

Part I.—The Vapour Pressures of Acetone.

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These measurements were undertaken at the request of Dr. H. E. Watson who required the values of the vapour tensions of acetone at low temperatures in connection with experiments on the losses of acetone during distillation.

The only previous measurements of the vapour pressures of acetone are by Regnault (*Mém. de l'Acad. Petersb.* 1862, 26, 339) and they are for temperatures above 20°C.

An interpolation formula calculated from Regnault's results is given by Ramsay and Young (*Physico-Chemical Tables*, John Castell Evans. Vol. I p. 512). Although there is a remarkably good agreement between the observed and calculated figures in the whole interval from 30° to 130°C, unfortunately this agreement ceases to exist for the extreme values, the errors being 10% and 29% at 20° and 140°C respectively. From this it is evident that Ramsay and Young's formula serves no purpose for temperatures lower than 30° and any extrapolation below 20° is out of the question.

Experimental.

The method selected for the present series of determinations was the statical one, where the liquid under examination is enclosed in an air-free vessel so as to remain in equilibrium with its own vapour. The main objection to this method lies in the difficulty of completely removing all traces of air from the substance under examination. This was overcome by repeatedly freezing the acetone in liquid air and by exhausting the space above the frozen substance by means of a Toepler mercury pump. The vapour pressure of solid acetone at the boiling point of liquid air is exceedingly small and the above method for removing any dissolved air was found to be very effective. Another important condition for the successful working of the statical method is to expose as frequently as possible a fresh surface of the liquid to the vapour. This was fulfilled by using a platinum stirrer which was continuously kept in action during an experiment with the

help of an electro-magnet and metronome. The stirrer also ensured the uniformity of the temperature of the liquid.

Fig. 1 shows diagrammatically the general arrangement of the apparatus. The manometer M had two branches each of 25 mm. bore meeting below in a common tube. The lower extremity of this tube was open, and dipped into a vessel of mercury resting on a platform which could be raised and lowered by means of screws. It was thus possible to take all readings with a rising meniscus. Both the mercury surfaces were shaded in exactly the same way. One branch of the manometer was connected to a pump through a phosphorus pentoxide tube, and during an experiment it was maintained thoroughly exhausted and dry. The other branch was in direct communication with the tube containing acetone. The difference of levels in the manometer was therefore always the actual vapour pressure. The heights of the mercury columns were read off directly by means of a vertical cathetometer placed at a distance of one meter and graduated to read to 0.01 mm. (Fig. 1. p. 56)

By exhausting the whole manometer and connecting the two sides by means of the tap P, the cathetometer crosswire could be levelled, and any zero correction determined.

The acetone under examination was contained in a thin-walled glass tube 24 mm. diameter, 270 mm. long and provided with a side tube fused on directly to one leg of the manometer. A platinum stirrer was placed inside the tube and the quantity of the liquid adjusted to such a height that its surface was always broken by the action of the stirrer. This tube was closed by means of a rubber cork carrying a thermo-couple (not shown in the diagram) and no leakage was to be detected even on long standing.

For maintaining a constant temperature a large Dewar's cylindrical silvered vacuum vessel, filled with a suitable freezing mixture was used.

For determining temperatures a mercury and a pentane thermometer were at first tried, but it was found that the former was difficult to read at the lower temperatures and the latter possessed a considerable lag, thus proving unfit for any comparatively rapid determinations as required in these experiments. A copper-constantan thermo-couple consisting of two pairs of junctions in series was therefore made and calibrated. Alternate junctions were placed together in thin-walled glass sheaths about 5 mm. diameter; junctions 1 and 3 were always immersed in ice and junctions 2 and 4 in the bath of unknown temperature.

The calibration was effected by measuring directly the thermo-electromotive force in micro-volts by means of a direct reading potentiometer. A small Weston element was previously compared with a standard element and was used for all measurements on the potentiometer.

A galvanometer of the uni-pivot type was simultaneously calibrated in terms of micro-volts and in terms of temperatures throughout its scale.

The degree of accuracy which it was hoped to attain in making the temperature measurements was 0.1°C . Several difficulties were however experienced and it is doubtful whether the values can be considered accurate to more than 0.3° or perhaps at best 0.2° . An attempt was first made to use the melting points of bromobenzene, mercury and chlorobenzene as given by Timmermanns (Proc. Roy. Dub. Soc. 1912, 25, 310) for the fixed points. By carefully drying and redistilling bromo- and chlorobenzene into a closed freezing-point apparatus and stirring with a magnetic stirrer, sharp freezing points were obtained. The freezing point of mercury was also determined several times with consistent results and in addition the transition point of sodium sulphate.

The E. M. F. s in micro-volts and the assumed temperatures were :—

	E. 10^{-6}v	$t^{\circ}\text{C}$
Sodium sulphate	+1212	+32.38
Bromobenzene	-1033	-30.6
Mercury	-1309	-38.89
Chlorobenzene	-1479	-45.0

The E. M. F. s actually measured were twice the above, as two couples in series were used.

On attempting to draw a curve through these points, however, there seemed to be a very decided irregularity if the freezing points of the organic substances were to be included. Consequently two parabolic formulae were constructed and examined to find out, if possible, the probable extent of any deviation in the region between 0° and -30° . The value -38.89° recently obtained by Henning (Ann. d. Physik 1914, 43, 282) was taken for the freezing point of mercury.

A curve passing through the freezing point of mercury, zero and the transition point of sodium sulphate is given by the equation $E = 35.71 t + 0.0529 t^2$ while one through zero, the

freezing point of mercury and a sample of liquid air for which t was assumed to be -190° and E found to be -4710 micro-volts is represented by $E = 35.95 t + 0.0588 t^2$. All temperatures between 0° and -50° corresponding to the same E. M. F. and calculated by these two equations agree with each other within 0.1° , so that it is highly probable that the equations represent the true shape of the curve. Consequently it was decided to use the first equation for determining temperatures and to neglect the values from the freezing points of the organic liquids. It is interesting to note that the values obtained for bromobenzene and chlorobenzene respectively, when this was done, were -30.3° and -44.3° or 0.2° and 0.6° higher than Timmermanns' values, allowing for the difference between the mercury values adopted. It is difficult to account for these discrepancies.

The galvanometer deflection d was very nearly a linear function of the E. M. F. as may be seen from the following table.

$d \times 30$	E
300	294
600	594
900	899
1200	1209
1500	1525

It would naturally have been possible to obtain an equation connecting directly the galvanometer deflection and the temperature, but it was thought preferable to introduce the E. M. F. s as well because a galvanometer constant may vary, while the E. M. F. is an absolute measure available for future reference, also one parabolic equation was not suited to express both the galvanometer scale and the temperature variations with the E. M. F.

Before starting an experiment, the glass tube, platinum stirrer and thermo-couple were carefully cleaned and washed with the pure acetone. The cork was inserted into the tube, cemented with a mixture of beeswax and resin and the acetone in the glass tube was frozen in liquid air with constant stirring. The air, contained in the space above, was removed by means of a mercury pump. The acetone was then allowed to warm up to room temperature and frozen in liquid air for the second time. In this operation only a small quantity of occluded air could be obtained and on repeating this process a few times, it was possible to remove all the occluded air. At this stage the measurements of vapour pressure were made. By changing the temperatures of the

liquid, in which the acetone tube was immersed, and noting the corresponding pressures as indicated by the manometer, a number of points could be obtained.

The thermostat vessel was filled with ice for the temperature of 0°C .; for temperatures down to -15°C . various mixtures of ice and salt were employed and the temperature could be held constant for long periods. Alcohol cooled in liquid air supplied the other temperatures as far as -50°C . A number of observations were taken in each case, with rising and falling temperatures, since it was not quite easy to maintain these low temperatures constant longer than a quarter of an hour. The difference between the values obtained was, however, very slight, as it was found that equilibrium between vapour and liquid was reached quite rapidly, the usual time being about two minutes.

Results.

The experiments extended for a considerable period and there was good agreement between results obtained at different times. The accompanying table I contains the values observed from -50° to 0°C , and also a few figures above the latter temperature obtained with a calibrated mercury thermometer, for a sample of acetone which had been made by a fermentation process. It appeared to be very pure but its specific gravity at 25° was only 0.7909 which corresponds to a water content of 2.0% according to the measurements of Squibb (*Journ. Amer. Chem. Soc.* 1895, 17, 187.) The measurements could not be extended to higher temperatures, as it was not possible to measure pressures above 150 mm. in the apparatus.

The first column gives the galvanometer deflexions.

The second column gives the thermo-electromotive force expressed in micro-volts.

The third column gives the observed vapour pressures in millimeters of mercury corrected for temperature and reduced to sea level and 45° latitude, the latter being an appreciable quantity in Bangalore.

The fifth column gives the pressures in millimeters calculated from a smoothed curve as explained below.

TABLE I.
Vapour pressures of Fermentation Acetone, $d_{20}^{25} = 0.7909$.

defl.	E. M. F. 10^{-6} volts.	t°C	p. mm. (obs.)	p. mm. (smoothed)
		14.4	139.0	139.6
		14.2	138.2	138.0
		10.1	112.7	113.2
		5.2	88.63	88.63
0.0	0.0	0.0	67.22	67.22
- 2.1	- 61	- 1.7	61.90	61.50
- 4.1	- 121	- 3.4	55.79	56.17
- 8.1	- 237	- 6.7	46.87	46.87
- 8.2	- 240	- 6.8	46.68	46.68
- 8.3	- 243	- 6.9	46.48	46.46
- 8.9	- 261	- 7.4	45.10	45.10
-10.8	- 318	- 9.0	41.09	41.03
-11.0	- 324	- 9.2	40.73	40.64
-12.1	- 357	-10.1	38.71	38.47
-12.2	- 360	-10.2	38.16	38.25
-12.9	- 380.5	-10.8	37.04	37.04
-15.0	- 443.5	-12.7	33.03	33.19
-16.9	- 500.5	-14.3	30.13	30.12
-17.2	- 509.5	-14.6	29.72	29.70
-17.8	- 527.5	-15.1	28.63	28.63
-18.8	- 558	-16.0	27.42	27.36
-20.1	- 597	-17.2	25.27	25.36
-22.0	- 654.5	-18.9	22.73	22.92
-24.6	- 734	-21.2	19.68	19.80
-26.4	- 788.5	-22.9	18.05	17.85
-27.1	- 810	-23.5	17.36	17.21
-27.9	- 834.5	-24.2	16.64	16.48
-28.0	- 837.5	-24.3	16.29	16.44
-31.5	- 945	-27.6	13.15	13.26
-32.8	- 985	-28.8	12.30	12.26
-33.1	- 994	-29.1	11.88	12.03
-34.1	-1025	-30.0	11.34	11.30
-34.9	-1050	-30.8	10.72	10.72
-35.1	-1056	-31.0	10.60	10.62
-37.6	-1133.5	-33.4	8.90	9.00
-38.2	-1152.5	-34.0	8.66	8.64
-38.3	-1156	-34.1	8.70	8.57
-41.0	-1240	-36.7	7.15	7.15
-41.8	-1266	-37.6	6.71	6.74
-43.1	-1307	-38.8	6.09	6.13
-44.1	-1338	-39.8	5.79	5.71
-44.8	-1361	-40.5	5.48	5.39
-44.9	-1364	-40.6	5.29	5.34
-45.0	-1367	-40.7	5.28	5.33
-47.1	-1433	-42.9	4.51	4.51
-47.7	-1452	-43.5	4.27	4.27
-48.5	-1477	-44.3	3.97	4.03
-48.6	-1480	-44.4	4.02	4.02
-49.0	-1493	-44.8	3.94	3.87
-51.0	-1556	-46.8	3.24	3.24
-51.8	-1581	-47.7	3.02	3.02

Table II gives similar results for a sample of commercial "extra pure" acetone which was dried with calcium chloride before use. The centre fraction with boiling point constant to within 0.1° was distilled directly into the measuring tube. Two such samples were prepared, and were slightly different from each other, the one having $d_{25}^{25} 0.7871$ corresponding to 0.74 per cent of water (Squibb loc. cit.), and the other having $d_{25}^{25} 0.7865$ corresponding to 0.48 per cent of water. This difference, however, did not appreciably affect the vapour pressures of the two samples and therefore the results obtained with both of these are included in the table.

TABLE II.

Vapour pressures of commercial "extra pure"
Acetone $d_{25}^{25} = 0.7865$.

defl.	E. M. F. 10^{-6} volts.	$t^\circ\text{C}$	p. mm (obs.)	p. mm. (smoothed)
18.8	557.5	15.3	154.39	154.4
17.8	527.5	14.5	148.32	148.4
17.5	518.5	14.2	146.63	146.6
0.0	0.0	0.0	69.51	69.51
— 4.1	— 121	— 3.4	57.90	58.12
— 4.9	— 141	— 4.1	57.45	56.26
— 7.6	— 223	— 6.3	49.67	49.58
—13.2	— 389.5	—11.1	38.08	37.81
—14.5	— 428.5	—12.2	35.13	35.22
—14.7	— 434.5	—12.4	34.81	34.82
—16.8	— 497.5	—14.2	31.48	31.30
—20.2	— 600	—17.3	26.25	26.08
—23.1	— 688	—19.9	22.36	22.29
—24.2	— 721.5	—20.9	20.99	20.95
—24.6	— 733.5	—21.2	20.59	20.49
—24.9	— 743	—21.5	19.96	20.12
—31.1	— 933	—27.2	14.24	14.07
—31.6	— 948	—27.7	13.85	13.63
—34.1	—1025	—30.0	11.64	11.69
—35.0	—1053	—30.9	11.14	11.04
—35.5	—1068.5	—31.4	10.68	11.69
—35.9	—1081	—31.8	10.40	10.39
—36.1	—1087	—32.0	10.27	10.24
—38.5	—1162	—34.3	8.83	8.75
—41.0	—1240	—36.7	7.48	7.39
—47.9	—1458	—43.7	4.43	4.37

To eliminate, as far as possible, experimental errors the values found were smoothed as follows.

The logarithms of the pressures were plotted against the temperatures giving an approximately straight line. This could be represented by the equation $Y=0.028X+1.80$ where Y is the logarithm of the pressure and X the corresponding temperature.

The length of the perpendicular upon this line from a point X^1, Y^1 is proportional to $Y^1-0.028 X^1-1.80$. The lengths of these perpendiculars from all experimental points were calculated and another curve was constructed in which the lengths of the perpendiculars were plotted against respective temperatures. All slight deviations were magnified in this diagram and it was therefore possible to run a smooth curve through the various points. From this curve the "smoothed" pressures were calculated back for the given temperatures.

Separate smooth curves were constructed for Tables I and II and it is to be seen that the vapour pressures in the first sample are lower than those in the second; this is also natural since the substance employed in later experiments contained less water.

It is also to be seen that the corresponding vapour pressures in both the tables are proportional, the ratio being 0.9670 throughout the series.

Values are calculated for the vapour pressures of acetone from the results entered in table II for definite intervals of temperature. They are given in the accompanying table III.

TABLE III.

Vapour pressures of Acetone.

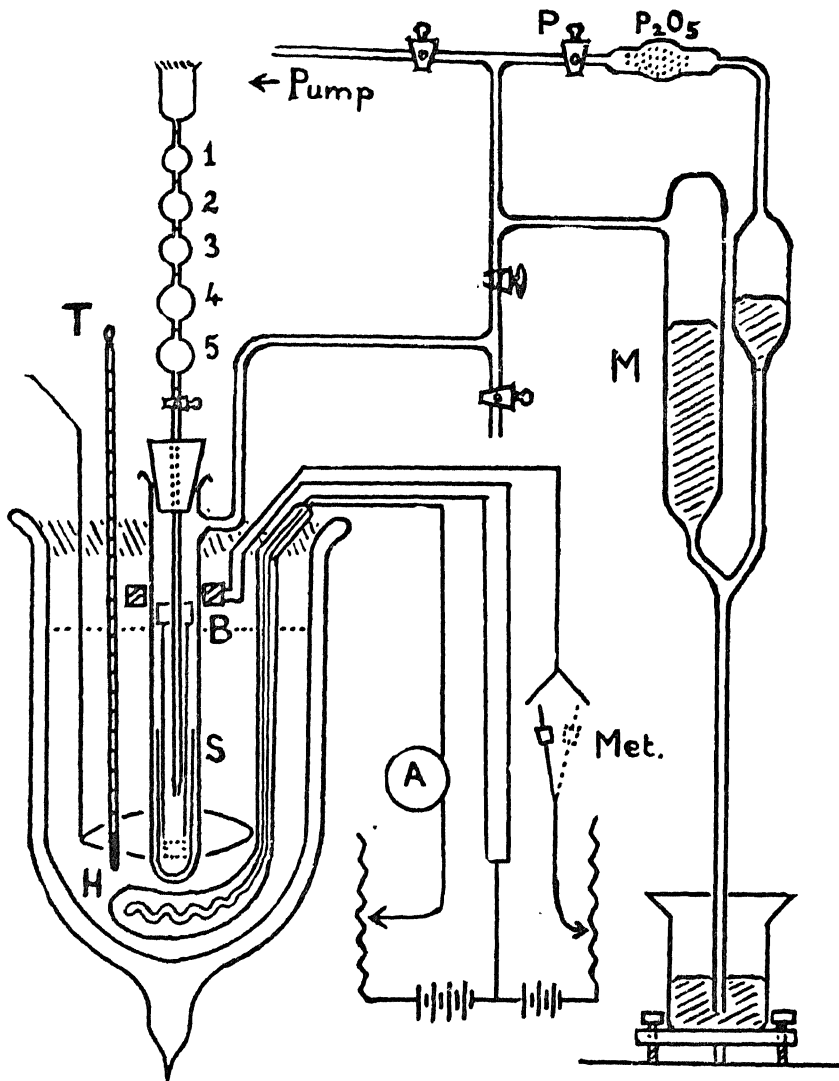
t°C	p. mm.
+15	151·8
+10	117·4
+ 5	90·36
0	69·51
- 5	53·27
-10	40·12
-15	30·02
-20	22·05
-25	16·26
-30	11·70
-35	8·32
-40	5·81
-45	3·92
-50	2·54

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DIAGRAM 1

(pp. 48, 60)



1,2,3,4,5 WATER BULBS

A AMPERE-METER

B MAGNETIC STIRRER

H ELECTRIC HEATER

M MANOMETER

Met METRONOME

S SILVER SOLUTION-TUBE

T THERMOMETER

DIAGRAM 2

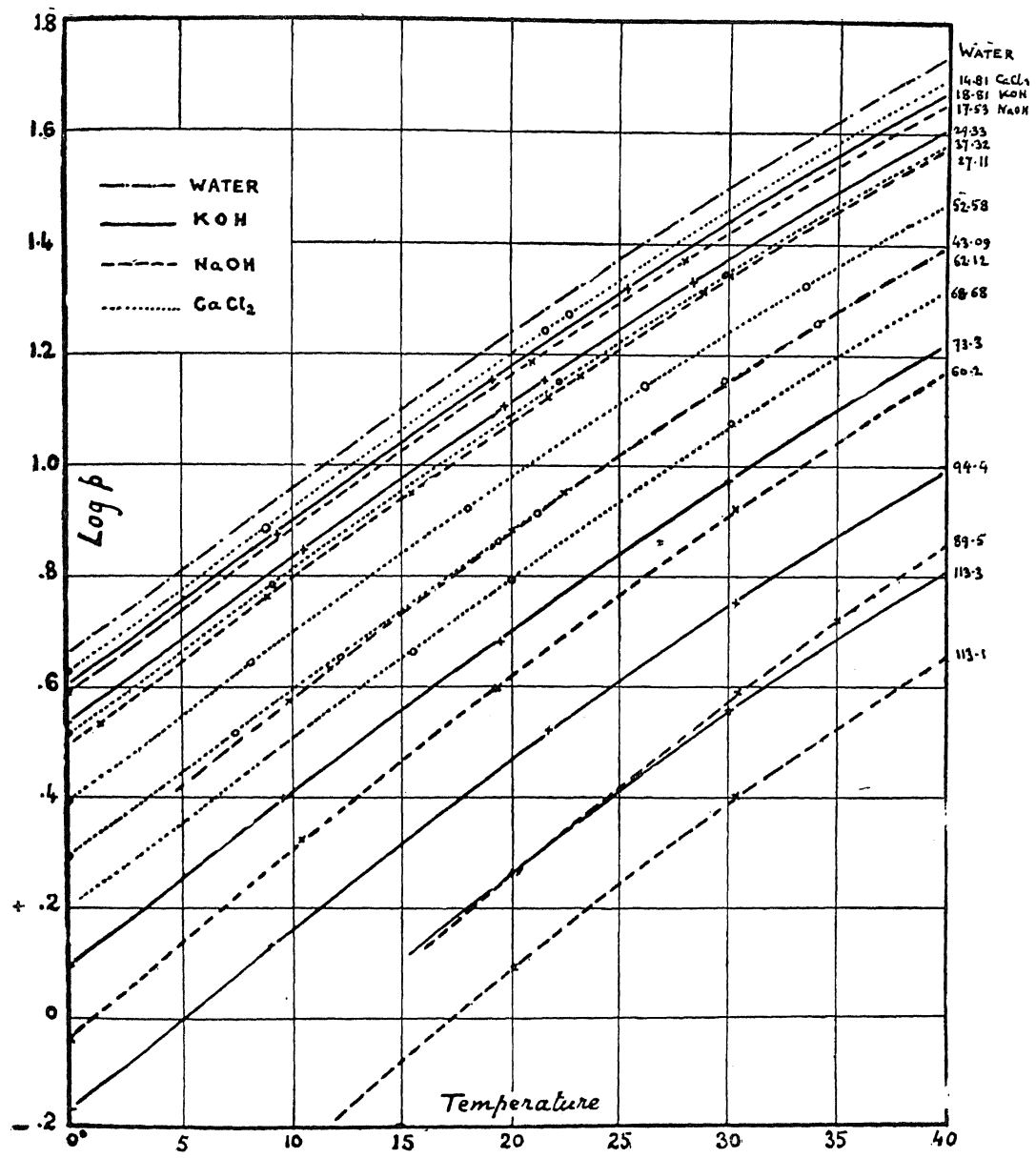


DIAGRAM 3

