Summary

Anhydrous potassium sulfate was found to be insoluble in all the alcohols used, and sodium sulfate is soluble in only three of the alcohols. The solubility of sodium sulfate in methyl alcohol increases with a rise in temperature. In ethyl and isopropyl alcohols, the solubility of sodium sulfate reaches a maximum and then decreases. The solubilities of the sulfates in alcohols follow the general trend of their solubilities in water, that is, the sodium being more soluble than the potassium sulfate.

The chlorides of both sodium and potassium in methyl alcohol show a slight decrease in solubility with temperature. In ethyl, n-propyl and isopropyl alcohols both salts pass through a maximum solubility and then decrease, the potassium decreasing more rapidly than the sodium chloride. In the butyl alcohols there is a slight increase in solubility with rise of temperature for both salts.

The solubility of all the salts decreases as the molecular weight of the alcohol increases.

Rolla, Missouri

THE COMPRESSIBILITY ISOTHERMS OF METHANE AT PRESSURES TO 1000 ATMOSPHERES AND AT TEMPERATURES FROM −70 TO 200°

By Hamline M. Kvalnes and V. L. Gaddy

The formation of methane as a side reaction in high pressure syntheses involving hydrogen and carbon monoxide and its use as a reactant have emphasized the need of compressibility data for the gas over a wide pressure and temperature range. Previously existing data on the compressibility of methane are for the temperature range 0 to 200° at pressures to 300 atmospheres. Amagat[1] determined the compressibility of methane for temperatures between 14.7 and 100.1° at pressures from 40 to 300 atmospheres. The absolute volumes are not given but only PV relative to the volume of a certain manometric tube. Burrell and Robertson[2] measured an isotherm at 15° to a pressure of forty atmospheres. Keyes, Smith and Joubert[3] determined five isotherms for the temperatures 0, 50, 100, 150 and 200° at pressures to about 300 atmospheres. Later Keyes and Burks[4] improved the apparatus used by Keyes, Smith and Joubert, and redetermined the data for the same temperatures and approxi-

[1] Amagat, *Ann. Chim. Phys.*, 22, 367 (1881).
[2] Burrell and Robertson, Bureau of Mines Technical Paper No. 158 (1917).
[3] Keyes, Smith and Joubert, *J. Math. Phys. Mass. Inst. Tech.*, 1, 191 (1922).
[4] Keyes and Burks, This Journal, 49, 1403 (1927).

mately the same pressure range. In the present work the data are extended to cover the temperature range −70 to 200° at pressures to 1000 atmospheres.

Method, Apparatus and Calibrations.—The method and apparatus used in the present experiments are, for the most part, the same as those already fully described in papers from this Laboratory dealing with the compressibility of carbon monoxide, hydrogen, nitrogen and mixtures of the latter two.[5] The only modification made in the equipment consisted in simplifying the former purification train to contain only two low temperature traps, one packed in ice and the other in solid carbon dioxide.

The 20-cc. bronze pipet used at the lower pressures was calibrated with hydrogen before and after the zero degree work on methane. All other pipet calibrations were made with methane at 0°.

All temperatures were controlled by hand in a manner similar to that formerly described[5] for control of temperatures below 0°. The thermocouple was the same as that used in the aforementioned work and has since then been compared with another copper–constantan thermocouple calibrated by the Bureau of Standards at temperatures of −25.92, −50.42 and −70.50°. The latter calibration was made against a platinum resistance thermometer, "standardized in the manner provided in the definition of the International Temperature Scale." It was considered accurate to about one microvolt, which is equivalent to about 0.03° in the temperature range −25 to −70°. The comparison indicated that the low temperatures were −24.99 ± 0.03°, −49.93 ± 0.03° and −69.90 ± 0.03°, for the listed temperatures of −25, −50 and −70°.

Calculations.—To determine the compressibility factor at a given pressure and temperature by the method employed in this work, it is necessary to measure the quantity of gas contained in a pipet of known volume at the given pressure and temperature. To do this the gas is allowed to expand into a larger volume where it is measured at 25° and at a pressure ranging from 480 to 1000 mm., according to the quantity of gas obtained. It is desired, however, to know the volume of gas at 760 mm. and 0°. The temperature change is calculated by using the temperature coefficient of expansion α for the gas. For gases such as hydrogen and nitrogen it is sufficiently accurate to correct the gas to 760 mm. by the ideal gas law. Methane, however, differs significantly from the ideal gas even at atmospheric pressure. The value for PV at 760 mm. and 0° is given in the "I. C. T."[6] as 0.9976. PV was assumed equal to 1 at zero pressure and the value for any other pressure was taken

[5] Bartlett, THIS JOURNAL, **49,** 68 (1927); **49,** 687 (1927); **49,** 1955 (1927); Bartlett, Cupples and Tremearne, *ibid.,* **50,** 1275 (1928). Bartlett, Hetherington, Kvalnes and Tremearne, *ibid.,* **52,** 1363 (1930); **52,** 1374 (1930).

[6] "International Critical Tables," Vol. III, p. 3.

from a straight line through the two points. Using the above correction for change of compressibility with pressure, samples measured at the two extremes of the pressure range checked to within 0.05%.

Gas.—The 500 cubic feet of methane gas required for this investigation were made available to the Fixed Nitrogen Research Laboratory through the courtesy of the du Pont Ammonia Corporation. It was prepared from a mixture of hydrogen and methane by condensation at the temperature of liquid air and subsequent fractional distillation to remove traces of dissolved hydrogen. The previous history of the gas precluded the presence of nitrogen. Ordinary methods of analysis failed to show any other impurities. Other tests[7] indicated a purity of 99.88 ± 0.02%.

Experimental Results

The experimental results are given in Table I. Each PV value with the exception of those given for zero and one atmosphere pressure is the average of two or more separate determinations. At all temperatures determinations were made at pressure intervals sufficiently small accurately to define the shape of the isotherms. At the lowest temperatures this necessitated obtaining a few data at pressure intervals of five atmospheres.

The PV value at zero pressure and 0° was taken as the reciprocal of the aforementioned "I. C. T." value of 0.9976, which agreed to better than 0.1% with the value obtained by extrapolation of the PV–P curve through the points at 1, 30 and 40 atmospheres. The remaining values at zero pressure were calculated, using the ideal gas temperature factor, while those at one atmosphere were taken from a curve drawn through the zero, 20, 30 and 40 atmosphere points.

Figure 1 is a plot of the isotherms obtained by dividing each PV value by the value at zero pressure for that temperature. The curves thus all have the same origin, that is, $PV = 1$, at zero pressure. They are drawn through every experimentally determined point, and in all cases give smooth curves.

Discussion

The data obtained by Keyes and Burks[4] on the compressibility of methane have been incorporated in Table I. Their results are given in specific volumes so that it was necessary to calculate the corresponding PV values and plot them for the pressures given in order to obtain the values of the table at the even pressures. No extrapolations beyond the range of pressures examined by Keyes and Burks were made. The error in plotting was less than 0.05%.

The range of temperature and pressure in this work duplicates the

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[7] Dr. Rossini of the Bureau of Standards used some of this gas in an investigation to be published in the *Bureau of Standards Journal of Research*. He found by analysis 0.12% of CO, and combustion ratios of carbon to hydrogen checked this value.

TABLE I

THE COMPRESSIBILITY FACTORS, PV, FOR METHANE

Atm.	−70°	−50°	−25°	0°	+25°	+50°	+100°	+150°	+200°
0	0.7455	0.8189	0.9106	1.0024	1.0942	1.1859	1.3695	1.5530	1.7365
1	.7410	.8150	.9075	1.0000	1.0922	1.1845	1.3686	1.5525	1.7363
20	.6473	.7402	....	....	1.0549	....	....	....	....
30	.5910	.6991	.8183	0.9303	....	1.1412	1.3411	1.5370	1.7311
	....	....	....	.9292[a]	....	....	....	....	....
40	.5244	.6547	.7873	.9065	1.0198	1.1284	....	....	....
	....	....	....	.9057[a]	....	1.1267[a]	....	....	....
50	.4425	.6069	....	.8833	....	....	1.3268	1.5319	1.7309
	....	.....	....	.8827[a]	....	....	1.3269[a]	....	....
60	.3366	.5551	.7243	.8611	0.9871	1.1020	....	1.5305	1.7306
	....'	....	....	.8603[a]	....	1.1014[a]	1.3205[a]	1.5280[a]	1.7301[a]
65	.2912	....	....	....	....	....	....	....	....
70	.2633	.5059	....	....	....	....	....	....	....
80	.2556	.4604	.6651	.8199	.9569	1.0806	....	....	....
	....	....	....	.8185[a]	....	1.0792[a]	1.3098[1]	1.5248[a]	1.7322•
90	....	.4266	....	....	....	....	....	....	....
100	.2808	.4088	.6167	.7853	.9319	1.0636	....	....	....
	....	....	....	.7836[a]	....	1.0612[a]	1.3018[a]	1.5237[a]	1.7357[a]
120	.3175	.5095	.5877	.7604	.9126	1.0498	....	....	....
	....	....	....	....	....	1.0476[a]	1.2965[a]	1.5241[a]	1.7414[a]
140	.3543	.4304	.5801	.7457	.9003	1.0408	....	....	....
	....	....	....	....	....	1.0390[a]	1.2939[a]	1.5272[a]	1.7485[a]
160	.3915	.4601	.5891	.7425	.8949	1.0367	....	....	....
180	.4288	.4924	.6079	.7482	.8970	1.0373	1.2995	....	....
	....	....	....	....	....	....	1.3000[a]	1.5398[1]	1.7668[1]
200	.4656	.5269	.6319	.7631	.9048	1.0437	1.3076	1.5504	1.7760
	....	....	....	....	....	....	....	1.5497[a]	1.7788[a]
250	.5567	.6142	.7066	.8184	.9469	1.0776	1.3364	....	1.8107
	....	....	....	....	....	....	....	....	1.8151[a]
300	.6458	.7025	.7879	.8886	1.0062	1.1286	1.3785	1.6234	1.8534
400	.8185	.8750	.9561	1.0468	1.1499	1.2608	1.4929	1.7268	1.9586
500	.9867	1.0433	1.1221	1.2086	1.3064	1.4106	1.6277	1.8542	2.0803
600	1.1487	1.2071	1.2862	1.3709	1.4659	1.5653	1.7729	1.9935	2.2131
700	1.3066	1.3661	1.4466	....	....	....	....	....	....
800	1.4631	1.5246	1.6046	1.6894	1.7801	1.8781.	1.0744	2.2828	2.4949
900	1.6154	1.6782	1.7607	....	....	....	....	....	....
1000	1.7656	1.8287	1.9110	2.0000	2.0892	2.1845	2.3757	2.5797	2.7861

[a] Keyes and Burks, THIS JOURNAL, **49**, 1403 (1927).

pressure range of Keyes and Burks[4] at 0 and 50°, while at the three higher temperatures they duplicate only the extremes of the pressure ranges. Throughout the entire pressure range for 0 and 50°, the present results are higher than those of Keyes and Burks by 0.05 to 0.20%. At 100, 150 and 200° agreement of the two sets of data appears satisfactory except at 60 atmospheres at 150° and at 200 and 250 atmospheres at 200°. Here the maximum deviation, which occurs at 250 atmospheres at 200°, amounts to 0.24%.

The order of taking the data presented in Table I was very irregular. In the course of a day determinations would often be made at three or four different temperatures over a comparatively small pressure range. This manner of collecting the data minimized the chance that any one isotherm might contain a constant error peculiar to itself. The regularity of the data, as a whole, attests the accuracy of the method.
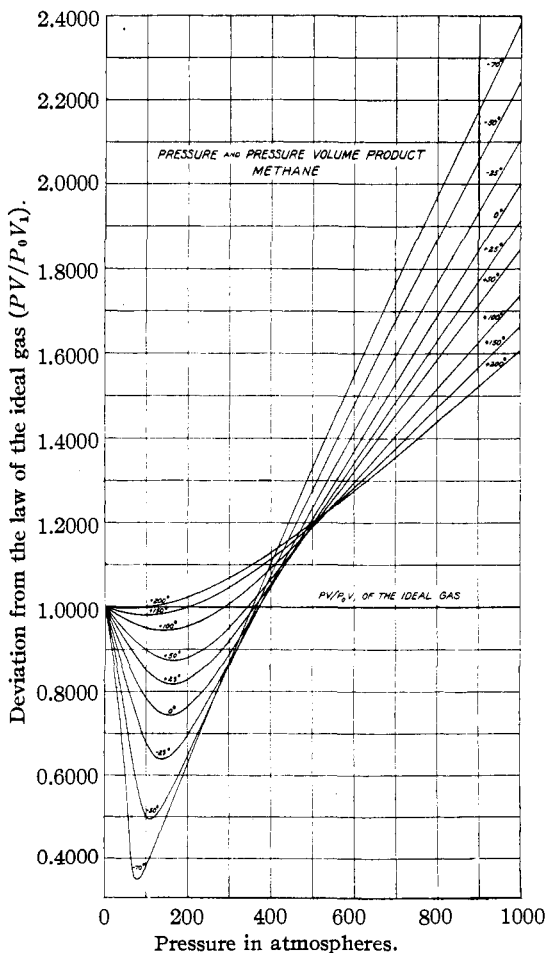

Fig. 1.

Two lines of evidence indicate that adsorption did not occur on the walls of the pipet to any appreciable extent. First, when gas was allowed to expand from the pipet at high pressure, there was no increase in the quantity of gas obtained after the outlet valve was completely opened. Second, two pipets having wall surfaces in the ratio 1:4 and volumes in

the ratio 1:16 gave results agreeing to 0.05% or better at 70 atmospheres and −50° and at 80 atmospheres and −25°.

Below 100° the isotherms show great curvature at all pressures. Above 370 atmospheres this is in such a direction that the slope of the isotherm decreases with increase in pressure. The 100° isotherm is straight through the 500–1000 atmosphere range, while through this same range the slopes of the 150 and 200° isotherms increase with increase in pressure.

The "unique point" found in nitrogen[5] at 380 atmospheres and with carbon monoxide[5] at 375 atmospheres is duplicated in methane at 533 atmospheres for the 100 to 200° range. This indicates that through a certain temperature range every gas may exhibit this phenomenon. Below the "unique" temperature range the PV isotherms will deviate with decreasing temperature toward the isotherm of the gas and liquid at the critical temperature and above this range will deviate toward the isotherm of the ideal gas, becoming identical with it at infinite temperature. Hydrogen at −70° is already above the range, nitrogen is within it from 100 to −70°, while carbon monoxide is within it for the temperature interval −70 to 200°.

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Summary

The compressibility isotherms of methane have been determined to 1000 atmospheres at nine temperatures through the range −70 to 200°. In the range of pressure and temperature duplicated, the results are in agreement with those of Keyes and Burks. With the exception of the pressure interval 500–1000 atmospheres at 100° the compressibility isotherms have considerable curvature.

WASHINGTON, D. C.