long time. I have observed this in the investigation of the system ether-anthraquinone, but only in the case that the liquid phase was very viscous.

When we have not to do with a viscous liquid phase, but as here, with a solid solution, the said phenomenon of retardation will be able to appear the sooner.

It will, no doubt, not require any further elucidation now why ROYSTON, when he did not heat up to 1030°, but to 720°, had to find less cementite after cooling. It is possible that he did 'not reach the line $a's'$, then, but sf on the line ss', so that first a-iron deposited.

Further I think that it is clear why up to now the temperature of the metastable mixed crystal eutectic point has, indeed, been observed, but not once that of the stable mixed crystal eutectic point. To enable us to pursue the stable equilibrium between martensite mixed crystals and graphite to the point S a so slow cooling is required, that a thermic determination is quite impossible. The only method which may possibly yield a reliable result is the dilatometrical, when an active catalyser shall have been found for the transformation under consideration.

These considerations do not seem devoid of interest to me because they are of general application, and give a plausible explanation of the mutual relation between the internal equilibrium in a homogeneous phase, and the heterogeneous equilibrium that may arise from it.

Anorganic Chemical Laboratory of the University.
Amsterdam, Nov. 19, 1911.

Chemistry. — "*Determinations of vapour tensions of nitrogen tetroxide.*" By Dr. F. E. C. SCHEFFER and Mr. J. P. TREUB. (Communicated by Prof. A. F. HOLLEMAN).

1. In 1884 RAMSAY and YOUNG published a paper on vapour tension determinations of ice and camphor[1]). They demonstrated that statical and dynamical methods yield concordant results, and that therefore, just as the P-T-line of liquids can be determined from boiling-point determinations at varying pressure, also the P-T-line of the solid-gas-equilibrium may be found by the observation of sublimation temperatures at varying pressure.

In a later investigation, however, it appeared that solid substances which dissociate at their transition to vapour, in many cases according to the dynamic method[2]) furnish values for the vapour tension which

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[1]) Phil. Trans. **175**. 37 (1884).
[2]) Phil. Trans. **177**. 71 (1886).

deviate from the statically determined ones. A full discussion and explanation of this behaviour is found in VAN ROSSEM's thesis for the doctorate [1]. In the evaporation of solid substance we have in this case a superposition of two velocities, the velocity of evaporation of the molecule as such, and the velocity of dissociation in the vapour. If the first velocity is small with respect to the second, stable equilibrium will exist at any moment between the solid substance and the vapour surrounding it, and the same values will be found according to the two methods of determination. If, however, the first velocity is great with regard to the second, the solid substance will be surrounded by a vapour which is little dissociated, at least less than is the case for the stable coexistence. Then the substance can be heated to a higher temperature than in the former case. Hence the dynamically determined P-T-line, whose situation will depend on the rapidity of the heating, will lie at higher temperature, resp. at lower pressure, than the statical one.

A similar deviation between P-T-lines determined statically and dynamically, is however not known for liquids. We disregard here the generally very small differences which may occur in consequence of a certain excess of pressure which the boiling (or sublimating) substance must exert to emit its vapour to the surrounding space, which must cause the substance to assume a somewhat higher temperature corresponding to the somewhat higher pressure in the immediate neighbourhood. The differences described above are of an entirely different order of magnitude. Nitrogen tetroxide, which RAMSAY and YOUNG also included in their above described investigation, gives concordant results in the determinations, made according to the two different methods; this conclusion is based on the observations collected in the following table. (p. 538).

The statical values given in the above table were obtained by making use of the compressibility of a large glass reservoir, filled with mercury and provided with a narrow capillary ; the displacement of the mercury meniscus in the capillary tube furnishes a measure for the pressure exerted by the nitrogentetroxide against the reservoir. The two observations marked with an asterisk, have not been measured directly, but have been found by determining the difference of pressure between 0° and the temperatures 13,9 and 19,6, in which it was assumed that the pressure determined statically and dynamically would agree at 0°. A difference which might eventually exist between the values at 0° obtained by the two

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1) VAN ROSSEM. Thesis for the doctorate and Z. ph. Ch 62, 257 (1908). See also Z. ph. Ch. 72. 458 (1910).

TABLE I.

T	P (in millim. of mercury)		T	P (in millim. of mercury)	
	statical	dynamical		statical	dynamical
— 26	68.6		— 4.3		204.5
— 25.2	69.6		— 3.1	225.3	
— 21.0	84.6		0.0		257.5
— 19.35		86.5	2.2		291.0
— 19.1	96.0		4.0		316.5
— 18.15		91.8	5.7		344.0
— 18.0	96.0		7.9		390.5
— 17.0	101.6		9.7		426.0
— 14.6		113.5	11.4		467.5
— 13.0	132.2		12.1		483.0
— 12.7		127.0	13.9	536.8*	
— 11.5	149.4		14.2		536.0
— 11.0	150.2		15.8		578.5
- 10.0	155.7	147.5	17.0		613.5
— 9.6	152.0		18.5		660.5
— 8.7	161.7		19.6	687.1*	
— 8.0	167.5		20.9		738.5
— 6.7		177.0	21.5		752.0
— 5.3	200.0				

methods would, therefore, render a correction to the two determinations in question indispensable. A glance at the above table must really lead us to the conclusion that if there is a difference between the determinations in the two series, it will certainly be a slight one, and that it can probably be accounted for by the above mentioned excess of pressure. Moreover the dynamic determinations yield a very regular course of the P-T-line, and it is just this regularity that leads us to expect that the velocity of the homogeneous vapour equilibrium will be great with respect to that of the evaporation, because otherwise a variation in the rapidity of working, as was already alluded to above, would probably have affected the regularity of the observations.

Lately, however, a paper by GUYE and DROUGININE [1]) appeared, in which some vapour pressure determinations of nitrogen tetroxide are mentioned These values, which were obtained by a statical method, however, deviate perceptibly from the values found dynamically by RAMSAY and YOUNG ; GUYE and DROUGININE's line lies at lower temperature, resp. higher pressure than that of RAMSAY and YOUNG, and these deviations come particularly into the foreground in the temperature region where only the two statical values marked in the above table with an asterisk, have been given. --

If, accordingly, these two values, which have both been found indirectly, were not correct, and if those of GUYE and DROUGININE on the contrary, were, we should have found an example in the nitrogen peroxide for which the velocity in the homogeneous equilibrium is not (as is usually the case) very great with respect to the velocity of evaporation.

This last consideration led us to seek a statical method which would enable us to determine the vapour tensions of the nitrogentetroxide accurately, and to remove the said contradiction.

Such an investigation was the more attractive as the P-T-line of the nitrogentetroxide possesses a point of inflection according to GUYE and DROUGININE's determinations. Vapour pressure curves of simple substances have, as far as is known, without exception P-T-lines which are all convex seen from the temperature axis. For a dissociating substance, however, as nitrogen-tetroxide, whose internal vapour equilibrium between the molecules N_2O_4 and NO_2 is accurately known by numerous investigations, the existence of such a point of inflection does not seem impossible however. If we namely consider the system NO_2—N_2O_4 as a pseudo-binary system, we shall expect that the vapour pressure curve of the NO_2, which would indicate the coexistence between liquid and vapour, which both consist exclusively of molecules NO_2 lies at higher pressure, resp. lower temperatures than the tension curve of the N_2O_4, as is indicated in the figure 1. The vapour curve, which indicates the stable coexistence of the equilibrium liquid and vapour, will lie close to the N_2O_4 curve at low temperatures, at higher temperatures, however, the dissociation taking place endothermically, it will approach the NO_2 curve, and in this way it may give rise to a point of inflection G. GUYE and DROUGININE's line actually shows such a point of inflection between 0° and the boiling-point. Also for this reason it seemed important to us to repeat the determinations of the vapour

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[1]) Journ. de Ch. ph. 8. 473 (1910).

tension with great care, because with accurate knowledge of these values it is also possible to calculate the change of the degree of

FIG.1
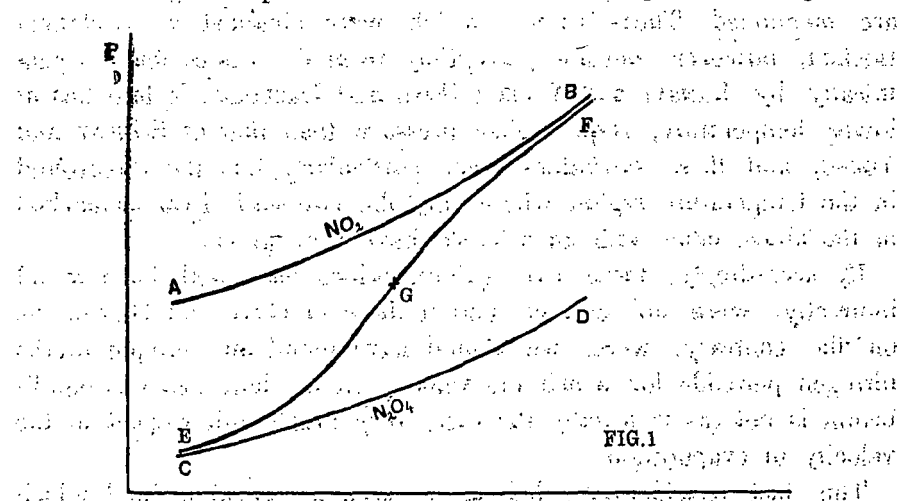
dissociation of the vapour along the line of coexistence by the aid of the data concerning the internal vapour equilibrium, as will appear further on.

2. The reason that our knowledge of the vapour tensions of nitrogen tetroxide is still small is to be found in the first place in the violent action which takes place between N_2O_4 and mercury, even when both have been dried by phosphorpentoxide. Hence the use of a mercury manometer in which the mercury of the manometer comes into contact with the N_2O_4, is excluded. GUYE and DROUGININE have evaded this difficulty by applying an air cushion, between the mercury manometer and the vessel with nitrogen tetroxide, so that the pressure of the nitrogen tetroxide was transferred by the air to the manometer. This method is, however, certainly attended with drawbacks. Even apart from the solution of air in the nitrogen tetroxide, an eventual mixture of air with the gaseous tetroxide produces already an increase of pressure. The determinations can be correct only when the vapour in the immediate neighbourhood of the liquid (resp. solid substance) is pure tetroxide, i.e., when the air has not penetrated so far.

For the above reason we have rejected the use of a mercury manometer. As we mentioned above, RAMSAY and YOUNG carried out their statical determinations by making use of the compressibility of a thin-walled glass reservoir. When in May of this year we were endeavouring to find a similar method of measuring the pressure, which rests on the deformation of a thin glass wall, a paper appeared

by JACKSON [1]), in which a glass manometer was described which had enabled him to determine pressures below one atmosphere accurately to tenths of millimeters of mercury. This glass spring, founded on the principle of the Bourdon metal barometer, which different from the before proposed models can be made easily and rapidly after some practice, yields a very efficient apparatus for measurements of vapour tensions of substances which attack mercury, like nitrogen tetroxide. We have varied the shape, sensitiveness and size of the glass manometer in numerous ways, and have at last succeeded in modifying the method in such a way that it is possible to carry out determinations of the vapour tension also at higher pressure. In this communication we will discuss the determinations made up to three atmospheres; the description of the experiments at higher pressure, which have already been carried out to about 60 atmospheres, and which if possible will be continued to the critical pressure, will be postponed with the determination (by another method) of the critical temperature (158°,2) to a following communication.

3. Glass manometer for pressures below three atmospheres.

The shape of the glass manometer which was used by us, has been represented in fig. 2; it is the same as that of fig. 2 of the cited paper by JACKSON. A glass tube of about 5 mm. external section is drawn out on one side; near the drawn end the tube is blown up and drawn out to the shape of an ellipsoid, which is then reduced to the shape of fig. 2 by one-sided heating. If now an increase of
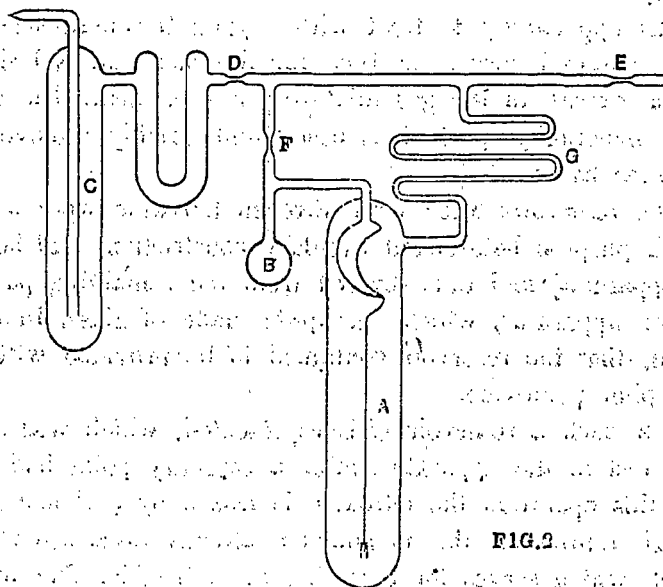

FIG.2

[1]) Journ. Chem. Soc. 99 1066 (1911).

pressure of some millimeters of mercury caused a definite deviation of the needle-shaped prolongation, the glass spring was fused into a wide vessel A, as will be clear from fig. 2 without further description. On the wide tube A two marks have been made in such a way that in case of equal internal and external pressure the end of the needle is exactly between these two marks; we may also make a mark on one side, and a scale on the other side to be able easily to determine eventual deviations from the zero position after the scale has been gauged. As for our purpose an accuracy of about 1 mm. of mercury sufficed, we have not made any attempts as yet to make the manometer more sensitive. In our opinion it is, however, certainly possible (among others with improved arrangement for reading — see Jackson) to raise the accuracy to tenths of millimeters of mercury.

4. *The preparation of nitrogen tetroxide and the filling of the apparatus.*

The substance was prepared according to the method described by Guye and Drouginine by bringing NO, generated from a solution of natrium nitrite by means of moderately diluted sulphuric acid and dried by sulphuric acid and phosphorpentoxide, into contact with oxygen dried in the same way; then the N_2O_4 vapours are condensed, after a repeated contact with phosphorpentoxide, in a tube placed in carbonic acid and alcohol. Generally two such tubes were used in the preparation; an inner tube fused into the two reservoirs then afforded an opportunity to treat with oxygen the obtained substance, which is coloured green or blue for the case that NO should be present in excess in the gas mixture for a moment. The green or blue hue eventually present is easily and quickly removed, when the substance has melted.

Then the reservoirs filled with nitrogen tetroxide were melted off (for which purpose beforehand capillary constrictions had been made in the apparatus) and thus severed from the remaining part of the preparative apparatus, which was quite made of glass. In this care was taken, that the reservoir continued to be provided with a tube with phosphor pentoxide.

In fig. 2 such a reservoir C is represented, which was sealed at D to the rest of the apparatus, after a capillary point had been cut open; in this operation the tetroxide is frozen by carbonic acid and alcohol. A represents the manometer already described in § 3, B the vessel which serves for receiving the tetroxide. The whole apparatus was then connected with a Gaede-pump at E, and evacuated

while the reservoir remained, cooled to —80°. After the capillary constriction at E had been fused to, part of the nitrogen tetroxide was distilled over from C to B, and after the two vessels C and B had been cooled again down to —80° the connection at D was melted off.

Now we had still to break the capillary constriction at E in a rubber tube connected with the GAEDE-pump and exhausted, to melt off the constriction at F, which was made possible by the glass spring G, and to admit with slow heating of B continually so much air through E that the pointer does not move too far from the marks to prevent breaking of the apparatus.

5. Pressure measurement.

For temperatures below the temperature of the room the pressure was determined by surrounding B with a large vacuum vessel filled with alcohol, which was brought to and kept at the required temperature by the insertion of small pieces of solid carbonic acid. A stirrer ensured uniformity of temperature throughout the vacuum vessel. The temperatures were read from an ANSCHUTZ-thermometer, which was controlled by the aid of thawing ice and mercury. The pressure was determined by the aid of a mercury manometer connected with E (fig. 2) by rubber.

For determinations at temperatures above the temperature of the room the whole apparatus was immersed in a large waterbath up to F, and the pressure, obtained by pumping air by means of a cycle pump into the righthand part of the apparatus, was read from a mercury manometer $2^1/_2$ meters long, when adjustment of the pointer between the two marks has been obtained.

It may finally be mentioned that as a control experiment a not filled apparatus, in which F and G were connected by means of rubber, was brought at different pressures and temperatures, and it was ascertained that no appreciable change of the position of the pointer on the scale could be perceived, so that the zero position appeared to be independent of the temperature and pressure.

6. Results.

' The obtained results have been collected in the following table; the pressures are given in millimeters of mercury of 0°, and if necessary corrected to 45° N.Lat.

It is clear from the above table and the corresponding graphical representation (Fig. 3), that the P-T line of the nitrogen tetroxyde presents a perfectly normal shape; there is no question of the

TABLE II.

Equilibrium solid-gas		Equilibrium liquid-gas			
T	P (mm. mercury)	T	P (mm. mercury)	T	P (mm. mercury)
— 36	18	— 23	70	16.5	608
— 28	34	— 20	85	19.2	690
— 23	53	— 18	96	21.45	770
— 20	70	— 15	115	24.3	873
— 14	114	— 13	128	27.4	1007
— 10.8	146	— 10.8	146	29.55	1108
		— 6.9	180	32.55	1263
		— 5.3	198	35.65	1447
		— 2.6	227	39.0	1668
		— 0.6	256	41.15	1825
		+ 0.8	276	43.2	1982
		4.1	328	45.65	2189
		7.7	393	47.2	2329
		11.0	463	48.7	2478
		12.4	497		
		15.0	565		

appearance of a point of inflection in the investigated range of temperature. If we compare these values found statically with values determined by the two different methods by RAMSAY and YOUNG, which is possible for pressures below one atmosphere, the two series of observations appear to be almost identical. Nor do the two statical values determined indirectly, which have been indicated by an asterisk, in Table I, deviate appreciably from our observations. Accordingly our observations present the same deviations from GUYE and DROUGININE's observations as were mentioned in § 1 concerning RAMSAY and YOUNG's series of observations. Moreover on comparison of the two tables it, will be clear that our determinations of the equilibrium, of undercooled liquid-vapour agree with the observations of RAMSAY and YOUNG at the same temperatures. Prof. RAMSAY was so kind as to inform us in answer to a question concerning this that these obser-
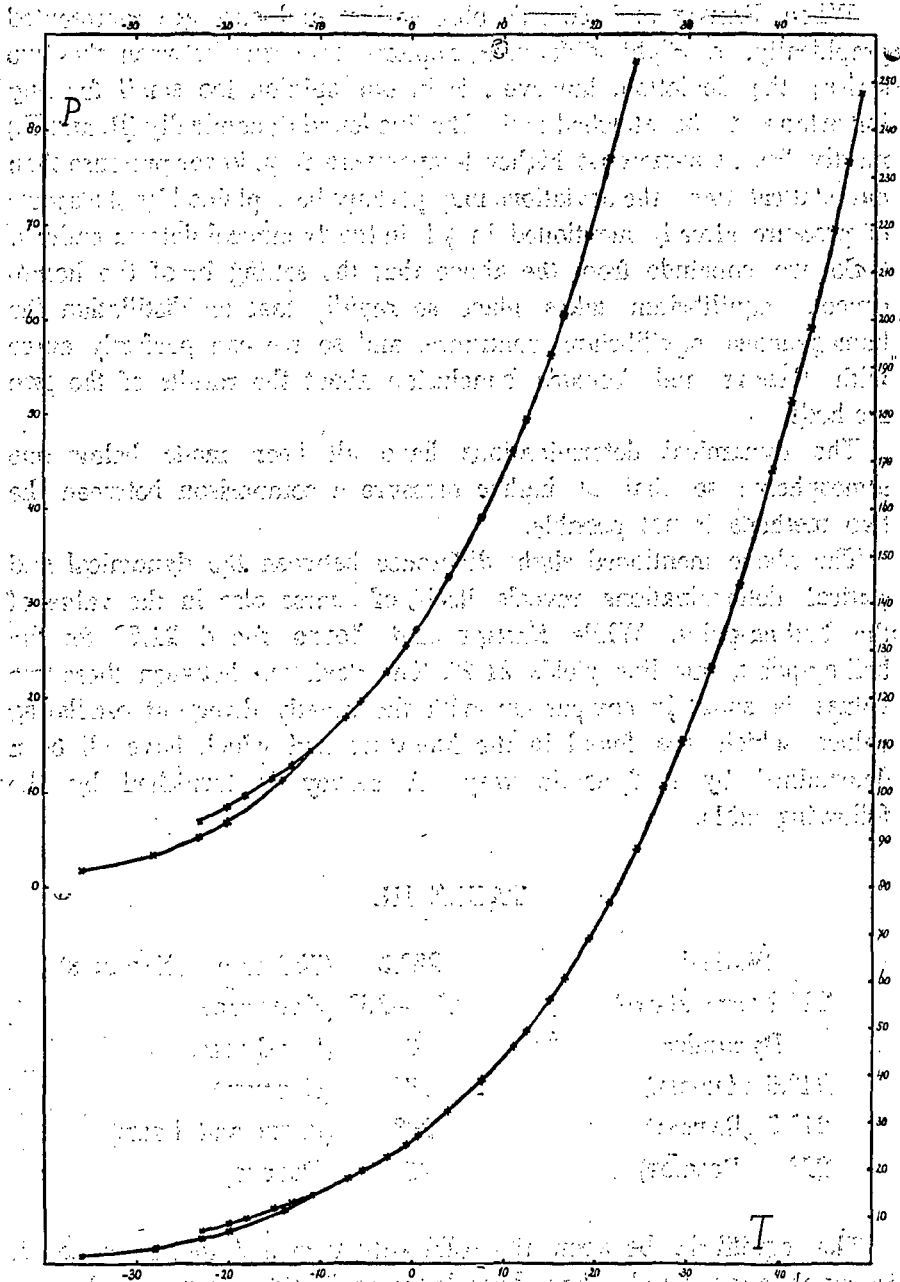
Fig. 3.

vations had really been made with undercooled liquid, not with solid substance [1]).

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[1] It has been stated by GUYE and DROUGININE (loc. cit. 498), that RAMSAY and YOUNG in agreement with them have found no break between the lines of the liquid-gas, resp. solid-gas equilibrium. This conclusion is erroneous on account of

When RAMSAY and YOUNG's observations and ours are represented graphically, a slight difference appears to occur between the two 'series; the deviation, however, is in our opinion too small for any importance to be attached to it. The line found dynamically (R. and Y.) mostly lies at somewhat higher temperature resp. lower pressure than our statical line; the deviations may perhaps be explained by the excess of pressure already mentioned in § 1 in the dynamical determinations.

So we conclude from the above that the setting in of the homogeneous equilibrium takes place so rapidly that on distillation the homogeneous equilibrium continues, and so we can perfectly agree with RAMSAY and YOUNG's conclusion about the results of the two methods,

The dynamical determinations have all been made below one atmosphere; so that at higher pressure a comparison between the two methods is not possible.

The above mentioned slight difference between the dynamical and statical determinations reveals itself of course also in the value of the boiling-point. While RAMSAY and YOUNG found 21.7° for the boiling-point, our line yields 21.2°. The deviation between these two values is small in comparison with the greatly divergent oscillating values which are found in the literature and which have all been determined by a dynamic way. A survey is furnished by the following table.

TABLE III.

Statical	22°.5	(750 mm.) (NADEJDIN)
21°.2 (see above)	25'—26°	(HASENBACH)
Dynamical	26°	(GAY-LUSSAC)
21°.6 (THORPE)	26°	(GEUTHER)
21°.7 (RAMSAY)	26°	(BRUNI and BERTI)
22° (PELIGOT)	28°	(DULONG)

The equilibria between the solid substance and the gasphase set in much more slowly than those between liquid and gas. To be able to indicate the point of intersection of the solid-gas line with the vapour pressure line in fig. 3, we have determined the melting-point under the saturation pressure by slow heating starting from the

the reason given in the text that R. and Y. have only examined equilibria between liquid and gas, resp. undercooled liquid-gas. In R. and Y.'s observations cited in the paper by G and D. some misprints seem to occur,

equilibrium solid-gas. The appearance of the first slight quantity of liquid took place at — 10°.8. The melting proceeding very slowly, we have kept the mass for a long time between —11° and —10°. At last we could observe that also the last quantity of solid substance disappeared at —10°.8. So no appreciable melting range appeared during the melting. A comparison between the melting point found by us under the saturation pressure and the melting points given in the literature is found in the subjoined table.

TABLE IV.

— 9° (Péligot)	—10°.95 (Bruni and Berti)
— 9°.6 (Guye and Drouginine)	—11°.5 to —12° (Müller)
—10°.14 (Ramsay)	—13°.5 (Frietsche)
—10°.8 (see above)	

From the above survey it appears that our value for the melting-point agrees with that of Bruni and Berti, and that it lies lower than the two melting-points of Ramsay and Guye, which have also been found in recent times. Though as a rule decidedly the more importance is to be attached to the melting-points the higher they lie, at least for so far as the formation of mixed crystals is excluded, yet the value found by us does not seem less probable to us than the two last mentioned for the following reasons. Guye and Drouginine's determination was carried out with a pentane thermometer, for which a correction of about two degrees was necessary for the emerging part, which can account at least for part of the found difference. Ramsay determined the melting-point with a view to an investigation of the constant of the lowering of the melting-point which is, of course, independent of the absolute value of the melting-point; also in the apparatus used for this it will, probably, have been inevitable, that a part of the thermometer emerged from the apparatus.

Moreover we have prepared a quantity of nitrogen peroxide in the way indicated by Ramsay by addition of N_2O_3, prepared from strong nitric acid and arsenictrioxide, to strong nitric acid and phosphorpentoxide. The decoloration of the N_2O_3 soon appears when a sufficient quantity of the N_2O_5 formed from the nitric acid and phosphorpentoxide is present. The obtained liquid was poured off from the phosphoric acid formed and the rest of the P_2O_5, and five fractions from this were received in tubes provided with capillaries by distillation through a phosphor pentoxide tube. With none of these fractions a final melting-point was found that lay higher than

— 10.9°, even when the observable melting range only amounted to some tenths of degrees. In these determinations, which were made in a bath of carbonic acid and alcohol, which could be kept constant for a long time by insertion of bits of carbonic acid, the tubes were heated very slowly, while they were continually shaken ; the temperature was read on an Anschützthermometer, the mercury thread of which was quite immersed in the bath.

If the heating took place at the rate of about 0.1° per minute, a melting point which was appreciably too high was found in spite of the shaking of the tubes. Whether the melting-point of the N_2O_4 can depend on the circumstances to which it was subjected previously, and the deviations can possibly be explained by the formation of mixed crystals of N_2O_4 and NO_2, will have to be decided by a further investigation by Prof. SMITS and one of us.

§ 7. The nitrogen tetroxide may justly be called the classical example of dissociation. Numerous scientists have been engaged with the experimental determination and specially with the theoretical considerations and calculations. As basis of these calculations serve the determinations of the vapour density of dissociating N_2O_4 under varying temperature and pressure. From these determinations among which those of the two brothers NATANSON[1]) are the most accurate, different theorists have derived several expressions for the constant of dissociation as function of the temperature. The great variety in the proposed formulae is owing for the greater part to the different values ascribed to the specific heats of the NO_2 and N_2O_4. As these are not sufficiently known in their dependence on the temperature, it is only possible to determine this relation roughly.

Among the calculations carried out with the greatest accuracy, those by SCHREBER[2]) deserve a foremost place.

With the aid of his recalculated expression :

$$log \frac{4 \; x^2}{1-x^2} \; \frac{P}{T} = 9.13242 - \frac{2866.2}{T},$$

which represents the observed densities with sufficient accuracy the degree of dissociation can, accordingly, be calculated for given temperature and pressure.

We have carried out these calculations for the values of the pressure and the temperature along the P-T line to get an impression of the change of the degree of splitting up of the N_2O_4 along the

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[1]) Wied. Ann. **24** 454 (1885); **27** 606 (1886).

[2]) Z. ph. Ch. **24** 651 (1897).

vapour pressure curve. Beforehand little is to be said about this course; an increase of temperature at constant pressure will promote the splitting up, because the dissociation takes place endothermically, increase of pressure on the other hand will oppose it. Now increased temperature always accompanies increased pressure along the P-T line, and it remains the question which influence is the greater one. This consideration had already led us, in connection with the reasoning of § 1, to the possibility of a point of inflection in the P-T line. The absence of a point of inflection in the P-T line (according to § 6) in the temperature region examined by us here corresponds to a gradual change of the degree of dissociation as function of T along the P-T line; it appears from the subjoined table that the degree of dissociation increases with the temperature, that in other words the ascending temperature exerts a greater influence on the splitting than the increasing pressure on the formation of N_2O_4-molecules.

TABLE V.

T	$100\ x$	T	$100\ x$
—20	8	20	15
—10	9	30	18
0	11	40	20
10	13	50	23

It will perhaps be superfluous to emphasise particularly that these values of the degree of dissociation expressed in percentages in the above table, are only intended as a rough calculation, because SCHREBER's formula is only an approximate formula, and these values have, moreover, been found by extrapolation to the region where the gas phase in equilibrium reaches its point of condensation; for a survey of the course of the degree of dissociation and the last ·mentioned conclusion, however, the above table is perfectly sufficient in our opinion.

Anorg. Chem. Laboratory of the University of Amsterdam.

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