have been studied. Both solutions contain ruthenium in the bivalent condition.

When chlorine and carbon monoxide are passed over hot ruthenium, the dichloride is formed, but it is difficult to chlorinate the ruthenium completely.

Ruthenium dichloride is insoluble in the ordinary solvents, but is soluble in dil. alcohol, and to some extent in diluted organic hydroxides and acids.

The solution of the dichloride in dil. alcohol is not colloidal, but is very slightly ionized.

LEXINGTON, VIRGINIA

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, No. 155]

THE PRESSURE-VOLUME-TEMPERATURE RELATION FOR GASEOUS ETHYL ETHER

BY JAMES A. BEATTIE[1]

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This investigation was begun with the purpose of studying the mechanism of vaporization by a consideration of the pressure-volume-temperature data on the liquid and gaseous phases of a substance, and of studying the accuracy with which the equation of state suggested by Keyes[2] represents the experimental data. The particular form which the equation takes when no change is occurring in the molecular species of the substance under consideration, is $p = \frac{RT}{v-\delta} - \frac{A}{(v+1)^2}$, $\delta = \beta e^{-(\alpha/v)}$. H. B. Phillips pointed out to the author that the potential energy term $A/(v + 1)^2$ in the above quotation was almost equivalent to $A/v^2 e^{-m/v}$ where $m = 2l$. This latter term has been found to fit the data slightly better[3] than the algebraic form, especially for the liquid phase, and also to have a better theoretical significance. For future work the equation will be used in this modified form.

It will be noticed that this equation, which was deduced for the case that the molecular complexity of the fluid is not changing (neither association nor dissociation taking place) requires that the pressure be a linear function of the temperature when the volume is held constant. For testing the correctness of this condition, it is better to measure isometrics directly, rather than to calculate them from isothermal data, and hence in this work the isometric method was used.

Ethyl ether was the substance chosen for this study, since there is a large

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[1] National Research Fellow in Chemistry.

[2] Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917).

[3] See Tables IV and V of this article and also Smith and Taylor, THIS JOURNAL, **45**, 2107 (1923).

range of both gas and liquid phases above room temperature (critical point about 194°). In the gas phase a wide range of densities can be studied without the use of high pressures. Ether vapor departs widely in its behavior from the perfect gas laws and is therefore a more severe test on the accuracy of the functions in the equation of state than many gases. It has the further advantage of being easily obtained in a high degree of purity.

The only measurements over any considerable range of values for gaseous ether are those of Ramsay and Young,[4] and Keyes and Felsing.[5] The former measured isothermals, and by graphical methods obtained isometrics. They came to the conclusion that the isometrics are straight throughout the entire region from specific volumes of 2 to 300 cc. per g. However, Keyes and Felsing in a consideration of these data decided that at densities smaller than 15 cc. per g. the isometrics begin to show a curvature.

Keyes and Felsing, whose work was of a preliminary character, measured directly along constant volume lines. Their work covers specific volumes from 13 to 50 cc. per g., and they came to the same conclusion from their own work as they drew from the measurements of Ramsay and Young, although their actual data differ considerably from those of the latter.

In the present paper are presented what are believed to be the most accurate pressure-volume-temperature data so far obtained. They will be used for applying a most exacting test to the equation of state, and determining accurate values for the constants of gaseous ether.

The Experimental Method

There are three variables—pressure, specific volume and temperature—the choosing of any two of which fixes the third. The method of this investigation was to place a definite mass of the ether in a piezometer kept at constant temperature, and to cause the gas to occupy several different volumes by the injection of definite amounts of mercury, and to measure the resulting pressures. The data thus obtained extended over a range of specific volumes from 2.5 to 35 cc. per g., at temperatures between 150° and 325°. The pressure measurements extended from about 11 to 200 atmospheres.

The Thermostat and Temperature Measurements.—The thermostat is shown at A, Fig. 1.

It consisted of a steel tube 20 cm. in diameter and 50 cm. long, with an electric heater wound on the outside, enclosed in a much larger can, with about 15 cm. of magnesia insulation between. The inner vessel was sunk below the surface of the outer one, the insulation extending to the top of the latter so as to reduce the heat loss as much as possible. The fluid used for the bath was heavy cylinder oil, which even at 325° did

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[4] Ramsay and Young, *Z. physik. Chem.*, **1**, 440 (1887).

[5] Keyes and Felsing, THIS JOURNAL, **41**, 589 (1919).

not decompose sufficiently rapidly to cause any inconvenience. The inner vessel contained a tightly fitting steel top with split plugs for the introduction of the necessary parts.

The bath was thoroughly stirred by means of a set of propeller blades which drew the oil down through a steel tube, at the top of which was a heating coil, and forced it out at the bottom against the regulator. The latter was a thin steel tube filled with mercury, having at the top the usual means for operating a relay, which controlled the flow of current in the internal heating coil.

Enough current was constantly passed through the external coil to raise the temperature of the bath to within about 2° of the desired temperature, the rest of heating being accomplished in the internal coil, and was regulated as described above.

The temperature was measured by a platinum thermometer of the flat type, resistances being measured on a Mueller bridge. The bridge was thermostatted and the resistances calibrated just before the measurements. The ice point of the thermometer was measured each day and the steam benzophenone and naphthaline points determined from time to time, satisfactory checks being obtained throughout the period over which the measurements extended.

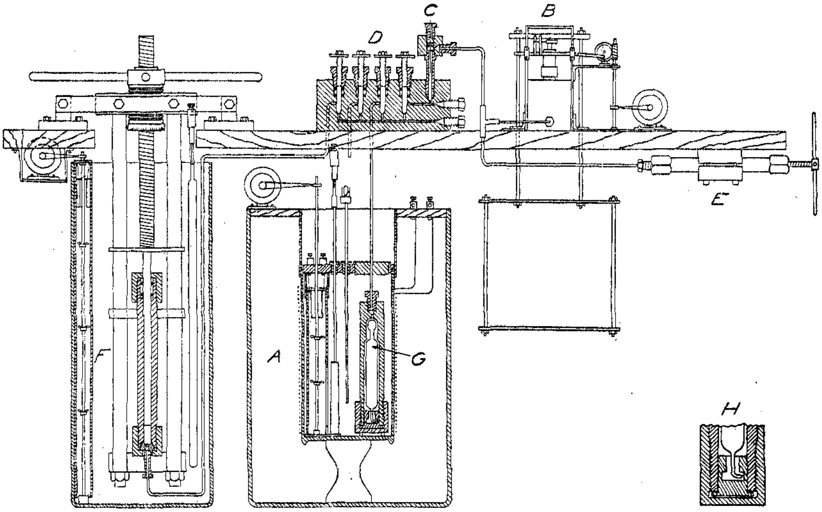

Fig. 1.—The compressibility apparatus.

The automatic regulation of the bath temperature was satisfactory to 300°, constancy to ±0.002° being obtained; but at 325° hand regulation was used, a switch operated by hand taking the place of the relay, in which case a temperature variation of ±0.005° was allowed.

The piezometer containing the gas was placed in the thermostat in such a manner that the bath fluid could circulate around it in all directions.

The Pressure Gage.—The gage, B, Fig. 1, was of the dead-weight piston type with mechanical oscillation, similar to that used by Keyes and Brownlee.[6] The piston constant was about 0.734 mm. of mercury at standard conditions per gram weight on the pan.

The gage was calibrated against a mercury column. The temperature of the column was kept as constant as possible by enclosing it in a channel-

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[6] Keyes and Brownlee, THIS JOURNAL, 40, 25 (1918).

shaped wooden frame, the front of which was closed with heavy cardboard. The temperature was obtained by averaging the readings of a series of mercury thermometers placed one meter apart, and the length of the mercury column was measured on a steel scale kept under a constant tension, which was also applied when calibrating it against a standard meter. Two different grades of oil—"Lard" and "Heavy Medium" designated by L. and H. M. in the table—were used to lubricate the piston, but no specific effect due to the oil could be detected. Table I contains a résumé of the calibration data. In the third column is given the height of the mercury corrected for the tape error; in the fourth, this height has been reduced to 0°, 45° latitude and sea level. In Col. 5 is the correction for the oil levels and the weight of a column of air equivalent to that of the mercury height; in Col. 6 is the correction for the compressibility of the mercury, and in Col. 7 is the fully corrected height of the column while in Col. 8 is the total weight on the piston.

Table I

Calibration of the Piston Gage

Oil	Mean temp. of column °C.	True height in mm.	Height under standard cond. Mm.	Oil and air heights corr. Mm.	Compressibility corr. Mm.	Corr. height in mm.	Total wt. on pan G.	Piston constant Mm./g.	Deviation from mean × 10^5
H. M.	21.19	8953.4	8916.81	−56.77	+0.20	8860.24	12070.01	0.734071	+4.7
H. M.	22.83	8956.9	8917.64	−56.77	.20	8861.07	12072.01	.734018	−0.6
H. M.	21.61	8961.4	8924.11	−56.77	.20	8867.54	12081.21	.733994	−3.0
H. M.	20.12	8955.9	8921.03	−56.77	.20	8864.46	12076.31	.734037	+1.3
L.	21.71	9006.4	8968.75	−57.22	.20	8911.73	12141.01	.734019	−0.5
L.	21.64	6987.8	6958.68	−57.04	.12	6901.76	9402.74	.734016	−0.8
L.	21.73	5001.6	4980.68	−56.86	.06	4923.88	6707.98	.734033	+0.9
L.	22.86	8997.4	8957.93	−57.22	.20	8900.91	12126.71	.733992	−3.2
H. M.	20.92	9007.9	8971.53	−56.78	.20	8914.95	12145.01	.734042	+1.8
H. M.	21.27	6992.3	6963.63	−56.60	.12	6907.15	9409.72	.734044	+2.0
H. M.	22.40	9011.4	8972.61	−56.78	.20	8916.03	12147.01	.734010	−1.4
L.	20.20	9001.4	8966.23	−56.78	.20	8909.65	12138.11	.734023	−0.1
L.	20.74	9011.4	8975.31	−56.78	.20	8918.73	12150.01	.734051	+2.7
H. M.	20.69	6990.8	6962.86	−56.60	.12	6906.38	9409.22	.734001	−2.3
H. M.	21.88	6992.8	6963.36	−56.60	.12	6906.88	9409.72	.734015	−0.9
							Av.	.734024	±1.7

Piston constant, 0.73402 ± 0.00002 mm./g.

To determine when pressure equilibrium had been reached, the device shown at C, Fig. 1, was used.

This consisted of a steel needle projecting into a capillary, and insulated electrically from the rest of the block. Mercury filled the block D to the point of the needle, the position of which was not affected by pressure, and above was oil which communicated the pressure to the piston gage. The oil leak at the gage was compensated for by addition from the injector shown at E.

The steel needle and the block D were connected in series with a telephone and the 2-volt terminals of a transformer. When there was not sufficient weight on the pan to balance the pressure in the piezometer the mercury level rose at C and made contact with the needle, causing a buzzing in the telephone; when too much weight was on the pan the circuit was broken. This gave a delicate means of detecting pressure equilibrium, as at pressures below 50 atmospheres 1 g. was sufficient to cause the circuit to make or break.

The Volume Measuring Device.—The volume of the gas in the piezometer G, Fig. 1, was varied by the injection of mercury from the compressor F.

This consisted of a very uniform steel rod passing through a packing into a thick steel tube filled with mercury. The packing was linen cloth soaked in ceresin wax, at the top and bottom of which were hard rubber rings to prevent the piston from dragging any of the wax with it. The piston was moved in and out by means of a threaded portion passing through a long Tobin bronze nut, at the upper and lower surfaces of which were roller bearings to reduce the friction and wear of turning the nut. At the lower end the head of the nut was divided into a hundred parts, and also a revolution counter was attached, so that the number of whole turns and fractions could be determined. The piston was 22.2 mm. ($^7/_8$ in.) in diameter, and the pitch of the thread was 10 in 14 mm. (18 per inch) so that a thousandth of a turn, which could be easily estimated, varied the volume by about 0.5 cu. mm.

The temperature of the compressor was kept constant by a kerosene bath, which was stirred, heated and regulated as shown in Fig. 1, and it was measured with a platinum thermometer, the regulation being to ±0.001°, while the bath temperature was 30°.

The piston was calibrated by weighing the amount of mercury expelled for each ten turns, using an extremely fine glass tip cemented to the end of the steel capillary leading from the compressor.

In making a measurement, mercury was expelled from the compressor and passed through a capillary to the block D, containing 4 steel stopcocks, one shutting off the compressor, one the piezometer, one the piston gage, and one leading to a vacuum pump. In the block and connecting steel capillaries was about 1.5 cc. of mercury. The temperature of the block was measured, and correction for the thermal expansion made.

From the block the mercury passed down through a capillary and between the steel and glass vessels G, then up through the glass capillary and into the gas space.

The Piezometer.—It has been found that ether decomposes at high temperatures when in contact with iron, but no decomposition takes place at 325° when held in glass containers. Hence the piezometer G consisted of a glass vessel of about 96 cc. capacity surrounded by a steel jacket.

The piezometer was made of Pyrex glass and annealed. At one end was a small bulb connected to the main part of the vessel by a capillary. This bulb and capillary were calibrated with mercury, since it was intended to determine the amount of ether present by measuring the volume of the liquid phase at 0°, where the density is accurately known, and correcting for the amount of the gas phase in the main portion of the piezometer. At the other end was a fine capillary. The volume of the piezometer was determined for various heights, and also its total capacity at 30°, as well as the volume per unit length of the capillaries.

The steel bomb was closed by a soft steel-washer, made by heating cold rolled steel to 1100° in a stream of hydrogen.[7] It was confined between the body and cap of the bomb in such a way that it could not flow. The

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[7] This washer was suggested by Dr. Keyes and, as stated above, gave excellent results.

lock nut was separate from the cap, so that in tightening, the latter would not turn on the washer and scar it. This joint has been opened and closed, heated to 325° many times, and subjected to a pressure of 1000 atmospheres without leaking.

Method of Filling the Piezometer

The ether was purified by shaking with concd. sulfuric acid, then treating it several times with an alkaline permanganate solution, and washing it with water after each treatment. This was followed by treatment with sulfuric acid, calcium chloride, and finally by several distillations from sodium.

Dry ether was introduced into Flasks AA, Fig. 2, and distilled back and forth many times. It was frozen after each distillation by means of liquid air, and evacuated each time with a diffusion pump. The purpose of this was to remove all traces of dissolved gases that might have been present. At B is shown a device similar to that used by Young[8] to test the completeness of the removal of air. It consisted of an inverted bell which could be raised by a magnet, thus collecting some of the gas phase. If this disappears promptly under the small hydrostatic pressure of the liquid phase, it is taken to indicate the absence of permanent gases.

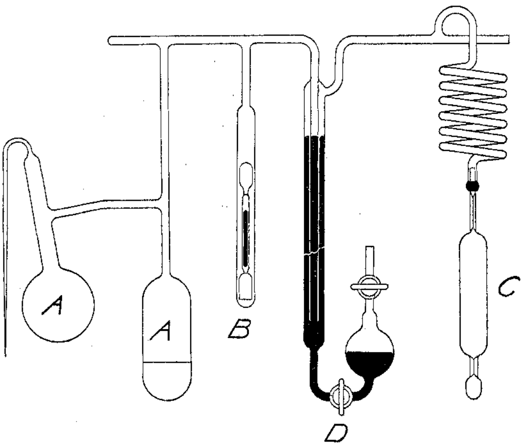

Fig. 2.—The loading apparatus.

The piezometer C was connected to the filling apparatus by a cement and evacuated for two days, while being heated constantly to 360°. It was then connected to the ether supply by means of the greaseless stopcock at D, the ether distilled in, and frozen by means of liquid air. The piezometer was sealed off as near the line to which it had been calibrated as possible and the capillary bent as shown at H, Fig. 1.

The amount of ether present was determined both by measuring the volume of liquid present and correcting for the amount of vapor as described above; and by direct weighing, using a vessel similar in shape to the piezometer as a counterpoise. These weighings extended over two weeks with widely different room temperatures and barometric pressures. The results were concordant to 0.1 mg., and the two methods agreed to 0.2 mg.

Experimental Method

A blank run was first made to determine the compressibility of the apparatus. The glass piezometer was evacuated, sealed off, and placed in the steel casing, the bend in the capillary fitting into a slot in the cap of the bomb as shown at H, Fig. 1.

The bomb was closed, connected to the block D, and placed on its side in a thermostat at 30°. The compressor was so filled that mercury just

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[8] Young, *Phil. Mag.*, **20**, 797 (1910).

appeared on the end of its capillary when the reading on the head was zero. The piston was withdrawn slightly and the capillary also attached to the block D.

The block and the space around the glass piezometer were then evacuated, the pressure gage B being disconnected and a blank plug substituted. The vacuum was shut off and mercury forced into the bomb from the compressor, until the space around the piezometer and also the block up to the detection needle at C were filled. The gage was connected, and with each of the three stopcocks open exactly one turn several measurements at different pressures were made. From these data, by extrapolation, could be obtained the compressor setting, for the case that the pressure outside the piezometer was the same as that inside, namely a vacuum. This was called the "zero set."

The bomb was then set upright, and the glass piezometer in rising up broke the capillary at a point where a file scratch had been previously made. Mercury was run in until the vessel was completely filled. The compressibility of the whole apparatus was determined at 30° and at each of the temperatures used in the final measurements. From a plot of compressibility in terms of Δv (volume of mercury in bomb at any temperature and pressure minus that present at 30° and zero pressure—the "zero set") against the pressure, for each isotherm, the change in volume due to the temperature and pressure in question could be read off.

The bomb was opened and filled with ether, and care was taken to have as nearly as possible the same amount of glass present as in the blank run. A zero set was again made at 30° but this time the extrapolation was made to the vapor pressure of the ether, in order to have the pressure inside and outside the piezometer the same. The measurements were then made on the compressibility of the ether vapor, the piston settings being made so that at each temperature the gas occupied precisely the same set of volumes, thus giving isometrics as well as isotherms.

The observed pressure was corrected for the barometric height, the oil level difference between the gage and the needle point, and the mercury level difference between the needle point and the height of the mercury in the piezometer, as well as the capillary depression of the mercury in the capillary at the detecting needle. The level of the mercury inside the piezometer was determined from a plot of the height against volume of mercury in the lower part of the piezometer made from the original calibration of the vessel. For any piston setting the amount of mercury in the piezometer was known, hence its height in the vessel was determined from the plot. For purposes of reducing the height of the mercury column to zero its temperature was divided into three sections. The application of these corrections which are accurately determinable give the pressure exerted by the gas at the temperature and volume in question.

The same amount of mercury was in the system during the final measurements as in the calibrations, since the compressor was also filled to the end of the capillary for each set of measurements and the block D completely cleaned out after each set. The volume of the glass in the piezometer was slightly different in the two sets of runs. A correction for this, which, however, was too small to affect the results, was applied.

To calculate the compressor setting for a desired density of gas, it was necessary to know approximately the pressure exerted by the substance for the specific volume and temperature in question. For this purpose the equation of state based on the work of Ramsay and Young was used. From the plot of the compressibility of the apparatus against pressure at each temperature could then be obtained the change in volume Δv from the zero set at 30° due to the temperature and pressure expansion of the steel and the mercury. Suppose it is desired to cause the gas to occupy a space V. A correction must be applied due to the fact that in the preliminary runs this space was occupied by mercury at the temperature T of the piezometer, whereas in the final measurements this mercury was in the compressor at 30°, where it occupied a smaller volume. Hence the volume V must be multiplied by the ratio of the density of mercury at $t°$ to that at 30°. A further slight correction is necessary since the compressibility of mercury is a function of temperature as well as pressure. The densities used were obtained from Landolt and Börnstein's "*Tabellen*," and the temperature function of compressibility from the work of Bridgman.[9] The latter correction was too small to affect the results appreciably. There is then added the compressibility of the apparatus, Δv, obtained as described above.

Subtracting this corrected volume from the inside volume of the piezometer at 30° gave the amount of mercury that must be injected from the zero set to give the desired space for the gas. The setting of the compressor could then be determined from its calibration.

The Experimental Data

As stated in the introduction, the data were taken along isometrics in order to test, among other things, the linearity of the constant-volume lines. For each density an equation of the form

$$p = \psi T - \phi \qquad (1)$$

was determined. In Table II are given the observed data together with the pressures calculated from the best straight line that can be put through the isometrics. The constants of this line are also given. The value of 0° on the absolute temperature scale was taken as 273.13°. It can be seen that for the smaller densities the observed data lie on a straight line within the experimental error, which it is believed is about 0.01 atmosphere

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[9] Bridgman, *Proc. Am. Acad.*, **57**, 347 (1911).

up to 50 atm. However, at 12 cc. per g. a curvature of the measured isometric is clearly shown and this increases as the density becomes greater.

TABLE II

COMPARISON OF OBSERVED PRESSURES WITH THOSE CALCULATED BY ASSUMING THE ISOMETRIC LINES TO BE STRAIGHT

Temperatures in °C. The first line gives the observed pressure; the second is that calculated and the third is the first minus the second.

Volume cc./g.	150	175	200	225	250	275	300	325
	$p=0.03698T-4.460$							
35	11.190	12.112	13.049	13.957	14.890	15.796	16.732	17.665
	11.187	12.112	13.036	13.961	14.885	15.810	16.734	17.659
	0.003	0.000	0.013	−0.004	0.005	−0.014	−0.002	0.006
	$p=0.04416T-6.033$							
30	12.667	13.756	14.847	15.966	17.076	18.165	19.276	20.394
	12.652	13.756	14.860	15.964	17.068	18.172	19.276	20.380
	0.015	0.000	−0.013	0.002	0.008	−0.007	0.000	0.014
	$p=0.05468T-8.644$							
25	14.479	15.859	17.229	18.604	19.958	21.322	22.708	24.050
	14.493	15.860	17.227	18.594	19.961	21.328	22.695	24.062
	−0.014	−0.001	0.002	0.010	−0.003	−0.006	0.013	−0.012
	$p=0.07140T-13.315$							
20	16.880	18.678	20.471	22.250	24.038	25.841	27.601	29.390
	16.896	18.681	20.466	22.251	24.036	25.821	27.606	29.391
	−0.016	−0.003	0.005	−0.001	0.002	0.020	−0.005	−0.001
	$p=0.10145T-22.962$							
15	....	22.492	25.036	27.578	30.120	32.639	35.194	37.713
	....	22.501	25.037	27.573	30.110	32.646	35.182	37.718
	....	−0.009	−0.001	0.005	0.010	−0.007	0.012	−0.005
	$p=0.12730T-32.203$							
12.5	....	24.825	28.023	31.214	34.400	37.586	40.755	43.930
	....	24.844	28.026	31.209	34.391	37.574	40.756	43.939
	....	−0.019	−0.003	0.005	0.009	0.012	−0.001	−0.009
	$p=0.16851T-48.138$							
10	....	....	31.579	35.808	40.028	44.238	48.430	52.638
	....	....	31.589	35.802	40.015	44.227	48.440	52.653
	....	....	−0.010	0.006	0.013	0.011	−0.010	−0.015
	$p=0.24374T-79.797$							
7.5	....	....	35.502	41.626	47.730	53.805	59.908	65.973
	....	....	35.524	41.617	47.711	53.804	59.898	65.991
	....	....	−0.022	0.009	0.019	0.001	0.010	−0.018
	$p=0.41145T-155.869$							
5	....	....	38.775	49.107	59.378	69.718	79.936	90.182
	....	....	38.800	49.087	59.373	69.659	79.945	90.232
	....	....	−0.025	0.020	0.005	0.059	−0.009	−0.050
	$p=1.26107T-548.036$							
2.5	....	....	48.490	80.221	111.821	143.296	174.608	206.100
	....	....	48.614	80.141	111.668	143.194	174.721	206.248
	....	....	−0.124	0.080	0.153	0.102	−0.113	−0.148

Pressures in atmospheres $T=t$ °C. + 273.13

The accuracy of the equation of state can now be examined in the light of the data given in Table II. This equation has the form

$$p = \frac{RT}{v-\delta} - \frac{A}{v^2}e^{-(m/v)} \quad \text{where } \delta = \beta e^{-(\alpha/v)} \tag{2}$$

which requires the pressure to vary linearly with the temperature at constant volume. It should be borne in mind that in this form the equation[2,5] holds only when the molecular species of the fluid under consideration does not vary. When the association or dissociation is occurring (and it is assumed that when the isometrics begin to show curvature, this is what is taking place) the Keyes equation in this *particular* form is not applicable. The ψ and ϕ of Equation 1 become $\frac{R}{v-\delta}$ and $\frac{A}{v^2}e^{-m/v}$ and the accuracy of these functions can be tested for those densities for which the measured isometrics are substantially straight.

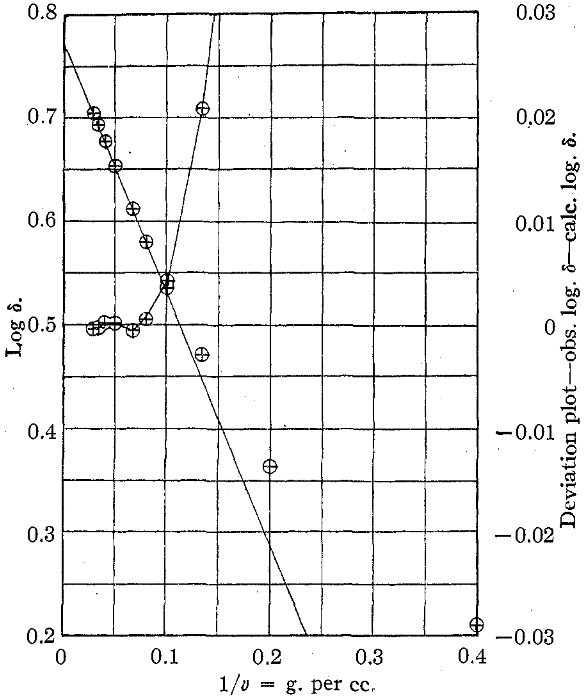

Fig. 3.—Plot of $\log_{10}\delta$ against $1/v$ and deviation plot. The equation of the straight line is $\log_{10}\delta = 0.77325 - \frac{2.4240}{v}$.

$$\text{Since } \psi = \frac{R}{v-\delta} \tag{3}$$

the value of δ can be calculated for the set of values of ψ and v given in Table II. In this case R is the gas constant in cc. per atm. per degree C., and per gram and is for ether 1.1074, since its value in cc. per atm. per degree C. and per mole was taken as 82.056, and the molecular weight of ether as 74.096 (H = 1.0076, O = 16, C = 12.005). In Table III are given the values of δ so calculated (under the column headed "δ obs.") together with the corresponding specific volumes. To test the accuracy of the function used to represent δ, a graph of log δ against $1/v$ was made. This, according to the equation of state, should be a straight line. Hence, a straight line was passed through the points and a deviation plot of Δ log δ against $1/v$ made (Fig. 3). The equation of the straight line chosen is given in Table III, together with the values of δ and log δ calculated from it. It will be seen that the delta function holds very satisfactorily in the region in which the isometrics are straight lines, that is, from larger specific volumes to 15 cc. per g., (and it is quite good even at 10 cc. per g.) but as the isometrics begin to curve, the discrepancy between the observed and calculated deltas increases, as would be expected. The values for the greater densities are, however, given to complete the table.

TABLE III

COMPARISON OF OBSERVED δ AND $\left(\frac{\partial P}{\partial T}\right)_v$ WITH THAT CALCULATED FROM THE EQUATION OF STATE

Volume Cc./g.	Log δ			δ in cc.			$\left(\frac{\partial P}{\partial T}\right)_v$ in atm. per °C.		
	Obs.	Calc.	Obs.-calc.	Obs.	Calc.	Obs.-calc.	Obs.	Calc.	Obs.-calc.
35	0.70364	0.70399	−0.00035	5.054	5.058	−0.004	0.03698	0.03698	0.00000
30	.69223	.69245	− .00022	4.923	4.926	− .003	.04416	.04417	− .00001
25	.67651	.67629	.00022	4.748	4.746	.002	.05468	.05468	.00000
20	.65225	.65205	.00020	4.490	4.488	.002	.07140	.07139	.00001
15	.61109	.61165	− .00056	4.084	4.089	− .005	.10145	.10149	− .00004
12.5	.57990	.57933	.00057	3.801	3.796	.005	.12730	.12723	.00007
10	.53504	.53085	.00419	3.428	3.395	.033	.16851	.16766	.00085
7.5	.47085	.45005	.02080	2.957	2.819	.138	.24375	.23657	.00717
5	.36342	.28845	.07497	2.309	1.943	.366	.41145	.36225	.04920
2.5	.21005	− .19635	.40640	1.622	0.636	.986	1.26107	.59410	.66697

$$\log \delta = 0.77325 - \frac{2.4240}{v}; \quad \delta = 5.9327e^{-5.5815/v}.$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-\delta} = \frac{1.1074}{v-\delta}.$$

In Tables IV and V are given the data used in examining the two forms for the ϕ values. For the algebraic form $\phi = \frac{A}{(v+1)^2}$, it is necessary only to write $v + 1 = \sqrt{A}/\sqrt{\phi}$ and it can then be seen that a plot of $1/\sqrt{\phi}$ against v should be a straight line. This graph is given in Fig. 4, and in Table IV are the values of $1/\sqrt{\phi}$ and ϕ obtained from Table II together with those calculated from the equations, $1/\sqrt{\phi} = 0.009714 + 0.013235\ v$ and $\phi = 5709/(v + 0.734)^2$. For the exponential form $\phi = \frac{A}{v^2}\ e^{-m/v}$ can be written $\log v^2\phi = \log A - \frac{2.3m}{v}$, and hence the log $v^2\phi$ should vary linearly with $1/v$. The plot is given in Fig. 5 and the observed and calculated values of log $v^2\phi$ and ϕ, in Table V. The equations used are $\log v^2\phi = 3.75656 - \frac{0.6375}{v}$, and $\phi = \frac{5709}{v^2}e^{-1.468/v}$. It can be seen that in

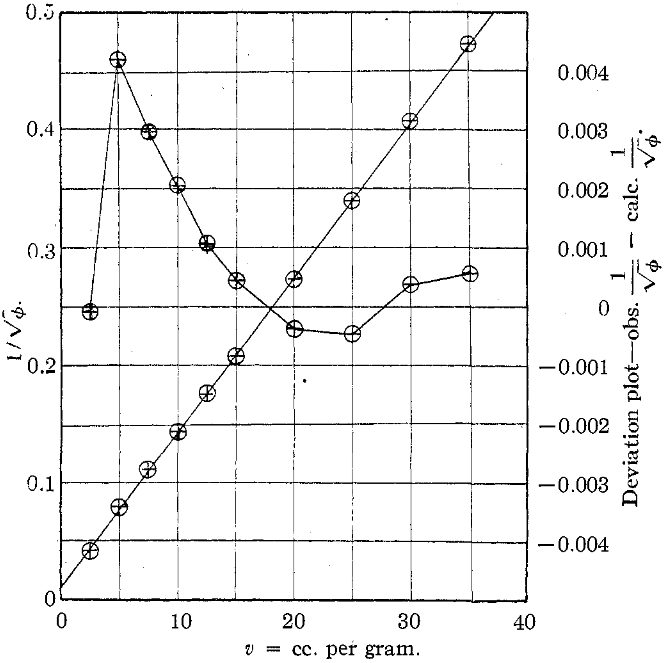

Fig. 4.—Plot of $\frac{1}{\sqrt{\phi}}$ against v and deviation plot. The equation of the straight line is $\frac{1}{\sqrt{\phi}} = 0.009714 - 0.013235\,v$.

TABLE IV

COMPARISON OF OBSERVED ϕ WITH THAT CALCULATED FROM ALGEBRAIC FORM OF THE EQUATION OF STATE

Volume Cc./g.	$\frac{1}{\sqrt{\phi}}$			ϕ in atms.		
	Obs.	Calc.	Obs.-calc.	Obs.	Calc.	Obs.-calc.
35	0.47351	0.47294	0.00057	4.460	4.471	− 0.011
30	.40713	.40676	.00037	6.033	6.044	− .011
25	.34013	.34059	− .00046	8.644	8.621	.023
20	.27405	.27441	− .00036	13.315	13.280	.035
15	.20869	.20824	.00045	22.962	23.061	− .099
12.5	.17622	.17515	.00107	32.203	32.597	− .394
10	.14413	.14206	.00207	48.138	49.549	− 1.411
7.5	.11195	.10898	.00297	79.797	84.205	− 4.408
5	.080098	.075889	.004209	155.869	173.638	−17.769
2.5	.042716	.042802	− .000086	548.036	545.858	2.178

$$\frac{1}{\sqrt{\phi}} = 0.009714 + 0.013235\,v;\quad \phi = \frac{5709}{(v + 0.734)^2}$$

the gas phase there is little choice between these two equations for ϕ, the exponential type holding perhaps slightly better for the larger densities, but both giving good results down to volumes of 15 cc. per g. Exactly the same value of A was used for the two equations, and m was taken as exactly twice 1.

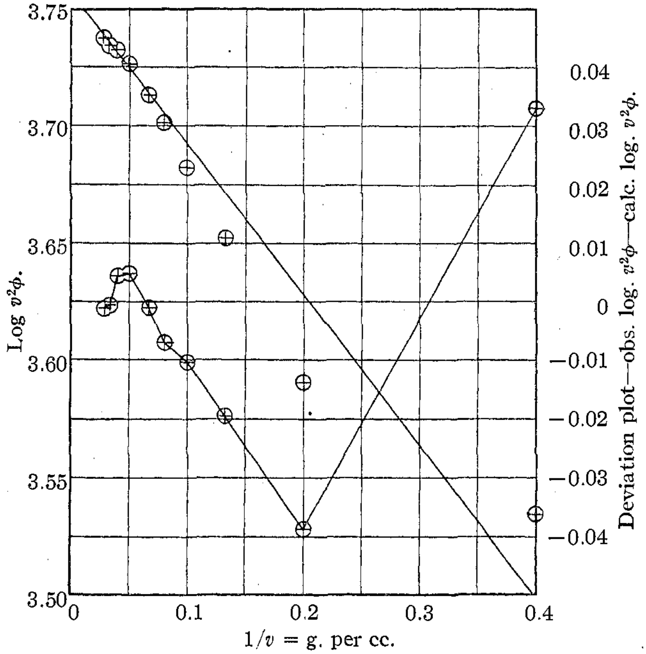

Fig. 5.—Plot of $\log_{10} v^2\phi$ against $1/v$ and deviation plot. The equation of the straight line is $\log_{10} v^2\phi = 3.75656 - \frac{0.6375}{v}$.

TABLE V

COMPARISON OF OBSERVED ϕ WITH THAT CALCULATED FROM EXPONENTIAL FORM OF EQUATION OF STATE

Volume Cc./g.	log ϕv^2			ϕ in atmospheres		
	Obs.	Calc.	Obs.-calc.	Obs.	Calc.	Obs.-calc.
35	3.73747	3.73835	−0.00088	4.460	4.469	− 0.009
30	3.73478	3.73531	− .00053	6.033	6.041	− .008
25	3.73259	3.73106	.00153	8.644	8.614	.030
20	3.72640	3.72468	.00172	13.315	13.262	.053
15	3.71319	3.71406	− .00087	22.962	23.008	− .046
12.5	3.70172	3.70556	− .00384	32.203	32.489	− .286
10	3.68249	3.69281	− .01032	48.138	49.296	− 1.158
7.5	3.65211	3.67156	− .01945	79.797	83.453	− 3.656
5	3.59070	3.62906	− .03836	155.869	170.263	−14.394
2.5	3.53469	3.50156	.03313	548.036	507.785	40.251

$$\log \phi v^2 = 3.75656 - \frac{0.6375}{v}; \quad \phi = \frac{5709}{v^2} e^{-1.468/v}$$

The Keyes equation for ether vapor becomes, therefore,

$$p = \frac{1.1074}{v-\delta}T - \frac{5709}{(v+0.734)^2}; \qquad \delta = 5.9327\,e^{-5.5815/v}$$

$$\text{or } \log\delta = 0.77325 - \frac{2.4240}{v} \tag{A}$$

$$T = t^\circ\text{C.} + 273.13$$

and the equation as modified by Phillips

$$p = \frac{1.1074}{v-\delta}T - \frac{5709}{v^2}e^{-1.468/v} \quad \text{where } \log v^2\phi = 3.75656 - \frac{0.6375}{v} \tag{B}$$

ϕ being the second term on the right hand side of the equation.

In Table VI are given the values of the pressures calculated from Equation B, together with those measured in the present investigation. It can be seen that to a specific volume of 15 cc. per g., (that is, in the region where the isometrics are substantially straight lines) the measured pressures are quite accurately reproduced, but at greater densities where presumably the molecular species of the substance is changing more rapidly, great discrepancies appear. It is hoped to consider this region in a later article.

Table VI

Comparison of Observed Pressure with That Calculated by the Equation of State

Temperatures in °C. In the first line is the observed pressure in atmospheres; in the second that calculated; and the third is the first minus the second.

Volume Cc./g.	150	175	200	225	250	275	300	325
35	11.190	12.112	13.049	13.957	14.890	15.796	16.732	17.665
	11.178	12.103	13.027	13.952	14.876	15.801	16.725	17.650
	0.012	0.009	0.022	0.005	0.014	−0.005	0.007	0.015
30	12.667	13.756	14.847	15.966	17.076	18.165	19.276	20.394
	12.649	13.753	14.857	15.961	17.066	18.170	19.274	20.378
	0.018	0.003	−0.010	0.005	0.010	−0.005	0.002	0.016
25	14.479	15.859	17.229	18.604	19.958	21.322	22.708	24.050
	14.523	15.890	17.257	18.624	19.991	21.358	22.725	24.092
	−0.044	−0.031	−0.028	−0.020	−0.033	−0.036	−0.017	−0.042
20	16.880	18.678	20.471	22.250	24.038	25.841	27.601	29.390
	16.945	18.730	20.515	22.300	24.084	25.869	27.654	29.439
	−0.065	−0.052	−0.044	−0.050	−0.046	−0.028	−0.053	−0.049
15	....	22.492	25.036	27.578	30.120	32.639	35.194	37.713
	....	22.473	25.010	27.547	30.084	32.622	35.159	37.696
	....	0.019	0.026	0.031	0.036	0.017	0.035	0.017
12.5	....	24.825	28.023	31.214	34.400	37.586	40.755	43.930
	....	24.527	27.707	30.888	34.069	37.250	40.430	43.611
	....	0.298	0.316	0.326	0.331	0.336	0.325	0.319
10	....	....	31.579	35.808	40.028	44.238	48.430	52.638
	....	....	30.029	34.220	38.412	42.603	46.795	50.986
	....	....	1.550	1.588	1.616	1.635	1.635	1.652

Accuracy Required of the Constants

It is perhaps of interest to discuss the error allowable in the constants of the equation in order to calculate the pressure to any desired accuracy.

$$\text{Since } \phi = \frac{A}{v^2}\, e^{-m/v}$$

$$\begin{aligned} \Delta\phi &= \frac{\phi}{A}\,\Delta A \qquad (1) & & \text{and} & \Delta\phi &= -\frac{\phi}{v}\Delta m \qquad (2) \\ \frac{\Delta\phi}{\phi} &= \frac{\Delta A}{A} & & & \frac{\Delta\phi}{\phi} &= -\frac{\Delta m}{v} \end{aligned}$$

$$\text{and since } \psi T = \frac{RT}{v-\delta}$$

$$\begin{aligned} \Delta(\psi T) &= \frac{\psi T}{R}\,\Delta R \qquad (3) & & \text{and} & \Delta(\psi T) &= \frac{\psi T}{v-\delta}\Delta\delta \\ \frac{\Delta(\psi T)}{\psi T} &= \frac{\Delta R}{R} & & & \frac{\Delta(\psi T)}{\psi T} &= \frac{\Delta\delta}{v-\delta} \end{aligned}$$

Now $\delta = \beta e^{-\alpha/v}$, whence $\Delta\delta = e^{-\alpha/v}\Delta\beta - \beta/_v\, e^{-\alpha/v}\Delta\alpha$ from which we get by substitution in the equation above

$$\begin{aligned} \Delta(\psi T) &= \frac{\psi T}{v-\delta} e^{-\alpha/v}\Delta\beta \qquad (4) & & \text{and} & \Delta\psi T &= -\frac{\psi T}{v-\delta}\frac{\delta}{v}\Delta\alpha \quad (5) \\ \frac{\Delta(\psi T)}{\psi T} &= \frac{e^{-\alpha/v}}{v-\delta}\Delta\beta & & & \frac{\Delta\psi T}{\psi T} &= -\frac{\delta}{v(v-\delta)}\Delta\alpha \end{aligned}$$

In Table VII are given the errors in each constant, which would cause an error of 0.01 atmosphere in the calculated pressure, for the two specific volumes 50 and 15 cc. per g. at 250°. The allowable error in each constant should be divided by 5 if it is required to know the pressure to 0.01 atmosphere.

Table VII

Errors in the Constants of the Equation of State Each Capable of Producing 0.01 Atmosphere Error in the Calculated Pressure

These divided by 5 give the allowable error which would produce a total error of 0.01 atmosphere in the pressure.

$t = 250$°C.

	$v = 50$ cc./g.			$v = 15$ cc./g.		
Constant	Value	Absolute error	Error %	Value	Absolute error	Error %
R	1.1074	0.00085	0.077	1.1074	0.00021	0.019
β	5.9327	.039	.66	5.9327	.0030	.050
α	5.5815	.33	5.8	5.5815	.0075	.14
A	5709	26	0.45	5709	2.5	.043
m	1.468	0.23	15	1.468	0.0065	.44
δ	5.306	...	..	4.089	...	..
ψT	12.96	...	..	53.092	...	..
ϕ	2.22	...	..	23.008	...	..
P	10.74	...	..	30.084	...	..

Summary

An apparatus for measuring the pressure-volume-temperature properties of gaseous substance with great accuracy has been described.

The isometrics of ethyl ether from a specific volume of 2.5 to 35 cc. per g. and from 175° to 325° have been measured. It was found that from 15 cc. per g. to the smallest densities the isometrics were substantially straight within the experimental error of the measurements. At densities greater than 15 cc. per g. the isometrics show a curvature which becomes greater as the density increases.

From the experimental data the Keyes equation of state for ether vapor was determined. This is $p = \frac{1.1074}{v-\delta}T - \frac{5709}{(v+0.734)^2}$; $\log_{10}\delta = 0.77325 - \frac{2.4240}{v}$; $T = t°\text{C.} + 273.13$.

A modification of the last term of the Keyes equation, suggested by H. B. Phillips has been examined and found to hold as well as or slightly better than the original form. In this case the equation is $p = \frac{1.1074}{v-\delta}T - \frac{5709}{v^2}e^{-\frac{1.468}{v}}$ where $\log v^2\phi = 3.75656 - \frac{0.6375}{v}$, ϕ being the last term on the right hand side of the equation. In these equations v is the specific volume in cc. per gram, and p the pressure in atmospheres of 760 mm. of mercury at 0° and under standard conditions of gravitation.

The equation reproduces the measured pressures with great accuracy from the largest specific volumes to 15 cc. per g., that is, in the region of straight isometrics. At greater densities the equation in its present particular form cannot be used. The form which the equation takes in this region, where presumably the molecular species is changing (association or dissociation occurring) will be examined in a later article.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR., CHEMICAL LABORATORY, HARVARD UNIVERSITY]

A COMPARISON OF THE ATOMIC WEIGHTS OF TERRESTRIAL AND METEORIC COBALT. V. THE ANALYSIS OF COBALTOUS CHLORIDE

BY GREGORY PAUL BAXTER AND MERRILL JAMES DORCAS

RECEIVED NOVEMBER 20, 1923

The question of the identity of elementary material from different sources has received considerable attention at various times.

Even before the existence of isotopes was suspected many such comparisons were carried out.[1] More recently the matter has received especial

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[1] See especially copper: Richards, *Proc. Am. Acad. Arts Sci.*, **23**, 178 (1887); nickel: Richards and Cushman, *ibid.*, **33**, 102 (1897); calcium: Richards, THIS JOURNAL, **24**, 374 (1902); sodium and silver: Richards and Wells, *Carnegie Inst. Pub.*, **28**, 13, 17 (1905).