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NOMENCLATURE

C = composition parameter, $x_i/(x_i + x_h)$
K_j = vapor-liquid equilibrium constant for j component, y_j/x_j
P_k = pressure at point of convergence, p.s.i.a.
P_c = critical pressure, p.s.i.a.
t_c = critical temperature, ° F.
x_h = mole fraction in liquid phase of component of lowest volatility
x_i = mole fraction in liquid phase of component of intermediate volatility
x_j = mole fraction in liquid phase of j component
y_j = mole fraction in vapor phase of j component
π = pressure, p.s.i.a.

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Vapor Pressures of Silicon Tetrachloride–Carbon Tetrachloride Mixtures

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VAPOR PRESSURE of silicon tetrachloride–carbon tetrachloride systems at 30°, 40°, and 50° C. are presented. The constant of the symmetrical van Laar equation which satisfies the total vapor pressure data is given as a linear regression against reciprocal temperature. Wood (*2*) obtained data on this system using chemical analysis but his results do not show thermodynamic consistency. The procedure and apparatus have been described previously by Ryder, Kamal, and Canjar (*1*).

EXPERIMENTAL COMPOUNDS

Baker Analytical Reagent grade carbon tetrachloride and Fisher Scientific Technical grade silicon tetrachloride were used in the experimental work. No attempt was made to determine purity of the reagents.

VAPOR-LIQUID EQUILIBRIUM THEORY

At low pressures, the total pressure exerted by a binary mixture may be written as

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

If log γ does not vary much with pressure as in the present work, the Gibbs-Duhem equation can be assumed valid

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

and equations which satisfy the Gibbs-Duhem criteria such as the van Laar equations

$$\log \gamma_1 = \frac{Ax_2^2}{[(A/B)\,x_1 + x_2]^2} \qquad (3)$$

$$\log \gamma_2 = \frac{Bx_1^2}{[x_1 + (B/A)\,x_2]^2} \qquad (4)$$

can be used to describe the variation of log γ with composition.

If $A = B$, the van Laar equations reduce to

$$\log \gamma_i = B(1 - x_i)^2 \qquad (5)$$

By expressing γ_i as a sum of an infinite series

$$\gamma_i = 1 + B(1 - x_i)^2 + (B/2)\,(1 - x_i)^4_T \qquad (6)$$

and ignoring all but the first two terms, Equation 1 may be written as

$$P_t = x_1(1 + Bx_2^2)\,P_1^\circ + x_2(1 + Bx_1^2)\,P_2^\circ \qquad (7)$$

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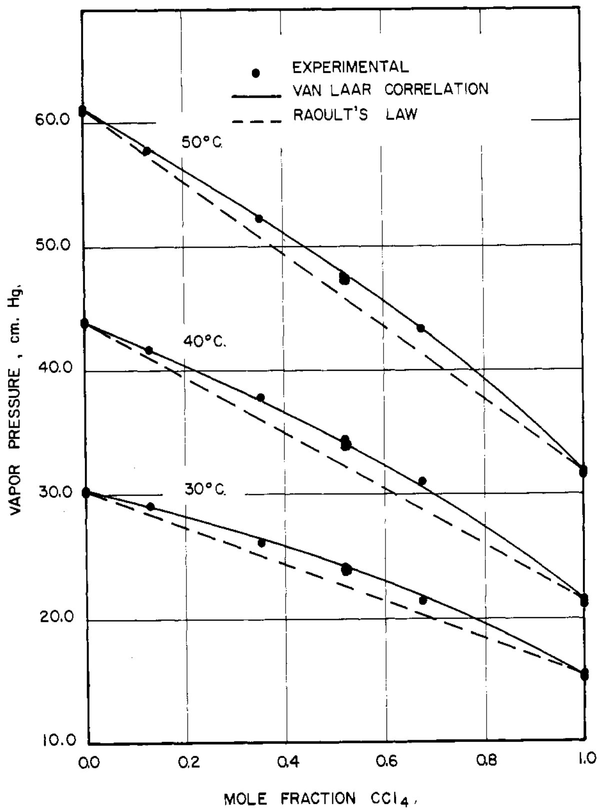

Figure 1. Experimental vapor pressure of $SiCl_4$-CCl_4 mixtures vs. mole fraction CCl_4

or

$$B = \frac{P_t - x_1P_1^\circ - x_2P_2^\circ}{x_1x_2(x_2P_1^\circ + x_1P_2^\circ)} \tag{8}$$

B can be calculated directly from experimental data by Equation 8.

Analysis of the experimental data presented here indicates that the assumption $A = B$ in the van Laar equation is justified for this particular system. The maximum error introduced into the calculation by the approximation of the infinite series is about 0.5 mm. Hg. The experimental variance is greater than 0.5 mm. Hg.

RESULTS

Table I. Experimental Total Vapor Pressure Data for CCl_4-$SiCl_4$ System

(Total vapor pressure, cm. of Hg)

Run No.	Mole Fraction CCl_4	30.0° C.	40.0° C.	50.0° C.
7	1.0000	15.25	21.23	31.61
3	1.0000	15.34	21.28	31.72
5	1.0000	15.40	21.51	31.85
8	0.6863	21.43	31.02	43.30
2-A	0.5244	23.94	34.00	47.21
2-B	0.5244	23.92	33.94	47.41
1-A	0.5224	23.92	34.40	47.58
1-B	0.5224	23.79	34.10	47.47
2	0.5219	24.14	33.99	47.25
6	0.3518	26.08	37.85	52.22
9	0.1279	29.08	41.70	57.81
4	0.0000	30.37	43.84	60.98
1	0.0000	30.20	43.91	61.20

The variation in B with reciprocal absolute temperature can be represented by an equation with a relative uncertainty of 10% in the range of experimental temperatures

$$B = -1.5399 + \frac{0.5483 \times 10^3}{T} \tag{10}$$

if logarithms to the base e are used in Equation 5.

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

$$y_i/x_i = \gamma_i P_i^\circ / P_t \tag{11}$$

Figure 1 compares the experimental data with the total pressure calculated from the van Laar equations using the value of the van Laar constant predicted by Equation 10. Table I summarizes the results of the experimental work.

NOMENCLATURE

A, B = van Laar constants
P_t = total vapor pressure of mixture (cm. Hg)
P_i° = vapor pressure of pure component i (cm. Hg)
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
log = natural logarithm, $\log_e$

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