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Vapor Pressures of Titanium Tetrachloride–Carbon Tetrachloride Mixtures

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VAPOR PRESSURE DATA for carbon tetrachloride–titanium tetrachloride systems are presented. Constants for the Van Laar equations which satisfy the total vapor pressure data are given for temperatures of 30°, 40°, and 50° C. Vapor liquid equilibrium data for this system were obtained by Nasu (*4*) who employed chemical analysis and conventional equilibrium techniques. However, Nasu's results are not consistent with standard thermodynamic tests.

EXPERIMENTAL COMPOUNDS

Chemicals used were Fisher Scientific reagent grade, carbon tetrachloride and Fisher Scientific Co. purified grade titanium tetrachloride.

PROCEDURE AND APPARATUS

Due to the extreme reactivity of titanium tetrachloride with the moisture in the atmosphere to form hydrogen chloride and titanium dioxide, it was necessary to handle the materials inside a Berkley-type dry box in which an atmosphere of dry nitrogen was maintained.

Vapor-liquid equilibrium data were obtained by measuring the total vapor pressure of different mixtures of the compounds at temperatures 30, 40, and 50° C. A glass spring manometer (modified Bourdon gage) was used in conjunction with static equilibrium equipment, as suggested by Kamal (2) and modified by Ryder (5). The sample and glass manometer were kept in an oil bath where the temperature was controlled to within ±0.1° C.

Compositions of samples were determined by weighing and negligible error was introduced in their preparation. Care was taken that no moisture or foreign gases were available to interfere in the measurements.

The major components of the experimental apparatus for measuring the vapor pressure of pure carbon tetrachloride and carbon tetrachloride–titanium tetrachloride mixtures are shown in Figure 1.

A 250-ml. sample preparation and introduction flask, *A*, is fitted with invertible vent and ground glass joint for connection to the vaporization chamber.

Pressure regulation system, *B*, consists of a 500-ml. gas sample bottle and two volume-calibrated glass tubing chambers between stopcocks 8 and 10.

A vaporization chamber is formed by the ground glass seal between vaporization chamber dome, *D*, and vaporization chamber jacket, C. A ground glass joint, *D*, forms the mouth of the jacket. The liquid bulb capacity is 250 ml. and the total vaporization chamber volume with *D* in place is approximately 525 ml. *D* houses a sample introduction tube at stopcock 3, a glass spring manometer (modified Bourdon gage), *E*, and a pressure release vent at stopcock 4 which interconnects both sides of the glass spring manometer diaphragm. A glass pointer needle extending into the vaporization chamber from the glass spring manometer diaphragm and a fixed glass reference pointer indicate the balancing of internal and external diaphragm pressures.

A variable level mercury manometer, *F*, is used for measuring the pressure on the regulated (internal) side of the glass spring manometer diaphragm.

A leveling bulb, *G*, controls the mercury level in manometer, *F*, for precision pressure regulation.

VAPOR-LIQUID EQUILIBRIUM DATA THEORY

The total vapor pressure of a binary system may be expressed by

$$P_T = \gamma_1 x_1 P_1^\circ + \gamma_2 x_2 P_2^\circ \qquad (1)$$

If log γ does not vary much with pressure, the following relationship may be assumed valid:

$$x_1 \left(\frac{\partial \operatorname{Log} \gamma_1}{\partial x_1} \right)_T = x_2 \left(\frac{\partial \operatorname{Log} \gamma_2}{\partial x_2} \right)_T \qquad (2)$$

In the present work, this condition is satisfied, and the van Laar equation can therefore be used to represent log γ.

$$\operatorname{Log} \gamma_1 = \frac{A x_2^2}{\left(\frac{A}{B} x_1 + x_2 \right)^2} \qquad (3)$$

$$\operatorname{Log} \gamma_2 = \frac{B x_1^2}{\left(x_1 + \frac{A}{A} x_2 \right)^2} \qquad (4)$$

By trial and error, constants *A* and *B* satisfying Equations 1, 3, and 4 can be determined.

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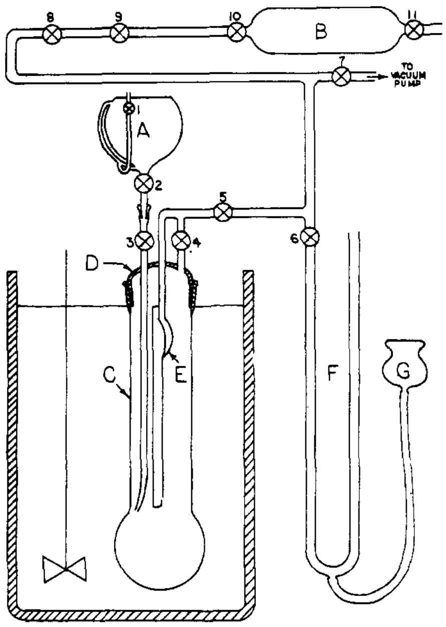

Figure 1. Schematic drawing of experimental apparatus

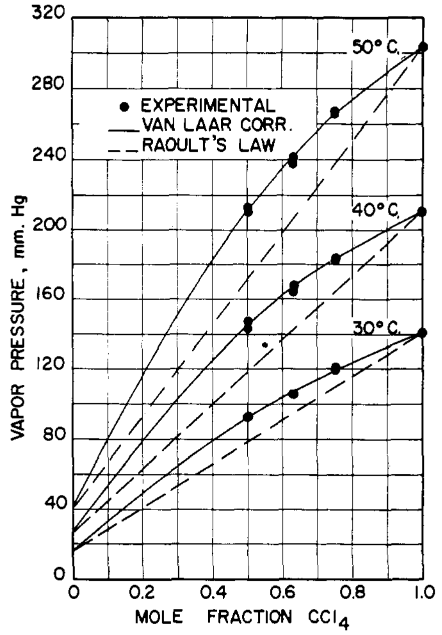

Figure 2. Experimental vapor pressure of $TiCl_4$-CCl_4 mixtures vs. mole fraction CCl_4

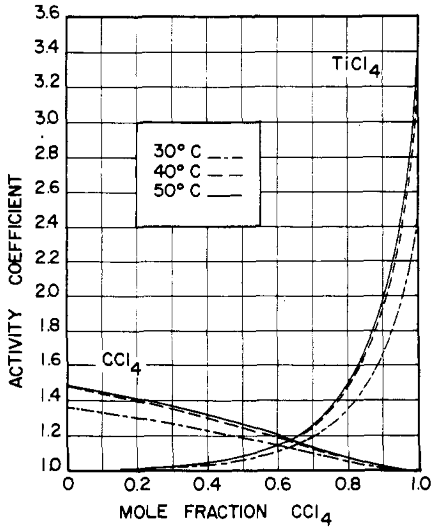

Figure 3. Computed activity coefficients for $TiCl_4$ and CCl_4 vs. mole fraction CCl_4

RESULTS

Figure 2 is a graphical representation of the experimental results presented in Table I. Figure 3 represents activity coefficients corresponding to vapor pressure measurements. Values for the van Laar equations are given below.

Temp., ° C.	A	B
30.0	0.133	0.390
40.0	0.170	0.510
50.0	0.170	0.530

Van Laar Equations

$$\text{Log}\ \gamma_{CCl_4} = \frac{A x^2_{TiCl_4}}{\left(\frac{A}{B}\ x_{CCl_4} + x_{TiCl_4}\right)^2}$$

$$\text{Log}\ \gamma_{TiCl_4} = \frac{B x^2_{CCl_4}}{\left(x_{CCl_4} + \frac{B}{A}\ x_{TiCl_4}\right)^2}$$

The recommended equations for the variation of A and B with temperature are:

$$\text{Log}\ A = 0.8464 - \frac{522.18}{T}$$

$$\text{Log}\ B = 1.7437 - \frac{652.57}{T}$$

The vapor-liquid equilibrium distribution ratios for this system can be obtained from the following relation:

$$\frac{y_i}{x_i} = \frac{\gamma_i P_i^\circ}{P_T}$$

Uncertainty in activity coefficients in the temperature range from 30° to 50° C. is less than 3% for the liquid compositions of 50 mole %. The uncertainty becomes greater for the activity coefficient of a component as its concentration becomes smaller. The uncertainties also increase as the above equations are extrapolated to higher temperatures. Vapor pressure data for the pure components can be obtained (*1*, *3*).

Table I. Experimental Total Vapor Pressure Data for CCl_4-$TiCl_4$ System

		Total Vapor Pressure, Mm. of Hg at		
Run No.	x_{CCl_4}	30.0° C.	40.0° C.	50.0° C.
2	1.0000	139.8	211.6	303.8
3	1.0000	142.3	210.6	303.3
4	1.0000	139.8	210.2	305.6
5	1.0000	142.2	209.2	300.6
7	0.7476	120.7	182.5	267.6
9	0.7501	119.7	183.4	265.8
10	0.6304	105.6	167.5	241.5
11	0.6311	105.7	164.0	237.6
6	0.5007	92.5	147.4	213.4
8	0.4988	92.6	143.5	210.7

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NOMENCLATURE

A, B = van Laar constants
P_T = total vapor pressure of mixture
P_i° = vapor pressure of pure component i
T = absolute temperature, ° K.
x_i = mole fraction of component, i, in liquid mixture
y_i = mole fraction of component, i, in vapor in equilibrium with liquid mixture
γ_i = activity coefficient of component i

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