tie-lines were then obtained by finding the compositions at which curves of constant activity of *n*-propanol intersected the binodal curve. The resultant liquid and vapor three-phase curves are shown, in projection, in Figure 7. The three-phase curves cover a range of boiling points of only about 3°C.

The system does not form a ternary azeotrope, homogeneous or heterogeneous. The vapor and liquid surfaces are rather flat, however, in the region between the homogeneous water-propanol azeotrope and the heterogeneous water-butanol azeotrope. This is evident on inspection of two isothermal sections of the phase diagram at 89° and 91°C, as shown in Figure 8.

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Nomenclature

B_{ij} = second virial coefficient, cm^3 mol^{-1}
G^E = excess Gibbs free energy of mixing, J mol^{-1}
G_{ij} = parameter of Renon-Prausnitz equation
g_{ij} = parameter of Renon-Prausnitz equation
H^E = excess enthalpy of mixing, J mol^{-1}
P = total pressure, mm Hg
P_i^0 = pure component vapor pressure, mm Hg
R = gas constant, J K^{-1} mol^{-1}
T = Kelvin temperature, K
t = Celsius temperature, °C
V^E = excess volume of mixing, cm^3 mol^{-1}
W_i = wt %
x_i = liquid phase mole fraction
y_i = vapor phase mole fraction

Greek Letters

α_{ij} = parameter of Renon-Prausnitz equation
γ_i = liquid phase activity coefficient
η = refractive index (sodium D-line)
ρ = density, g cm^{-3}
τ_{ij} = parameter of Renon-Prausnitz equation

Subscripts

1 = water
2 = *n*-propanol
3 = *n*-butanol
i,j,k,l,r = running variables

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Integral Isobaric Heat of Vaporization of Benzene-1,2-Dichloroethane System

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Integral isobaric heats of vaporization of benzene-1,2-dichloroethane mixtures were measured at pressures of 684 and 760 mm of Hg using a modified Dana's apparatus. The results were found to be linear with composition.

Latent heat of vaporization is a very important property needed in the design and operation of chemical plants. Several investigators have therefore devised methods for the determination of this property. Very little data (*1, 2, 6–10, 12, 13, 15*) are available on heat of vaporization of mixtures.

The first published work on latent heats of mixtures was by Dana (*2*) who worked at atmospheric pressure and cryogenic temperatures. Apart from other sources of error, the main source of error in his experimentation was due to heat leak because of the considerable temperature gradient between the system and the surroundings. Subsequently, attempts have been made (*6–10, 12, 13*) to minimize the heat leak and reduce other sources of error involved. The best modification was due to Shettigar et al. (*9*) who introduced a liquid meter also to avoid changes in the equilibrium condition of the experiment.

Experimental

Materials. Benzene used was of Pro analysi grade produced by Sarabhai Merck Ltd., India, with a reported boiling range of 80–81°C. This material was subjected to the thiophene test. Thiophene was removed by treating it with concentrated sulfuric acid and distilling it after separation and washing it with distilled water. Benzene then was dried over calcium chloride, filtered, and further purified in a distillation column. Only the middle fractions of the distillate were collected. Table I gives a comparison of the experimentally determined physical properties with the literature values.

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Table I. Physical Properties of Purified Components

Component	Normal bp, °C		Refractive index at 30°C		Density at 30°C, g/cc	
	Obsd	Lit.	Obsd	Lit.	Obsd	Lit.
Benzene (*3*)	80.10	80.10	1.49474	1.49468	0.8684	0.86837
1,2-Dichloroethane (*4*)	83.50	83.47	1.43889	1.43929	1.2386	1.23847

Table II. Latent Heats of Vaporization of Benzene–1,2-Dichloroethane Mixtures

Pressure, 684 mm Hg			Pressure, 760 mm Hg		
Mol % benzene	Bp, °C	Latent heat of vaporization cal/g-mol	Mol % benzene	Bp, °C	Latent heat of vaporization, cal/g-mol
0.00	79.9	7782	0.00	83.50	7740 (7650)[a]
17.87	79.3	7732	16.59	82.9	7690
49.00	78.3	7605	35.35	82.2	7595
67.50	77.7	7522	48.04	81.8	7578
85.25	77.1	7475	67.93	81.1	7495
100.00	76.7	7407 (7393)[a]	100.00	80.1	7357 (7360)[a]

[a] Values from ref. *5* and *11*.

1,2-Dichloroethane used was of the L.R. grade. This was washed with dilute solutions of potassium hydroxide and then with distilled water. It was dried over phosphorus pentoxide and distilled twice. The purified sample was stored in an amber-colored bottle in a desiccator. This was tested for its purity by determining its physical properties. The experimentally determined physical properties were then compared with the literature values. Data are given in Table I.

Analysis of mixtures. The refractive index of synthetic mixtures of benzene and 1,2-dichloroethane prepared was measured using a Pulfrich refractometer with a monochromatic (sodium D line) light source. A chart was prepared with the mole fraction of benzene plotted against the refractive index of the mixture. The composition of the required mixture was read from the above calibration curve. The refractive index-composition data fitted the relationship of

$$x = 18.089\,\eta_D{}^{30} - 26.0176 \tag{1}$$

where x = mole fraction of benzene and $\eta_D{}^{30}$ = refractive index of the mixture at 30°C with an average absolute error of 1.3% and a maximum error of 2.1%.

Apparatus and procedure. The apparatus used was essentially the same as the one used by Shettigar and coworkers (*9*). It consisted of a preheater, a calorimeter, and a liquid meter. The preheater was a 3-liter four-necked flask with stirring arrangement. The calorimeter was a glass tube 1 cm in diam and 6 cm long surrounded by a jacket of 4 cm diam and the liquid bath. The jacket was evacuated to 10^{-4} mm Hg. The heater for the calorimeter was made of Nichrome wire which can supply 250 cal/min. The required constant potential difference to the calorimeter heater was provided by means of a rectifying circuit. The liquid meter was designed in such a way that the liquid in the meter was siphoned automatically to the preheater. As the prevailing atmospheric pressure is 684 mm Hg, a pressure unit was added to the apparatus to enable the measurements to be made at 760 mm Hg. The apparatus and procedure are described in detail elsewhere (*9*).

Results. No experimental data are available on latent heat of vaporization of benzene-1,2-dichloroethane system. Therefore experiments were conducted to determine this property at pressures of 684 and 760 mm Hg. The results obtained are given in Table II along with the boiling point data. The boiling points reported in Table II compare well with the values reported by Timmermans (*14*). However, the values reported by Timmermans seem to be slightly higher.

The latent heat of vaporization of the mixture varies linearly with composition according to the equations

$$\Delta H_m{}^v = 7745.9 - 380.9\,x \tag{2}$$

$$\Delta H_m{}^v = 7789.2 - 379.3\,x \tag{3}$$

where $\Delta H_m{}^v$ = latent heat of vaporization of the mixture and x = mole fraction of benzene for 760 and 684 mm of Hg, respectively. The maximum error in using Equation 2 was 0.21% and the average absolute deviation was 0.13% while for Equation 3, the maximum error was 0.15% and the average absolute deviation was 0.1%. The value reported for each composition represents average values of four readings for that composition. The maximum deviation among different values for a particular composition was ±0.4%.

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