II. *On Evaporation and Dissociation.*—Part I.

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[Plates 1, 2.]

§ 1. The phenomena exhibited by gases when exposed to varying temperatures and pressures have been shown by many eminent observers to be explicable by an extension to molecules of the laws of motion of matter which are known to be true in the case of large bodies. Such molecules of gas are supposed to be in a state of very rapid motion, the free path of each molecule bearing a very large ratio to the diameter of the molecule. As a liquid is formed by the condensation of a gas, it is clear that its molecules are in closer proximity to each other, and that the average free path of each molecule in the liquid state cannot be nearly so great as in the gaseous state. It was pointed out by Naumann (Ann. d. Chem. u. Pharm., 1870, 155, 325; see also Ramsay, Proc. Roy. Soc., 1880, April 22 and December 16) that it is conceivable that an explanation of the closer proximity of molecules in a liquid than in a gas may be that two or more gaseous molecules have united to form complex molecular groups, analogous to those complex molecules which are known as chemical compounds, in which two or more elements exist in combination.

On the other hand, it is held by some that the difference between gas and liquid is due solely to the greater proximity of the molecules in the liquid state, by reason of which they come within the sphere of mutual attraction, but do not necessarily coalesce to form groups of molecules analogous to the group of atoms in the molecule of a compound.

These views also apply to the molecular constitution of solids; it is generally held that solids differ from liquids only in the arrangement and restrained motion of their molecules.

§ 2. In support of the first view the following points have been urged:—

(*a.*) The rotation of the plane of polarised light is supposed to point to molecular grouping in liquids and solids, which does not exist in gases.

(*b.*) The existence of allotropic forms of elements, and of isomorphous forms of compounds, and the fact that heat is evolved or absorbed during passage from the one form to the other.

(*c.*) The abnormal vapour-density of sulphur and selenium among elements, and of the compound nitric peroxide appear to be undoubtedly due to the existence of complex molecules. It is to be remarked that in these cases molecular grouping occurs before the liquid condition is attained.

(*d.*) The abnormal vapour-densities of all substances at temperatures near their boiling-points, shown especially by acetic and homologous acids. Here also the grouping, if any, must occur in the gaseous state.

§ 3. The phenomena stated in (*a*) and (*b*) are explained equally well, it may be remarked, by a systematic arrangement of gaseous molecules, and do not necessarily imply union of those molecules to form more complex molecular groups; while as regards (*d*) it appears almost certain that the abnormality common to non-dissociable vapours near their condensing-points at high temperatures and corresponding high pressures, is due simply to a deviation from AVOGADRO's law, for it disappears, at least in the case of alcohol, on lowering temperature and pressure, so as to keep the vapour nearly saturated. With acetic acid vapour, on the contrary, the abnormality, which is considerable at the ordinary boiling-point, increases greatly with reduction of temperature and pressure. It might be expected that a decrease of temperature would tend towards the formation of complex molecular groups; while it is difficult to imagine a rise of temperature, even if accompanied by a rise of pressure, bringing about this result.

§ 4. If it be true that liquids consist of more complex molecular groups than gases, that each such complex molecule is composed of a definite number of gaseous molecules, and that the molecule of a liquid may be regarded as a chemical compound of *like* gaseous molecules, then the phenomena attending the change from the solid or liquid to the gaseous state should be similar both with stable and dissociable bodies.

§ 5. Certain analogies are evident on first inspection.

(1.) To convert a liquid into gas, work must be done

(*a.*) in overcoming molecular cohesion;

(*b.*) in expansion against pressure, which may be that of the atmosphere.

If liquids consist simply of gaseous molecules in such proximity that they exercise mutual attraction on each other, the work is wholly expended in these two directions; if, on the contrary, molecules of a liquid are more complex than those of its gas, work is also done

(*c.*) in decomposing the complex molecules;

(*d.*) in imparting increased velocity to the resulting gaseous molecules.

The last assertion (*d*) will hold if the mean energy of each of the liquid molecules is equal to the mean energy of each of the gaseous molecules in contact with it. It is known, at any rate, that no heat change occurs when a saturated vapour is brought in contact with its liquid at the same temperature and pressure. Since the energy of any molecule is proportional to its mass, and to the square of its velocity, and since the mean energy of one of the complex molecules is equal to the mean energy of a single gaseous molecule, it follows that the square of the velocity of the complex molecule is $\frac{1}{n}$th of that of the gaseous molecule, where n represents the number of gaseous molecules condensed to form a complex molecule. It follows, then, that after the complex molecule has been resolved into its constituent simpler molecules, heat must be imparted to each of the latter to increase its velocity, until the energy, $\frac{1}{2}MV^2$, becomes equal to that of the remaining molecules. (See NAUMANN, 'Thermochemie,' p. 93, ed. 1882).*

(*e.*) If molecules, in becoming gaseous, acquire increased velocity, it is obvious that owing to their collision, the motion of the atoms in the molecule is also increased, a certain proportion of energy being absorbed.

Supposing the existence in liquids of complex molecular groups, the analogy is evident between the evaporation of a liquid and the vaporization of such a compound as is stable when solid or liquid, but dissociates partly or completely when gasified. In the first case the simple molecules are like each other; in the second, generally unlike.

§ 6. (2.) The density of gases is found in some cases to increase as the temperature falls to the condensing-point. This may be explained by assuming the existence of complex gaseous molecules (PLAYFAIR and WANKLYN, Trans. R. S., Edin., xxii. (3), 441; 'Annalen,' 122, 245; also NAUMANN, 'Annalen,' 155, 325); or it may be viewed, as before stated, as caused by greater molecular proximity, when mutual attraction comes into play. Similarly with those substances in which dissociation takes place in the gaseous state, the density of the mixture of gases increases with fall of temperature; and this is doubtless caused by the increase in number of complex molecules. (As regards this statement, see § 3.)

§ 7. Solids and liquids, when confined in a closed space, give off from their surfaces gaseous molecules, until there exists in that space a certain number. These gaseous molecules are termed collectively, a *saturated vapour*. After this limit, conditioned by the temperature of the liquid and gas, is reached, evaporation is balanced by condensation; the pressure exerted by the vapour is termed the *vapour-pressure* (vapour-tension) of the substance. Similarly, substances which are known to dissociate, when confined in a limited space, give off vapour, or a mixture of vapours, the molecules of which are wholly, or in part, simpler than those forming the solid or liquid. Such a vapour, or mixture of vapours exerts a pressure conditioned by the temperature. This pressure has been termed the *pressure* (or tension) *of dissociation*. As in the case of bodies that do not dissociate into unlike molecules, the pressure is dependent on the temperature,

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* Exception may be taken to the above statement on the ground that it is yet unknown to what the energy of a liquid is due; and that the relation between energy and temperature, with liquids, has not been ascertained.

and at a given temperature it reaches a maximum, owing to equilibrium being established between dissociation and recombination, as well as between evaporation and condensation, if the latter occurs. We have already shown ('Transactions,' Part I., 1884, p. 37) that in the case of solids, where unlike molecules are not formed when change to a gaseous condition occurs, the curve which represents the maximum pressure attainable by the vapour of a solid at different temperatures represents also the maximum temperature to which the solid can be heated under different pressures, when there is free surface for evaporation. This has long been known to hold for liquids. If the work done in dissociating complex molecules of a solid or liquid into unlike simpler gaseous molecules is analogous to that expended in converting a stable solid or liquid into gas, it seems not unnatural to expect that the above relation between temperature and pressure should hold good for such bodies as dissociate in passing from the solid or liquid into the gaseous state.

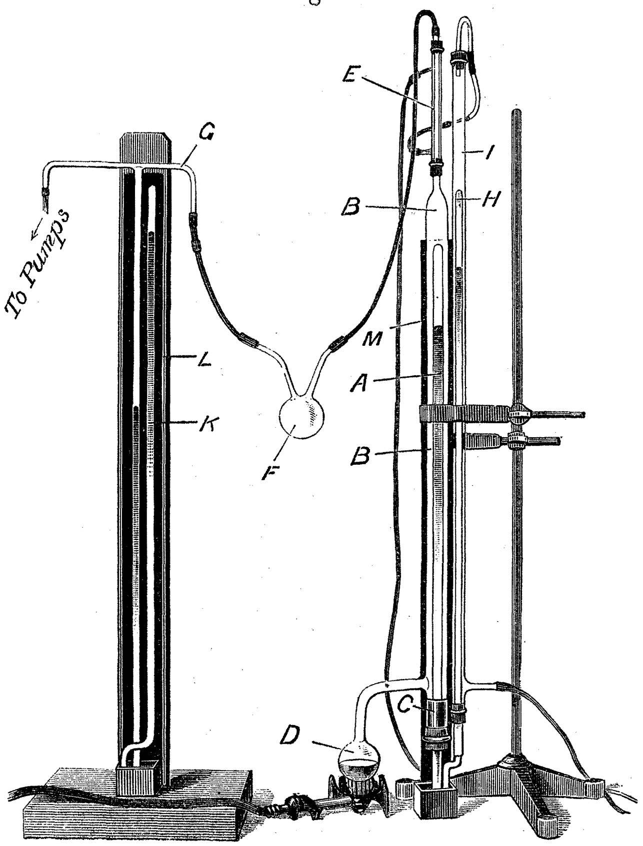
In the present memoir, the relations between temperature and pressure in the case of dissociating substances will be studied.

Description of General Methods.

§ 8. *Temperature of Volatilization under different Pressures.*—The method employed has already been described in the 'Transactions,' Part II., 1884, p. 461. It was often found more convenient to heat the substance in the still, by means of a vapour-jacket instead of a paraffin or sulphuric-acid bath. Care must be taken that the temperature of the vapour is at least 30° to 40° higher than that registered by the thermometer. For high temperatures, the vapour of aniline, methyl-salicylate, bromonaphthalene, or mercury was used as a jacket; and for very high temperatures, it was preferable to use a still with a short tube, with the stem of the thermometer outside of the apparatus. This, of course, necessitated a somewhat troublesome correction, in order to ascertain the true temperature; for different parts of the stem of the thermometer were heated to different temperatures. In many cases, air was introduced into the previously calibrated thermometer to prevent sublimation of mercury in the stem. Although the results are uniformly given in arithmetical order, yet readings were taken sometimes after raising, sometimes after lowering the pressure.

§ 9. *Vapour-pressure (Pressure of Dissociation) at different Temperatures.*—The customary method was employed of introducing the substance into a barometer-tube, heating the tube, and comparing the height of the column of mercury with that in a barometer placed in the same trough. The methods of introducing liquids or solids into the experimental tube, so as to exclude air and moisture, have been already described in the memoir referred to above. As it was necessary to heat the experimental tube to any desired temperature, and to maintain that temperature constant for any length of time, the following method was resorted to as the only practicable one. The experimental tube A was surrounded with a jacket B, and passed through an indiarubber cork, inserted into the lower opening of the jacket. In order to prevent this cork from being attacked by the hot condensed liquid, it was covered with a layer of mercury C. (It may be remarked here that it was found that the slight volatilization of this mercury did not affect the temperature, even at a temperature of 280°, with bromonaphthalene as a jacket, owing probably to the constant presence of a layer of liquid on its surface.) The pure liquid, the vapour of which served to heat the experimental tube, was boiled in a bulb, D, fused on to the side of the jacket. A narrow tube was fused on to the top of the jacket, and was surrounded by a short condenser, E. On issuing from the condenser, the upper extremity of the narrow tube was coupled, by means of lead tubing, with a reservoir, F, the object of which was to collect any liquid which might accidentally pass the condenser. A second lead tube joined F with the gauge G, and the gauge was connected with a Carre's air-pump, as well as with a Sprengel pump, a large reservoir being interposed in order to ensure constancy of pressure. A barometer, H, stood in the same trough as the experimental tube A, and was surrounded by a jacket of water of known temperature, I. On account of the gradual escape of air from the glass into the vacuous space, the barometer was boiled out from time to time. Another barometer,

Fig. 1.



K, stood in the same trough as the gauge G. The heights of the mercury were read in both cases by means of the two scales L and M, graduated on plate-glass mirror; parallax in reading was thus avoided. By means of this arrangement, the pressure in the jacket could be maintained constant for hours together, thus ensuring a constant temperature. In order to obtain any desired temperature between that of the atmosphere and 360°, the following liquids were used:—alcohol, chlorobenzene, bromobenzene, aniline, methyl-salicylate, bromonaphthalene, and mercury. These liquids have the advantage of being very stable, and of being easily obtained in large quantity in a nearly pure state, and at a low price.

The vapour-pressures of all these liquids were determined with great care; and as this method of obtaining constant known temperatures may prove serviceable to others, we have published separate papers on the subject. (Trans. Chem. Soc., 47, p. 640 and 49, p. 37.)

Results of Experiments.

§ 10. *Chloral Hydrate.*—The dissociation of the vapour of chloral hydrate $CCl_3.CH\left.\begin{matrix}OH\\OH\end{matrix}\right\}$, into chloral, $CCl_3.CHO$, and water, H_2O, has been shown by NAUMANN to be complete even at 78·5°, under a pressure of 162 millims. The vapour-density determined by him was 40·85, the theoretical vapour-density of a mixture of the vapours of chloral and water being 41·3, while that of undissociated chloral hydrate is 82·6 ('Berichte,' 1876, p. 822). Experiments have been made by MOITESSIER and ENGEL on the distillation of chloral hydrate, and on its vapour-pressure under different conditions ('Comptes Rendus,' 86, p. 971; 88, pp. 285 and 861; 90, p. 98). WÜRTZ has shown that the vapour of chloral hydrate behaves to an anhydrous salt as though it contained water ('Comptes Rendus,' 84, p. 977; 86, p. 1170; see also FRIEDEL, Bull. Soc. Chim., 43, p. 56; TROOST, 'Comptes Rendus,' 100, p. 834); and also that the vapours of anhydrous chloral and of water do not evolve heat when mixed ('Comptes Rendus,' 89, pp. 190, 337, 429, 1063). NAUMANN points out that the temperature of decomposition of chloral hydrate lies so low that the minuteness of its vapour-pressure probably precludes a determination of its vapour-density at that temperature ('Thermochemie,' p. 135). So long as it retains the solid state, however, it is proved by its physical properties to be a compound. It was, therefore, deemed specially important to determine whether the curve representing its pressures of dissociation was identical with that exhibiting its volatilizing points under different pressures.

§ 11. Pressures of Dissociation of Chloral hydrate in Barometer-tube.

Temperature.	Pressure.	Time required for equilibrium.
°	millims.	
12·7	6·8	After standing over night.
27·9	19·0	34′
39·9	35·8	20′
50·8	72·0	24
56·1	96·2	Constant at once.
63·3	146·4	,, ,,
78·2	318·3	,, ,,

The chloral hydrate began to melt and partly liquefied at 50·8°. These results confirm those of Moitessier and Engel. The general form of the curve based on these numbers is remarkably similar to that of an ordinary vapour-pressure curve. (Plate 1.)

§ 12. Temperatures of Volatilization of Chloral hydrate.

The bulb of a thermometer was covered by dipping it repeatedly in melted chloral hydrate, and allowing it to solidify until it had acquired a sufficiently thick deposit. A bath of sulphuric acid was used to heat the tube. The temperature rose gradually; the pressure remaining nearly constant. At 51·8° the substance was still perfectly solid, although above its ordinary melting-point, 50·6°; the pressure registered 11·4 millims. The temperature then rose to 57°, while the pressure rose to 12·3 millims.; after this the pressure rose only 0·1 millim., while the temperature rose to 64°. Even at 64° no sign of melting was to be noticed. The experiment was then discontinued, and the melting-point of the sublimed chloral hydrate compared with that of the portion left on the thermometer. It was found to be 50·6° for both. The substances had, therefore, apparently undergone no change on heating. It is right to observe, however, that a specimen of chloral hydrate, which had been repeatedly melted, and which was examined after two years, left on treatment with water an insoluble residue, the melting-point of which was above 130°. The melting-point of the residue on the thermometer-bulb, however, showed that it did not consist of this substance, which is possibly a polymeride.

§ 13. In the second experiment, with the temperature at 50·2°, the pressure was 7 millims.; the temperature rose to 55°, pressure rising to 7·4. It was impossible to lower the pressure further, for vapours given off by the chloral hydrate attacked the mercury of the Sprengel pump, forming mercurous chloride; this is a remarkable circumstance, for chloral hydrate had no perceptible action on the mercury in the barometer-tube, at a much higher temperature. After this experiment, the chloral hydrate adhering to the bulb of the thermometer was carefully examined, and it was found that the bulb was completely coated, and that the substance was in perfect contact with it. The minimum thickness was 0·8 millim., and the hydrate extended 12 millims. below the bulb and about 30 millims. above it. The hydrate was therefore undoubtedly heated above its usual melting-point without melting.

§ 14. The third experiment began with a temperature of 52° and a pressure of 9·2 millims. Air was then admitted, so as to raise the pressure to 24 millims., while the temperature was rising. The registered temperature was 53°. More air was admitted from time to time, and the following readings were taken :—

Pressures	40·3	53·0	53·0	60·6
Temperatures. . .	52·0	50·0	49·0	49·0 (melting).

As soon as the substance began to melt, air was removed by pumping. When the pressure was reduced to 40·3 millims., the temperature being 48·4°, the substance entirely solidified, and after further reduction of pressure to 23 millims., the temperature rose to 51°. Air was then admitted, so as to raise the pressure to 61·6 millims., when the hydrate melted. It is noticeable from this experiment, that admission of air, to increase the pressure, lowered the temperature, and its removal raised the temperature; and that the substance melted only when the temperature had fallen below its ordinary melting-point; and that the pressure at which fusion occurred was in this, and in other similar cases, about 60 millims.

§ 15. Confirmation of the above results was obtained with a fourth series.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure	Temperature.
millims.	°	millims.	°	millims.	°
7·4	50·0	41·0	56·0	42·0	50·0
7·5	52·0	40·0	53·7	falling	53·0
7·6	54·0	47·5	53·0	,,	54·0
7·7	55·0	59·6	52·0	,,	55·0
8·1	56·0	59·6	51·0	,,	56·0
8·1	57·0	59·6	50·7	..	..
Substance solid ; air admitted.		Melting ; air removed by pumping.		Pressure increased to 64 millims. Substance melted.	

§ 16. In the fifth series, to ascertain if the chloral hydrate would melt if the pressure were high, and the temperature raised towards the melting-point, the substance was heated at a pressure of 24 millims. It began to melt when the temperature registered was 24°. It was evident that the heat had not had time to penetrate to the interior. The substance was cooled, and again heated at a pressure of 16·5 millims. The hydrate melted only when in contact with the stem of the thermometer, where it was evidently heated by conduction. These observations were confirmed by a sixth experiment, in which the pressure was 25 millims., and the temperature registered, when fusion began, 37°. After cooling and lowering the pressure to 15·2 millims., the temperature rose on again heating to 55°, without the substance melting. As these results are so very unusual, it was deemed advisable to check the experiments, showing the possibility of heating the chloral hydrate above its melting-point without its fusing; entirely similar results were obtained in two separate series of experiments.

§ 17. The general conclusion to be drawn from these experiments is, that the relations between temperature and pressure with chloral hydrate differ from those shown in the case of bodies which do not dissociate, and indeed that a fall of pressure allows of a rise of temperature, and that a rise of pressure lowers the temperature of this dissociating body. It is also to be remarked that this substance undergoes no change in composition, so long as it remains solid, while it is known that when the liquid hydrate is distilled, separation into its constituents takes place, and that the residuum has a different composition from that of the distillate (Naumann, 'Berichte,' 1879, p. 738).

§ 18. As the results of a determination of the vapour-pressures of chloral by Moitessier and Engel are meagre, it was thought worth while to determine these constants by the still-method, as chloral attacks mercury, and another cause of error is the formation of a small quantity of hydrogen chloride when chloral is heated.

VAPOUR-PRESSURE of Chloral.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
5·3	−13·0	29·6	18·0	248·6	65·2
7·5	− 6·9	37·9	22·7	296·6	69·7
8·4	− 5·0	49·8	28·2	358·3	74·8
10·3	− 1·0	61·9	32·0	415·0	79·7
12·3	+ 2·0	62·9	32·7	463·3	82·7
13·6	4·0	72·6	35·9	518·0	85·3
15·7	6·5	79·1	37·5	565·0	88·6
16·5	6·9	83·8	38·9	608·0	90·7
17·0	8·0	95·5	41·9	671·5	93·8
18·3	9·2	121·3	47·6	704·9	95·3
20·1	10·8	160·0	54·0		
21·6	12·8	200·7	59·7		

§ 19. It will be noticed from § 10 that Naumann found the vapour-density at 78·5° under a pressure of 162 millims. to point to complete dissociation. But the vapour-pressure of chloral hydrate at 78·5° is 322 millims., hence the vapour in his experiments was very far from being saturated. Since dissociation decreases with increase of pressure, it was deemed possible that at pressures nearer saturation, dissociation might not be complete. The following experiments were carried out to test this point:—

A quantity of substance was roughly weighed (about 0·016 gram.), so calculated that its vapour would exert a pressure nearly that of saturation at 60°; and its vapour-density was then determined by Hofmann's method; the tube was heated by alcohol boiling under reduced pressure.

Weight.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage of molecules decomposed.
grm.	millims.	cub. centims.			per cent.
0·01587	113·3	33·64	3811	43·08	91·74
..	107·0	36·14	3867	42·46	94·54
..	102·5	37·76	3870	42·42	94·72
The temperature was then raised to 78·2°					
..	119·6	34·58	4136	41·87	97·28

The temperature was raised to 131·8° by a jacket of chlorobenzene vapour, and two readings of pressure and volume were taken. From these the values of P.V. were respectively 4835 and 4829; as it is certain that dissociation must be complete at this temperature, the actual weight of substance was calculated from the mean value of P.V., and the number obtained was employed in the above calculation of vapour-densities. It is thus evident that at 60°, and at pressures near that of saturation, dissociation is not quite complete. In this, and in all other cases in which dissociation was nearly complete, a very long time elapsed before the whole of the substance had evaporated.

§ 20. *Butyl-chloral Hydrate,* $C_3H_4Cl_3.CH\left\{\begin{matrix}OH\\OH\end{matrix}\right.$.—This body resembles chloral hydrate in dissociating into butyl-chloral and water. Its vapour-density has been determined by Engel and Moitessier in Hofmann's apparatus at 160°, and found to point to complete dissociation. It is stated by these experimenters that it begins to boil at 100°, and that the water distils off, leaving butyl-chloral, boiling at 165°. Butyl-chloral hydrate was found to separate on heating into two layers, the upper of which consisted mainly of butyl-chloral. A few determinations of vapour-pressures were made by Moitessier and Engel, and the following numbers were obtained by them :—

Temperature.	Pressure.
°	millims.
16·8	18·3
46·0	62·8
65·0	125·0
78·4	331·0
100·0	Over 760.

§ 21. PRESSURES of Dissociation of Butyl-chloral hydrate in Barometer-tube.

Temperature.	Pressure.	Time required for equilibrium.
°	millims.	
15·0	5·8	2 hours
35·0	23·1	81′
16·0	9·5	Stood all night.
35·0	25·9	51′
50·0	49·5	52′
60·0	86·0	95′
70·0	189·7	73′
77·8	307·0	28′
85·0	428·0	7′
90·0	569·7	2′

The curve is represented in Plate 1.

§ 22. TEMPERATURES of Volatilization of Butyl-chloral Hydrate.

The thermometer-bulb was coated as usual, and the still was jacketed with aniline vapour. The initial pressure was 2·15 millims. The temperature rose gradually to 68·5°, and then fell again to 66·5°; the pressure falling to 2·0 millims. The pressure was then raised to 6·8 millims.; the temperature continued to fall very slowly to 66°. On raising pressure to 15·2 millims., temperature fell to 65·5°; and with a pressure of 28·5 millims. temperature remained constant. When pressure was raised to 52·7 millims. temperature rose to 66°; pressure was increased to 65·9 millims., when temperature rose gradually to 69·7°, when the substance in contact with the stem of the thermometer became moist. On reducing pressure to 21·8 millims. solidification immediately ensued; but as the substance had largely evaporated, readings of temperature were doubtful.

A second series of experiments was made. The initial pressure was 1·9 millims., the temperature rising to about 63°. On raising pressure to 3·8 millims., no alteration in temperature was noticed. At 26·1 millims. temperature rose slowly to 64·5°. Pressure was then reduced to 13·9 millims., and the temperature fell to 63°. The reduction of pressure was continued until it reached 2·8 millims.; the temperature fell to 62·5° when the pressure was 5·5 millims., and gradually rose again to 64°. Pressure was then raised to 48 millims., and temperature rose to 68°. With rise of pressure to 65·2 millims., temperature rose to 69·2°, and the upper portion of the substance melted. On reducing pressure to 22 millims. solidification occurred, and temperature fell to 65·4°.

§ 23. It will be seen that these results are most erratic; but it is to be noted that the total range of temperature was only from 62·5° to 69·2°, while the pressure varied from 1·9 millims. to 65·9 millims. The only conclusion to be drawn is that temperature and pressure are independent of each other.

§ 24. *Chloral methyl-alcoholate*, $CCl_3CH\begin{cases}OH\\OCH_3\end{cases}$.—This substance is formed by direct combination of chloral and methyl alcohol, with evolution of a large amount of heat. It has been little investigated. Its boiling-point is given by MARTINS and MENDELSSOHN-BARTHOLDY at 98° ('Berichte,' III., p. 443), and by JACOBSEN at 106° ('Annalen,' 157, p. 243). The melting-point is stated by JACOBSEN to be 50°. We find it, however, to be 40·2°. These numbers are discordant, but it is to be noticed that the numbers given by JACOBSEN are with methyl and ethyl compounds of chloral invariably 8° to 10° higher than those given by other observers.

The methyl alcohol used by us in preparing this body was made from pure crystals of methyl oxalate, and was carefully dried. It was mixed with chloral, and the resulting compound was crystallized over sulphuric acid. The crystallization of both ethyl and methyl compounds, from their solution in the respective alcohols, is extremely beautiful. The crystals grow upwards out of the liquid, and assume the form of luxuriant vegetation.

§ 25. PRESSURES of Dissociation of Chloral methyl-alcoholate in Barometer-tube.

Temperature.	Pressure.	Time required to establish equilibrium.	Remarks.
°	millims.		
17·0	8·8	1 h.	Solid.
35·0	17·0	16′	,,
40·0	18·1	Constant at once.	,,
45·0	21·3	15′	Liquid.
40·0	14·9	35′	Liquid, cooled below M.P.
35·0	10·3	50′	,, ,, ,, ,,
50·0	30·7	8′	Liquid.
55·0	40·0	5′	,,
60·0	56·6	2′	,,
65·0	73·2	4′	,,
70·0	98·5	5′	,,
78·05	154·2	3′	,,

The level of the mercury in the trough was then raised, and the tube allowed to cool; complete condensation occurred, and after 16 h. the mercury was in complete contact with the solid at the top of the tube. The level was then lowered.

Temperature.	Pressure.	Time required to establish equilibrium.	Remarks.
°	millims.		
18·0	9·3	48′	Solid.
85·0	218·9	12′	Liquid.
90·0	281·4	19′	,,
95·0	358·4	7′	,,
100·0	452·8	6′	,,
105·0	566·2	26′	,,

It will be noticed that the liquid has apparently a lower vapour-pressure than the solid. At 35° the vapour-pressure of the solid is 17 millims., and of the liquid only

10·3 millims. Now, as we have already shown, that with stable substances the solid has invariably a lower vapour-pressure than the liquid ('Transactions,' Part II., 1884, p. 461), and as from theoretical considerations this must be so; and as it is also evident that the melting of chloral methyl-alcoholate must be accompanied by absorption of heat, for when the liquid substance is allowed to cool below its solidifying point, temperature rises when solidification begins; it appears to us necessary to account for this phenomenon by the supposition that the products of dissociation are soluble in the liquid, and are therefore prevented from exerting their full pressure. Similar phenomena have been observed with the ethyl alcoholate, and it was noticed that when liquefaction commenced pressure fell at once. (The curve is given in Plate 1.)

§ 26. TEMPERATURES of Volatilization of Chloral methyl-alcoholate.

The initial pressure in the still was 2·2 millims. On heating with aniline vapour, the temperature gradually rose more and more slowly to 40·6° without alteration of pressure. On raising pressure to 5·5 millims., the substance melted completely at once. The melting pressure lies, therefore, between 2·2 and 5·5 millims. Here, again, no relation between temperature and pressure is observable.

§ 27. It was noticed that the vapour-pressure of the methyl alcoholate in the barometer-tube was lower than that of the hydrate at the same temperatures, in spite of the fact that methyl alcohol is more volatile than water; and it appeared likely that the substance would be more stable than the hydrate. This was found to be the case by the following determinations of vapour-density. It will be noticed that while the vapour-pressure at 78·5° is 160 millims., the density was determined at 131·4 millims.

VAPOUR-DENSITIES of Chloral methyl-alcoholate.

Weight.	Temperature.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage number of molecules decomposed.
	°	millims.	cub. centims.			per cent.
0·0203	78·5	131·4	33·53	4406	50·32	78·06
—	"	117·0	38·03	4450	49·82	79·84
—	132·1	148·6	38·01	5648	45·24	100·0
—	"	134·7	42·28	5695	44·86	"
—	"	150·9	37·58	5671	45·06	"

The theoretical vapour-density of the dissociated substance is 44·8.

§ 28. *Chloral ethyl-alcoholate,* $CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right.$.—Formed by direct combination of anhydrous chloral with ethyl alcohol. It was crystallized from its solution in ethyl alcohol. It is stated by JACOBSEN to melt at 56° (*loc. cit.*); by LIEBEN at 46° ('Berichte,' III., p. 909; and we find its melting-point to be 46·5°. The boiling-point is given by Lieben as 115°. Its vapour-density has been determined by Lieben, and found by Dumas's method to be 53·12 at 157°, and 50·38 at 198°. Würtz has also determined the vapour-density by Hofmann's method, and found at 100°, with a pressure of 247·6 millims., the vapour density to be 48·07. The theoretical density of the mixture of chloral and alcohol is 48·3. By Dumas's method the alcoholate would be submitted to fractional distillation, which would entail a residue containing excess of chloral; and it is more likely that the higher vapour-density obtained by Lieben is to be ascribed to this cause than to incomplete dissociation.

§ 29. Vapour-pressures of Chloral ethyl-alcoholate in Barometer-tube.

Series I.

Temperature.	Pressure.	Time.	Remarks.
°	millims.		
14·0	13·5	2 days	Solid.
35·0	24·4	22′	„
45·0	23·1	13′	Trace of liquid showing.
50·0	24·7	22′	Liquid.
55·0	34·6	5′	„
60·0	46·6	9′	„
65·0	62·7	3′	„
70·0	84·0	5′	„
75·0	111·8	3′	„
78·0	130·0	3′	„
Cooled to 50·0	24·7	45′	Recombination.
„ 35·0	9·8	23′	Still falling; liquid, cooled below solidifying point.
12·0	11·2	18 hours	Solid.
35·0	24·3	19′	„
85·0	187·3	31′	Liquid.
90·0	242·2	15′	„
95·0	308·8	5′	„
100·0	387·8	10′	„
105·0	487·7	10′	„
109·4	585·4	9′	„

§ 30. Series II.

Temperature.	Pressure.	Time.	Remarks.
°	millims.		
15·0	9·1	1 hour	Solid.
35·0	22·8	19′	„
40·0	24·7	25′	„
45·0	25·1	15′	„
50·1	25·9	37′	Liquid.
60·0	47·1	12′	„
Cooled to 40·0	14·7	112′	Still liquid.
„ 35·0	12·4	50′	Still liquid; pressure falling slowly.
35·0	19·9	16′	Solid.

Here, again, the pressures in the solid are higher than in the liquid state, and probably for the same reason. On referring to the curve in Plate 1 it will be noticed that that portion representing the pressure in contact with liquid below the melting-point is continuous with that above the melting-point; whereas the pressure of the vapour in contact with solid is somewhat irregular, as is also the case with the methyl compound.

§ 31. TEMPERATURES of Volatilization of Chloral ethyl-alcoholate.

Series I.—The initial pressure was 2 millims.; the temperature of the alcoholate, heated by aniline-vapour, rose more and more slowly until it reached 47·7°. The pressure was then raised to 8·1 millims., when the substance melted.

Series II.—At a pressure of 2·55 millims. the temperature rose to 47°; air was admitted so as to raise the pressure to 6·1 millims., the alcoholate at once melted, and did not re-solidify on reducing pressure to 5·1 millims. It was thus impossible to detect any relationship between temperature and pressure.

§ 32. VAPOUR-DENSITIES of Chloral ethyl-alcoholate.

Weight.	Temperature.	Pressure.	Volume.	P. V.	Vapour-density.	Percentage number of molecules decomposed.
grm.	°	millims.	cub. centims.			per cent.
0·02066	78·35	111	38·42	4265	52·88	82·68
		117·7	36·28	4270	52·82	82·89
		122·9	34·68	4262	52·95	82·44

It is thus evident that this body is not wholly dissociated at 78·35° when the pressure bears the ratio to that of saturation of 111 or 123 to 130.

We propose to study in greater detail the dissociation of these interesting substances, as revealed by their vapour-densities; these determinations, however, suffice to show that they are capable of existing partially undissociated.

§ 33. *Ammonium Carbamate.*—The formula of pure ammonium carbamate is $CO\begin{cases}NH_2\\ONH_4\end{cases}$; but from the nature of our experiments we were compelled to use the commercial salt, the composition of which is variable.

The dissociation pressures of this substance have been very accurately determined by NAUMANN ('Berichte,' 1871, p. 782); by ISAMBERT ('Comptes Rendus,' 97, p. 1212); and by MOTESSIEIR and ENGEL ('Comptes Rendus,' 93, p. 595). As the results of all three observers agree with each other, a redetermination was unnecessary. Suffice it to say that they give a regular curve of the usual form, reproduced in Plate 1.

It is also known from numerous experiments by NAUMANN ('Annalen,' 160, p. 5, and

'Berichte,' 1871, p. 780); by Bineau ('Annales,' 67, p. 240); and by H. Rose (Pogg. Ann., 46, p. 363), that the vapour-density of ammonium carbamate is 13·0, corresponding to complete dissociation into $2NH_3+CO_2$. It might, therefore, be expected to yield results somewhat analogous to those obtained with chloral hydrate.

§ 34. Temperatures of Volatilization of Ammonium Carbamate.

As it was impossible to coat the bulb of the thermometer in the usual way with this substance, a block of commercial carbamate was drilled with a hole, which the thermometer exactly fitted; and it was then turned in a lathe to form a cylinder of convenient size. The following numbers refer, therefore, to commercial carbamate, or, as it is usually termed, carbonate of ammonia. The apparatus was the same as that employed for chloral hydrate. To ensure thorough condensation of the evolved gases, tubes containing pumice-stone, moistened with sulphuric acid, and stick-potash were interposed between the apparatus and the pump. The jacket was the vapour of boiling aniline.

The first series consisted of two readings, every care being taken to keep the pressure low. The pressures were 5 and 9 millims. respectively, and the temperatures 62° and 64°.

The second series gave the following numbers :—

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature
millims.	°	millims.	°	millims.	°
100	65·8	145·5	64·2	130	66·0
115	65·4	162·0	67·7	210	66·0
130	64·5	156·0	68·0	202	65·4
139	63·5	144·0	67·4	200	65·0
145	63·3	130·0	66·5		

From these experiments it will appear that, as in previous cases, pressure and temperature are independent of each other. The maximum temperature attained was 68°, although the temperature of the jacket was over 180°. The results are shown in Plate 1.

§ 35. *Ammonium Chloride*, NH_4Cl.—This substance has given rise to long discussions. The solution of ammonium chloride is known to dissociate on boiling, for ammonia is first evolved, and the residual liquid is acid (Fittig, 'Annalen,' 128, p. 189). Its vapour density corresponds to a mixture of NH_3 and HCl at 350° and atmospheric pressure (Deville and Troost, 'Comptes Rendus,' 56, p. 895), and also at higher temperatures. Horstmann, from not very concordant results, concluded that its vapour-density is greater at 300° and a pressure of from 40 to 60 millims., than at 360° under normal pressure ('Berichte,' 1869, p. 299). At 360° Deville found that on mixing the gases heat was evolved, necessarily implying some combination; Wanklyn, however, states that combination is only partial. **Marignac** calculated the latent heat of vaporization of NH_4Cl and found it to be 706 calories; while **Favre** and **Silbermann** give the heat of combination of NH_3 and HCl as 743·5 or 715·5 calories, calculating by different methods. **Horstmann** determined the vapour-pressure by distilling the substance in an iron tube closed by a cork in which were three holes; one for a manometer, one for a thermometer, and one for exhausting air, and so lowering pressure. And from his observations, the details of which he does not record, he constructed a curve showing the relations of pressure and temperature ('Berichte,' 1869, p. 137). On referring to this curve it will be seen that his results closely agree with those obtained by us. **Than** contradicts **Deville**'s results as regards rise of temperature on mixing the gases, by experiments conducted on a different principle; at 350° he found no evolution of heat, or, more correctly, noticed no contraction, while between 330° and 340° contraction occurred ('Annalen,' 131, p. 129). The well-known experiments on the diffusion of the hot vapour of ammonium chloride point to at least partial dissociation.

§ 36. VAPOUR-PRESSURES of Ammonium chloride in Barometer-tube.

For temperatures between 98° and 280° an ordinary barometer-tube was used. As mercury-vapour at 280° exerts a pressure of 155·17 millims., it was first advisable to determine whether a mixture of mercury-vapour and another vapour on which it had no action could be relied on as giving the sum of their pressures.

A barometer-tube was boiled out, and jacketed with bromonaphthalene, no substance being introduced. At a pressure of 755·9 millims., and at a temperature as determined by the vapour-pressure of bromonaphthalene of 280·1° (see § 9), the vapour-pressure of mercury, after all corrections had been introduced, was found to be 158·8 millims. On cooling there was a certain amount of air present which had been given off from the walls of the barometer-tube. The pressure exerted by this air was read at 24°, and was found to be 10·6 millims. The volume occupied by this air was (23·3 millims. × by area of the tube), while at 280·1° it was (159·3 millims. × by area of tube); hence the pressure at the higher temperature was found by the equation

$$\frac{10{\cdot}6 \times 23{\cdot}3 \times 553{\cdot}1}{159{\cdot}3 \times 297} = 2{\cdot}9 \text{ millims.}$$

The vapour-pressure of mercury is therefore $158{\cdot}8 - 2{\cdot}9 = 155{\cdot}9$ millims. This is identical with that given by **Regnault**, for mercury-vapour at 280·1°.* This tube without being emptied was inverted and again boiled out *in vacuo*. Bromonaphthalene was then introduced, and the tube was jacketed with bromonaphthalene vapour, boiling under reduced pressure. The temperature was occasionally raised by increasing the pressure, and readings were taken. The results obtained were always too low, and were variable. The cause of this turned out to be the slow rate at which the mercury-vapour diffused through the layer of liquid bromonaphthalene on the surface of the mercury,

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* From our revised table of the vapour-pressures of mercury the pressure at 280·1° is 157·7 millims.

for on lowering the temperature the pressure of the bromonaphthalene vapour, after the pressure of mercury-vapour had been subtracted, was found to be the same as that under which the bromonaphthalene which jacketed the tube, was boiling. The detailed results are as follows:—

Temperature.	Pressure of bromonaphthalene in jacket.	Total pressure in barometer-tube.	Vapour-pressure of mercury.	Δ.	Corrected to 0°.
°	millims.	millims.	millims.		millims.
238·2	290·6	346·7	55·5	291·2	290·1
			(54·1)*	292·6	291·5

The level of the mercury was fluctuating about 1 millim.

It is thus seen that the combined vapour-pressure of these two substances is equal to the sum of the two vapour-pressures taken separately.

§ 37. A fresh tube was boiled out, and ammonium chloride was introduced. On heating with vapours of different liquids under different pressures the following results were obtained:—

Temperature.	Pressure.	Duration of experiment.
°	millims.	
98·2	0·2	Constant
122·9	3·5	23′
132·0	3·9	10′
140·9	4·3	Constant
151·9	4·7	7′
165·9	4·9	8′
183·3	5·5	34′
200·0	9·1	36′
210·1	12·3	60′
223·0	18·1	32′
241·9	32·1	29′
251·4	48·8	43′
261·3	72·5	65′
271·1	99·4	11′
280·7	144·4	?

The last observation admitted of no regular time-curve, on account of the difficulty of forcing up the vapour. A constant result was finally obtained at the pressure given.

§ 38. After cooling, a permanent gas remained, exerting a pressure of 50·2 millims. This after two days had fallen to 44 millims. The tube was then inverted, which removed some of the gas, and after being placed in position, was again heated. The atmospheric pressure was 760 millims., hence the boiling-point of bromonaphthalene was 280·3°. The pressure now rose to 145·9 millims., almost identical with the former reading. After again cooling, the pressure was 35 millims. On introducing water, a portion, at least, of the permanent gas was dissolved. As the pressure thus obtained was identical within limits of error of experiment with that yielded by the still-

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* From our table.

method, which will afterwards be given, and as this was not the case with other dissociating substances, the highest reading was repeated.

§ 39. The vapour-pressure of mercury was redetermined in the same manner as before; the tube was jacketed with bromonaphthalene at a pressure of 752·2 millims.; the temperature corresponding was 280°. The vapour-pressure was found, after the necessary corrections, to be 156 millims. After cooling, the pressure due to air was 1·7 millim.; this, corrected as before, gives a pressure of 0·6 millim. at the higher temperature. The pressure of the mercury-vapour is therefore 155·4 millims. From REGNAULT'S numbers, 155·2 is the pressure at this temperature.*

This tube, without being emptied, was boiled out again *in vacuo*, and some ammonium chloride, prepared from pure hydrochloric acid and ammonia, and previously strongly heated, was introduced with the usual precautions. The tube was again jacketed with bromonaphthalene vapour, boiling at a pressure of 755·7 millims., corresponding to the temperature 280·1°; the pressure read was 145·4 millims., a number agreeing very closely with those previously obtained, viz., 144·4 and 145·9 millims.

§ 40. When the tube cooled, a permanent gas remained, which exerted a pressure of 18·3 millims. This amounts to a pressure at the higher reading of 4·2 millims. As a very long time was allowed so as to make certain of no further rise when the ammonium chloride was heated, the presence of this gas cannot be accounted for by a gradual decomposition of the ammonia, for we have shown (Chem. Soc. J., 1884, p. 88) that ammonia begins to decompose only at about 500°, even when hydrochloric acid is absent. It might, however, be due to some extent to the action of hydrochloric acid on mercury. On inclining the tube, this gas formed a bubble of considerable size at the top. Water was then introduced, and almost complete absorption occurred. It appears certain, then, that gaseous hydrogen chloride and ammonia, when perfectly dry, combine very slowly. In any case, the error, owing to presence of permanent gas, amounted to only 4·2 millims.

§ 41. It was deemed advisable to ascertain the vapour-pressure of ammonium chloride at still higher temperatures, and for that purpose the ordinary arrangement was inadmissible. We, therefore, adopted a method, the principle of which will be seen from the accompanying diagram. A is a tube, at the closed end of which a mass of ammonium chloride was placed above the constriction at B. This was done before the tube had been bent. Mercury was then introduced, occupying the level shown. This tube was surrounded by a jacket, C, containing a little mercury; and was closed by a tight-fitting indiarubber cork, D, through which the open end of the tube, A, projected. The tube A was connected by means of lead-tubing with a differential gauge, E, behind which stood a graduated mirror scale, and with a force and exhaust-pump, G, so that pressure on the mercury in A could be increased or diminished to a known amount at will. The pressure exerted on the mercury in the

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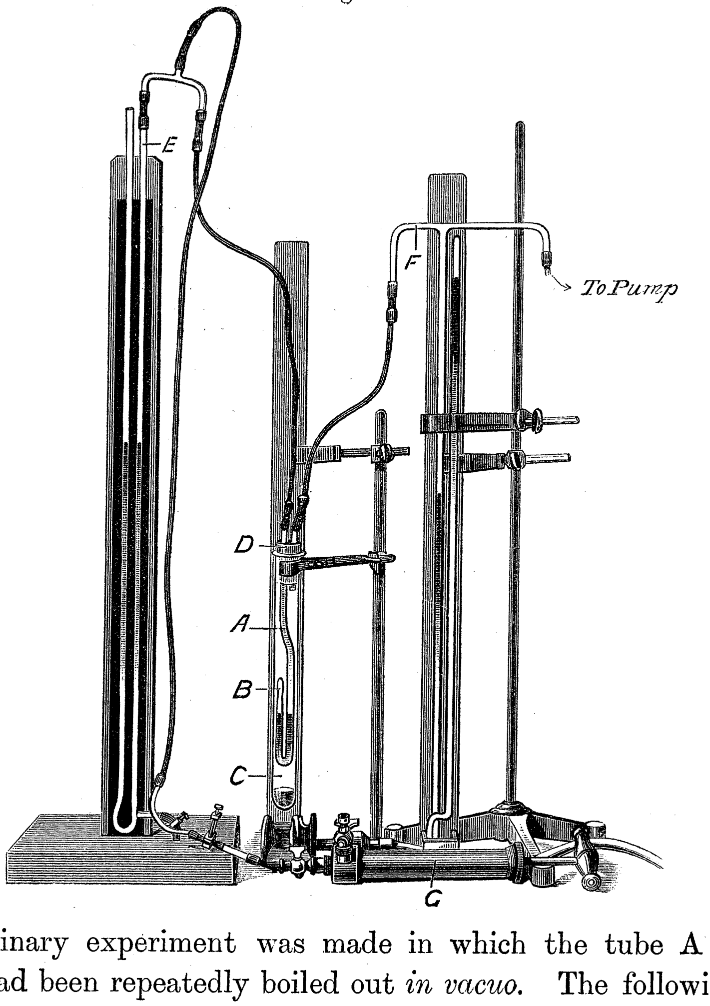
* From our revised table, 157·35 millims.

closed limb of A was equal to atmospheric pressure plus or minus the difference of levels in the differential gauge, plus or minus the difference of levels in the tube A, all reduced to 0°.

§ 42. Through a second hole in the indiarubber cork D a tube passed to a gauge, F, and from that to an exhaust-pump. The mercury in C could thus be caused to boil under any desired pressure, heating A to corresponding temperatures. For the measurement of these temperatures, Regnault's data for the vapour-pressures of mercury were used.

Fig. 2.



§ 43. A preliminary experiment was made in which the tube A contained only mercury, which had been repeatedly boiled out *in vacuo*. The following results were obtained:—

Pressure under which mercury boiled.	Pressure in A.	Δ.
millims.	millims.	millims.
267·6	266·7	0·9
378·3	377·0	1·3
755·0	751·8	3·2

The error in pressure is thus seen to be less than 0·5 per cent., and corresponds to an extremely minute difference in temperature; in the last instance it is barely 0·20°.

§ 44. In experiments on the vapour-pressures of ammonium chloride it was unnecessary to boil out the tube A, for it was possible to ensure absence of air by raising the pressure, heating the substance, and then reducing pressure so as to allow gas to escape. The mass of solid ammonium chloride could not pass the constriction. At a temperature of 320° it was considered certain that all air had been removed when this operation had been repeated six times, a considerable interval of time elapsing between each escape. A large number of preliminary experiments showed that the pressure rose steadily, and as this was considered at first to be due to dissociation, time-curves were constructed. In order, as we imagined, to shorten the time required, the pressure in the differential gauge was raised before each reading, so as to keep the volume of gas constant.

§ 45. For the sake of clearness the experiments are arranged in the order of temperature. At 290° vapour was allowed to escape, and a reading was immediately taken, with the following result:—

Temperature.	Pressure.
°	millims.
290	188·5
300	250·6
,,	252·5
310	342·4
,,	342·1
320	445·9
,,	443·7
330	597·6
,,	596·0

§ 46. A considerable number of experiments were made at 320° and 340°, pressure being allowed to rise.

At 320°, the following initial readings were obtained:—449·7 millims. and 447·7 millims. Having noticed that pressure steadily rose, after these readings had been taken, it was resolved to construct time-curves, so as to ascertain the rate of increase, and the final value. But it was found that this rate was sensibly constant during any one experiment, although it differed in each experiment, and was always slower after each escape of vapour. Since the explanation of the results which we propose to give was only arrived at after careful examination of these time-curves, it is necessary to give the numbers in detail. The third column will be explained later.

I. TEMPERATURE, 320°. Rate of increase of pressure, 1 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
449·2	0	449·2	0
451·1	5	446·1	5
457·2	11	446·2	11
463·1	17	446·1	17

II. TEMPERATURE, 320°. Rate, 0·85 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
449·3	0	449·3	0
449·1	4·2	444·9	5
456·2	9·3	446·9	11
460·2	13·6	446·6	16
462·7	16·1	446·6	19

III. TEMPERATURE, 320° (much vapour let out). Rate, 0·545 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
447·5	0	447·5	0
448·1	2·7	445·4	5
453·9	5·4	448·5	10
457·6	9·8	447·8	18
470·3	20·7	449·6	38

IV. TEMPERATURE, 320°. Rate, 0·513 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
449·7	0	449·7	0
451·7	2·6	449·1	5
457·4	10·8	446·6	21
468·1	19·0	449·1	37

V. TEMPERATURE, 320°. Rate, 0·481 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
446·0	0	446·0	0
448·8	2·4	446·4	5
453·9	5·3	448·6	11
460·8	8·7	452·1	18
463·8	14·9	448·9	31
474·7	25·0	449·7	52
481·6	32·7	448·9	68

VI. TEMPERATURE, 320° (tube re-filled). Rate, 0·683 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
447·1	0	447·1	0
465·1	25·3	439·8	37
510·0	58·8	451·2	86
554·5	102·5	452·0	150
610·0	164·0	446·0	240
662·5	225·5	437·0	330
706·3	266·5	439·8	390

VII. TEMPERATURE, 320° (large amount of vapour allowed to escape). Rate, 0·297 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
438·4	0	438·4	0
447·1	8·9	438·2	30
458·1	26·7	431·4	90
477·5	49·0	428·5	165
517·8	78·7	438·3	265

VIII. TEMPERATURE, 320°. Rate, 0·2142 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
438·4	0	438·4	0
445·4	5·1	440·3	24
461·3	23·3	438·0	109
478·4	43·7	434·7	204
496·0	58·7	437·3	274
511·8	71·5	440·3	334

IX. TEMPERATURE, 340°. Rate, after about 20′, 0·495 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
728·1	0	728·1	0
765·7	6·4	759·3	13
784·3	17·3	767·0	35
806·6	34·6	772·0	70
813·8	52·0	761·8	105
825·2	54·4	770·8	110
838·8	71·8	767·0	145

X. Temperature, 340°. Rate, 0·385 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
684·2	0	684·2	0
748·2	2·3	745·9	6
758·6	7·3	751·3	19
774·2	20·0	754·2	52
786·9	32·7	754·2	85
793·3	44·7	748·6	116

XI. Temperature, 340°. Tube re-filled. Rate, after 20′, 1·02 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
720·7	0	720·7	0
761·8	7·1	754·7	7
780·9	20·4	760·5	20
804·0	44·9	759·1	44
827·8	68·3	759·5	67
859·2	98·9	760·3	97

XII. Temperature, 340°. Rate, after 20′, 0·372 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
730·9	0	730·9	0
755·8	1·9	753·9	5
774·7	9·3	765·4	25
787·0	23·1	763·9	62
796·3	34·2	762·1	92
810·8	45·4	765·4	122

XIII. Temperature, 340°. Rate after 20′, 0·300 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
714·4	0	714·4	0
756·3	1·2	755·1	4
769·9	6·6	763·3	22
775·0	12·6	762·4	42
782·2	20·1	762·1	67
835·8	68·4	767·4	228
886·0	123·9	762·1	413

XIV. TEMPERATURE, 340°. Rate, 0·191 millim. per minute.

Pressure read.	Time × rate.	Pressure recalculated.	Time.
millims.		millims.	′
767·4	0	767·4	0
800·3	35·1	765·2	184
805·0	40·3	764·7	211
809·0	48·9	760·1	256
839·2	77·0	762·2	403
845·9	86·5	759·4	453
857·9	95·1	762·8	498
866·9	103·3	763·6	541
870·1	110·0	760·1	576

§ 47. As in all these experiments the volume was kept nearly constant, a constant increase of pressure denotes a constant evolution of gas. This would not have been the case had the volume been allowed to increase. It seemed impossible that such results could have been produced by dissociation; and as it was believed that this constant evolution of gas was due to the action of hydrochloric acid on mercury, this supposition was put to the test. On heating mercury with ammonium chloride for three hours to 330–340° in a sealed tube, it was proved, on treating the contents with water, that mercury had entered into solution as chloride. This has also been noticed by THAN ('Annalen,' 131, p. 131). It would appear that the rate of action depends on the quantity, and therefore on the surface of the solid ammonium chloride present; for it diminished after each escape of gas. It was, therefore, possible to calculate the pressure due to the vapour of ammonium chloride or of its products of dissociation; for it may be considered certain that the rate of action of ammonium chloride on mercury during one experiment is constant. By deducting the product of the constant rate of increase of pressure into the time, from the read pressures, the true vapour-pressure, or dissociation-pressure of ammonium chloride at each time of reading could be calculated. It will be seen that at 320° the vapour-pressure is constant throughout the whole experiment; while at 340° the pressure due to ammonium chloride rises rapidly during the first twenty minutes, and then remains constant. Now, although both the initial and final pressures with different experiments at 340° differed widely from each other, yet, calculating in this way, the result varies within very small limits. We are unable to account for the rise in vapour-pressure during the first twenty minutes at 340°, and not at 320°; had it occurred also at 320° we should have ascribed it to the usual rise of pressure accompanying dissociation before equilibrium is established; but, as will afterwards be shown, dissociation is complete at both temperatures; there is no doubt, however, that the temperature of the ammonium chloride must have been greatly lowered at first by volatilization, and it may be due to this cause.

Since at 320° the initial pressure is the same as that obtained by recalculation, the numbers first given for the lower temperatures, and probably for 330° may be considered as correct.

The mean results at 320° and at 340° are:—

Temperature.	Pressure.
	millims.
320	444·7
340	759·6

Some of the experiments described above were made with ordinary commercial ammonium chloride; but the later ones were all made with material prepared from pure hydrochloric acid and "volcanic" ammonia, which, as is known, is free from hydrocarbons.

§ 48. TEMPERATURES of Volatilization of Ammonium Chloride.

A very clear block of commercial ammonium chloride was cut into pieces of suitable size, each of which was drilled with a hole to receive the bulb of the thermometer, and was then cut into a cylindrical shape. Owing to the very high temperature attained by the ammonium chloride, and the sudden heating, the thermometers were frequently broken; each thermometer was carefully calibrated before air was introduced, and their readings served so far to check each other. Although this method appears somewhat crude, yet the concordance of the results to be given shows its reliableness.

SERIES I.—Pressure Raised by Admission of Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
5·9	199·3	65·0	256·6	449·8	315·5
6·2	202·5	74·9	259·0	495·2	319·4
30·2	237·9	81·9	262·6	520·1	320·5
37·9	240·7	89·8	264·1	596·6	325·6
38·1	241·3	100·6	267·7	640·9	327·7
45·6	247·8	109·9	269·9	709·6	331·3
59·9	252·8	122·1	273·3	760·3	333·4

SERIES II.—Pressure Raised by Admission of Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·4	178·5	16·9	220·5	349·8	307·3
1·5	179·3	25·3	229·9	399·5	311·9
2·2	183·3	31·6	235·9	400·4	313·2
3 1	187·5	41·0	244·4	447·7	315·2
3·6	191·1	82·8	263·9	499·8	318·9
4·4	194·7	95·5	266·7	502·5	320·9
4·5	196·8	125·8	275·9	553·7	321·8
4·5	193·3	150·7	280·3	602·3	324·0
8·3	202·1	194·5	289·3	652·6	327·0
9·1	206·0	201·0	289·0	652·9	327·8
12·6	212·2	249·7	296·0	707·7	329·5
16·1	219·6	293·0	302·6	763·3	330·7
16·3	220·5	300·9	302·2		

SERIES III.—Pressure Raised by Admission of Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
3·3	191·7	112·8	273·0	457·7	318·5
6·1	204·6	169·6	284·7	510·3	321·4
9·7	211·4	180·1	287·4	574·5	325·8
20·8	226·9	217·2	292·8	589·9	327·1
37·7	242·5	305·0	303·5	640·4	329·5
65·5	257·1	322·8	306·3	720·2	333 9
77·1	262·4	383·0	311·5		
113·4	272·6	443·0	316·2		

SERIES IV.—Pressure Raised by Admission of Hydrogen Chloride.

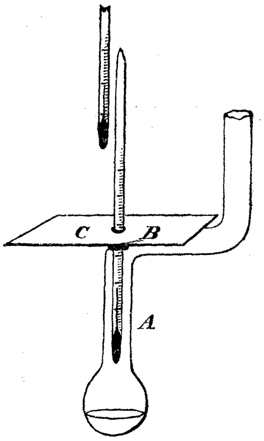
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
3·9	195·5	77·0	261·2	292·4	301·7
12·0	214·7	102·6	267·3	304·6	302·2
19·3	224·2	123·6	273·4	362·9	308·1
31·5	236·9	135·4	277·0	426·3	314·0
34·1	239·3	146·7	278·8	489·3	319·4
42·4	244·5	171·0	283·5	496·7	318·4
57·8	253·2	206·2	290·0	614·4	326·3
70·7	258·9	253·4	296·2	705·7	331·7

During these experiments the tube was jacketed with the vapour of boiling mercury; the readings are given in arithmetical order, but were taken sometimes with rising, sometimes with falling pressure.

§ 49. The results of all these experiments are shown in Plate 1; where it will be seen that the curve representing the temperatures of volatilization under different pressures is sensibly identical with that representing pressures of dissociation and vapour-pressures at different temperatures.

§ 50. It will be noticed that at the highest temperatures the numbers representing temperatures of volatilization fall below the vapour-pressure curve: and since the temperatures of the jacket of mercury-vapour used for heating the block of ammonium chloride was only about 20° higher than the highest temperatures registered by the thermometer imbedded in the block, it was deemed advisable to make an independent determination of the temperature of vaporization under normal pressure. For this purpose a calibrated thermometer into which air had been admitted was heated with mercury-vapour under circumstances as similar as possible to those of the actual experiment. In the woodcut, A represents a wide tube bent twice at right angles, with a bulb blown at one end. At B a hole was blown, to admit the thermometer, which was kept in position by a plug of asbestos. The upper part of the thermometer was protected from hot air-currents by a sheet of asbestos cardboard, C; the mean temperature of the upper part of the stem of the thermometer was ascertained in the ordinary way. The result was as follows:—

Fig. 3.



Reading of thermometer	351·0°
Stem heated by mercury-vapour up to graduation	110°
Mean temperature of upper portion of stem	33°
Correction for calibration at 351°	− 3·65°
Rise of zero-point owing to heating	1·9°
Corrected temperature 351·0°+12·3°−3·65°−1·9°=357·85°	
Barometer	762·1 millims. at 0°
From REGNAULT's table, interpolated.	Temperature=357·6°*

This close approximation between a mercurial thermometer and an air thermometer might excite surprise; but we have frequently noticed that these particular German-

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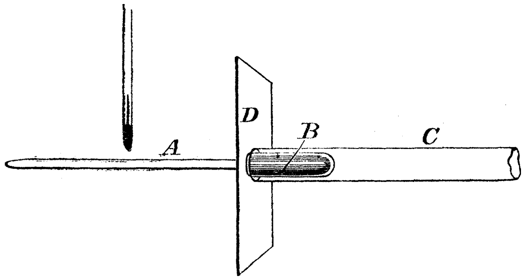
* From our revised table, 358·3°.

glass thermometers give results closely agreeing with air thermometer readings up to 280°. It may be concluded that the temperatures shown by this thermometer, corrected in this way, are in sufficiently close agreement with those of REGNAULT'S air thermometer.

§ 51. The temperature of volatilization of ammonium chloride was then determined under ordinary pressure with the apparatus shown in the wood-cut (fig. 4). A block of ammonium chloride, B, was drilled with a hole to receive the bulb of a thermometer, A, and was placed horizontally at one end of an open combustion-tube, C. The stem of the thermometer was protected by a sheet of asbestos, D. The block was heated by applying the flame of a BUNSEN burner to the combustion-tube, and the temperature registered by the thermometer was read, when constant.

Fig. 4.



Reading of thermometer	329·5°
(Stem was heated up to graduation 30°.)	
Mean temperature of cool portion of stem	30·4°
Correction for calibration at 329·5°	−3·65
Zero-point after experiment	Unaltered
Corrected temperature	329·5 + 14·4 − 3·65 − 1·9 = 338·35°
Barometer	762·1 millims. at 0°

By the barometer-tube method, the mean-pressure at 340° was, as before mentioned, 759·6 millims. The difference, which is less than 2·0°, may well be due to error of experiment.

§ 52. SOME Experiments on the Vapour-density of Ammonium Chloride.

These experiments were carried out by HOFMANN'S method at 280° under pressures varying from 85 millims. to 135·8 millims. The pressure of the vapour in contact with solid, at 280°, is about 145 millims. This temperature is perhaps the only one in which HOFMANN'S method can be applied ; for at higher temperatures the vapour-pressure of mercury becomes too great, and atlower temperatures, the vapour-pressure of ammonium chloride is too small.

No serious error can be introduced by the action of the hydrochloric acid on the mercury, because the volume of the gas is so large, the surface of contact with the solid so small, and the action so slow at that temperature.

The HOFMANN's tube was exhausted, filled with mercury, and jacketed with bromonaphthalene, boiling at 752·3 millims. pressure; the temperature was, therefore, 280°, at which the vapour-pressure of mercury is 157·35[*] millims.

I. Height of barometer as read on scale	115·0	millims.
,, mercury in HOFMANN's tube	272·3	,,
Difference	157·3	,,
Correction for heated column of mercury	13·3	,,
Pressure	170·6	,,
Pressure reduced to 0°	169·7	,,
Weight of ammonium chloride	0·00434	grm.

The ammonium chloride was introduced while the tube was still hot, and the following readings were taken :—

Height of barometer as read on scale	112·8	millims.
,, mercury in HOFMANN's tube	359·1	,,
Difference	246·3	,,
Correction for heated column of mercury	9·3	,,
Pressure	255·6	,,
Pressure reduced to 0°	254·6	,,

The tube containing ammonium chloride carried with it a little air, the pressure of which, at the higher temperature and volume, was calculated to be 0·25 millim.

Volume before addition of ammonium chloride	43·94	cub. centims.
,, after ,, ,, ,,	63·50	,,
Pressure due to air at smaller volume	169·7 − 157·35	millims.
,, ,, larger ,,	$\frac{12{\cdot}35 \times 43{\cdot}94}{63{\cdot}5} = 8{\cdot}6$	,,
Total pressure due to air at larger volume	8·6 + 0·25 = 8·85	,,
Pressure due to NH_4Cl	= 254·6 − 157·35 − 8·85 = 88·4	,,
Vapour density of $NH_4Cl (H=1)$	13·29	,,
Vapour density of $NH_3 + HCl$	13·37	,,

The body is thus seen to be totally dissociated.

II. Weight of substance	0·0087	grm.
Barometer, corrected	749·4	millims.
Temperature of bromonaphthalene vapour	279·8°	
Vapour-pressure of mercury	156·6	millims.

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[*] In revising proofs, we have substituted for the vapour-pressures of mercury determined by REGNAULT, our revised numbers, which we believe to be more accurate.—[May 22, 1886.]

	Pressure (uncorr.).	Correction for column of hot mercury.	Pressure corrected to 0°.	Pressure due to air.	Pressure of ammonium-chloride vapour.	Volume.	P. V.	Vapour-density.
	millims.	millims.	millims.	millims.	millims.	cub. centims.		
(1)	146·8	14·1	160·3	3·7	..	41·66	..	..
(2)	286·8	7·6	293·3	2·1	134·6	73·52	9,896	15·09
(3)	286·5	7·5	292·9	2·1	134·2	74·11	9,946	15·06
(4)	286·2	7·4	292·5	2·0	133·9	74·57	9,985	14·96
(5)	285·2	7·2	291·3	1·95	132·75	75·41	10,010	14·92
(6)	282·3	6·7	287·9	1·7	129·6	77·75	10,077	14·82
(7)	281·2	6·45	286·55	1·55	128·4	78·78	10,115	14·77
(8)	286·2	7·5	292·6	1·6	134·4	73·91	9,934	15·04
(9)	287·0	7·75	293·65	2·1	134·95	72·73	9,815	15·23
(10)	280·1	6·5	285·5	1·55	127·35	78·56	10,005	14·94

Of these determinations, (1) was with mercury alone, in order to determine the amount of air present. From the rest it would appear that the vapour of ammonium chloride is not wholly dissociated at pressures near those of saturation; the percentage number of molecules decomposed varying from 75·57 to 81·04 within the limits of these experiments. It may also be noticed that, in general, the higher the pressure, the higher the vapour-density.

§ 53. In the case of ammonium chloride it appears that the temperature of volatilization depends on the pressure, and that the curve representing the temperatures of volatilization under different pressures is coincident with that representing the vapour-pressures at different temperatures. But on inspecting the curve (Plate 1) showing the relation between temperature and pressure for ammonium chloride it will be noticed that the temperatures of volatilization, represented by crosses, lie in all cases lower than the circles representing pressures. Two corrections have not been applied, both of which would raise the temperatures of volatilization, because we were unable to estimate the exact amount. The temperatures of volatilization were ascertained by means of a mercurial thermometer, but the others, indirectly by an air thermometer. The thermometers were not compared beforehand, and, having been broken during the experiments, a comparison is now impossible. Thermometers belonging to the same batch, which were made of German soda-glass, have been subsequently compared, and to make their readings coincide with those of an air thermometer require to have their readings raised 1·0° at 220°, 1·2° at 230°, 1·4° at 250°, and 1·5° at 280°. If this correction were applied it is obvious that the results of the two methods would form the same curve. Above 280° this comparison has not been made.

Another correction would appear to be requisite for the highest temperatures, owing to the temperature of the jacket of mercury-vapour being too near that of the block of ammonium chloride. Of this we can form no estimate, but it should be noticed that the single observation at the atmospheric pressure, by a method which is free from both these objections, agrees closely with the point obtained by the barometer-tube method. This is shown by the large cross on the diagram.

§ 54. *Phthalic Acid*, $C_6H_4(COOH)_2$.—This acid melts at 184° (LOSSEN), decomposing into water and phthalic anhydride, $C_6H_4(CO)_2O$. ADOR ('Annalen,' 163, p. 230) states that large crystals melt at 213°, while, when powdered, the melting-point is 203°.

PRESSURES of Dissociation of Phthalic Acid in Barometer-tube.

Temperature.	Pressure.	Duration of experiment.
°	millims.	′
30·8	4·7	19
59·8	20·8	46
78·0	28·8	62
100·0	41·2	84
116·0	51·9	140
131·95	61·7	151
131·6	60·1	125
143·6	111·9	423
149·9	164·6	384
149·8	163·1	18
154·9	215·5	363
159·5	327·3	257
164·6	443·2	142

The tube was here refilled, as the original quantity of substance was deemed insufficient; the remaining numbers of this series will be referred to under succinic acid.

Temperature.	Pressure.	Duration of experiment.
°	millims.	
165·3	514·3	67′
168·7	629·6	Constant
Recombination 165·0	518·7	122′
168·1	618·7	118′

The results of these experiments are graphically represented in Plate 2. The form of the curve appears to differ somewhat from that of an ordinary vapour-pressure curve, for the curvature is more abrupt on approaching the horizontal portion. This peculiarity will be referred to later.

§ 55. TEMPERATURES of Volatilization of Phthalic Acid.

As phthalic acid dissociates on liquefying, the bulb of a thermometer was first covered with cotton-wool, and dipped repeatedly into a boiling aqueous solution of the acid. The thermometer was then hung in a bell-jar over sulphuric acid for several days until dry. The requisite temperature was obtained by jacketing with vapour of bromonaphthalene, boiling at about 280°. The condenser was cooled by a freezing mixture.

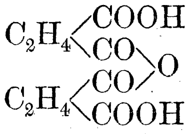
Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·05	191·9	9·8	201·7	87·3	196·9
3·5	198·4	142·0	210·1	32·2	168·6
6·4	199·4	46·9	177·1		
30·4	202·9	22·8	159·5		

When the pressure was raised to 142 millims. the anhydride was left behind, and condensed as liquid on the sides of the tube, crystallizing on the colder parts. After the experiment, on removing the freezing mixture, the solid which had passed into the condenser liquefied partially, the liquid containing crystals. There had therefore been a separation of water. The solid in the condenser was evidently acid, and not anhydride, so that at very low pressures the acid had passed over undecomposed : it was then only after the pressure had been raised that decomposition took place, and it is probable that the substance had then melted, though it was difficult to observe this on the cotton-wool. The phthalic acid condensed in very small crystals, forming an opaque mass : the anhydride, in long transparent crystals. There was a distinct line of demarcation between the two. The last five numbers, which differ entirely from the others, are evidently the temperatures of volatilization of the anhydride, and the former ones of the acid. These numbers are reproduced in a separate curve. The temperatures of volatilization of the acid are plotted in Plate 2, and it is to be observed that, although there is an indication of a curve of the usual form, it completely differs from that obtained by the other method.

§ 56. *Succinic Acid*, $C_2H_4(COOH)_2$.—This acid melts at 180°, and is said to boil at 235° with formation of the anhydride, $C_2H_4(CO)_2O$. The acid used in these experiments was recrystallized, and kept over phosphoric anhydride.

PRESSURES of Dissociation of Succinic Acid in Barometer-tube.

A very large number of experiments were made with this substance. In the first three series the numbers obtained gave, when graphically represented, curves with double flexure; and so long as the same amount of substance was employed recombination at any given temperature reached the same point as regards pressure as did decomposition. The curves obtained from these series were fairly concordant. But, on increasing the amount of substance, the pressures for given temperatures were much higher, and the double flexure tended to disappear. With phthalic acid it is possible that the vertical trend of the curve might have been due to an insufficient amount of substance; but this cannot have been the case with succinic acid. As the pressure of dissociation of succinic acid appears to depend on the amount of substance present, and is capable of being altered at will, and as the number of experiments made on this subject comprise several thousand readings, and lasted over six weeks, we content ourselves with reproducing the results in the form of curves. (See Plate 2.) It may be generally stated that the larger the amount of substance the higher the pressure at which the double flexure appears. It may possibly be that succinic acid has the power of forming intermediate anhydrides of some such type as



$$\left.\begin{matrix}C_2H_4\left\langle\begin{matrix}COOH\\CO\end{matrix}\right.\\C_2H_4\left\langle\begin{matrix}CO\\COOH\end{matrix}\right.\end{matrix}\right\rangle O$$

and that its abnormal behaviour is to be accounted for on the supposition of their existence, but this is merely a conjecture.

§ 57. TEMPERATURES of Volatilization of Succinic Acid.

The bulb of the thermometer was dipped repeatedly into the melted acid until a sufficiently thick layer had accumulated. For low pressures the condenser was cooled by a freezing mixture, and the tube was jacketed with vapour of methyl salicylate.

SERIES I.

Pressure.	Temperature.
millims.	°
0·9	153·7
2·3	166·8
2·5	169·3

SERIES II.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·55	160·7	6·4	174·7	75·4	175·1
1·65	161·5	7·4	176·0	107·8	174·3
1·70	161·0	12·5	176·8	139·3	174·1
1·90	162·4	15·6	176·1	168·7	174·2
2·1	162·4	17·1	176·5	220·4	174·5
3·0	167·3	30·9	175·6	275·1	174·5
4·3	170·2	51·1	175·8		

The substance melted after the pressure had been raised to 275·1 millims.; the melting-pressure must therefore occur between the pressures 220·4 and 275·1 millims. After the experiments were finished the melting-point of the acid still adhering to the thermometer bulb was compared with that of the original substance, and they were found to be identical at 181·0°. Here, again, it is noticeable that the results of the two methods are widely divergent. (Plate 2.)

§ 58. *Aldehyde-Ammonia*, $CH_3.CH\left\{\begin{matrix}NH_2\\OH\end{matrix}\right.$.—This substance was suspected to decompose on heating, in spite of SCHRÖDER's having found its vapour-density normal at 160° ('Berichte,' 4, p. 470); and it will be seen later that our experiments prove the justice of this conclusion. The substance smells at once of aldehyde and ammonia. It is said to melt between 70° and 80°, and to distil undecomposed at 100°.

§ 59. PRESSURES of Dissociation in Barometer-tube.

Temperature.	Pressure.	Duration of experiment.
°	millims.	
21·3	7·0	12 hours.
28·9	13·5	83 minutes.
39·7	32·9	88 „
45·2	49·8	27 „
50·0	83·6	Not constant after 249 minutes.
54·6	144·2	„ „ 718 „
55·7	176·2	Constant after 75 minutes.
60–60·8	307 4	Not quite constant after 25 hours.

It was evident from the discoloration of the substance at the higher temperatures that it had partly decomposed; the results, however, point to gradual dissociation, accompanied at the higher temperatures with some decomposition. The curve is given in Plate 2.

§ 60. TEMPERATURES of Volatilization of Aldehyde-ammonia.

The condenser was cooled by a freezing mixture. The thermometer-bulb was covered with cotton-wool, and dipped repeatedly into the melted substance. The tube was jacketed with the vapour of chlorobenzene.

SERIES I.—Pressure raised by admitting Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
2·8	26·1	33·0	56·2	403·3	78·2
3·25	29·2	63·4	61·5	53·3	60·3
3·85	33·2	124·1	67·2	511·1	81·2
8·5	42·7	265·0	74·2		

SERIES II.—Pressure raised by admitting Air.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
1·95	24·3	95·5	65·1	349·3	76·7
2·4	27·1	161·3	69·2	153·2	68·8
2·8	28·9	198·1	70·9	445·7	79·2
12·9	47·1	250·9	73·1		
21·6	52·6	300·4	74·9		

SERIES III.—Pressure raised by admitting Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
6·3	38·2	38·0	59·0	185·0	72·2
6·45	39·55	53·7	61·2	216·3	73·2
9·5	44·3	67·8	63·2	249·5	74·8
10·8	46·3	79·5	64·5	278·3	75·9
12·55	48·2	95·6	65·4	205·2	73·4
15·6	50·5	114·0	67·2	140·1	70·3
21·5	53·7	136·0	68·7		
28 6	56·6	156·5	70·2		

SERIES IV.—Pressure raised by admitting Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
4·0	35·6	44·0	60·2	229·8	73·9
21·4	52·2	53·3	62·1	303·6	76·2
48·8	60·2	81·7	66·0	300·1	76·0

SERIES V.—Pressure raised by admitting Ammonia-gas.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
9·7	42·3	150·3	69·2	551·4	81·4
11·1	45·1	239·4	73·1	606·3	82·8
23·5	52·6	314·9	75·3	641·8	83·2
66·8	62·3	382·0	77·2	711·7	85·2
68·8	63·0	435·5	78·6	736·1	85·8
108·2	66·6	506·4	80·3		

SERIES VI.—Pressure raised by admitting Aldehyde-vapour, prepared at the time from Aldehyde-ammonia and Sulphuric Acid, and dried over P_2O_5.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
8·45	42·1	67·5	63·9	309·9	75·1
10·15	44·3	99·7	65·8	348·1	76·3
23·6	54·2	139·8	68·8	403·1	77·7
37·7	59·1	175·1	70·8	462·4	78·9
44·4	61·0	215·8	72·1	553·1	80·3
49·8	62·0	266·0	73·9	616·9	81·4

When air or aldehyde was admitted to raise the pressure the cotton-wool became discoloured by a brown resinous substance; this was not the case when the pressure was raised by admitting ammonia-gas (LIUBAWIN, 'Berichte,' 8, p. 1684). Although the results obtained on raising pressure with air, ammonia, and aldehyde are somewhat divergent, yet a very large difference of pressure is caused by a slight alteration in temperature, and the results of observations with any one of these substances show equal discordance among each other. This is not surprising considering the nature of the compound. (Plate 2.)

§ 61. VAPOUR-DENSITIES of Aldehyde-ammonia.

The vapour-densities were determined by HOFMANN'S method at 78·25° and at 131·8°.

Weight.	Temperature.	Pressure.	Volume.	P.V.	Vapour-density.	Percentage number of molecules decomposed.
	°	millims.	cub. centims.			
0·0353	78·25	294·1	73·06	21,487	17·93	70·11
”	”	280·0	76·86	21,521	17·90	”

A long time had to elapse before pressure became constant and the vapour acquired its maximum volume.

Weight.	Temperature.	Pressure.	Volume.	P.V.	Vapour-density.	Percentage number of molecules decomposed.
	°	millims.	cub. centims.			
0·0353	131·8	324·1	79·78	25,857	17·17	77·64 (?)

A certain amount of yellow resin had deposited on the surface of the mercury at the higher temperature, which accounts for the dissociation being apparently incomplete. At the lower temperature no decomposition was observed.

The dissociation of this substance was evidently far from complete, and it will be seen that the curve representing temperatures of volatilization approaches more nearly to the usual form of a vapour-pressure curve. The pressure, 280–290 millims., lies considerably below that obtained by the still method at 78·25°, which is about 420 millims., and it is very far below saturation, as indicated by experiments with the barometer-tube.

§ 62. *Paraldehyde and Metaldehyde.*—It was thought that some results might have been obtained from these substances. Paraldehyde is a liquid of the formula $C_6H_{12}O_3=3C_2H_4O$, obtained by treating aldehyde with a minute quantity of sulphurous anhydride, cyanogen, or certain other substances. Its vapour-density is said to be normal for the formula $C_6H_{12}O_3$ (BEILSTEIN, 'Handbuch der Organischen Chemie,' p. 28). It boils at 124° (KEKULÉ and ZINCKE), at 123·2° to 123·5° (BRÜHL). When distilled with a little sulphuric acid it changes totally to aldehyde (WEIDENBUSCH).

A portion boiling at 122·6° was employed for the following experiments. When heated in a barometer-tube it was found to attack the mercury; it was therefore well shaken with mercury and redistilled. The pure substance does not appear to decompose, and the results obtained by the two methods were practically identical.

Metaldehyde is a solid crystalline body, produced by the action of gaseous hydrogen chloride, or sulphurous anhydride on aldehyde in a freezing mixture. It is insoluble in the ordinary solvents, and sublimes without melting at 112–115°, and when heated under pressure to 120° it changes completely into aldehyde. Its dissociation-pressure was determined in a barometer-tube.

Temperature.	Pressure.	Time.
°	millims.	
17·0	11·8	24 hours
50·4	282·0	216′
,,	332·0	216′+380′=596′
,,	339·4	596′+75′=671′

The rise of pressure was 2·4 millims. in the last 35′.

Temperature.	Pressure.	Time.
°	millims.	
60	459·0	335′

The pressure rose 14·3 millims. in the last 60′.

We have evidently here to deal with a substance the equilibrium of which is established only after a very long time. It was allowed to cool, and stood for ten days; combination was gradually taking place, as shown by the gradual rise of the mercury.

§ 63. *Nitrogen Peroxide.*—This substance was prepared in the following manner. A mixture of arsenious oxide, sulphuric acid, and nitric acid was heated; the vapour evolved was led through a U-tube containing arsenious oxide, and then through a drying-tube filled with phosphoric anhydride. It then entered a U-tube, provided with a bulb, which was placed in a freezing mixture. To avoid decomposition, the apparatus was constructed, as far as possible, in one piece. After redistillation the substance, which had a deep-red colour, was used for the following experiments.

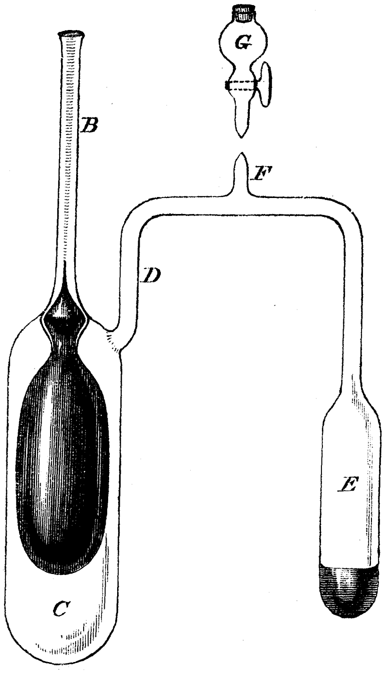
The vapour-density of nitric peroxide in presence of nitrogen was first determined by PLAYFAIR and WANKLYN ('Annalen,' 122, p. 249). From their results they concluded that at 100° the gas consists chiefly of NO_2, and at the ordinary temperature of N_2O_4. MÜLLER ('Annalen,' 122, p. 15), and DEVILLE and TROOST ('Comptes Rendus,' 64, p. 237) determined its vapour-density by DUMAS' method, with very concordant results. NAUMANN ('Annalen,' Suppl., 6, p. 203) calculated from their data the percentage number of molecules decomposed at different temperatures, and found that at 26·7° it contained 80·04 p.c. of molecules of N_2O_4; while at 135°, 1·31 p.c. of the total number of molecules was left undecomposed. The curve constructed from NAUMANN'S numbers presents the usual double flexure of a dissociation-curve. At the boiling-point, under normal pressure, 21·7°, it is evident that less than 20 p.c. is dissociated. DE LA FONTAINE ('Archives Phys. Nat.' (2), 28, p. 271) drew attention to the remarkable change of colour which nitric peroxide gas shows on heating; and as the liquid also grows lighter in colour when cooled, it appears probable that dissociation still proceeds in the liquid state (NAUMANN, 'Thermochemie,' ed. 1882, p. 138). From these and similar results WILLARD GIBBS has constructed a formula, showing on thermodynamical principles the rate of dissociation of nitric peroxide.

§ 64. VAPOUR-PRESSURES of Nitric Peroxide.

As liquid nitric peroxide quickly attacks mercury, it was impossible to determine its vapour-pressure by the usual method. Tolerably accurate results were obtained by the following device. An apparatus of the form given in the annexed drawing was employed.

A large bulb A of about 50 ccs. capacity, very thin walled, yet strong enough to resist the pressure of the atmosphere, was sealed to a graduated glass tube of thermometer-bore, B, and was fused into an encasing bulb, C, the walls of which were much thicker. From the upper part of C a tube, D, projected vertically for some distance, and was then bent twice at right angles. The other extremity of this tube was enlarged at E; a T-piece, F, was sealed to the horizontal portion of the tube; the bulb A was filled with mercury, by exhausting it, and allowing mercury to enter. The bulb C was placed in a vessel with a perforated bottom, containing finely-pounded ice, which was heaped round the lower portion of the graduated stem, and continually renewed. As the bulb A forms an extremely delicate thermometer, in which 60° of the arbitrary scale corresponded to 1° of temperature, it was only after several hours that the temperature became constant. When absolute constancy of temperature had been attained, the T-tube F was connected with the pump and with a gauge, and air was removed from the apparatus; the diminution of pressure caused the bulb A to expand, and the mercury in the graduated stem to fall. This fall was found to be sensibly equal for equal decrease of pressure; and from the mean of a great number of readings a change of 9·04 millims. pressure was found to be equivalent to 1° of the scale; hence $\frac{1}{10}$° corresponded to about 1 millim.

Fig. 5.



A perfectly air-tight stopcock was then fused on to the T-tube F, and the apparatus was dried by exhausting the air with a CARRE'S pump. The apparatus was then pumped empty of air with the mercury-pump, and the stopcock was closed. A reservoir, G, which had been sealed to the stopcock, was then filled with liquid nitric peroxide, and the stopcock was opened so as to admit two or three cubic centimetres of the liquid. The stopcock was then closed, and removed by sealing.

As the height of the mercury in the graduated stem had been read before introducing the nitric peroxide, and as the introduction of the liquid caused a rise of the mercury corresponding to the pressure of its vapour, the apparatus acted as a barometer for temperatures below 0°. The vapour-pressure was regulated by the coldest part of the apparatus. The bulb E was placed in a well-stirred mixture of ice and hydrochloric acid, in contact with a thermometer, and the temperature and the position of the mercury in the graduated scale were read, with the following results:—

§ 65.

Scale readings.*	Pressure.	Temperature.
	millims.	°
115·0	68·6	−26
114·9	69·6	−25·2
113·3	84·6	−21·0
112·0	96·0	−19·1
112·0	96·0	−18·0
111·4	101·6	−17·0
108·0	132·2	−13·0
106·1	149·4	−11·5
106·0	150·2	−11·0
105·4	155·7	−10·0
105·8	152·0	− 9·6
104·7	161·7	− 8·7
104·1	167·5	− 8·0
100·5	200·0	− 5·3
97·7	225·3	− 3·1

§ 66. To obtain readings at a higher temperature, the bulb C was placed in running water, the temperature of which was almost constant, and mercury was removed from the graduated stem for convenience in reading. The readings obtained by this method correspond with those obtained by the still-method, to be hereafter described. It was accordingly assumed that they would correspond at 0°. The bulb E was placed in melting ice, and the position of the mercury in the graduated stem was noted. The ice round E was now replaced by running water at a temperature of 13·9°, and the alteration in position of the mercury in the scale read. Since the temperature of the running water was not absolutely constant, this was repeated several times, and the mean result taken as correct. It was found as the mean of six experiments that an alteration of temperature from 0° to 13·9° produced a rise of mercury of 30·9 scale divisions, corresponding to an increase of pressure of 279·3 millims. As the pressure at 0° found by the other method is 257·5 millims., the pressure at 13·9° is therefore 279·3+257·5=536·8 millims.

§ 67. A direct reading at 19·6 was taken by placing the apparatus in a large tank of water of that temperature, the temperature of the room being some degrees higher. The mercury in the scale read 81·0°. The point of the T-tube was broken, so as to communicate with the atmosphere, and the height of the mercury was again read. It was 73·2°. This difference was 7·8°, or allowing for the cooling of the water during one minute, 7·7°. Multiplied by 9·04, this difference is equivalent to 69·5 millims. Subtracting from the pressure of the atmosphere at the time, 756·6, the true pressure in the apparatus was found to be 687·1 millims.

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* It should be mentioned that the scale was inverted, so that a lower reading corresponds to a higher pressure.

§ 68. MAXIMUM Temperatures at Different Pressures.

In these experiments the only differences from the ordinary arrangement were—a stopcock was used instead of an indiarubber tube and clip to admit the liquid; as nitric peroxide attacks cotton-wool, the bulb of the thermometer was covered with asbestos; warm water was used as a jacket, and the condenser was placed in a good freezing mixture.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
86·5	−19·35	257·5	0·0	483·0	12·1
91·8	−18·15	291·0	+2·2	536·0	14·2
113·5	−14·60	316·5	4·0	578·5	15·8
127·0	−12·7	344·0	5·7	613·5	17·0
147·5	−10·0	390·5	7·9	660·5	18·5
177·0	− 6·7	426·0	9·7	738·5	20·9
204·5	− 4·3	467·5	11·4	752·0	21·5

§ 69. On reference to the curves (Plate 1) it will be seen that the results by both methods agree as closely as could be expected from the nature of the first. In this respect the behaviour of nitrogen peroxide is similar to that of ammonium chloride; but while the latter is completely dissociated at its volatilizing point under normal pressure, the former has suffered only very partial dissociation.

NOTE.—Quite recently E. and L. NATANSON ('WIEDEMANN'S Annalen,' 24, p. 454) have determined the relations between the specific heat and vapour-density of nitrogen peroxide under varying pressures, and at a constant temperature. They find that while the vapour-density increases, the specific heat decreases with rise of pressure, and conclude from this that the alteration of density of nitrogen peroxide is due to the dissociation of N_2O_4 into $2NO_2$.

§ 70. *Acetic Acid.*—The sample of acetic acid used was the same as that employed by us in determining the different vapour-pressures of the solid and liquid acid (see 'Transactions,' 1884, Part II.). It was perfectly pure, boiling with absolute constancy at 118·7°, at a pressure of 765·2 millims., and melting at 16·4°. The large stock of acid contained a little water; but on fractionation, after one-third had distilled over, the remainder always boiled constantly to the last drop. The various determinations were made with portions fractionated at different times.

PLAYFAIR and WANKLYN (Trans. Roy. Soc., Edin., 22, Part III., p. 441) were the first to suggest that, as the vapour-density of acetic acid at low temperatures is nearly double that which it possesses at high temperatures, its formula at low temperatures is $C_4H_8O_4$; and that on heating, this molecule splits into two of the formula $C_2H_4O_2$. An increase of density in the neighbourhood of the condensing-point is a common property of all gases; and NAUMANN concludes ('Annalen,' 155, p. 325) that, although acetic acid may exhibit this behaviour, yet that its abnormal density is to be explained chiefly on **Playfair** and **Wanklyn's** supposition. **Horstmann** and others take the opposite view. So far, then, it is an open question whether acetic acid dissociates or not.

§ 71. Numerous determinations of the vapour-pressures of acetic acid have been made by **Regnault** ('Mémoires de l'Académie', xxvi., p. 51–60), **Bineau** ('Annales' [3], 18, p. 226), **Landolt** ('Annalen,' Suppl., 6, p. 157), and **Wüllner** (Pogg. Ann., 103, p. 529). Their results show absolutely no concordance. Thus at 15°, **Bineau** finds a vapour-pressure of 7 millims.; while **Landolt** finds 15 millims.; and **Regnault's** determinations vary from 8·5 millims. to 10·4 millims. At higher temperatures the various determinations are even less concordant. At 80°, for example, the difference between determinations by **Landolt** and by **Wüllner** amounts to 85 millims. **Regnault** attributed his discordant results to the presence of water in those samples which gave a lower pressure, and of acetone in those giving a higher pressure. It will be seen that our very numerous determinations exhibit perfect accordance with each other. The vapour-pressures and the temperatures of volatilization at low temperatures have already been given by us in the paper referred to; above 20° the results are as follows:—

§ 72. VAPOUR-PRESSURES of Acetic Acid in Barometer-tube.

SERIES I.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
21·2	12·7	39·2	32·2	63·2	100·7
24·5	14·6	43·8	39·7	66·0	113·4
29·15	18·55	48·1	49·9	68·7	127·7
31·0	20·45	51·5	58·7	71·1	142·5
33·2	23·2	54·9	68·3	73·4	157·0
34·4	24·25	57·6	77·4	75·5	170·1
35·6	26·45	60·2	88·5	78·1	190·7

SERIES II.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
25·9	15·05	45·1	42·65	66·15	114·6
28·3	17·7	49·6	52·9	68·15	126·0
30·95	20·25	53·2	63·6	70·05	136·1
34·3	25·25	57·0	75·5	72·95	153·6
37·4	29·2	59·9	86·5	74·6	164·5
40·8	34·5	63·2	101·2	77·95	188·1

After the completion of these experiments it was found, on inclining the tube, that absolutely no air was present.

SERIES III.

Temperature.	Pressure.	Temperature.	Pressure.	Temperature.	Pressure.
°	millims.	°	millims.	°	millims.
62·5	97·2	93·7	340·0	108·3	551·6
74·3	163·4	105·2	499·9	109·3	574·4
83·0	229·9	94·1	345·6	..	..

§ 73. MAXIMUM Temperatures at Different Pressures.*

SERIES I.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
236·3	83·9	78·7	57·4	28·3	36·1
194·4	78·8	66·7	53·5	22·9	32·7
156·2	73·2	53·7	49·2	16·8	27·2
131·9	69·1	51·7	48·5	12·9	22·4
96·3	61·8	41·7	43·8		

SERIES II.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
146·3	71·6	34·3	40·1	17·45	27·3
58·1	50·5	28·9	36·9	12·65	21·4
51·3	48·2	21·8	31·3		

SERIES III.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
14·5	23·4	14·35	23·0	12·45	20·9

SERIES IV.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
15·95	25·6	13·05	22·05	12·85	21·68

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* In this case, as well as in that of nitric peroxide, it is inadmissible to use the expression "temperature of volatilization," which by definition applies only to solids. (Phil. Trans., 1884, I.) Nor is "boiling-point" a correct term, for ebullition does not take place. With liquids which are known not to dissociate, the expression "vapour-pressure" may of course be used.

Series V.

Pressure.	Temperature.	Pressure.	Temperature.	Pressure.	Temperature.
millims.	°	millims.	°	millims.	°
717·9	117·15	460·3	103·3	242·1	84·6
657·5	114·1	425·2	100·6	228·0	83·4
642·6	113·4	396·3	98·6	215·2	81·65
623·8	112·4	376·4	97·4	199·5	79·8
587·1	110·4	344·3	94·5	177·3	76·4
540·0	107·45	307·9	91·4	127·5	68·5
501·8	105·45	267·8	87·5	87·6	59·6
				55·6	49·65

The shortness of series III. and IV. is accounted for by the fact that they consist of the higher numbers of series which have been elsewhere given. The results by both methods are shown in Plate 2.

§ 74. It was thought possible that the hydrochloride of ethylamine, and that chlorine hydrate might yield serviceable results. The former gave off a permanent gas, and grew pasty when heated; the temperature rose steadily to above 300° with no sign of a check.

The chlorine hydrate, prepared by bringing a thermometer-bulb covered with cotton-wool, and soaked with water, in contact with chlorine at a low temperature, melted suddenly when the pressure was lowered, with rapid evolution of chlorine, while the temperature rose to 0°. This unusual behaviour perhaps deserves further investigation,* but as it did not come under our programme, it was not further followed.

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* (Since writing the above, the matter has been made the subject of experiment by H. Le Chatelier, "Comptes Rendus," 99, p. 1074; he finds that solid chlorine hydrate has a higher vapour-pressure than the liquid hydrate, if the latter exists, and is not a mere solution of chlorine in water. It may be remembered that similar results with chloral ethyl- and methyl-alcoholates are described by us in § 25).

§ 75. Discussion of Results.

For the sake of clearness we tabulate the results already described :—

Name of substance.	Vapour-density shows—	Temperature of volatilization.	Vapour-pressure, or pressure of dissociation.
Chloral hydrate	Dissociation almost complete at 78°	Independent of pressure	Curve of ordinary form.
Butyl chloral-hydrate . .	Complete dissociation at 160°	Independent of pressure	Curve of ordinary form.
Chloral methyl-alcoholate	At 78·5°, about 78 per cent. dissociated	Independent of pressure	Curve of ordinary form.
Chloral ethyl-alcoholate .	At 78°, 82·5 to 83 per cent. dissociated	Independent of pressure	Curve of ordinary form.
Ammonium carbamate .	Total dissociation . . .	Constant at about 65° under all pressures	Curve of ordinary form.
Ammonium chloride . .	Dissociation very nearly complete at 280°	(Curves	identical.)
Phthalic acid	Vapour-density not determined; dissociation probably very large, no constant melting-point	Rudimentary curve at low pressures	Abrupt change of direction of curve.
Succinic acid	Vapour-density not determined; dissociation probably less complete than with phthalic acid, constant melting-point	Curve more obvious than with phthalic acid	Appears to depend on amount of substance present; curve shows double flexure.
Aldehyde-ammonia . . .	70 per cent. dissociated at 78·25°, under reduced pressure	Curve of usual form . .	Curve of usual form, but pressure higher than by other method.
Paraldehyde	No dissociation	(Curves	identical.)
Metaldehyde	. . . .	. . . .	Equilibrium established only after very prolonged heating.
Nitrogen peroxide . . .	Dissociation small below 20°	(Curves	identical.)
Acetic acid	Vapour - density abnormally high, especially at low temperature	(Curves	identical.)
Ethylamine hydrochloride	No results		
Chlorine hydrate . . .	No results		

§ 76. It is evident that these substances may be divided into two groups : that in which the curves representing temperatures of volatilization and vapour-pressures are identical; and that in which these curves are distinct. The members of the first class behave like ordinary solids and liquids; and the class includes the three substances, ammonium chloride, nitrogen peroxide, and acetic acid; with the first of these dissociation is nearly complete sixty degrees below the temperature of volatilization under normal pressure; with the second dissociation amounts to less than 20 per cent. at its boiling-point; while with acetic acid it is uncertain whether true dissociation takes place. The second group, which contains the rest of these substances, with the exception of paraldehyde, which is stable, may be divided into two sections: that in which pressure has no apparent influence on the temperature of volatilization, and that in which its influence is partial.

§ 77. Judging from the determinations of vapour-density which have been made, it may fairly be stated that those substances which show the greatest amount of dissociation also show the greatest divergence between the curves, and the least connexion between pressure and temperature of volatilization. Thus with chloral hydrate, the dissociation of which is almost complete, the temperature of volatilization is independent of pressure, and with ammonium carbamate, which is completely dissociated, this is also noticeable. Again, with succinic and phthalic acids, the former of which, judging from its melting-point, is probably more stable than the latter, the curve representing temperatures of volatilization of the former is more obvious than that of the latter; and with aldehyde ammonia, the two curves of which have the same general form and which are not widely divergent, the determination of vapour-density shows that the dissociation is only 70 per cent. at 78·25°, under greatly reduced pressure. Again, with the alcoholates of chloral, which appear to show the same behaviour as chloral hydrate in the still, the melting-pressure is so low, and the rate at which they volatilize so rapid, that any small indication of temperature being influenced by pressure might well have escaped observation. Moreover, we are not able at present to compare the relative stability of these bodies with that of phthalic and succinic acids. Had we to deal with this class alone it would have appeared that the statement at the beginning of this paragraph might be general; but ammonium chloride forms so marked an exception that this view can hardly be sustained without qualification.

§ 78. It is also to be noticed that the chloral compounds with water and with the alcohols belong to the class of dihydric alcohols, or their methyl or ethyl derivatives. Thus aldehyde itself, when mixed with water, evolves heat, and undergoes contraction; and this behaviour would point to the formation of the dihydric alcohol

$$CH_3CH\begin{cases}OH\\OH\end{cases}.$$

Now such a union, if this constitution be accepted as correct, involves the breaking down of a molecule of water, and the partial molecular rearrangement of aldehyde, so that from CH_3CHO there is formed $CH_3CH(OH)_2$. With the methyl and ethyl compounds the substance produced is at once a monohydric alcohol, and a methyl or ethyl ether, thus:—

$$CCl_3CH\begin{cases}OH\\OCH_3\end{cases}, \text{ and } CCl_3CH\begin{cases}OH\\OC_2H_5\end{cases}.$$

In the case of ammonium carbamate its formation involves the breaking down of one molecule of ammonia, and the formation of an ammonium group, NH_4, and of an amido group, NH_2: and this necessitates the actual transfer of an atom of hydrogen from one nitrogen-atom to the other, thus:—

$$OCO+2NH_3=OC\begin{cases}ONH_4\\NH_2\end{cases}.$$

Again, aldehyde-ammonia is usually viewed as a dihydric alcohol, in which one hydroxyl group is replaced by an amido group, and this again involves the breaking down of a molecule of ammonia, its formula being $\mathrm{CH_3CH}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}\right.$. Lastly, the combination of phthalic or succinic anhydride with water involves the breaking down of a molecule of water, thus :—

$$\mathrm{C_2H_4(CO)_2O+H.OH=C_2H_4(COOH)_2}\ ;$$
$$\mathrm{C_6H_4(CO)_2O+H.OH=C_6H_4(COOH)_2}.$$

In all these cases the behaviour in the still differs from that in the barometer-tube.

§ 79. The three remaining substances, nitrogen peroxide, acetic acid, and ammonium chloride, give identical vapour-pressures by both methods; and in this their behaviour does not differ from that of stable solids or liquids. It is, therefore, to be surmised that these substances must show some essential difference in constitution from the others, and we shall consider them in detail.

Nitrogen peroxide, when dissociated, may have one of two formulæ, either $\mathrm{N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$ or $\mathrm{N}\left\langle\begin{smallmatrix}\mathrm{O}\\ |\\ \mathrm{O}\end{smallmatrix}\right.$. It is indifferent for our purpose which is accepted; but, taking the first as correct, there are three ways of representing the union of two molecules of $\mathrm{NO_2}$ to form $\mathrm{N_2O_4}$. First: Simple union of the nitrogen atoms thus :— $\begin{smallmatrix}\mathrm{O}\backslash\!\!\backslash\\ \mathrm{O}/\!\!/\end{smallmatrix}\mathrm{N}-\mathrm{N}\begin{smallmatrix}/\!\!/\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{smallmatrix}$. Second: Union through the oxygen atoms :—$\mathrm{O=N-O-O-N=O}$. Third (and the hypothesis has been recently advanced yb Divers): Union of a nitrogen atom of the one molecule with an oxygen atom of the other, the result being a nitrate of nitrosyl, $\begin{smallmatrix}\mathrm{O}\backslash\!\!\backslash\\ \mathrm{O}/\!\!/\end{smallmatrix}\mathrm{N-O-N=O}$.

Now, none of these methods of representation involves the breaking down of a molecule, but only a partial molecular re-arrangement, such as takes place in the aldehyde group, CHO, which does not involve an alteration in position of the atoms.

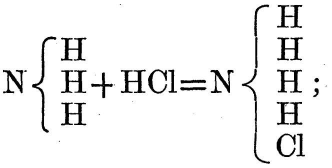
§ 80. Passing to acetic acid, it has been suggested by Playfair and Wanklyn that the abnormal vapour-densities point to a molecule of the formula $\mathrm{C_4H_8O_4}$, and the formula deduced by Willard Gibbs from the observations of these experimenters and others is based on this assumption. If this view is correct, the only structural formula applicable is

$$\begin{matrix}\mathrm{CH_3-C}\left\{\begin{matrix}\mathrm{OH}\\ \mathrm{O}\end{matrix}\right.\\ \mathrm{CH_3-C}\left\{\begin{matrix}\dot{\mathrm{O}}\\ \mathrm{OH}\end{matrix}\right.\end{matrix}$$

where the oxygen of the two carboxyl groups forms the connecting link. Here again there is no breaking down of a molecule.

But experiments which we have made on the density of the saturated vapour of this substance show clearly that the density increases more and more rapidly with fall of temperature, until at 50° the density is more than 55, that of the molecule $C_4H_8O_4$ being 60; and some isolated determinations by a method, of the reliability of which we are in some doubt at present, appear to indicate that at 20° the vapour-density may be as high as 70, and there is no doubt that the trend of the curve representing the relation of saturated vapour-density to pressure or temperature would, if prolonged and if no sudden change of direction occurs, give vapour-densities at low pressures and temperatures considerably higher than 60. We have shown in a paper, recently presented to the Society, that alcohol, and also ether, which may be regarded as typical of liquids in general, do not show this increase in the density of their saturated vapours with fall of temperature and pressure. We are at present engaged in a study of the thermal properties of acetic acid, which we hope will definitely decide this point. If the vapour-density of acetic acid is really higher than 60, at low temperatures no structural formula can represent the method of combination of the molecules.

§ 81. The formation of ammonium chloride is usually believed to be attended by the change of valency in nitrogen from triad to pentad, and to be accompanied by the breaking down of the molecule of hydrogen chloride, thus :—



$$\mathrm{N}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\end{matrix}\right. + \mathrm{HCl} = \mathrm{N}\left\{\begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{H}\\\mathrm{Cl}\end{matrix}\right. ;$$

and the existence of the extremely stable phosphorous pentafluoride is a strong argument in support of this view.

But if it be held, there appears no reason why we should not place in the same class potassium hydrogen fluoride, KHF_2, and hydroplatinichloric acid, H_2PtCl_6, and other similar compounds.

On the other hand, such compounds may be placed in the class of "molecular combinations;" but if this be done it must be conceded that such compounds are not always to be distinguished from "atomic combinations" by any ordinary tests of stability.

Now ammonium chloride, although it agrees with acetic acid and with nitrogen peroxide in its behaviour as regards vapour-pressures, differs from them in respect of its dissociating into dissimilar molecules. It is thus evident that the agreement in behaviour of these three substances with that of ordinary solids and liquids cannot be ascribed to the similarity of the molecules produced by dissociation.

§ 82. As nitrogen peroxide and acetic acid in their dissociation do not require a breaking down of a molecule such as water or ammonia, and as ammonium chloride agrees with them in its behaviour as regards vapour-pressure; and as this agreement, as has already been shown, does not depend on the amount of dissociation, for there are some bodies in the other class totally dissociated, and some partially dissociated;

it may be surmised that in the act of combination of ammonia with hydrogen chloride, the molecule of hydrogen chloride is not split but combines as a whole. Should this conjecture not be accepted as correct it will be necessary to seek for an explanation of the phenomena observed, by some relations yet to be discovered. Should it be accepted, the classification of those substances in which an evident molecular rupture takes place, suggested in § 77, may still be adopted; and it is probable that an idea of the amount of dissociation may be gathered from the relation of the two curves.

§ 83. Some points still remain to be discussed.

Vapour-pressures of substances undergoing partial dissociation.—A substance capable of exerting vapour-pressure, and at the same time capable of dissociating, exerts a pressure which is the sum of the vapour-pressures of the undecomposed substance, and of the bodies resulting from its dissociation. If these two pressures could be determined separately by experiment we should have two separate curves, the resultant of which would be that representing the pressure determined by the barometer-tube method.

The curve representing the true vapour-pressure of the dissociating body would, to begin with, show increase of pressure with rise of temperature. But at a certain temperature pressure must decrease with rise of temperature, for if the temperature be sufficiently raised dissociation is complete, and there is no true vapour-pressure. The curve must, therefore, have the general form A, fig. 6 or fig. 7.

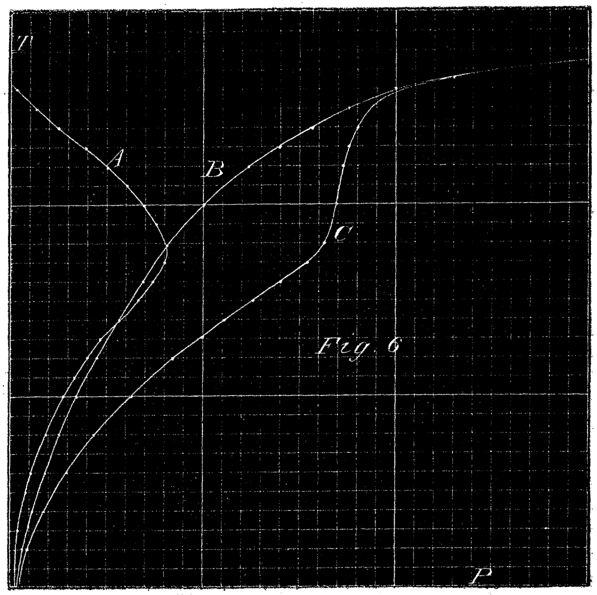
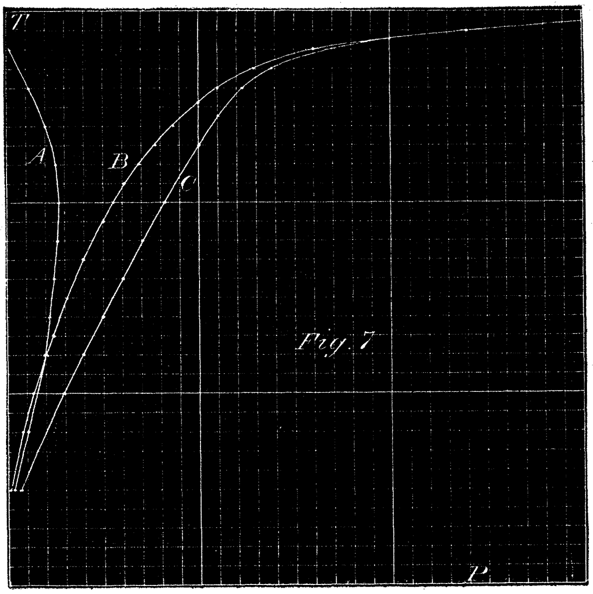
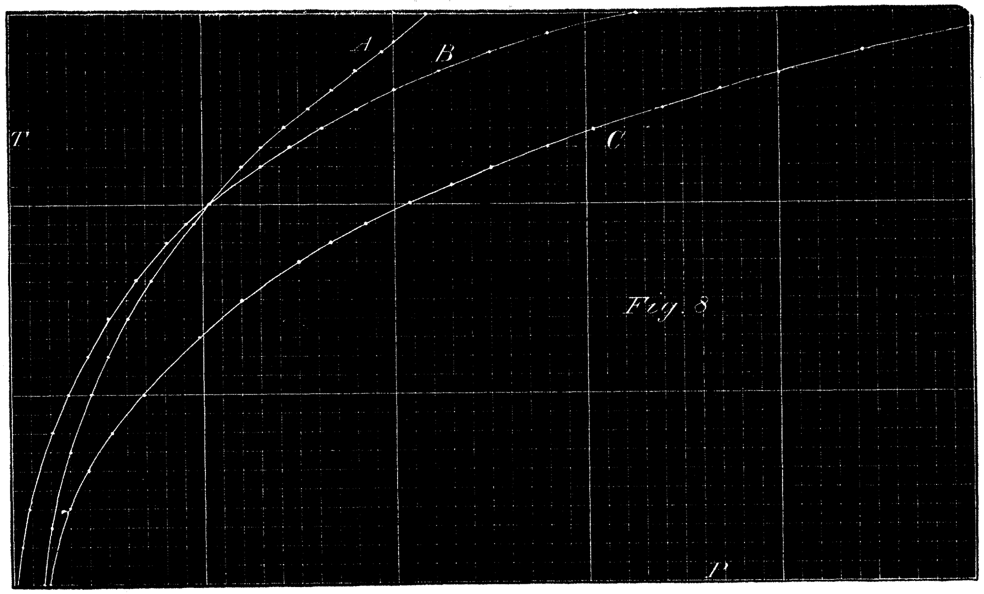


Fig. 6

At the same time the products of dissociation exert a pressure which increases more and more rapidly with rise of temperature (as in *B*, figs. 6, 7, 8). Now the combination of two such curves might yield a curve of double flexure, as shown in *C*, fig. 6;

and an indication of this may possibly be seen with succinic acid. Or it may give a curve with an abrupt change of direction, as in *C*, fig 7, and phthalic acid may afford an example of this. Or, lastly, the curve may be indistinguishable from an ordinary vapour-pressure curve (*C*, fig. 8), as is the case with most substances.

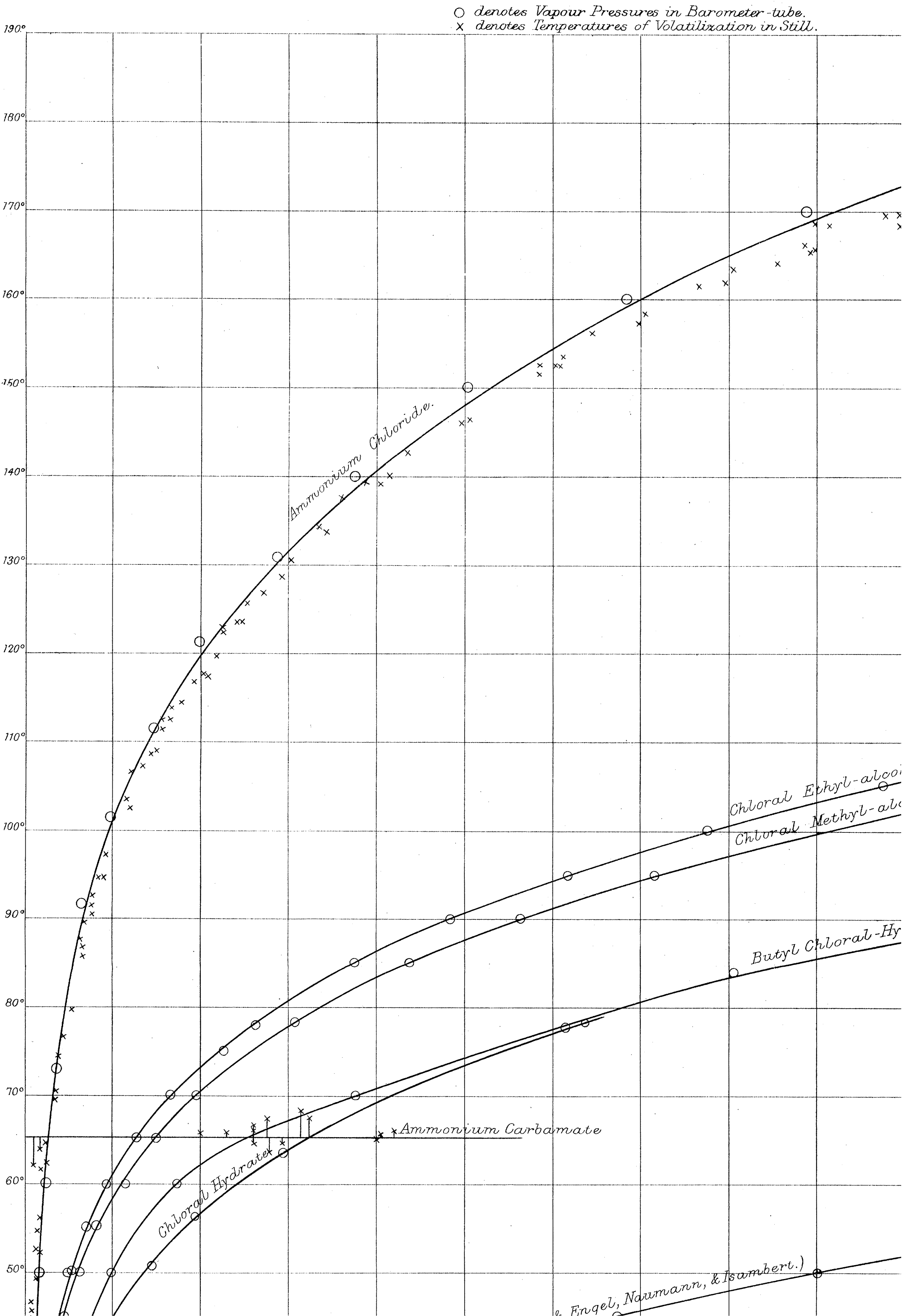


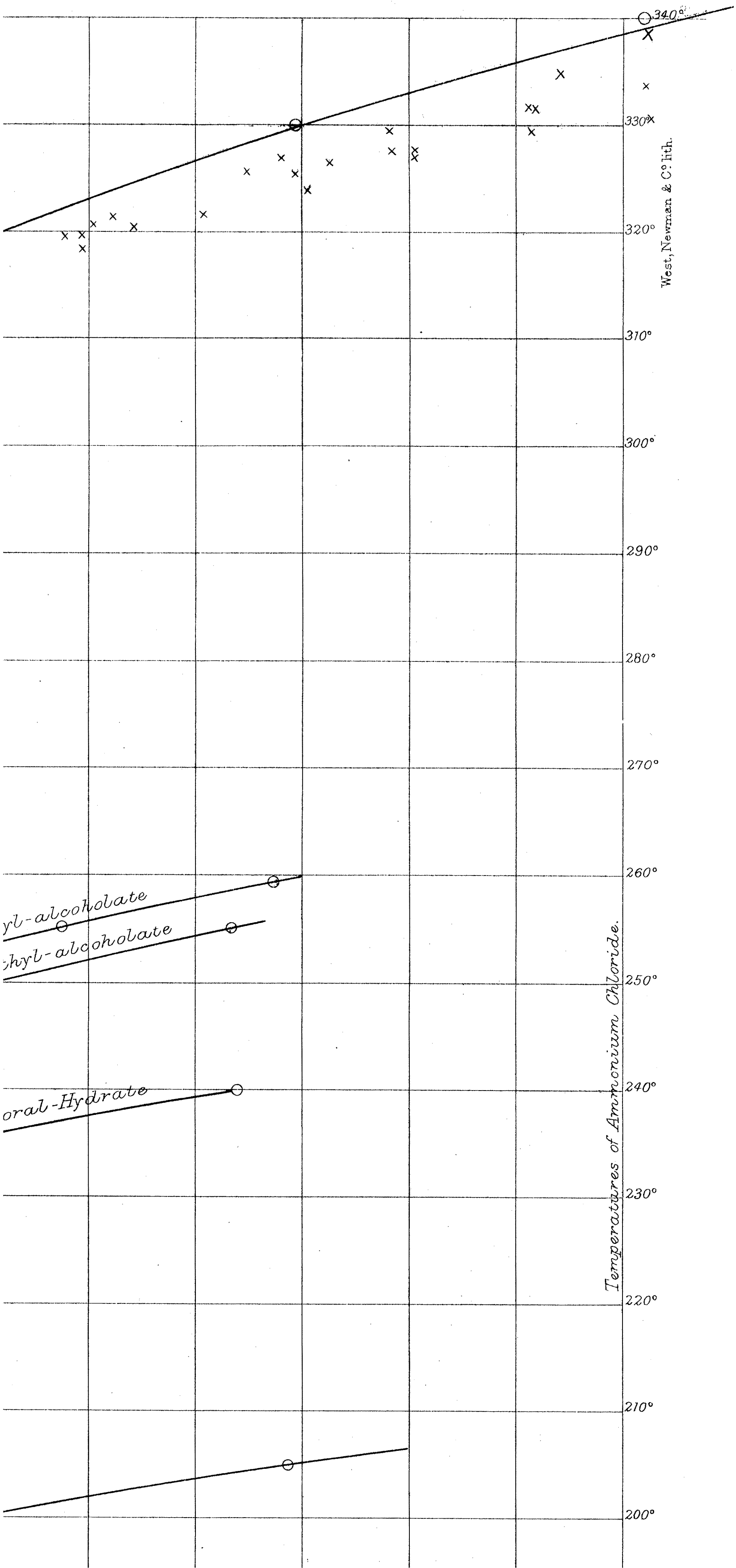


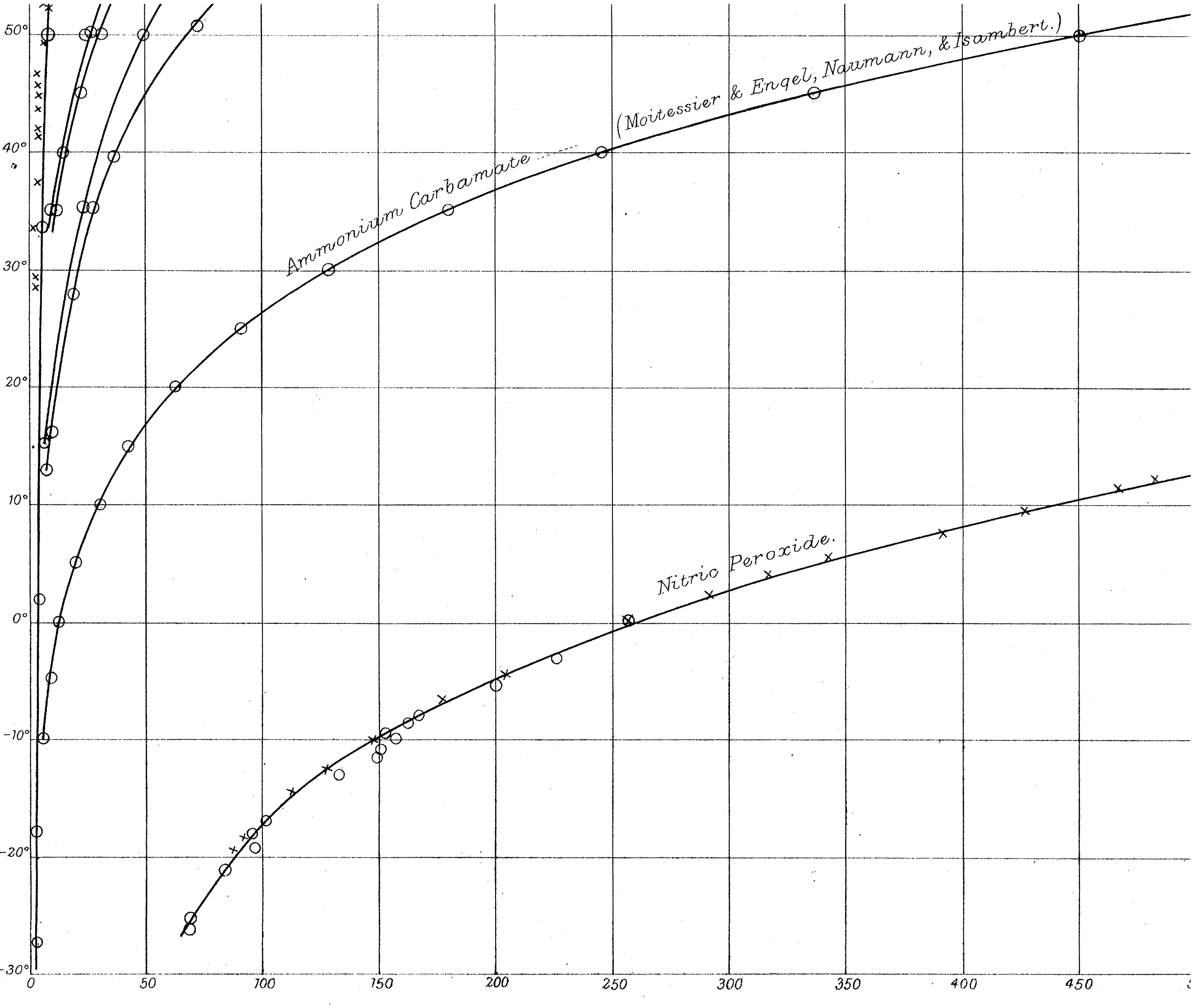
§ 84. *Influence of one of the products of dissociation on the amount of dissociation.*—The results of Horstmann, Moitessier and Engel, and Isambert have shown that the presence of excess of one of the products of dissociation diminishes the amount of dissociation. Their experiments were made by introducing a known quantity of one of the products of dissociation into a barometer-tube, in which the dissociable substance was being heated. WÜRTZ has also shown that the vapour-density of a dissociable compound is increased in presence of one of its components, which necessarily implies a decrease of dissociation. Now, it has been found by us from experiments with aldehyde ammonia and ammonium chloride that it is immaterial how pressure is raised in determining temperatures of volatilization; but the two cases are very different. In the former the gas in excess is mixed with, and acts on the vapour evolved from the dissociable body, while in the latter it is a question of the action on the solid of the gas introduced, since after the component vapours have left the surface of the solid, any action on them would have no influence on the solid. It appears most likely that the solid is always surrounded by its own vapour, so that it is doubtful whether the introduced gas ever comes in contact with the solid at all.

§ 85. *Difference of behaviour of dissociable solids from dissociable liquids when evaporating from a free surface.*—So long as the body is solid the residue has always its original composition; but a liquid separates into its components, the more volatile passing over first. This was found to be the case with chloral hydrate and with phthalic and succinic acids, and no doubt holds good with others. It amounts to a proof that the solid substance, in volatilizing, does not pass through the state of liquid. It would also show that a solid, so long as it remains a solid, cannot dissociate; while a liquid may undergo increased dissociation with rise of temperature, thus forming a mixture from which the more volatile constituent separates first.

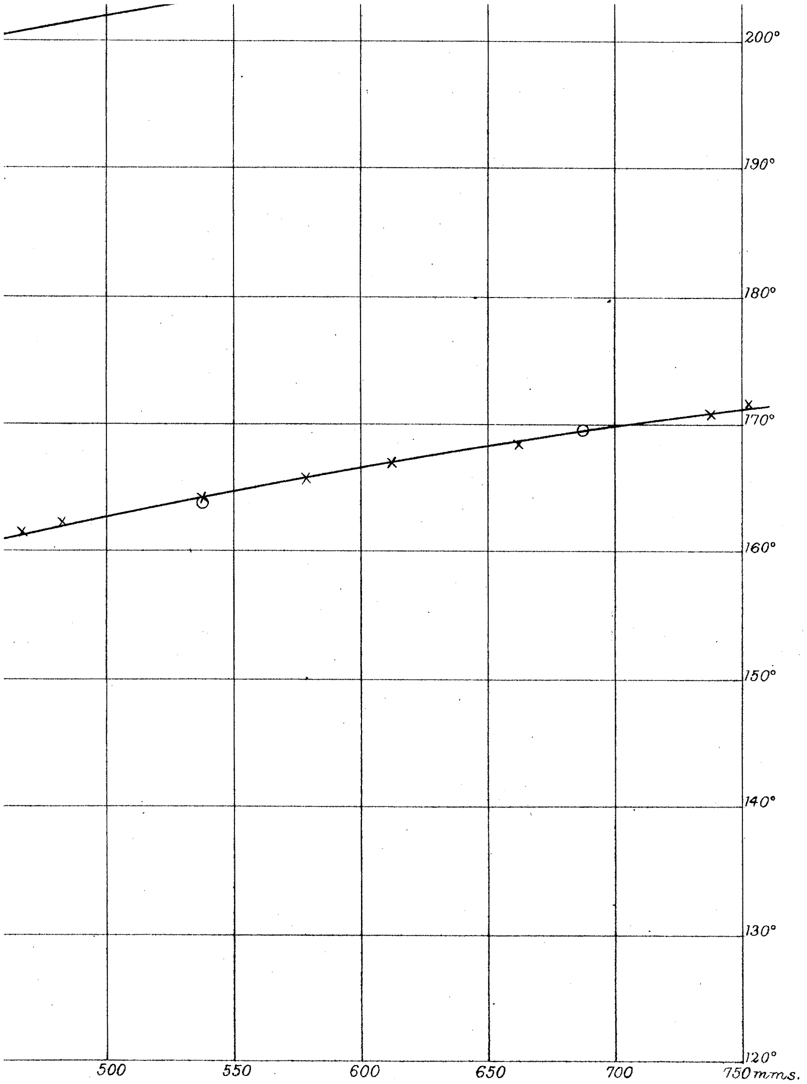
§ 86. We have shown in the preceding pages that there is no essential difference, in certain cases of dissociation, between the behaviour of dissociating and evaporating bodies; but in others, where a deeper chemical change may be supposed to occur, an essential difference exists, as shown by a comparison of the curves representing, on the one hand, temperatures of volatilization under different pressures, and, on the other, vapour-pressures, or pressures of dissociation, at different temperatures. The precise nature of this difference is as yet unexplainable, in our present state of ignorance of the molecular and atomic constitution of chemical substances.


○ denotes Vapour Pressures in Barometer-tube.
× denotes Temperatures of Volatilization in Still.
190°
180°
170°
160°
150°
140°
130°
120°
110°
100°
90°
80°
70°
60°
50°
Ammonium Chloride.
Chloral Ethyl-alco
Chloral Methyl-alc
Butyl Chloral-Hy
Ammonium Carbamate
Chloral Hydrate
Engel, Naumann, & Isambert.)

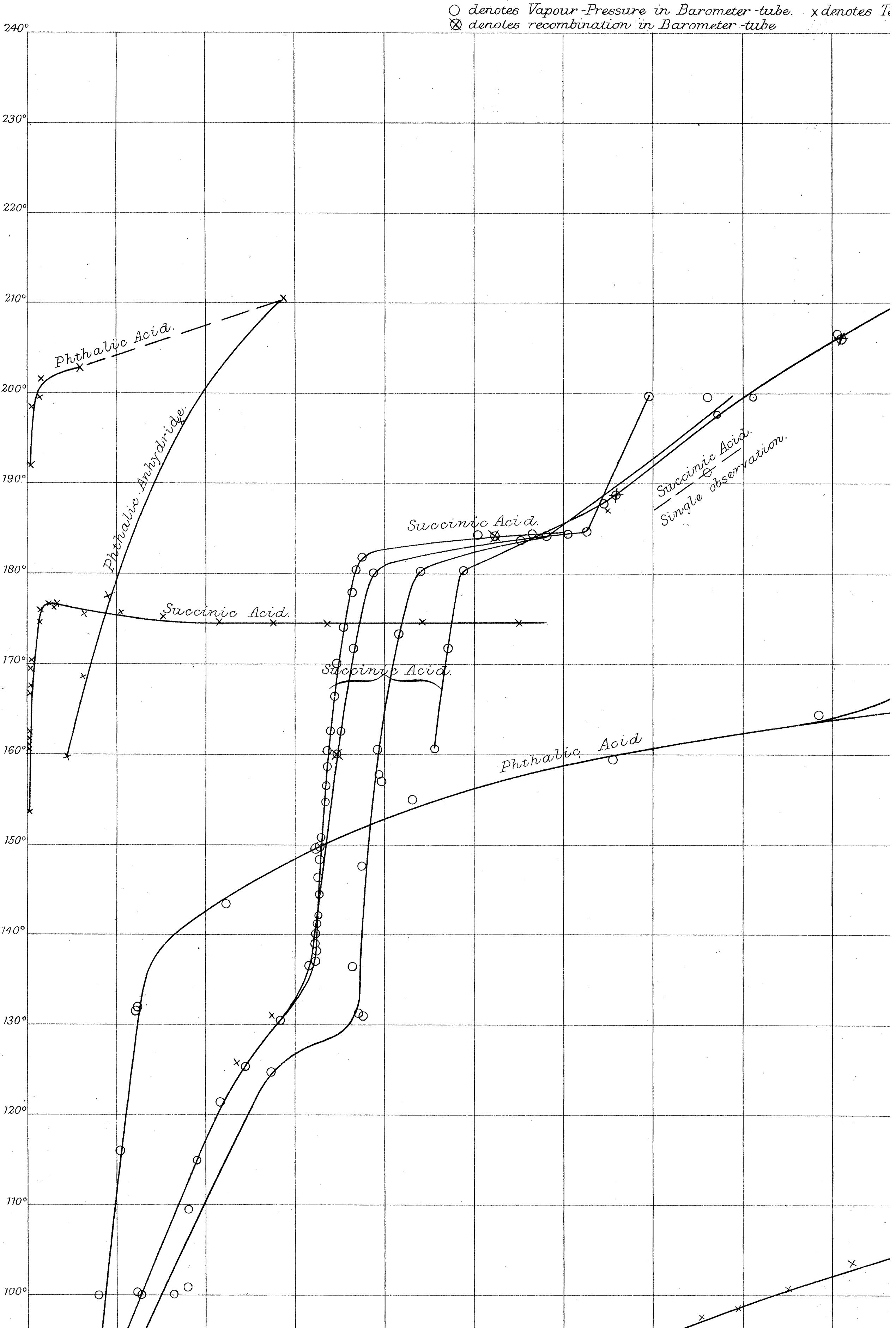

340°
330°
320°
310°
300°
290°
280°
270°
260°
250°
240°
230°
220°
210°
200°
yl-alcoholate
hyl-alcoholate
oral-Hydrate
Temperatures of Ammonium Chloride.
West, Newman & C°. lith.



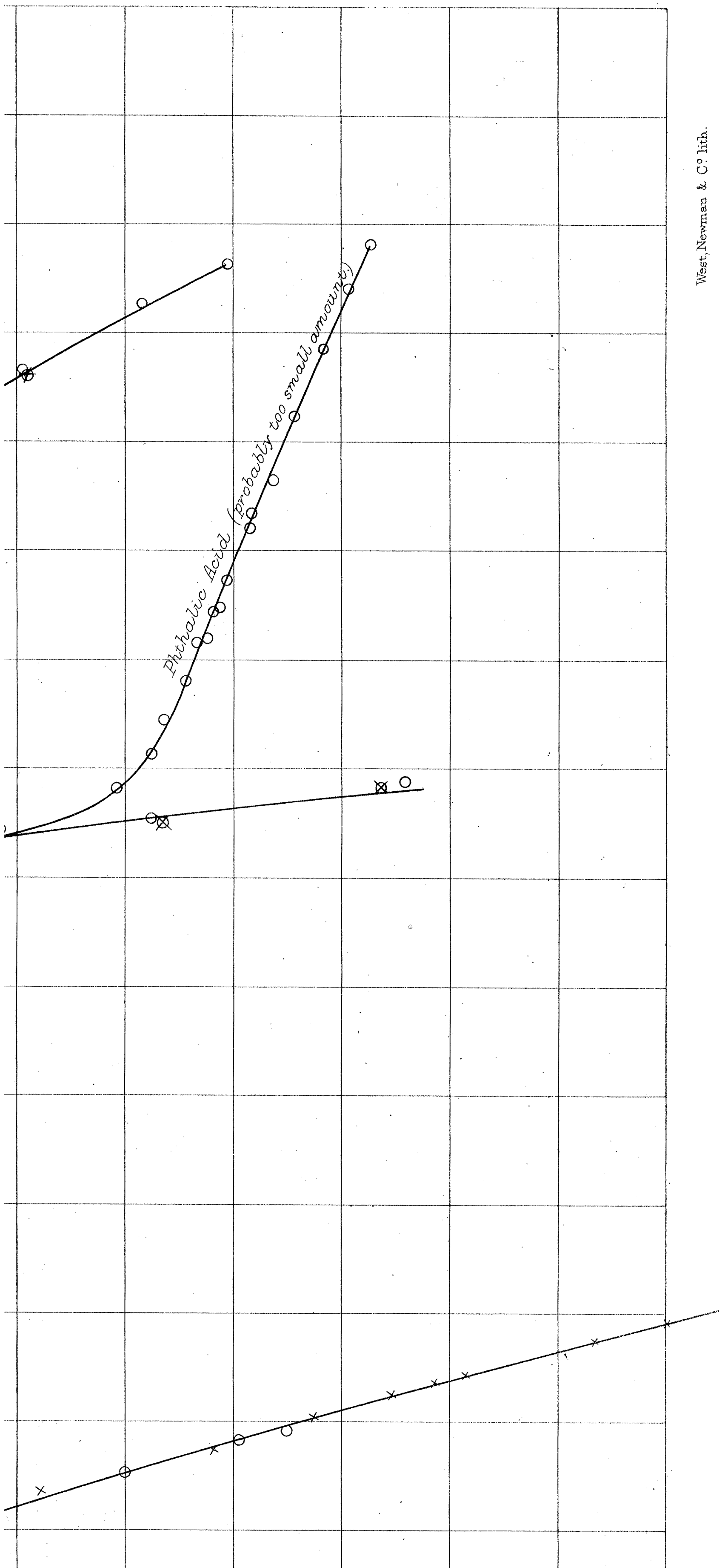
Ramsay & Young.


200°
190°
180°
170°
160°
150°
140°
130°
120°
500
550
600
650
700
750 mms.

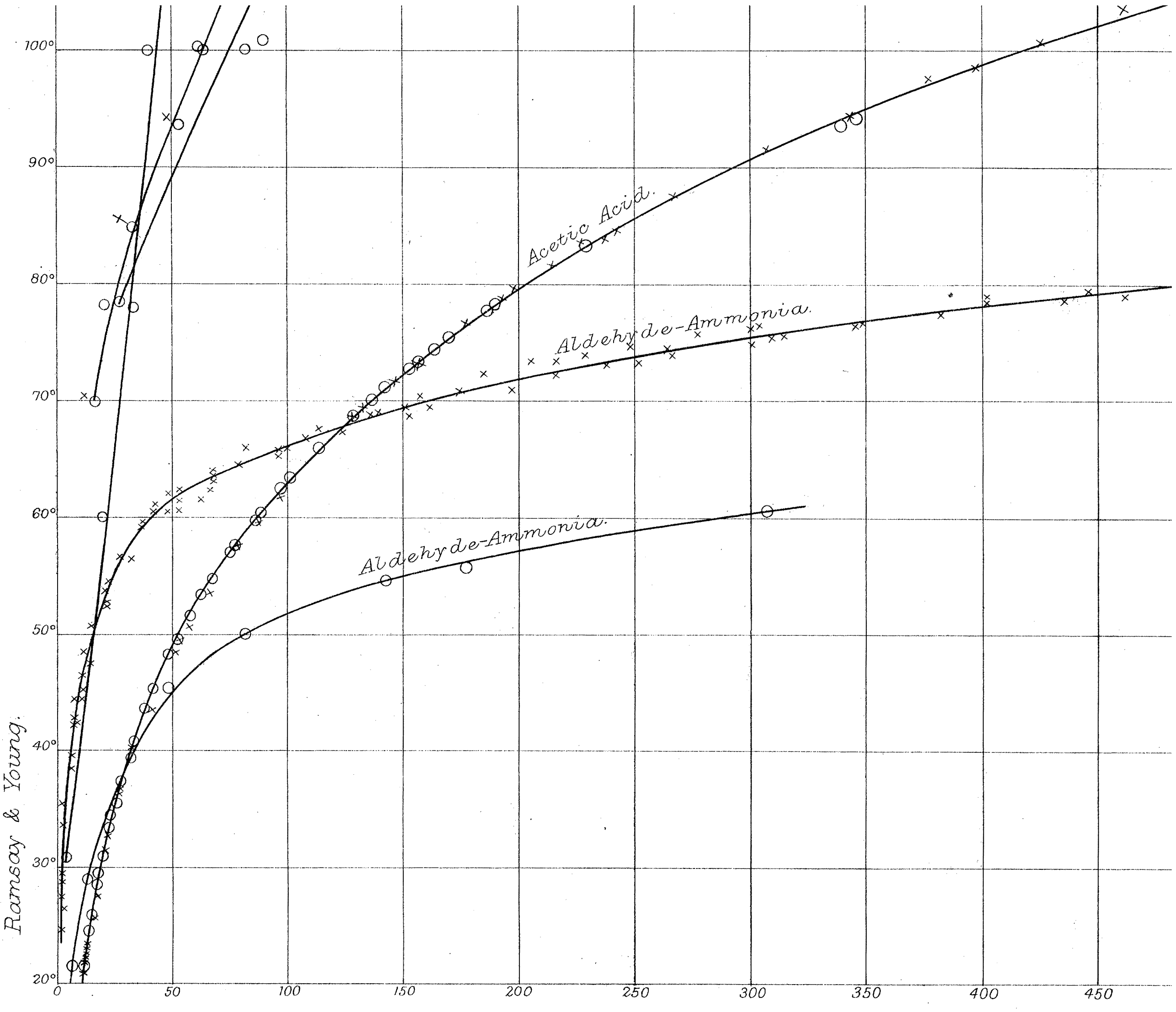
Phil. Trans. 1886. Plate 2.

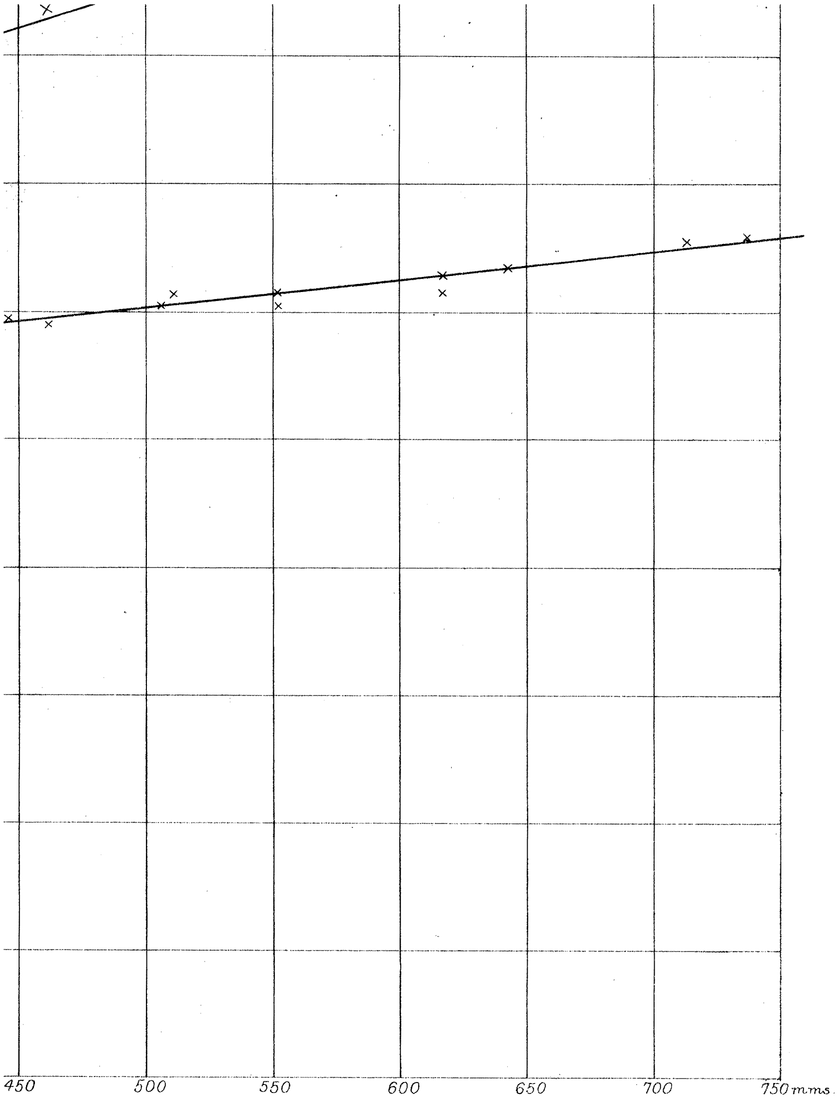


denotes Temperature of Volatilization in Still.

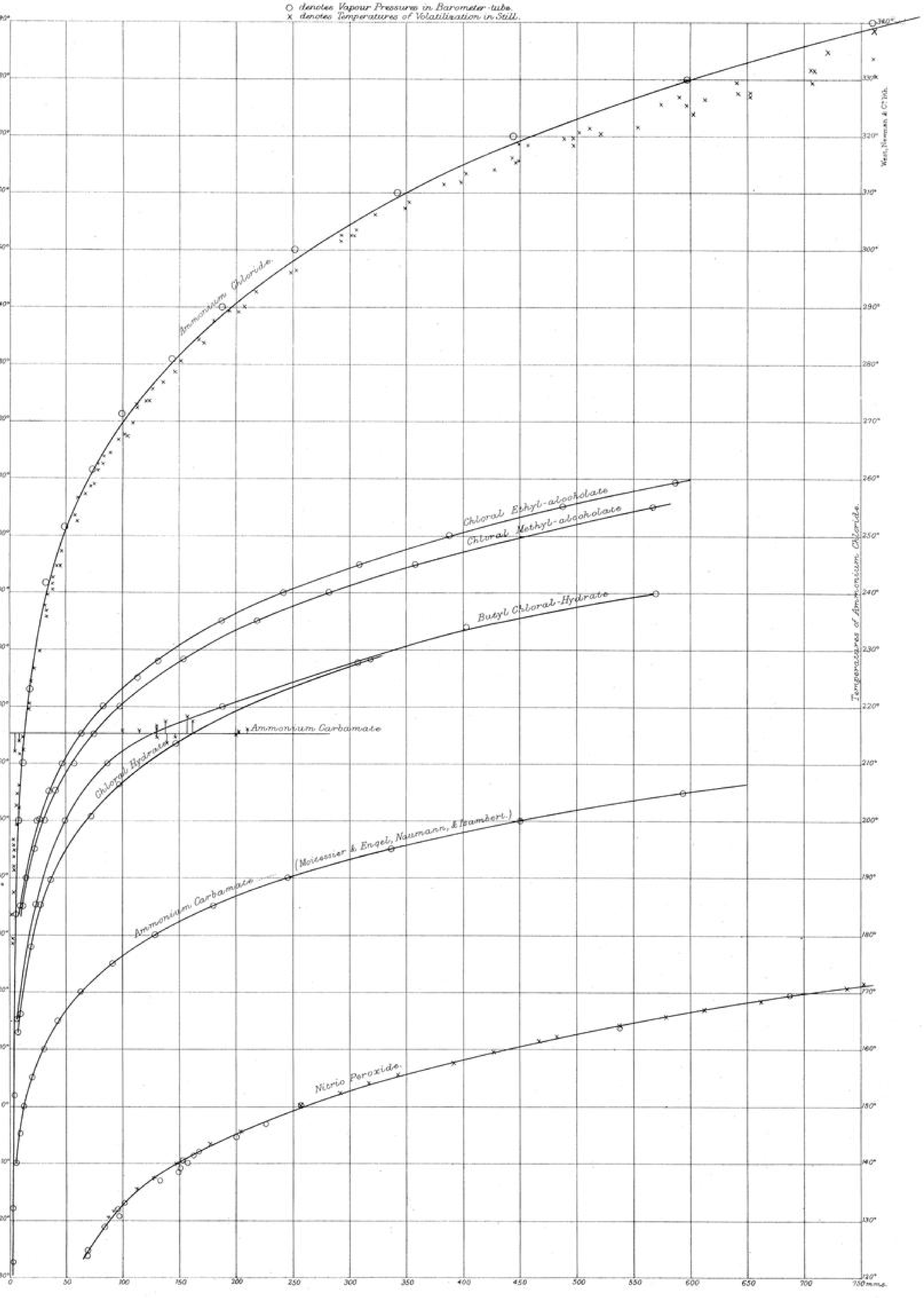


West, Newman & Co. lith.


Ramsay & Young.
100°
90°
80°
70°
60°
50°
40°
30°
20°
0
50
100
150
200
250
300
350
400
450
Acetic Acid.
Aldehyde-Ammonia.
Aldehyde-Ammonia.

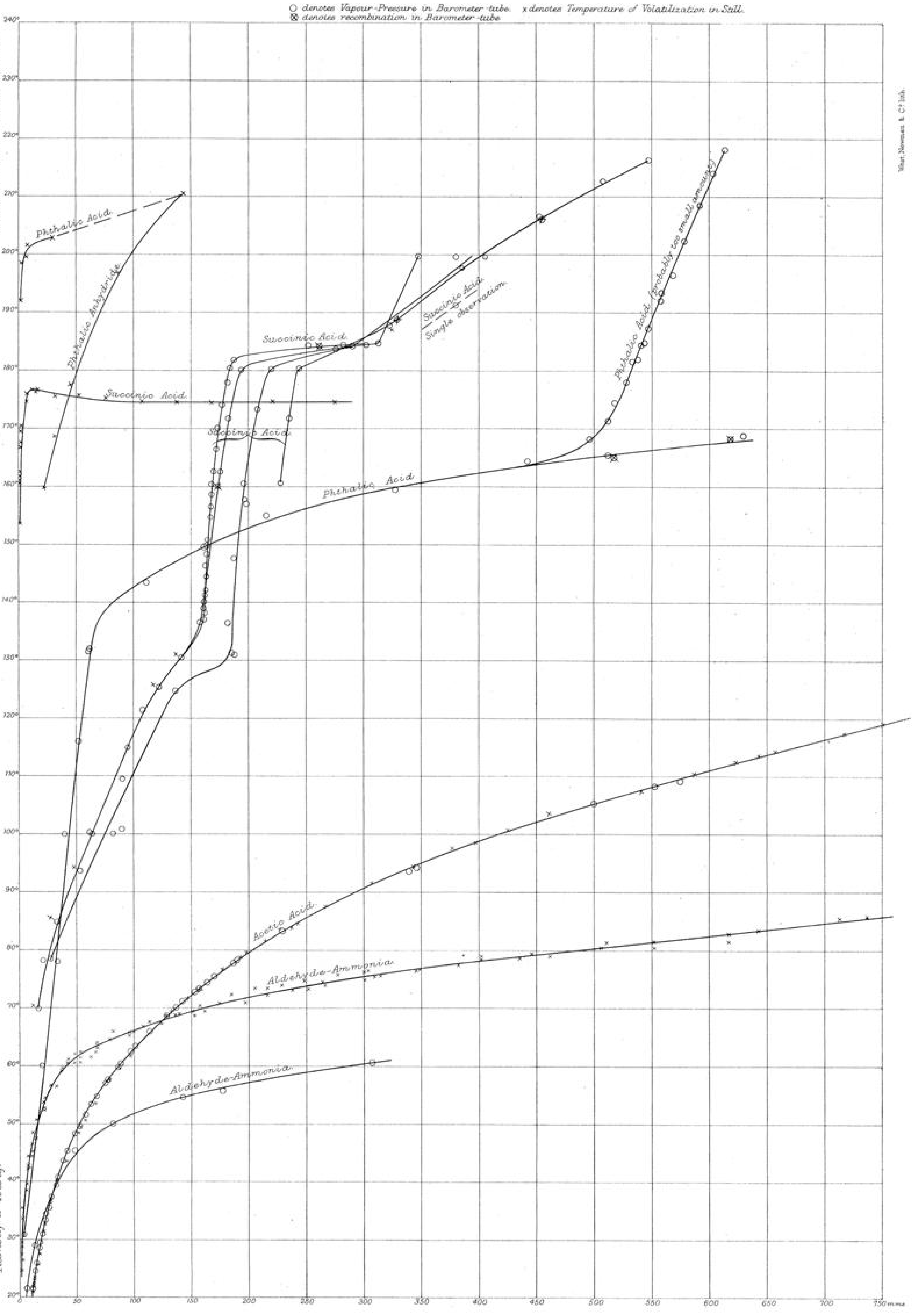

450
500
550
600
650
700
750 mms.

Phil. Trans. 1886. Plate 1.



Ramsay & Young.

West, Newman & Co lith.



Ramsay & Young.

West, Newman & C° lith.