(41) Lambert, J.D., Cotten, K.J., Pailthorpe, M.W., Robinson, A.M., Scrivens, J., Vale, W.R.F., Young, R.M., *Proc. Roy. Soc. (London)* **A231**, 280 (1955).
(42) Lenoir, J.M., Comings, E.W., *Chem. Eng. Progr.* **47**, 223 (1951).
(43) Lenoir, J.M., Junk, W.A., Comings, E.W., *Ibid.*, **49**, 539 (1953).
(44) Mann, W.B., Dickins, B.G., *Proc. Roy. Soc. (London)* **A134**, 77 (1931).
(45) Michels, A., Botzen, A., Friedman, A.S., Sengers, J.V., *Physica* **22**, 121 (1956).
Physica **22**, 121 (1956).
(46) Milverton, S.W., *Proc. Roy. Soc. (London)* **150**, 287 (1935).
(47) Misic, Dragoslav, Thodos, George, *A.I.Ch.E. Journal* **7**, 267 (1961).
(48) Moser, E., Dissertation, Friedrich-Wilhelms, Universität zu Berlin, 1913.
(49) Nothdurft, Walter, *Ann. Physik* **28**, 137 (1937).
(50) Nuttall, R.L., g unnings, D.G., *J. Res. N.B.S.* **58**, 271 (1957).

(50) Nuttall, R.L., Gunnings, D.G., *J. Res. N.B.S.* **58**, 271 (1957).
(51) Powers, R.W., Mattox, R.W., Johnston, H.E., *J. Am. Chem. Soc.* **76**, 5968 (1954).
(52) Richter, G.N., Sage, B.H., J. CHEM. ENG. DATA **4**, 36 (1959).
(53) Rothman, A.J., *U.S. Atomic Energy Comm., Tech. Inform. Service*, **UCRL-2339** (1954).
(54) Rothman, A.J., Bromley, L.A., *Ind. Eng. Chem.* **47**, 899 (1955).
(55) Schleirmacher, A., *Ann. Physik* **34**, 623 (1888).
(56) Schleirmacher, A., *Ibid.*, **36**, 346 (1889).
(57) Schmidt, E., *Forschungsheim-Warmefsch.* No. **5**, Munich (1924).
(58) Schneider, Ernst, *Ann. Physik* **79**, 177 (1926).
(59) *Ibid.*, **80**, 215 (1926).
(60) Schottky, W.F., *Z. Elektrochem.* **56**, 889 (1952).
(61) Sellschopp, Wilhelm, *Forsch. Gebiete Ingenieurw.* **5**, 162 (1934).
(62) Sherratt, G.G., Griffiths, E., *Phil. Mag.* (7) **27**, 68 (1939).
(63) Sounders, Jr., Mott, Matthews, C.S., Hurd, C.O., *Ind. Eng. Chem.* **41**, 1037 (1949).
(64) Stefen, J., *Berichte der Wiener Akademie* **65**, II, 45 (1872).
(65) *Ibid.*, **72**, II, 69 (1875).
(66) Stice, J.E., M.S. thesis, Illinois Institute of Technology, Chicago, 1952.
(67) Stiel, L.I., Thodos, George, *A.I.Ch.E. Journal* **7**, 611 (1961).
(68) *Ibid.*, **8**, 229 (1962).
(69) Stolyarov, E.A., *Zhur. Fiz. Khim.* **24**, 279 (1950).
(70) Stolyarov, E.A., Ipatiev, V.V., Teodorovich, P., *Ibid.*, **24**, 166 (1950).
(71) Thomas, L.B., Golike, R.C., *J. Chem. Phys.* **22**, 300 (1954).
(72) Timroth, D., Vargaftik, N.B., *J. Phys. (USSR)* **11**, 101 (1940).
(73) Todd, G.W., *Proc. Roy. Soc. (London)* **A83**, 19 (1909).
(74) Trautz, M., Zundel, A., *Ann. Physik* (5) **17**, 345 (1933).
(75) Ubbink, J.B., *Physica* **14**, 165 (1948).
(76) Ubbink, J.B., de Haas, W.J., *Ibid.*, **10**, 451 (1943).
(77) *Ibid.*, **10**, 465 (1943).
(78) Uhlir, Jr., Arthur, *J. Chem. Phys.* **20**, 463 (1952).
(79) Vargaftik, N.B., *Zhur. Tekh. Phiz.* **4**, 341 (1937).
(80) Vargaftik, N.B., Oleshchuk, O.N., *Izvest. VTI* **15**, No. 6, 7–15 (1946).
(81) Vargaftik, N.B., Parfenov, I.D., *J. Exptl. Theoret. Phys. (USSR)* **8**, 189 (1938).
(82) Vargaftik, N.B., Smirnova, E.V., *Zhur. Tekh. Fiz.* **26**, 1251 (1956).
(83) *Ibid., Soviet Phys. Tech. Phys.* **1**, 1221 (1957).
(84) Vargaftik, N.B., Tarzemanov, A.A., *Topoenergetika* **6**, No. 9 (1959).
(85) Vines, R.G., *Australian J. Chem.* **6**, 1 (1953).
(86) Vines, R.G., Bennett, L.A., *J. Chem. Phys.* **22**, 360 (1956).
(87) Vines, R.G., *Project Squid Paper No.* **59-HT-2** (1959).
(88) Wassiljewa, Alexandra, *Physik. Z.* **5**, 737 (1904).
(89) Weber, S., *Ann. Physik* (4) **54**, 437 (1917).
(90) Weber, S., *Ibid.*, **54**, 481 (1917).
(91) *Ibid.*, **82**, 479 (1927).
(92) Wilner, T., Borelius, G., *Ibid.*, **4**, (5), 316 (1930).
(93) Winkelmann, A., *Ibid.*, **156**, 497 (1875).
(94) Wooley, H.W., Scott, R.B., Brickwedde, F.G., *J. Research NBS* **4**, 379 (Nov. 1948).
(95) Ziebland, Hans, Burton, J.T.A., *Brit. J. Appl. Phys.* **6**, 416 (1955).
(96) Ziegler, E., Dissertation, Universität zu Halle, Germany, 1904.

RECEIVED for review November 19, 1962. Accepted March 28, 1963. The support of one of the authors, Dragoslav Misic, by the Petroleum Research Fund is gratefully acknowledged.

Vapor Pressures of Silicon Tetrachloride–Titanium Tetrachloride Mixtures

REID B. CROOKSTON and LAWRENCE N. CANJAR
Department of Chemical Engineering, Carnegie Institute of Technology, Pittsburgh, Pa.

Liquid phase activity coefficients for silicon tetrachloride–titanium tetrachloride solutions are presented. The activity coefficients were calculated from total pressure–composition data for the 30°, 40°, and 50° C. isotherms. The results have been correlated using the two suffix van Laar equations.

LIQUID PHASE activity coefficients for silicon tetrachloride–titanium tetrachloride solutions are presented. The activity coefficients were calculated from total pressure–composition data for the 30°, 40°, and 50° C. isotherms with glass Bourdon tubes serving as the pressure sensing elements. The results have been correlated using the two suffix van Laar equations. The van Laar constants, A and B, were determined so as to give a "least-squares fit" to the data.

EXPERIMENTAL COMPOUNDS

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

PROCEDURE AND APPARATUS

Because both silicon tetrachloride and titanium tetrachloride react with the water vapor in air, it was necessary to isolate these chemicals from contacting air throughout the test work. Sample preparations were carried out using the equipment and arrangement shown in Figure 1. Each chloride was transferred from its commercial bottle to a flask, such as the one shown at the top of Figure 1, in a Berkley-type dry box, filled with dry nitrogen. A large volume of vapor was then withdrawn from each flask to remove the nitrogen contaminants. With the proper manipulation of the stopcocks shown in Figure 1, first titanium tetrachloride and then silicon tetrachloride was allowed to flow into the previously evacuated sample flask. Compositions were determined by difference of weights. The four-way joint permitted the transference route to be purged or evacuated as desired.

The experimental pressure measurements were made using the arrangement diagramed in Figure 2. During a test, the sample was contained in a glass vessel, denoted as the "glass-spring assembly" in Figure 2, that was entirely submerged in a constant-temperature bath. Six glass Bourdon tubes, mounted as shown, served as pressure sensing elements. Their deflections were registered by the relative alignment of markers at the ends of two, twenty-centimeter needles. The sensitivity of the equipment was 0.6 mm. of mercury. Throughout a test, stopcocks 3 and 4 were closed and 5 was open. The pressure inside the glass Bourdon tubes could be both controlled and measured. To determine the total pressure of a solution, first, the pressure inside the glass Bourdon tubes was adjusted so that it equaled the solution pressure, a condition indicated by exact alignment of the markers. Then the pressure inside the glass Bourdon tubes was read from the manometer. Very precise pressure regulation was possible by adjustment of the height of the mercury bulb of the variable-level mercury manometer. Deflections of the markers were magnified by a cathatometer.

THEORY

The total pressure of a binary solution with an ideal gas phase is

$$P = \gamma_1 x_1 P_1^\circ + \gamma_2 x_2 P_2^\circ \tag{1}$$

For pressures less than atmospheric, the constant pressure constraint may be removed from the Gibbs-Duhem equation, which may then be written:

$$x_1\left[\frac{\partial \log \gamma_1}{\partial x_1}\right]_T = x_2\left[\frac{\partial \log \gamma_2}{\partial x_2}\right]_T \tag{2}$$

In the present work, the two suffix van Laar equations, Equations 3 and 4, which satisfy the Gibbs-Duhem criteria, were found to successfully correlate the data.

$$\log \gamma_1 = \frac{A x_2^2}{\left[\frac{A}{B} x_1 + x_2\right]^2} \tag{3}$$

$$\log \gamma_2 = \frac{B x_1^2}{\left[\frac{B}{A} x_2 + x_1\right]^2} \tag{4}$$

Substituting Equations 3 and 4 into 1 gives the final working equation

$$P = x_1 P_1^\circ\, 10^{\frac{A x_2^2}{[(A/B)\, x_1 + x_2]^2}} + x_2 P_2^\circ\, 10^{\frac{B x_1^2}{[(B/A)\, x_2 + x_1]^2}} \tag{5}$$

The van Laar constants, A and B, in Equation 5 were determined, for each isotherm, using a Bendix G–20 computer so that the sum of the squares of the differences between the pressure measurements and the pressures given by Equation 5, at the same liquid composition, be a minimum. In other words, for each isotherm, A and B were determined so as to minimize

$$SS = \sum\left[P_j - x_{1j} P_1^\circ\, 10^{\frac{A x_{2j}^2}{[(A/B)\, x_{1j} + x_{2j}]^2}} - x_{2j} P_2^\circ\, 10^{\frac{B x_{1j}^2}{[(B/A)\, x_{2j} + x_{1j}]^2}}\right]^2 \tag{6}$$

where subscript j refers to a data point.

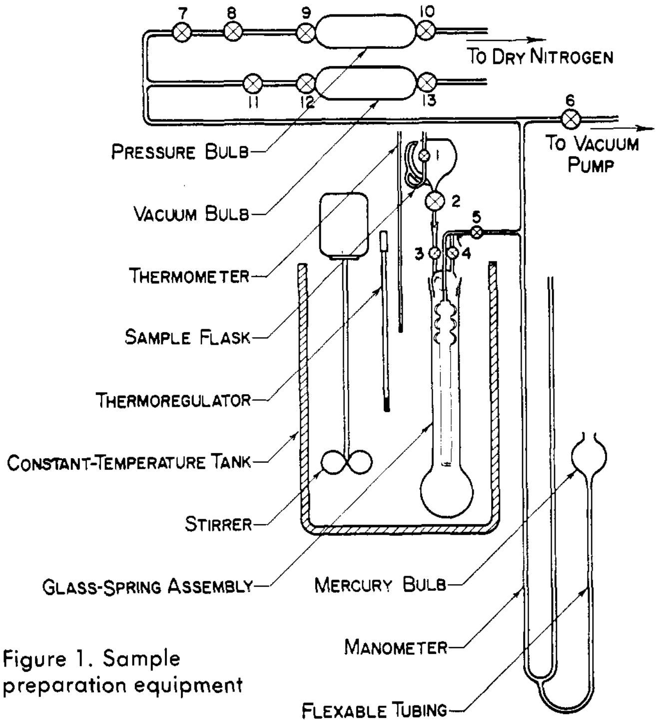

Figure 1. Sample preparation equipment

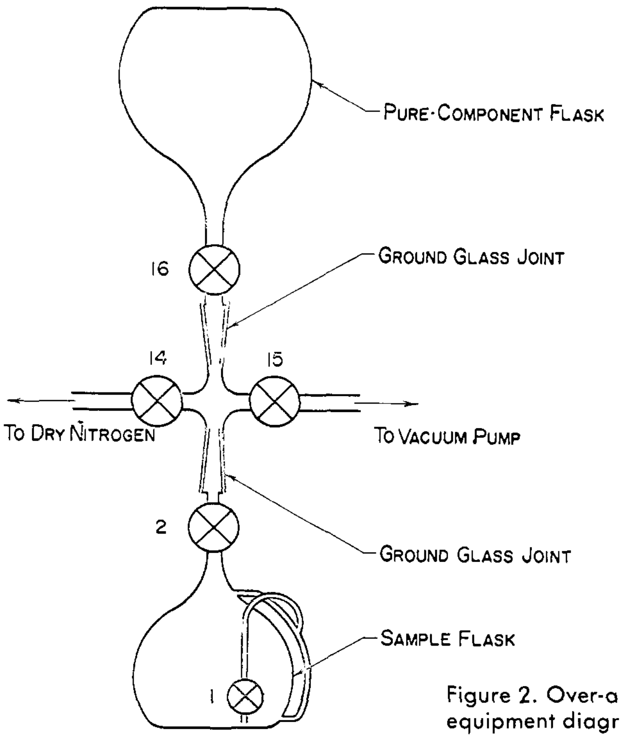

Figure 2. Over-all equipment diagram

Table I. Pressure in Mm. of Mercury

Carbon Tetrachloride

Run No.	30° C.	40° C.	50° C.
1	141.7	210.9	307.6
2	141.8	212.2	308.7
3	141.1	211.2	308.4

Silicon Tetrachloride—Titanium Tetrachloride

	30° C.		40° C.		50° C.	
Run No.	mol fraction $SiCl_4$	pressure mm. of Hg	mol fraction $SiCl_4$	pressure mm. of Hg	mol fraction $SiCl_4$	pressure mm. of Hg
1	0.0000	15.0	0.0000	24.9	0.0000	39.9
2	0.0000	14.2	0.0000	23.8	0.0000	38.1
3	0.2517	100.8	0.2503	148.2	0.2487	209.2
4	0.2517	100.5	0.2503	149.5	0.2487	209.8
5	0.5034	167.9	0.5018	244.6	0.4998	343.8
6	0.5034	169.6	0.5018	244.6	0.4998	345.6
7	0.7690	234.3	0.7679	341.0	0.7663	478.4
8	0.7690	233.7	0.7679	338.3	0.7663	476.4
9	1.0000	291.1	1.0000	424.1	1.0000	600.6
10	1.0000	291.6	1.0000	423.7	1.0000	602.1

RESULTS

The equipment and method were checked by measuring the vapor pressure of pure carbon tetrachloride and comparing them with the values of Stull (*2*), who accumulated and analyzed a large amount of vapor pressure data with considerable rigor. The average difference between the values obtained in this work, presented in Table I, and those of Stull is 1.1 mm. of mercury.

The experimental data for the titanium tetrachloride-silicon tetrachloride solutions is also presented in Table I. Small corrections have been made in the liquid compositions to correct for certain vaporizations, such as the vapor which occupied the space above the liquid during the tests. For example, the original composition of the liquid charged to the apparatus during Run 6 of Table I was 0.5118. A complete description of these corrections is given in reference (*1*). Figure 3 is a graphical representation of the data, least-squares curves, and Raoult's Law lines. The vapor pressures of pure carbon, titanium, and silicon tetrachlorides are shown plotted *vs.* reciprocal temperature in Figure 4, and the connecting lines are straight as would be expected over such a temperature range. Table II presents the van Laar constants that gave a least-squares fit to the data and the corresponding minimum sum of squares for each isotherm. The van Laar constants in Table II apply to the following equations where the logatithms are to the base ten. These equations are plotted in Figure 5.

Table II. van Laar Constants and SS

Isotherm	*A*	*B*	Sum of Squares
30° C.	0.13992	0.16886	2.840
40° C.	0.16055	0.15193	8.260
50° C.	0.16050	0.12625	5.572

$$\log \gamma_{SiCl_4} = \frac{A x^2_{TiCl_4}}{[(A/B)\, x_{SiCl_4} + x_{TiCl_4}]^2} \tag{7}$$

$$\log \gamma_{TiCl_4} = \frac{B x^2_{SiCl_4}}{[(B/A)\, x_{TiCl_4} + x_{SiCl_4}]^2} \tag{8}$$

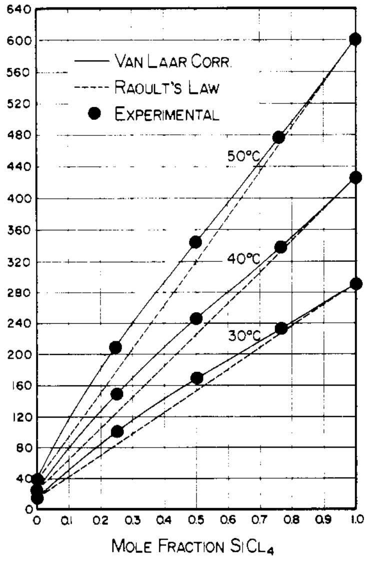

Figure 3. Total pressure *vs.* mole fraction $SiCl_4$

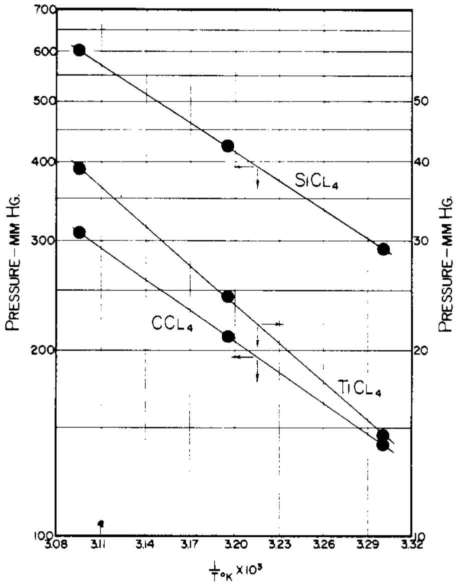

Figure 4. Vapor pressure plot

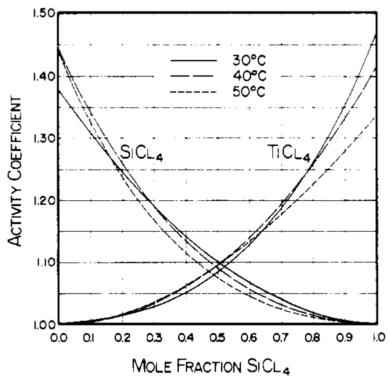

Figure 5. Activity coefficients plot

NOMENCLATURE

A, B = van Laar constants
P = total pressure of mixture
P_i° = vapor pressure of pure component i
SS = sum of squares
x_i = mole fraction of component i in the liquid phase
γ_i = activity coefficient of component i in the liquid phase

LITERATURE CITED

(1) Crookston, R.B., M. S. Thesis, Carnegie Institute of Technology, Chemical Engineering Department, 1962.
(2) Stull, D.R., *Ind. Eng. Chem.* **39**, 517 (1947).

RECEIVED for review March 5, 1963. Accepted June 17, 1963.

Thermodynamic Functions of Methane

ROBIN S. McDOWELL and F. H. KRUSE
Los Alamos Scientific Laboratory, University of Calif., Los Alamos, N. M.

Standard-state thermodynamic functions for gaseous methane are reported for the temperature range 60° K. to 5000° K., taking into consideration low-temperature quantum effects, anharmonicity, centrifugal distortion, and vibration-rotation interaction.

ALTHOUGH METHANE is a thermodynamically important molecule, no tables of its thermodynamic functions appear to have been published in which the rigid-rotator, harmonic oscillator (RRHO) approximation was abandoned. The best available values (*11*) are based on an RRHO calculation performed in 1944 (*10*). Spectroscopic information on methane has increased to the point where now the higher-order corrections can be applied. This paper reports the standard state thermodynamic functions for gaseous methane from 60° K. to 5000° K., taking into consideration low-temperature quantum effects, anharmonicity (*16*), centrifugal distortion (*8*), and vibration-rotation interaction (*9*).

The functions were calculated for an ideal gas at 1 atm. pressure. The RRHO values were obtained using the Viney (*15*) rotational partition function. Correction terms were included for anharmonicity through the second order (*i.e.*, terms varying as T^2 at high temperatures). The contribution of nuclear spin was not included. Separate calculations were made for $C^{12}H_4$ and $C^{13}H_4$ using $C^{13}H_4$ frequencies and anharmonicities calculated as previously described (*7*). The maximum difference in C_p°/R between these calculations and the values obtained using $C^{12}H_4$ frequencies and anharmonicities and a mean molecular weight (based on 1.11% $C^{13}H_4$) was only 0.0002. Since this is less than the probable error introduced by uncertainties in the molecular constants, the values reported here are based on the $C^{12}H_4$ constants and the mean molecular weight. Physical-scale constants (*3*) were used with hc/k = 1.43880 cm. deg. and a translational entropy constant of −1.16552. Calculations were carried out on an IBM 7090 computer.

The molecular constants selected for this work are listed in Table I.

Because of the extreme complexity of the methane spectrum, due in large part to the high degeneracy of most bands and the resultant opportunity for various types of interaction, the selection of a suitable set of constants is difficult. This will probably be the situation for some time to come, since the finer points of the spectra of tetrahedral molecules are only now beginning to be studied in detail (*4*, *5*) and the effect of higher-order perturbations of such molecules on their thermodynamic functions

Table I. Molecular Constants of Methane

Mass = 16.04757 amu. (physical scale) (*14*)
Rotational Constants (*13*)
B_0 = 5.2406 cm.$^{-1}$
D_0 = 1.23×10^{-4} cm.$^{-1}$
σ = 12
Vibrational Constants (cm.$^{-1}$)

	$i = 1$	$i = 2$	$i = 3$	$i = 4$
ν_i (*2, 13*)	2916.7	1533.6	3018.9	1305.9
X_{1i} (*7*)	−64.6	0	−65.0	0
X_{2i}		0	−15.0	−11.2
X_{3i}			−17.5	−12.0
X_{4i}				−6.0
α_i	−0.025	−0.11	0.037	0.045