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THE VAPOR PRESSURES, DENSITIES AND SOME DERIVED QUANTITIES FOR ETHER AT LOW TEMPERATURES

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Introduction

This investigation was initiated to obtain better values for the saturation specific volumes of ethyl ether to be used in connection with the equation of state of the liquid phase. Incidental to the present investigation, further experience was gained in the operation and possibilities of the improved type of cryostat. In addition to the density measurements from $+70^{\circ}$ to -120° , vapor-pressure measurements were made in the temperature interval $+20^{\circ}$ to -60° .

Regnault¹ measured the vapor pressures and densities of ether above 0° . Later Young² obtained values over a range extending from slightly below 0° to the critical temperature. Seitz, Alterthum and Lechner³ have published densities from the freezing point of ether to 0° . Mündel⁴ measured a few vapor pressures at about the temperature of solid carbon dioxide, at one atmosphere (-78.5°). However, due to the fact that the pressures are very low below -70° , his results are only serviceable in giving the magnitude of the pressures.

In measuring the densities Young used a pycnometer of the U type such as is employed for liquids with low vapor pressures. Ether has an appreciable vapor pressure even at 0° , so that this is possibly not the best type of pycnometer. For the higher temperatures, Young floated ether on top of mercury in a jacketed manometer tube, determining the mass of ether by measuring the volume at a known temperature and density.

Seitz, Alterthum and Lechner measured the density from -110° to 0° . A borosilicate glass pycnometer was used of the same form as that employed in this investigation. The pycnometer had a long and rather large capillary to avoid the necessity of reloading to cover the temperature range. The temperatures, to the freezing point of mercury, were measured with a mercury thermometer, and lower temperatures were obtained by means of 2 Reichsanstalt calibrated pentane thermometers graduated to 0.1. To refrigerate the cryostat to -75° solid carbon dioxide was introduced into the bath from time to time, and for lower temperatures liquid air was dropped upon the surface of the petroleum-ether bath. The ether was purified by drying an imported "purest" ether over sodium.

¹ Regnault, *Mém. Acad.*, **26**, 339 (1862).

² Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374-443 (1910).

³ Seitz, Alterthum and Lechner, *Ann. Physik*, **49**, 90 (1916).

⁴ Mündel, *Z. physik. Chem.*, **85**, 435 (1913).

Keyes and Felsing⁵ drew up a table of the most probable densities of ether from the work referred to above and from some measurements at 0° and -33° by Kenny and by Keyes and Felsing. They considered the densities above zero as measured by Young to be more accurate than those of Seitz, Alterthum and Lechner. Both sets of data seem to be about as accurate as the experimental procedure would permit.

Apparatus and Method

For the density measurements the apparatus consisted of the cryostat, a quartz pycnometer, loading apparatus and the resistance thermometer. The same cryostat, loading apparatus and thermometer were used for the density measurements as were subsequently used with the addition of a special manometer for the vapor-pressure measurements.

The Cryostat.—The cryostat, shown in Fig. 1 consists of a large Pyrex Dewar tube L of about 6.3 cm. inside diameter. Inside this is a smaller Dewar tube S also of Pyrex glass, with a tube leading out from the bottom at D so that the amount of air between the walls of the inner tube could be varied at will. The inner tube contains a stirrer and heater H. Several designs of bimetallic regulators were tried, but they were not found to be as satisfactory as hand regulation. The outer Dewar tube was filled with liquid air or liquid ammonia as a cooling medium. Liquid air was found to be best for all temperatures, however, due to the convenience in handling. The inner tube was filled with bath liquid which would not freeze at the temperature at which it was used. Kerosene and gasolene were used for the higher temperatures, and from -40° to -120° petroleum ether or pentane was used.

The cryostat is of an improved design similar in principle to that first used by Cardoso⁶ in his work on the critical constants of certain gases. If one has a good vacuum pump and regulates the degree of exhaustion very carefully until heat transfer between the bath and the cooling medium is small, good regulation can easily be obtained. It was found that, with a resistance thermometer sensitive to changes in temperature of 0.001° and with rapid stirring, the temperature could be maintained constant to within at least 0.01° by hand regulation. Pyrex glass was used in constructing the cryostat because of its greater thermal resistance as compared with soda glass. The Dewar tubes were annealed before pumping. Thus far there has been no loss of Dewar tubes due to sudden or unequal cooling with the liquid air.

The Pycnometer.—The quartz pycnometer shown at P in Fig. 1 had an approximate volume of 7.6 cc. The capillary was very uniform, having a volume of 0.0133 cc.

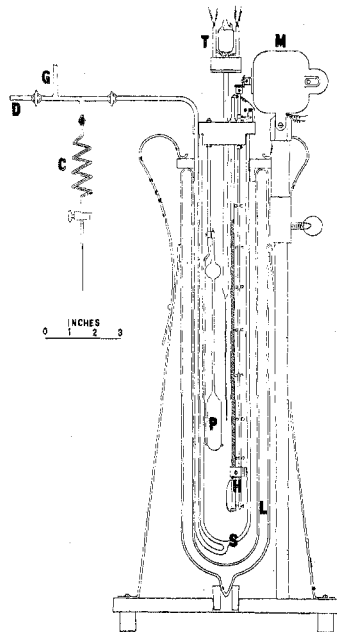


Fig. 1.

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

⁶ Cardoso, *J. chim. phys.*, **15**, 317 (1915).

per cm. length. Above the capillary was a bulb of approximately 2.5 cc. capacity. The pycnometer was connected to the loading apparatus shown in Fig. 2 by means of a quartz-to-glass ground joint. The pycnometer was calibrated by filling with mercury, boiling to expel air and moisture, and weighing before and after determining the height in the capillary at various temperatures. This gave calibrations both of the bulbs and of the capillary, using the densities of mercury as determined by Callendar and Moss.

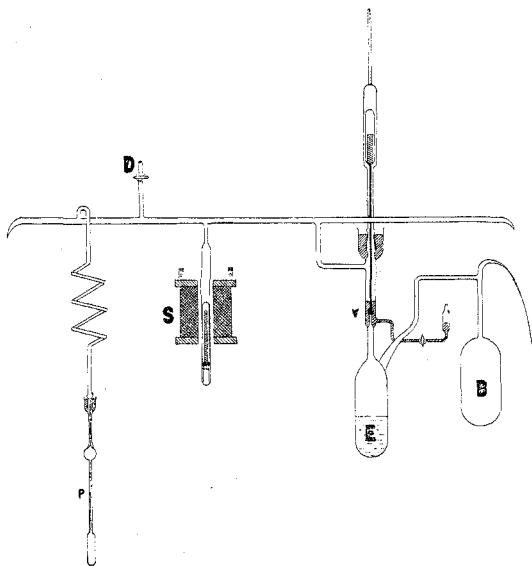


Fig. 2.

with mercury and reading the volume under a pressure of 1 atmosphere. The pycnometer was then evacuated and the volume read again. The change in volume was found to be 0.000307 cc. per atmosphere for the volume used.

The expansion of quartz with rising temperature has been measured by a number of observers. Holborn and Henning⁷ measured the mean coefficient of expansion over 250° intervals. Scheel and Chappuis⁸ determined the mean coefficient between 15° and 57°, and 15° and 100°. They give an equation to represent their results. Harlow⁹ measured the cubical expansion from 0° to 100°. Henning¹⁰ observed the coefficient against glass from -191° to 16° and obtained the value -4.64×10^{-7} cm. per cm. length per degree C. This value is only approximate but it shows that, on the average, quartz expands in cooling to liquid air temperatures.

Scheel and Dorsey¹¹ determined the coefficient for 20° intervals from 0° to -160°. The expansion was measured by observing the shift of interference fringes. The temperature was measured by surrounding the quartz ring used with a calibrated resistance element. The temperatures were obtained by dipping the container to different depths in liquid air. Randall¹² made measurements above zero using the same principle.

⁷ Holborn and Henning, *Ann. Physik*, **10**, 446 (1903).

⁸ Scheel and Chappuis, *Wiss. Abhand. Phys.-Tech. Reichsanst.*, **4**, 54 (1904).

⁹ Harlow, *Proc. Phys. Soc. London*, **24**, 30 (1912).

¹⁰ Henning, *Ann. Physik*, **22**, 606 (1907).

¹¹ Scheel and Dorsey, *Phys. Rev.*, **27**, 101 (1907).

¹² Randall, *ibid.*, **30**, 216 (1910).

Since the volume of the capillary was small, the pycnometer had to be refilled for each temperature, and in some cases several fillings were made at the same temperature. It is difficult to mark graduations on quartz, and hence the height in the capillary was determined by means of a cathetometer and the bottom of the pycnometer was taken as the reference mark.

Quartz was used instead of glass in constructing the pycnometer because its coefficient of expansion is very small and the consequent corrections are small. Also, quartz is a pure substance and has a coefficient which does not vary with different samples as does that of glass. The dilatation of the pycnometer with pressure was obtained by filling

The Scheel and Dorsey values seem to be the most consistent below zero and Randall's results are best above zero. It was found that the equation

$$\log (\alpha + 19) = \log 34.79 - \frac{50.789}{T} \tag{1}$$

best represented all values between -200° and $+50^{\circ}$ within the limits of experimental accuracy. This was integrated graphically for the mean coefficient from 0° to -25° ,

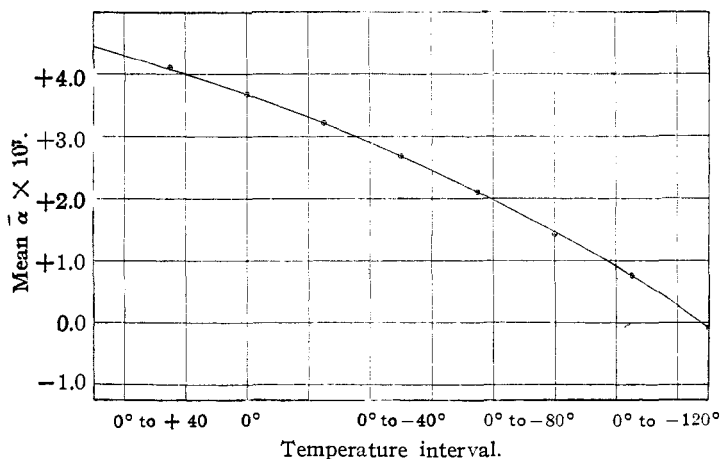


Fig. 3.—Mean coefficient of expansion of quartz plotted against temperature interval.

TABLE I
MEAN EXPANSION COEFFICIENTS OF QUARTZ

$\alpha \times 10^7$ calculated from the equation: $\log (\alpha + 19) = 1.5414 - \frac{50.789}{T}$

$$\bar{\alpha} = \frac{34.79 \int_{T_1}^{T_2} \frac{2.3b}{\epsilon T} - 19}{T_2 - T_1}$$

$T^{\circ}_{\text{abs.}}$	$1/T \times 10^3$	α observed $\times 10^7$	α calc. $\times 10^7$	Deviation	Interval of values $^{\circ}\text{C.}$	Temp. range 0° to $^{\circ}\text{C.}$	Mean $\bar{\alpha} \times 10^7$ (calc.)
113	8.85	-6.65 ^a	-6.63	-0.02	20	+ 50	+4.46
153	6.54	-2.97 ^a	-2.80	-0.17	20	+ 25	+4.11
183	5.46	-0.64 ^a	-0.63	-0.01	20	0	+3.67
193	5.18	-0.468 ^a	-0.02	-0.45	20	- 25	+3.21
203	4.93	+0.55 ^a	+0.55	0.00	20	- 50	+2.68
233	4.29	2.110 ^a	2.06	-0.05	20	- 75	+2.09
273	3.66	3.60 ^a	3.67	+0.07	20	-100	+1.42
309	3.236	4.27 ^b	4.83	+0.56	15- 56	-125	+0.76
322	3.106	4.23 ^c	16- 81.7	-150	-0.09
331	3.021	4.90 ^b	15-100	-175	-1.09
407	2.457	4.79 ^d	17-250

^a Scheel and Dorsey.

^b Scheel and Chappuis.

^c Randall.

^d Henning and Holborn.

and 0° to -50° , 0° to -75° , 0° to -100° , 0° to -125° , 0° to -150° , and 0° to -175° . These values were plotted with the temperatures and from the plot the mean coefficient

of linear expansion from 0° to t° could be read off. Table I contains observed and calculated values of mean coefficient, $\bar{\alpha}$. The plot is given in Fig. 3. From the values given, it is seen that the coefficient of expansion of quartz, in addition to being small, changes sign at about -80° and that at about -147° the pycnometer would have the same volume as at 0° . Evidently quartz is well suited for density work as regards its expansion behavior.

Loading Apparatus.—The loading apparatus shown in Fig. 2 was used to store the ether supply and keep it from contact with air, moisture and gaseous impurities.

The pycnometer P was connected by a quartz-to-glass ground joint as shown in the diagram. To load the pycnometer the ether was frozen and the parts of the apparatus previously open to the air evacuated through D by the mercury diffusion pump backed by a rotary oil pump. In testing for air in the apparatus, an iron rod with a glass bell attached was lifted by the solenoid S, whereupon ether could be distilled over, sufficient in amount to cover the bell when it was lowered. If there is any air present, the vapor phase will not collapse promptly under the slight hydrostatic head of liquid ether when the bell is dropped. The storage bulb E was finally warmed and the pycnometer cooled with liquid ammonia. The distillation was arrested again by cooling the storage bulb with liquid air, when sufficient ether had distilled over.

The pycnometer, after it was cooled with liquid air, was sealed from the storage apparatus with the oxygen-gas flame. It was found by trial that the amount of ether decomposed in sealing off the pycnometer was negligible, due to the very low vapor pressure at the temperature of liquid air. The amount of quartz lost by vaporization was also tested for and found to be negligible.

The same loading apparatus was employed to furnish the ether for the vapor-pressure measurements, being sealed to the vapor-pressure apparatus at L, Fig. 4, and then sealed off.

The Thermometer.—A platinum resistance thermometer T, Fig. 1, was used as already stated. This thermometer was calibrated at the ice, steam and naphthalene points to get the constants of the Callendar equation. The Callendar formula is not applicable at low temperatures as was shown by Henning.¹³ The Henning corrections were used at first but later corrections obtained by actual comparison of the resistance thermometer with the hydrogen thermometer of Keyes, Townshend and Young¹⁴ were used. The thermometer was calibrated by Townshend and Young down to the boiling point of liquid oxygen.

A purchased thermometer bridge, thermostated in this laboratory, was calibrated against U. S. Bureau of Standards' standardized resistances by means of a Carey-Foster bridge.

The Manometer and Vapor-pressure Apparatus.—A mercury manometer was used having a steel base and steel stopcocks as shown at A in Fig. 4. The arm, B, on the right had a sealed-in platinum needle which served as a fixed point for that arm. The contact was made by means of a buzzer amplifier system as shown. The interrupted low voltage direct current from I was amplified by the vacuum tube H and transmitted to the telephones T. Mercury was fed into the system to balance the pressure by means of the reservoir E, through the gas trap D and the final adjustment made with the small compressor C. The system was evacuated through V before loading with mercury or ether. The ether was stirred with the electromagnetic stirrer G operated by the metronome J.

The diameters of the 2 arms of the manometer were measured over the entire length of the tubes, before assembling, by weighing the mercury withdrawn from known

¹³ Henning, *Ann. Physik*, **40**, 345, 653 (1913).

¹⁴ Keyes, Townshend and Young, *J. Math. Phys. Mass. Inst. Tech.*, **1**, No. 4 (1922).

lengths of column. This gave means of correcting for differences in capillary depression. The diameter of the tubes was large (1.3 cm.) in order to decrease the capillary depression. The same cathetometer was used as in the density work.

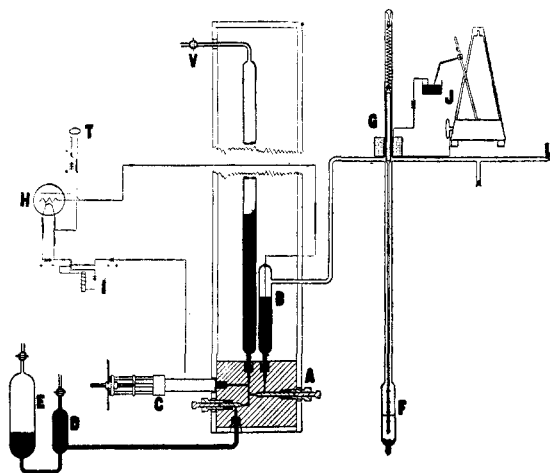


Fig. 4.

Preparation of Material.—The c. p. ether of trade was further purified by first shaking with conc. sulfuric acid until fresh portions produced no change of color. Then it was allowed to stand over a fresh quantity of acid overnight. After this treatment it was washed with water and poured into a saturated solution of potassium permanganate, containing 20 g. of sodium hydroxide per liter, to oxidize any aldehydes. After 24 hours the alkaline permanganate was removed and the treatment repeated. The ether was then washed, treated again with conc. sulfuric acid for a short time, washed, dried over calcium chloride and distilled. After drying over sodium ribbon it was again distilled. The ether was then allowed to stand over sodium ribbon for several weeks with additions of freshly prepared ribbon every few days. It was finally loaded into the bulb B of the storage apparatus (Fig. 2) from which it was distilled into the pycnometer or vapor-pressure apparatus through the 1-way valve V.

Experimental Data

Density of Liquid Ether.—The densities observed and calculated are given in Table II. Since the density is almost a linear function of the

TABLE II
DENSITIES AND SPECIFIC VOLUMES OF ETHER

No.	Temperature ° C.	Density Calc.	Sp. vol. Calc.	Density Obs.	Values of other observers
1	-120	0.86195	1.16016	0.86195	0.8620 ^a
2	-115	0.85699	1.16687
3	-110	0.85200	1.17371	0.85192	0.8517 ^a
4	-105	0.84699	1.18065
5	-100	0.84196	1.18770	0.8415 ^a
6	-95	0.83690	1.19489
7	-90	0.83182	1.20218	0.8313 ^a
8	-85	0.82672	1.20960

TABLE II (Continued)

No.	Temperature °C.	Density Calc.	Sp. vol. Calc.	Density Obs.	Values of other observers
9	- 80	0.82159	1.21715	0.82141
10	- 75	0.81643	1.22484	0.81640
11	- 70	0.81126	1.23265	0.81114	0.8106 ^a
12	- 65	0.80606	1.24060
13	- 60	0.80084	1.24869
14	- 55	0.79559	1.25693
15	- 50	0.79032	1.26532	0.79032	0.7899 ^a
16	- 45	0.78502	1.27385	0.78510
17	- 40	0.77970	1.28254	0.77970
18	- 35	0.77436	1.29139	0.77425
19	- 30	0.76899	1.30041	0.7690 ^a
20	- 25	0.76360	1.30959
21	- 20	0.75819	1.31893
22	- 15	0.75275	1.32846
23	- 10	0.74729	1.33817	0.7474 ^a
24	- 5	0.74180	1.34807	0.73620 ^b
25	0	0.73629	1.35816	0.73629	0.73635 ^c
26	+ 5	0.73069	1.36857
27	10	0.72503	1.37925	0.7248 ^b
28	15	0.71930	1.39024
29	20	0.71352	1.40150	0.71349	0.7135 ^b
30	25	0.70768	1.41307
31	30	0.70177	1.42497	0.7019 ^b
32	35	0.69580	1.43719	0.69576
33	40	0.68976	1.44978	0.68979	0.6894 ^b
34	45	0.68367	1.46269
35	50	0.67751	1.47599	0.6764 ^b
36	55	0.67129	1.48967	0.67116
37	60	0.66501	1.50374	0.66501	0.6658 ^b
38	65	0.65866	1.51823
39	70	0.65226	1.53313	0.6532 ^b

^a Seitz, Alterthum and Lechner.^b Young.^c Keyes and Felsing.

temperature, it was decided to use a series equation. The following equations represent the observed values to one part in seven thousand:

$$\delta = 0.73629 - 0.001138t - 0.000001237t^2 \quad (2)$$

$$\delta = 0.73629 - 0.0011044t - 0.0000004772t^2 \quad (3)$$

Equation 2 holds for the densities above 0° and Equation 3 holds below 0°. It is believed that the densities are correct to at least one part in 7000.

The Vapor Pressures.—The vapor pressures were measured from -60° to +20°. Since the cathetometer was graduated to 0.02 mm., it is probable that the vapor pressures are not more accurate than 0.05 mm. At least two check observations were obtained for every temperature and in many cases more. The equation below, relating the vapor pressure to the temperature, shows good agreement with the observations to 0°.

Above 0°, however, there is a slight trend away from the observations. The equation cannot be expected to give accurate extrapolated values in spite of the good agreement with the observed values.

$$\log p = - (2168.599/T) + 13.882702 - 0.01814165 T + 0.00001718195 T^2 \quad (4)$$

In the equation, p is the vapor pressure in millimeters of mercury and T

TABLE III
OBSERVED VAPOR PRESSURES

No.	Temp. ° C.	Vapor	V. p. calc.	No.	Temp. ° C.	Vapor	V. p. calc.
		pressure observed Mm.	from Eq. 4 Mm.			pressure observed Mm.	from Eq. 4 Mm.
1	-60.799	3.95	3.91	10	-16.578	80.67	80.65
2	-55.748	5.93	5.96	11	-11.637	104.79	104.87
3	-50.873	8.77	8.76	12	- 6.698	134.76	134.76
4	-45.998	12.62	12.62	13	+ 0.009	186.13	186.18
5	-41.125	17.78	17.85	14	+ 4.975	233.73	233.69
6	-36.231	24.77	24.85	15	9.937	290.62	290.50
7	-31.329	34.03	34.06	16	14.903	358.15	357.99
8	-26.421	45.81	46.00	17	19.871	437.70	437.51
9	-21.502	61.31	61.31

TABLE IV
CALCULATED VAPOR PRESSURES

No.	Temp. ° C.	Temp.	Vapor pres.	Vapor pres. of
		° Abs.	calc.	other observers
1	-65	208.135	2.70	
2	-60	213.135	4.19	
3	-55	218.135	6.32	
4	-50	223.135	9.36	
5	-45	228.135	13.57	
6	-40	233.135	19.28	
7	-35	238.135	26.93	
8	-30	243.135	37.00	
9	-25	248.135	49.94	
10	-20	253.135	66.75	{ 68.90 ^a
11	-15	258.135	87.82	{ 62.99 ^b
12	-10	263.135	114.10	{ 114.72 ^a
13	- 5	268.135	146.52	{ 111.81 ^b
14	0.000	273.135	186.10	{ 184.39 ^a
				{ 184.90 ^b
15	+ 5	278.135	233.95	{ 286.83 ^a
16	10	283.135	291.29	{ 291.78 ^b
17	15	288.135	359.41	
18	20	293.135	439.56	{ 432.78 ^a
				{ 442.36 ^b
19	25	298.135	533.78	

^a Regnault.

^b Young

is the absolute temperature. The value 273.135° for the ice point on the absolute scale was used for all calculations. The observed and calculated values are given in Table III.

In Table IV are given the values of the vapor pressure for every 5° over the interval measured. The values of Regnault and of Young are also given for comparison.

The apparatus described in this paper was not applicable for measuring vapor pressures above room temperature. It is noticed that the pressure obtained at 0° does not agree with that of Regnault or of Young. Since the zero point is most reproducible, this temperature was investigated very carefully with two different loadings of fresh ether and the values thus obtained agreed with the original one.

TABLE V
DERIVED QUANTITIES FOR ETHER

No.	Temp. $^\circ\text{C}.$	V_1 calc. from Eq. 6	V_1 from other observers	$\lambda \frac{\text{cal.}}{\text{g.}}$ calc. from Clap. Eq.	λ obs.	$\lambda - p(\Delta v)$ or ΔU in	$C_{S_1} - C_{S_2}$
						cal. g.	cal. g. $^\circ$
1	-65	64927	104.52	...	98.94	-.6932
2	-60	42836	103.56	...	97.84	-.6762
3	-55	29034	102.64	...	96.78	-.6601
4	-50	20040	101.62	...	95.64	-.6641
5	-45	14128	100.67	...	94.56	-.6291
6	-40	10160	99.74	...	93.50	-.6148
7	-35	7426.9	98.805	...	92.43	-.6010
8	-30	5515.5	6127 ¹⁹	97.890	...	91.38	-.5878
9	-25	4166.7	4581 ¹⁹	96.975	...	90.35	-.5750
10	-20	3177.2	3484 ¹⁹	96.073	...	89.32	-.5628
11	-15	2459.6	2616 ¹⁹	95.161	...	88.28	-.5508
12	-10	1927.1	1992 ¹⁹	94.265	...	87.26	-.5393
13	- 5	1526.8	1551 ¹⁹	93.378	...	86.26	-.5281
14	0	1222.3	1225.5 ¹⁹ 1209.2 ²	92.493	94.0 ¹⁵	85.25	-.5172
15	+ 5	987.9	953 ¹⁹	91.603	93.5 ¹⁸	84.25	-.5066
16	10	805.63	763.4 ¹⁹ 791.1 ²	90.719	92.52 ¹⁷	83.25	-.4962
17	15	662.65	628.9 ¹⁹	89.837	$\left\{ \begin{array}{l} 15.5^\circ \\ 89.25^{16} \end{array} \right.$	82.26	-.4860
18	20	549.49	526.3 ¹⁹ 534.8 ²	88.963	87.54 ¹⁷	81.29	-.4760
19	25	458.58	446.8 ¹⁹	88.083	...	80.31	-.4661
20	0.138	90.50 ¹⁵
21	11.813	88.83 ¹⁵

¹⁵ Ramsay and Young, *Phil. Trans.*, **178A**, 329 (1887).

¹⁶ Winkelman, *Wied. Ann.*, **9**, 208, 358 (1880).

¹⁷ Mills, *THIS JOURNAL*, **31**, 1123 (1909).

¹⁸ Beattie, unpublished *Thesis*, *Mass. Inst. Tech.*, 1918.

¹⁹ Battelli, *Ann. chim. phys.*, **6**, 25 (1892).

Discussion of Data and Calculation of Derived Quantities.—
The Clapeyron equation²⁰

$$\lambda = T (v_1 - v_2) \frac{dp}{dT} \quad (5)$$

was used to calculate the latent heats of evaporation, λ . The values of the specific volume of the liquid (v_2) were obtained from Table II. The values of v_1 given in Table V were obtained from the perfect gas law and, for the higher temperatures, from the equation

$$p = \frac{RT}{v_1 - 6.25} - \frac{5796.2}{v_1^2} \quad (6)$$

which is the equation given by Keyes and Felsing⁵ simplified to the form of van der Waals' equation. The values of the specific volume of the vapor, v_1 given by various observers are also listed in Table V. The latter are erratic, indicating possibly that the equation of state gives values which are at least as reliable as the measured volumes. The values of Battelli²¹ were plotted against the temperature to a very large scale and the volumes read at the even temperatures in order to compare them with the calculated values.

The rate of change of the vapor pressure with the temperature along the saturation curve was obtained from Equation 4 by differentiating, giving

$$\left(\frac{dp}{dT}\right)_{\text{sat.}} = \left(\frac{4993.395}{T^2} - 0.04177279 + 0.000079126T\right) p \quad (7)$$

The values of the heat of vaporization, in calories per gram, calculated from the above, are given in Table V and were used to calculate the internal energy change which is also listed in Table V. The internal energy change was obtained by subtracting the pressure-volume work, $p \Delta v$, from the latent heat.

The thermodynamic equation,

$$\left(\frac{\partial U}{\partial v}\right)_T = T \left(\frac{\partial p}{\partial T}\right)_v - p \quad (8)$$

gives a general relation between the internal energy and the volume. From the Keyes²² equation we obtain

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

and Equation 8 becomes

$$\left(\frac{\partial U}{\partial v}\right)_T = \frac{RT}{v - \delta} - p = \frac{A}{(v + b)^2} \quad (9)$$

²⁰ The subscript 1 refers to the vapor phase and the subscript 2 to the liquid phase in all the following discussion.

²¹ Ref. 19, pp. 25, 38.

²² Keyes, *Proc. Nat. Acad. Sci.*, **3**, 323 (1917). $p = \frac{R}{v - \delta} T - \frac{A}{(v + b)^2}$.

Hence the internal energy change from v_2 to v_1 is obtained by integrating Equation 9

$$\left[\Delta U = \int_{v_2}^{v_1} dU = \int_{v_2}^{v_1} \frac{A}{(v+l)^2} dv = A \left(\frac{1}{v_2+l} - \frac{1}{v_1+l} \right) \right]_T \quad (10)$$

Equation 10 is true, provided the liquid phase is composed of the same type of molecules as the vapor phase or it might still be true if the molecules of the liquid were all doublets and the vapor specific volume large enough to make the term $\frac{A}{v_1+l}$ negligible. The change in internal energy on evaporation might, therefore, be accurately represented by an equation of the form

$$\Delta U = \frac{A}{v_2+l}$$

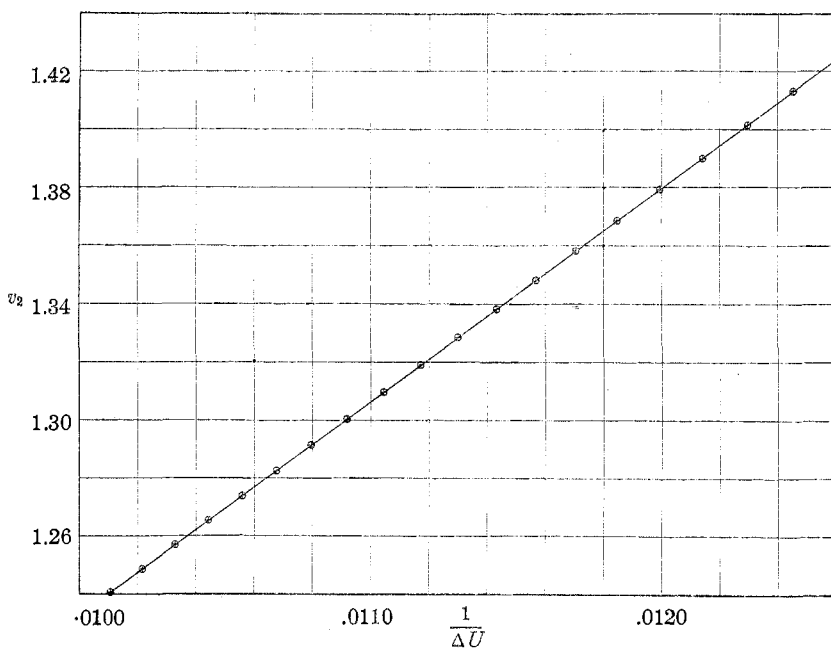


Fig. 5.

where v_1 is large. More conveniently arranged

$$\frac{1}{\Delta U} = \frac{v_2}{A} + \frac{l}{A} \quad (11)$$

Equation 11 is linear in v_2 and $1/\Delta U$. The plot given in Fig 5 shows how closely this deduction holds. The equation for the straight line drawn in Fig. 5 is

$$\frac{1}{\Delta U} = \frac{v_2}{73.423} - 0.006791 \quad (12)$$

where ΔU is in calories per gram and v_2 in cc. per gram.

Some information on the difference in specific heats of the saturated vapor and liquid may be obtained from the observed and derived quantities given above. The logarithm of the latent heat was plotted against the logarithm of the absolute critical temperature minus the absolute temperature. This gives almost a straight line. The equation of this curve, shown in Fig. 6, was obtained.

$$\log \lambda = 3.165779 - 1.423343 \log (T_c - T) + 0.3939349 [\log (T_c - T)]^2 \quad (13)$$

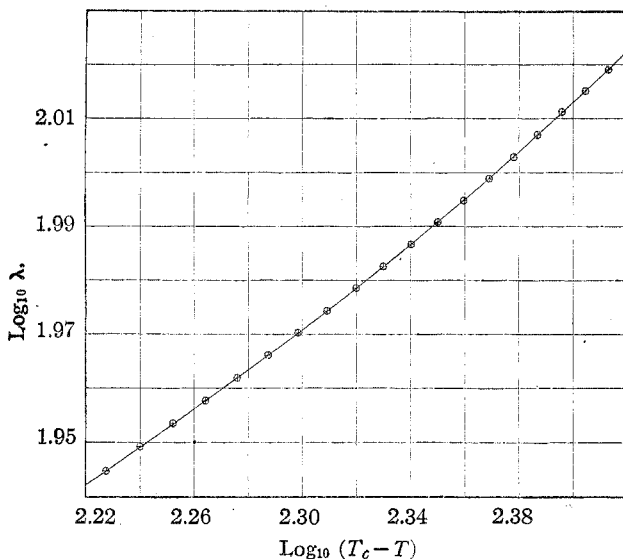


Fig. 6.

Equation 13 when differentiated gives

$$\left(\frac{d\lambda}{dT}\right) = [1.42334 - 0.78587 \log (T_c - T)] \frac{\lambda}{(T_c - T)} \quad (14)$$

By means of the thermodynamic equation

$$C_{s1} - C_{s2} = \left(\frac{d\lambda}{dT}\right) - \frac{\lambda}{T} \quad (15)$$

the difference in saturation specific heats of the vapor and liquid may be calculated. These values are given in Table V. If the specific heat of one phase is known, the value for the other phase may be obtained.

Battelli,²³ Regnault,²⁴ Hartung,²⁵ S. Lussano,²⁶ and Beattie¹⁸ have measured the specific heat of liquid ether. Regnault gives the equation

$$C_{s2} = 0.529 + 0.000592t$$

where t is degrees centigrade and C_{s2} is in calories per gram per degree. The values of these observers, together with the values for every 10°

²³ Battelli, Landolt-Börnstein, "Tabellen," 1912.

²⁴ Ref. 1, p. 262.

²⁵ Hartung, *Trans. Faraday Soc.*, 11, 64 (1915).

²⁶ S. Lussano, *Nuovo cimento*, 7, 304 (1914).

calculated from Regnault's equation, are given in Table VI. Since Regnault's equation seems to represent the data fairly well, it was used to calculate the specific heats of the liquid phase.

TABLE VI
SPECIFIC HEATS OF ETHER

Temp. ° C.	$C_{s_2} \equiv C_{p_2}$ Obs.	Observer Ref. no.	C_{p_1} calc.	C_{p_1} obs. ²⁸
-50	0.517	23
- 2	0.523	23
-40	0.505	24	0.317	...
-30	0.511	24	0.325	...
-20	0.517	24	0.337	0.355
-10	0.523	24	0.349	0.364
0	0.529	24	0.361	0.372
10	0.535	24	0.373	0.381
20	0.541	24	0.386	0.390
25	0.544	24	0.393	0.394
18.5	0.541	(obs. 17° to 20°) ²⁵
22.7	0.540	26
1.164	0.574	18
13.367	0.583	18

In the equation

$$C_{p_1} - C_{p_2} = C_{s_1} - C_{s_2} + T \left(\frac{\partial p}{\partial T} \right)_{\text{sat.}} \left[\frac{\partial v_1}{\partial T} - \frac{\partial v_2}{\partial T} \right]_p \quad (16)$$

the value of C_{s_2} is given from Regnault's data, the value of $C_{s_1} - C_{s_2}$ is obtained from Table VI, and $\left(\frac{\partial p}{\partial T} \right)_{\text{sat.}}$ from Equation 7.

The expression for $\left(\frac{\partial v_1}{\partial T} \right)_p$ was obtained by differentiating equation (6) and is

$$\left(\frac{\partial v_1}{\partial T} \right)_p = \frac{v - \beta}{T} \left(\frac{1}{1 - \frac{2A}{RT} \left[\frac{(v - \beta)^2}{v^3} \right]} \right)$$

$\left(\frac{\partial v_2}{\partial T} \right)_p$ as given by Tyrer²⁷ is 0.0020 at 0° and hence could be neglected in the calculations without introducing any error.

The values of C_{p_1} calculated from this equation are also given in Table VI. E. Wiedmann²⁸ gives the equation $C_p = 0.3725 + 0.0008536t$ for the specific heat of the vapor. Values calculated from this equation are given in Table VI. Of course the calculated values cannot be very accurate since $d\lambda/dT$ contains the second derivative of p as a factor and λ/T contains the first derivative. Moreover, the values of C_{s_2} are not very accurate.

In conclusion, we desire to thank Professor Keyes of this Laboratory

²⁷ Tyrer, *Z. physik. Chem.*, **87**, 175 (1914).

²⁸ Wiedmann, *Wied. Ann.*, **2**, 195 (1877).

at whose suggestion the investigation was started and whose advice and assistance were of great help during its progress.

Summary

1. The densities and vapor pressures of ether have been measured over the lower temperature range.
2. From these and an equation of condition, the latent heats of evaporation and the change in internal energy on evaporation were calculated.
3. A relation connecting the specific volume of the liquid and the internal energy change on evaporation is given.
4. From the latent heats there was obtained the difference in saturation specific heats of the vapor and liquid, and from these, when compared with Regnault's values for the liquid, some values of the specific heat of the vapor at constant pressure were deduced.

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**THE CONDUCTANCE OF SOLUTIONS OF SALTS IN PHENOL
AT 50°**

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Introduction.—The manner in which the conductance of an electrolyte in solution varies as a function of the concentration is largely governed by the dielectric constant of the solvent medium. In solvents of high dielectric constant, the equivalent conductance decreases continuously with increasing concentration up to very high concentrations. With solvents of intermediate dielectric constant—in the neighborhood of 20—the equivalent conductance decreases with increasing concentration at low concentration and apparently approaches a more or less constant value in the neighborhood of normal concentration. With solvents of dielectric constant lower than 20, the conductance decreases with increasing concentration at low concentration, and passes through a minimum at higher concentration, after which the conductance increases as the concentration increases. At concentrations considerably above normal, the conductance in all cases ultimately decreases with increasing concentration, presumably as a result of the influence of the increasing viscosity of the solutions. Finally, in solvents of very low dielectric constant the conductance increases with increasing concentration, beginning with the lowest concentrations at which reliable conductance measurements are available. This transformation of the form of the conductance curve as a consequence of the change in the value of the dielectric constant of the solvent medium is a very general phenomenon. It is strikingly illustrated by the conductance curves of a salt in a given sol-