Binary Vapor-Liquid Equilibria Involving 1,2-Dichloroethane and 1,1,1- and 1,1,2-Trichloroethane

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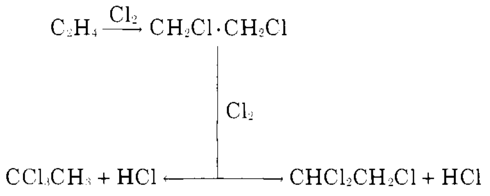
Vapor-pressure equilibrium data for three binary systems: 1,2-dichloroethane–1,1,1-trichloroethane, 1,2-dichloroethane–1,1,2-trichloroethane, and 1,1,1- and 1,1,2-trichlorethane were obtained. The activity coefficients for these systems deviated only slightly from the ideal. Some thermodynamic inconsistencies were noted.

CHLORINATION of ethylene in a medium of ethylene dichloride at temperatures below 50° C. produces 1,2-dichloroethane. Two major by-products, 1,1,1- and 1,1,2-trichloroethane, result from substitutive chlorination of the 1,2-dichloroethane. The preponderant by-product is the 1,1,2-isomer, but small quantities of the 1,1,1-isomer may also be present. The reactions are:



A distillation column was designed for the purification of the crude 1,2-dichloroethane. Vapor-liquid equilibrium data were obtained for the three binary system involved. Ternary vapor-liquid equilibrium data will be obtained at a later date.

MATERIALS

Reagent grade liquids were used. 1,1,1- and 1,1,2-trichloroethanes (Fluka and Buchs) and 1,2-dichloroethane (Riedal) were each fractionated, and the fraction corresponding to its boiling point (within about 0.5° C. range) was collected. The purity of each was tested by determining the carbon, hydrogen, and chlorine contents, density, and refractive index. Vapor phase chromatographic analysis indicated that the liquids were very pure. Their refractive indices closely agreed with literature data (*7, 8, 12*). The principal physical properties of the solvents are summarized in Table I.

Vapor pressure data for the systems—obtained from International Critical Tables (*10*), Perry's Handbook (*4*)

Table I. Physical Properties of the Liquids

	Boiling Point, ° C.		
	Lit. 760 mm. of Hg	Exptl. 710 mm. of Hg	Ref.
1,1.1-Trichloroethane	74.10	71.7–72.5	(*4, 8, 12*) •
	74.20		(*10*)
1,2-Dichloroethane	83.47	81.0–81.5	(*7*)
	83.70	81.0–81.5	(*4*)
1,1,2-Trichloroethane	113.7	111.2–111.4	(*7, 10*)
	113–114		(*12*)

	Density, G./Cc.		
	Lit.		
	20° C.	25° C.	Ref.
1,1,1-Trichloroethane	1.3390	1.3314	(*8*)
	1.3492	. . .	(*12*)
1,2-Dichloroethane	1.25309	1.24579	(*7*)
	1.2520	. . .	(*12*)
1,1.2-Trichloroethane	1.43968	1.43194	(*7*)

	Refractive Index				
	Lit.			Exptl.	
	20° C.	25° C.	30° C.	30° C.	Ref.
1,1,1-Trichloroethane	1.3314	1.4359		1.4320	(*8*)
	1.43838	. . .		. . .	(*12*)
1,2-Dichloroethane	1.44476	1.44210	1.43929	1.4391	(*7*)
	1.4443	. . .	. . .	. . .	(*12*)
1,1.2-Trichloroethane	1.47124	1.46868	1.46600	1.46600	(*7*)

and from equations proposed by Kissell and Manning (*11*)—were smoothed out, and the final vapor pressure–temperature curves for the three solvents are shown in Figure 1.

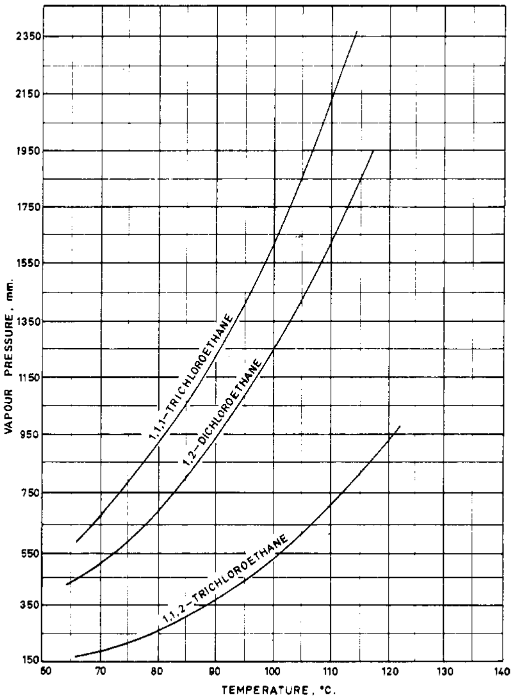


Figure 1. Vapor pressures of 1,1,1-trichloroethane, 1,2-dichloroethane, and 1,1,2-trichlorethane

1,2-DICHLOROETHANE–1,1,1-TRICHLOROETHANE SYSTEM

The activity coefficients for this system were estimated by the Carlson-Colburn method (*3*). For this purpose, boiling point data were obtained at 710 mm. of Hg pressure. Normally, one first obtains isothermal vapor-liquid equilibrium data necessary for calculating the activity coefficients. But it has been established that for liquids differing by less than 10° C. in their boiling points, there is negligible error in using van Laar and Margules equations for isobaric conditions as well (*5, 6, 14, 15*). Since the difference in boiling points of these compounds is less than 10° C., isobaric boiling point data were used in the Carlson-Colburn method (which was originally developed for isothermal data). The van Laar equations derived on the basis of the boiling point data are:

$$\log \gamma_1 = \frac{0.1634\, x_2^2}{(0.71\, x_1 + x_2)^2}$$

$$\log \gamma_2 = \frac{0.2304\, x_1^2}{(x_1 + 1.41\, x_2)^2} \qquad (1)$$

Activity coefficients determined from Equation 1 were used in Equation 2:

$$y_1 = \frac{(\gamma_1 P_1 x_1)/(\gamma_2 P_2 x_2)}{1 + (\gamma_1 P_1 x_1)/(\gamma_2 P_2 x_2)} \qquad (2)$$

to determine isobaric vapor-liquid compositions at a total pressure of 710 mm. of Hg, the normal atmospheric pressure at Poona.

Vapor-liquid equilibrium data for this system were also determined experimentally at 710 mm. of Hg using an Othmer still. To test reproducibility, several series of runs were made, each series covering the entire range of compositions in 10 to 12 experimental points. Compositions in the 1,2-dichloroethane– 1,1,1-trichloroethane mixtures were determined (to within 1%) by refractive index measurements at 30° C.

The experimental data and the values calculated from the boiling point data are plotted in Figure 2. Since these agree closely, Equation 1 may be considered an accurate expression for the activity coefficients of this system at 710 mm. of Hg. The experimental *x*, *y*, and temperature values of the system are presented in Table II.

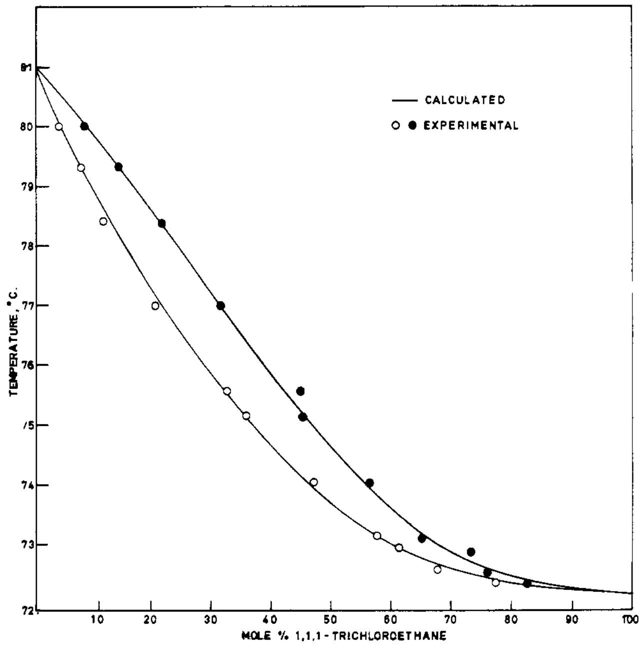


Figure 2. Vapor-liquid equilibrium curves for the system 1,1,1-trichloroethane–1,2-dichloroethane

Table II. Experimental *x*, *y*, and temperature data for the system 1,2-dichloroethane–1,1,1-trichloroethane

Temp., ° C.	*x*	*y*
72.30	1.000	1.000
72.40	0.775	0.825
72.65	0.675	0.760
73.00	0.610	0.730
73.20	0.575	0.655
74.10	0.470	0.565
75.20	0.350	0.452
75.60	0.315	0.445
77.00	0.205	0.315
78.40	0.120	0.215
79.30	0.075	0.140
80.00	0.045	0.080
81.00	0.000	0.000

THE SYSTEMS 1,2-DICHLOROETHANE–1,1,2-TRICHLOROETHANE AND 1,1,1-TRICHLOROETHANE–1,1,2-TRICHLOROETHANE

In each of these systems, the difference in boiling points between the two liquids is considerably more than 10° C., and it is not possible to apply either the isothermal equations for isobaric data or the Carlson-Colburn method.

Because activity coefficients of the 1,2-dichloroethane–1,1,2-trichloroethane system were nearly unity over the whole range of compositions, the system is considered ideal. The data of Portnov and Seferovich (*13*) suggest that the system is nonideal, but according to subsequent data of Kissell and Manning (*11*) the system is ideal. The author's data confirm the findings of Kissell and Manning. The data of Portnov and Seferovich is regarded as inconsistent with the Gibbs-Duhem equation. Activity coefficients indicate the 1,1,1- and 1,1,2-trichloroethane system is also ideal.

In both of these systems, the values of γ_2 ranged from 0.85 to 1; while the values of γ_1 were unity or slightly higher. These data are thermodynamically inconsistent, but results of this kind have been reported earlier (*1*, *2*, *9*) in studies of ideal systems.

All the compounds were redistilled in a rectification column of over 70 theoretical plates; fractional values of γ_2 again were obtained. Pure liquids were then run in the Othmer still and the refractive indices of vapor and liquid determined. These were identical for each of the two liquids, thus suggesting the absence of impurities (at least of the kind that could be detected by refractive index measurements). These observations confirm the view of Van Winkle and coworkers (*2*, *9*) that for systems approaching ideality such thermodynamic inconsistencies are likely.

NOMENCLATURE

P = vapor pressure of pure component, mm. of Hg.
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase
γ = activity coefficient

Subscripts

1 = refers to low boiling component
2 = refers to high boiling component

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Low Temperature Phase Equilibria of the Gas-Liquid System Helium-Neon-Nitrogen

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Vapor and liquid composition data were obtained for the gas-liquid systems helium-nitrogen, neon-nitrogen, and helium-neon-nitrogen at 82.70° K. and 113.13° K. from 6.4 to 50 atm. From the observed linear relation between the compositions of helium and neon in the vapor phase for the binary and ternary mixtures at constant temperature and pressure, semiempirical equations relating the compositions of the phases were derived from which smoothed and interpolated liquid composition data were calculated.

THE SOLUBILITY of helium gas in liquid nitrogen (*1*–*3*, *6*) and of helium-neon gas mixtures in liquid nitrogen (*7*) have been reported. The literature data for the ternary gas-liquid system (*7*) are of limited value and cannot be used for process calculations. No data have been reported for the solubility of neon gas in liquid nitrogen. Measurements were undertaken, therefore, on the binary solutions of neon and helium gases in liquid nitrogen, and on the ternary solutions of helium-neon gas mixtures in liquid nitrogen at pressures up to 50 atm. The liquid phase compositions were correlated and extended throughout the experimental pressure range by semiempirical equations derived from standard thermodynamic relations and the Henry's Law constant for neon in helium-nitrogen mixtures.

EXPERIMENTAL

Materials. The purity of the gases neon, nitrogen, and helium were determined by mass spectrometer. The anslyses given in Table I show that no further purification of the gases was necessary for the phase equilibrium studies. Liquid and vapor samples taken from the equilibrium cell were also analyzed by mass spectrometer using calibration mixtures prepared with an accuracy of ±0.4%.

Apparatus and Procedure. The technique used for obtaining equilibrium between a liquid solution and its gas phase is known as the "once-through-flow" method. In this procedure, a feed gas of composition lying between the estimated equilibrium compositions of the two phases is brought near to the temperature of the system and passed through the liquid phase. The vapor and liquid pahses are withdrawn continuously at a rate such that the mass balance of each component in the system is maintained. The advantages of this method are that the feed gas composition needs to be known only approximately, and the technique used for withdrawing samples ensures that the liquid sample truly represents the equilibrium composition. The latter is a particularly important consideration at low