Table II. Measured and Estimated Entropies at 298.15° K. in Gibbs per Mole

Compound	$S°_{298}$ Measured	$S°_{298}$ Estimated	% Diff.
KOH	18.85	14.2	−24.7
K_2CO_3	37.17	33.6	−9.6
K_2SiO_3	34.93	35.2	0.8
LiCl	14.19	13.5	−4.9
Li_2SiO_3	19.08	23.8	24.7
MgS	12.03	12.6	4.7
$SnSO_4$	33.12	30.3	−8.5
$AlCl_3 \cdot 6H_2O$	76.03	82.5	8.5

LITERATURE CITED

(1) Andon, R. J. L., Counsell, J. F., McKerrell, H., Martin, J. F., *Trans. Faraday Soc.* **59**, 2702 (1963).
(2) Brown, H. C., Boyd, A. C., *Anal. Chem.* **27**, 156 (1955).
(3) Cox, B., *J. Chem. Soc.* **1954**, 3251.
(4) Furukawa, G. T., Reilly, M. L., Piccirelli, J. H., *J. Res. Natl. Bur. Std.* **68A**, 651 (1964).
(5) Hildenbrand, D. L., Kramer, W. R., McDonald, R. A., Stull, D. R., *J. Am. Chem. Soc.* **80**, 4129 (1958).
(6) Hu, T., Hepler, L. G., J. CHEM. ENG. DATA **7**, 58 (1962).
(7) JANAF Thermochemical Tables, Dow Chemical Co., Thermal Research Laboratory, Midland, Mich.
(8) Justice, B. H., J. CHEM. ENG. DATA, 14, 4 (1969).
(9) Kelley, K. K., King, E. G., U. S. Bur. Mines, Bull. **592** (1961).
(10) Latimer, W. M., "Oxidation Potentials," 2nd ed., Appendix III, Prentice-Hall, New York, 1952.
(11) Oetting, F. L., McDonald, R. A., *J. Phys. Chem.* **67**, 2737 (1963).
(12) Shirley, D. A., *J. Am. Chem. Soc.* **82**, 3841 (1960).
(13) Stull, D. R., *Anal. Chim. Acta* **17**, 133 (1957).

RECEIVED for review April 14, 1969. Accepted September 8, 1969. Work supported in part by the Advanced Research Projects Agency, Propellant Chemistry Office, and monitored by the Air Force Flight Test Center under Contract Nr. AF 33(616)-6149.

Volumetric Behavior of a Polar-Nonpolar Gas Mixture: Trifluoromethane-Tetrafluoromethane System

HOWARD B. LANGE, JR.,[1] and FRED P. STEIN
Department of Chemical Engineering, Lehigh University, Bethlehem, Pa. 18015

Compressibility factors were determined for the polar-nonpolar gaseous system, $CF_3H—CF_4$, for six compositions at temperatures between −30° and 95° C., and at temperatures as low as −70° C. for CF_4. The data extend to pressures as high as 1238 p.s.i.a. and are accurate to better than one part per thousand. Values are given for the constants in the Martin-Hou equation of state which correlate the volumetric data with average deviations of less than 0.5% for the pure components and 1.1% for the mixtures. Second and third virial coefficients were determined from the data; the virial coefficients for the pure gases and the interaction virial coefficients are presented. Intermolecular-potential-function parameters are given for CF_4, which correlate the second virial coefficient for this gas within its experimental uncertainty between −70° and 500° C.

THE APPARENT NEED for volumetric data on gas mixtures containing polar components, as well as a need for such data to interpret some vapor-liquid equilibrium data (*12*), prompted the determination of the volumetric behavior of the $CF_3H—CF_4$ system. Of the available methods of volumetric measurement, the Burnett method was selected as having the best combination of accuracy and efficiency.

The Burnett method is an isothermal experiment in which successive portions of a test gas, confined in a primary chamber, are allowed to expand into a secondary chamber, which is discharged and evacuated after each expansion. For each expansion, comparison of the ratio of the pressures before and after the expansion to the known volume ratio of the two chambers indicates the nonideality of the test gas. The Burnett method has been described in detail (*1, 13*).

[1] Present address, Babcock and Wilcox Co., Research Center, Alliance, Ohio 44601

EXPERIMENTAL

The experimental pressures were measured by balancing a hydraulic pressure generated by a dead-weight gage against the test-gas pressure, using a sensitive differential-pressure transducer (DP-cell). The latter employed a thin metallic diaphragm, the position of which was sensed by a magnetic-reluctance circuit. The pressure-measurement system had a sensitivity of 0.001 p.s.i. and an over-all accuracy of 0.01 p.s.i. The test-gas pressure was continually monitored on a recorder, except during and immediately following expansions, as a check for leaks and as evidence of the restoration of thermal equilibrium after each expansion.

The temperatures of the chamber walls, as well as that of the constant-temperature bath, were measured with an accuracy of 0.01° C. The calculations included corrections for small departures from run temperature. A very small portion of the test gas was at room temperature, because the DP-cell was located outside of the constant-temperature bath. A correction for this unthermostated test gas was included in the calculations in a fashion similar to that used by previous investigators (*3*).

The dead-weight gage was manufactured by the Ruska Instrument Corp. The weights were calibrated by Ruska against class S standards and were checked prior to this work for internal consistency. The piston area was certified by Ruska, based on light-wave micrometer readings accurate to 5×10^{-6} inch.

The temperature scale was established by calibration of the thermopiles *in situ* against a platinum-resistance thermometer previously calibrated by the National Bureau of Standards.

The mixtures were analyzed with a Beckman Instruments, Inc., GC-2A gas chromatograph which used an electronic integrator for the determination of peak areas. Each mixture was compared on the chromatograph to a standard of the same nominal composition. The standards were prepared by mixing the pure components to a total pressure of approximately 2 atm. The compositions of the standards, as determined from the mixing pressures, were then corrected for slight departures from ideality using second virial coefficients. Sufficient time was allowed for the homogenization of all gas mixtures. The estimated uncertainty in the reported compositions is 0.5% of the lesser mole fraction. The CF_4 used in this work was 0.996 pure; the 0.004 air impurity was determined chromatographically as described above. The CF_3H was quoted as 0.9998 pure by the supplier, E. I. du Pont de Nemours & Co. The compressibility factors and second virial coefficients presented below were corrected for this small air impurity.

Measurement of a vapor pressure in this apparatus provides a convenient cross check among the independently established pressure, temperature, and purity of material. Accordingly, the vapor pressure of CF_3H was measured at 0° C.; the value found was 362.47 p.s.i.a. Martin and Hou (*11*) report an experimental value of 363.3 at 0° C. and a smoothed value of 362.61 p.s.i.a.

EXPERIMENTAL DATA

Two or three series of expansions were carried out at each condition of temperature and composition, the experimental pressures being staggered to define the isotherm better. The accuracy of the compressibility factors given in Table I varies between 3 and 7 parts

Table I. Experimental Compressibility Factors

Mole Fraction CF_4 = 1.0

Pressure, P.S.I.A.	Compressibility Factor 95.00° C.	40.00° C.	0.00° C.	−30.00° C.	−50.00° C.	−70.00° C.
1200	0.9075	0.7839	0.5825	[a]		
1000	0.9186	0.8111	0.6309	[b]		
800	0.9303	0.8433	0.7019	[c]		
600	0.9445	0.8802	0.7802	0.6000		
500	0.9528	0.8993	0.8191	0.6915	[d]	
400	0.9612	0.9189	0.8573	0.7668	0.6389	
300	0.9707	0.9391	0.8945	0.8333	0.7600	
250	0.9753	0.9490	0.9126	0.8640	0.8087	0.7058
200	0.9797	0.9589	0.9306	0.8933	0.8524	0.7843
150	0.9849	0.9692	0.9484	0.9213	0.8930	0.8480
100			0.9653	0.9483	0.9303	0.9040

Pressure, P.S.I.A.	Mole Fraction CF_3H = 0.0505, −50.00° C.	Mole Fraction CF_3H = 0.0505, −70.00° C.	Mole Fraction CF_3H = 0.0872, −50.00° C.	Mole Fraction CF_3H = 0.0872, −70.00° C.
400	0.6311		0.6192	
350	0.6993		0.6913	
300	0.7550		0.7515	
250	0.8056		0.8025	
200	0.8493	0.7803	0.8482	0.7764
150	0.8911	0.8462	0.8899	0.8439
100		0.9030		0.9019

Mole Fraction CF_3H = 0.193

Pressure, P.S.I.A.	95.00° C.	40.00° C.	0.00° C.	−30.00° C.	−50.00° C.
1200	0.8934	0.7557	0.5230		
1000	0.9055	0.7888	0.5775		
800	0.9210	0.8267	0.6643	[e]	
600	0.9386	0.8686	0.7571	0.5294	
500	0.9479	0.8903	0.8018	0.6506	[f]
400	0.9577	0.9122	0.8449	0.7423	
300	0.9676	0.9343	0.8860	0.8184	0.7333
250		0.9452	0.9059	0.8527	0.7900
200		0.9560		0.8850	0.8397
150				0.9153	0.8845

(Continued)

Table I. (Continued)

Pressure, P.S.I.A.	Compressibility Factor 95.00° C.	40.00° C.	0.00° C.	−30.00° C.	−50.00° C.	−70.00° C.
	Mole Fraction CF_3H = 0.410					
1200	0.8610	0.6909	[g]			
1000	0.8795	0.7351	0.4413			
800	0.9003	0.7862	0.5616			
600	0.9233	0.8404	0.6979			
500	0.9354	0.8676	0.7579			
400	0.9478	0.8947	0.8130			
300	0.9606	0.9216	0.8643	0.7790		
250	0.9671	0.9348	0.8886	0.8224		
200	0.9734	0.9479	0.9121	0.8629		
150			0.9350	0.9001		
	Mole Fraction CF_3H = 0.607					
1200	0.8232	0.6049				
1000	0.8474	0.6643				
800	0.8750	0.7341				
600	0.9046	0.8048	0.6062			
500	0.9199	0.8395	0.6957			
400	0.9358	0.8736	0.7705			
300	0.9516	0.9063	0.8361			
250	0.9599	0.9225	0.8661	[h]		
200	0.9679	0.9385	0.8950	0.8328		
150				0.8798		
100				0.9226		
	Mole Fraction CF_3H = 0.8407					
1200	0.7597	0.4322				
1000	0.7921	0.5182				
800	0.8311	0.6324				
600	0.8732	0.7402				
500	0.8947	0.7898	[i]			
400	0.9161	0.8361	0.6885			
300	0.9370	0.8799	0.7862			
250	0.9476	0.9013	0.8279			
200		0.9218	0.8665			
150			0.9025	0.8434		
100			0.9365	0.9008		
	Mole Fraction CF_3H = 1.0					
650	0.8340	0.6365				
600	0.8467	0.6743				
500	0.8728	0.7418				
400	0.8987	0.8017				
350	0.9115	0.8299	0.6692			
300	0.9245	0.8566	0.7348			
250	0.9373	0.8824	0.7901			
200	0.9498	0.9073	0.8392			
150		0.9315	0.8839	[j]		
100		0.9551	0.9251	0.8814		

[a] P = 1216.070, Z = 0.3851.
[b] P = 1025.151, Z = 0.3569.
[c] P = 745.116, Z = 0.4456.
[d] P = 466.481, Z = 0.4989.
[e] P = 665.690, Z = 0.4119.
[f] P = 331.716, Z = 0.6914.
[g] P = 1210.740, Z = 0.4056.
[h] P = 224.926, Z = 0.8074.
[i] P = 447.166, Z = 0.6305.
[j] P = 142.699, Z = 0.8199.

in 10,000, tending to be poorer at the higher pressures and lower temperatures. The absence of high-pressure data for pure CF_3H at 40° and 95° C. is due to the fact that pure CF_3H would have condensed at room temperature in the DP-cell. The values presented in Table I are interpolations to round values of pressure. The original data at the experimentally measured pressures are available as a NAPS document.

CORRELATION OF VOLUMETRIC DATA

Constants for the Martin-Hou equation of state *(10)* have been determined previously for pure CF_4 and for pure CF_3H based on experimental data *(11)* for these gases. The numerical values, taken from technical bulletins available from Freon Products Division, E. I. du Pont de Nemours & Co., Inc., are shown in columns 2 and 4 of Table II. These constants, when used in the Martin-Hou equation,

$$P = \frac{RT}{(V-b)} + \frac{A_2 + B_2T + C_2e^{-kT/T_c}}{(V-b)^2} + \frac{A_3 + B_3T + C_3e^{-kT/T_c}}{(V-b)^3} + \frac{A_4 + B_4T}{(V-b)^4} + \frac{A_5 + B_5T + C_5e^{-kT/T_c}}{(V-b)^5} + \frac{A_6 + B_6T}{e^{av}} \quad (1)$$

predict pressures at the densities measured in this work which are in close agreement with the experimental

Table II. Recommended Values of Martin-Hou Constants for CF_4–CF_3H System

Martin-Hou Constant	CF_4	Interaction	CF_3H
A_2	-1.675376×10^4	-1.936576×10^4	-2.294265×10^4
A_3	3.002263×10^3	-7.452064×10^{-1}	-4.282594×10^3
A_4	1.152582×10^4	2.614219×10^4	4.971046×10^4
A_5	-2.366137×10^4	-4.438648×10^4	-6.511159×10^4
A_6	5.838823×10^7	6.635878×10^7	7.502357×10^7
B_2	1.653808×10^1	1.678043×10^1	1.702634×10^1
B_3	8.745026×10^0	1.764664×10^1	2.654826×10^1
B_4	-2.350832×10^1	-4.562773×10^1	-8.855969×10^1
B_5	4.785193×10^1	6.644246×10^1	1.086551×10^2
B_6	-9.263923×10^4	-1.015967×10^5	-1.114202×10^5
C_2	-1.467135×10^5	-2.471400×10^5	-7.833461×10^5
C_3	3.679677×10^5	9.773246×10^5	2.039583×10^6
C_5	-2.553920×10^5	-6.251347×10^5	-1.244522×10^6
k	4.00	4.69	5.50
T_c	409.50	469.52	538.33
a	7.51278	7.46949	7.42645
b	0.13200	0.10977	0.08753
R	10.73168	10.73168	10.73168

Units: p.s.i.a., cu. ft. per lb.-mole, ° R.

pressures (average deviations of 0.24% for CF_4, 0.43% for CF_3H, and maximum deviations of about 1% for both gases). The largest deviations occur at the highest pressures and in the vicinity of the critical point.

A quadratic composition dependency is usually assumed for the Martin-Hou constants,

$$K = y_1^2 K_{11} + 2\, y_1\, y_2\, K_{12} + y_2^2 K_{22} \tag{2}$$

where K is any Martin-Hou constant, subscript 1 refers to CF_4, and 2 refers to CF_3H. The interaction constants, K_{12} in Equation 2, which best correlate the mixture data are listed in Table II. Only interaction constants bearing some rational relationship to the pure-gas constants were considered (*9*). The values given predict the experimental pressures for the mixtures with an average deviation of 1.1% and a maximum deviation of 2.8%.

Table III. Second Virial Coefficients for CF_4–CF_3H System (Cc./gram-mole)

Temp., ° C.	B_{11} (CF_4)	B_{12}	B_{22} (CF_3H)
95	-45.75 ± 0.2	-51.13 ± 1.0	-109.50 ± 0.2
40	-77.26 ± 0.2	-85.28 ± 1.4	-165.50 ± 0.2
0	-110.87 ± 0.2	-122.75 ± 1.4	-233.60 ± 0.4
−30	-146.36 ± 0.2	-159.33 ± 1.8	-311.60 ± 1.0
−50	-177.71 ± 0.5		
−70	-216.75 ± 0.7		

VIRIAL COEFFICIENTS

The coefficients of the second and third terms in the virial equation

$$Z = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \frac{D(T)}{V^3} + \cdots \tag{3}$$

were determined from plots of $(Z - 1)V$ *vs.* $1/V$. They are given for the pure gases in Tables III and IV. Also given in Tables III and IV are the second and third interaction virial coefficients, which were calculated from the composition dependencies of the virial coefficients of the mixtures and which refer to Equations 4 and 5 (*6*). The virial coefficients of CF_4 at 0° C. reported here are in good agreement with values reported elsewhere (*5*).

$$B(T) = y_1^2 B_{11}(T) + 2y_1\, y_2\, B_{12}(T) + y_2^2 B_{22}(T) \tag{4}$$

$$C(T) = y_1^3 C_{111}(T) + 3y_1^2\, y_2\, C_{112}(T) + 3y_1\, y_2^2\, C_{122}(T) + y_2^3 C_{222}(T) \tag{5}$$

The estimated accuracies of the virial coefficients are given in the tables. The temperature dependencies of the virial coefficients are shown in Figures 1 and 2. In Figure 2, the expected low-temperature maximum in the third virial coefficient (*2*) is in evidence, but is not fully defined by these data.

The linearity of the $(Z - 1)V$ *vs.* $1/V$ plots indicated that Equation 3. truncated after the third term, is

Table IV. Third Virial Coefficients for CF_4–CF_3H System (Cc. per gram-mole)^2

Temp., ° C.	C_{111} (CF_4)	C_{112}	C_{122}	C_{222} (CF_3H)
95	4890 ± 150	4700 ± 500	4200 ± 300	8410 ± 250
40	6030 ± 125	4950 ± 200	7100 ± 200	$11{,}630 \pm 100$
0	7070 ± 100	6400 ± 200	$10{,}250 \pm 300$	$15{,}700 \pm 175$
−30	8660 ± 100	7200 ± 500	$11{,}800 \pm 600$	$15{,}000 \pm 1000$
−50	9645 ± 300			
−70	9320 ± 500			

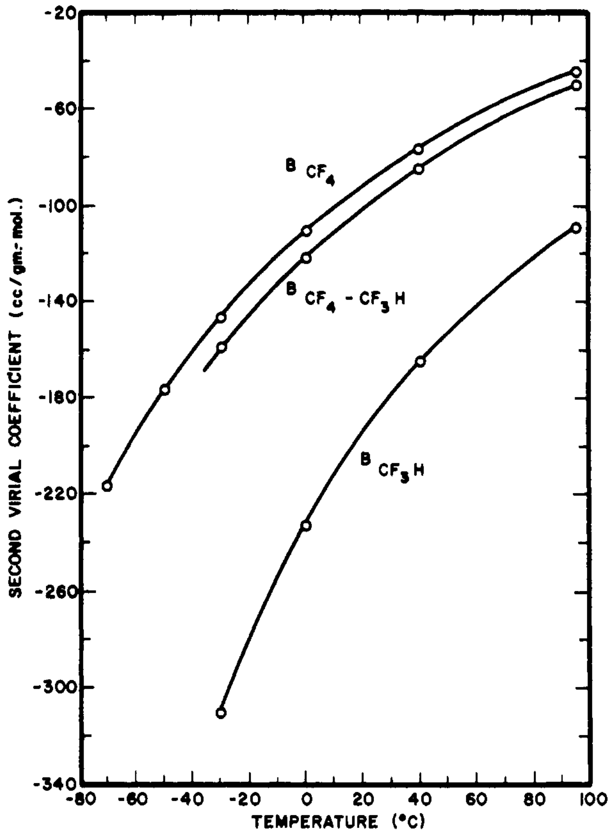

Figure 1. Second virial coefficients

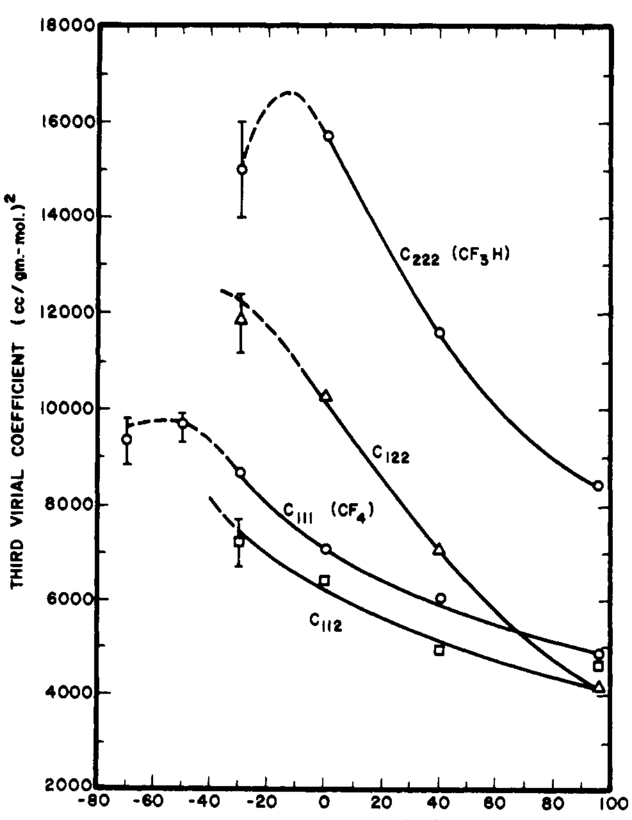

Figure 2. Third virial coefficients

Table V. Optimum Values of Parameters for CF_4 for Spherical-Shell and Spherical-Kihara Functions

Spherical-Shell Function	
Equilibrium separation, r_o, A.	4.60 ± 0.01
Core diameter, d, A.	2.585 ± 0.005
Energy parameter, ε/k, ° K.	302.75 ± 0.1
Spherical-Kihara Function	
Collision diameter, σ, A.	4.33 ± 0.01
Core radius, a, A.	0.715 ± 0.005
Energy parameter, ε/k, ° K.	287.625 ± 0.1

valid, within the limits of accuracy of the compressibilities measured here, to pressures as high as approximately 0.9 times the critical pressure at temperatures below approximately 1.1 times the critical temperature and to still higher pressures at higher temperatures.

CORRELATION OF SECOND VIRIAL COEFFICIENTS OF CF_4

The second virial coefficients of CF_4 reported here, together with values at temperatures as high as 500° C. reported by other investigators (*5, 7*), were correlated within their experimental accuracies using either the spherical-shell (*4*) or a spherical Kihara (*8*) intermolecular potential-energy function. The generalized second virial coefficient is given in tabulated form for each of the functions in the references cited. The optimum values of the function parameters for CF_4 are given in Table V. The second-virial-coefficient data used at temperatures above the range of this work are considered accurate to 0.3 cc. per gram-mole, based on the accuracy of the volumetric data from which they were obtained.

ACKNOWLEDGMENT

The donation of samples of CF_4 and CF_3H by the Freon Products Division, E. I. du Pont de Nemours & Co., is sincerely appreciated. Fellowship support from NDEA is gratefully acknowledged and appreciated.

NOMENCLATURE

B = second virial coefficient, cc./gram-mole (except in Equation 1)
C = third virial coefficient, (cc./gram-mole)^2 (except in Equation 1)
K = general Martin-Hou constant
P = absolute pressure, p.s.i.a.
T = absolute temperature, ° R, or ° K.
V = molar volume
y = mole-fraction
Z = compressibility factor

Subscripts

c = critical property
1 = refers to CF_4
2 = refers to CF_3H (except in Equation 1)

LITERATURE CITED

(1) Burnett, E. S., *J. Appl. Mech., Trans. A.S.M.E.* 58, A136 (1936).

(2) Chueh, P. L., Prausnitz, J. M., *A.I.Ch.E. J.* **13**, 896 (1967).
(3) Crain, R. W., Sonntag, R. W., *Advan. Cryog. Eng.* **11**, 379 (1965).
(4) DeRocco, A. G., Hoover, W. G., *J. Chem. Phys.* **36**, 916 (1962).
(5) Douslin, D. R., Harrison, R. H., Moore, R. T., McCullough, J. P., *Ibid.*, **35**, 1357 (1961).
(6) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," p. 153, Wiley, New York, 1954.
(7) Kalfoglou, N. K., Miller, J. G., *J. Phys. Chem.* **71**, 1256 (1967).
(8) Kihara, T., *Rev. Mod. Phys.* **25**, 831 (1953).
(9) Lange, H. B., Ph.D. thesis, Lehigh University, Bethlehem, Pa., 1969.
(10) Martin, J. J., *Ind. Eng. Chem.* **59**, No. 12, 34 (1967).
(11) Martin, J. J., Hou, Y. C., *A.I.Ch.E. J.* **5**, 125 (1959).
(12) Piacentini, A., Stein, F. P., *Chem. Eng. Progr. Symp. Ser. No.* 81, **63**, 28 (1967).
(13) Silberberg, I. H., Kobe, K. A., McKetta, J. J., J. Chem. Eng. Data **4**, 314 (1959).

Received for review April 21, 1969. Accepted September 2, 1969. For supplementary material, order NAPS Document 00648 from ASIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y., 10001, remitting $1.00 for microfiche or $3.00 for photocopies.

Pressure-Volume-Temperature-Concentration Relation of Aqueous NaCl Solutions

ALLEN M. ROWE, JR., and JAMES C. S. CHOU[1]
School of Mechanical Engineering, Oklahoma State University, Stillwater, Okla.

The derivatives $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ of NaCl solutions have been experimentally determined in the temperature range 0° to 175° C. for NaCl concentrations of 0 to 25 grams per 100 grams of solution and pressures up to 350 kg. per sq. cm. An interpolation formula which describes the pressure-volume-temperature-concentration (*P-v-T-x*) relation has been developed to fit these experimental results and the density data from the literature.

BECAUSE of the importance of converting salt water to potable water, there is considerable interest in the thermodynamic properties of aqueous NaCl solutions. The petroleum industry is also interested in these properties for predicting steam drive and aquifer performance. Pressure, specific volume, temperature, and concentration data are the basic data required for calculating thermodynamic properties of solutions. Although no equation can be found to represent the relations among the properties in an absolutely correct manner without understanding the fundamental nature of the substances and their interactions, an empirical equation which adequately represents the property relations can be used to interpolate the experimental data, facilitate calculations involving integration and differentiation, and provide a concise representation of a large mass of data. An efficient evaluation of the properties is nearly impossible without interpolation formulas.

A survey of literature indicated the lack of experimental data on compressibility for NaCl solutions at temperatures above 40° C.; measurements were therefore made to determine the values of the derivative $\left(\frac{\partial v}{\partial P}\right)_{T,x}$ for 0, 5, 10, 15, 20, and 25% of NaCl in solutions at 21.7°, 50.9°, 81.0°, 119.4°, 146.9°, and 174.4° C., up to pressures of 350 kg. per sq. cm. By using test results and low-pressure density data from the literature, a formula was then improvised to describe the *P-v-T-x* relations. The estimated maximum deviation of the observations from this formula was less than 1.5 p.p.t. over the entire region investigated.

[1] Present address, Department of Mechanical Engineering, University of Hawaii, Honolulu, Hawaii

EXPERIMENTAL

The compressibilities of a liquid are often experimentally determined by measuring the total change in specific volume caused by the change in pressure from 1 to *P* atm. However, this experiment was designed to obtain the differential change in specific volume associated with a small pressure change at pressure *P*, at the fixed temperature, by using a calibrated positive displacement pump. The apparatus used is shown in Figure 1. The vessel used for testing the solutions was made of stainless steel, surrounded by three electrical heating coils of 650 watts each, and insulated by a 1.5-inch layer of mineral wool. The electric current through the coil was controlled by a variable resistor that maintained the desired temperature of the solution in the vessel. To minimize temperature variation of the solution, 415 feet of 0.01-inch o.d. nickel-chromium wire was placed inside the vessel to distribute the heat uniformly through the solution. The pump piston, which was calibrated to 0.01 cc. of piston displacement, could be advanced or retreated at uniform speed of 0 to 100 cc. of