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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  $\beta$  was isomer of  $\alpha$ , also a figure like fig. 6 would be possible.

*Note.* When according to form. 14 we calculate the pressure corresponding with the temperature of  $695^\circ$ , 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  $696^\circ + 273^\circ = 968^\circ$ , 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:

$$f = 0,4343 \left( \frac{T_1 \ln p_1 - T_2 \ln p_2}{T_1 - T_2} - \ln p_k \right)^{1)}$$

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

from $200^\circ$ to $300^\circ$	$f = 3,11$
" $300^\circ$ " $400^\circ$	$f = 2,84$
" $400^\circ$ " $500^\circ$	$f = 2,60$
" $500^\circ$ " $600^\circ$	$f = 2,40$

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

<sup>1)</sup> In the preceding communication the term  $\ln p_k$  had been erroneously omitted.

a change of volume. Then, however, a reaction occurs, at which the quantities of some phases increase, those of other phases decrease, and only after disappearance of one of the phases, pressure, temperature and composition of the phases can change.

May the composition of a phase  $F_1$  be given by the quantities  $(x_1)_1 (x_2)_1 (x_3)_1 \dots (x_{n-1})_1$  and 1 or  $1 - (x_1)_1 - (x_2)_1 \dots (x_{n-1})_1$  that of a phase  $F_2$  by:

$(x_1)_2 (x_2)_2 (x_3)_2 \dots (x_{n-1})_2$  and 1 or  $1 - (x_1)_2 - (x_2)_2 \dots (x_{n-1})_2$  of the  $n$  components. We express in the same way the compositions of the phases  $F_3, F_4, \dots F_{n+2}$ . Let occur between these  $n+2$  phases the reaction:

$$y_1 F_1 + y_2 F_2 + y_3 F_3 + \dots + y_{n+2} F_{n+2} = 0 \quad \dots \quad (1)$$

$y_1 F_1$  means  $y_1$  quantities of the phase  $F_1$ , each of which has the composition given above;  $y_2 F_2$  etc. have the same meaning. It is evident that these reaction-coefficients  $y_1 \dots y_{n+2}$  cannot have all the same sign. In order to know reaction (1) it is not necessary to know the  $n+2$  reaction-coefficients  $y_1 \dots y_{n+2}$  themselves, the reaction is viz. determined by their  $n+1$  relations.

From the condition, that at the reaction the total quantity of each of the  $n$  components rests unchanged, the  $n$  relations follow:

$$\left. \begin{aligned} y_1 + y_2 + y_3 + \dots + y_{n+2} &= 0 \\ y_1 (x_1)_1 + y_2 (x_1)_2 + y_3 (x_1)_3 + \dots + y_{n+2} (x_1)_{n+2} &= 0 \\ y_1 (x_2)_1 + y_2 (x_2)_2 + y_3 (x_2)_3 + \dots + y_{n+2} (x_2)_{n+2} &= 0 \\ \dots &\dots \\ y_1 (x_{n-1})_1 + y_2 (x_{n-1})_2 + y_3 (x_{n-1})_3 + \dots + y_{n+2} (x_{n-1})_{n+2} &= 0 \end{aligned} \right\} \quad \dots \quad (2)$$

As we have only  $n$  conditions for the determination of the  $n+1$  ratios, (2) and therefore also (1) may be satisfied in infinitely many ways, or in other words: the reaction between the  $n+2$  phases of an invariant equilibrium can take place in infinitely many ways.

Now we put the condition that the total volume remains the same at the reaction; the reaction is then: "isovolumetrical". When we represent the volumina of the above-mentioned quantities of the phases  $F_1, F_2$  etc. by  $v_1, v_2$  etc. then it follows:

$$y_1 v_1 + y_2 v_2 + y_3 v_3 + \dots + y_{n+2} v_{n+2} = 0 \quad \dots \quad (3)$$

Now we have  $n+1$  equations [viz. the  $n$  equations (2) and equation (3)]; the  $n+1$  ratios of the reaction-coefficients are consequently determined and therefore also the proceeding of the reaction (1). Consequently we find that an isovolumetrical reaction between the  $n+2$  phases of an invariant equilibrium is completely determined.

We might just as well have posed instead of (3) the condition that the reaction takes place without addition or withdrawal of heat. As the entropy remains the same then, we call such a reaction an "isentropical reaction". When we represent the entropies by  $\eta_1, \eta_2$  etc., then the condition is:

$$y_1\eta_1 + y_2\eta_2 + y_3\eta_3 + \dots + y_{n+2}\eta_{n+2} = 0 \quad \dots \quad (4)$$

Then we have again  $n + 1$  equations, so that also an isentropical reaction between the  $n + 2$  phases of an invariant equilibrium is completely defined.

It is evident that the coefficients  $y_1, y_2$  etc. in the isovolumetrical reaction (1) are others than in the isentropical reaction (1). Further it is also evident that, dependent on the direction of the reaction, we must add or withdraw heat with an isovolumetrical reaction and that we must change the volume with an isentropical reaction.

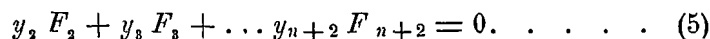
Now we imagine at  $T_0$  and under  $P_0$  that the  $n + 2$  phases  $F_1 \dots F_{n+2}$  are together; we let the isovolumetrical or isentropical reaction take place and we let this proceed until one of the phases disappears. Then an equilibrium of  $n$  components in  $n + 1$  phases arises, which is consequently monovariant. In this way  $n + 2$  monovariant equilibria may occur. As in each of these equilibria one of the phases of the invariant point fails, we represent, for the sake of abbreviation, a monovariant equilibrium by putting between parentheses the missing phase. Consequently we shall represent the equilibrium  $F_2 + F_3 + \dots F_{n+2}$  by  $(F_1)$ , the equilibrium  $F_1 + F_3 + F_4 + \dots F_{n+2}$  by  $(F_2)$ , etc. From the invariant equilibrium, therefore, the  $n + 2$  monovariant equilibria  $(F_1), (F_2), (F_3) \dots (F_{n+2})$  may occur.

Each monovariant equilibrium exists at a whole series of temperatures and corresponding pressures; consequently it is represented in the  $P, T$ -diagram by a curve, which goes through the invariant point  $P_0 T_0$ . Therefore in this point  $n + 2$  curves intersect one another. Each of these curves is divided by the invariant point into two parts; the one represents stable conditions the other metastable conditions. We shall always dot the metastable part. (See e. g. the fig. 1, in which these curves are indicated in the same way as the equilibria, which they represent).

When we consider only stable conditions, we may say:  $n + 2$  monovariant curves proceed from an invariant point of a system of  $n$  components.

In order to define the direction of these curves in the  $P, T$ -diagram, we may use the following thesis<sup>1)</sup>: the systems which are formed on addition of heat at an isovolumetrical reaction exist at higher — those which are formed on withdrawal of heat exist at lower temperatures. The systems which are formed on decrease of volume at an isentropical reaction exist under higher — those which are formed on increase of volume exist under lower pressures.

Let us consider now the equilibrium  $(F_1) = F_2 + F_3 + \dots F_{n+2}$ , which is represented in fig. 1 by curve  $(F_1)$  at a temperature  $T_a$  and under a pressure  $P_a$ , which are represented by the point  $a$ . On addition of heat under a constant pressure or on change of volume at a constant temperature a reaction, which is completely defined, occurs between these  $n+1$  phases. Let us write this reaction:



The  $n$  relations between the  $n+1$  reaction-coefficients are fixed then by the  $n$  equations (2) in which, however, we must omit all terms which refer to the phase  $F_1$ , [consequently  $y_1, (x_1)_1, (x_2)_1$  etc.].

Now we let reaction (5) occur until one of the phases of the equilibrium  $(F_1)$  disappears; then an equilibrium of  $n$  phases arises, which is consequently bivariant. In all  $n+1$  bivariant equilibria can arise from the equilibrium  $(F_1)$ . As in each of these equilibria two of the phases of the invariant point are wanting, we represent a bivariant equilibrium by putting between parentheses the failing phases.  $(F_1 F_2)$  represents consequently the equilibrium  $F_3 + F_4 + \dots F_{n+2}$ . From the equilibrium  $(F_1)$ , therefore, the bivariant equilibria  $(F_1 F_2), (F_1 F_3) \dots (F_1 F_{n+2})$  may arise in the manner, which is treated above.

In a bivariant equilibrium  $P$  and  $T$  can be considered as independent variables; each bivariant equilibrium can, therefore, be represented in the  $P, T$ -diagram by the points of the plane of this diagram, consequently by a region.

Consequently  $n+1$  bivariant regions, which may arise from the equilibrium  $(F_1)$ , go through each monovariant curve  $(F_1)$ . Each of these regions is divided into two parts by the curve  $(F_1)$ , the one part represents stable conditions, the other metastable conditions. When we limit ourselves to the stable parts of these regions, we may say: in a system of  $n$  components  $n+1$  bivariant regions start from each monovariant curve.

<sup>1)</sup> F. A. H. SCHREINEMAKERS. Heterog. Gleichgewichte von H. W. BAKHUIS ROOZEBOM. III': we find herein the proofs for ternary systems on p. 220—221 and 298—301. These, however, are also true for systems of  $n$  components.

The  $n + 1$  regions starting in fig. 1 from curve ( $F_1$ ), are situated partly at the one and partly at the other side of this curve; also it is evident that the regions, which are situated on the same side of the curve, cover one another. Hence it follows immediately that several bivariant equilibria can occur under a given  $P$  and at a given  $T$ .

In order to determine on which side of the curve ( $F_1$ ) the stable part e.g. ( $F_1 F_2$ ) of a bivariant region is situated, we let the reaction (5) take place in such a way, that the phase  $F_2$  disappears from the equilibrium ( $F_1$ ). This may always take place, when the quantity of  $F_2$  in the equilibrium ( $F_1$ ) has been taken small enough. If we let this reaction proceed under a constant pressure, we have to state whether heat must be added or supplied, when we let it take place at a constant temperature, we must determine whether the volume increases or decreases. We may then apply the following rules: at the right of the curve we find the bivariant equilibria, which arise on addition of heat; at the left of the curve those which arise on withdrawal of heat. Above the curve we find the bivariant equilibria, which arise on decrease of volume; beneath the curve those, which arise on increase of volume.

For the meaning of "at the right", "at the left", "beneath" and "above" is assumed that the  $P$ - and  $T$ -axes are situated as in fig. 1.

When we apply the considerations, mentioned above, to each of the  $n + 2$  curves ( $F_1$ )...( $F_{n+2}$ ) then we obtain the division of the  $\frac{1}{2}(n+2)(n+1)$  divariant regions between the different curves and around the point  $O$ .

The following is apparent from the previous considerations. When we know the compositions of the phases, which occur in an invariant point and the changes in entropy and volume which take place at the reactions, then we are able to determine in the  $P, T$ -diagram the curves starting from this point and the division of the bivariant regions.

## 2. *Some general properties.*

Now we will put the question whether anything may be deduced concerning the position of the curves and the regions with respect to one another, when we know the compositions of the phases only and not the changes of entropy and volume which the reactions involve.

This question is already dissolved for binary <sup>1)</sup> and ternary <sup>2)</sup>

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Z. f. Phys. Chemie 82 59 (1913) and F. E. C. SCHEFFER, these Communications October 1912.

<sup>2)</sup> F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOOM III' 218.

systems, the way which we have followed then [viz. with the aid of the graphical representation of the  $\psi$ - and the  $\zeta$ -function] is not appropriate however to be applied to systems with more components. The following method is much simpler and leads to the result desired for any system.

We consider an invariant point with the phases  $F_1, F_2, \dots, F_{n+2}$  and two of the curves starting from this point, viz.  $(F_1) = F_2 + F_3 + \dots + F_{n+2}$  and  $(F_2) = F_1 + F_3 + \dots + F_{n+2}$ . (see fig. 1). Between the stable parts of these curves the region  $(F_1 F_2) = F_3 + F_4 + \dots + F_{n+2}$  is situated. When we consider stable conditions only, this region terminates at the one side in curve  $(F_1)$ , at the other side in curve  $(F_2)$ . Now it is the question in which of the two angles  $(F_1) O (F_2)$  the region  $(F_1 F_2)$  is situated, viz. in the angle which is smaller or in the angle which is larger than  $180^\circ$ .

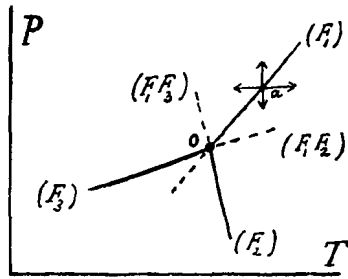


Fig. 1.

The first case has been drawn in fig. 1 in the latter case the region  $(F_1 F_2)$  should extend itself over the metastable parts of the curve  $(F_1)$  and  $(F_2)$ . We call the angle of the region  $(F_1 F_2)$  in the point  $o$  the region-angle of  $(F_1 F_2)$ ; we can prove now: "a region-angle is always smaller than  $180^\circ$ ."

In order to prove this we imagine in fig. 1 the region  $(F_1 F_2)$  in the angle  $(F_1) o (F_2)$ , which is larger than  $180^\circ$ . The stable part of this region then extends itself on both sides of the metastable part of curve  $(F_1)$  and also of  $(F_2)$ . This now is in contradiction with the property that the stable part of each region, which may arise from a curve, is situated only at one side of this curve. Hence it follows, therefore, that the region-angle must be smaller than  $180^\circ$ .

Therefore, when we will draw in fig. 1 the region  $(F_1 F_3)$ , this must be situated in the angle  $(F_1) O (F_3)$ , which is smaller than  $180^\circ$ . As in fig. 1  $(F_3)$  and  $(F_2)$  are drawn on different sides of  $(F_1)$ , the regions  $(F_1 F_3)$  and  $(F_1 F_2)$  fall outside one another; when we had taken  $(F_2)$  and  $(F_3)$  on the same side of  $(F_1)$ , the two regions should partly cover one another.

Another property is the following: every region, which extends itself over the metastable or stable part of a curve  $(F_p)$  contains the phase  $F_p$ , or in other words: each region which is intersected by the stable or the metastable part of a curve  $(F_p)$  contains the phase  $F_p$ . In an invariant point the  $n + 2$  phases  $F_1 F_2 \dots F_{n+2}$  occur; consequently around this point  $\frac{1}{2}(n + 2)(n + 1)$  bivariant regions extend themselves. In  $n + 1$  of these regions the phase  $F_1$  is wanting,

viz. in  $(F_1F_2), (F_1F_3) \dots (F_1F_{n+2})$ ; in all the other [viz. in  $\frac{1}{2}n(n+1)$  regions] it is present however. The same applies to every other phase.

Now we imagine in fig 1 the curves  $(F_1), (F_2) \dots (F_{n+2})$  to be drawn. The  $n + 1$  regions in which the phase  $F_1$  does not occur, all start from the stable part of the curve  $(F_1)$ ; none of those regions can therefore, extend itself over the stable part of curve  $(F_1)$ . When, therefore a region extends itself over the stable part of the curve  $(F_1)$ , then it must consequently contain the phase  $F_1$ . As every region-angle is however smaller than  $180^\circ$ , none of the  $n + 1$  regions, in which the phase  $F_1$  does not occur, can extend itself over the metastable part of the curve  $(F_1)$ ; the regions, which extend themselves over this part, consequently contain all the phase  $F_1$ .

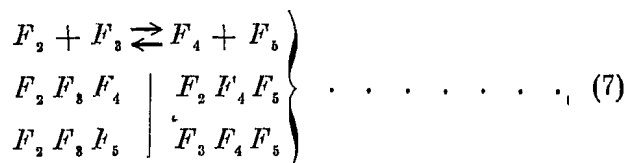
Consequently we find: each region, which extends itself over the metastable or stable part of a curve  $(F_p)$ , contains the phase  $F_p$ .

We must keep in mind with this that the metastable part of a curve is always covered by one or more regions, but this is not always the case with the stable part. Further it is also apparent that the reversé of the previous thesis viz. "all regions which contain themselves the phase  $F_p$  extend themselves over the metastable or stable part of the curve  $(F_p)$ " need not be true; this is only always the case in unary systems. Later we shall still refer to these and other properties.

Now we shall deduce a thesis, which is of great importance for the determination of the position of the curves with respect to one another. For fixing the ideas we take an invariant point with the phases  $F_1, F_2, F_3, F_4$  and  $F_5$  and we consider the curve  $(F_1) = F_2 + F_3 + F_4 + F_5$  starting from this point. Between the four phases of this equilibrium on addition or withdrawal of heat a reaction occurs, which is, as we have seen above, completely defined by the compositions of the phases. Let this reaction be for instance:



Consequently four bivariant regions start from the curve  $(F_1)$  viz.  $F_2F_3F_4, F_2F_3F_5, F_2F_4F_5$  and  $F_3F_4F_5$ . It follows from (6) that the regions  $F_2F_3F_4$  and  $F_2F_3F_5$  are situated at the one side and the regions  $F_2F_4F_5$  and  $F_3F_4F_5$  at the other side of curve  $(F_1)$ . We write this:



When we should know the changes in entropy and volume,







We firstly determine now the position of (2). It is apparent from equation 11 that the curves (1) and (2) are situated at different sides of (3), as (1) is taken at the right of (3), (2) must, therefore, be situated at the left of (3). It is apparent from equation 13 that the

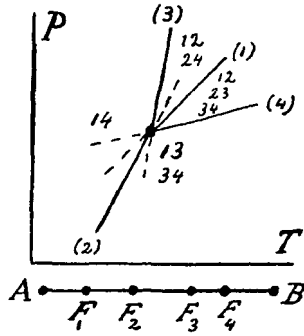


Fig. 2.

curves (2) and (3) are situated at different sides of (1); as (3) has been taken at the left of (1), (2) must consequently be situated at the right of (1).

Therefore, we find . curve (2) is situated at the left of (3) and at the right of (1); it is situated, therefore, as is drawn in fig. 2 between the metastable parts of (1) and (3).

Now we determine the position of (4).

It is apparent from equation 11 that (1) and (4) are situated at the same side of (3); (4) is, therefore, situated at the right of (3). It is apparent from equation (13) that (3) and (4) are situated at different sides of (1); consequently (4) is situated at the right of (1).

Consequently we find: curve (4) is situated at the right of (1) and (3); it is situated, therefore, as is also drawn in fig. 2, between the stable part of (1) and the metastable part of (3).

From fig. 2 still follow the relations:

$$2 \supseteq 1 + 3 \quad . . . . (14) \quad 3 \supseteq 1 + 4 \quad . . . . (16)$$

and

$$(2) |(4)| (1) (3) \quad . . . . (15) \quad (3) |(2)| (1) (4) \quad . . . . (17)$$

As the position of the curves with respect to one another, is already fixed in fig. 2, we need no more the relations 14—17, they may however be useful as a confirmation. From (15) follows that (1) and (3) are situated at the one side and (2) at the other side of (4); in accordance with (17) (1) and (4) are situated at the one side and (3) at the other side of (2). We see that this is in accordance with fig. 2. Consequently we find the following rule:

when we call, going from the one component towards the other, the phases occurring in a quadruplepoint  $F_1, F_2, F_3$  and  $F_4$  then the order of succession of the curves, if we move in the  $P, T$ -diagram around the quadruplepoint, is 1, 3, 2, 4 or reversally.

We have assumed at the deduction above that curve (3) is situated at the left of (1); when we take (3) at the right of (1) we find the same order of succession.

Now we shall seek the position of the 6 bivariant regions. From curve (1) = 2 + 3 + 4 the regions 23, 24 and 34 are starting. The region 23 extends itself between the curves (1) and (4); it is indicated in fig. 2 by 23. The region 24 is situated between the curves (1) and (3); the region 34 is situated between the curves (1) and (2) and therefore, extends itself over curve (2) [fig. 2]. [We keep in mind with this that each region-angle is smaller than  $180^\circ$ .]

When we act in the same way with the regions which start from the curves (2), (3) and (4) we find a partition of the regions as in fig. 2.

Previously we have deduced: each region, which extends itself over the stable or metastable part of curve ( $F_p$ ) contains the phase  $F_p$ . We see the confirmation of this rule in fig. 2. The metastable part of curve (1) intersects the region 14, the stable part of this curve the region 12; both the regions contain the phase 1. The metastable part of curve (2) intersects the regions 12 and 24, which contain both the phase 2; the metastable part of curve (3) intersects the regions 13 and 34 which contain both the phase 3. The metastable part of curve (4) intersects the region 14, the stable part of this curve is covered by the region 34; both the regions contain the phase 4.

The following is apparent from the preceding considerations. In all binary systems the partition and the position of the curves and the regions will respect to one another starting from a quadruple-point, is always the same; it can be represented by fig. 2.

(To be continued).

**Chemistry.** — “*Compounds of the Arsenious Oxide.*” II. By Prof. F. A. H. SCHREINEMAKERS and Miss W. C. DE BAAT.

*a. Introduction.*

By RÜDORFF<sup>1)</sup> and others compounds are prepared of the  $As_2O_3$  with halogenides of potassium, sodium and ammonium.

These compounds were obtained by treating solutions of arsenites (viz. solutions of  $As_2O_3$  in a base) with the corresponding halogenides.

RÜDORFF describes the compound  $As_2O_3 \cdot NH_4Cl$ , which we have found also; he also describes the compound  $(As_2O_3)_2 \cdot KCl$ , which we have not found.

In order to obtain these compounds, we have, however, worked in quite another manner; for this we have brought together water,

<sup>1)</sup> FR. RÜDORFF. Ber. 19 2668 (1886), 21 3051 (1888).