LITERATURE CITED

(1) Campanile, V.A., Lantz, V., *Anal. Chem.* **26**, 1394 (1954).
(2) Chu, K.Y., Thompson, A.R., J. CHEM. ENG. DATA **7**, 358 (1962).
(3) Eykman, I., *Rec. Trav. Chim.* **14**, 185 (1895).
(4) Gladstone, J.H., Dale, T.P., *Phil. Trans.* **153**, 317 (1863).
(5) Kurtz, S. S., Jr., Ward, A. L., *J. Franklin Inst.* **222**, 563 (1936).
(6) Lorentz, H. A., *Wied. Ann.* **9**, 641 (1880).
(7) Lorenz, L., *Ibid.*, **11**, 70 (1880).
(8) Manufacturing Chemists' Association Research Project, June 30, 1965.
(9) Newton, I., "Opticks," book II, p. 245 (1704).
(10) Sumer, K. M., Thompson, A. R., J. CHEM. ENG. DATA **12**, 489 (1967).
(11) Tseng, Y. M., Thompson, A. R., *Ibid.*, **9**, 264 (1964).

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Vapor-Liquid Equilibrium Data for Benzene-Alkylbenzene Systems

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Isobaric vapor-liquid equilibrium data are reported for the following benzene-alkylbenzene systems: benzene-toluene, benzene-ethylbenzene, and benzene–*n*-propylbenzene. Within the experimental error, these systems obey Raoult's law.

THE SYSTEM benzene-toluene, the simplest member of the benzene-alkylbenzene class of mixtures, obeys Raoult's law closely (*6*). The purpose here is to present thermodynamic data for two other benzene-alkylbenzene systems: benzene-ethylbenzene and benzene–*n*-propylbenzene.

Equilibrium data at atmospheric pressure for the system benzene-ethylbenzene were obtained by Makh and Azarova (*3*), who reported an average relative volatility $\alpha = 7$. The theoretical value, assuming that Raoult's law is obeyed, is $\alpha = 5$. Makh and Azarova also studied the system benzene-toluene and reported a relative volatility $\alpha = 3.5$ (*3*). The theoretical value, assuming that Raoult's law is obeyed, is $\alpha = 2.4$. Since several other studies have shown that the system benzene-toluene obeys Raoult's law (*6*), the authors concluded that the data of Makh and Azarova contain serious errors.

EXPERIMENTAL

Chemicals. Reagents (Eastman Kodak Co.) were further purified by fractionation. The final properties of the reagents are recorded in Table I.

Apparatus. The equilibrium apparatus (Figure 1) is a recirculation type. The main components of the apparatus are the boiler, the vapor-liquid separator, the vapor condenser, the traps for the liquid and vapor condensate. The boiler is provided with internal and external heating units. Vapor generated within the boiler rises through the Cottrell tube and enters the separator. The separated liquid drops to the liquid trap, where samples are withdrawn using a hypodermic needle, and overflows back to the boiler.

Table I. Properties of Reagents

	Refractive Index at 25° C.		Boiling Point, ° C.	
Material	Experimental	Literature (*1*)	Experimental	Literature (*1*)
Benzene	1.49791	1.49792	80.08	80.100
Toluene	1.49413	1.49414	110.62	110.625
Ethylbenzene	1.49318	1.49320	136.18	136.186
n-Propylbenzene	1.48961	1.48951	159.24	159.217

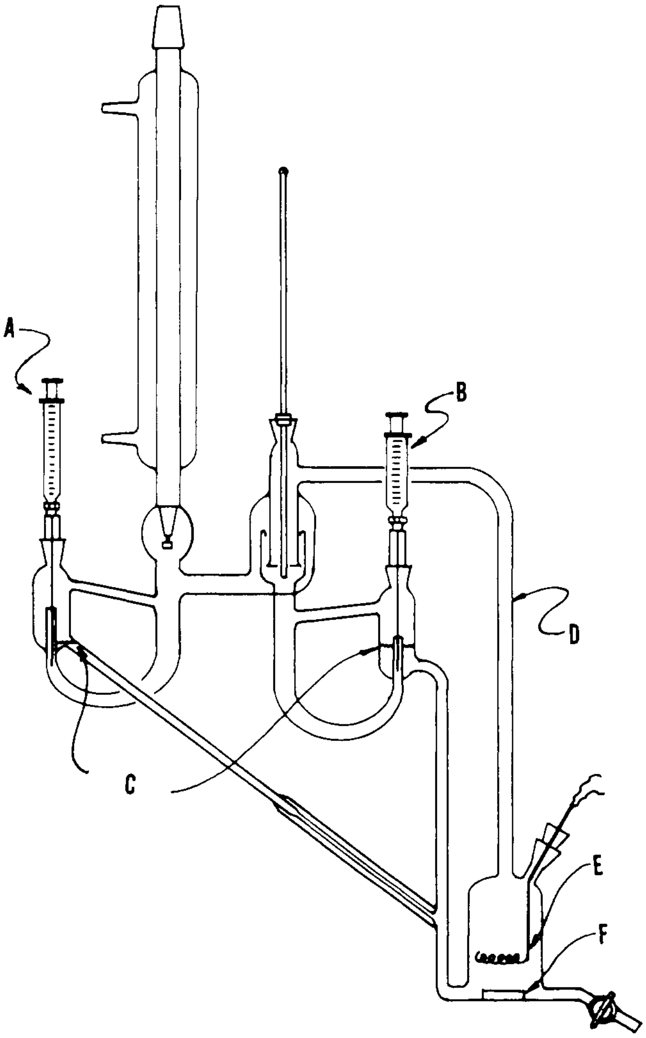

Figure 1. Diagram of equilibrium still

A. Condensate sample
B. Liquid sample
C. Operating levels
D. Cottrell tube
E. Internal heater
F. Stirrer

Table II. Phase Equilibria at 1 Atm.

t, ° C.	x_1	y_1	$x_1 - x_1^{ideal}$	$y_1 - y_1^{ideal}$
		Benzene (1) – Toluene (2)		
110.62	0.000	0.000		
107.04	0.081	0.170	0.000	0.002
99.84	0.268	0.455	0.002	–0.004
91.96	0.505	0.710	–0.006	–0.006
80.08	1.000	1.000		
		Benzene (1) – Ethylbenzene (2)		
136.18	0.000	0.000		
135.31	0.009	0.033	0.001	0.003
134.54	0.017	0.059	0.002	0.004
132.93	0.030	0.106	0.001	–0.002
119.99	0.165	0.458	0.000	–0.005
109.65	0.302	0.664	–0.002	–0.005
101.86	0.438	0.785	0.003	–0.005
93.95	0.601	0.879	0.003	–0.007
88.01	0.753	0.937	0.003	–0.005
82.95	0.902	0.979	0.000	–0.002
81.62	0.945	0.989	–0.001	–0.001
81.09	0.966	0.993	0.001	0.000
80.08	1.000	1.000		
		Benzene (1)-*n*-Propylbenzene (2)		
159.24	0.000	0.000		
158.38	0.005	0.028	0.001	0.003
156.58	0.014	0.078	0.001	0.004
150.36	0.050	0.241	0.004	0.006
138.33	0.126	0.496	0.007	0.007
122.69	0.248	0.726	0.005	0.004
96.50	0.604	0.938	0.011	0.000
93.29	0.668	0.955	0.012	0.002
85.61	0.846	0.984	0.008	0.000
82.02	0.944	0.995	0.004	0.000
81.23	0.965	0.997	0.000	0.000
80.08	1.000	1.000		

Vapor from the separator is condensed, drops into the vapor condensate trap, overflows, and rejoins the recirculating liquid stream. The combined liquid and vapor condensate streams re-enter the base of the boiler in the path of a magnetically driven stirrer. The Cottrell tube and the separator are insulated and covered with a heating tape. The temperature of the insulation, measured by a thermometer placed between the insulation and the heating tape, is maintained about 5° C. below the equilibrium temperature. The accuracy of the equilibrium temperature, measured by the calibrated thermometer in the separator, is ±0.05° C. The composition of the liquid and vapor condensate samples is obtained by means of gas chromatography; the maximum error in the chromatographic analysis is ±0.005 mole fraction. Additional details concerning the apparatus and the procedure have been reported (*2*).

Procedure. All equilibrium runs were allowed to reflux for 6 to 8 hours before the samples were taken, even though a constant temperature in the separator was attained in about 1 hour. The liquid in the hypodermic needles was displaced several times after the equilibrium temperature was attained. Liquid and vapor condensate samples were withdrawn simultaneously. The temperature at the separator (adjusted for emergent stem errors) and barometric pressure were recorded before taking the samples.

RESULTS

Isobaric vapor-liquid equilibrium data at 1 atm. for the mixtures benzene-toluene, benzene-ethylbenzene, and benzene-*n*-propylbenzene are reported in Table II. The pressure varied from 744 to 771 mm. of Hg; the temperatures given in Table II have been corrected (*2*) to 1 normal atm. (760 mm. of Hg).

Activity coefficients were calculated using the equations:

$$Py_1 = P_1^\circ C_1 \gamma_1 x_1 \tag{1}$$

$$Py_2 = P_2^\circ C_2 \gamma_2 x_2 \tag{2}$$

The quantities C_1 and C_2 arise from deviations of the gas phase from the perfect gas law and were calculated using the equations (*7*):

$$\ln C_1 = \frac{(P - P_1^\circ)\ (v_1^L - B_{11}) - y_2^2 \delta_{12} P}{RT} \tag{3}$$

$$\ln C_2 = \frac{(P - P_2^\circ)\ (v_2^L - B_{22}) - y_1^2 \delta_{12} P}{RT} \tag{4}$$

The second virial coefficients B_{11}, and B_{22}, and B_{12} ($\delta_{12} = 2B_{12} - B_{11} - B_{22}$) were estimated by means of the generalized correlation of Pitzer *et al.*(*5*) using published critical constants (*1*). Vapor pressures for the pure materials were calculated by the Antoine equation using constants obtained from (*1*).

The assumption that the vapor is a perfect gas ($C_1 = C_2 = 1$) yields errors in the relative volatility as large as 4, 8, and 14% for the mixtures benzene-toluene, benzene-ethylbenzene, and benzene-*n*-propylbenzene, respectively. Since the pressure is only 1 atm., such large corrections to the perfect gas law are rather surprising at first sight. But, for data taken at atmospheric pressure, the pressure of the light component is always larger than 1 atm. For example, in the case of the system benzene-*n*-propylbenzene, the vapor pressure of benzene varies from 1 to 7 atm.

The excess Gibbs free energy, g^E, was calculated by means of the equation:

$$g^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \tag{5}$$

Within the limit of experimental error, g^E is a quadratic function of composition:

$$g^E/RT = Ax_1x_2 \tag{6}$$

The value of the constant A for each mixture is reported in Table III. The limit of error for g^E at the equimolar composition, as shown in Table III, is 4 to 13 cal. per mole.

The quantity A, although independent of composition for these mixtures, varies with temperature according to the thermodynamic relation (*7*):

$$\frac{h^E}{Rx_1\,x_2} = -\,T^2\,\frac{\partial}{\partial T}\left(\frac{g^E}{RTx_1x_2}\right) = -\,T^2\,\frac{dA}{dT} \tag{7}$$

For the mixture benzene-ethylbenzene, the value of the excess enthalpy at 20° C. and at the equimolar composition is h^E = 26 cal. per mole (*4*). Equation 7 shows that the change in the value of A, ΔA, over the boiling point range 80° to 136° C. (ΔT = 56° C.) is only 0.02. Since the latter value is smaller than the limit of experimental error for A, the procedure of ignoring the temperature dependence of A is justified.

Table III. Excess Gibbs Free Energies for Benzene–Alkylbenzene Systems, 1 Atm.

System	$A = g^E/RTx_1x_2$	g^E at $x_1 = 0.5$ Cal./Mole
Benzene-toluene	0.01 ± 0.02	2 ± 4
Benzene-ethylbenzene	0.01 ± 0.04	2 ± 7
Benzene-*n*-propylbenzene	–0.06 ± 0.07	–11 ± 13

The difference between the experimental composition and the composition calculated by means of Raoult's law ($\gamma_1 = \gamma_2 = 1$) is recorded for each data point in Table II. These differences are generally smaller than the estimated limit of experimental error in the composition (± 0.005 mole fraction).

CONCLUSION

For the vapor-liquid equilibria at 1 atm. and within the experimental error stated previously, the benzene-alkylbenzene systems benzene-toluene, benzene-ethylbenzene, and benzene–*n*-propylbenzene obey Raoult's law.

NOMENCLATURE

A = a constant, Equation 6
B_{ij} = second virial coefficient for i–j interactions
C_i = a dimensionless correction for vapor phase imperfections
g^e = excess Gibbs free energy
h^e = excess enthalpy
P_i° = vapor pressure of pure i
P = pressure
R = gas constant
t = temperature, ° C.
T = temperature, ° K.
v_i^L = molar volume of pure liquid i
x_i = mole fraction of i in liquid phase
y_i = mole fraction of i in gas phase
α = relative volatility = (x_1y_2/y_1x_2)
γ_i = activity coefficient of i in liquid phase

LITERATURE CITED

(1) American Petroleum Institute, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953.
(2) Hollenbach, G. E., M. S. thesis, School of Chemical Engineering, University of Pennsylvania, Philadelphia, Pa., 1962.
(3) Makh, G.M., Azarova, Z.N., *Zhur. Prikladnoi Khim. (J. Appl. Chem.)* **19**, 585 (1946) (in Russian).
(4) Meares, P., *Trans. Faraday Soc.* **49**, 1133 (1953).
(5) Pitzer, K.S., Lippmann, D.Z., Curl, R.F., Jr., Huggins, C.M., Peterson, D.E., *J. Am. Chem. Soc.* **77**, 3427 (1955).
(6) Rowlinson, J.S., "Liquids and Liquid Mixtures," p. 150, Butterworths, London, 1959.
(7) Van Ness, H.C., "Classical Thermodynamics of Non-Electrolyte Solutions," pp. 82, 122, Macmillan, New York, 1964.

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Correlation of Some Thermodynamic Properties of Nitriles

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Available thermodynamic data for nitriles are partitioned and correlated to yield contributions to S° and ΔH_f° from several different types of groups in nitriles. These groups are formed to take account of possible perturbations of portions of the molecule by neighboring groups. Testing of these partitioned contributions for self-consistency, which is done wherever possible, shows that the correlations are satisfactory.

QUANTUM chemical theories must ultimately be tested against experimental information, or, as in the case of semi-empirical theories, they may require calibration with empirical data. In addition, it may be possible to formulate quantum chemical techniques analogous to the group contribution methods of thermodynamics. To date few if any attempts have been made to employ thermodynamic results for any of these purposes. In connection with work from this laboratory on the quantum chemistry of nitrogen compounds (*7-9, 11*), and in particular on the nature of the CN bond (*10*), accurate thermodynamic data on nitriles were required. The paucity of such information soon became apparent from an examination of the literature. Hence, the only convenient alternative was to resort to calculation of the required values by one of the many additivity methods. One of the best of such techniques is the "second-order" method of Benson and Buss (*1*), but unfortunately, only one of the group contributions listed by them contains a nitrile group. Therefore, the available values of the thermodynamic properties of nitriles were used to attempt to complete the group contribution terms given for nitriles by Benson.

METHOD

The best available data which was employed in this work is listed in Table I. In the case of most of the compounds, the results given are the only data available for the gas phase. In some cases, such as that of malononitrile and succinonitrile, older data are available and are referred to in the references. In all cases, the most recent data have been taken as the best available, since the previous results are usually much older, sometimes having been obtained in the nineteenth century. Reliability of data is not always directly related to its age, of course, as can be seen by noting the comparisons made with some of the older data (*3*). Hence, wherever necessary, comparisons of experimental methods were made. This paper will deal with the gas phase at 298.16° K. only.

The method of Benson and Buss was then applied to each of the nitriles in succession. However, to do this, an appropriate partitioning of the nitriles into new groups, some which had not been considered by Benson, was required. The first group contribution which appeared to be appropriate for consideration was that of C_t—$(N_t)(C)$, which, in Benson's notation, is that for the carbon atom of the nitrile group, where the nitrile group carbon is attached to a single bonded carbon atom. C_t and N_t refer to triple bonded carbon and nitrogen atoms, respectively. Then acetonitrile is composed of one C_t—$(N_t)(C)$ group and one C—$(H)_3(C_t)$ group, the contributions of which must be summed.

A symmetry correction of $-R \ln 3 = -2.2$ is then applied to the entropy term for acetonitrile. The term y, which