CCLXXXV.—*A Differential Method for the Measurement of the Vapour Pressure of Liquids.*

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FOR the purpose of some projected experiments on the intensive drying of liquids, it seemed desirable to find a method of measuring precisely the vapour pressure of a liquid without the use of a mercury manometer, the mercury column of which might be expected to retain traces of water and so retard complete drying. It seemed that such a method could be developed were the liquid itself to be used as the manometric liquid (compare Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412). Some advantages of the method are (1) that the measurements are made in the absence of any foreign gas, Campbell's results (*Trans. Faraday Soc.*, 1915, **10**, 197) having shown that the vapour pressure of a liquid is, in certain cases, substantially altered by the presence of a gas; (2)

that the use of a relatively light liquid as the manometric substance materially increases the accuracy of the determination; and (3) that in dealing with intensively dried liquids the vapour-pressure measurements would be made in a vessel of simple form which could be sealed off from the main apparatus and examined at leisure. The method finally evolved was to seal up the liquid, free from gas, in a simple **U**-tube, and then to observe the difference of level between the liquid in the two limbs maintained at different constant temperatures, and to repeat the observations for successive steps in temperature difference. Unfortunately, it seems impossible to establish absolute values without one such value for reference, but given that one value, the differential curve serves as a valuable check on existing curves and can be used to advantage where the slope of the curve is of greater importance than the absolute position. The method was worked out and tested by experiments on benzene and water, and was then applied to a redetermination of the vapour-pressure curve for bromine. Such a redetermination seemed very desirable, as our knowledge of the vapour pressure of liquid bromine rests almost solely on the experiments of Ramsay and Young (J., 1886, **49**, 453).

FIG. 1.

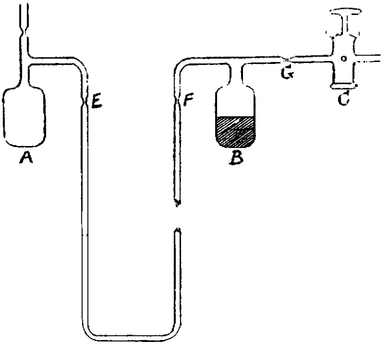
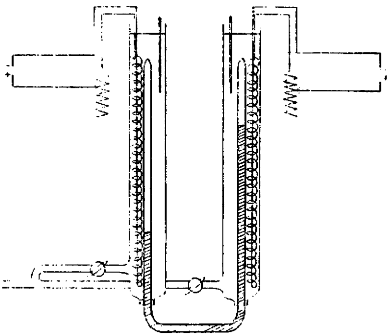


FIG. 2.



The apparatus used consists essentially of a **U**-tube of about 6 mm. bore and with limbs about 60 cm. long and 10 cm. apart. The tube is filled with the liquid to be examined by means of a subsidiary apparatus which is sealed off prior to making the observations. The **U**-tube and filling apparatus are shown in Fig. 1. The purified liquid is placed in bulb A, frozen with a mixture of solid carbon dioxide and ether, and the apparatus exhausted through the mercury-sealed tap, C, by means of a mercury vapour pump. On being allowed to melt, the solid in A gives up the major part of the dissolved gases and by a sufficient number of repetitions of this process the liquid can be rendered gas-free. A large number of experiments gave evidence that the process must be repeated at least three times, and that some liquids retain gas more persistently than others and may require to be frozen and melted in a vacuum six to eight times. When the liquid is almost gas-free, it is distilled slowly into B so as to drive before it any gas which may have been absorbed by the walls of the tube. Bulb A is then taken off by sealing the constriction E. The liquid, now in B, is again frozen, the apparatus exhausted as completely as possible, and the vacuum tap, C, removed by sealing at G. Finally, the liquid is distilled into the U-tube until the latter is a little more than half full, and the bulb B is disconnected by sealing the constriction F.

Fig. 2 shows the U-tube set up for measurements. The two limbs are enclosed in wide glass jackets filled with water, the temperature of which can be kept constant to within 0·05° by means of the internal heating coils. The water is stirred very efficiently by a steady stream of air. The temperature of the jackets is indicated by the two standardised thermometers readable to 0·01°.

The procedure is as follows. The temperature of the left-hand jacket is raised above that of the right-hand one until there is a considerable difference between the levels of the liquid in the two limbs of the U-tube. The temperature of each jacket is then kept constant for 30 minutes, by which time equilibrium is established, and the difference of levels read by means of a cathetometer reading to 0·01 mm. This is repeated after adjusting the temperature of the right-hand jacket to that which the left-hand one had in the previous case and again establishing a difference of levels by raising the temperature of the left-hand jacket. By this means one obtains a series of differential readings which can be reduced to mm. of mercury at 0°, account being taken of the change in density of the liquid with temperature.

Vapour Pressure of Benzene.

The data for benzene (Table I) obtained by this method illustrate clearly how the differential readings are transformed into mm. of mercury. The numbers (1) and (2) refer to the two limbs of the U-tube.

The benzene was purified by fractional distillation, the fraction used distilling within a range of 0·1°. The vapour pressure of benzene at 17·4° being accepted as 65·3 mm. Hg (Young, J., 1889, **55**, 486), the values at higher temperatures follow from the differential measurements. These are in Table II and are shown plotted against temperature in Fig. 3.

TABLE I.

Temp.		Height of column (cm.).		Density of benzene at temp. of jacket.		Height of equivalent column of water (cm.).		Differential V. P. in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
23·6°	17·4°	10·52	46·02	0·874	0·880	9·20	40·53	23·20
29·2	23·6	8·33	48·50	0·868	0·874	7·23	42·38	26·04
33·5	29·2	10·03	47·34	0·863	0·868	8·66	41·10	24·03
37·2	33·5	10·84	46·96	0·859	0·863	9·31	40·53	23·13
40·8	37·2	8·77	49·10	0·855	0·859	7·50	42·18	25·69
43·7	40·8	10·80	47·67	0·852	0·855	9·20	40·76	23·37
46·5	43·7	9·53	48·92	0·849	0·852	8·09	41·68	24·88
48·8	46·5	11·43	47·47	0·846	0·849	9·68	40·30	22·69
51·3	48·8	8·93	49·82	0·844	0·846	7·54	42·18	25·66
53·2	51·3	12·73	46·72	0·842	0·844	10·72	39·43	21·27
54·8	53·2	13·63	46·12	0·840	0·842	11·45	38·84	20·29

TABLE II.

Temp.	23·6°	29·2°	33·5°	37·2°	40·8°	43·7°
V. P. (mm.) ...	88·5	114·5	138·6	161·7	187·4	210·8
Temp.	46·5°	48·8°	51·3°	53·2°	54·8°	
V. P. (mm.) ...	235·6	258·3	284·0	305·3	325·6	

It can be seen that even up to temperatures of 50° and above the new values fall well on Young's curve. It is noteworthy that any error in the method is cumulative, and if serious, would show more and more clearly as one approached the higher temperatures. Above 50°, it was found difficult to keep the temperature of the jackets within the set limits of constancy and therefore the determinations were not carried beyond that point.

Vapour Pressure of Water.

Similar experiments to the above were carried out with distilled water and yielded equally good results. These are in Table III and are plotted in Fig. 3, together with the accepted values (see Landolt-Börnstein, " Physikalisch-Chemische Tabellen," 1923).

TABLE III.

Temp.		Height of column (cm.).		Density of water at temp. of jacket.		Height of column corrected for density (cm.).		Differential V. P. in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
33·8°	15·1°	10·40	45·55	0·994	0·999	10·34	45·51	25·89
43·7	33·8	10·20	47·05	0·991	0·994	10·11	46·76	26·98
49·4	43·7	13·70	44·30	0·988	0·991	13·54	43·90	22·36
51·9	43·7	5·20	51·50	0·987	0·991	5·13	51·10	33·83
26·9	15·1	20·10	38·65	0·996	0·999	20·02	38·61	13·69
39·1	26·9	11·10	46·35	0·992	0·996	11·01	46·16	25·87
46·8	39·1	11·60	45·95	0·989	0·992	11·48	45·57	25·09

In this case the assumed value for the vapour pressure is 12·91 mm. at 15·1°, taken from the accepted curve; it is evident that the method again holds good over the temperature range covered by the experiments, *viz.*, 15—50°. Table IV gives the actual vapour pressures derived from the differential results.

TABLE IV.

Temp.	26·9°	33·8°	39·1°	43·7°	46·8°	49·4°	51·9°
V. P. (mm.)	26·6	38·8	52·5	65·8	77·6	88·1	99·6

FIG. 3.

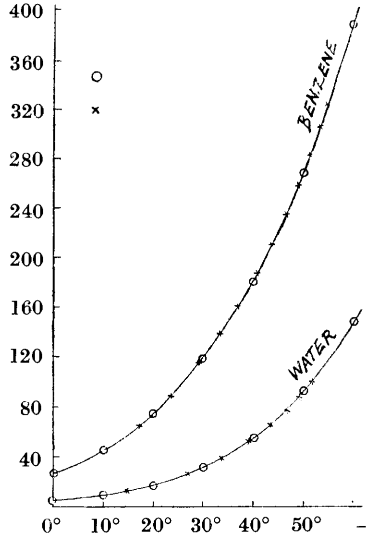
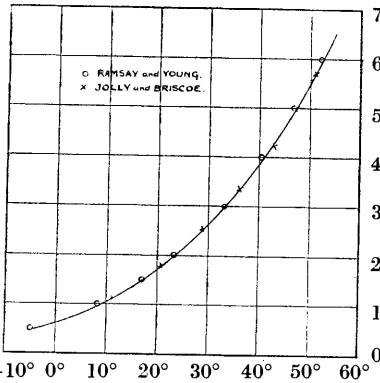


FIG. 4.



Temperature.

⊙ { *Accepted values for water.* / *Young's values for benzene.*
× *Differential values.*

Ordinates represent V. P. in mm. Hg.

Redetermination of the Vapour Pressure of Bromine.

At first it was supposed that if one could obtain a series of differential vapour pressures, construct a curve on some assumed value, and extrapolate to some low temperature at which the vapour pressure is sensibly zero (*i.e.*, within the experimental error), then it would be possible to determine the error of the assumed value. The assumed curve, being constructed from differential measurements, would have the correct slope but probably the wrong absolute position. Hence, by shifting it bodily by an amount equal to the difference between the extrapolated value at the very low temperature and zero pressure, the true curve for bromine could be obtained.

An attempt was made to do this, but instead of plotting pressure against temperature, the latter was plotted against $T \log p$, a straight line resulting. Although this could be extrapolated easily to lower temperatures, it deviated in the region of — 60° and beyond, turning towards — ∞ and thus leading to erroneous conclusions. It is about the temperature of — 60° that the vapour pressure of bromine can be assumed to be zero.

It became necessary, therefore, to get some independent value for the pressure at any one temperature in order to fix the absolute position of the vapour-pressure curve; the value accepted was that of Ramsay and Young at 20·7°, namely, 178·7 mm. of mercury.

The bromine used for the differential measurements was purified and dried by distillation successively from potassium bromide and concentrated sulphuric acid, the head and tail fractions being rejected in each case. The differential measurements are shown in Table V.

TABLE V.

Temp.		Height of column (cm.).		Density of bromine at temp. of jacket.		Height of equivalent column of water (cm.).		Differential *V. P.* in mm. Hg.
(1).	(2).	(1).	(2).	(1).	(2).	(1).	(2).	
20·7°	11·1°	16·45	45·40	3·117	3·152	51·28	143·10	67·57
28·9	20·7	14·75	47·67	3·088	3·117	45·55	148·60	75·80
36·1	28·9	13·62	49·85	3·064	3·088	41·73	153·90	82·50
42·8	36·1	12·76	51·13	3·041	3·064	38·80	156·70	86·78
47·2	42·8	14·44	49·55	3·026	3·041	43·70	150·70	78·75
51·0	47·2	17·13	47·65	3·012	3·026	51·60	144·20	68·16

On combining Ramsay and Young's value at 20·7° with the differential values the following absolute values were obtained :

Temp.	11·1°	20·7°	28·9°	36·1°	42·8°	47·2°	51·0°
V. P. (mm.)	111·1	178·7	254·5	337·0	423·8	502·5	570·7

Fig. 4 shows these values plotted together with those of Ramsay and Young. It is evident that the form of Ramsay and Young's curve is closely confirmed by the differential measurements.

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