.8	6.8	6.9	6.3	6.3	6.5
Total trimethylbenzenes	47.6	47.6	47.8	43.1	43.1	43.3	40.1	40.1	40.3	37.6	37.7	37.9	35.7	35.7	35.9	34.2	34.2	34.4	33.2	33.2	33.4	32.1	32.1	32.3
1,2,3,4-Tetramethylbenzene	2.0	2.3	2.2	2.9	3.3	3.2	3.7	4.1	4.0	4.3	4.8	4.7	5.1	5.7	5.6	5.5	6.2	6.0	6.0	6.7	6.5	6.3	7.1	6.9
1,2,3,5-Tetramethylbenzene	13.4	14.8	14.7	14.1	15.7	15.5	14.4	16.1	15.9	14.3	16.1	15.9	14.8	16.6	16.3	14.8	16.5	16.3	14.8	16.5	16.3	14.7	16.4	16.2
1,2,4,5-Tetramethylbenzene	9.9	11.1	10.9	10.1	11.2	11.1	9.9	11.0	11.0	9.7	10.8	10.7	9.3	10.3	10.3	9.4	10.4	10.5	9.2	10.3	10.3	8.9	9.9	9.9
Total tetramethylbenzenes	25.3	28.2	27.8	27.1	30.2	29.8	28.0	31.3	30.9	28.3	31.7	31.3	29.2	32.6	32.2	29.7	33.1	32.8	30.0	33.5	33.1	29.9	33.4	33.0
Pentamethylbenzene	2.0	2.4	2.4	2.6	3.2	3.1	3.0	3.7	3.5	3.4	4.1	4.1	4.1	5.1	4.9	4.4	5.4	5.1	4.7	5.8	5.5	4.9	6.0	5.8
Hexamethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1

Tetramethylbenzene Disporportionation Equilibria

Methylbenzene	0.3	0.3	0.4	0.2	0.2	0.3	0.2	0.2	0.3	0.2	0.2	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0
1,2-Dimethylbenzene	1.1	1.0	1.3	0.9	0.9	1.2	0.9	0.8	1.1	0.8	0.8	1.0	0.6	0.6	0.7	0.4	0.4	0.6	0.3	0.3	0.4	0.2	0.2	0.3
1,3-Dimethylbenzene	2.0	2.0	2.5	1.9	1.8	2.3	1.8	1.8	2.2	1.8	1.7	2.2	1.5	1.4	1.8	1.2	1.2	1.5	0.9	0.9	1.1	0.8	0.8	1.0
1,4-Dimethylbenzene	0.9	0.9	1.1	0.9	0.9	1.0	0.8	0.8	1.0	0.8	0.8	0.9	0.6	0.6	0.8	0.6	0.5	0.6	0.4	0.4	0.5	0.4	0.3	0.4
Total dimethylbenzenes	4.0	3.9	4.9	3.7	3.6	4.5	3.5	3.4	4.3	3.4	3.3	4.1	2.7	2.6	3.3	2.2	2.1	2.7	1.6	1.6	2.0	1.4	1.3	1.7
1,2,3-Trimethylbenzene	2.1	2.1	2.3	1.9	1.9	2.1	1.8	1.8	2.0	1.6	1.6	1.8	1.3	1.3	1.5	1.0	1.0	1.2	0.7	0.7	0.8	0.5	0.5	0.5
1,2,4-Trimethylbenzene	11.2	11.0	12.2	11.3	11.1	12.4	11.6	11.3	12.6	11.8	11.6	12.9	11.7	11.4	12.7	11.4	11.2	12.5	10.8	10.6	11.9	10.6	10.4	11.6
1,3,5-Trimethylbenzene	3.3	3.1	3.6	3.5	3.3	3.7	3.7	3.6	4.0	4.0	3.9	4.3	4.2	4.1	4.6	4.7	4.5	5.0	5.0	4.9	5.4	7.0	6.8	7.7
Total trimethylbenzenes	16.6	16.2	18.1	16.7	16.3	18.2	17.1	16.7	18.6	17.4	17.1	19.0	17.2	16.8	18.8	17.1	16.7	18.7	16.5	16.2	18.1	18.1	17.7	19.8
1,2,3,4-Tetramethylbenzene	10.6	10.7	10.7	10.1	10.2	10.2	9.5	9.6	9.6	9.0	9.1	9.1	8.0	8.1	8.1	7.0	7.1	7.1	5.8	5.9	5.9	4.4	4.5	4.5
1,2,4,5-Tetramethylbenzene	24.9	24.7	24.7	25.3	25.2	25.2	25.7	25.7	25.7	26.4	26.3	26.2	27.0	27.0	26.8	27.8	27.7	27.7	28.3	28.2	28.3	29.1	29.1	29.1
1,2,4,5-Tetramethylbenzene	15.2	15.1	15.0	15.9	15.7	15.7	16.6	16.3	16.2	16.5	16.3	16.3	18.3	18.0	18.2	19.4	19.2	19.2	20.4	20.1	20.2	21.8	21.5	21.5
Total tetramethylbenzenes	50.7	50.5	50.4	51.3	51.1	51.1	51.8	51.6	51.5	51.9	51.7	51.6	53.3	53.1	53.1	54.2	54.0	54.0	54.5	54.2	54.4	55.3	55.1	55.1
Pentamethylbenzene	26.5	27.2	24.6	26.5	27.1	24.5	26.2	26.9	24.3	26.0	26.7	24.1	26.0	26.7	24.0	25.9	26.6	24.1	27.1	27.7	25.2	25.1	25.8	23.3
Hexamethylbenzene	1.9	1.9	1.6	1.6	1.7	1.4	1.2	1.2	1.0	1.1	1.0	0.9	0.7	0.7	0.6	0.5	0.5	0.4	0.2	0.2	0.2	0.1	0.1	0.1

Pentamethylbenzene Disproportionation Equilibria

1,2,3-Trimethylbenzene	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
1,2,4-Trimethylbenzene	0.6	0.6	0.8	0.5	0.5	0.7	0.5	0.4	0.6	0.4	0.4	0.5	0.3	0.3	0.4	0.2	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1
1,3,5-Trimethylbenzene	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Total trimethylbenzenes	0.9	0.9	1.1	0.8	0.8	1.0	0.8	0.8	0.9	0.7	0.7	0.8	0.4	0.4	0.5	0.3	0.3	0.4	0.2	0.2	0.2	0.2	0.2	0.2
1,2,3,4-Tetramethylbenzene	3.8	3.8	4.1	3.5	3.5	3.8	3.1	3.0	3.3	2.7	2.7	2.9	2.1	2.1	2.3	1.6	1.6	1.8	1.0	1.0	1.1	0.6	0.6	0.6
1,2,3,5-Tetramethylbenzene	8.9	8.7	9.6	8.7	8.5	9.4	8.3	8.1	9.0	7.9	7.7	8.5	7.2	7.1	7.8	6.5	6.3	7.0	5.1	5.0	5.5	3.7	3.6	4.0
1,2,4,5-Tetramethylbenzene	5.4	5.2	5.8	5.5	5.3	5.9	5.3	5.2	5.7	4.9	4.7	5.3	4.9	4.7	5.2	4.5	4.4	4.8	3.7	3.5	3.9	2.7	2.7	3.0
Total tetramethylbenzenes	18.1	17.7	19.5	17.7	17.3	19.1	16.7	16.3	18.0	15.5	15.1	16.7	14.2	13.9	15.3	12.6	12.3	13.6	9.8	9.5	10.5	7.0	6.9	7.6
Pentamethylbenzene	57.4	57.4	57.5	58.6	58.7	58.7	61.3	61.5	61.5	63.6	63.8	63.8	67.8	67.9	67.9	71.9	72.0	71.9	77.7	77.8	77.9	84.4	84.4	84.4
Hexamethylbenzene	23.6	24.0	21.9	22.9	23.2	21.2	21.2	21.5	19.6	20.2	20.5	18.7	17.6	17.8	16.3	15.2	15.4	14.1	12.3	12.5	11.4	8.0	8.1	7.4

[a] All quantities expressed as per cent.

Figure 1. Disproportionation of toluene

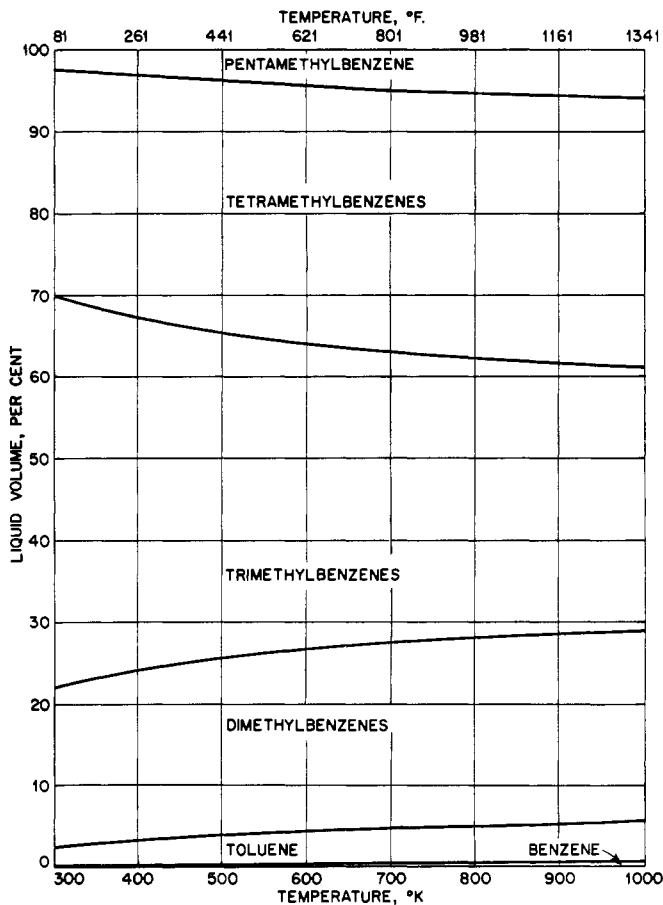Figure 2. Disproportionation
of dimethylbenzenes

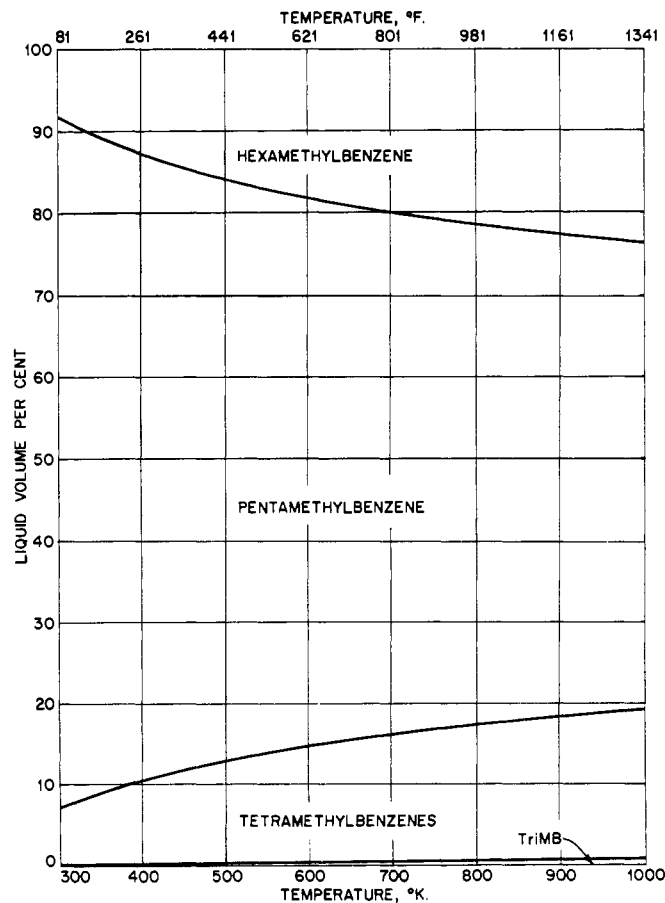Figure 3. Disproportionation of trimethylbenzenes

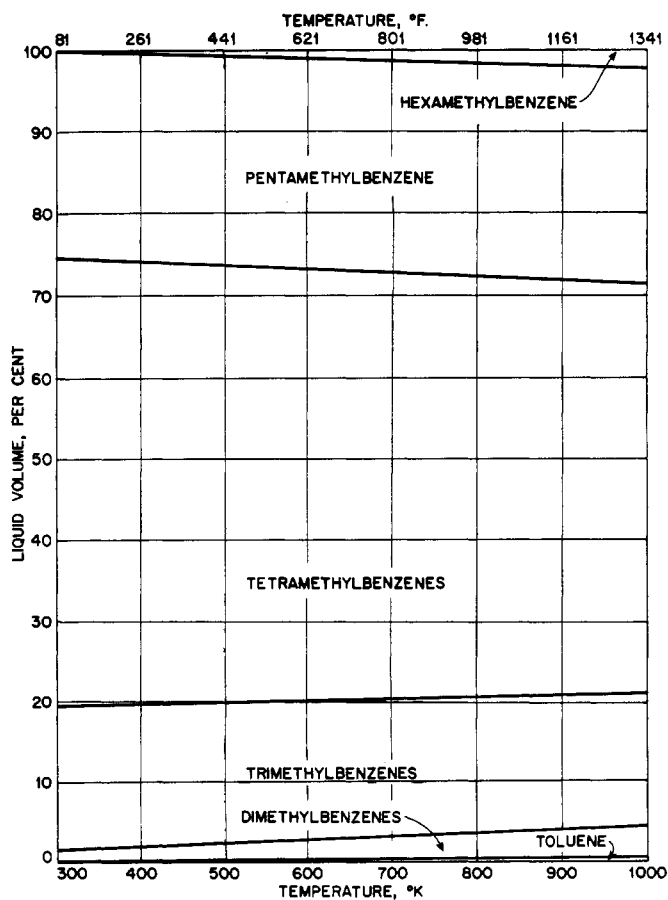
Figure 4. Disproportionation of tetramethylbenzenes

Figure 5. Disproportionation of pentamethylbenzenes

N_7 directly. Likewise, one can determine the other constituents of the equilibrium mixture. The $\sum N$ is found and should be equal to unity. The mole fraction of each component is further multiplied by the number of methyl groups in its structure. For methylbenzene disproportionation $\sum CH_3$ should be 1; dimethylbenzenes, 2; etc. N_1 and N_2 are systematically changed until the two criteria are fulfilled. A graphical method for rapid convergence is described by Smith (5).

The procedure outlined above was programmed on a Burroughs E-101 to permit convenient application of the successive approximation method. The resulting theoretical equilibrium concentrations derived from disproportionation of mono-, di-, tri-, tetra-, and pentamethylbenzenes at 100° K. increments from 300° to 1000° K. are given in Table I on mole, weight, and liquid volume per cent bases. The liquid volume per cent data are plotted in Figures 1 through 5.

An independent series of calculations of the equilibria presented in this article has been published (1). The results of the former investigation are given in a considerably different form from those of the current study; a binomial distribution function was employed to show that statistical distribution of the methyl groups is approached as temperature increases.

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