Heats of Mixing of Benzene and Cyclohexane

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THE HEATS OF mixing at 90° C. of benzene and cyclohexane have been determined in the precision calorimeter described previously (*1*). These and other data will be of interest for thorough evaluation of models for describing interactions in solution (*3*) in terms of group contributions and interactions. Sufficient reliable experimental measurements have not been reported for an adequate number of mixtures of nonelectrolytes to enable rigorous checks on recent theories.

The calorimetric data are summarized in Table I and Figure 1 over a range of concentrations. Similar data for the benzene-cyclohexane binary at 25° C. were published by Scatchard and associates (*4*). A qualitative comparison of the investigation of Scatchard with the current study shows agreement. The heats of mixing at 90° C. of solutions containing approximately 50% mole benzene are about 20% smaller than at 25° C., and there is a slight asymmetry in the energy-concentration curves. Theoretical energies of mixing at 25° C. and 50° C. are shown in Figure 1. These values were computed from relationships derived from regular solution theory (*2*). The behavior of the benzene-cyclohexane binary departs considerably from predictions:

Table I. Experimental Integral Heats of Mixing Benzene and Cyclohexane at 90° C.

Benzene			Cal./Mole	
Wt. %	Mole %	Cal./mole	Cyclohexane	of Mixt.
10.9	11.6	388	50.3	45.2
21.6	22.9	406	120.8	93.1
26.1	27.5	357	135.9	98.5
30.8	32.4	345	165.5	111.9
41.0	42.8	306	229	131.1
50.7	52.5	270	300	142.4
50.6	52.4	268	297	141.1
64.7	66.4	209	415	139.3
73.8	75.2	131	397	98.6
81.9	83.0	90.0	441	74.8
91.2	91.8	41.2	464	37.8

The experimental and theoretical heats of mixing differ by almost an order of magnitude, and the calculated temperature coefficient is only roughly approximated. A satisfactory theory to account for these observations has not been developed at the present time.

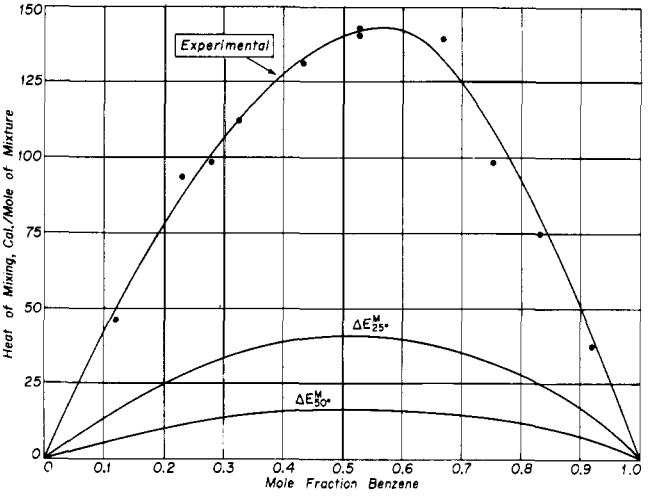

Figure 1. Experimental integral heats of mixing of benzene-cyclohexane at 90° C.

LITERATURE CITED

(1) Nicholson, D.E., J. CHEM. ENG. DATA 5, 35 (1960).
(2) *Ibid.*, p. 309.
(3) Redlich, O., Derr, E.L., Pierotti, G.J., *J. Am. Chem. Soc.* **81**, 2283 (1959).
(4) Scatchard, G., Wood, S.E., Mochel, J.M., *J. Phys. Chem.* **43**, 119 (1939).

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