Calculated Equilibria of the Methylbenzenes and Benzene from 298° to 1000° K.

CLARK J. EGAN
California Research Corp., Richmond, Calif.

METHYL group transfer is a predominant reaction of methylbenzenes in the presence of acid-type catalysts, such as those used in catalytic cracking and isomerization. This transfer reaction is somewhat slower than isomerization, and it proceeds stepwise, the products from the first transfer undergoing subsequent transfer reactions. Equilibrium with respect to isomerization and methyl group transfer involves a large number of species. The equilibrium is usually not attained in catalytic reactions in the temperature range of 600 to 1000° F. because of side reactions, such as cracking.

Data on the thermodynamic properties of the methylbenzenes were extended recently to include the tetra-, penta-, and hexamethylbenzenes (*2*). These data, in conjunction with those reported for the remaining methylbenzenes (*3*), may be used to calculate the isomerization and methyl transfer equilibria involving the 12 methylbenzenes and benzene in the ideal gas state.

The equilibrium distribution of the methylbenzenes is presented here as a function of the average number of methyl groups per ring in the equilibrium mixture. Equilibria involving larger groups than methyl on the ring were not considered.

METHOD AND RESULTS

The 13 simultaneous equations that need to be solved comprise six equations for isomerization equilibria, five equations for methyl group transfer equilibria, one equation defining the average number of methyl groups per ring in the equilibrium mixture, and one equation normalizing the sum of the mole fractions to unity. These equations were conveniently solved with a digital computer at intervals in the range of 0.1 to 0.3 for the average number of methyl groups per ring.

The free energy data given by Hastings and Nicholson (*2*) were used for eight of the methylbenzenes. Some ΔF_f^0 values listed in Table V of their paper are in error, especially those for hexamethylbenzene. The corrected values of ΔF_f^0 in kilocalories per mole are tabulated below:

Temp., ° K.	1,2-Dimethylbenzene	1,2,3-Trimethylbenzene	Pentamethylbenzene	Hexamethylbenzene
298.16			29.479	31.125
300			29.774	31.474
400		41.143		50.804
500				70.704
600	56.115			90.977
700		76.758		111.224
800			115.105	132.154
900				152.799
1000				173.732

The values for the remaining substances were those given by Taylor and others (*3*).

Two sets of eight graphs are used. The first set shows the equilibrium concentration of each individual isomer at 100° intervals from 298° to 1000° K. Figure 1 is the first in this set, and Figure 2 is the eighth. In the second set (Figure 3 is the last of this group), the concentration of the total C_8's, C_9's, and C_{10}'s at equilibrium is plotted. (Copies of the remaining figures are available upon request from the Technical Information Center, California Research Corp., P.O. Box 1627, Richmond, Calif.)

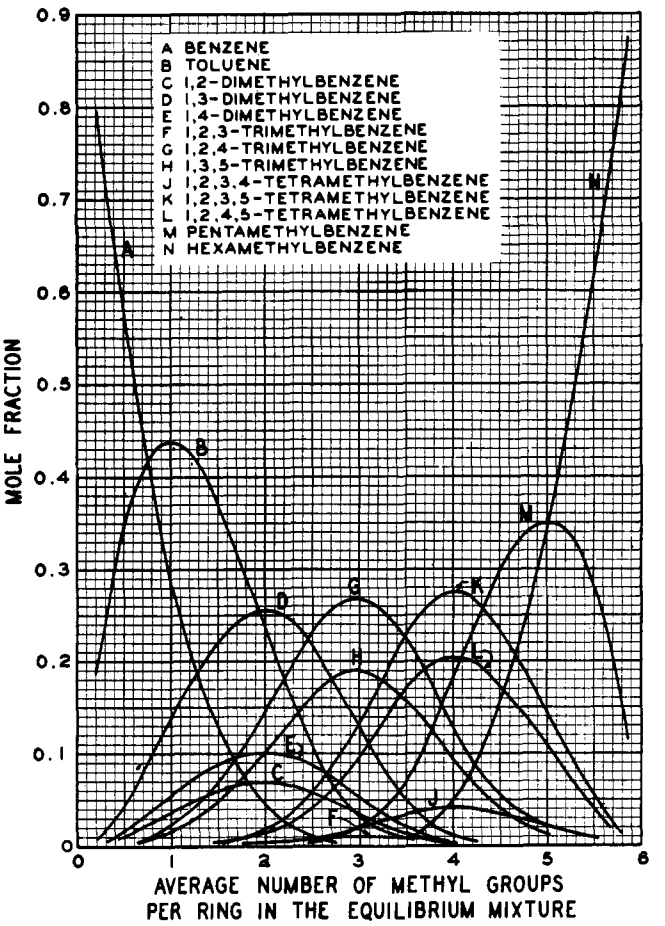

Figure 1. Equilibrium concentration of methylbenzenes in ideal gas state at 298.16° K.

Figure 4 is a cross plot that shows the effect of temperature on the maximum concentration of selected methylbenzenes. For most of the isomers, the temperature effect is small; therefore, the charts presented can be used over a range of ± 100° F. without introducing significant error.

DISCUSSION

The large effect of the methyl transfer reaction is apparent. For example, when there is an average of two methyl groups per ring in the equilibrium mixture corresponding to an over-all composition equivalent to a dimethylbenzene, the most abundant species at equilibrium above 600° K. (620° F.) is toluene rather than any one of the dimethylbenzene isomers. Also, above about 800° K.

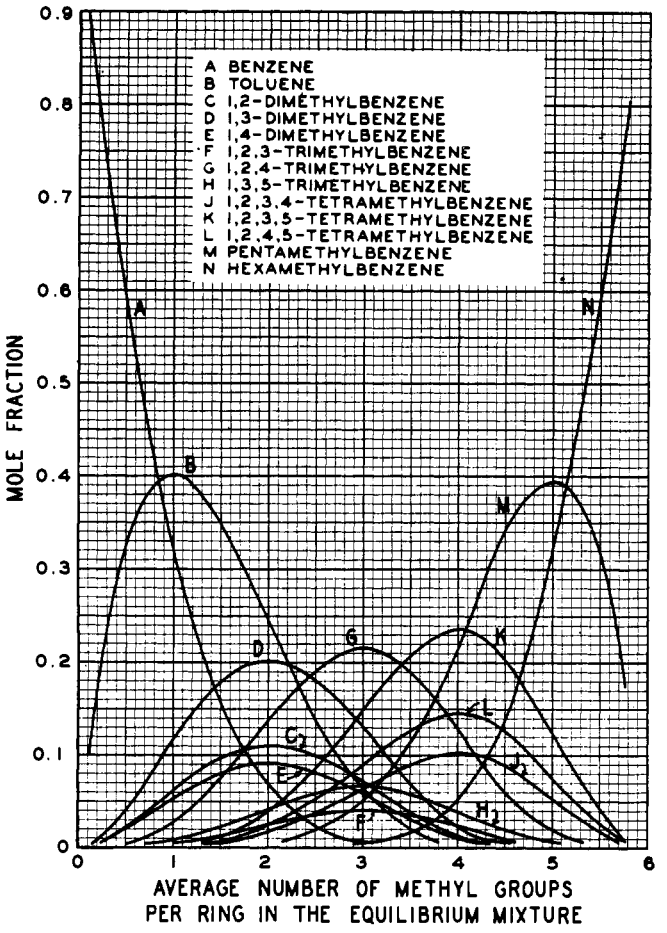

Figure 2. Equilibrium concentration of methylbenzenes in ideal gas state at 1000° K.

(980° F.) when there is an average of three methyl groups per ring in the equilibrium mixture, the concentration of C_8 and C_{10} methylbenzenes almost equals the concentration of C_9 methylbenzenes.

The dashed curves in Figure 3 show the mole fraction of total methylbenzenes of a given molecular weight expected from a statistical distribution of methyl groups. This mole fraction is given by the binomial distribution (*1*).

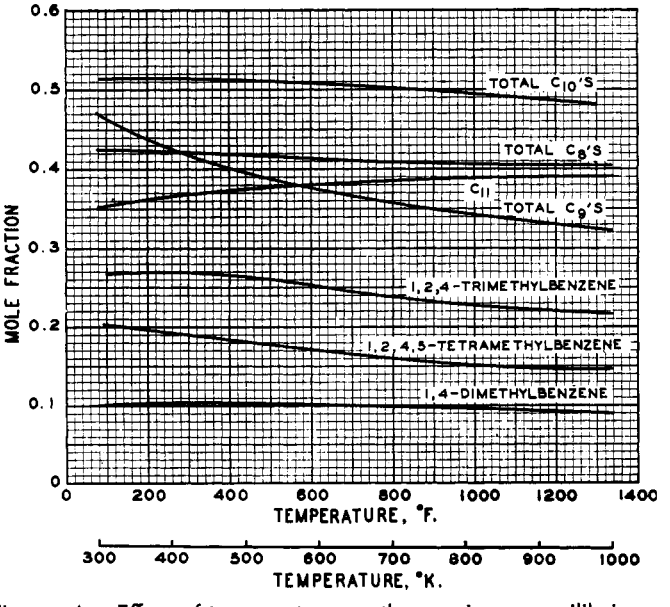

Figure 4. Effect of temperature on the maximum equilibrium concentration of several methylbenzenes

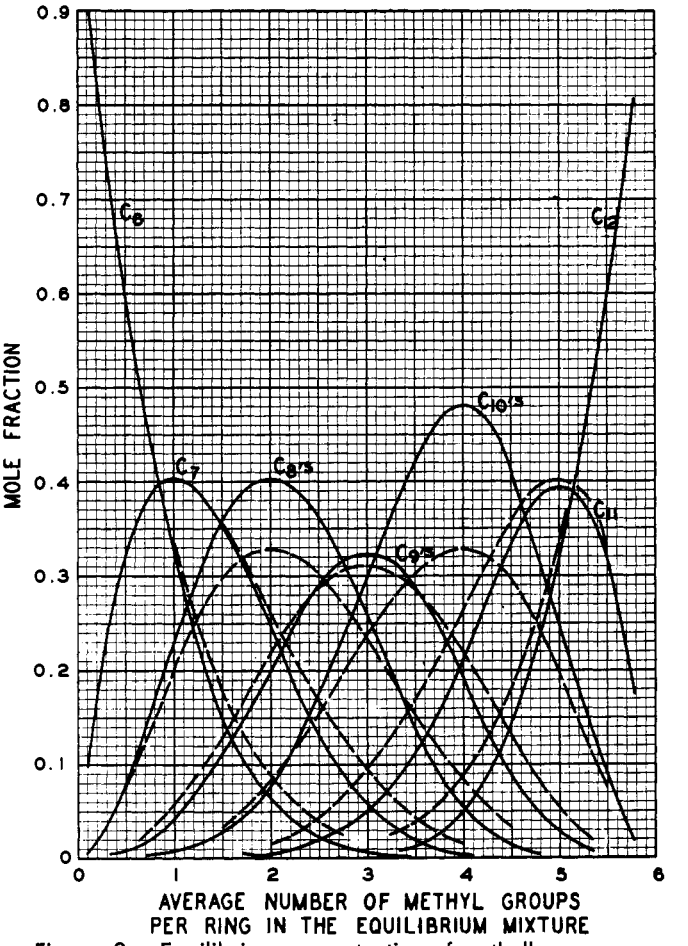

Figure 3. Equilibrium concentration of methylbenzenes in ideal gas state at 1000° K.

Dashed curves show statistical distribution of methyl groups

$$\frac{6!}{N!\ (6-N)!}\left(\frac{x}{6}\right)^{N}\left(\frac{6-x}{6}\right)^{6-N}$$

where

N = number of methyl groups per molecule

x = average number of methyl groups per ring over the whole distribution

The statistical distribution is being approached as the temperature is increased. The distribution of isomers of the C_8, C_9, and C_{10} methylbenzenes also approaches the statistical distribution as the temperature is increased.

One application of these equilibrium data is in increasing the yield in an isomerization reaction of a given methylbenzene. Here methyl group transfer is an undesirable reaction that reduces the yield of the desired isomer. This side reaction may be repressed by addition of the proper concentration of the products of the reaction to the feed stock.

ACKNOWLEDGMENT

The author is indebted to E.B. Reid, Leonard Tornheim, and P.W.M. John for the mathematical analysis, and programming, and to K.S. Pitzer for helpful suggestions.

LITERATURE CITED

(1) Feller, William, "Introduction to Probability Theory and Its Application," 2nd. ed., Vol. I, p. 137, Wiley, 1957.

(2) Hastings, S.H., Nicholson, D.E., *J. Phys. Chem.* **61**, 730 (1957).

(3) Taylor, W.J., Wagman, D.D., Williams, M.G., Pitzer, K.S., Rossini, F.D., *J. Research Natl. Bur. Standards* **37**, 95 (1946).

RECEIVED October 14, 1959. Accepted April 6, 1960.