

*Citation:*

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**Chemistry.** — “*Determinations of the vapour tension of nitrogen tetroxide*”. By Dr. F. E. C. SCHEFFER and J. P. TREUB. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of May 25, 1912).

1. In a previous treatise<sup>1)</sup> we communicated the results of an inquiry into the vapour tensions of nitrogen tetroxide. In these determinations we made use of a method which had been applied before by different investigators (LADENBURG, RAMSAY and YOUNG, BODENSTEIN, JOHNSON and JACKSON) in measurements of vapour tensions of substances which could not be brought into contact with mercury. Of the forms of the manometer proposed by the said investigators we chose that described by JACKSON, because this manometer can be very easily constructed, and the accuracy which we wanted to reach, can be easily obtained by means of this apparatus. Moreover by means of this manometer it seemed possible to us to devise a method to determine the vapour pressures of substances attacking mercury up to the critical pressure. As a sequel to the determinations to three atmospheres given in the preceding paper, we shall give a description here of this method for higher pressure, and state the results which make the vapour tension line of the nitrogen tetroxide up to the critical temperature known to us.

2. *Critical temperature.* Before entering upon the description of the vapour tension determinations at higher pressure, we will first mention a determination of the critical temperature, which we did not carry out with the measurements of the vapour tension, but in another way independent of these. A thickwalled tube of combustion glass provided with a capillary constriction was connected by means of a ground glass junction with the reservoir with nitrogen tetroxide. After the tube had been evacuated by means of the GAEDÉ-pump (with cooling of the nitrogen tetroxide with a carbonic acid alcohol mixture), and the connection with the pump had been melted off, the tube was filled by the liquid being distilled over, so that the liquid took up a volume that was somewhat smaller than half that of the tube. Then the latter was melted off at the capillary constriction, and heated in a bath of paraffin oil.

The liquid, which is almost colourless in the neighbourhood of

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<sup>1)</sup> These Proc. Vol. 14, p. 536.

the melting-point, and has a yellow brownish colour at the temperature of the room, becomes darker with rise of temperature; at about  $50^{\circ}$  it is already dark brown, and the transparency diminishes gradually with ascending temperature. The vapour which has a lighter colour at equal temperature on account of its slighter density, also gets darker with increasing temperature, so that above  $100^{\circ}$  the meniscus between liquid and vapour can hardly be distinguished. Hence the critical phenomenon of this darkbrown liquid and vapour has not been directly observed. The only value of the critical temperature recorded in the literature, has, accordingly, not been determined by an optical, but by another way.

For the determination of the critical temperature NADEJDINE <sup>1)</sup> made use of a very ingenious method, which, however, has not yielded accurate results. A tube was provided with a balance-knife in the middle so that it could execute regular oscillations round the state of equilibrium. If now the tube is filled with nitrogen tetroxide, regular oscillations are impossible, the tube inclines to the side where the liquid is. With rise of temperature above the critical however, the tube fills homogeneously, and gets in equilibrium. The temperature, at which this setting in of the equilibrium takes place, was considered to be the critical temperature; it amounted to  $171,2^{\circ}$  C.

We have, however, succeeded in observing the critical phenomenon directly optically. With incident and transmitted light there is nothing to be observed of the critical phenomenon in our tubes of about 3 mm. bore (thickness of the wall 3 mm.). Even the use of an arc lamp did not bring a change. When, however, we threw the light on the tube (in a bath of paraffin oil), and directed our eye so that the light that was reflected on the inner wall of the tube, could reach our eye, we could clearly distinguish the demarcation between liquid and vapour. In one of the tubes we saw the meniscus quickly shift to one of the extremities on rise of temperature, and disappear suddenly. In another tube, the volume of which pretty well agreed with the critical volume of the filling, the line of demarcation disappeared suddenly about in the middle of the tube. Both tubes yielded  $158,2^{\circ}$  C. for the temperature at which the demarcation between liquid and vapour disappeared. We have repeatedly carried out these determinations independently of each other; the obtained values agreed within  $0,2^{\circ}$ . So the critical temperature amounts to  $158,2^{\circ}$ , and accordingly differs considerably from the value given by NADEJDINE.

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<sup>1)</sup> Beibl. 9, 721 (1885).

3. *The vapour tension determinations.* The apparatus used by us for the vapour tension determinations, is represented in fig. 1. The

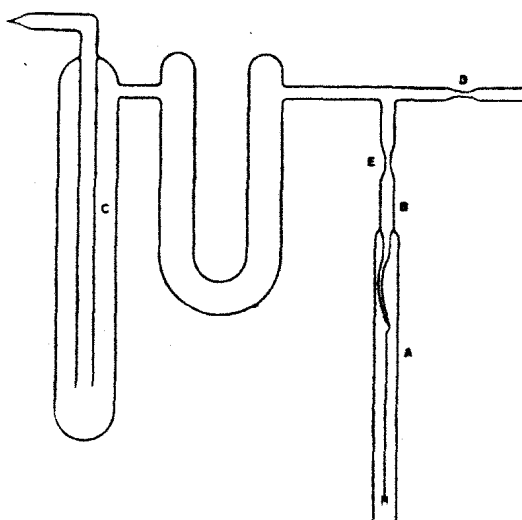


Fig. 1.

manometer, which is fused into the tube *A*, differs from the one described in our previous communication only in this that it is more elongated and smaller; the length of the curved part amounts to three or four cm., while the tube *A* has an external diameter of 10 mm. and a length of 22 or 23 cm. The entire apparatus serving for the measurements has a length of about 28 cm. after the constriction at *E* has been

melted off. On the outer tube *A* two marks have been made, so that the end of the needle is just between the two marks when the internal and external pressure is the same. The manometer can resist an excess of pressure of one atmosphere, and can therefore be evacuated; then the end of the needle reaches the inner wall of *A* in some of the apparatus used by us. The sensitivity reached with this shape of apparatus varies between  $\frac{1}{20}$  and  $\frac{1}{10}$  atmosphere.

Before the apparatus was filled the reservoir *C* with the nitrogen tetroxide was cooled by means of a mixture of carbonic acid-alcohol, and evacuated by means of a GAÈDE-pump through *D*. Then the constriction *D* was melted off, and a quantity of nitrogen tetroxide was distilled over through the *U*-tube with phosphorus-pentoxide into *B*; for this purpose a cylindrical vessel was placed round the tube *A* by means of a cork, which vessel could be filled with alcohol cooled by carbonic acid. When a sufficient quantity of liquid was distilled over, the apparatus was separated from the filling apparatus by melting off at *E*, after the nitrogen tetroxide in *B* and *C* had been brought to  $-80^{\circ}$ .

We have applied two different methods for the determination of vapour tensions.

*a.* For our first determinations we made use of the arrangement indicated in Fig. 2*a*. The apparatus *AB* was slid into a thickwalled combustion tube, so that it rested on the constriction at *C* with a copper spiral, which is not drawn in the figure. At the lower end of the combustion tube a combustion capillary *D* of 3 mm. bore

and with a wall of 3 mm. thickness was fused to the apparatus, which was cemented into a mounting for CAILLETET experiments. The upper end of the combustion tube was fused to by means of an oxygen gas flame. After evacuation with a water-jet pump the combustion tube was filled with a glycerin-water mixture, and screwed into a CAILLETET-pressure-cylindre filled with the same liquid. Then a cylindrical glass jacket was put round the combustion tube by means of a rubber stopper prepared for high temperatures, in which jacket different liquids were electrically heated under varying pressure till they boiled (by means of the heating wire wrapped

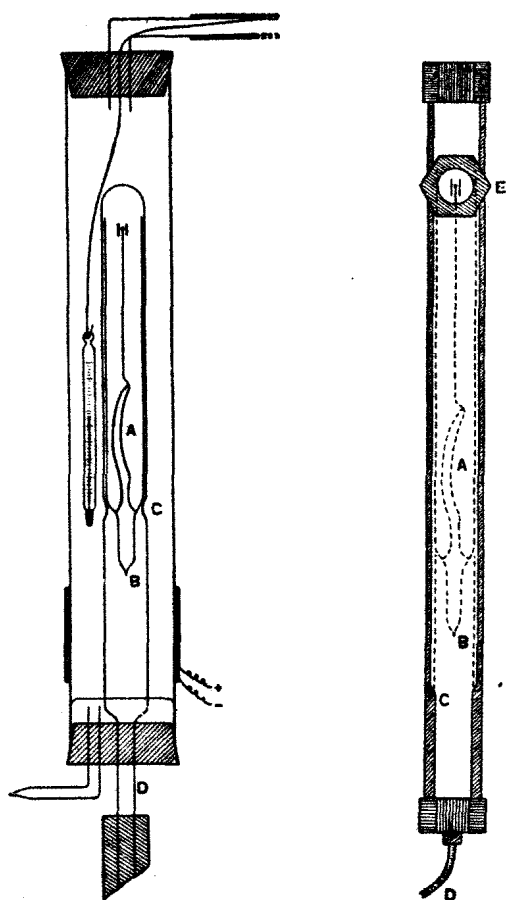


Fig. 2a.

Fig. 2b.

round the tube and drawn in fig. 2a). The rubber stopper was protected against the action of the boiling liquid by a layer of mercury. The condensation ring of the boiling liquid was always raised to above the extremity of the combustion tube, the temperature was

read on an Anschützthermometer (which had been compared with a normal thermometer) the mercury bulb of which was at a level with the nitrogen tetroxide.

For the determination of the pressure this was regulated by means of a CAILLETET-pump in such a way that the needle was exactly between the marks on the tube *A*, and read on a SCHÄFFER and BUDENBERG metal manometer gauged by means of a pressure-balance. The liquids which we have used for heating, were successively alcohol, toluene, xylol, and aniline; the bumping was prevented by a stream of air-bubbles, which were sucked in through the tube that passed through the stopper.

The results obtained by this method, will be described in § 4. The experiments arranged in this way always finished up with an explosion; the highest pressure we reached was 67 atmospheres. The critical pressure, however, lying higher, we were obliged to have recourse to another method for the determination of the higher vapour-tensions.

*b.* In our further experiments we abandoned the use of a combustion tube, and replaced it by a copper tube. In this we had first of all to face the difficulty to arrange it in such a way that the reading of the position of the manometer needle was possible. For this purpose near the end of the tube two transverse tubes were adjusted, which could be closed by means of perforated screws, one of which (*E*) has been drawn in fig. 2*b*. The hole through these screws was closed with a glass plate, which was pressed to the tube by the screw. To make this arrangement tight at high pressure was at first attended with great difficulties. We tried to reach this by screwing the glass plates to the tube between rings of leather; it was, however, impossible to get a sufficient closure in this way.

Then we pressed the plates between plaster of Paris, and between copper, made soft by being made red-hot, always, however, with a negative result. After these futile attempts we cemented the plates in loose steel mountings, and screwed these mountings with copper plates into the tube. As cement we tried first a mixture of soluble glass, zinc oxide, and magnesium oxide; once we succeeded in this way to obtain a sufficient closure up to 100 atmospheres, generally, however, the soluble glass showed cracks, which allowed the liquid in the copper tube to get through on increase of pressure. At last we succeeded in cementing the glass plates into the steel mounting by means of an enamel obtained by melting from sodium- and potassium carbonate, silicium oxide, and lead oxide. By heating with a Tecluburner this enamel melted, and entirely filled the narrow opening between

glass and steel, and continued to close after it had been cooled, up to a pressure of 150 atmospheres.

Now the apparatus *AB* was slid into the tube; it rested on the constriction *C* by means of a loose glass tube that tightly fitted in the copper tube; the length of this tube was chosen so that the end of the manometer needle was exactly between the two glass plates in the holes in the screws, so that it was possible to read the position with an incandescent lamp placed behind it. The narrow copper tube *D*, which formed the connection with the CAILLETET-pump, was fastened to the lower end of the copper tube by means of a screw. Now the tube was quite filled with the glycerin water solution, and closed at the top with a screw:

So in this way we had obtained an arrangement which could resist pressures of about 150 atmospheres. It only remained to us to find a method to heat this copper tube to varying temperatures.

We have tried to use an oil-bath for the heating, and to place the tube in the bath in such a way that the end in which the glass plates were, projected above the bath. This was required for the accurate reading of the needle, and to have at the same time an opportunity to clean the glass panes when in course of time the screws began to leak a little in consequence of the increase of temperature. This method of heating, however, appeared to give unreliable results in spite of different modifications. It appeared that the part that projected above the liquid caused a loss of heat, so that the temperature of the nitrogen tetroxide remained lower than the temperature in the oil-bath, so that at a definite temperature always too low pressures were found compared with the results according to the method *a*.

At last we were more successful with another quite different method of heating. The copper tube was quite surrounded by two tightly fitting spirals of hard lead. Through both these spirals an oil-stream was passed, so that the two streams ran in opposite directions; one stream flowed spirally round the tube from below upwards, the other in the opposite direction. The oil-stream was obtained by means of a rotating pump worked by an electromotor, which pressed the oil from a pan heated by two Tecluburners through the spirals. The tube and the heating-spirals surrounding it were first enveloped with thick asbestos cord, and then with a thick layer of cotton waste to prevent emission of heat as much as possible; the inlet and exit tubes were isolated in the same way.

The temperature was read on an Anschütz thermometer, which was placed between the spirals and the tube and of which the part

of the scale that was to be read, was placed behind an opening in the isolation material. Besides this thermometer opening only two small apertures were made in the isolation layer, through which the two small panes remained visible.

4. *Results.* The results obtained by the methods described in the preceding paragraph, have been collected in Table I. They have been made with five apparatus; the determinations in the neighbourhood of the critical temperature have been carried out with an apparatus which was about half filled with liquid at the ordinary temperature, and the volume of which was therefore somewhat smaller than the critical volume. From our determinations at the temperatures in the immediate neighbourhood of  $T_k$  we have determined the critical pressure graphically. The extrapolation that is required for it, can certainly be executed within the error of one atmosphere. Yet we think that we must consider the critical pressure accurate up to two atmospheres. We have namely no perfect certainty that the observations at the highest temperatures refer to the heterogeneous equilibrium. The possibility cannot be entirely excluded that these observations represent a line in the homogeneous liquid region, though these determinations yield a practically continuously progressing curve with those at lower temperatures; if this should be the case, the deviation from the real vapour-tension curve is so slight, that the accurate value of the critical pressure could only be found by means of an extrapolation formula, drawn up from observations at lower temperature. In this, however, we also meet with difficulties, as then the extrapolation would have to take place over a greater range of temperature; we return to this extrapolation in a following paragraph. So we find 100 atmospheres for the critical pressure, in which we must consider a maximum deviation of two atmospheres possible. It will, moreover, be difficult to reach a greater accuracy, as it will not be possible to observe the critical pressure at the same time with the measurement of the pressure without complicating the arrangement considerably. Besides this would give rise to new experimental difficulties, because the critical phenomenon in itself is so very difficult to observe. A manometer which was filled for about two thirds with liquid, presented a sudden deviation from the vapour tension line at about  $140^\circ$ ; the pressure rose abnormally rapidly (about 6 atm. per degree) with slight rise of temperature, much more rapidly than the vapour tension line, even in the neighbourhood of the critical circumstances. So this apparatus is quite filled with liquid at  $140^\circ$ , and the abnormal rise of pressure was



TABLE I.

<i>t</i>	<i>p</i>	Method	<i>t</i>	<i>p</i>	Method
54.25	4.1	<i>a</i> (alcohol)	109.8	26.8	<i>a</i> (xylol)
59.6	4.95	<i>a</i> (alcohol)	110.2	26.8	<i>b</i>
64.95	6.1	<i>a</i> (alcohol)	110.3	27.0	<i>a</i> (xylol)
70.1	7.3	<i>a</i> (alcohol)	110.8	27.2	<i>b</i>
72.7	8.0	<i>b</i>	114.5	30.8	<i>a</i> (xylol)
74.7	8.7	<i>a</i> (alcohol)	115.5	31.3	<i>a</i> (xylol)
78.3	9.7	<i>a</i> (alcohol)	115.7	31.6	<i>a</i> (xylol)
78.3	9.6	<i>b</i>	119.2	35.3	<i>a</i> (xylol)
79.7	10.1	<i>b</i>	120.0	35.7	<i>b</i>
81.7	10.8	<i>a</i> (toluene)	120.5	36.3	<i>a</i> (xylol)
82.7	11.1	<i>b</i>	125.35	41.6	<i>a</i> (xylol)
86.7	12.9	<i>b</i>	125.5	41.8	<i>a</i> (xylol)
87.1	13.0	<i>b</i>	131.1	48.8	<i>a</i> (xylol)
88.5	13.6	<i>a</i> (toluene)	131.5	49.3	<i>b</i>
92.3	15.3	<i>b</i>	134.9	54.4	<i>a</i> (xylol)
93.7	16.1	<i>a</i> (toluene)	139.1	60.5	<i>a</i> (aniline)
98.15	18.6	<i>a</i> (toluene)	142.6	66.6	<i>a</i> (aniline)
100.7	20.3	<i>a</i> (xylol)	142.9	66.4	<i>b</i>
100.9	20.3	<i>a</i> (xylol)	151.2	82.4	<i>b</i>
101.45	20.5	<i>b</i>	152.4	84.5	<i>b</i>
101.6	20.7	<i>a</i> (toluene)	156.2	93.6	<i>b</i>
104.5	22.6	<i>a</i> (toluene)	157.4	97.2	<i>b</i>
105.6	23.3	<i>a</i> (xylol)	$T_k$ 158.2	$P_k$ 100	extrapolation
105.9	23.7	<i>a</i> (xylol)			

therefore owing to the heating of the homogeneous liquid at constant volume.

With every determination in Table I the method used for the observation is given; the pressures are given in atmospheres. In the first four determinations and in the sixth the pressure was not determined by means of a SCHÄFFER and BUDENBERG manometer, but with an air-manometer (air-isotherm of AMAGAT).

It will be clear from the table and the corresponding graphical representation (fig. 3) that there is sufficient harmony between the results obtained by the two methods of observation.

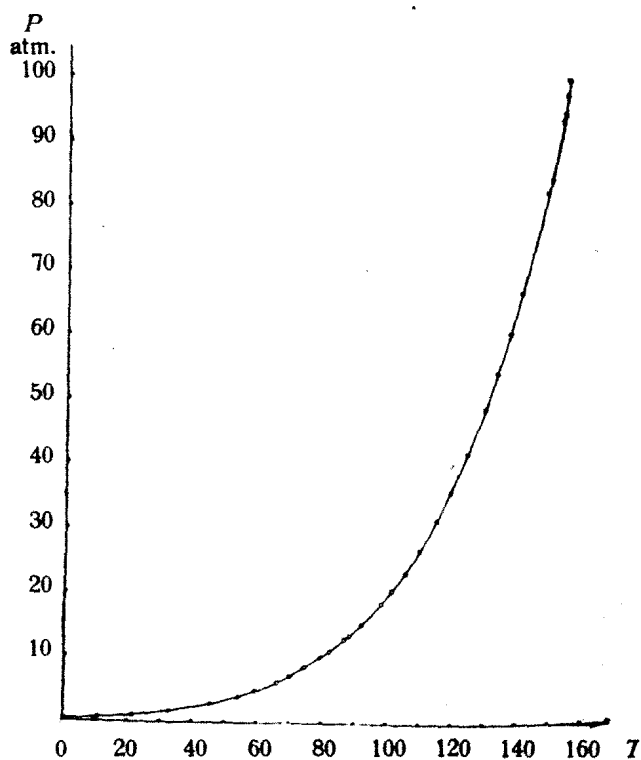


Fig. 3.

By way of control of the pressure measurements we have exposed one of our manometer tubes, after being opened, in the copper tube to the same pressures and temperatures as occurred in our determinations. Then it appeared that in none of the observations a correction was required for a change of the zero position.

5. As for the nitrogen tetroxide we have to do with a substance which is in dissociation, for which the values of the degree of the dissociation appreciably vary both in the liquid state and in the vapour state corresponding with it — for the vapour we already gave some values for the degree of dissociation in our preceding communication — it seemed desirable to calculate the value of  $f$  from VAN DER WAALS'S empirical equation with the aid of our observations. If for this purpose in the equation:

$$-\log \frac{P}{P_k} = f \frac{T_k - T}{T}$$

we substitute the values  $p_k = 100$  and  $T_k = 158.2 + 273 = 431.2$ , our observations yield values of  $f$  varying with the temperature, as will be clear from the subjoined table II.

TABLE II.

$t$	$T$	$P$	$f$	$t$	$T$	$P$	$f$
7.0	280.0	$\frac{1}{2}$	4.25	100.5	373.5	20	4.5
21.2	294.2	1	4.3	123.8	396.8	40	4.6
46.6	319.6	3	4.35	138.8	411.8	60	[4.7]
79.4	352.4	10	4.5	150.0	423.0	80	[5.0]

The value of  $f$  appears really to reveal the dissociation; it lies, namely, much higher than that of normal substances ( $\pm 3$ ), even higher than that of substances as water and alcohol. It appears at the same time that  $f$  rises with the temperature, whereas the reverse takes place for water and alcohol.

So the inclination of the  $P$ — $T$ -line increases more rapidly with rising temperature than for a normal substance.

In the graphical representation, which occurs in the Theoretische Chemie of Prof. NERNST <sup>1)</sup>, in which  $-\log \frac{P}{p_k}$  is taken as ordinate,

$\frac{T_k}{T} - 1$  as abscissa, nitrogen tetroxide yields therefore a line, which in opposition to that of water and alcohol is concave seem from below, and yields a branch of the fanlike sheaf of lines, which lies still higher than all those indicated in the graphical representation.

We have put the last two values for  $f$  in table II between parentheses, as these change resp. 0.1 and 0.2 by a change of one atmosphere in the value of  $P_k$ , and are therefore distinctly inferior to the preceding ones in accuracy.

6. As appears from the change of colour of liquid and vapour with rising temperature the increase of the degree of dissociation is accompanied by an increase of darkening of the colour according to table IV of our former communication. Hence the supposition naturally suggests itself, that the brown colour is owing to the split molecules, whereas the unsplit molecules are colourless. This supposition has been confirmed by the investigation of SALET <sup>2)</sup>, who has

<sup>1)</sup> p. 237 (1909).

<sup>2)</sup> C. r. 67. 488 (1868).

succeeded in getting quantitative data about the homogeneous equilibrium by a colorimetric method, which data accord well with the determinations from the vapour densities. As the colour of the liquid and the vapour gets darker and darker towards the critical temperature, the degree of dissociation will probably be great at  $T_k$ .

In order to get a criterion about the degree of the dissociation we have calculated the values of  $a$  and  $b$  from the equation of state (as the result of a discussion of one of us with prof. VAN DER WAALS). By substitution of  $T_k = 431.2$  and  $P_k = 100$ , we find:

$$a = \frac{27}{64.273^2} \frac{T_k^2}{P_k} = 0,0105 \text{ and}$$

$$b = \frac{1}{8.273} \frac{T_k}{P_k} = 0,00197.$$

If to get an approximative estimation we now consider the  $b$  as an additive quantity, we can calculate the theoretical  $b$  for  $NO_2$ , resp.  $N_2O_4$ , from the tables of the  $b$ -values, and compare them with the values found above.

From the values for nitrogen and oxygen we find in this way for  $NO_2$  and  $N_2O_4$ , resp. 0,00226 and 0,00452.

Calculation with the aid of the data about nitrogen oxide and oxygen, resp. nitrogen mon-oxide and oxygen, yields for  $NO_2$  and  $N_2O_4$ , 0,00186 and 0,00372, resp. 0,00200 and 0,00400.

So we draw the conclusion from these values, that the fluid phase for the critical circumstances consists for by far the greater part of split molecules.

7. The complex behaviour of the nitrogen tetroxide leads us to expect an intricate equation for the  $PT$ -line. Caloric data, which can be of use to us to find the vapour tension equation, are not sufficiently known. For this we must of course know the heat of evaporation and the specific heats along the border-line. The specific heats which are known, refer to unsaturated vapours as far as the vapour state is concerned. Accordingly they would have to be corrected in accordance with the change of the degree of dissociation with the pressure. The heat of dissociation in the homogeneous vapour is known pretty accurately, and so this correction might be applied at those temperatures for which the degree of dissociation in the saturated vapour is known (see preceding communication Table IV). The specific heat of the liquid is almost quite unknown. So even if the heat of evaporation at one temperature were known with sufficient accuracy, the unknown dependence of the specific heats on the

temperature would yet render the drawing up of a formula by the aid of the caloric data impossible.

We will only calculate the value of the heat of evaporation from our vapour-tension determinations by the aid of the equation of CLAPEYRON, which can only be applied for low pressures, because the specific volumes along the border line are unknown at higher pressure. From the equation:

$$T \frac{dP}{dT} = \frac{Q}{V_{gas} - V_l}$$

we find, neglecting  $V_l$  with respect to  $V_{gas}$  and applying the law of BOYLE-GAY-LUSSAC:

$$P V = (1 + x) RT,$$

in which  $x$  represents the degree of dissociation

$$Q = \frac{(1 + x) RT^2}{P} \frac{dP}{dT}.$$

In order to calculate  $\frac{dP}{dT}$  we have represented our determinations at low pressure by an empirical formula. By the aid of the data:  $t = -23, p = 70 \text{ m.M.}; t = 11,0, p = 463 \text{ m.M.}; t = 48.7, p = 2478 \text{ m.M.}$  from our former communication we derive the values  $a = 1325.6$ ,  $b = 3.354$ ,  $c = -0.8950$  for the constants  $a$ ,  $b$ , and  $c$  in the equation:

$$\log p = -\frac{a}{T} + b \log T + c$$

This equation represents our observations of the preceding communication very well. It may be remarked here in passing that this expression can represent the observations at higher pressure even up to about 120' and 36 atmospheres. At higher pressures the curve calculated from the equation deviates slightly towards lower pressure; in the immediate neighbourhood of  $T_k$  the deviations become greater; still even at  $T_k$  the deviation amounts only to about three atmospheres. It is remarkable that this formula drawn up from observations below 3 atmospheres, is able to represent the vapour-tension line of this complicated substance so accurately.

If we now differentiate the obtained expression we find:

$$0.4343 \frac{1}{p} \frac{dp}{dT} = \frac{1325.6}{T^2} + 0.4343 \frac{3.354}{T},$$

which yields after substitution:

$$Q = \frac{1325.6}{0.4343} (1 + x) R + 3.354 (1 + x) RT.$$

If in this expression we substitute the values  $R = 1,985$ ,  $t = 21,2$ , and  $x = 0.15$ , which two last refer to the boiling point, we find for the heat of evaporation at the boiling-point:

9200 calories.

The experimental determinations of BERTHELOT and OGIER<sup>1)</sup> appreciably differ from this value. From a number of values which differ pretty considerably from each other, which, however, all of them lie lower than the above mentioned one, they consider 8600 calories the most probable. We, however, think that we have to prefer our calculation, the more so as the determinations which have served for our calculation, just lie in the temperature region over which RAMSAY and YOUNG's investigation extended, and the determinations of the latter do not practically differ from ours.

In conclusion we wish to avail ourselves of this opportunity to express our thanks to Prof. SMITS for his advice in the experimental difficulties experienced by us, and for the interest shown by him in our work.

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**Physics.** — *“Electric double refraction in some artificial clouds and vapours.”* (Third part). By Prof. P. ZEEMAN and C. M. HOOGENBOOM.

18. The results obtained with the sal-ammoniac fog might be explained by postulating the existence of two varieties of sal-ammoniac crystals. This hypothesis was put forward in § 17. In the textbooks on crystallography, which were at the disposition of the authors, nothing however, relating to dimorphism of sal-ammoniac could be found. This seemed rather unfavourable to the proposed explanation. We are much indebted therefore to Dr. F. E. C. SCHEFFER, who gave us some references to the chemical-crystallographical literature, from which it appears that the dimorphism of sal-ammoniac is a well-known fact (see v. GROTH, *Chemische Kristallographie*. Band I. S. 167. 1906).

STAS<sup>2)</sup> while sublimating  $\text{NH}_4\text{Cl}$  had observed a phenomenon closely resembling the transformation of polymorphous substances; he did not try however an explanation and it seems that he did not think of dimorphism.

<sup>1)</sup> Ann. de Ch. et de Ph. (5) 30 398 (1883).

<sup>2)</sup> STAS. Untersuchungen über die chemischen Proportionen u.s.w. deutsch von Aronstein. S. 54. Leipzig 1867.