III. *The Influence of Pressure on the Temperature of Volatilization of Solids.*

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Communicated by Sir Andrew C. Ramsay, *LL.D., F.R.S.*

Received June 5,—Read June 21, 1883.

1. The experiments to be described in this paper were undertaken in order to ascertain whether solids have definite volatilizing* points under different pressures, as liquids have definite boiling-points, and whether these pressures are identical with their vapour-tensions at those temperatures.

It has been long known that arsenic, which volatilizes without melting under atmospheric pressure, melts when the pressure is raised; and some years ago Carnelley proved that ice, mercuric chloride, and camphor do not melt below certain pressures peculiar to each substance; but above these pressures they melt when heated. He proposed the term "critical pressure" to denote that pressure below which a solid cannot melt. Preliminary experiments appeared to show that the solid might be raised in temperature above its ordinary melting-point without melting; but it has since been experimentally proved that this is not the case.

In January, 1881, shortly after the publication of Carnelley's experiments, one of us read a paper before the Chemical Society of the Owens College, in which it was pointed out that, theoretically, at pressures below the triple point of Jas. Thomson, water should be unable to exist as such. It was at that time experimentally undecided whether ice could be heated above 0° C. or not; and the annexed diagram (fig. 1) was designed to show the relations of solid, liquid, and gas, to temperature and pressure.

A somewhat similar diagram was subsequently published in 'Nature' by Peterssen, (June 23rd, 1881), which, however, did not show Jas. Thomson's ice-steam line, and in which the triple-point was placed below, instead of above 0°. This was pointed out in a letter to 'Nature' (July 14th, 1881).

2. Although it appeared extremely probable that the temperature of a solid corresponding to a definite vapour-tension is identical with the temperature at which it

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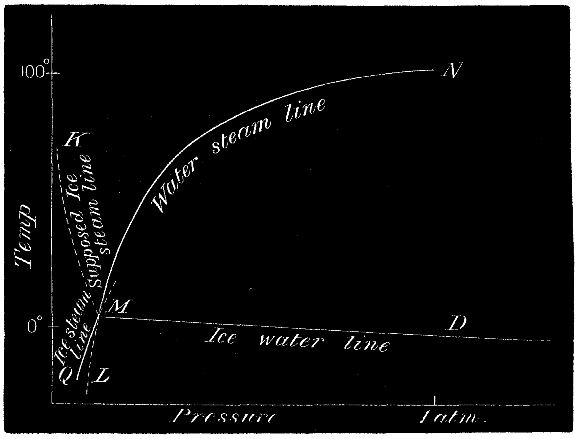
* By the term "volatilizing" we wish to imply the condition of a solid analogous to that of a liquid when it is said to be "boiling"; and not the mere passing off into vapour analogous to *evaporating* in the case of a liquid; in other words, the "volatilizing point" of a solid at a given pressure is the maximum temperature to which the solid can attain under that pressure.

volatilizes under the same pressure, yet it has never been satisfactorily proved. It is true that Mr. J. B. HANNAY states that in experiments performed to disprove the possibility of raising the temperature of ice above 0°, for which a Florence flask was used, the bulb being placed in a freezing mixture, while the neck, in which a thermometer surrounded with ice was suspended, was heated by a BUNSEN'S flame, the temperature of the bulb or condenser was nearly identical with that of the ice. From our experiments we know that the temperatures of the freezing mixture and of the condenser are never identical, and Mr. HANNAY failed to describe any arrangement by which the internal temperature of the condenser could be found.

Fig. 1.



The experiments of PETTERSSEN are more conclusive. By connecting the apparatus with a manometer he found that when the block of ice surrounding the thermometer was at any given temperature, the pressure in the manometer roughly corresponded to the vapour-tension of ice at the same temperature; but as he published the results of only two experiments, and as the errors are comparatively large, the question could not be regarded as settled.

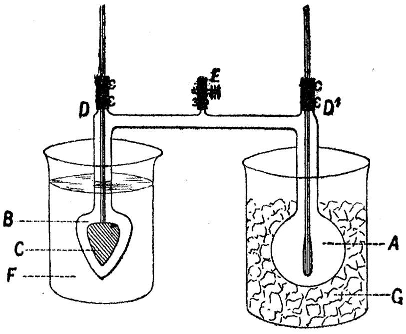
3. We resolved first to study the behaviour of ice at low pressures. For this purpose an apparatus was constructed which we afterwards found to have some resemblance to that described by BOUTLEROW (I. Russ. Phys. Chem. Soc., 1881, i., 316). The annexed figure (fig. 2) shows its form.

It was found that the leakage of air into the apparatus through the indiarubber connexions was extremely minute, and that an almost perfect vacuum could be maintained for several days.

4. The plan of operation was as follows:—Both bulbs were filled with water through the opening at E, and the water was boiled down until reduced to the volume of the bulb B. While the water was boiling, the screw-clip at E was closed, and the flames then removed. After cooling, the water was transferred to B, which was placed in a freezing mixture. When the water was frozen the bulb was gently

warmed, and the water which had melted from its interior surface transferred to A. The bulb A was then surrounded by a freezing mixture, and by gently warming B, all ice in contact with the sides was removed. The bulb B was now surrounded with boiling water, and the temperatures registered by the thermometers in A and B were carefully observed, while the temperature of the freezing mixture was altered from time to time.

Fig. 2.



A. Bulb, named condenser, placed in freezing-mixture.
B. Pear-shaped bulb, containing a block of ice, C, frozen round thermometer.
D, D'. Narrower tubes fused on to the wider tubes, through which the thermometers passed, secured by wired indiarubber connexions.
E. Exit tube for steam, closed by indiarubber tube and screw-clip.
F. Hot bath of water or paraffin.
G. Freezing mixture of hydrochloric acid and ice.

During freezing the phenomenon of supersaturation was nearly always observed. The temperature fell occasionally as low as —11°, while the water was still liquid. A sudden formation of ice then occurred, and the temperature rose to 0°. After remaining constant for some time while ice was being formed on the sides of the bulb, we were surprised to find the temperature fall below 0° (on one occasion as low as —10°), before the whole of the water was frozen. This we afterwards ascertained to be owing to the thermometer transferring heat to the ice with which it was in contact, and which was cooled by the freezing mixture, for the temperature of the water had not fallen below 0°.

5. The pressure in the apparatus could be increased only by raising the temperature of the condenser or by admitting air. The former has the effect of increasing the total pressure of water-vapour, and also of the air already contained in the apparatus, and can be calculated from the tables of tension of vapour in contact with ice, given by REGNAULT. An attempt was made to measure the pressure of the air present by inverting the apparatus and transferring all the air to one bulb, and then reading the difference in level of the water in the two limbs; but as the apparatus itself is such a delicate air-thermometer, it was found impossible to obtain satisfactory results. The amount of air was therefore calculated by a method which will appear hereafter.

6. The first series of readings gave the following results :—

Number of readings.	Mean temperature of condenser.	Mean temperature of bulb.	Difference.	Difference calculated.
7	−11°·1	−8°	3°·1	3°·2
1	− 9·2	−6·4	2·8	2·8
4	− 8·05	−5·6	2·45	2·5
4	− 5·5	−3·3	2·2	2·3
6	− 3·2	−1·3	1·9	1·9

The second series gave similar numbers :—

Number of readings.	Mean temperature of condenser.	Mean temperature of bulb.	Difference.	Difference calculated.
4	−17°·7	−9°·35	8°·35	8°·35
1	−16·7	−8·9	7·8	7·9
3	−15·5	−8·3	7·2	7·4
4	−14·5	−7·6	6·9	6·9
3	−13·6	−6·8	6·8	6·5
1	−12·7	−6·3	6·4	6·2

At this point the bulb of the thermometer became slightly exposed, and it is seen that the temperature shown by this thermometer rises more rapidly :—

Number of readings.	Mean temperature of condenser.	Mean temperature of bulb.	Difference.	Difference calculated.
2	−11°·45	−5°·45	6°·0	5°·7
3	−10·6	−4·5	6·1	5·4
9	− 9·0	−3·2	5·8	4·9
10	− 7·3	−1·5	5·8	4·4

It is to be observed that in each case the thermometer in the ice-bulb shows a higher temperature than that in the condenser, and that as the temperature rises the difference decreases.

7. The question arises :—On what does this difference depend? The answer which naturally occurred to us was that the temperature of the ice depends on the pressure in the apparatus, which in its turn depends on the temperature of the condenser. Assuming the truth of this hypothesis, it was possible to calculate the pressure exerted by the air in the apparatus for any one temperature in the following way :— In the first series of experiments the tension, ascertained by REGNAULT'S tables, corresponding to the temperature −3°·2 in the condenser, is 3·59 millims.; that corresponding to the temperature −1°·3 of the ice is 4·16 millims. Assuming the temperature of the ice wholly to depend on the pressure in the apparatus, the pressure would

be 4·16 millims., of which 3·59 millims. are due to the tension of vapour in the condenser, while the difference between 4·16 and 3·59=0·57 millim. must be due to air. Since this pressure of air is nearly constant throughout the experiment, the slight variation being due to difference in temperature of the apparatus, which can be approximately allowed for, it is possible to calculate from REGNAULT's table the variation in temperature of the ice caused by altering the temperature of the condenser. For instance, the lowest temperature of the condenser in series I. is $-11^{\circ}\cdot 1$; this corresponds to a pressure of 1·905 millims.; the total pressure in the apparatus is therefore $1\cdot 905+0\cdot 570=2\cdot 475$ millims., and the corresponding temperature is $-7^{\circ}\cdot 9$; the temperature observed being $-8^{\circ}\cdot 0$.

In the second series the pressure of the air found as above is 1·08 millims., the lowest temperature being taken as the basis of calculation. The agreement between the calculated and found differences is seen to be close until the bulb became exposed, when its temperature rose more rapidly.

8. As it was sufficiently proved by these experiments, which were confirmed by numerous others, that our hypothesis is fairly in agreement with experimental evidence, it was decided next to admit small quantities of air, and to ascertain what rise in temperature the ice underwent. But as a very small amount of air causes a great difference in temperature, we were unsuccessful in measuring the exact amount of each addition. In order to do this, it was necessary to have as nearly as possible a perfect vacuum in the apparatus. For this purpose a litre of distilled water was boiled down to about 200 cub. centims. and introduced, while almost at its boiling-point, into the apparatus. The thermometers were not inserted until steam was issuing rapidly from the three orifices. Before inserting them they were held for some time in the steam, so as to remove any adhering film of air. It was evident that the bulbs were nearly vacuous, for two columns of water enclosing vapour came completely together without showing any trace of a bubble of air. It is right here to observe that all attempts to produce a complete vacuum with the SPRENGEL's pump which we then possessed were totally unsuccessful.

After the apparatus was in order the freezing mixture was changed, and the temperature of the ice fell to -17°; the temperature of the thermometer in the condenser, however, fell very slowly, owing possibly to absence of convection currents. The temperature of the ice rose, while that of the condenser fell, until at -13° they were equal, and remained constant for a considerable time. It thus appears that the temperature of volatilization of the ice is -13° when the pressure in the apparatus is equal to the vapour-tension of ice at that temperature. A minute quantity of air was then introduced; the temperature of the condenser was now $-12^{\circ}\cdot 6$, while that of the ice rose at once to $-6^{\circ}\cdot 7$, and then remained stationary. On a second addition of air, with the condenser at $-12^{\circ}\cdot 9$, the temperature of the ice rose to $-1^{\circ}\cdot 5$ Thus, with no air, the difference between the readings of the two thermometers was 0°; after the first addition, $5^{\circ}\cdot 9$, and after the second addition of air, $11^{\circ}\cdot 4$.

9. In Section 7 it was stated that the alteration of the temperature of the condenser influenced the pressure in the apparatus. Indeed, any alteration in the temperature of the apparatus must influence the pressure due to air; hence it follows that if the temperature of the bath is altered, the pressure in the apparatus must also be altered. When the temperature of the bath is kept constant the pressure due to air alters only with alteration in the temperature of the condenser, and its change is therefore very small. To ascertain the effect of changing the temperature of the bath, the following experiment was made:—

Temperature of bath.	Temperature of condenser.	Temperature of ice.	Pressure. millim.	Difference found.	Difference calculated.
75°	−11°	−6°·3	0·890	4°·7	4°·7
85	−10·8	−6·1	0·905	4·7	4·8
100	− 9·5	−5·0	0·930	4·5	4·4
110	− 9·1	−4·7	0·948	4·4	4·4
120	− 8·8	−4·3	0·962	4·5	4·35
140	− 8·2	−3·7	0·990	4·5	4·25

In this experiment the capacities of the condenser, of the bulb, and of the whole apparatus were known; the pressure (0·89 millim.) was calculated from the lowest reading, and the difference in pressure was calculated from the observed temperatures and volumes of the various parts of the apparatus.

The agreement between the observed and calculated results is sufficient to give probability to the above hypothesis.

10. These results, although fairly conclusive, are all deduced from the behaviour of one substance, ice, which on account of its low melting-point and vapour-tension offers considerable difficulties in manipulation. Acetic acid was chosen, and the following series of results were obtained, the method of experiment being precisely similar to that followed with ice. Acetic acid melts at 16°·4.

	Temperature of bath.	Temperature of condenser.	Temperature of ice.	Difference.
a. Preliminary	Cold	−14°·9	+ 6°·6	21°·5
	Cold	− 6·0	9·7	15·7
	100	− 4·9	9·9	14·8
	70	− 4·3	8·8	13·1
	70	− 2·7	10·9	13·6
	Cold	+ 1·0	13·6	12·6
b. Apparatus free from air . . .	75	+ 0·9	+ 0·6	+ 0·3
	75	12·2	11·9	0·3
c. x cub. centims. of air introduced (The absolute amount of air was not measured).	80	− 0·6	5·9	6·5
	80	+ 0·9	6·3	5·4
	80	2·3	6·9	4·6
	80	4·3	7·9	3·6
	80	12·9	15·0	2·1
d. 2x cub. centims. of air introduced	65	− 8·2	7·0	15·2
	65	− 6·4	7·4	13·8
	65	− 5·8	7·6	13·4
	65	− 4·9	7·9	12·8
	65	− 3·7	8·1	11·8
	80	+ 2·1	9·9	7·8
	69	3·1	10·9	7·8
	67	5·6	11·8	6·3
	80	8·9	14·9	6·0
e. 3x cub. centims. of air introduced	73	− 3·4	12·1	15·5

11. Benzene gave a good semi-transparent block of ice, but its vapour caused the indiarubber connexions to leak; moreover, its rate of volatilization was so rapid that it only partially solidified in the receiver, even at −15°. The consequence was that the temperature of the benzene ice was apparently much lower than that of the thermometer in the condenser. Although acetic acid vapour solidified at once on reaching the condenser, yet the rapid current of vapour evidently warmed the thermometer in the condenser, for its readings are apparently too high.

12. Naphthalene was next tried, the apparatus being in this case exhausted with the pump.

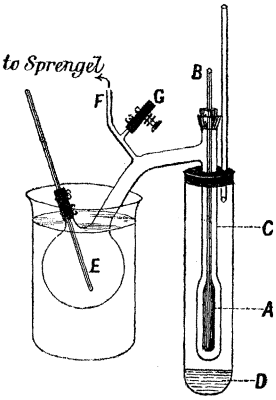
Temperature of bath.	Temperature of condenser.	Temperature of naphthalene.	Difference.
100°	−4°·9	73°·0	77°·9
„	−4·1	73·65	77·75
„	−3·6	74·15	77·75
„	−2·45	74·5	76·95
„	−1·6	74·75	76·35
„	−0·5	75·15	75·65
„	+0·4	75·6	75·20
„	+1·0	76·35	75·35
„	+2·3	76·8	74·50

The results with acetic acid and naphthalene generally agree with those obtained with ice; the differences at low temperatures being greater than at high temperatures. Owing to the low vapour-tension of naphthalene (9 millim.) at its melting-point (79·2), and to the want of data regarding its vapour-tension at lower temperatures, it was not thought worth while to make more extended experiments.

13. Camphor presents unusual facilities for the study of this question. Its melting-point is 175°; its vapour-tension at that temperature is 354 millims., and at 20° is 1 millim.; a great range is thus secured.

The apparatus, however, had to be modified in order to permit the tube containing the thermometer which supported a block of camphor to be jacketed with a vapour, and also to prevent stoppage of the passage by condensation of camphor vapour. It is represented in the accompanying figure (fig. 3).

Fig. 3.



A. Block of camphor round thermometer B, inserted in tube.

C, D. Jacketing tube containing aniline, the vapour of which could be made to surround C.

E. Condenser.

F. Tube connected with SPRENGEL'S pump.

G. Indiarubber tube, closed by screw-clip, through which air could be admitted to alter pressure.

The thermometer was coated by dipping it repeatedly into melted camphor until a sufficiently thick layer had accumulated. The tube C was closed by an indiarubber cork through which the thermometer passed. The condenser E was placed in cold water during the experiment.

On establishing a fair vacuum, and boiling the aniline so as to jacket the tube containing the camphor with aniline-vapour at 184°·5, the temperature of the camphor rapidly rose, but no sublimation took place until the temperature had nearly reached its upper limit. The camphor then rapidly sublimed, and its temperature and the pressure indicated by a manometer connected with the air-pump were read. The pressure was then altered, and other readings taken. At very low pressures the camphor-vapour passed over into the condenser, which in these cases was cooled with a freezing mixture ; but at higher pressures condensation took place in the tube connecting the condenser with the heated tube.

Pressure.	Temperature of camphor.	Pressure.	Temperature of camphor.
millims.	°	millims.	°
1·7	41·2	92·8	136·3
7·2	48·9	105·0	140·3
15·4	92·4	109·4	141·7
27·2	101·0	155·1	147·0
35·0	109·4	197·6	154·3
46·0	116·7	218·5	157·9
66·3	127·4	240·7	160·1
88·6	134·2	297·8	168·0

14. When pressure was gradually increased to 370 millims. the camphor melted, and a drop hung from the end of the solid camphor coating the thermometer. By lowering the pressure to 358 millims. this drop solidified. The pressure of the solidification point was confirmed by a second experiment, but the pressure of melting seemed to vary.

15. The tension of camphor vapour in a barometer tube was next determined. When carried out with only ordinary precautions it was found impossible to exclude moisture, which rendered the results false. Correct results were obtained in the following manner. The upper end of the barometer-tube was drawn into a capillary, and connected with a SPRENGEL's pump ; the whole tube was then jacketed, and surrounded with the vapour of boiling aniline, while a current of dry air was drawn through it. Some camphor was then introduced by the lower end, which was immediately dipped under hot mercury. The mercury was then pumped up the inclined tube ; after it had reached a certain level, the camphor solidified, and adhered to the side of the tube. While the mercury rose further, bubbles of camphor vapour rushed up the tube, carrying with them all air and water vapour. After the mercury had entered the capillary portion of the tube the jacketing tube was slipped down, and the capillary tube was sealed through the mercury. We think it right to give details of the method of operation, as we found it a matter of extreme difficulty to expel all moisture and air. The temperatures given were obtained by jacketing the barometer-tube with the vapours of various pure liquids.

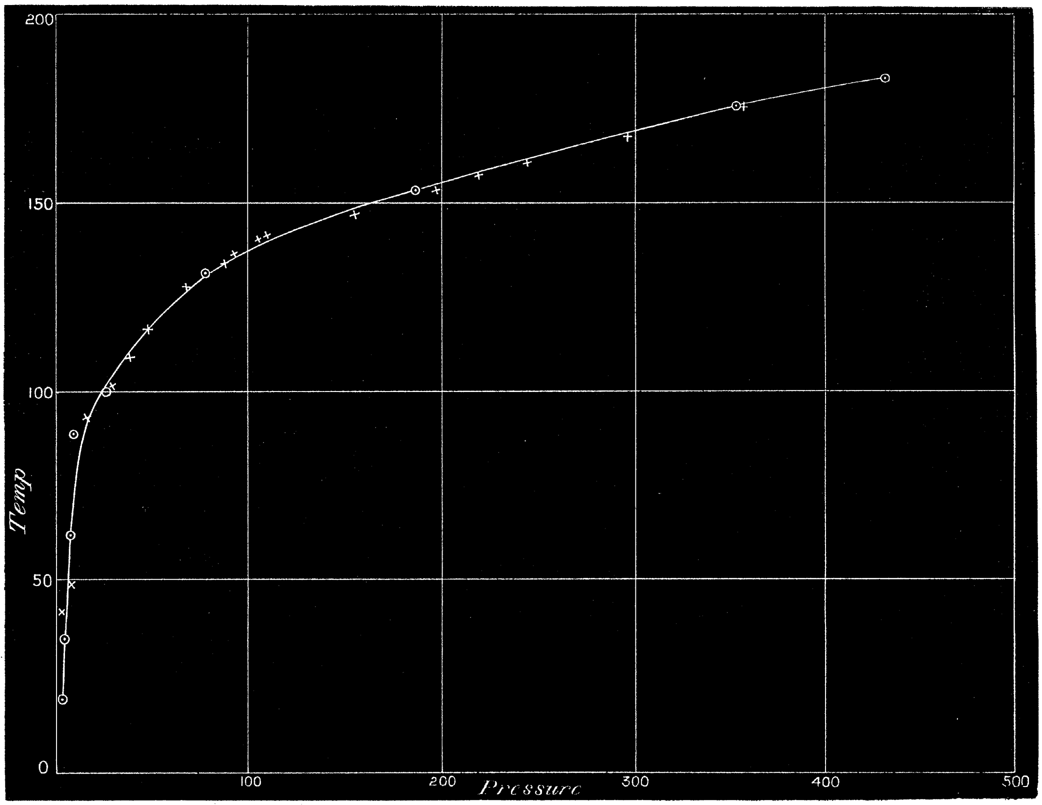
Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.
20·0	1·0	132·0	78·1
35·0	1·8	154·0	188·8
62·4	6·4	175·0*	354·0
78·4	9·5	184·5	431·0
100·0	22·6		

* Melting-point of camphor (GAY-LUSSAC, Ann. Chim. Phys., ix., 78).

The tension was observed three times when the camphor solidified in the barometer-tube. The readings differed only by 3·5 millims., and as a mean gave 350 millims. The tension at which solidification took place in the bulb-apparatus was observed to be 358 millims. The mean of both determinations is 354 millims.

The annexed figure (fig. 4) shows the curve obtained from both sets of results; the pressures corresponding to temperatures of vaporization being indicated by a cross; the vapour-tensions by a dot surrounded by a circle.

Fig. 4.



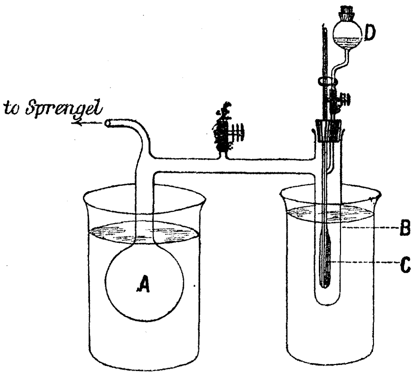
16. It is thus proved that in the case of camphor the pressures corresponding to the temperatures of volatilization coincide with the vapour-tensions of solid camphor at these temperatures; and it appears that this assertion can also be made of ice.

It may be advisable here to point out the difference between the evaporation of a liquid and of a solid. When the bottom of a vessel containing a liquid is heated, the whole of the liquid becomes hot owing chiefly to convection currents, and evaporation takes place only at its surface. When the temperature has reached the boiling point, either superheating or ebullition must take place. It would thus seem that the surface is not large enough to afford escape for the gaseous molecules, and in the former case the temperature of the liquid rises indefinitely, whereas in the latter the liquid increases the extent of its surface by the formation of bubbles. In the case of a solid it is obvious that the surface is of limited extent, and it might therefore be expected that the solid should rise in temperature. Reasoning thus, the possibility of the existence of hot ice was maintained by CARNELLEY and other writers in a series of letters which appeared in 'Nature' during the years 1881 and 1882.

On the other hand, a liquid in the spheroidal state presents a free surface of evaporation in every direction, and yet, although exposed to the radiation of a white-hot surface, its temperature does not rise to the boiling-point (BALFOUR STEWART, 'Treatise on Heat,' 3rd edition, p. 124); and we find that when water is heated in a platinum basin by means of a blowpipe flame impinging on its surface, its temperature cannot be raised above 90°. In these cases the surface appears to be large enough to allow all vapour to escape with sufficient rapidity to prevent superheating.

If, then, the rate of evaporation at the surface of a solid is capable of indefinite increase, however much heat the solid receives, it follows that solids have definite temperatures of volatilization or volatilizing-points, corresponding to definite pressures, as liquids have definite boiling-points.

Fig. 5.



A. Condenser from which exit-tube leads to SPRENGEL'S pump and manometer.
B. Tube in which thermometer C is suspended, placed in hot bath.
C. Thermometer, with bulb covered with cotton-wool.
D. Bulb containing liquid which could be admitted to apparatus by turning screw-clip, so as to trickle down the thermometer-stem, and moisten the cotton-wool.
E. Clipped indiarubber tube for admission of air.

17. It occurred to us that it would be advisable to ascertain if the boiling-points or maximum temperature of evaporation of liquids under conditions as nearly as possible identical with those to which the solids already mentioned were exposed are the same as the temperatures corresponding to their vapour-tensions. To enable this to be done, the apparatus was modified as shown in the figure (fig. 5).

By using a casing of cotton-wool round the thermometer bulb the liquid was exposed to radiated heat in the same manner as the solids were. The vapour-tensions of water found in this way were identical with those of REGNAULT.

18. This method of determining vapour-tensions has great advantages compared with the usual method. For it is extremely difficult to obtain a number of constant temperatures when a long tube is heated, and the pressures depend on those temperatures; whereas by the method described, the temperature depends on the pressure, which can be varied at will by exhausting with the pump or by introducing air.

19. The experiments described have shown that solids have definite temperatures of volatilization, as liquids have definite boiling-points, depending on the pressure to which they are subjected, and that these temperatures are *sensibly* coincident with those of their vapour-tensions. That they cannot be *absolutely* identical is evident; for there must be a certain excess of pressure to produce a flow of vapour from the evaporating substance to the surrounding space, and consequently the evaporating substance must have a higher temperature corresponding to the higher pressure in its immediate neighbourhood. But by the ordinary method of measuring vapour-tensions, where the body emitting vapour is placed in the vacuous space above the mercury in a barometer tube, no flow is possible, and hence the level of the mercury is a true measure of the tension.

Our results, we venture to think, show that with solids as with liquids this difference, even when rapid evaporation is taking place, is an extremely minute one. They also show that the ice-steam line of JAS. THOMSON (see diagram, fig. 1, M, L) is the upper temperature limit of ice at pressures below the critical one.