CCLIV.—*The Vapour Pressure of Ethyl Acetate from 0° to 100°.*

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HAVING prepared large quantities of pure ethyl acetate for the work described in the preceding communication, the authors thought it worth while to find its vapour pressure at various temperatures, especially as they had at their command means of maintaining constant pressures not hitherto at the disposal of other workers (Trans., 1911, **99**, 984).

I.—For temperatures above 15° the boiling point was determined at constant pressure in the manner described in the above-mentioned paper (*ibid.*, p. 989). At each pressure a complete fractionation of 100 grams of pure ethyl acetate was made, the temperature recorded being that at which Δ per cent. was a maximum (see Wade, Trans., 1905, **87**, 1656).

TABLE I.

Experimental Boiling Points of Ethyl Acetate.

Pressure in mm.	Boiling point.	$dt/dp.$	Pressure. in mm.	Boiling point.	$dt/dp.$
60	16·20°	0·325	612	70·78°	0·048
73	20·00	0·28	760	77·15	0·04
78	21·30	0·27	900	82·40	0·035
175	38·48	0·14	980	85·05	0·032
327	53·66	0·08	1175	90·95	0·028
444	61·83	0·062	1444	97·82	0·024

Anschütz thermometers were used; they had been compared with standard thermometers, and well known fixed points had also been used in calibrating them. The temperatures are reduced to the hydrogen scale in the latitude of Paris.

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The vapour pressures and dt/dp plotted against the boiling points are represented in the two curves in Fig. 1.

A large-scale curve was drawn by plotting $\log p$ against the temperature. From this curve $\log p$ was read at a given temperature, and the corresponding pressure calculated. In this way the results given in column (a) of table II were found.

FIG. 1.

AB = dt/dp . CD = vapour pressure curve.

Another way in which the pressure at any temperature was found was by plotting the values of $\Delta \log p / \Delta t$ against the mean t . Then the vapour pressure at any temperature was calculated from the formula:

$$\log p_t = \log p_{t_1} + \frac{\Delta \log p}{\Delta t} \cdot (t - t_1).$$

The values are given in column (b) of table II; for convenience the values at 0° and 10° are added from table VI. The values obtained by Young and Thomas (Trans., 1893, **63**, 1216) are given in column (e).

TABLE II.

Temp.	From log. curve. (a.)	By log. difference from nearest experimental value. (b.)	Mean mm. (c.)	dp/dt . (d.)	Values (in mm.) of Young and Thomas. (e.)
0°			24.1	1.45	24.3
10			42.9	2.4	42.7
15	56.2	56.3	56.3	3.1	
20	72.6	73.0	72.8	3.7	72.8
30	118.5	119.0	118.7	5.7	118.7
40	186.2	186.7	186.4	8.0	186.2
50	282.5	282.6	282.5	11.4	282.2
60	415.4	414.8	415.1	15.7	415.4
70	596.5	595.7	596.1	20.8	596.3
80	832.8	833.6	833.2	27.1	832.7
90	1138.0	1140.0	1139.0	34.7	1130.0
100	1537.0	1535.0	1536.0	43.9	1515.0

The agreement with the results of Young and Thomas is very good, except at 90° and 100°, where the values for the pressure obtained by the authors exceeds the previous values by 9 mm. and 21 mm. respectively. Young and Thomas used the static method, which usually gives high values for the vapour pressure.

The authors carefully tested the point by doing three distillations, with the following results:

TABLE III.

Pressure in mm.	Boiling point.	Reduced to 1470 mm.
1471.7	98.49°	98.45°
1472.3	98.49	98.44
1470.7	98.46	98.44

These results correspond with a vapour pressure of 1535 mm. at 100° and a boiling point of 99.16° under a pressure of 1500 mm.

The value given in column (c) of table II was thus confirmed, proving that the values of Young and Thomas were low. In order to make further tests, the following curves were drawn: (a) p plotted against t ; (b) $\log p$ against t ; (c) first differences against mean t ; (d) second differences against mean t . The high values of column c fell exactly on these curves, whilst there was no doubt that the values of Young and Thomas were off the curves, especially in the case of the last two curves, which tend to magnify any errors.

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In the following table the boiling points of ethyl acetate at various pressures are given.

TABLE IV.

Pressure in mm.	Boiling point.	dt/dp .	Pressure in mm.	Boiling point.	dt/dp .
25	0·61°	0·68	700	74·72°	0·043
50	12·75	0·37	760	77·15	0·040
75	20·54	0·27	800	78·71	0·038
100	26·15	0·20	900	82·40	0·035
150	34·93	0·155	1000	85·70	0·0315
175	38·48	0·14	1100	88·77	0·0293
200	41·73	0·121	1200	91·65	0·028
300	51·44	0·086	1300	94·33	0·026
400	58·98	0·068	1400	96·82	0·0246
500	65·12	0·056	1500	99·16	0·0232
600	70·19	0·048			

II.—Vapour Pressures below 15°.

For low pressures the apparatus sketched in Fig. 2 was used.

The end (a) of the T-piece is joined to the manometer, and the end (b) to the manostat, air reservoir, and air pump. The thick-walled capillary (c) is drawn out to a long, very fine point, which presses against the bottom of the flask. The top of this capillary is joined to a Drechsel bottle containing concentrated sulphuric acid, so that only dry air enters the flask. The quantity of air required to promote steady boiling is very small, not more than 1 c.c. in thirty minutes, as the bubbles which enter through the fine capillary are extremely minute. The thermometer dips below the surface of the liquid. The flask rests on a thin layer of cotton-wool, and no artificial external heat is used.

When the pressure, as regulated by the manostat, had reached a constant value, the boiling point remained steady for an indefinite period. As soon as the pressure was altered the temperature adjusted itself with remarkable rapidity to a new constant value. With the room at 20° the temperature of the boiling liquid could be kept steadily at 0°, the deposit of dew forming a protective coating against the external heat.

FIG. 2.

The experimental results are given in table V, and are represented on the curve in Fig. 3.

TABLE V.

Pressure in mm.	Boiling point.	Pressure in mm.	Boiling point.
24.9	0.60°	30.6	4.0°
25.7	1.15	33.4	5.7
26.6	1.60	34.0	6.05
26.9	1.80	37.3	7.5
27.0	1.95	45.0	10.7
27.2	2.00	47.2	11.6
28.2	2.5	50.0	12.7

FIG. 3.

AB=vapour pressure curve. CD= dt/dp .

The values in column (a) of table VI were read from this curve. The first differences were smoothed, giving the final values in column (b) and the values of dt/dp in column (c). The latter values are plotted against the temperature in Fig. 3.

TABLE VI.

Temp.	(a.) Vapour pressure from curve, in mm.	(b.) Smoothed value of pressure, in mm.	(c.) dt/dp , in mm.
0°	24·1	24·1	0·69
1	25·6	25·6	0·66
2	27·2	27·2	0·625
3	28·7	28·8	0·595
4	30·5	30·5	0·535
5	32·3	32·3	0·535
6	34·2	34·2	0·51
7	36·3	36·2	0·48
8	38·5	38·3	0·455
9	40·7	40·5	0·435
10	43·1	42·9	0·415
11	45·6	45·4	0·395
12	48·3	48·0	0·38
13	50·9	50·7	0·36
14	—	53·5	0·35
15	—	56·4	0·34

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