lution figures, and also resolutions of the abnormal sign, can appear, and that negative rotation might arise in consequence.

The thought suggests itself to try whether the observed rotation constants can be explained in this way. For this purpose it is necessary to represent these constants by a formula as required by theory, with one or more ultraviolet frequencies. It will have to appear at the same time that the index of refraction can be represented by a formula of the form required by theory, with the same frequencies, besides ultrared ones.

It will be communicated in a following paper what a treatment of the results of our observations in this sense will have yielded.

Chemistry. — *"On Tension Lines of the System Phosphorus."* IV. By Prof. A. SMITS and S. C. BOKHORST. (Communicated by Prof. J. D. VAN DER WAALS.)

(Communicated in the meeting of April 23, 1915.)

1. *New determinations of the vapour pressure of liquid white phosphorus.*

In the first communication under this title [1]) among others the vapour pressure line of the liquid white phosphorus was discussed. This line, which had been determined by us according to the statical and dynamical method up to 336°, had such a course, that it could not be considered as the metastable prolongation of the vapour pressure line of the liquid violet phosphorus.

Now it appeared that this result was to be ascribed to this that the vapour pressure above 325° increased with the temperature to an abnormal degree.

This circumstance added to the fact that the temperature was always increased as quickly as possible in the vapour tension determination to prevent all the white phosphorus from being converted before the determination could be made, led us to suppose that the results might be faulty at these high temperatures in consequence of spontaneous heating of the mass brought about by the conversion:

$$\text{white } P \rightarrow \text{violet } P + \alpha \text{ Cal.}$$

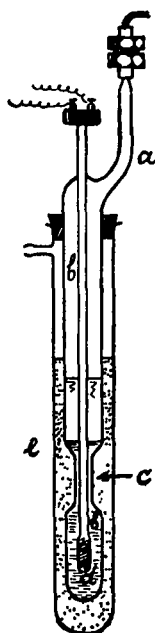
[1]) These Proc. Vol. XVI, p. 1174.

As this conversion is accompanied by a pretty great generation of heat (4.4 Cal. at the ordinary temp.), and the velocity of this reaction is already pretty great above 325°, it would be possible that the temperature of the phosphorus had been higher than that of the surrounding bath, whereas it had been assumed that inside and outside the apparatus there always prevailed the same temperature.

To avoid this possible error, not the temperature of the bath, but that of the phosphorus had to be measured.

For this purpose with application of the dynamic method according to Smith[1]) the tube of the thermo-element was fused into the vapour pressure apparatus, so that always the temperature of the phosphorus was determined.

Afterwards when it had appeared that through the contact with stearine the boiling point of the phosphorus was absolutely not influenced, the apparatus was used represented in fig. 1. Into the inner tube a which has a constriction at c a resistance thermometer has been fused, which reaches to the lowest widening. This inner tube is filled up to above the constriction with pure white phosphorus, which is then shut off by a layer of stearine. All this takes place in vacuum. In the outer jacket e also stearine is brought, which is heated under different pressures.

Just as for the other apparatus also now the temperature is determined at which the phosphorus under a definite pressure begins to boil. This method has this advantage that without any difficulty the experiment can be made with larger quantities, and the temperature can be indicated very quickly and very accurately.

By these two improved methods the following results were now found:

Fig. 1.

Temp.	Pressure in atm.
331 8°	2.47
332.9°	2.61
342.0	2.95
355.7	3.88

[1]) Americ. Chem. Soc. 32, 897 (1910).

2. *The vapour pressure formula for the liquid phosphorus.*

When we supplement our former measurements up to 300° by the above mentioned results, we get what follows:

P in atm.	$t.$	$T \ln p$	P in atm.	$- t$	$T \ln p$
0.04	169.0	—1423	0.69	261.4	— 198
0.07	181.3	—1208	0.74	265.5	— 162
0.09	185.5	—1104	1.00	280.5	— 0
0.18	206.9	— 823	1.38	298.6	+ 185
0.20	210.0	— 777	2.47	331.8	+ 547
0.32	229.8	— 573	2.61	332.9	+ 582
0.42	237.9	— 443	2.95	342.0	+ 665
0.54	252.0	— 323	3.88	355.7	+ 852

That the last four points fit in very well with the others, follows clearly from the following graphical representation (Fig. 2), in
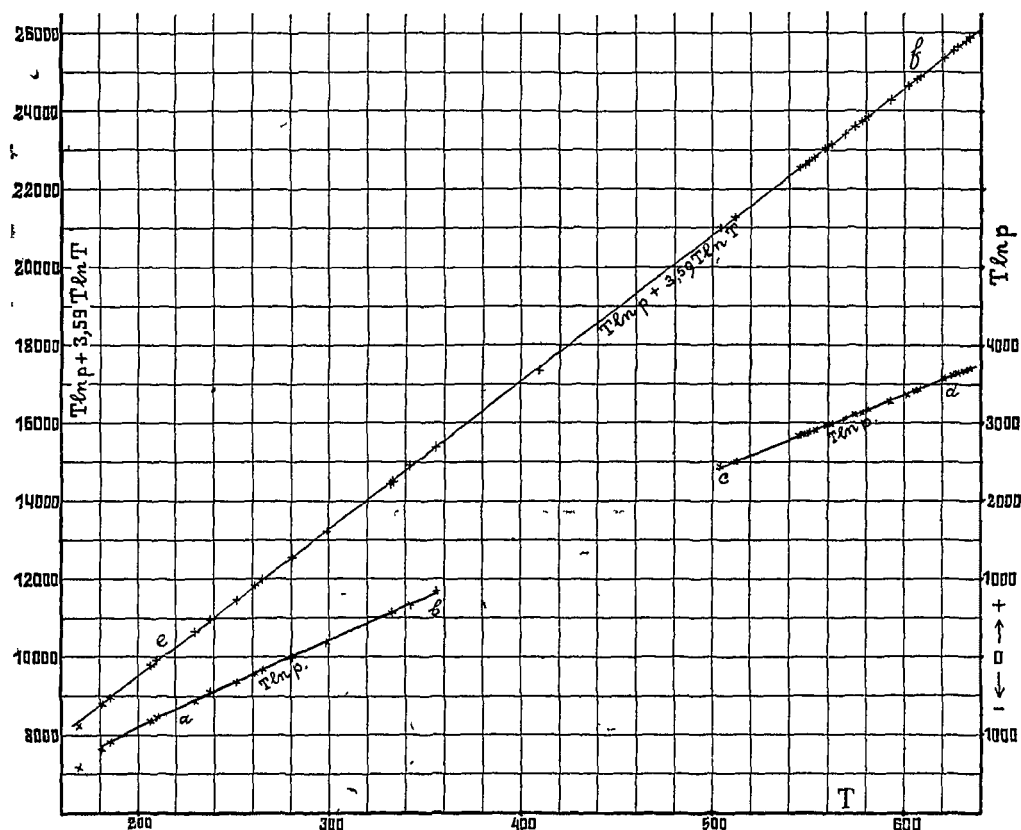

Fig. 2.

which the quantity $T \ln p$ is plotted as function of T (the line ab). We see from this that the different points yield an almost straight line, whose shape is exceedingly little concave with respect to the temperature axis. This had accordingly proved that the preceding determinations had been vitiated by the spontaneous heating of the white phosphorus in conversion.

If in the same diagram we now give $T \ln p$ as function of T also for the liquid violet phosphorus, we get the already discussed straight line cd.

The consideration of these two lines ab and cd brings us at once to the conviction that they belong together, i.e. that they are two parts of one and the same curve, the intermediate part of which cannot be realized here.

It follows then from this that the second part cd cannot be perfectly straight in reality, no more than the first part ab, and that there must be a rational formula to be found, which represents both portions with sufficient accuracy.

To find this formula the following course is taken.

The line ab which represents $T \ln p$ as function of T for the liquid white phosphorus, is only very slightly curved. If we now assume for a moment that this line is straight, then as was already shown before, the constant C can be found by the aid of two points, on the application of the relations:

$$T_1 \ln p_1 = -\frac{Q}{R} + C T_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and

$$T_2 \ln p_2 = -\frac{Q}{R} + C T_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If this value of C is substituted in one of the above equations, then follows from this the value for Q, which indicates the molecular heat of evaporation.

If this is done, we find $Q = 12.17$ kg. cal., 9.96 kg. cal. being found for the mol. heat of evaporation of the liquid violet phosphorus. The latter result was obtained in the same way as here the Q for the liquid white phosphorus was calculated viz. on the assumption that Q is no temperature function.

Now this is, evidently, indeed not the case, for $T \ln p$ plotted as function of T is no perfectly straight line.

We can now accept by approximation that 12.17 kg. cal. is the mean value of the heat of evaporation of the liquid white phosphorus in the temperature interval from 160° to 360°, and that this heat

of evaporation will therefore about agree with the mean temperature of 260°. Thus we can also consider the value of 9.96 kg. cal. as the mean heat of evaporation of the liquid violet phosphorus over the temperature range from 512° to 630 , so that this heat of evaporation will about hold for the mean temperature of 571°. Thus we arrive at the result that the heat of evaporation from 260° to 571° decreases by 2210 gr. cal., so that we have at a rough approximation

$$\frac{dQ}{dT} = -7,106 \qquad \ldots \ldots \ldots \quad (4)$$

If we now start from the equation:

$$\frac{d\ln p}{dT} = \frac{Q}{RT^2} \cdot \qquad \ldots \ldots \ldots \quad (5)$$

and write:

$$Q_T = Q_o + a\,T \qquad \ldots \ldots \ldots \quad (6)$$

we find by integration:

$$\ln p = -\frac{Q_o}{RT} + \frac{a}{R}\ln T + C \qquad \ldots \ldots \quad (7)$$

and as according to (6)

$$\frac{d\,Q_T}{d\,T} = a$$

we can substitute the value given by (4) for a. Then equation (7) becomes

$$\ln p = -\frac{Q_o}{RT} - 3.59\ln T + C \;^1) \qquad \ldots \ldots \quad (8)$$

To see whether this formula satisfied, the following graphical method was applied : Let us write equation (8) as follows :

$$T\ln p + 3.59\;T\ln T = -\frac{Q_o}{R} + C\,T \, . \qquad \ldots \ldots \quad (9)$$

we see at once that when this relation satisfies, $(T\ln p + 3,59\;T\ln T)$ plotted as function of T, will have to yield a straight line.

As appears from fig. 2, the thus obtained points lie really on a straight line ef, so that it has thus been proved that the relation (6) represents the change of the heat of evaporation with the temperature with sufficient accuracy.

In case of an exceptionally rapid heating, when the result was of course less accurate, a pressure of 7,36 atm. was observed at 409°,3, from which the value 1362 follows for $T\ln p$. In comparison with the

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1) We may just state here that instead of 3.59 we might as well have taken 3 or 4, for the course by which we have come to this value, is a rough approximation.

line discussed just now this value is slightly too low; this proves that the vapour was no longer perfectly saturate with respect to the white liquid phosphorus, which we think by no means astonishing.

By means of the linear relation (9) the constant C may now again be easily found in the following way from the value which the first member possesses at two different temperatures.

$$T_1 \, lnp_1 + 3.59 \, T_1 \, ln \, T_1 = - \frac{Q_0}{R} + C \, T_1 \ . \quad . \quad . \quad . \quad (10)$$

$$T_2 \, lnp_2 + 3.59 \, T_2 \, ln \, T_2 = - \frac{Q_0}{R} + C \, T_2. \quad . \quad . \quad . \quad (11)$$

from which follows that :

$$C = \frac{(T_2 lnp_1 + 3.59 T_2 ln T_2) - (T_1 lnp_2 + 3\,59 T_1 ln T_1)}{T_2 - T_1} = tg\alpha. \quad . \quad (12)$$

In this way we find $C = \mathbf{37.62}$.

If we substitute this value in (9), we get :

$$T \, ln \, p + 3.59 \, T \, ln \, T = - \frac{Q_0}{R} + 37.62 \, T. \quad . \quad . \quad . \quad (13)$$

3. *Calculation of Q_0 and of the vapour tension.*

By means of this relation we can now calculate the value of $\dfrac{Q_0}{R}$ from the different observations.

The result of this calculation is recorded in the following table. (see p. 112).

In the fifth column the found values for $\dfrac{Q_0}{R}$ are given, which give as mean the value 8257, from which follows that $Q_0 = 16{,}35$ kgs. cal.

The sixth column gives the discrepancies which the different results present from the mean, and it appears from this that they are comparatively small, and now exhibit the positive sign, now the negative sign.

If this value for $\dfrac{Q_0}{R}$ is substituted in equation (13), we get :

$$T \, ln \, p + 3.59 \, T \, ln \, T = 37.62 \, T - 8257 \quad . \quad . \quad . \quad (14)$$

by the aid of which we can now calculate the pressures for the different observation temperatures.

We find the result of this calculation in column 7.

These calculated pressures harmonize on the whole as well with the observed ones, as can be desired under the given circumstances. This is shown most convincingly by the last column, which gives the difference between the calculated and the observed pressure. It is evident that this difference should not be considered in itself, but

p in atm.	t	$T\ln p$	$T\ln p +$ 3.59 $T\ln T$	$\dfrac{Q_0}{R}$	$\Delta\,\dfrac{Q_0}{R}$	Calc. p in atm.	Δp
0.04	169.0	— 1423	8242	8386	+ 129	0.05	+ 0.01
0.07	181.3	— 1208	8771	8320	+ 63	0.08	+ 0.01
0.09	185.5	— 1104	8982	8267	+ 10	0.09	0.00
0.18	206.9	— 823	9814	8240	— 17	0.17	— 0.01
0.20	210.0	— 777	9939	8232	— 25	0.19	— 0.01
0.32	229.8	— 573	10655	8261	+ 4	0.32	0.00
0.42	237.9	— 443	10995	8225	— 32	0.40	— 0.02
0.54	252.0	— 323	11482	8268	+ 11	0.55	+ 0.01
0.69	261.4	— 198	11852	8252	— 5	0.68	— 0.01
0.74	265.5,	— 162	11995	8263	+ 6	0.75	+ 0.01
1	280.5	0	12554	8269	+ 12	1.02	+ 0.02
1.38	298.6	+ 185	13212	8288	+ 31	1.46	+ 0.08
2.47	331.8	547	14453	8300	+ 43	2.65	+ 0.18
2.61	332.9	582	14518	8276	+ 19	2.70	+ 0.09
2.95	342.0	665	14943	8294	+ 37	3.13	+ 0.18
3.88	355.7	852	15395	8257	0	3.88	0.00
. . . .	. . . .	. . . . . .	. . . . . .	. . . .	. . . . .	. . . .	. . . . . .
(7.36	409.3	1362	17346	8322	+ 65	8.10)	
. . . .	. . . .	. . . . . .	. . . . . .	. . . .	. . . .	. . . .	. . . . . .
23.2	504	2443	21007	8224	— 33	22.2	— 1.0
24.3	512	2504	21288	8244	— 13	23.9	— 0.4
31.9	545.5	2834	22543	8247	— 10	31.6	— 0.3
32.4	548	2855	22633	8253	— 4	32.2	— 0.2
33.0	550	2878	22712	8249	— 8	32.7	— 0.3
33.6	553	2903	22820	8254	— 3	33.5	— 0.1
34.5	555.5	2934	22920	8248	— 9	34.2	— 0.3
35.4	559	2967	23050	8250	— 7	35.1	— 0.3
35.5	560	2973	23083	8254	— 3	35.4	— 0.1
35.9	562	2990	23156	8257	0	35.9	0.0
37.6	569	3054	23414	8268	+ 5	37.8	+ 0.2
38.8	574	3099	23598	8266	+ 9	39.2	+ 0.4
40.3	578	3146	23756	8259	+ 2	40.4	+ 0.1
41.1	581	3173	23867	8261	+ 4	41.3	+ 0.2
44.2	593	3281	24309	8270	+ 13	44.9	+ 0.7
47.0	602	3369	24648	8270	+ 13	47.7	+ 0.7
48.6	606.5	3416	24821	8266	+ 9	49.1	+ 0.5
49.0	608	3429	24876	8268	+ 11	49.6	+ 0.6
53.9	621	3564	25374	8258	+ 1	53.9	0.0
55.6	625.5	3610	25546	8256	— 1	55.5	— 0.1
56.5	627.5	3633	25625	8252	— 5	56.2	— 0.3
57.7	632	3670	25788	8258	+ 1	57.8	+ 0.1
58.6	634	3692	25866	8256	— 1	58.5	— 0.1

in connection with the absolute value found in the first or in the sixth column.

Besides the vapour pressure line of violet phosphorus, also that for liquid phosphorus is indicated in fig. 4, from which it is seen how the observed vapour pressures lie on the line drawn according to formula (14).
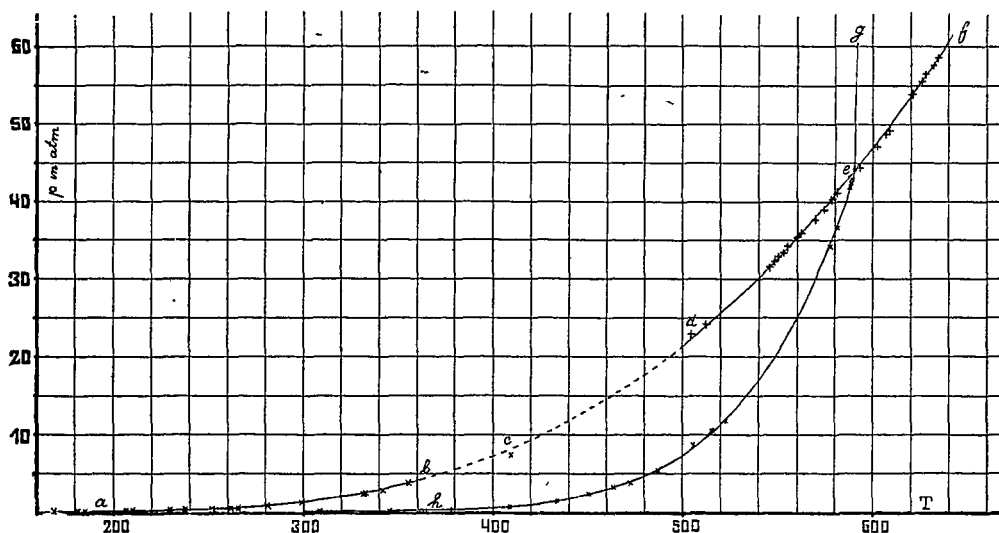

Fig. 3.

4. Conclusions.

The result of this investigation is so important for this reason that it was not known before whether there was any connection between the liquid white, and the liquid violet phosphorus. BAKHUIS ROOZEBOOM[1]) pointed out the possibility that the liquid white phosphorus had to be looked upon as supercooled liquid violet phosphorus, but he also expressed the opinion that it might also be that the phosphorus entirely agreed with the cyanogen, and that the vapour pressure line of the liquid white phosphorus terminated below the melting-point of the violet form in a critical point.

Up to a short time ago we thought for three reasons that this latter supposition of BAKHUIS ROOZEBOOM's would be the correct one. First of all the shape of the vapour pressure line of the liquid white phosphorus found some time ago pointed to the fact that this line could not be the prolongation of that of the liquid violet one. In the second place it could be calculated from the determinations of ASTON and RAMSAY [2]) of the surface tension that the liquid white phosphorus must reach its critical point at ± 422°. And in the third

[1]) Lehrbuch Heterog. Gleichgewichte 171 and 176.
[2]) Journ Chem Soc. 65, 173 (1894).

8

place the peculiar way in which, as Stock and Gomolka [1] were the first to find, red phosphorus can suddenly deposit from supercooled molten violet phosphorus and its vapour, seemed to point to a critical phenomenon.

In virtue of these three circumstances which seem to be in agreement with each other, we concluded phosphorus and cyanogen to be systems of the same type, and devised a diagram for the pseudo system of phosphorus, which was in close connection of that of cyanogen.

Now for the first time the question raised by Bakhuis Roozeboom, has been answered, and it has now appeared that the three above mentioned circumstances misled us at first. Phosphorus does not belong to the same type as cyanogen and the liquid white phosphorus must be really taken as supercooled liquid violet phosphorus.

The first determinations of the vapour tension were faulty at the highest temperature. Aston and Ramsay's determinations of the surface tension of liquid white phosphorus (which were only two, indeed) appear not to justify a calculation of the critical temperature, and the just mentioned phenomenon, which was observed by Stock and Gomolka, must be ascribed to this that the number of nuclei possesses a strongly pronounced maximum at a definite degree of supercooling, so that a spontaneous crystallisation, which proceeds with very great velocity, suddenly occurs there.

We see with great satisfaction that the system phosphorus can be represented in a simpler way than we thought at first in consequence of the non-existence of the supposed complication.

The P,T-projection of the system phosphorus for so far as it is known now, is schematically represented in the subjoined fig. 6. .
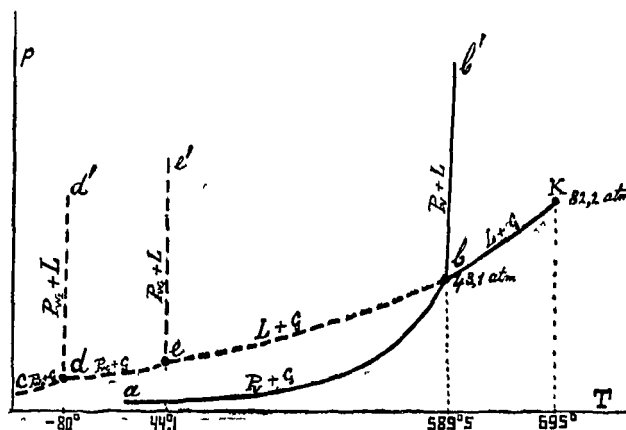

Fig. 4.

[1] Ber. 42, 4510 (1909).

With regard to the TX-fig. we must point out, that as was already remarked by us before [1], the pseudo-system of the phosphorus is most probably ternary, and that the third kind of molecules which has been left unconsidered up to now, plays probably a principal part in the change of the point of solidification of the white phosphorus. To simplify the representation we can disregard this third kind of molecules and take the pseudo system as binary, at least when our point of consideration is the connection between the white and the violet phosphorus.

Now the difference in properties between the white and the violet phosphorus, just as the difference in volatility and melting point suggest with great probability that we have to do here with a system of molecule-kinds, which differ in *size*. Hence we have probably to do here with the case of *association*. and the violet
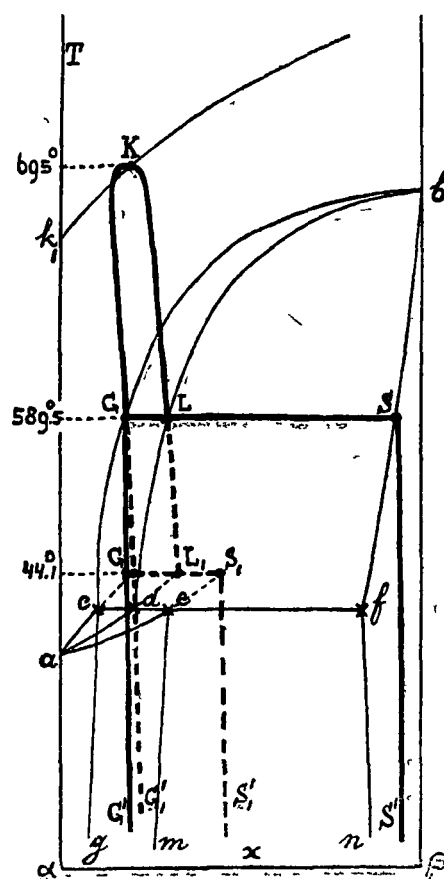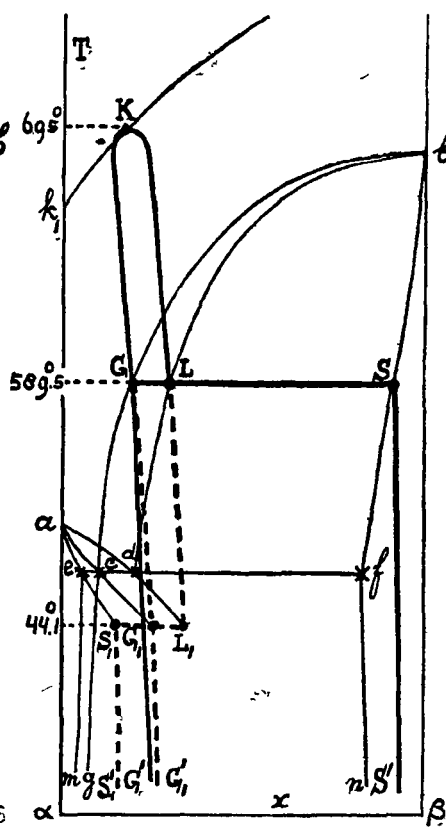

Fig. 5.   Fig. 6.

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[1] Z. f. phys. Chem. **88**, 621 (1914).

phosphorus will differ from the white chiefly in this that it contains a much larger proportion of associated molecules.

In this case the pseudo system, as was already explained several times, will possess no eutectic point, and then this pseudo system with the unary system lying in it, can be given schematically by fig. 5. If the pseudo-component β was isomer of α, also a figure like fig. 6 would be possible.

Note. When according to form. 14 we calculate the pressure corresponding with the temperature of 695°, which is the critical temperature of the liquid phosphorus according to W. A. WAHL's measurements, we find **82.2** atm. This is therefore the critical pressure, for which we found 83.56 in our preceding communication by means of the assumed linear relation

When we calculate the b-value from the critical pressure **82,2** atm. and the absolute critical temperature of 696° + 273° = **968°**, and from this the size of the phosphorus molecule, we find **4.33**; we found **4.26** before, which makes no difference of any importance

According to the formula:

$$j = 0,4343 \left(\frac{T_1 \ln p_1 - T_2 \ln p_2}{T_1 - T_2} - \ln p_k \right) \text{[1]}$$

the following values are found for the value of f at different temperatures:

from 200° to 300° $f = 3,11$
„ 300° „ 400° $f = 2,84$
„ 400° „ 500° $f = 2.60$
„ 500° „ 600° $f = 2,40$

Amsterdam, April 19, 1915.   *Anorg. Chemic. Laboratory*
of the University.

Chemistry. — *"In-, mono- and divariant equilibria"* I. By Prof. F. A. H. SCHREINEMAKERS.

1. Introduction.

When $n + 2$ phases occur in an equilibrium, which is composed of n substances, then it is invariant; the composition of the phases, the pressure and the temperature are perfectly defined then. In a P,T-diagram this equilibrium is represented by a point; we shall call this pressure and this temperature P_0 and T_0.

As this equilibrium is completely determined in every respect neither the composition of the phases, nor the pressure or the temperature can change on addition or withdrawal of heat or on

[1] In the preceding communication the term $\ln p_k$ had been erroneously omitted.