Solubility, Vapor Pressure, and Liquid Density in the System Carbon Dioxide–Methylene Chloride

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THE CARBON dioxide–methylene chloride system is of interest for possible propellant applications in aerosol packaging, but none of the required equilibrium data were found to be available in the literature. Equilibrium values of total pressure, liquid composition, and liquid density at 70° F. and from 15 to 300 p.s.i.a. were measured.

To obtain these data within the desired accuracy, an equilibrium cell was designed which would ensure attainment of true static equilibrium between gas and liquid phases under carefully measured total pressure, and provide for sampling the equilibrium liquid phase only (without changing the equilibrium composition due to the sampling procedure itself), for determination of liquid density and composition. Thus, a by-product resulting from this work is an apparatus and technique which are applicable, in general, to the determination of similar equilibrium data in gas solubility work at high pressures where conventional glass systems cannot be used.

APPARATUS AND PROCEDURE

General Outline of Method. The apparatus design was kept as simple as possible, while maintaining enough accuracy to measure liquid densities to within ±0.2%, liquid composition to within ±0.25 weight %, and pressures to within ±0.25 p.s.i.

Technical grade methylene chloride was degassed by distillation and transferred to a specially designed equilibrium cell under vacuum. The cell was then overpressurized with carbon dioxide from a storage cylinder, and the system brought to equilibrium by rocking the cell in a constant temperature bath until constant pressure was established. The cell was designed so that a liquid sample could be isolated in a calibrated volume, disconnected, and weighed while under pressure to determine liquid densities. Liquid phase composition data were then obtained by analyzing the entire isolated sample. This was done by expanding the vaporized sample through a series of sodium hydroxide solutions to extract the carbon dioxide. The solutions were then titrated with standardized hydrochloric acid to determine carbon dioxide content.

Equilibrium Cell. The equilibrium cell design was based on the static method (*1, 2, 5, 10*) rather than the dynamic method (*8, 9*), because it is simpler and does not require repeated analyses of the liquid phase to determine when equilibrium has been attained. Using this method, the liquid and gas were charged to a volume, and then the system was closed while equilibrium was established.

Figure 1 shows the equilibrium cell mounted so that it can be rocked in the constant temperature bath. A key point in design was the arrangement of the cell so that a liquid sample could be isolated in a calibrated volume at equilibrium and separated. This permitted the sample to be weighed accurately for density measurements, and then vaporized and purged through the analysis train for accurate composition determination. Isolation and analysis of a liquid phase sample was an important feature, since in much of the reported literature, a portion of the liquid phase had been expanded directly from the equilibrium cell into an evacuated sampler or into the analysis apparatus, thus neglecting concentration gradients near the valve and the volume change due to the sample displacement. This had probably resulted in the expanded gas not carrying along all the liquid that belongs with it (*6, 8*). Since the maximum pressure, in this investigation, was on the order of 20 atm., it was possible to isolate the sample simply rather than to use a mercury displacement technique necessary at much higher pressures (*1, 4, 8*). This was effectively accomplished by dividing the cell into three sections, a vapor chamber, *A*; a liquid chamber, *B*; and an interface chamber, *C*; connected by two 3/4-inch high pressure ball valves, *D* and *E*, (Jamesbury Type D22TT) (Figure 1). When both valves were open, the combined volumes were available for contacting the liquid and gas. After equilibrium had been attained, the liquid end was slowly lowered until the cell was vertical, to prevent trapping gas bubbles. Both ball valves were then closed, trapping the interface in the middle chamber. The small 1/8-inch Hoke needle valve, *F*, was then opened which released the pressure so that joint *G* could be taken apart, isolating liquid and vapor separately.

A detailed drawing of the vapor chamber is shown in Figure 2. It was designed for a volume of 150 cc. to be used with a special sample transfer procedure, which allowed a vapor sample to be weighed accurately before it was analyzed. Originally, it was planned to measure vapor phase composition in addition to the liquid phase relationships. Vapor samples were isolated and analyzed properly, but the results were high in methylene chloride content. This was apparently due to the vaporization of the liquid film present on the walls of the vapor chamber. For this reason the vapor phase will not be discussed further here.

The interface chamber is also detailed in Figure 2. The volume was arbitrarily taken at about 70 cc. to be sure that the interface always occurred in this section.

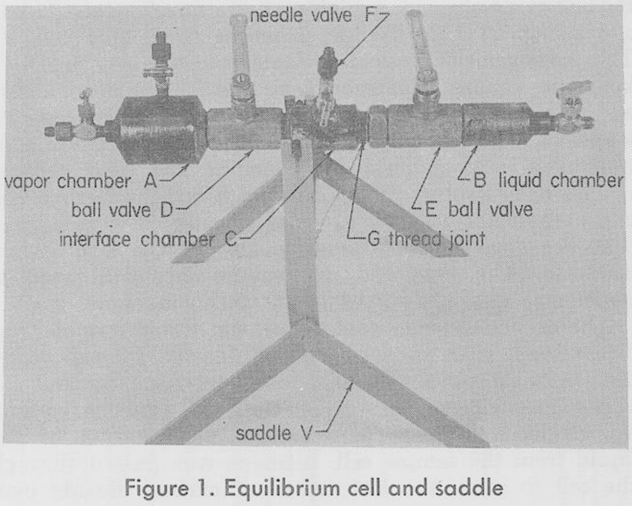

Figure 1. Equilibrium cell and saddle

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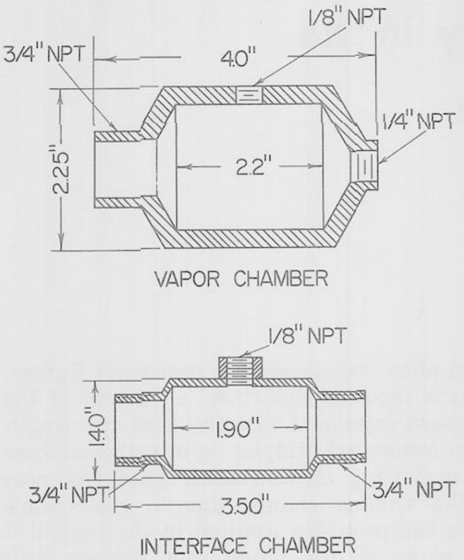

Figure 2. Vapor and interface chambers

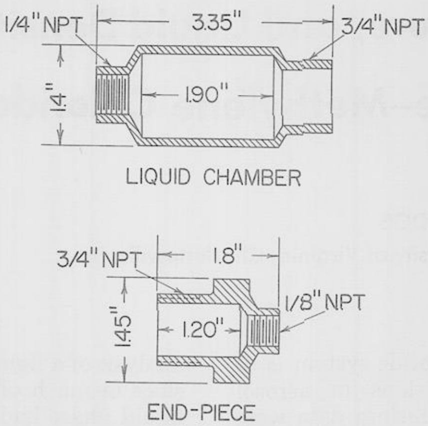

Figure 3. Liquid chamber and end piece

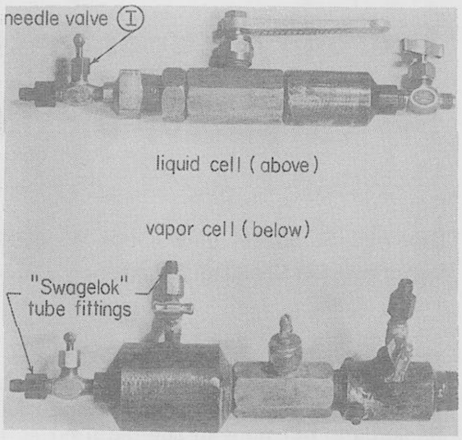

Figure 4. Liquid and vapor samples isolated at equilibrium conditions

Since it was desired to measure liquid densities to within ±0.2%, the liquid cell was designed for a volume of about 50 cc. (Figure 3) based on a possible error of ±0.01 cc. in calibration and ±0.01 gram in weighing the cell. It was necessary to calibrate the volume of the cell as a function of pressure, because of slight compression of the Teflon valve packings and the void space in the valve body. This was accomplished in a reproducible manner using deaerated, distilled water.

After the liquid sample had been isolated at equilibrium it was removed from the bath, disconnected, and dried very carefully with acetone and compressed air. A special end piece, detailed in Figure 3 and shown in position in Figure 4, was attached immediately and evacuated through needle valve *I*. The ball valve was then opened, allowing the liquid to expand into the extra volume. This prevented unnecessary strains on the cell, when the ambient temperature was higher than the equilibrium isotherm. The cell was then weighed accurately on a 1500-gram capacity analytical balance. From a knowledge of the equilibrium pressure, the calibrated volume of the cell, and the sample weight, liquid densities were determined. The sample was then ready for the analysis procedure.

Auxiliary Apparatus. The equilibrium cell, pressure measuring system, and other equipment necessary for bringing about equilibrium conditions are shown arranged for a run in Figure 5.

The cell pressure was measured by a stationary 8 ½-inch Ashcroft pressure test gage, *J*, graduated in 1-pound increments from 0 to 300 pounds, indirectly attached to the cell at *M* through a high-pressure manometer, *K*, and a $^1/_{16}$-inch in I.D. flexible, stainless steel tube coil, *L*. This arrangement prevented damage to the test gage. To keep the volume expansion from the cell at a minimum and to prevent condensation in the gage, the manometer was filled with mercury and the gage and extension pipe were filled with mineral oil. Mercury was used because it does not dissolve carbon dioxide. Since the flexible coil and manometer were always under water, it was assured that the gage pressure reading was at the equilibrium isotherm. The gage and manometer were calibrated in position by means of a dead weight testing machine.

The carbon dioxide content of the liquid sample was determined, after measuring liquid density, by vaporizing the entire sample slowly and completely and passing the vapor through an absorption train of aqueous sodium hydroxide. Following the complete vaporization of the liquid from the sample cell, nitrogen was passed through the cell to carry the last traces of carbon dioxide over into the absorption system. The entire absorption train was maintained above 50° C. to prevent condensation of the methylene chloride, and a final stage containing barium chloride was included to provide a visual check that no carbon dioxide was escaping the sodium hydroxide stages. The absorption solution was then titrated with hydrochloric acid to determine carbon dioxide in the usual manner (*3*).

RESULTS

The liquid density results are plotted *vs.* liquid composition in Figure 6. Individual samples deviated from the mean curve values by less than 0.1% in most cases and the maximum deviation found was 0.2%. Four significant figures were achieved in the density values, since the cell volume, of approximately 50 cc., was calibrated to the nearest ±0.01 cc., and the liquid samples, of approximately 65 grams, were weighed to the nearest ±0.01 gram.

The liquid density values decrease, in a nearly linear manner, as total pressure increases up to 130 p.s.i.g. At that point the curve changes slope, and densities decrease

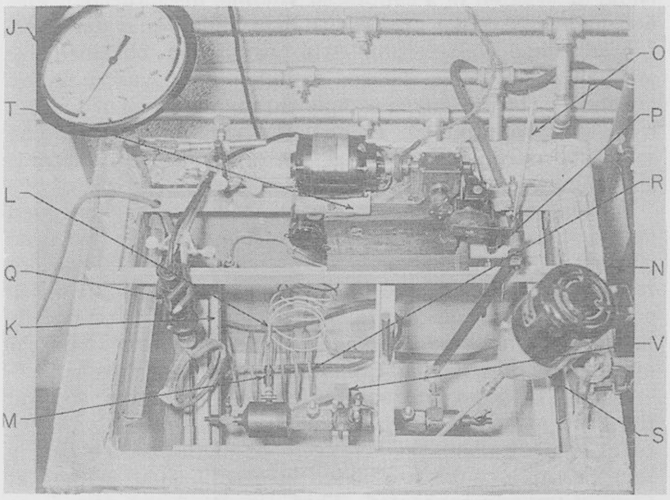

Figure 5. Entire equilibrium apparatus

J.	Pressure gage	*P.*	Thermoregulator
K.	Manometer	*Q.*	Heater
L.	Tube coil	*R.*	Water coil
M.	Connection	*S.*	Electric stirrer
N.	Water bath	*T.*	Rocking mechanism
O.	Thermometer	*V.*	Saddle

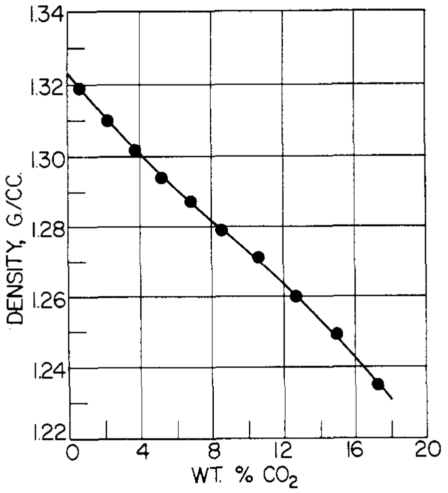

Figure 6. Liquid density vs. weight per cent of CO_2 dissolved in methylene chloride at 70° F.

more rapidly with further increase in pressure, indicating that the solubility of carbon dioxide is increasing more rapidly. This increased solubility effect above 130 p.s.i.g. was verified by the curve of total pressure *vs.* liquid composition.

The only literature density value available for comparison was that of pure methylene chloride, which is 1.325 grams per cc. at atmospheric pressure (*7*). The experimental value of 1.322 grams per cc. differs by 0.2%. Based on this accuracy and the precision of the individual measurements, the curve should represent well the density relationship with total pressure for the system.

The total absolute pressure is plotted *vs.* liquid phase composition in Figure 7. Individual sample variation from the mean curve was about 0.05 weight % in most cases, but a few varied as much as 0.2 weight %. Composition values were determined to three significant figures as a result of the normality and volume of the absorbing solutions, and the titration procedure used.

The concentration of dissolved carbon dioxide increases linearly with total pressure up to about 145 p.s.i.a. At that point the curve changes slope, and the concentration increases more rapidly with further increase in pressure. The similar characteristics of the density and composition curves, above and below 145 p.s.i.a., indicate that the experimental results are consistent.

The linear relationship between total pressure and concentration of dissolved gas is characteristic of an ideal solution in which Henry's law applies to the solute and Raoult's law to the solvent. Under these conditions, applying Dalton's law to the gas phase permits calculation of the Henry's law constant from measurements of total pressure and composition through the relationship,

$$P_t = HX_{CO_2} + 7.1(1 - x_{CO_2})$$

where

P_t = total pressure, p.s.i.a.
H = Henry's law constant, p.s.i.a.
x_{CO_2} = mole fraction carbon dioxide in liquid
7.1 = vapor pressure of pure methylene chloride, p.s.i.a., at 70° F. (*7*)

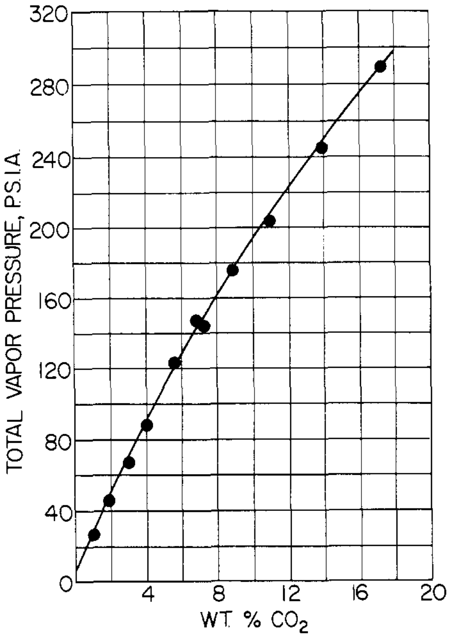

Figure 7. Total vapor pressure vs. weight per cent of CO_2 dissolved in methylene chloride at 70° F.

The value of *H* for the linear portion of the curve was found to be 1085 ± 5 p.s.i.a. at 70° F. Henry's law with this value of *H* successfully describes the solubility up to about 145 p.s.i.a. and 13 mole % of dissolved carbon dioxide. At higher pressures, the law predicts solubilities less than the experimental values, reaching a deviation of −10% at 300 p.s.i.a. and 30 mole % of dissolved carbon dioxide (experimental).

LITERATURE CITED

(1) Dean, M.R., Tooke, J.W., *Ind. Eng. Chem.* **38**, 389 (1946).
(2) Frolich, K., Tauch, E.J., Hogan, J.J., Peer, A.A., *Ibid.*, **23**, 548 (1931).
(3) Griffin, C.W., "Inorganic Quantitative Analysis," p. 137-42. Philadelphia, Blakiston Co., 1954.
(4) Holder, C.H., Maass, O., *Can. J. Research* 18, *Sect. B*, 293 (1940).
(5) Ipatieff, V.N., Monroe, G.S., *Ind. Eng. Chem., Anal. Ed.* **14**, 166 (1942).
(6) Lackowicz, S.K., *J. Imp. Coll. Eng. Soc.* **8**, 51 (1954).
(7) Solvay Process Div., Allied Chemical Corp., "Methylene Chloride, Chloroform, Methyl Chloride, Carbon Tetrachloride," p. 22.
(8) Wan, S.W., Dodge, B.F., *Ind. Eng. Chem.* **32**, 95 (1940).
(9) Wiebe, R., Gaddy, V.L., Heins, C., *Ibid.*, **24**, 823 (1932).
(10) Wiebe, R., Tremearne, T.H., *J. Am. Chem. Soc.* **55**, 975 (1933).

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