DISCUSSION

Table II contains the experimental isothermal x, y, P equilibrium data obtained at 50°, 75°, and 100° C. Figure 1 is a plot of the equilibrium data at 100° C. and is typical of the data at 75° and 50° C. also. The vaporization equilibrium constants, K, for the formic acid and valeric acid at the three temperatures are tabulated in Table II and plotted against pressure in Figure 2. Neither of these plots indicates the presence of an azeotrope in the system.

Because the vapor phase of this system behaves as a nonideal gas and since PVT data for the vapor are not available, it is not possible to check the thermodynamic consistency of the data.

NOMENCLATURE

K = y/x = vaporization equilibrium constant
P = Pressure, mm. of Hg
T = Temperature, ° C.
x = Mole fraction in the liquid phase
y = Mole fraction in the vapor phase

Subscripts

F = formic acid
V = valeric acid

LITERATURE CITED

(1) Dreisback, R.R., "Physical Properties of Chemical Compounds," Vol. **III**, *Adv. Chem. Ser.* No. **29**, 441 (1961).
(2) Gilmont, R., *Ind. Eng. Chem. Anal. Ed.* **18**, 633 (1946).
(3) Hipkin, H., Myers, H.S., *Ind. Eng. Chem.* **46**, 2524 (1954).
(4) Perry, J.H., Ed., "Chemical Engineers Handbook," 3rd ed., p. 160, McGraw-Hill Book Co., New York, N. Y., 1950.
(5) Pimentel, G.C., McClellan, A.L., "The Hydrogen Bond," pp. 194, 256, H. Feeman and Co., San Francisco, Calif., 1960.
(6) Udovenko, V.V., Airapotova, R.P., *J. Gen. Chem. (Russian)* **17**, 425 (1947).
(7) Washburn, E.W., Ed., "International Critical Tables," Vol. 3, p. 437, McGraw-Hill Book Co., New York, N.Y., 1928.
(8) *Ibid.*, Vol. 7, pp. 12, 34, 1930.

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Volumetric Properties of Supercritical Hydrogen Sulfide

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The volumetric properties of hydrogen sulfide were measured in a constant volume apparatus over the temperature range from 373° K. to 493° K. and a pressure range from 90 atm. to 1700 atm. The compressibility factors and virial coefficients at 20° intervals of this temperature range have been calculated. The virial expression given calculates the volumetric properties within 1% at temperature between 373° K. and 493° K. at pressures greater than 200 atm. and within 3% at pressures less than 200 atm. The density range covered by these measurements was between 8 and 24 moles per liter.

DURING the course of an investigation in the supercritical region of hydrogen sulfide, it became necessary to extend the region in which the volumetric properties of hydrogen sulfide were known. Thus, measurements in this laboratory, in the supercritical state only, extended the pressure range to 1700 atm. and the temperature range to 220° C. The results were expressed in the form of a virial equation in density.

Several investigations on the volumetric properties of hydrogen sulfide are reported in the literature. Giauque and Blue (*3*) measured the vapor pressure of hydrogen sulfide from 16° K. to the boiling point (212.8° K.). Cardoso (*1*) measured the vapor pressure of the coexisting phases between the boiling point (212.8° K.) and the critical point (373.6° K.). Beyond the critical point, Reamer, Sage, and Lacey (*5*) studied hydrogen sulfide to 171° C. and pressures to 680 atm.

EXPERIMENTAL

Measurements were made in a constant-volume apparatus having a total volume of 138.06 cc. This method was preferable to the variable volume method, because it circumvented the problem noted by Reamer, Sage, and Lacey (*4*) that the mercury used as a volume changing element reacted with the hydrogen sulfide at temperatures in the neighborhood of 170° C.

The stainless steel vessel and the associated fittings were manufactured by Pressure Products Industries (Hatboro, Pa.). Pressures were measured by an Astra Gauge Corporation Bourdon tube gauge that covered a pressure range from 0 to 30,000 p.s.i. and that had been calibrated to 0.25% accuracy of full scale against a dead weight gage at a minimum of five points. The dead weight gage was calibrated by the National Bureau of Standards for the Astra Corporation. The standard deviation in the piston and cylinder effective area was 57 p.p.m. The fractional change in the effective area per unit change in pressure was 8.85×10^{-9} p.s.i. with a standard deviation of 0.62×10^{-9} p.s.i. (NBS Monograph 65) (*2*). An oil bath, capable of maintaining the set temperature across the length of the vessel within ±0.5° C., was used to establish isothermal conditions during the course of the measurements. A mercury thermometer which had been calibrated against a copper-constantan thermocouple in a stirred oil bath was used for temperature measurement. The copper-constantan thermocouple was calibrated in accordance with NBS circular 590 (*6*) (ice point and boiling point of H_2O as primary points, freezing points of mercury and tin as secondary

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points). The accuracy of the calibration was 0.3° C. The accuracy of the temperatures reported for PVT data was ±0.5° C. and determined by the oil bath used for PVT measurements.

The hydrogen sulfide used during these experiments was C.P. grade gas furnished by the Matheson Company. The gas was subjected to further purification by passing it through two cryogenic traps maintained at −45° C., a tube containing silica gel, and a 0.22-micron Millipore filter.

A known quantity of hydrogen sulfide was measured into the previously evacuated vessel by metering it through a Brooks Instrument Company Rotameter that had been specifically calibrated for mass flow of hydrogen sulfide. The rotameter was calibrated attached to the H_2S purification system operating under a specific set of conditions (15 p.s.i.g., 0.22-micron filter, cryogenic traps at −45° C.). Under these conditions, the standard deviation in the weight of H_2S was ±0.07 gram per minute. Comparison of the amount metered into the high pressure vessels with the amount actually present as determined by weighing into a calibration vessel indicates the calibration is accurate to 0.5%. Pressure readings were made on the constant density system as the temperature was increased in a stepwise manner to 220° C. and then decreased in

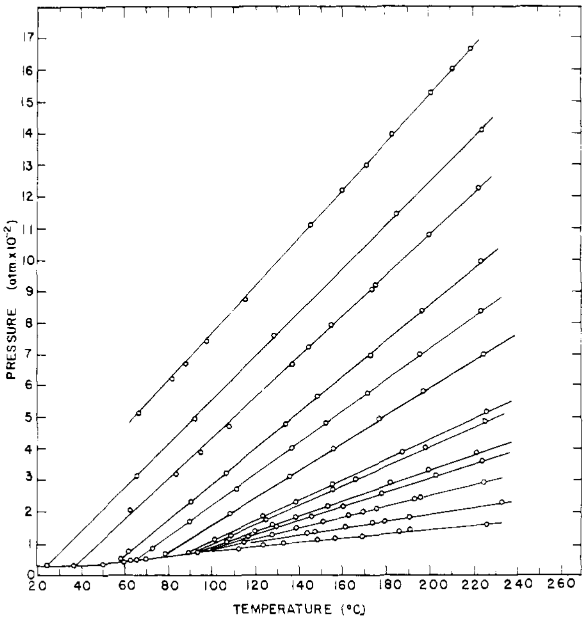

Figure 1. Isopycnic lines for H_2S above the critical point (uncorrected data)

The densities of the 13 Isopycnic lines from highest to lowest are: 21.25, 20.40, 19.55, 18.20, 17.85, 17.00, 16.15, 15.30, 14.45, 13.60, 12.75, 11.90, and 11.05 (moles/liter)

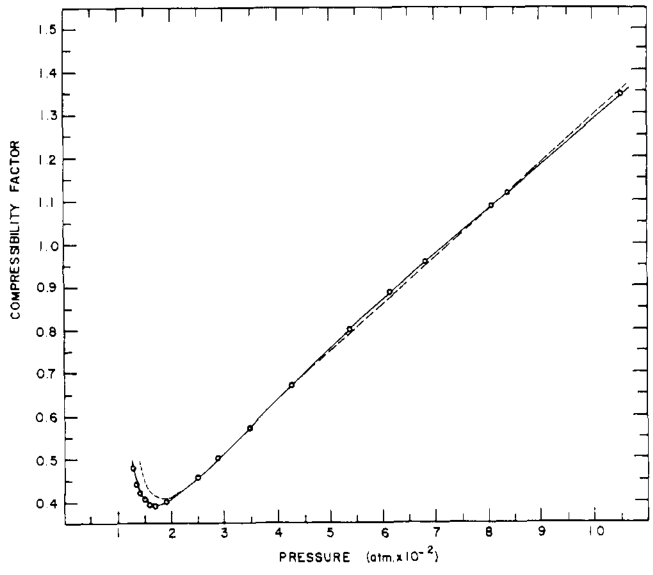

Figure 3. Comparison of corresponding state theorem (3) and the experimental virial equation for the 413° K. isotherm

The points are experimental data. The solid line was calculated from the virial coefficients given. The dashed line from the corresponding states theorem

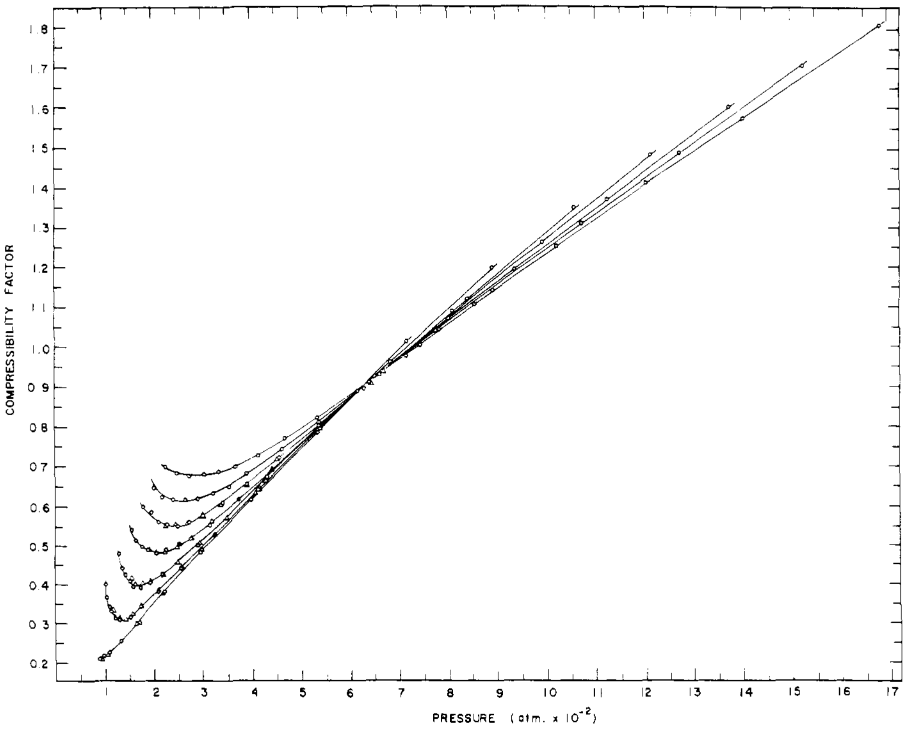

Figure 2. Virial expressions for H_2S compared with these experiments, ○, and with the data of Reamer, Sage, and Lacey (4), ▽

The temperatures of the isotherms shown are 373°, 393°, 413°, 433°, 453°, 473°, and 493° K. from the lowest to the highest curves (left hand side)

Table I. Observed and Calculated Values for the Pressure and

Density, Moles/ Liter	373° K.				393° K.				413° K.				433° K.	
	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}
8.00	...	...	...	...	103	0.399	103	0.399	130	0.480	130	0.478	154	0.542
9.00	...	...	...	...	106	0.365	107	0.368	135	0.443	136	0.447	164	0.513
10.00	...	...	...	...	111	0.344	111	0.344	144	0.424	143	0.423	177	0.498
11.00	...	...	...	...	116	0.330	115	0.325	152	0.408	151	0.406	189	0.484
12.00	...	...	...	...	121	0.313	121	0.313	161	0.395	161	0.396	205	0.480
13.00	...	...	...	...	130	0.310	129	0.307	173	0.393	174	0.395	227	0.491
14.00	90	0.210	93	0.216	140	0.310	140	0.309	192	0.405	192	0.404	252	0.507
15.00	99	0.216	97	0.211	153	0.316	156	0.322	217	0.427	216	0.424	277	0.520
16.00	110	0.225	109	0.223	178	0.345	179	0.346	249	0.459	248	0.458	316	0.556
17.00	133	0.256	132	0.253	208	0.379	211	0.385	290	0.503	293	0.508	373	0.618
18.00	167	0.303	168	0.305	256	0.441	257	0.443	350	0.574	353	0.578	443	0.693
19.00	223	0.383	222	0.381	324	0.528	322	0.525	434	0.674	431	0.670	538	0.797
20.00	297	0.485	297	0.486	413	0.640	410	0.635	535	0.789	534	0.788	657	0.925
21.00	398	0.619	400	0.623	533	0.787	528	0.780	669	0.940	668	0.938	810	1.086
22.00	533	0.792	536	0.795	682	0.961	685	0.966	838	1.124	839	1.125	989	1.265
23.00	715	1.016	711	1.010	890	1.200	892	1.202	1054	1.352	1055	1.353	1213	1.484

Table II. Coefficients of the Virial Expressions for Single Phase Hydrogen Sulfide

						Estimated Standard Errors[a]	
T° K.	B	C	D	E	F	This work	Reamer *et al.* (4)
373	-6.966×10^{-2}	...	...	3.74×10^{-6}	0.9×10^{-7}	0.005	0.013
393	-1.354×10^{-1}	1.026×10^{-2}	-3.647×10^{-4}	...	3.6×10^{-7}	0.005	0.007
413	-1.040×10^{-1}	6.048×10^{-3}	-1.667×10^{-4}	...	2.4×10^{-7}	0.003	0.008
433	-9.002×10^{-2}	4.912×10^{-3}	-1.165×10^{-4}	...	2.1×10^{-7}	0.007	0.008
453	-7.206×10^{-2}	2.886×10^{-3}	-2.156×10^{-5}	...	1.6×10^{-7}	0.005	0.004
473	-6.399×10^{-2}	2.412×10^{-3}	$+1.20 \times 10^{-6}$	...	1.4×10^{-7}	0.008	...
493	-5.256×10^{-2}	1.524×10^{-3}	$+3.836 \times 10^{-5}$	...	1.2×10^{-7}	0.010	...

[a] Estimated standard errors of the fit of the virial expressions to these experiments and to the data of Reamer, Sage, and Lacey.

a stepwise manner. A small sampling vessel was used to remove part of the hydrogen sulfide from the experimental apparatus. The exact amount of gas removed was determined by weighing. The resultant lower density system was used to make another set of measurements.

RESULTS

A correction to take into account that portion of the system (about 4% of the total volume) that could not be thermostatted at the temperature of the oil bath had to be made on the pressure-temperature data shown in Figure 1. Density correction values were compiled using the data of Reamer, Sage, and Lacey (*5*) as a standard (Table I).

The corrected values of the temperature, pressure, and density shown in Table I were used to calculate the compressibility factor;

$$Z = \frac{PV}{RT} \tag{1}$$

for hydrogen sulfide, also tabulated in Table I.

Coefficients for a virial equation of the form

$$Z = 1 + B(T)\rho + C(T)\rho^2 + D(T)\rho^3 + E(T)\rho^4 + F(T)\rho^5 \tag{2}$$

were determined by a least squares procedure for seven isotherms differing by 20° C. between 373° K. and 493° K. The coefficients are shown in Table II. A comparison between the data observed in this investigation, the data of Reamer, Sage, and Lacey (*5*), and the virial expressions is shown in Figure 2. Values of the compressibility factors and pressures calculated from the virial expressions are shown in Table I.

DISCUSSION

Use of the virial expression for the calculation of the volumetric properties of hydrogen sulfide is restricted to temperatures between 373° K. and 493° K. and to densities between 8 and 24 moles per liter. Under these circumstances, the maximum error in using these equations is 1% at pressures exceeding 200 atm. and 3% at pressures less than 200 atm. The estimated standard error for the virial equation at each temperature is given in column 7 of Table II. The values listed in the last column are the estimated standard errors for these equations and the data of Reamer, Sage, and Lacey (*5*). The major source of error arises because the Bourdon tube gage could be read only to accuracy of 3 atm. The correction procedure also contributes to the error, but the error is small in comparison with the gage reading error.

Even though the amount of data that could be taken at the lowest temperature, 373° K., was limited and of poorer quality than the higher pressure and temperature data, virial coefficients were calculated for this temperature. They should be used with caution because of these limita-

Compressibility Factor as Functions of Temperature and Density

433° K.		453° K.				473° K.				493° K.			
P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}	P_{corr}	Z_{corr}	P_{calc}	Z_{calc}
154	0.542	178	0.599	179	0.602	201	0.647	201	0.648	226	0.698	227	0.701
165	0.515	196	0.586	194	0.579	218	0.624	220	0.629	249	0.684	249	0.685
176	0.496	209	0.562	209	0.562	240	0.618	239	0.616	274	0.677	274	0.677
189	0.484	227	0.555	226	0.553	264	0.618	261	0.612	304	0.683	301	0.676
204	0.479	246	0.552	246	0.552	289	0.621	287	0.616	335	0.690	332	0.684
224	0.484	272	0.563	271	0.561	320	0.634	318	0.630	368	0.700	369	0.702
248	0.498	301	0.578	302	0.581	353	0.650	356	0.655	413	0.729	414	0.731
280	0.525	341	0.612	342	0.614	397	0.682	403	0.693	467	0.770	468	0.772
321	0.565	390	0.656	393	0.660	462	0.744	463	0.745	533	0.824	536	0.828
376	0.622	456	0.722	457	0.723	537	0.814	536	0.813	613	0.891	608	0.884
446	0.698	537	0.803	539	0.806	628	0.899	629	0.901	714	0.981	722	0.992
538	0.796	644	0.913	642	0.909	742	1.006	732	0.992	852	1.108	848	1.103
654	0.920	778	1.046	771	1.037	889	1.145	886	1.141	1018	1.258	1002	1.238
801	1.074	934	1.197	931	1.193	1071	1.314	1060	1.301	1202	1.415	1188	1.399
987	1.263	1123	1.373	1129	1.381	1273	1.491	1273	1.491	1402	1.575	1415	1.590
1220	1.493	1372	1.605	1372	1.605	1525	1.708	1532	1.716	1684	1.810	1688	1.814

tions. This is evident from the pattern of coefficients for the isotherms at higher temperatures.

Agreement between the corrected pressures observed during this investigation and the pressures calculated from the compressibility chart of Nelson and Obert (*4*) based on the theorem of corresponding states is excellent over the pressure and temperature range investigated (Figure 3).

NOMENCLATURE

P_{corr} = observed pressure, atmospheres.

Z_{corr} = compressibility factor calculated from the observed values of the pressure at the given temperature and density.

P_{calc} = pressure calculated from the virial expressions for the given density and temperature.

Z_{calc} = compressibility factor calculated from the virial expressions at the given temperature and density.

LITERATURE CITED

(1) Cardoso, E., *Gazz. Chim. Ital.* **51**, 153 (1921).

(2) Cross, J.L., "Reduction of Data for Piston Gage Pressure Measurements," *Natl. Bur. Std. (U.S.) Monograph* **65**, June 17, 1963.

(3) Giauque, W.F., Blue, R.W., *J. Am. Chem. Soc.* **58**, 831 (1936).

(4) Nelson, L.C., Obert, E.F., *Trans. ASME* **76**, 1057 (1954).

(5) Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **42**, 140 (1950).

(6) Roeser, W.F., Lonberger, S.T., "Methods of Testing Thermocouples and Thermocouple Materials," *Natl. Bur. Std. (U.S.) Circ.* **590**, February 6, 1958.

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Ternary Systems

Water-Acetonitrile-Salts

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Effectiveness in salting water out of acetonitrile was determined for 23 salts. Seven were effective, seven were ineffective, and nine precipitated the salt. Solubility data, equilibrium tie lines, and the plait point were determined for water-acetonitrile with four of these salts at 25° C.: sodium bromide, sodium nitrate, ammonium nitrate, and diammonium phosphate. A novel method of correlating the tie lines is proposed, applying the principle of rectilinear diameters to the equilibrium tie lines.

IN A CONTINUING study of water-acetonitrile-salt systems (*2, 3, 4*), salting-out effectiveness of nine salts of potassium, eight of ammonium, and seven of sodium was studied. Salts which bring about formation of two liquid phases upon addition of acetonitrile to the saturated salt solution are held to be effective in salting water out of acetonitrile. Binodal curves and equilibrium tie lines were determined experimentally for water-acetonitrile-sodium bromide, water-acetonitrile-sodium nitrate, water-acetonitrile-ammonium nitrate, and water-acetonitrile-diammonium phosphate.

EXPERIMENTAL

Results of salting-out effectiveness studies are given in Table I. Ineffective salts are those which failed to form two liquid phases. In some cases, the acetonitrile caused precipitation of the salt.

Binodal curves were determined by the well-known cloud point method. Starting in each case with a sample of approximately 1.5 grams of saturated salt solution, acetonitrile was added dropwise from a buret until a cloud point was reached. Water was added dropwise from a buret to