MOLE FRACTION OF ETHYLENE DICHLORIDE IN
LIQUID OR VAPOUR

Figure 1. t-x-y Diagram
⊙ Liquid ● Vapor

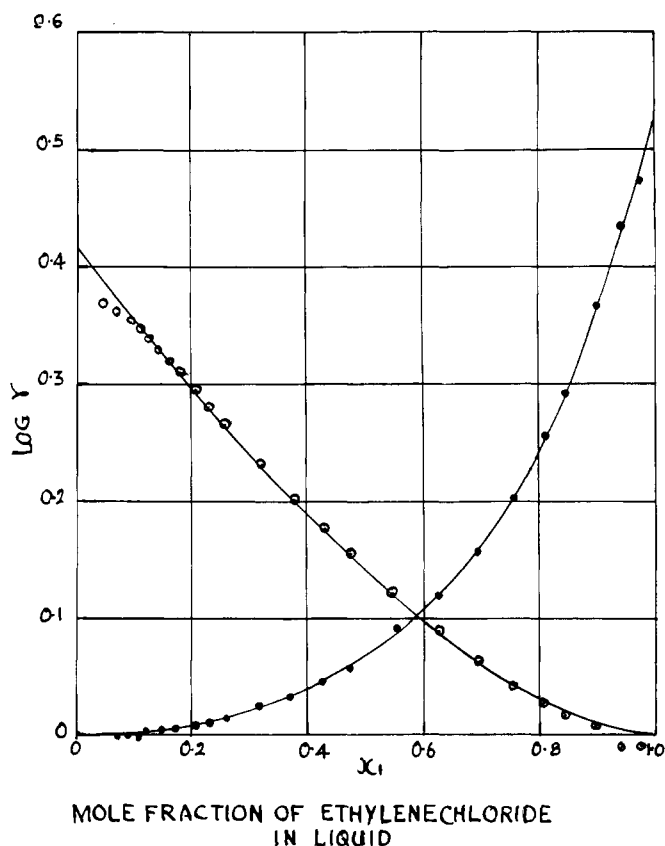## RESULTS AND DISCUSSION

The experimental vapor-liquid equilibrium data are presented in Table III. Figures 1 and 2 show t-x-y and log γ vs. x_1 (mole fraction of ethylene dichloride in liquid) plots, respectively.

The ratios of the activity coefficients were correlated by Chao's (1) modified Redlich-Kister equation

$$\log \frac{\gamma_1}{\gamma_2} = a + b\ (x_2 - x_1) + c\ (6x_1x_2 - 1)$$

where $a = 0.0313$, $b = 0.434$, and $c = 0.06$.

The individual activity coefficients were calculated by the method suggested by Nagata (6). The root mean square deviation in the calculation of the vapor composition is 0.3%. The calculated values of y_1 are shown in Table III.

The thermodynamic consistency was checked by Herington's (3) area test, showing $D < J$ ($D = 13.29$, $J = 14.62$).

MOLE FRACTION OF ETHYLENECHLORIDE
IN LIQUID

Figure 2. Log γ vs. x_1 plot
⊙ Log γ_1 ● Log γ_2

LITERATURE CITED

(1) Chao, K.C., Ind. Eng. Chem. 51, 93 (1959).
(2) "Chemical Engineers' Handbook" (Asian Edition), J.H. Perry, Ed., pp. 3-70, McGraw-Hill, 1963.
(3) Herington, E.F.G., J. Inst. Petrol. 37, 457 (1951), as cited by Hala, E., Pick, J., Fried, V., Vilim, O., "Vapour Liquid Equilibrium," p. 332, Pergamon, London, 1967.
(4) Jordan, T.E., "Vapour Pressures of Organic Compounds," p. 66, Interscience, New York, 1954.
(5) Mainkar, S.V., Mene, P.S., Ind. Chem. Eng. 9, 120 (1967).
(6) Nagata, I., J. Chem. Eng. Data 7, 360 (1962).
(7) Timmermans, J., "Physico Chemical Constants of Pure Organic Compounds," Elsevier, New York, 1950.

Isothermal Compressibility of Water at Various Temperatures

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An apparatus is described for the measurement of the isothermal compressibility of liquids at pressures up to 50 atm. and temperatures to 60° C. The apparatus has been used to measure the isothermal compressibility of water from 2° to 55° C. The results are discussed briefly and compared to the values obtained by other workers.

COMPRESSIBILITY measurements have been made both isothermally and adiabatically on aqueous solutions (6) and on water (1, 3-5, 7, 9-14). Most prior studies of isothermal compressibility have been made over extended pressure ranges, and very few measurements are available at or near 1 atm. Furthermore, only a very limited number of studies have been made of the compressibility of aqueous

solutions as a function of temperature. To remedy this situation somewhat, the authors have initiated a study of the isothermal compressibility of aqueous solutions at low pressures and as a function of temperature.

The present report describes the compressibility apparatus and some isothermal compressibility measurements made on water between 2° and 55°C. Recently,

various workers have carefully measured the isothermal compressibility of water at various temperatures (1, 9, 10) and have reviewed the earlier work (3–5, 7, 11–14). Kell and Whalley's work (10) appears to be the most extensive and accurate study to date made on the isothermal compressibility of water as a function of temperature and pressure.

EXPERIMENTAL

Description of Apparatus. The apparatus (Figure 1) which has been developed for the measurement of isothermal compressibility of various solutions consists of three basic units: the piezometer, the pressure cell, and the temperature bath.

The piezometer, C, is a cylindrical vessel, made of 7740 borosilicate glass (volume, about 450 ml.). The top of the piezometer is fitted with a 14/20 standard taper joint for filling. The glass stopper is forced into the joint to obtain a good seal, and held in place with two springs. A thin layer of Apiezon grease is placed on the stopper to prevent freezing. A precision bore capillary, E, (2 mm. in diameter × 56 cm. in length) is fitted to the bottom of the piezometer. Before use, the capillary is carefully calibrated by weighing various lengths (threads) of mercury. The piezometer is held in position in the pressure vessel by two stainless steel hose clamps, welded onto a 0.64-cm. diameter stainless steel rod. This rod is firmly fastened to the upper cover of the pressure vessel with four small bolts.

The pressure cell, H, is made entirely of brass except for a glass boiler tube (500 p.s.i. rating, 30 cm. long) that

Figure 1. Compressibility apparatus

encloses the upper portion of the capillary of the piezometer. The brass cylinder of the pressure vessel (8.7 cm. in diameter × 28 cm. in length; wall thickness, 0.64 cm.) is capped off on both ends by 1.9-cm.-thick brass plates. These plates are held against the cylinder by eight stainless steel bolts, each of which is torqued to 300 inch-pounds; teflon gaskets are used. Holes are drilled into the upper plate of the pressure vessel for the thermometer probe, A, the capillary, E, and a pressure inlet, D. A smaller brass plate (5.1 cm. in diameter × 1.9 cm. thick) is used to hold the boiler tube, J, in position around the capillary. This smaller plate is held fast against the boiler tube with six stainless steel bolts, again using teflon gaskets for seals. The pressure vessel was safety-tested to a maximum of 50 atm.

A 20.5-cm. "washer plate" (constructed of 0.64-cm.-thick PVC plastic) with three leveling bolts, G, is bolted to the lower plate of the pressure vessel for leveling the system on the bottom of a constant-temperature bath.

All parts of the pressure vessel and support are nickel-plated to minimize corrosion. A zinc block is placed in the temperature bath to obtain some control of the direction of whatever corrosion did occur.

The pressure vessel, boiler tube not included, is filled with ethylene glycol. The ethylene glycol serves a threefold purpose: as a conducting medium for thermal transfer, as a hydrostatic pressurizing medium, and as a safety precaution to minimize the explosive effect if the pressure cell fails. The entire apparatus is submerged in a large constant-temperature bath.

The wooden temperature bath, lined with polyester resin to prevent leakage, has a capacity of about 57 liters. A glass window is placed on one side of the bath for viewing the capillary. The temperature of the bath is regulated to ±0.001° C. with a Bailey Instrument Corp. temperature controller.

The temperature inside and outside of the pressure vessel was monitored with a Hewlett-Packard quartz crystal thermometer to determine when thermal equilibrium was established before and after compression. The thermometer is capable of measuring the temperature to 0.0001° C. with an accuracy of about 0.02° C. The probe or sensing element is reported by the manufacturer to be independent of the applied pressure. The authors assume that thermal equilibrium has been reached when the difference between the temperature probes, one inside and one outside the cell, returns to the original value before compression. For a 5-atm. change in pressure, it takes about one hour to dissipate the heat of compression. Stirring inside the cell is accomplished by using a submersible magnetic stirrer and a magnetic stirring bar enclosed in teflon, F. The temperature in the pressure vessel varies ±0.0005° C. over a 24-hour period. During the time of a measurement, 45 to 60 minutes, the temperature fluctuates less than ±0.0003° C. within the pressure cell, and it is expected that the fluctuations within the piezometer itself are considerably smaller.

Procedure. After the piezometer has been thoroughly cleaned with a solution of $KMnO_4$ in concentrated H_2SO_4 and carefully flushed with water, mercury is added and the amount determined by weighing—approximately 330 grams. The piezometer is then filled with degassed, freshly distilled water at about 60° C., immediately cooled to about 4° C., and capped. The amount of water is also determined at room temperature by weighing.

The temperature of the piezometer and its contents is raised to about 0.5° C. above the desired operating temperature, and the displaced mercury is collected and weighed. The piezometer is then attached to the support, B, and the pressure vessel assembled. After ethylene glycol, at the operating temperature, is added and the thermometer probe inserted, the entire apparatus is placed in the temperature bath.
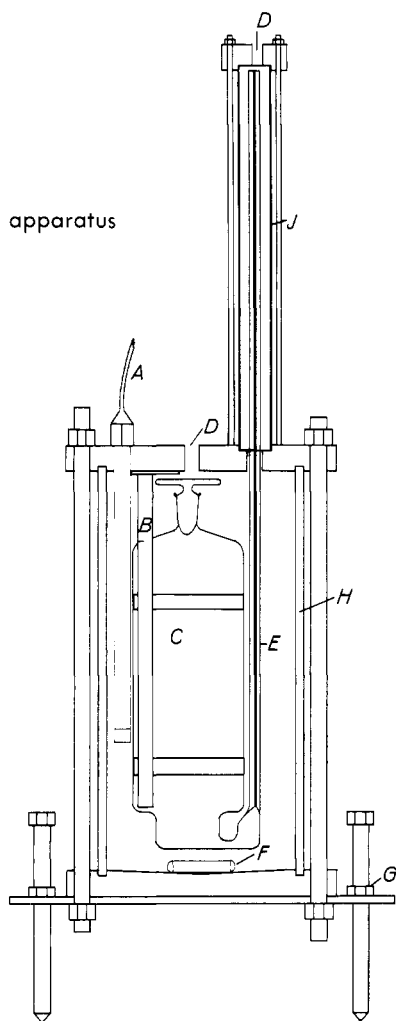
After thermal equilibrium is established in the pressure vessel, about 5 atm. of pressure is applied to the system, using compressed argon as the pressurizing agent. When thermal equilibrium is again reached—about one hour—the position of the mercury meniscus from the reference mark is recorded. The pressure change, ΔP, is measured with a Texas Instruments fused quartz precision pressure gage, and the change in position of the mercury column is measured with an Ole-Dick cathetometer. The pressure is increased another 5 atm. and the process repeated, to a pressure of about 15 atm. The accuracy of the Texas Instruments fused quartz precision pressure gage is reported by the manufacturer to be about 0.02%, traceable to the National Bureau of Standards. Since we are concerned with pressure differences, the accuracy of the instrument is not a limiting factor. The cathetometer is capable of measuring height differences to within ± 3 microns, which in this case corresponds to about $\pm 0.01\%$.

Materials. The water used in these experiments is prepared by feeding once-distilled water from a Barnstead still into a three-stage glass still, with the final condenser made of fused quartz. The first stage contains an acid permanganate solution, the second stage an alkaline permanganate solution, and the third stage only the distillate. The resistance of the water is measured with a flow-through conductivity cell connected in parallel with the still output, and the organic content is measured with a Beckman GC-5 with flame ionization dector. The water resistivity is 4 megaohm, with an organic content of less then 0.2 p.p.b. The mercury used for these experiments is purified by filtering and then triple distilling it under vacuum.

RESULTS AND DISCUSSION

The isothermal compressibility, K, of a liquid is defined by

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \qquad (1)$$

The actual quantities measured, Δh and ΔP—the change of the height of meniscus and the pressure change—are dependent upon the volume of the mercury (V_{Hg}), the volume of the water, V_{H_2O}, and the inside volume of the glass container, to a reference mark, V_t. The total volume of the system is

$$V_t = V_{H_2O} + V_{Hg} + Ah \qquad (2)$$

where A is the cross sectional area of the capillary, and h is the initial distance of the mercury meniscus below the reference mark on the top of the capillary.

Differentiating Equation 2 with respect to pressure, one obtains

$$\frac{\partial V_t}{\partial P} = -\frac{\partial V_{H_2O}}{\partial P} - \frac{\partial V_{Hg}}{\partial P} + \frac{h\partial A}{\partial P} + \frac{A\partial h}{\partial P} \qquad (3)$$

where the negative sign indicates a decrease in volume. From the theory of elasticity, assuming the glass is homogeneous and isotropic (1), one obtains

$$\frac{\partial A}{\partial P} = -\frac{2AK_g}{3} \qquad (4)$$

$$\frac{\partial V_t}{\partial P} = -V_t K_g \qquad (5)$$

where K_g is the isothermal compressibility of glass. Substituting Equation 1 for mercury and water and Equations 4 and 5 for glass into Equation 3, one obtains, upon rearranging

$$K_{H_2O} = -K_{Hg}\frac{V_{Hg}}{V_{H_2O}} + K_g\left(1 + \frac{V_{Hg}}{V_{H_2O}} + \frac{A\Delta h}{3V_{H_2O}}\right) + \frac{A\Delta h}{V_{H_2O}\Delta P} \qquad (6)$$

Table I. Compressibility of Water at Various Temperatures

Temp., °C.	P, Atm.[a]	$K \times 10^6$, Atm.$^{-1}$	Lit. Values[b], Atm.$^{-1}$
1.92	5.0	51.27	
	8.0	50.80	
	8.0	50.93	
		av. 51.00 ± 0.18	50.96
3.01	4.0	50.74	
	7.0	50.38	
		av. 50.56 ± 0.18	50.56
4.02	5.5	50.53	
	8.5	50.11	
		av. 50.32 ± 0.21	50.25
5.00	2.0	50.15	
	4.0	49.95	
	6.0	49.99	
		av. 50.03 ± 0.08	49.94
9.93	5.5	48.21	
	5.5	48.50	
	8.0	48.68	
	8.0	48.51	
	15.0	48.23	
		av. 48.43 ± 0.16	48.53
15.03	5.5	47.30	
	8.0	47.59	
		av. 47.44 ± 0.16	47.40
20.02	6.5	46.71	
	8.5	46.53	
		av. 46.62 ± 0.09	46.52
25.00	2.0	45.87	
	2.5	45.98	
	6.0	46.04	
	8.0	45.90	
		av. 45.94 ± 0.06	45.84
29.99	3.5	45.55	
	6.5	45.22	
	8.0	45.37	
	8.0	45.15	
	8.5	45.06	
		av. 45.27 ± 0.13	45.35
35.00	6.5	45.01	
	8.5	44.95	
		av. 44.98 ± 0.03	45.01
39.98	3.5	44.86	
	3.5	44.71	
	6.5	44.55	
	8.5	44.85	
		av. 44.74 ± 0.11	44.81
45.08	6.5	44.63	
	8.5	44.97	
		av. 44.80 ± 0.17	44.74
50.01	3.5	44.97	
	6.5	44.86	
	8.5	44.72	
		av. 44.85 ± 0.08	44.76
54.78	6.5	44.82	
	8.5	44.90	
		av. 44.86 ± 0.04	44.86

[a] Average pressure at which measurement was made. [b] Literature values were taken from Kell and Whalley (10)
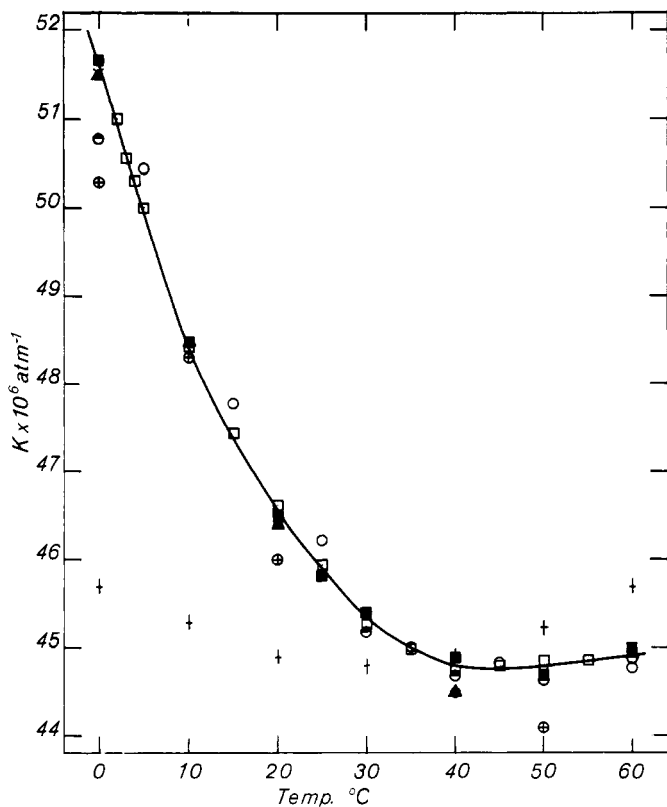
Figure 2. Plot of isothermal compressibility of water vs. temperature; the line represents smooth curve drawn through all the data
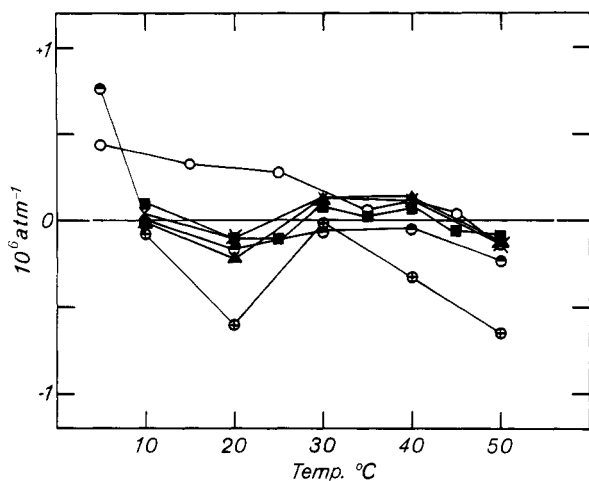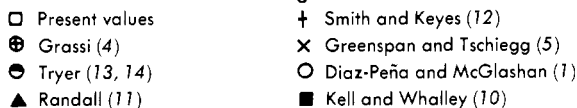
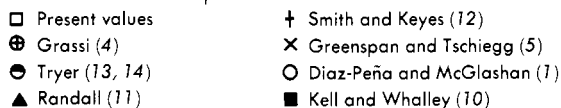|	
□ Present values	+ Smith and Keyes (12)
⊕ Grassi (4)	× Greenspan and Tschiegg (5)
● Tryer (13, 14)	○ Diaz-Peña and McGlashan (1)
▲ Randall (11)	■ Kell and Whalley (10)

Figure 3. Deviations plot of compressibility results compared to other workers

□ Present values	+ Smith and Keyes (12)
⊕ Grassi (4)	× Greenspan and Tschiegg (5)
● Tryer (13, 14)	○ Diaz-Peña and McGlashan (1)
▲ Randall (11)	■ Kell and Whalley (10)

where Δh is the change in the height of the mercury meniscus and ΔP is the change in the pressure. The compressibilities of water, K_{H_2O}, are calculated from the measured change in height, Δh, and the change in pressure, ΔP, using selected values for the compressibility of glass and mercury. Since the compressibilities of both mercury (1) and glass (8) have been reported at a few temperatures, it is assumed

that these quantities vary linearly with temperature. The pressure differential is corrected for the change in height of the mercury—i.e., head corrections.

The compressibilities of water at various pressures, 2 to 15 atm., and at various temperatures, 2° to 55° C., are given in Table I. Since a regular dependence of the compressibility on pressure was not detected over the small range of pressure covered at a given temperature, the results were averaged to obtain the compressibility of water at 1 atm. These averaged compressibility values are also listed in Table I, along with their average deviation from the mean. The average deviations vary from about ±0.1 to ±0.2 × 10⁻⁶ atm.⁻¹, and represent our estimated experimental error. Figure 2 shows a plot of the averaged experimental compressibility values of water vs. temperature, and those obtained by others (1, 4, 5, 10-14). Figure 3 gives a deviation plot for the present compressibility results compared to other workers (1, 4, 5, 10, 11, 13, 14), and showing excellent agreement with the recent work of Kell and Whalley (10).

The compressibility of water at various temperatures (° C.) have been fitted by a least squares "best fit" to the equation

$$K_{H_2O} = A + Bt + Ct^2 + Dt^3 + Et^4 + Ft^5 \qquad (7)$$

where $A = 0.5188 \times 10^{-4}$ atm.⁻¹, $B = -0.4705 \times 10^{-6}$ atm.⁻¹ deg.⁻¹, $C = 0.1833 \times 10^{-7}$ atm.⁻¹ deg.⁻², $D = -0.5883 \times 10^{-9}$ atm.⁻¹ deg.⁻³, $E = 0.1083 \times 10^{-10}$ atm.⁻¹ deg.⁻⁴, and $F = -0.7521 \times 10^{-13}$ atm.⁻¹ deg.⁻⁵. The root mean square deviation of the fit is 0.05×10^{-6} atm.⁻¹.

The minimum in the compressibility of water, at about 45° C., appears to be due to the opposed temperature coefficients of the compressibilities of the structured and nonstructured (or less structured) entities (2).

In future work, the authors plan to study the isothermal compressibility of aqueous solutions as a function of temperature, to shed some light on the structure of water and solute-solvent interactions.

LITERATURE CITED

(1) Diaz-Peña, M., McGlashan, M.L., Trans. Faraday Soc. 55, 2018 (1959).
(2) Feates, F.S., Ives, D.J.G., J. Chem. Soc. (London) 1956, p. 2798.
(3) Gibson, R.E., Loeffler, O.H., J. Am. Chem. Soc. 63, 898 (1941).
(4) Grassi, C., Ann. Chim. Phys. 31, 437 (1851).
(5) Greenspan, M., Tschiegg, C.E., J. Res. Natl. Bur. Std. 59, 249 (1957).
(6) Harned, H.S., Owen, B.B., "The Physical Chemistry of Electrolytic Solutions," ACS Monograph No. 137, 375, Reinhold, New York, 1958.
(7) Jessup, R.S., J. Res. Natl. Bur. Std. 5, 985 (1930).
(8) Jolley, E.L., Product Engineering, Corning Glass Works, Corning, New York, personal communication, 1968.
(9) Kell, G.S., J. Chem. Eng. Data 12, 66 (1967).
(10) Kell, G.S., Whalley, E., Phil. Trans. Roy. Soc. (London) 258, 565 (1965).
(11) Randall, C.R., J. Res. Natl. Bur. Std. 8, 79 (1932).
(12) Smith, L., Keyes, F.G., Proc. Am. Acad. Arts Sci. 69, 285 (1934).
(13) Tryer, D.J., J. Chem. Soc. (London) 103, 1675 (1913).
(14) Tryer, D.J., Ibid., 105, 2534 (1914).