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Chemistry. — “On the vapour pressure lines of the system phosphorus.” I. By Prof. A. SMIT^s, S. C. BOKHORST, and J. W. TERWEN. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of March 28, 1913).

1. On a former occasion ¹⁾ the result of a preliminary investigation about the vapour pressure lines of liquid white and liquid red phosphorus was communicated. It appeared already then that the vapour pressure lines of these two colourless liquid phases of the system phosphorus cannot be considered as two pieces of the same vapour pressure line.

The question under discussion being of the utmost importance, which ought to be decided with perfect certainty, it was resolved to determine the vapour pressure lines of liquid white and liquid red phosphorus as accurately and as far as possible.

2. *Determination of the vapour pressure line of liquid red phosphorus.*

We again made use of JACKSON'S glass spring manometer (see fig. 1 *ab*), which was now made of infusible glass, was filled with pure red phosphorus, and then exhausted and sealed off. This glass spring served as phosphorus reservoir and at the same time as indicator of the pressure.

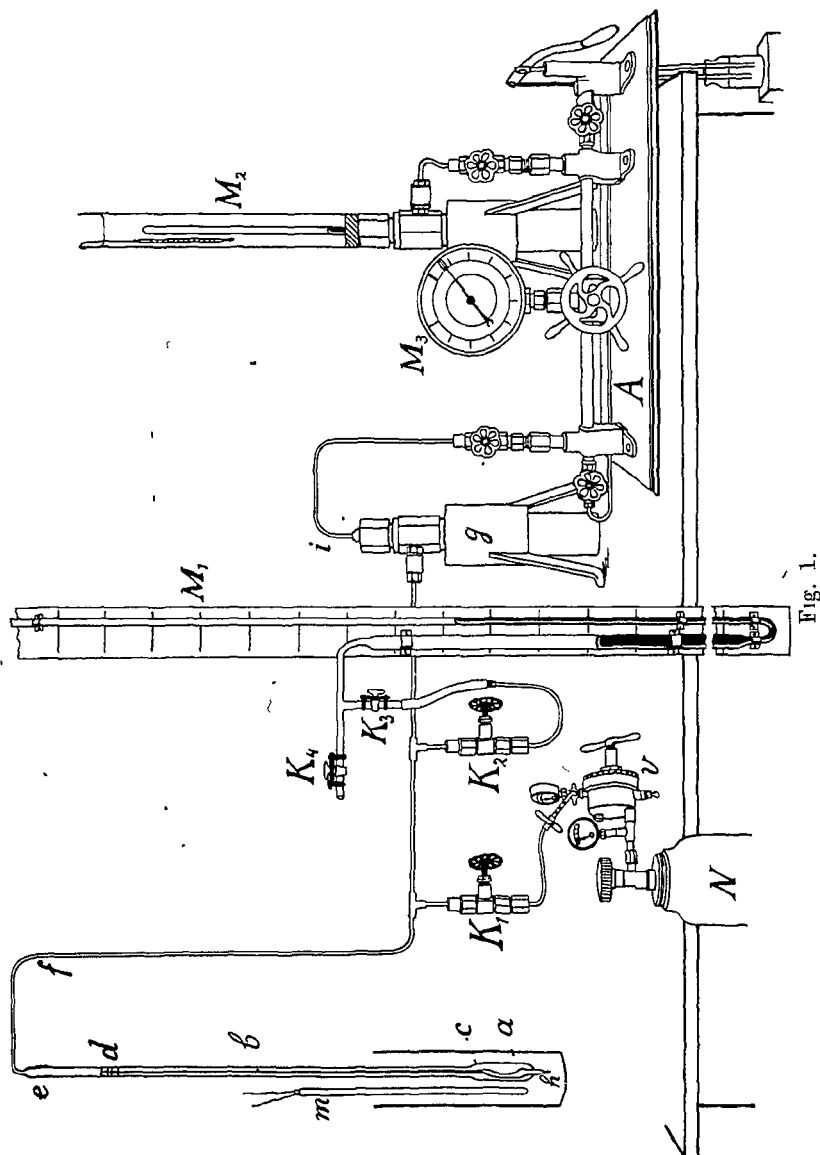
'Round the glass spring a wider vessel *c* had, namely, been sealed on beforehand, which ended into a somewhat narrower tube, which was electrolytically coated with copper at *e*, so that it could be soldered to the copper mounting *e*.

This copper mounting consisted of a copper coupling piece, in which a copper plate was used as packing. The said mounting was in connection with the cocks K_1 , K_2 by means of copper tubes, and the pressure cylindre *g*, which was filled with glycerin, and was connected with a SCHÄFFER and BUDENBERG'S hydrostatic press *A* with closed air manometer M_2 , and metal manometer M_1 .

The cock K_1 could effect the communication between the space round the glass spring and the carbonic acid cylindre *N*, and the cock K_2 could bring the same space into communication with the open manometer M_1 . A *T*-piece with the cocks K_3 and K_4 was sealed to this open manometer, K_4 being connected with the GAEDÉ pump. Before the beginning of every experiment the space round the glass spring was exhausted through this cock, to have an opportunity to indicate the zero-position of the needle of the glass spring on the tube *d*. This was effected by sticking two strips of paper

¹⁾ These Proc. XV, p. 885.

with marks put on them on the front and the back of the tube *d*, but above each other, in such a way that the two marks are in the same plane with the needle. When a vapour pressure determination was made, a copper bath with a molten mixture of KNO_3 and $NaNO_2$ was placed round the phosphorus manometer, in which a stirrer was continually moved up and down.¹⁾



¹⁾ In the preliminary experiments an air bath was used, with which no accurate determinations could be made, however, on account of the unequal temperature.

Then a gauged thermo-element and a gauged very sensitive resistance thermometer were placed in the bath for the temperature measurement, so that the temperature could be measured in two different ways. The bath was surrounded by a wider asbestos cylinder, burners placed under it ensuring a uniform heating.

In the determination of the vapour pressure line of the liquid red phosphorus the bath was slowly raised to a temperature above the melting point of this modification.

In order to bring the needle of the glass spring manometer to its zero position, the pressure in the space round this manometer had to be continually increased. At first this was effected by slowly admitting air through K_4 , K_2 and K_3 being open, but afterwards this was obtained by filling the tube between the valve V and the cock K_1 with CO_2 of higher pressure, after K_4 had been closed, and then carefully opening the cock K_1 . As the open manometer could indicate at most an excess of pressure of ± 4 atmospheres, K_2 was closed when this pressure had been reached, so that at higher pressure only the closed air manometer M_2 was used. In its turn the airmanometer was closed at pressures of about 10 atmospheres, and the metal manometer M_3 was read. It had appeared in preliminary experiments that the three different manometers corresponded with each other very satisfactorily.

When the red phosphorus was melted, the temperature was kept constant for some time, the needle was brought exactly to its zero position, and the pressure was read on the air manometer. Then the temperature was slightly raised or lowered; then again put at the same point, and the preceding operation was repeated to get an idea of the accuracy of the method. The result was that the error at these high temperatures and pressures amounted to less than 0,1 atm.

In this way we could determine the vapour pressure line of the molten red phosphorus up to a temperature of 634° , and a pressure of 58.6 atm., which may, indeed, be called a surprising result, for that a glass tube of a diameter of 2 cm. and a thickness of wall of 2 mm. can resist a pressure of 58 atmospheres at a temperature of 634° , was not expected by us, and in these experiments we were fully prepared for a violent explosion, which, however, fortunately did not take place. That the glass had not even been deformed was proved by this that when the experiment was over, the zero position appeared to have hardly changed.

We have been able to continue these vapour tension determinations of the liquid red phosphorus up to $\pm 85^\circ$ below the triple

point, which lies at **589.5** and **43.1** atm. The supercooled phosphorus then indeed was converted to the solid red phosphorus, but we succeeded in making the experiment in such a way that notwithstanding, the vapour space remained saturate with vapour of the liquid phase during the experiment. The method followed was this,

TABLE I.

$$C = 9.609$$

$$\left(\frac{Q}{R}\right)_{\text{meas.}} = 5031.4$$

Number of the manom	p atm.	t	T	$T \ln p$	$\frac{Q}{R}$	$\Delta \left(\frac{Q}{R}\right)$	calc. p atm.
30	23.2	504	777	2443.0	5023.2	- 8.2	23.0
28	24.3	512	785	2504.5	5038.6	+ 7.2	24.5
27	31.9	545.5	818.5	2834.1	5030.9	- 0.5	31.9
30	32.4	548	821	2855.5	5033.5	+ 2.1	32.5
28	33.0	550	823	2877.6	5030.6	- 0.8	33.0
27	33.6	553	826	2902.9	5034.2	+ 2.8	33.7
28	34.5	555.5	828.5	2934.0	5027.0	- 4.4	34.4
28	35.4	559	832	2967.4	5027.3	- 4.3	35.3
30	35.5	560	833	2973.3	5030.9	- 0.5	35.5
28	35.9	562	835	2989.9	5033.7	+ 2.3	36.0
27	37.6	569	842	3054.0	5036.8	+ 5.4	37.8
28	38.8	574	847	3098.6	5040.2	+ 8.8	39.2
28	40.3	578	851	3145.6	5031.7	+ 0.3	40.3
30	41.1	581	854	3173.4	5032.8	+ 1.4	41.1
28	44.2	593	866	3281.1	5040.4	+ 9.0	44.7
30	47.0	602	875	3368.8	5039.1	+ 7.7	47.4
28	48.6	606.5	879.5	3415.6	5035.6	+ 4.2	48.8
28	49.0	608	881	3428.7	5036.9	+ 5.5	49.3
30	53.9	621	894	3564.5	5026.0	- 5.4	53.6
30	55.6	625.5	898.5	3610.3	5023.5	- 7.9	55.2
30	56.5	627.5	900.5	3632.7	5020.2	- 11.2	55.9
30	57.7	632	905	3669.9	5026.3	- 5.1	57.4
30	58.6	634	907	3692.2	5023.3	- 8.1	58.1

that for every determination the temperature was raised above the triple point, and then was lowered as quickly as possible to a definite temperature, which was then kept constant for some time, till the vapour tension had become constant. Thus a constant vapour tension could be observed even at the lowest point $\pm 504^\circ$ during 5 minutes. On continuation of the experiment pretty suddenly a decrease set in, which pointed to this that at that moment the liquid phase had disappeared, and had been entirely converted to the solid red phosphorus.

That these vapour tensions under the triple point really refer to the saturate vapour could be proved by this that when after the determination of the vapour tension at 550° , the temperature was not first raised above the triple point temperature, but at once to 562° , a vapour tension was observed at this latter temperature, which fitted exactly in the found vapour pressure line. After this determination at 562° we heated at once to 574° , and also the vapour tension observed at this temperature lay on the line already found.

It follows, therefore, from this that the vapour at 562° and 574° was still saturated with the vapour of the liquid red phosphorus, so that it is perfectly sure that this must also have been the case just before and at the lower temperature 550° .

The results of the vapour tension determinations of the liquid red phosphorus are given in the subjoined table. In the first column one finds the number of the manometer, and in the second column the temperature, the third giving the pressure in atmospheres.

In the PT representation Fig. 2 these results are graphically represented by the line cmd , from which follows that the different observations yield a very regular curve. Only the last point at 512° lies too low.

The point n is the point where the vapour pressure line of the solid red phosphorus mn (more about this later) intersects the vapour pressure line of the liquid red phosphorus, so the triple point of the red phosphorus.

When the saturation heat is no temperature function, the vapour pressure formula

$$\frac{d \ln p}{dT} = \frac{Q}{RT^2} \dots \dots \dots (1)$$

on integration yields the expression:

$$\ln p = -\frac{Q}{RT} + C \dots \dots \dots (2)$$

or

$$T_{\text{vap}} = -\frac{Q}{R} + CT \quad \dots \quad (3)$$

from which follows that T_{vap} , represented as function of T , will yield a straight line.

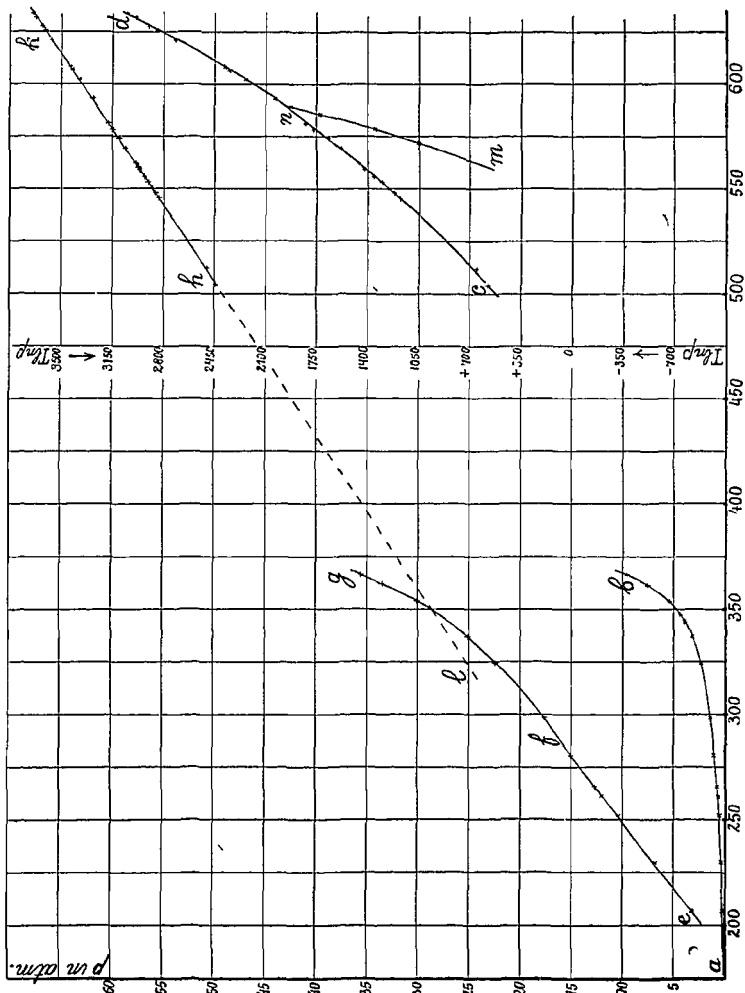


Fig. 2.

It is now interesting to examine what is found when T_{vap} is plotted against the temperature.

The points obtained in this way lay so nearly on a straight line that it was possible to unite nearly all the points on the same straight line, as the line hk shows; a proof therefore that the heat of evaporation in the examined temperature range is practically no temperature function.

This has the advantage that the constant C may be graphically

determined in a simple way. For this purpose the line is drawn so that as many points as possible lie on this line, and that the others, which deviate lie regularly on the left or the right of it. In this case the tangent of the angle α formed by this line and the temperature axis, will give the constant. This is immediately seen in the following way.

For two different points on this line we get namely.

$$T_1 \ln p_1 = -\frac{Q}{R} + CT_1 \dots \dots \dots (4)$$

and,

$$T_2 \ln p_2 = -\frac{Q}{R} + CT_2 \dots \dots \dots (5)$$

hence

$$C = \frac{T_2 \ln p_2 - T_1 \ln p_1}{T_2 - T_1} = \text{tga}$$

or

$$C = \frac{2,3025(T_2 \log p_2 - T_1 \log p_1)}{T_2 - T_1} \dots \dots \dots (6)$$

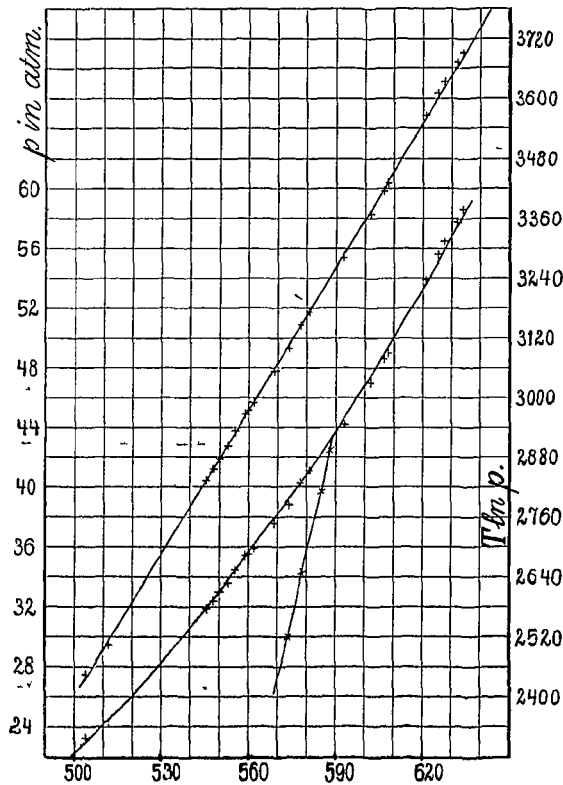


Fig. 3.

In this way the constant C is now determined. If we calculate the quantity $\frac{Q}{R}$ with this value of C from the different observations, we obtain the values given in the 6th column of table I. From this follows as mean value for Q 9,96 K. Cal.

In connection with the deviations from the mean value 5031,4 which the different values of $\frac{Q}{R}$ present (see column 7) it is to be expected that the above value for the heat of evaporation is pretty accurate. Finally the last column gives the calculated pressure when the values for C and $\frac{Q}{R}$ heading the table are used.

To give a better graphical survey of what has been found, the discussed lines are once more separately represented in Fig. 3.

The uppermost line again gives $T \ln p$ as function of T .

§ 3. *Determination of the vapour pressure line of liquid white phosphorus.*

If the difficulties in the preceding experiments were great, because many of the glass spring manometers already burst before the triple point of the red phosphorus had been reached, the difficulties in the following experiments were so great as to seem almost insuperable.

It is self-evident that the determination of the vapour tension of the white phosphorus at temperatures at which the conversion to solid red phosphorus still proceeds slowly, is attended with few difficulties.

Up to 312° this line had already been determined by JOLIBOIS¹⁾ with pretty great accuracy.

For the purpose we had in view, it was, however, necessary to carry these experiments up to as high temperatures as possible. In this we meet, however, with different difficulties. In the first place the molten white phosphorus begins rapidly to convert into the solid red modification from $\pm 280^\circ$ on rise of temperature, in consequence of which the liquid phase has disappeared in a comparatively short time, and the prevailing vapour tension, therefore, no longer corresponds with the vapour tension of the liquid phase at that temperature.

Hence to find points of the vapour pressure line of the liquid white phosphorus at higher temperatures, one has to heat the glass spring manometer as quickly as possible to a definite temperature, and then to keep the temperature constant for some time.

¹⁾ Thèses, Paris 1910.

By this mode of procedure we have actually succeeded in determining some points with the glass spring manometer at higher temperatures, but in the majority of the experiments the glass spring broke before the required temperature had been reached. This circumstance was owing to this that it often happens in case of rapid heating that part of the liquid white phosphorus is enclosed by a wall of red phosphorus. If now the tension in the space outside has become less than the tension of the enclosed liquid phosphorus, the wall of red phosphorus breaks at a certain difference of pressure, and the consequent sudden increase of pressure bursts the glass spring manometer.

As all attempts to prevent this enclosure of the liquid phosphorus failed, and with a few exceptions the experiments miscarried through this circumstance, we have finally tried to reach our end by another way, in which we have really succeeded. Instead of the statical method we have namely introduced the dynamic method, in the form given to it by SMITH ¹). The difficulty was, however, to find a suitable liquid, i. e. a liquid with a comparatively low melting-point, high boiling-point ($\pm 360^\circ$) and besides indifferent with respect to the phosphorus. We have succeeded in finding such a liquid, and

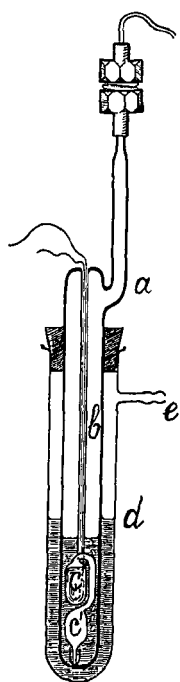


Fig. 4.
and to this we owe the final success of our endeavours in this direction. This liquid is melted stearin candle material or a mixture of stearic acid and palmitic acid. Instead of the glass spring manometer the apparatus represented in Fig. 4 was now attached to the apparatus Fig. 1. The former consists of a tube *a*, in which a vessel *c* is placed with a tube *c'*, which is bent downward and part of which is considerably widened, terminating in a capillary placed in a small wider tube. This apparatus, in which the vessel *c* contains white phosphorus, is quite immersed in the mixture of stearic acid and palmitic acid; and in the same liquid column, at the level of *c* is the extremity of the glass tube *b* fused to at the bottom, in which a thermo-element is placed. The tube *a*, which contains all this, is fastened airtight by means of a rubber stopper in the wider vessel *d*, also provided with the same fatty acid mixture, the side tube *e* of which serves to enable us to compress the air in *d* somewhat, and to raise the boiling point of the mixture, if necessary. By means

¹) Americ. Chem. Soc 32, 897 (1910).

of this arrangement it was now possible to determine the boiling-point of the liquid phosphorus under different pressures, and it is in this way that we have supplied the deficiencies which had continued to exist when the static method was applied. The phenomenon of inclosure of liquid phosphorus by solid red also often occurred by this way of procedure with the result that when the wall of the red phosphorus broke, a violent boiling of the liberated liquid took place, in which often part of the contents were flung outside from the vessel *c*.

However satisfactory this dynamic method was in the application, the velocity of conversion of the white phosphorus becomes so great above 360° that 366.4° is the highest temperature at which reliable measurements could still be made.

The result of the statical and the dynamical investigation is combined in the following table II, the results of JOLIBOIS' statical investigation being given in table III.

TABLE II

Method	Number of the man.	p atm.	t	T	$Tlnp$
dyn.	65	0.039	169.0	442.0	- 1433.9
"	65	0.070	181.3	454.3	- 1208.1
"	65	0.182	206.9	479.9	- 817.6
"	65	0.320	229.8	502.8	- 572.9
"	65	0.542	252.0	525.0	- 321.6
"	65	0.686	261.4	534.4	- 201.4
"	65	0.737	265.5	538.5	- 164.3
stat. and	dyn.	1.—	280.5	553.5	0.0
"	36	1.38	298.6	571.6	+ 184.9
"	35	2.36	324.5	597.5	+ 513.0
"	35	3.18	337.1	610.1	705.8
"	36	3.90	344.9	617.9	840.9
dyn.	54	3.94	343.9	616.9	845.8
"	59	4.38	347.5	620.5	916.5
"	60	5.39	353.9	626.9	1056.0
stat.	31	7.60	362.5	635.5	1291.8
dyn.	56	9.56	366.4	639.4	1443.5

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TABLE III.

p 'atm.	t	T	$T \ln p$
0.017	145	418	- 1703.1
0.064	173	446	- 1226.0
0.093	184	457	- 1085.4
0.124	192	465	- 970.7
0.157	200	473	- 875.7
0.178	205	478	- 825.0
0.253	219	492	- 676.2
0.366	235	508	- 510.6
0.418	239	512	- 446.6
0.464	244	517	- 397.0
0.499	247	520	- 361.4
0.543	250	523	- 319.4
0.591	254	527	- 277.2
0.633	257	530	- 242.2
0.675	259	532	- 209.1
0.705	262	535	- 187.0
0.797	268	541	- 122.7
0.850	273	546	- 88.7
0.925	275	548	- 42.7
0.990	279	552	- 5.5
1.034	281	554	+ 18.5
1.071	283	556	+ 38.1
1.122	285	558	+ 64.2
1.329	295	568	+ 161.5
1.437	299	572	+ 207.4
1.650	307	580	+ 290.4
1.817	312	585	+ 349.3

Graphically represented the line ab Fig. 2 is obtained. As the line ab shows, the higher temperatures are the most interesting, for it is from the vapour pressures found at those temperatures that it

appears with the greatest clearness that the vapour pressure line of liquid white phosphorus *cannot* be the prolongation of the vapour pressure line of liquid red phosphorus

This, however, follows still more clearly from the line *efg*, which gives *T_{lnp}* as function of *T*

In contrast with the line *hk* this line is *not* straight, but exhibits an ever increasing slope at higher temperatures. So the heat of evaporation is here undoubtedly a decided temperature function, which we shall discuss on a following occasion. The most convincing proof of the lack of correspondence of the vapour tension lines *ab* and *cd* is this that when the line *hk* is prolonged towards lower temperatures, it intersects the line *efg* at a rather large angle, from which it appears still more convincingly than from the lines *ab* and *cd*, that we have here certainly to do with two different curves in the same way as for the system *Cyanogen*.

To set forth still more clearly the regular course of the vapour pressure line *ab*, it has, just as the curve for *T_{lnp}*, been once more separately represented in Fig. 5. In this figure also the points

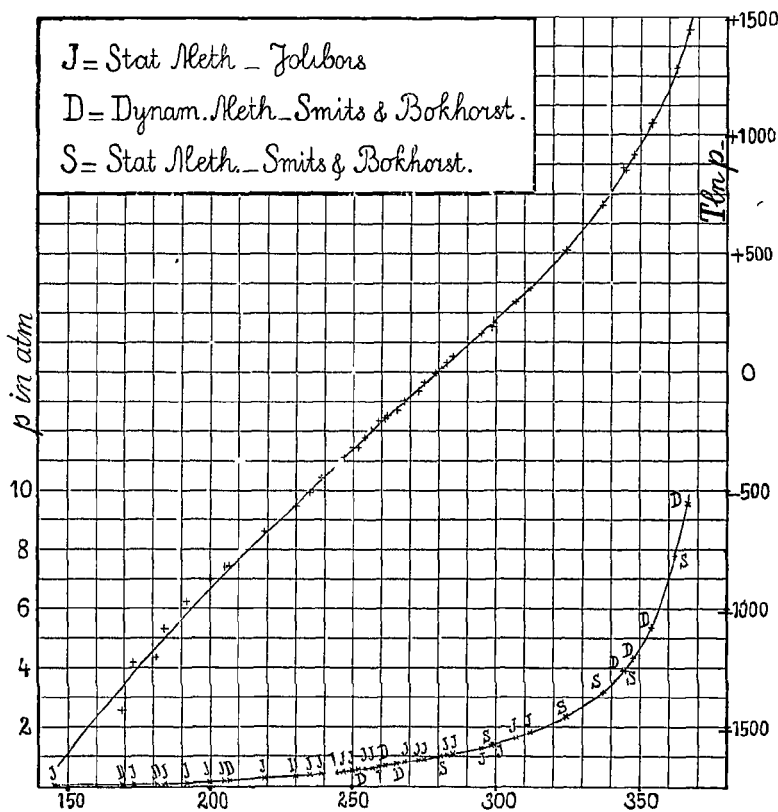


Fig. 5.

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determined by JOUBOIS are indicated, who, as also follows from the table, has only been able to continue his research up to 312° .

In a subsequent communication we shall give some theoretical considerations in connection with the results stated here, and also discuss the vapour pressure line of the solid modification, which we determined accurately already some time ago.

Anorg. Chem. Laboratory of the University.

Amsterdam, March 27, 1914.

Mathematics. — “*A bilinear congruence of rational twisted quartics.*”

By PROFESSOR JAN DE VRIES.

(Communicated in the meeting of March 28, 1914).

1. The base-curves of the pencils of cubic surfaces contained in a net $[\Phi^3]$ form a bilinear congruence. ¹⁾

If all the surfaces of the net have a twisted curve q^5 of genus *one* in common, and moreover pass through two fixed points H_1, H_2 , every two Φ^3 cut each other moreover along a rational curve q^4 , which rests on q^5 in 10 points. ²⁾

A third Φ^3 cuts q^4 in 12 points, of which 10 lie on q^5 ; the remaining 2 are H_1 and H_2 . Through an arbitrary point P passes *one* q^4 ; if P is chosen on a trisecant t of q^5 , then all Φ^3 passing through P contain the line t , and q^4 is replaced by the figure composed of t and a τ^3 , which cuts it, and meets q^5 in 7 points.

2. In order to determine the order of the ruled surface of the trisecants t , we observe that each point of q^5 bears two trisecants, so that q^5 is nodal curve of the ruled surface (t). We can now prove that a bisecant b , outside q^5 , cuts only *one* trisecant, from which it ensues that (t) must be of order five.

The bisecants b , which rest on the bisecant b_0 , form a ruled surface (b) of order 7, on which b_0 is a quadruple line. In a plane passing through b_0 lie three bisecants; as to each of those three lines the point of intersection of the other two may be associated, by which a correspondence (1,1) is brought about between the lines b and the points of q^5 , (b) is of genus *one*. A plane section of (b) has

¹⁾ See my communication in these *Proceedings*, volume XVI, p. 733. There I have considered the case that all Φ^3 have in common a twisted curve q^5 of genus *two*, so that a bilinear congruence of *elliptic* quartics is formed.

²⁾ See e.g. STURM, *Synthetische Untersuchungen über Flächen dritter Ordnung* (p p 215 and 233).