XVIII. *Influence of Change of Condition from the Liquid to the Solid State on Vapour-Pressure.*

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[Plates 18, 19.]

1. The object of this paper is to furnish an experimental proof of the theory advanced by Professor James Thomson (Brit. Assoc. Reports, 1871 and 1872, and Proc. Roy. Soc., vol. xxii., 27), that the pressure exerted by the vapour of a solid substance at a given temperature is less than that of the vapour of the substance in the liquid form at the same temperature. This theory was simultaneously brought forward by Kirchhoff (Pogg. Ann., vol. ciii., p. 206).

2. In confirmation of this theory, offered as a result of thermodynamic considerations and demonstrations, Professor Thomson made use of empirical formulæ, devised by M. Regnault, to represent the different parts of the experimentally derived curve for expressing relationship between temperature and pressure of water-gas in contact with ice and with water; and he showed that Regnault's results, when rightly interpreted, pointed to a discontinuity in the curve, occurring at a temperature nearly coincident with 0°, the melting-point of ice under normal pressure. Although Professor Thomson's conclusions bear remarkable testimony to the extreme accuracy of Regnault's work, yet the differences of pressure in the case of water and ice are so minute as to require, for trustworthy determination, much greater refinement than Regnault's methods admitted of.

3. That Professor Thomson's conclusions have not received general acceptance is best shown by the following translation from one of the most recent works on thermal chemistry, Naumann's 'Thermochemie' (Brunswick, 1882), p. 178:—"With naphthalene, a substance which is solid at 78°, when the temperature is raised, but when previously melted and cooled to 78° remains liquid, adhering in liquid drops to the walls of the vacuum-tube, I was able to observe that its vapour exerts the same pres-

sure whether evolved from and condensing to the solid or the liquid form. In accordance with these observations are former results of experiments on the vapour-pressures of ice and water, benzene, ethene bromide, acetic acid, cyanogen chloride, and carbon tetrachloride, all of which prove that in the passage of a substance from the solid to the liquid state no noticeable alteration in the curve of vapour-pressure occurs, but the curve preserves perfect regularity, both before and after the change."

4. In the following pages an experimental proof of the correctness of Professor JAS. THOMSON's theory will be given for camphor, benzene, acetic acid, and water. As these substances are representatives of very different chemical types, the law may be held to apply to all stable bodies in the liquid and solid states.

5. From its high tension at the melting-point, camphor promised results which might be expected to throw light on this question. The experiment was performed as follows :—

A barometer-tube was nearly filled with freshly distilled and filtered mercury, connected with a triple SPRENGEL pump, and a vacuum established. The mercury was then boiled throughout the whole length of the tube, by heating it from below upwards, with the flame of a BUNSEN burner, so as to remove air and moisture. Disconnecting from the pump, some fragments of previously fused pure camphor were placed on the surface of the mercury and kept in position by means of a coil of platinum gauze. The tube was again exhausted, and dry mercury was allowed to flow into the vacuous tube so as to cover the camphor and gauze. The tube was then disconnected from the SPRENGEL pump, and inserted in a trough of dry mercury. By this means the entire absence of air and moisture was ensured, and the method is a more convenient one than that described in the paper which we had the honour to lay before the Society in June of last year, entitled, "The Influence of Pressure on the Temperature of Volatilization of Solids" (Phil. Trans., 1884, p. 37).

The experimental tube was heated by means of aniline-vapour. Having previously made a set of numerous determinations of the vapour-pressure of aniline at different temperatures, we were able, by regulating the pressure, to surround the barometer-tube containing the camphor with vapour at any desired temperature between 120° and 184°·5.

It is not here necessary to give detailed observations of the vapour-pressures of camphor at lower temperatures; suffice it to say that they confirmed those obtained by this, and by another method described in the paper already referred to. For the purpose of this memoir we shall confine ourselves to pressures at temperatures near the melting-point.

6. The results were calculated according to the formulæ :—

$$P' = B - \{b - \beta - (l \times 0{\cdot}000181\ t') + p_{T}\},\ \text{and}$$

$$P = P' - (P' \times 0{\cdot}000169\ t) = \left(P' - P'\frac{0{\cdot}34}{100}\ \text{for}\ t = 20^\circ\right)$$

P = Pressure of vapour in millimeters of mercury, reduced to 0°.

P' = Pressure of vapour in millimeters of mercury at temperature of room.
B = Barometric height ,, ,, ,, ,,
b = Height of mercury in experimental tube.
β = Height of mercury in trough.
p_T = Pressure of mercury vapour at temperature T.
T = Temperature of aniline-vapour.
t = Temperature of room.
$t' = T - t$.
$l = b - \beta$.

VAPOUR-PRESSURES of camphor.

P'.	B.	b.	β.	$l \times 0\cdot000181\, t'$.	p_T.	P.	T.	State.
95·2	764·7	702·8	27·2	9·0	2·9	94·9	136°·0	Solid.
152·6	,,	645·1	28·8	8·7	4·5	152·1	149·8	,,
274·9	,,	520·0	31·7	6·4	7·9	274·1	168·0	,,
328·9	760·7	459·1	33·3	3·3	9·6	327·6	174·6	,,
351·8	764·7	441·3	33·7	4·7	10·0	350·6	176·7	,,
364·8	,,	427·9	34·1	4·4	10·5	363·6	178·3	Liquid.
372·5	760·7	414·0	34·3	2·1	10·6	370·3	178·9	,,
380·0	,,	406·2	34·5	1·9	10·9	378·7	179·5	,,
387·2	,,	399·0	34·8	1·7	11·0	385·9	180·3	,,
394·6	759·4	390·0	35·0	1·4	11·3	393·3	181·2	,,
395·3	760·7	390·5	35·0	1·5	11·3	394·0	181·3	,,
399·9	759·4	384·6	35·2	1·3	11·4	398·6	181·9	,,
402·1	,,	382·5	35·2	1·3	11·4	400·8	182·0	,,
406·6	,,	377·8	35·4	1·1	11·6	405·3	182·6	,,
408·7	,,	375·5	35·4	1·0	11·7	407·4	182·8	,,
414·1	,,	370·0	35·6	0·9	11·9	412·8	183·4	,,
422·4	,,	363·0	35·7	2·6	12·3	421·1	184·5	,,
595·2	750·2	176·7	40·0	1·4	19·7	593·2	198·7	,,
..	..	..	..	..	..	746·3	207·3	,,

For the last observation but one the tube was jacketed with the vapour of methyl benzoate boiling at 750·2 millims.; the last observation refers to the boiling-point of camphor under a pressure of 746·3 millims.

7. A graphic representation of the numbers obtained near the melting-point of camphor is given in the annexed curves. Curve No. I., Plate 18, gives a general representation of the vapour-pressures of camphor. Curve No. II. shows the vapour-pressures in the neighbourhood of the melting-point on an enlarged scale. It is to be noticed that the curves exhibit considerable irregularity about the melting-point, and that a prolongation of the portion above the melting-point would intersect the portion below the melting-point, as shown by dotted lines in Curve No. II.

8. As our anticipations were so far fulfilled we proceeded to investigate the behaviour of benzene and of acetic acid. The measurements obtained by means of a barometer-tube were not sufficiently accurate for our purpose, and therefore we employed the method described in the paper previously referred to, by means of which it was shown

that the maximum temperature to which a solid, having free surface for evaporation, can attain is that at which its vapour pressure is equal to the gaseous pressure to which it is exposed during distillation. The apparatus was modified as described in § 17 of that memoir. In reading pressures, parallax was avoided by the use of a mirror graduated in millimeters, standing vertically behind both gauge and barometer, and it was possible to read with confidence to the tenth part of a millimeter. (In testing this scale with a standard cathetometer by Mr. DARWIN, of Cambridge, the greatest deviation observed was 0·026 millim. in a range of 200 millims.) Only two readings were required, and these involved no correction at low pressures.

The cotton-wool having been moistened with benzene, the following readings were taken :—

9. VAPOUR pressures of benzene.

Temperature (corrected).	Pressure (observed).	Pressure (corrected).	State.
°	millims.	millims.	
9·60	44·55	44·40	Liquid
8·20	41·05	40·90	,,
6·32	37·20	37·10	,,
4·50	33·30	33·20	,,
4·46	34·15	34·05	,,
4·08	33·45	33·35	,,
4·01	32·50	32·40	,,
3·60	32·65	32·55	,,
3·00	31·50	31·40	Solid
2·98	32·00	31·90	Liquid
2·60	30·00	29·90	Solid
1·20	27·40	27·30	,,
0·90	26·80	26·70	,,
−0·20	25·60	25·50	,,
−1·28	23·40	23·40	,,
−1·72	22·35	22·35	,,
−2·80	20·80	20·80	,,
−3·77	19·60	19·60	,,
−4·80	17·90	17·90	,,
−5·21	17·60	17·60	,,

10. The boiling point of this specimen of benzene, which had been purified by recrystallization fifteen times and then carefully dried and fractionated, was 80° at a pressure of 755·7 millims.; it melted at 3°·3. From Professor V. MEYER's recent researches, however, it is probable that it still contained thiophene. The results are graphically shown in the accompanying curve, and it is evident on first inspection that the solid-gas curve is not continuous with the liquid-gas curve. We were unsuccessful in our attempts to cool benzene appreciably below its freezing-point without its solidifying.

11. As acetic acid promised favourable results in this respect we subjected it to experiment.

The results are given in the following table :—

For series IV., V., VI., VII., and VIII., a thermometer graduated in tenths of degrees was employed, and for series VII. and VIII. the barometer was refilled and again boiled out. It was easy to know when the acetic acid was solid and when liquid; for on lowering the pressure with liquid acid the temperature fell steadily and readings were taken, the pressure being kept constant for some time before each reading. As soon as the acid solidified, however, the temperature rose suddenly nearly to the melting-point, and then quickly fell to below its starting-point. Air was then carefully admitted to raise the temperature of the acid to near its melting-point, readings being taken from time to time; and on pressure being reduced by means of the pump, readings of the vapour-pressure of the solid acid were again taken, during fall of temperature.

12. Vapour-pressures of solid and liquid acetic acid.

Series I.

Temperature.	Pressure.	State.
	millims.	
27°·2	16·8	Liquid
22·4	12·9	,,
16·6	8·7	,,
13·2	6·9	Solid
5·4	3·5	,,
3·7	2·8	,,
−0·6	1·95	,,

Series II.

Temperature.	Pressure.	State.
	millims.	
27°·3	17·45	Liquid
21·4	12·65	,,
16·75	10·45	,,
15·6	9·15	,,
15·4	8·75	Solid

Series III.

Temperature.	Pressure.	State.
	millims.	
14°·2	8·3	Liquid
12·2	6·05	Solid
8·4	4·25	,,
7·2	4·05	,,
6·3	3·70	,,
1·85	2·35	,,
−5·6	1·30	,,

SERIES IV.

Temperature.	Pressure.	State.
°	millims.	
20·10	12·0	Liquid
18·60	11·1	,,
15·50	9·1	,,
13·70	8·1	,,
12·30	7·3	,,
10·70	6·75	,,
9·70	6·20	,,
8·72	4·60	Solid
8·58	5·95	Liquid

SERIES V.

Temperature.	Pressure.	State.
°	millims.	
15·15	8·40	Solid
13·96	7·30	,,
11·70	6·15	,,
10·40	5·30	,,
8·50	4·35	,,
6·68	3·85	,,
5·32	3·3	,,

SERIES VI.

Temperature.	Pressure.	State.
°	millims.	
15·70	9·25	Liquid
8·54	5·95	,,
7·06	5·25	,,
6·30	5·00	,,
4·20	4·25	,,

SERIES VII.

Temperature.	Pressure.	State.
°	millims.	
20·9	12·45	Liquid
14·72	8·50	,,
14·39	8·45	,,
10·60	6·50	,,
7·13	5·40	,,
4·70	4·75	,,
2·72	4·00	,,
11·39	5·75	Solid
8·40	4·65	,,
7·09	4·00	,,

SERIES VIII.

Temperature.	Pressure.	State.
°	millims.	
25·60	15·95	Liquid
22·05	13·05	,,
21·68	12·85	,,
19·20	11·05	,,
17·00	9·75	,,
16·41	9·45	Solid
16·32	9·15	,,
16·20	9·10	,,
16·09	8·95	,,
15·80	8·85	,,
15·6	8·55	,,
14·9	8·55	Liquid
14·85	8·00	Solid
14·58	7·95	,,
14·30	7·20	,,
13·30	6·75	,,
12·60	6·65	,,
12·10	6·05	,,
9·16	4·70	,,
6·41	3·75	,,
2·86	2·8	,,

13. On inspection of the curves representing the above numbers (Plate 19), the truth of Professor THOMSON'S theory is evident, for in the case of acetic acid, both the solid-gas curve and the liquid-gas curve have been obtained at temperatures below the melting-point.

14. An attempt was next made to measure these differences by the barometric method. As it is important in such experiments to ensure complete absence of air, the methods of introducing the liquid into the barometer tube may here be noticed. In the first series, the following method was employed. The little apparatus *a*, Plate 18, fig. 1, was partly filled with acetic acid, and exhausted with the pump, so as to remove dissolved air. A straight barometer, boiled out as usual, was placed in position. The little apparatus was removed from the pump, the point was broken off under the mercury, in the trough in which the barometer-tube stood, and a little of the acid forced up into the tube. There was a trace of air as large as a pin-point observable on slightly inclining the barometer-tube so as to bring the liquid to the top, which, however, was rapidly redissolved by the acetic acid.

15. Various attempts were made to secure constant low temperatures, which could be rapidly varied at will. The apparatus shown in *b*, Plate 18, fig. 1, was found best to answer the purpose. The tube, serving as a jacket to the upper portion of the barometer-tube containing the acid, was half-filled with ether, through which a current of dry air, regulated by means of a stop-cock, was drawn by an injector. The temperature rapidly fell, and remained constant so long as the rate of the current of air was not altered. The uniformity of the temperature of the ether was ensured by the violent agitation caused by the bubbles of air. Fresh ether was admitted from time to time

through the funnel, to replace that which had evaporated. The temperature was registered by a thermometer graduated in tenths of degrees, shown in the figure.

16. SERIES I.

Temperature.	Pressure.	State.
°	millims.	
19·4	11·0	Liquid
10·7	5·9	"
10·7	6·0	"
13·2	8·0	"
5·4	4·5	"
5·5	4·4	"
1·7	3·4	"
5·4	5·0	Solid
1·7	3·8	"
9·6	6·7	"
13·2	8·0	"
13·0	7·9	"

17. These numbers in their irregularity resemble those given by REGNAULT (Mem. de l'Institut, vol. xxvi.), and gave no indication of a difference in vapour-pressure between the liquid and solid states.

Thinking that the higher vapour-pressures of the solid acid might be due to the liberation of the small amount of dissolved air during solidification, another method of filling the tube was resorted to.

For the second series the method adopted was that previously employed for camphor; after a plain barometer-tube had been boiled out, liquid acetic acid was introduced, and after exhaustion was frozen. Mercury was then admitted, and while the acid was still solid, the tube was inverted over mercury; the acid on melting rose to the top. Even with this precaution a minute trace of air was still present.

18. SERIES II.

Temperature.	Pressure.	State.
°	millims.	
15·9	9·3	Liquid
18·1	10·4	"
16·85	9·6	"
16·3	9·3	"
15·7	9·1	"
12·3	6·3	"
7·7	5·1	"
1·6	4·0	Solid
4·7	5·1	"
11·9	7·8	"
13·4	8·3	"
8·7	6·3	"
5·55	5·1	"
4·6	5·0	"
1·5	4·1	"

19. As these results were still capricious the tube was filled by a third method, which ensured complete absence of air. The shape of the barometer-tube was modified, as shown in *c*, Plate 18, fig. 1. The tube, after exhaustion, was filled to within about an inch of the branch, and boiled out as usual. Air was then admitted, and about 1 cubic centimeter of acetic acid was introduced. The tube was again exhausted, and the acetic acid was gently warmed, so that its vapour might expel the last traces of air. While the pump was in action, mercury was admitted, the tube being placed in such a position that the acetic acid rose into the closed end of the tube near the junction. Disconnecting from the pump, the tube was inverted in mercury, when the acetic acid rose to its upper end. The absence of air was so complete that the liquid adhered for some time to the top of the tube, the mercury standing at several centimeters above the barometer level, and falling only after being violently shaken. This series includes only a few measurements below the melting-point, the majority being taken at higher temperatures for a different purpose.

20. SERIES III.

Temperature.	Pressure.	State.
°	millims.	
14·95	8·5	Liquid
4·30	4·5	Solid
10·80	6·7	,,

In this series it was found impossible to prevent the solidification of the acid below the temperature 14°·95, and as the results with the solid were still capricious the experiments were not continued. It may be mentioned, however, as a proof that no air was evolved during solidification, that after the acid in contact with the mercury had frozen, the mercury adhered to the solid even after lowering the level of the mercury in the trough.

21. It may be remembered that REGNAULT attributed his discordant results to the presence in his acetic acid of water, or of acetone, the former causing too low, the latter too high vapour-pressures. The acid which we used for these experiments was a portion of a stock of glacial acid, obtained for laboratory purposes several years ago. The liquid portion had been poured off from time to time, as required for laboratory use; a very complete series of fractionations has thus unwittingly been carried out, and it is now so pure that, at temperatures slightly below its melting-point, it is completely solid. This acid was fractionated; a portion containing water came over below 119°·1 (pressure=750·3 millims.); but after this temperature had been attained the whole of the liquid distilled with absolute constancy. Fractions were taken as required from time to time, as the liquid was found very apt to absorb moisture. The purity of this acid is best guaranteed by the absolute concordance of the determinations of vapour-pressures by the distillation method already given, as well as of those at

higher temperatures which form part of another investigation. The melting-point was found to be 16°·4.

22. In all these determinations of vapour-pressures by the barometer-tube method, the atmospheric pressure was ascertained by a barometer standing in the same trough as the experimental tube, and jacketed with flowing water at constant known temperature. The heights of the mercury in both tubes were read by a mirror-scale standing vertically behind them, and were corrected to zero. When necessary, corrections for capillarity were applied, but when possible, wide tubes, of approximately the same diameter, were employed.

As every care was taken we are unable to offer any explanation of these capricious results; they serve at least to account for REGNAULT'S want of success in his attempt to solve this problem.

23. Ethene dibromide was next experimented on, as it was one of the substances chosen by REGNAULT to decide this question. The new method was employed with the following results. The liquid was not quite pure, boiling from 130°–132°.

Temperature.	Pressure.	State.
°	millims.	
−1·7	1·35	Liquid
−1·9	1·25	"
−1·9	1·35	Solid

Owing to the extremely low pressures, the differences were too small to be measured.

24. REGNAULT states that he experimented on carbon tetra-chloride in the solid and liquid states. We found no sign of solidification even at −25°, and the body was therefore rejected as unsuitable for our purpose.

Vapour-pressures of liquid and solid water.

25. After devising the vapour-pressure apparatus we tested its accuracy by determining the vapour-pressures of ice and water between −15°·9 and 100°. The results agreed well with those calculated by means of REGNAULT'S formulæ; the minute differences, however, were not carefully noted at the time. Having acquired by the previous experiments the necessary dexterity of manipulation and accuracy in reading, we proceeded to the determination of the vapour-pressures of water and ice at low temperatures, which, on account of the extremely small differences to be observed, offers greater difficulties. It was first attempted to devise some means of measuring accurately small differences of pressure. One device was the use of a barometer and a gauge, of the ordinary diameter, to the upper ends of which were sealed narrower tubes bent almost at right angles, the bent portions lying in a nearly horizontal position, so that a slight alteration of pressure would produce a flow of the mercury through a

considerable length of tube. Another was the use of a glycerine barometer and gauge. A third was to suspend the barometer and the gauge from the arms of a balance, while the lower ends dipped into two troughs communicating with each other. The diameters of the tubes being known, the difference in level could be ascertained by a difference in weight. This last method promised success, but it was abandoned in favour of a much more simple one.

26. The principle of this method is to observe the temperatures of both ice and water while at the same pressure. Absolute accuracy in reading pressure is, as will hereafter be shown, not essential. The apparatus by which this was accomplished is shown in Plate 18, fig. 2.

A and B are the two thermometers, graduated in tenth-degrees, the bulbs of which are covered with cotton wool. The arrangements for introducing liquid, so as to moisten the cotton wool, are similar to those already described. The two vertical tubes dipped in water, the temperature of which was maintained at 35°–40°. The condenser differed but slightly from that previously used. The altered position of the exit tube C was found to be more favourable to condensation. The arrangement of the gauge and barometer is also shown in the figure. In order to ensure that the diameter of the gauge was the same as that of the barometer, the portion of the gauge D and the top of the barometer tube E were taken from adjacent portions of the same tube. The divisions on the mirror scale F were extremely fine, and an attempt was made to read to half-tenths of millimeters, with what success will be seen hereafter. In reading pressures, the level of the mercury in the trough was frequently altered, so as to avoid reading only at one part of the scale. As a rule, the mean of several readings is given. In order to facilitate exhaustion, the gauge was connected by means of a T-tube with a CARRÉ'S air-pump, as well as with a SPRENGEL pump, the former serving as a rough and the latter as a fine adjustment. In these experiments, after exhaustion by the CARRÉ pump, the lead tube connecting that pump with branch G of the T-tube was removed, and this junction served to admit air when desired. The india-rubber tubing, which was specially made for the purpose by Messrs. THORNTON, of Edinburgh, was very thick-walled, so as to avoid collapse on reduction of pressure, and was impervious to air. The india-rubber corks through which the thermometers passed were coated with paraffin. These precautions prevented any leakage whatsoever.

As before, a freezing mixture of pounded ice and hydrochloric acid surrounded the condenser.

27. Three thermometers were used, A and C by NEGRETTI and ZAMBRA, B by CETTI. Their zero-points were first determined, and a careful comparison of the scale below 0° was made by placing them in position, freezing water on the cotton wool covering both bulbs, and altering pressure. In this comparison both thermometers were under the same pressure, and the volatilizing point of ice being solely dependent on the pressure, both thermometers were under precisely the same conditions, and

must therefore register the same temperature. It was found that the two thermometers by NEGRETTI and ZAMBRA agreed throughout as to the length of their divisions; and a curve was constructed, showing the relation of the degrees on thermometer B to those of A.

28. It is worth recording that the zero-points of all the thermometers were lowered on reduction of pressure, but to very different amounts. The readings under atmospheric pressure of thermometers A and C, when placed in ice, being taken as identical, it was found that in a vacuum thermometer C stood 0°·5 lower than A. A similar phenomenon has been observed by MILLS. After coating thermometers with metals electrolytically, he noticed that the deposition of zinc and cadmium lowered the zero-points of his thermometers from 0·27 to 0·75 degree, while copper raised the zero-point in one case as much as 14·70 degrees (Proc. Roy. Soc., vol. 26, p. 504). MILLS made a comparison of this effect with that produced by raising or lowering atmospheric pressure.

The following table shows a comparison of thermometers A and B, by the method already mentioned:—

29.

Number of experiments, mean of.	Temperature of A.	Temperature of B.	Difference.
4	−2°·82	−3°·16	0°·34
1	3·72	4·10	0·38
3	4·66	5·06	0·40
2	5·06	5·53	0·47
2	+0·10	0·21	0·31
2	0·15	0·17	0·32
2	−2·33	2·68	0·34
1	3·62	4·04	0·42
1	1·80	2·18	0·38
1	2·92	3·34	0·42
1	3·87	4·30	0·43
4	4·59	5·09	0·50
3	4·35	4·77	0·42
2	4·93	5·38	0·45
1	0·66	1·00	0·34

The extreme variation in difference amounted to 0°·19. The difference was found to increase with fair regularity as the temperature fell.

30. From these numbers the following table was constructed by the graphic method:—Zero-points of A and B under the same conditions were respectively +0°·11 and −0°·21. A and C (of which the zero-point had been raised to 7°·23 for convenience of reading) were found to be identical throughout, hence their readings were accepted as correct, while those of B were corrected as given in the table below:—

Temperature.	Difference between A and B.	Correction for B.
0°	0°·32	0°·21
−1	0·34	0·23
−2	0·37	0·26
−3	0·40	0·29
−4	0·42	0·31
−5	0·45	0·34

31. A comparison of thermometers A and C was made before and after the experiments. They were first placed in melting ice, when A read 0°·18 and C, which had been altered in order to secure greater range, 7°·65. In vacuo the zero-points of these thermometers were 0°·11 and 7°·10 respectively. Thus thermometer A fell 0°·07, while C fell 0°·55, the difference being 0°·48. This was repeated after the experiments described in Series II., when A placed in melting ice read 0°·23, and C 7°·72, and in vacuo 0°·17 and 7°·13 respectively. Thus A fell 0°·06 and B 0°·59, the difference being 0°·53. This agrees with the comparison of the two thermometers at the atmospheric pressure and in a vacuum. At the same time, other readings of thermometer C were somewhat variable, and it was therefore deemed advisable to assume that the zero-point of C in Series II. was 7°·23. That this is so is shown by the fact that, taking this number as correct, the differences between the two thermometers disappeared at 0°. But even if 7°·13 were accepted as the zero-point of C it would not materially affect our results.

32. The experiments were conducted in the following manner:—Water was admitted so as to moisten the cotton-wool of both thermometers. Air was then removed as far as possible by means of the CARRÉ pump; it was then disconnected. The condenser was next cooled, when the temperature registered by both thermometers quickly fell to about −5°. Solidification then took place, the temperatures rapidly rising to 0°, and quickly falling again. The freezing-mixture was then removed, and a little air introduced, and one tube was jacketed with hot water. Both thermometers remained stationary at 0° for some time; the one which was warmed was allowed to rise to about +15°; the other thermometer remained below +3°. The freezing-mixture was then replaced, and air was slowly removed by the SPRENGEL pump. Under these circumstances it invariably happened that ice was formed on that thermometer, the temperature of which had not risen above 3°, as soon as the pressure fell below 4·6 millims., while the water on the other thermometer could be cooled to −5° without freezing by slowly reducing pressure. At a temperature between −5° and −6° it always froze. Between −5° and −0°, therefore, it was possible to obtain comparative readings.

33. In the tables which follow all the readings are given, except some preliminary ones made before the method of manipulation had been learned.

SERIES I.

A.	B.	Mean of A.	Mean of B.	A corrected (ice).	B corrected (water).	Difference.		Mean pressure.	
						Observed.	Calculated.	Observed.	Calculated.
°	°	°	°	°	°	°	°	millims.	millims.
-2·08	-2·69	-2·00	-2·61	-2·11	-2·35	0·24	0·28	3·80	3·88
-2·01	-2·61								
-1·92	-2·54								
-3·20	-4·00	-3·18	-3·97	-3·29	-3·67	0·38	0·46	3·50	3·52
-3·16	-3·94								
-3·42	-4·24	-3·40	-4·22	-3·51	-3·92	0·41	0·50	3·25	3·46
-3·39	-4·21								
-4·12	-5·07	-4·07	-5·03	-4·18	-4·71	0·53	0·62	3·20	3·26
-4·10	-5·04								
-4·03	-5·00								
-4·07	-5·02								
-4·04	-5·01								

SERIES II.

A.	C.	Mean of A.	Mean of C.	A corrected (ice).	C corrected (water).	Difference.		Mean pressure.	
						Observed.	Calculated.	Observed.	Calculated.
°	°	°	°	°	°	°	°	millims.	millims.
-3·34	+3·09	..	..	-3·51	-4·14	0·63	0·55	—	—
-3·52	+2·95	-3·42	+3·05	-3·59	-4·18	0·59	0·56	3·62	3·40
-3·32	+3·15								
-2·80	+3·84	..	..	-2·97	-3·39	0·42	0·43	3·77	3·60
-2·26	+4·40	-2·20	+4·45	-2·37	-2·78	0·41	0·35	3·95	3·76
-2·14	+4·51								
-1·79	+4·96	-1·74	+5·00	-1·91	-2·23	0·32	0·27	4·17	3·92
-1·70	+5·05								
-1·12	+5·67	..	..	-1·29	-1·56	0·27	0·20	4·17	4·12
-0·82	+6·15	-0·83	+6·15	-1·00	-1·08	0·08	0·16	4·30	4·26
-0·83	+6·15								
-0·07	+6·95	-0·06	+6·96	-0·23	-0·27	0·04	0·04	—	—
-0·05	+6·98								
-0·03	+7·00	..	..	-0·20	-0·23	0·03	0·03	—	—
-0·00	+7·05	..	..	-0·17	-0·18	0·01	0·02	—	—
+0·02	+7·08	..	..	-0·15	-0·15	0·00	0·02	—	—
+0·05	+7·10	..	..	-0·12	-0·13	0·01	0·01	—	—
+0·10	+7·15	..	..	-0·07	-0·08	0·01	0·01	—	—
+0·13	+7·20	..	..	-0·04	-0·03	-0·01	0·01	—	—
+0·17	+7·25	..	..	0·00	+0·02	-0·02	0·00	—	—
+0·17	+7·30	..	..	0·00	+0·07	-0·07	0·00	—	—
+0·17	+7·35	..	..	0·00	+0·12	-0·12	0·00	—	—

34. As the differences between the vapour-pressures of ice and of water given in the previous tables are generally greater than those calculated by Professor JAS. THOMSON from REGNAULT'S empirical formulæ, we proceeded to calculate the theoretical curve by the method given by Professor THOMSON, which may be expressed by the formula

vapour-pressure of ice at $(t-1)=\mathrm{P}_t-(\mathrm{P}'_t-\mathrm{P}'_{t-1})\left(\dfrac{\mathrm{H^V}_{t-\frac{1}{2}}+\mathrm{H^F}_{t-\frac{1}{2}}}{\mathrm{H^V}_{t-\frac{1}{2}}}\right)$.

where P $=$ vapour-pressure of ice.
P′ $=$ „ „ water.
$\mathrm{H^V}$ $=$ heat of vaporization of water.
$\mathrm{H^F}$ $=$ „ fusion of ice.
t $=$ temperature of ice.

The formula devised by Regnault for vapour-pressures of water between 0° and 100°, was held to apply to temperatures as low as $-15°$. Even if this is not strictly correct, the alteration in the differences between the vapour-pressures of water and ice would be inappreciable.

35. In calculating the results the following data were employed :—

(I.) Heat of vaporization of water at 0° $=606{\cdot}5$ calories (Regnault). ($\mathrm{H^V}$.)
„ „ „ $-0°{\cdot}5=606{\cdot}85$ „
„ „ „ $-1°{\cdot}5=607{\cdot}55$ „

and so on, increasing by 0·7 calorie for each degree.

(II.) Heat of fusion of ice at 0° $=79{\cdot}15$ calories (Regnault). ($\mathrm{H^F}$.)
„ „ „ $-0°{\cdot}5=78{\cdot}90$ „
„ „ „ $-1°{\cdot}5=78{\cdot}40$ „

and so on, decreasing by 0·5 calorie for each degree.

(III.) Specific heat of ice, 0·5 calorie (mean of various experiments).

(IV.) Ratio of difference of pressures for 1° of vapours of ice and water.

The ratio between 0° and $-1°$ was calculated thus :

$$\frac{606{\cdot}85+78{\cdot}90}{606{\cdot}85}=1{\cdot}130.$$

Between $-1°$ and $-2°$

$$\frac{607{\cdot}55+78{\cdot}40}{607{\cdot}55}=1{\cdot}129,$$

and so on.

(V.) Vapour-pressures of water from Regnault's empirical formula

$$\log e=a+b.\alpha^t-c.\beta^t, \text{ between } 0° \text{ and } -16°.$$

(It is noteworthy that the curve representing results calculated by Magnus from his own observations for temperatures below 0° runs parallel to that here given, with a difference varying between 0·075 and 0·081 millims.)

Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.
0	4·600	— 9	2·365
—1	4·281	—10	2·190
—2	3·983	—11	2·027
—3	3·703	—12	1·875
—4	3·441	—13	1·734
—5	3·196	—14	1·602
—6	2·966	—15	1·480
—7	2·752	—16	1·366
—8	2·552		

36. The vapour-pressures of ice and water may be taken as equal at 0°. The vapour-pressure of ice at —1° is calculated as follows :—

(1.) Difference between vapour-pressure of water at 0° and at —1°, $=4·600-4·281=0·319$ millim.

(2.) This difference, multiplied by the ratio between 0° and —1°, $=0·319\times 1·130=0·361$ millim.

(3.) Vapour-pressure of ice at 0°—difference of pressures between 0° and —1°, $=4·600-0·361=4·239$ millim.

In this manner the theoretical vapour-pressures of ice from 0° to —16° were calculated.

37. In the table below, under column A, are given the theoretical vapour-pressures of ice, calculated as above, and B gives results calculated by means of REGNAULT'S empirical formula E for temperatures between 0° and —32°.

Temperature.	Pressure.	
	A.	B.
°	millims.	millims.
0	4·600	4·600
— 1	4·239	4·263
— 2	3·903	3·941
— 3	3·587	3·644
— 4	3·292	3·368
— 5	3·016	3·113
— 6	2·757	2·876
— 7	2·516	2·658
— 8	2·292	2·455
— 9	2·082	2·267
—10	1·886	2·093
—11	1·704	1·933
—12	1·534	1·783
—13	1·376	1·646
—14	1·229	1·518
—15	1·093	1·400
—16	0·966	1·290

38. We have previously mentioned that in order to test the accuracy of our new method of determining vapour pressures, a careful set of determinations was made of the vapour-pressures of ice and water. The slight differences between the results obtained and those given in REGNAULT'S tables were considered at the time to be due to experimental error, for they were so small as to appear insignificant. On comparing these results, however, with the curve calculated from theory, it was found that they much more nearly coincided with it, than with REGNAULT'S curve. As they afford a striking confirmation of the results already given, they are here appended.

Temperature (corrected).	Pressure (observed).	Pressure calculated from theory.	Pressure calculated from REGNAULT'S formula.
°	millims.	millims.	millims.
− 2·6	3·7	3·708	3·75
− 3·7	3·2	3·378	3·45
− 5·6	2·85	2·856	2·96
− 6·7	2·55	2·580	2·72
− 9·7	1·95	1·942	2·13
−11·1	1·65	1·688	1·90
−13·3	1·45	1·330	1·60
−15·2	1·25	1·066	1·38
−15·9	1·00	0·980	1·29

39. Description of the curves (Plate 19).

No. I. Acetic acid. Curves drawn to follow the experimental results.

(*a*) Vapour-pressure of liquid acid.

(*b*) „ „ solid acid.

No. II. Water and ice.

(*a*) Curve for water calculated by RENAULT'S formula for pressures between 0° and 100°.

(*b*) Theoretical curve for ice, calculated from (*a*).

Our results for water are given as coinciding with (*a*), for it was assumed that the temperature of the thermometer surrounded by water was correct. This was done, for the object was to show differences of temperature at certain points in the curve, rather than the absolute relationship between temperature and pressure at any one point.

No. III. (*a*) Theoretical curve for ice.

(*b*) Curve from REGNAULT'S tables.

(*c*) Curve for water as in (II.).

The crosses denote the observations given in § 38; the circles the observations for ice given in § 33.

40. In the foregoing pages it has been proved: (1) that with camphor and benzene, the former in a barometer tube, and the second in the "still," the curve representing vapour-pressure of liquid above the melting-point is discontinuous with that of the solid below the melting-point: (2) that acetic acid shows this difference in a very

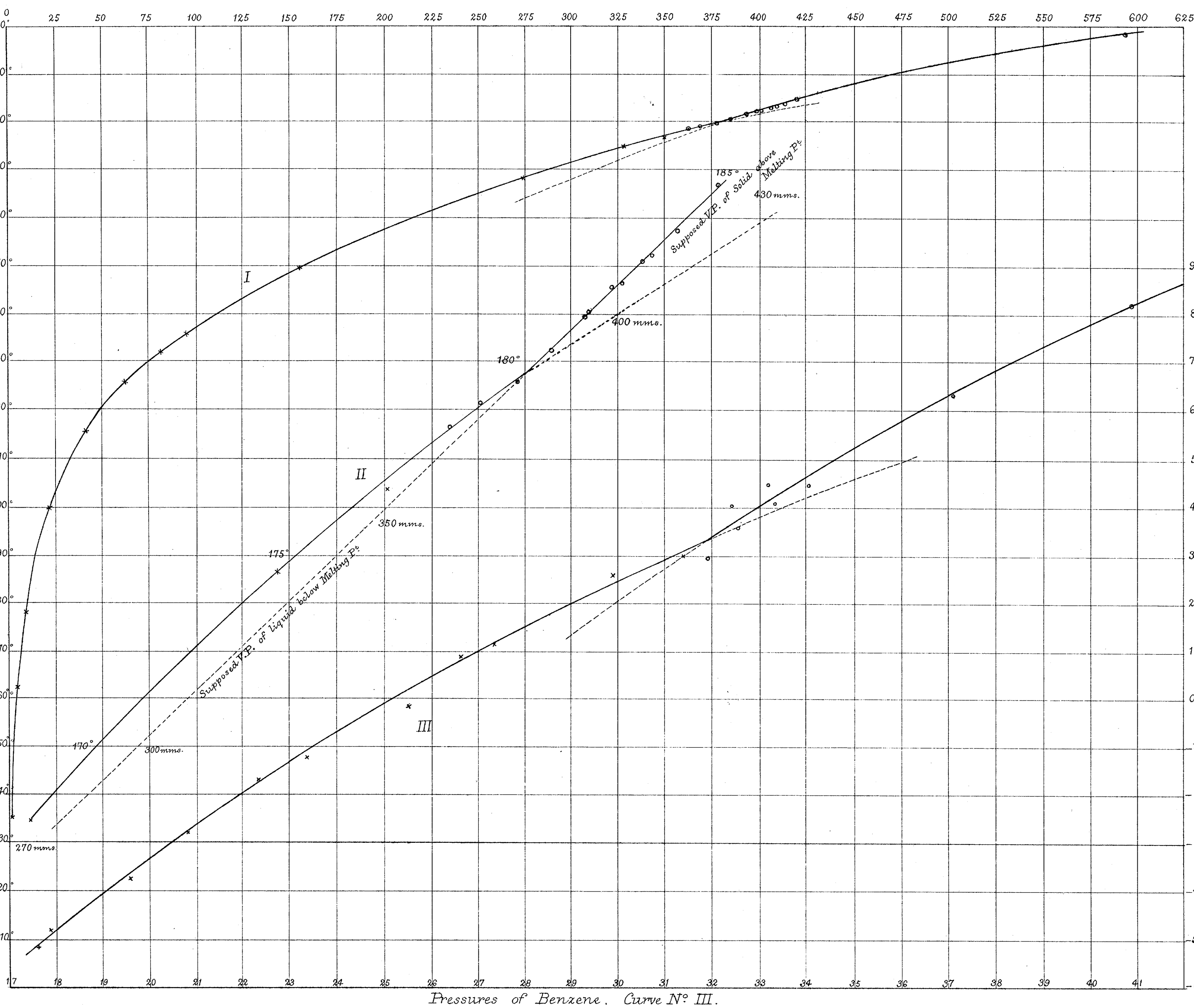
marked manner; and that, indeed, the curves representing vapour-pressure of solid and liquid below the melting-point are quite distinct: and (3) that, with water, as Professor THOMSON predicted, this difference is calculable from the known heats of vaporisation and fusion. It is to be regretted that similar data as regards acetic acid are not sufficiently complete or reliable to enable a similar calculation to be made.

ADDENDUM.

A new method of determining vapour-pressures of solids and liquids.

As this method has been fully described in this and in a previous paper (Phil. Trans., 1884, Part I., p. 37) it will not be necessary to enter into a detailed description of it. Our experience of the method has shown us that the results which it gives are more trustworthy, as well as more easily obtained than those which the older method yields; hence it may be well to point out its advantages.

1. There is no necessity to heat the whole apparatus to a known and uniform temperature. It is only necessary that the temperature of the bath should be kept 30° to 40° higher than that registered by the thermometer.
2. The temperature of the gauge and barometer are the same, and involve only a simple and small correction for the temperature of the column of mercury. The vapour-pressure of mercury is not introduced.
3. The gauge and barometer stand in the same trough, which may be placed at a distance from the still, and hence they are not subject to change of temperature.
4. The readings are more accurate, because the gauge and barometer need not be jacketed, and the scale may be placed immediately behind them.
5. The very great difficulty of filling an experimental tube, so as to ensure absence of air and moisture, is avoided.
6. In our apparatus, the temperature is dependent on the pressure, instead of the pressure being dependent on the temperature, and the pressure may easily be reduced or increased at will, and is of necessity constant throughout the whole apparatus.
7. A very much larger number of observations may be taken in the same time, and the influence of the errors of experiment, themselves much smaller, is thereby greatly reduced.
8. The labour involved in applying the corrections necessary when a barometer tube is used is avoided.



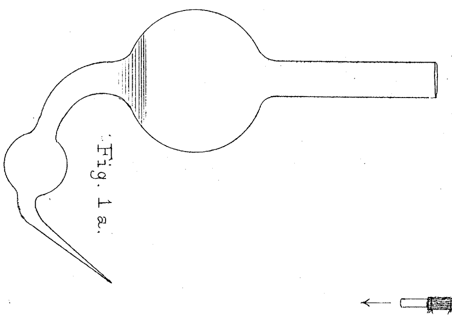
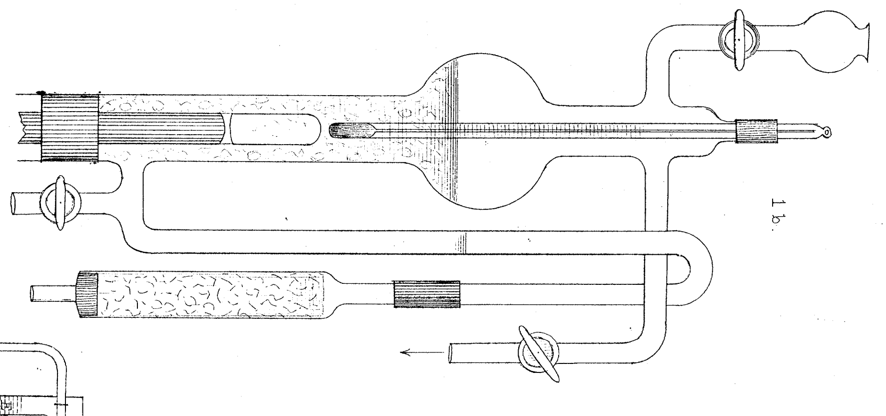


Fig. 1 a.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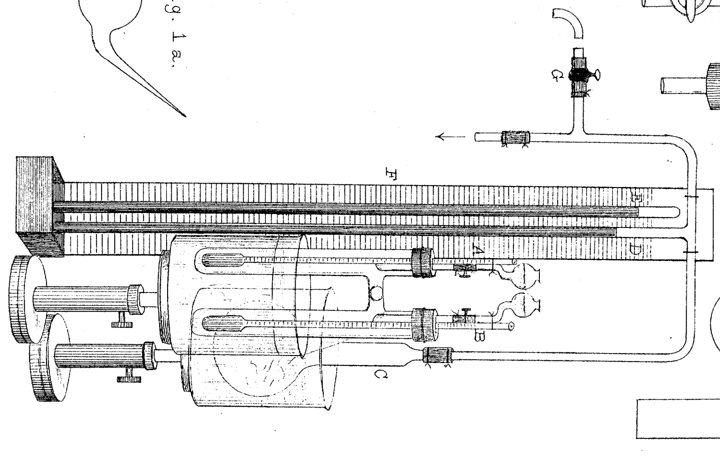
Fig. 2.


1 c.

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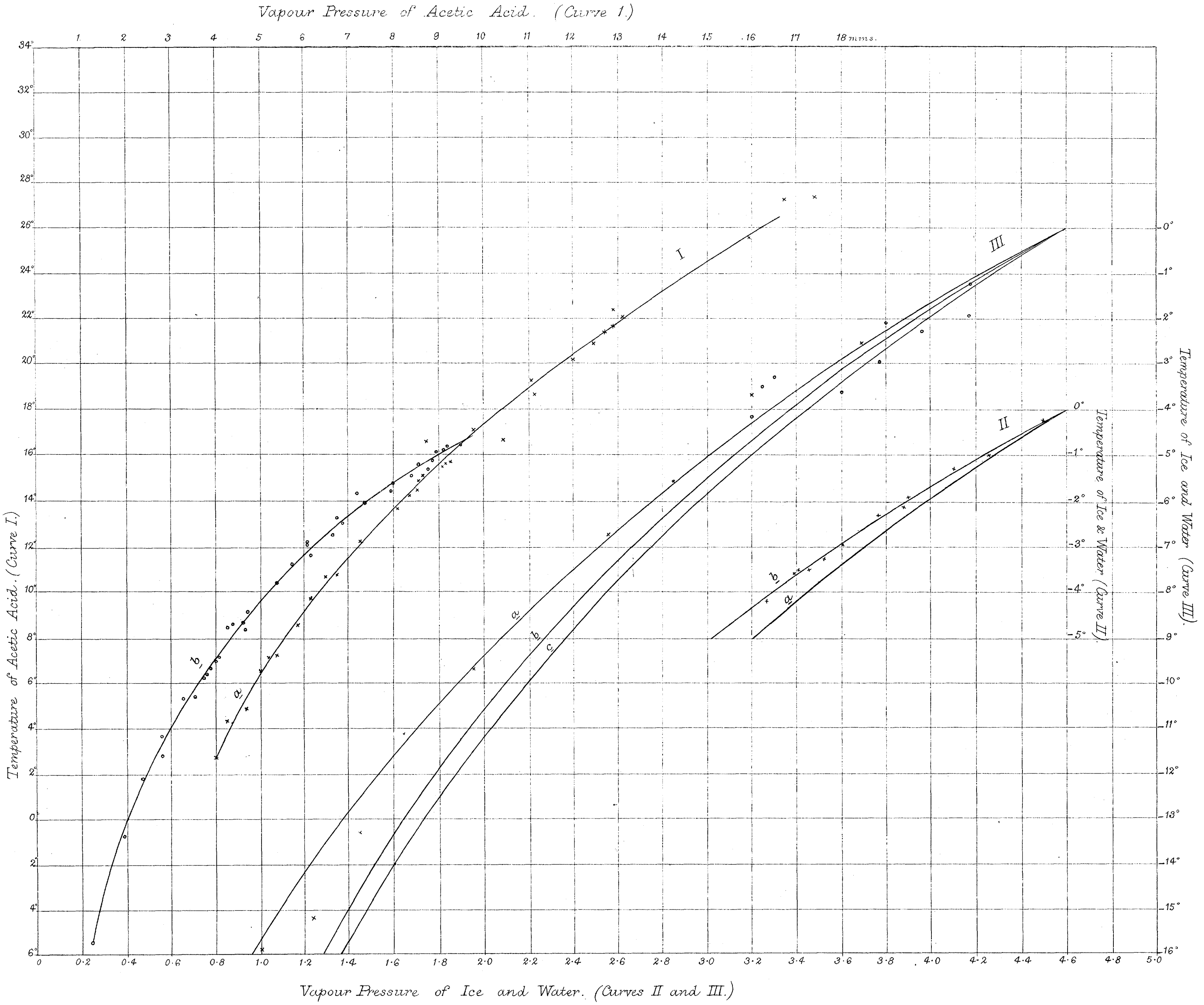
Ramsay & Young.

Phil. Trans. 1884. Plate 19.



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