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## **Chemistry**. — "In-, mono- and divariant equilibria." IX. By Prof. F. A. H. Schreinemakers.

(Communicated in the meeting of April 28, 1916).

13. The direction of the curves in the invariant point.

In the previous communications we have deduced the P, T-diagramtypes without knowing the changes in volume and entropy which occur at the reactions. When we know those also, however, then we may not only find the P, T-diagramtype, but also the diagram itself, viz. the direction of the curves in the invariant point.

We know that all reactions which may occur between the phases of an invariant point, are completely defined by two reactions. When we know also the changes in volume and entropy, which occur at those reactions, then those changes are known also for the other reactions.

Let one of the reaction-equations be:

 $l_1F_1 + l_2F_2 + \ldots + l_{n+2}F_{n+2} = 0.$  (1)

At the proceeding of this reaction a change in volume and a change in entropy occur; we represent the first by  $\Delta V_l$ , the second by  $\Delta \eta_l$ .

Where these changes present themselves we write them behind the reaction-equations and first the change in volume, afterwards the change in entropy. Consequently we write for (1):

$$l_1F_1 + \ldots + l_{n+2}F_{n+2} = 0 \qquad \Delta V_l \quad ; \quad \Delta \eta_l \quad . \quad . \quad (2)$$

Herein we may express  $\Delta V_l$  and  $\Delta \eta_l$  by:

$$\Delta V_l = l_1 v_1 + l_2 v_2 + \ldots + l_p v_p + \ldots + l_{n+2} v_{n+2} \quad . \quad . \quad (3)$$

$$\Delta \eta_l = l_1 \eta_1 + l_2 \eta_2 + \ldots + l_p \eta_p + \ldots + l_{n+2} \eta_{n+2} \quad . \quad . \quad (4)$$

Herein  $v_p$  and  $\eta_p$  represent the volume and the entropy of the unity of quantity of a phase  $F_p$ . We take as second reaction-equation:

$$m_1F_1 + \ldots + m_{n+2}F_{n+2} = 0 \qquad \Delta V_m \quad ; \quad \Delta \eta_m \ldots \quad . \tag{5}$$

When we deduce from (2) and (5) an arbitrary other reaction:  $(Kl_1+m_1)F_1+(Kl_2+m_2)F_2+\ldots=0$   $K\Delta V_l+\Delta V_m$ ;  $K\Delta \eta_l+\Delta \eta_m$ . (6) then the change in volume is  $K\Delta V_l+\Delta V_m$  and the change in entropy  $K\Delta \eta_l+\Delta \eta_m$ .

When we give to K such a value, that  $Kl_1 + m_1 = 0$ , then (6) represents the reaction, which may occur between the phases of the equilibrium  $(F_1)$  and the change in volume and entropy belonging to this reaction. Hence follows:

$$\left(\frac{dP}{dT}\right)_{1} = \frac{K\Delta\eta_{l} + \Delta\eta_{m}}{K\Delta V_{l} + \Delta V_{m}} = \frac{m_{1}\Delta\eta_{l} - l_{1}\Delta\eta_{m}}{m_{1}\Delta V_{l} - l_{1}\Delta V_{m}} \cdot \cdot \cdot \cdot \cdot (6)$$

by which is defined the direction of curve  $(\mathcal{F}_1)$  in the invariant point. In the same way we find the directions of the other curves.

Between all reactions in which n + 2 phases take part there are two special ones, viz. the isovolumetrical and the isentropical reaction (conf. communication I). At a reaction between the phases in the first the volume remains unchanged, in the second the entropy remains unchanged; in this latter case, therefore, heat is neither added nor withdrawn. We can easily deduce those reactions from (2) and (5). In order to find the isovolumetrical reaction we subtract the reactions from one another after having multiplied (2) by  $\Delta V_m$  and (5) by  $\Delta V_l$ ; in order to find the isentropical reaction we subtract the reactions from one another, after having multiplied (2) by  $\Delta \eta_m$  and (5)  $\Delta \eta_l$ . Let us write the isentropical reaction :

$$a_1F_1 + a_2F_2 + \ldots + a_{n+2}F_{n+2} = 0 \quad \Delta V \; ; \; 0 \; \ldots \; (7)$$

and the isovolumetrical reaction:

$$b_1F_1 + b_2F_2 + \ldots + b_{n+2}F_{n+2} \equiv 0$$
 0;  $\Delta\eta$ . (8)  
ce follows:

Hence follows:

$$(\lambda a_1 + b_1) F_1 + (\lambda a_2 + b_2) F_2 + \ldots \equiv 0 \quad \lambda \Delta V \quad ; \quad \Delta \eta \ldots \quad (9)$$

When we give to  $\lambda$  such a value that  $\lambda a_1 + b_1 = 0$ , then (9) represents the reaction which may occur between the phases of the equilibrium  $(F_1)$  and the change in volume and entropy belonging to this reaction. Hence follows:

$$\left(\frac{dP}{dT}\right)_{I} = \frac{\Delta\eta}{\lambda\Delta V} = -\frac{a_{I}\Delta\eta}{b_{I}\Delta V} \quad \text{of} \quad \frac{b_{I}}{a_{I}} \left(\frac{dP}{dT}\right)_{I} = -\frac{\Delta\eta}{\Delta V} \quad . \quad (10)$$

In the same way we find:

$$\frac{b_2}{a_2} \cdot \left(\frac{dP}{dT}\right)_2 = -\frac{\Delta \eta}{\Delta V} \quad ; \quad \frac{b_3}{a_3} \left(\frac{dF}{dT}\right)_3 = -\frac{\Delta \eta}{\Delta V} ; \quad \text{etc.}$$

Hence it appears that between the direction-coefficients of the tangents to the curve  $(F_1)$ ... in the invariant point the following relations exist:

$$\frac{b_1}{a_1} \left( \frac{dP}{dT} \right)_1 = \frac{b_2}{a_2} \left( \frac{dP}{dT} \right)_2 = \frac{b_3}{a_3} \left( \frac{dP}{dT} \right)_2 = \dots = -\frac{\Delta \eta}{\Delta V} \dots \quad (11)$$

From (11) follows the direction of each of the curves in the invariant point; this is however not yet sufficient to find the P, T-diagram. When  $\left(\frac{dP}{dT}\right)_1$  is e.g. positive, then this means that the

pressure along curve  $(F_1)$  increases at rising temperature, decreases at lowering temperature. Curve  $(F_1)$  may go, therefore, starting from the invariant point, towards higher P and T, or towards lower P and T, consequently in opposite-direction. In order to define the P,T-diagram we have to use therefore still other properties. For this we take:

1. the equilibria which are formed at an isentropical reaction with increase of volume, go towards lower pressures, starting from the invariant point; those, which are formed with decrease of volume, go towards higher pressures.

2. the equilibria, which are formed at an isovolumetrical reaction with increase of entropy (consequently on addition of heat) go towards higher temperatures, starting from the invariant point; those, which are formed with decrease of entropy (consequently on withdrawing of heat) go towards lower temperatures.

We now write the isentropical and isovolumetrical reactions (7) and (8):

$$a_1 F_1 + a_2 F_2 + \dots + a_{n+2} F_{n+2} = 0 \Delta V; 0$$
 (12)

$$\mu_1 a_1 F_1 + \mu_2 a_2 F_2 + \ldots + \mu_{n+2} a_{n+2} F_{n+2} = 0 \quad 0 \; ; \; \Delta \eta \quad (13)$$

in which we take the coefficients of the phase  $F_1$  positive; further we assume that in both the equations the phases are written in such order of succession, that the condition:

$$\mu_1 > \mu_2 > \ldots > \mu_p > \ldots > \mu_{n+2} \cdot \ldots \cdot (14)$$

is satisfied.

Now we may write for (11):

$$\mu_1 \left( \frac{dP}{dT} \right)_1 = \mu_2 \left( \frac{dP}{dT} \right)_2 = \mu_3 \left( \frac{dP}{dT} \right)_3 = \dots = -\frac{\Delta \eta}{\Delta V} . \quad (15)$$

When in (14) all the values of  $\mu$  are positive, then it follows from (15) that the direction-coefficients of the curves in the invariant point are either all positive or all negative. When we take into consideration absolute values only, then follows:

$$\left(\frac{dP}{dT}\right)_{1} < \left(\frac{dP}{dT}\right)_{2} < \cdots < \left(\frac{dP}{dT}\right)_{n+2} \cdots \qquad (16)$$

When  $\mu_1 \ldots \mu_{p-1}$  are positive and  $\mu_p \ldots \mu_{n+2}$  negative, then it follows, when we take into consideration absolute values only:

$$\left(\frac{dP}{dT}\right)_{1} < \dots < \left(\frac{dP}{dT}\right)_{p-1} \operatorname{and} \left(\frac{dP}{dT}\right)_{p} > \dots > \left(\frac{dP}{dT}\right)_{n+2}$$
(17)  
In this  $\left(\frac{dP}{dT}\right)_{p-1}$  may be as well larger as smaller than  $\left(\frac{dP}{dT}\right)_{p}$ .

 $\Delta V$  may be in (12) as well positive als negative; this depends on the direction, in which reaction (12) proceeds. When  $\Delta V$  is positive in the one direction, then it is negative in the opposite direction. Now we assume that  $\Delta V$  is the change of volume, when the reaction proceeds in such a way that the phases, which have a negative sign in (12), are formed, and that consequently the quantities of the phases, which have a positive sign, diminish. We call this direction: the "direction belonging to  $\Delta V$ ". When we let reaction (12) proceed in opposite direction, therefore in such a way that the quantities of the phases, which have a negative sign, diminish, then the change of volume is  $-\Delta V$ .

In (13) we assume the same; consequently  $\Delta \eta$  is the increase of entropy, when reaction (13) proceeds in such direction, that the phases, which have a negative sign, are formed.

For fixing the ideas now we shall assume that the series of signs of reaction-equation (12) is represented by:

$\boldsymbol{A}$	R	В	S	C	T		(18)
+	<i>—</i> …	$+ \cdots$		$+ \cdots$		•	(10)

In each group we give to the phases from left to right the indices 1, 2,...; in group  $A : A_1, A_2, \ldots$ , in group  $S : S_1, S_2, \ldots$ , etc.

When all ratios are positive in (14), then all phases have the same sign in (13) as in (12); when some of those ratios are negative, for instance beginning with  $\mu_p$ , then in (13) the phases  $F_1 \ldots F_{p-1}$  have the same sign, but  $F_p \ldots F_{n+2}$  the opposite sign as in (12). Then we obtain the two series of signs:

$\boldsymbol{A}$	R	$  B_a$	$B_b$ .	S		T'	l	
$+ \cdots$	···	+	$+ \cdots$	<i>—</i> …	+ • • •		$\Delta V; 0$	(19)
+			<u> </u>	$+ \dots$		+	$0; \Delta \eta$	(20)

The upper one represents the series of signs of reaction (12), the lower that of (13). With this we have assumed that the phase  $F_p$  is situated in group B; in the lower series of signs this group is divided then into two parts  $B_a$  and  $B_b$  with opposite sign.

We now let the isentropical reaction (12) between the phases of the invariant point occur in the direction belonging to  $\Delta V$ . As with this reaction the quantities of the phases, which have a positive sign in (12) or (19) diminish, from the invariant equilibrium, a monovariant equilibrium is formed, which we shall call  $(X_+)$ . Herein  $X_+$  represents, therefore, a phase with positive sign, consequently a phase from one of the groups A, B or C of (19).

When we let the isentropical reaction go in opposite direction, then

the quantities of the phases, which have a negative sign in (12) or (19) are diminished. Now from the invariant equilibrium a monovariant equilibrium  $(X_{-})$  is formed, in which  $X_{-}$  represents a phase with negative sign, therefore, a phase from one of the groups R, S or T of (19).

With the aid of the first of the properties mentioned above, which defines the direction of a curve from the sign of the change in volume at the isentropical reaction, we find:

 $I^{a}$ .  $\Delta V > 0$ . Starting from the invariant point the curves  $(X_{+})$  go towards lower- and the curves  $(X_{-})$  towards higher pressures.

I<sup>b</sup>.  $\Delta V < 0$ . Starting from the invariant point the curves  $(X_+)$  go towards higher- and the curves  $(X_-)$  towards lower pressures.

When we let the isovolumetrical reaction (13) occur between the phases of the invariant equilibrium and when we apply the second of the properties mentioned above, then we find:

II<sup>a</sup>.  $\Delta \eta > 0$ . Starting from the invariant point the curves  $(X_+)$  go towards higher- and the curves  $(X_{--})$  towards lower temperatures.

 $II^{5}$ .  $\Delta \eta < 0$ . Starting from the invariant point the curves  $(X_{+})$  go towards lower- and the curves  $(X_{-})$  towards higher temperatures.

	A	R	B <sub>a</sub>	Вђ	s	С			
	+		+ +,	+	   +	+	 +	$\Delta \mathcal{V}; 0$ 0; $\Delta q$	(a) (b)
$\Delta^P$ $\Delta T$	 +	+	 +		+		+ +	Δ <i>V</i> >0 Δ <i>n</i> >0	(c) (d)
$\Delta P$ $\Delta T$	+	 +	+	+ +		+		∆ <i>V</i> <0 ∆4<0	(e) (f)
$\Delta P$ $\Delta T$		+ +		~ +	+	 +	+	Δ <i>V</i> >0 Δq<0	(g) (h)
$\Delta^P$ $\Delta T$	+		+	+	 +	+	 +	∆ <i>V</i> <0 ∆4<0	(i) (k)
dP dT				· · ·	·		; ;		(/)

TABLE I.

Now we apply the rules  $I^{a}$  and  $I^{b}$  to the series of signs (19) and the rules  $II^{a}$  and  $II^{b}$  to the series of signs (20); viz. (19) is the series of signs of the isentropical-, (20) that of the isovolumetrical reaction. In the foregoing table the results are summarised.

In table I line *a* represents the series of signs of the isentropical reaction and line *b* that of the isovolumetrical reaction. In order to indicate that a curve goes, starting from the invariant point, towards higher or lower pressures, we write at the beginning of a rule  $\Delta P$  and further under each group a positive or negative sign; a positive sign indicates that  $\Delta P$  is positive, or in other words that the curves go towards higher pressures; a negative sign indicates that  $\Delta P$  is negative, therefore, that the curves go towards lower pressures.

The lines, beginning with  $\Delta T$ , indicate whether a curve goes, starting from the invariant point, towards higher or lower temperatures. A positive sign indicates that  $\Delta T$  is positive, therefore, that the curves go towards higher temperatures; a negative sign indicates that  $\Delta T$  is negative, therefore, that the curves go towards lower temperatures.

When we take  $\Delta V > 0$  [rules c and g] then, in accordance with  $I^a$  the curves of the groups A,  $\mathcal{B}_a$ ,  $\mathcal{B}_b$  and C go towards lower pressures, those of the groups R, S and T towards higher pressures. This is expressed by the signs in series c and g.

For  $\Delta V < 0$  [rule *e* and *i*] we find with the aid of  $I^b$  the series of signs *e* and *i*.

It is evident that in the rules c and g [viz.  $\Delta V > 0$ ] all signs are 'the opposite and in the series e and i [viz.  $\Delta V < 0$ ] all signs are the same as in the series of signs a.

With the aid of  $II^a$  and  $II^b$  we find from series b the series d, f,  $h_1$  and k. The series d and k [viz.  $\Delta \eta > 0$ ] have the same signs, the series f and h [viz.  $\Delta \eta < 0$ ] have the opposite signs as the series of signs b.

As it follows from (17), the arrows in the lower line of the table indicate the direction in which the absolute value of  $\frac{dP}{dT}$  increases for the different curves. Consequently it increases from curve  $(A_1)$ to the last curve of group  $B_a$ ; it decreases from the first curve of group  $B_b$  to the last curve of group T.

Table I represents the four possible cases, viz.  $\Delta V > 0$  and  $\Delta \eta > 0$  in series c and d;  $\Delta V < 0$  and  $\Delta \eta < 0$  in series e and f;  $\Delta V > 0$  and  $\Delta \eta < 0$  in series g and h;  $\Delta V < 0$  and  $\Delta \eta > 0$  in series i and k. The last rule l is true for each of those four cases. Now we can easily deduce the P,T-diagram for each of those cases.

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 $\Delta V > 0$  and  $\Delta \eta > 0$  [series c and d]. It appears at once from series c and d that the curves of group A go starting from the invariant point towards lower pressures and higher temperatures. In the P, T-diagram [fig. 1] of this group A the curves  $(A_1)$ ,  $(A_2)$ and  $(A_3)$  are drawn. The position of those three curves with respect to one another follows at once from the direction of the arrow in table I; hence it appears viz. that the absolute value of  $\frac{dP}{dT}$  is for -







curve  $(A_1)$  smaller than for  $(A_2)$ , for  $(A_2)$  smaller again than for  $(A_3)$ , etc.

Further it appears from table 1 that the curves of R go towards higher pressures and lower temperatures; of this group the curves  $(R_1)$ ,  $(R_2)$  and  $(R_3)$  are drawn. It appears from the direction of the arrow in table 1 that the absolute value of  $\frac{dP}{dT}$  for the curves  $A_1A_2A_3\ldots R_1R_2R_3$  increases from left to right. The curves of group R are situated, therefore, with respect to one another and to the curves of group A, as is drawn in fig. 1.

When we draw with the aid of the series c and d and the direction of the arrows, also the curves of the other groups, then we find fig. 1. Herein is only one curve drawn of each of the groups  $B_a$ ,  $B_b$ , S, C and T.

Consequently we find a P, T-diagram with five bundles of curves; each of the groups of signs R,  $B = B_a + B_b$ , S and C of the series of signs a produces a bundle of curves in the P, T-diagram, the groups of signs A and T produce together one single bundle only.

 $\Delta V < 0$  and  $\Delta \eta < 0$  [series *e* and *f*]. We obtain the same *P*,*T*-diagram as in fig. 1, with this great difference, however, that we have to change mutually the stable and metastable parts of the curves from fig. 1. Consequently we have to draw the dotted lines in fig. 1 and to dot the drawn lines.

 $\Delta V > 0$  and  $\Delta \eta < 0$  [series g and h]. It follows at once from series g and h that the curves of group A go, starting from the invariant point, towards lower pressures and temperatures, it is apparent from the direction of the arrow in table I that those curves must be situated with respect to one another as the curves  $(A_1)$ ,  $(A_2)$  and  $(A_3)$  in fig. 2. Further it appears from series g and h that the curves of group R go towards higher pressures and temperatures, it appears from the direction of the arrow in table I that those curves must be situated with respect to one another and to the curves of group A, as the curves  $(R_1)$ ,  $(R_2)$  and  $(R_3)$  in fig. 2.

When we draw, however, in the P, T-diagram also the curves of the other groups, then we find fig. 2. Herein only one curve is drawn of each of the groups  $B_a$ ,  $B_b$ , S, C and T.

Now we find again a P, T-diagram with five bundles of curves, each of the groups of signs R,  $B = B_a + B_b$ , S and C of series aproduces again a bundle of curves; the groups of signs A and Tproduce again together one bundle.

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 $\Delta V < 0$  and  $\Delta \eta > 0$  [series *i* and *k*]. We obtain the same *P*,*T*-diagram as in fig. 2, again with this great difference however, that we have to change mutually the stable and metastable parts of the curves in fig. 2.

In the four P, T-diagrams which we have deduced now, all curves, which belong to a same group [viz. group  $A, R, B_a, B_b$ , S, C and T] always go in the same direction of pressure and temperature. The curves of group A go, viz. starting from the invariant point in fig. 1 all towards lower P and higher T, in fig. 2 all towards lower P and T, the curves of group R go in fig. 1 viz. all towards higher P and lower T, in fig. 2 towards higher Pand T, etc. It appears from table 1 why this must be the case. As the groups C, R, and S in each of the P, T-diagrams form each a bundle of curves, the above mentioned is also true for those bundles of curves.

This is however no more the case for the bundles of curves A + Tand  $B = B_a + B_b$ ; the curves of bundle A + T all go in the same direction of temperature, but not in the same direction of pressure, the curves of bundle  $B = B_a + B_b$  all go in the same direction of pressure, but not in the same direction of temperature. We call such bundles "divergent"; bundle A + T is then divergent in direction of pressure, bundle  $B_a + B_b$  in direction of temperature; in fig. 3 bundle A + Tis divergent in both directions. We shall examine further under which conditions a similar divergency of a bundle may occur.

Deducing series of signs (20) from (19) we have assumed that in (14)  $\mu_1 \ldots \mu_{p-1}$  is positive and  $\mu_p \ldots \mu_{n+2}$  negative; in the two series the phases  $F_1 \ldots F_{p-1}$  have, therefore, the same sign and the phases  $F_p \ldots F_{n+2}$  therefore the opposite sign. Further we have assumed that the phase  $F_p$  is situated in group B; for this we have divided this group into the two groups  $B_a$  and  $B_o$ .

It may, however, also be the case that the phase  $F_p$  is the first of a group in the series of signs (19), consequently also in series a of table 1. We shall assume that it is the first of group S. Then in table 1 we need no more divide group B into the subgroups  $B_a$  and  $B_b$ , for the whole group B obtains then in all series of table 1 the same sign as group  $B_a$ . The two arrows in line l of table 1 must then reach the vertical line, which separates the B and S from one another.

Now we obtain again four P, T-diagrams, which we may represent

by the figs. 1 and 2 and by two other figures which we obtain when we mutually change the stable and metastable parts of the curves in

ε,

figs. 1 and 2. There is a great difference, however, in the position of the bundle of curves B. In the P, T-diagrams belonging to table 1, the bundle of curves B is viz. divergent in direction of temperature; this is no more the case in the four new diagrams. In each of the new diagrams viz. the whole bundle B goes in the same direction as group  $B_a$ ; in figs. 1 and 2 (and the two other P, T-diagrams) we have to turn the group  $B_b$  so far towards the group  $B_a$  until bundle Bdiverges no longer.

Let us now take the case that all values of  $\mu$  are positive in (14); the series of signs a and b in table 1 then become the same. Table 1 then passes into table 2, so that we obtain again four P, T-diagrams. Let us consider only the case  $\Delta V < 0$  and  $\Delta \eta > 0$ , consequently series i and k of table 2. It appears at once from those series that the curves of the groups A, B, and C all go towards higher pressures and temperatures, starting from the invariant point, and that those of the groups R, S, and T go towards lower pressures and temperatures. It appears from the direction of the arrow in table 2 that the absolute value of  $\frac{dP}{dT}$  increases from the

	A	R	В	S	C	T		
	+		+		+		ΔΥ,0	а 2
Δ <i>P</i> `		+		+		+	Δ <i>V</i> >0	
Δ7 	<del>+</del>		+		+	—	Δη>0	d 
Δ <i>T</i> '	+;···· 	+		+		+	$\Delta \eta < 0$ $\Delta \eta < 0$	e 
ΔP	<i>-</i>	+		+		+	∆ <i>V</i> >0	9
Δ <i>T</i>		+		+		+	∆q<0	h
۵P	+		+		+		∆ <i>V&lt;</i> 0	i
Δ <i>T</i>	+		+		+	·	Δη>0	k 
$\frac{dP}{dT}$						<del>`</del>		

TABLE 2.

first curve of group A to the last curve of group T. This direction of the arrow is in accordance with (16).

The corresponding P, T-diagram is easily found now; it is drawn in fig. 3; three curves are drawn of group A, of each of the other groups only one curve is drawn. The P, T-diagram shows this peculiarity that all curves are situated within two of the four quadrants; it follows from table 2 that this is the case for each of the four P, T-diagrams. The bundle A + T shows here the peculiarity





that it is divergent, as well in the direction of pressure as of temperature, and that it contains two succeeding curves, which make with one another an angle which is larger than  $90^{\circ}$ .

In all our considerations we have supposed up to now that the last group of the series of signs (19) is negative; it may of course also be positive. In order to consider this case we omit the group T from (19) and therefore also from (20) so that it disappears also from the tables, 1 and 2. Now it is evident that again we obtain the same P, T-diagrams which we have above, but that in those the curves of group T are missing. Consequently in the figs. 1 and 2 there is no more a bundle which is divergent in direction of pressure, and in fig. 3 no bundle which is divergent as well in direction of pressure as of temperature.

We represent the isentropical reaction, which may occur between the phases of an invariant point, by:

 $a_1F_1 + a_2F_2 + \ldots + a_pF_p + \ldots + a_{n+2}F_{n+2} = 0 \ \Delta V$ ; 0. (21) and the isovolumetrical reaction by:  $\mu_1 a_1 F_1 + \mu_2 a_2 F_2 + \ldots + \mu_p a_p F_p + \ldots + \mu_{n+2} a_{n+2} F_{n+2} = 0 \quad 0 : \Delta \eta \quad (22)$ 

We take  $a_1$  and  $\mu_1 a_1$  positive and we assume that the order of succession of the phases is chosen in such a way that the condition

$$\mu_1 > \mu_2 > \ldots > \mu_{p-1} > \mu_p > \ldots > \mu_{n+2} \quad \ldots \quad (23)$$

is satisfied.

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Now it appears from our previous considerations that we know, the P, T-diagram completely, viz. the directions of the curves in the invariant point, etc., when we know, besides the reactions (21) and (22) also the changes of volume and entropy  $\Delta V$  and  $\Delta \eta$  occurring with those reactions.

The isentropical reaction (21) alone is not sufficient to find the P, T-diagram, it is indeed sufficient, however, for defining the P, T-diagramtype; this follows viz. at once from the series of signs of this reaction. It is apparent from our previous considerations, that, when the last group of this series of signs is negative, we have to consider it as forming with the first a single group only. In the series of signs (19) the phases of A and T form, therefore, one single group only, which consists of the sub-groups A and T.

It is apparent from the following that the series of signs of the isentropical reaction, defines the P, T-diagramtype. Above we have found viz. that the number of bundles of curves is equal to the number of groups of signs and that each bundle contains as many curves as the group of signs contains phases. Further it was apparent that the bundles in the P, T-diagram and the groups in the series of signs have the same order of succession, if only we take in the series of signs, going from left to right, first the positive — and afterwards the negative groups. [In the series of signs (19) this order of succession is, therefore A + T B, C, R and S, which is in accordance with the figs. 1, 2 and 3].

The series, which indicates the signs of  $\Delta P$  has always either the same or the opposite signs of the series of signs of the isentropical reaction. Hence it follows that all curves, that liave the same signs in the isentropical series of signs, also go in the same direction of pressure. In series of signs (19) the phases of groups B, C and the sub-group A have all the same sign; the corresponding curves must go, therefore, all in the same direction of pressure, starting from the invariant point; in figs. 1 and 2 they go towards lower pressures, in fig. 3 towards higher pressures. The same is true for the curves of groups R, S and the sub-group T. It is apparent from all, this that the series of signs of the isentropical reaction (21)' defines still somewhat more than only the 'type of

the P,T-diagram; it defines viz. also which curves go in the same direction of pressure, starting from the invariant point.

When in (23) all values of  $\mu$  are positive, then all phases in (21) and (22) have the same sign; when  $\mu_1 \ldots \mu_{p-1}$  are positive and  $\mu_p \ldots \mu_{n+2}$  negative, then in (22)  $F_1 \ldots F_p$  have the same sign, but  $F_p \ldots F_{n+2}$  the opposite sign as in (21).

Now we shall examine which changes occur in a P, T-diagram, according to the position of  $F_p$  in the series of signs. In both reaction-equations (21) and (22) going from left to right,  $F_p$  may be the second or the third or the fourth phase, etc., and at last the  $(n + 2^{th})$  phase, consequently the last. When in (23) all values of  $\mu$  are positive, then this phase  $F_p$  is missing.

Let us assume, for fixing the ideas, that the series of signs of reaction (21) is represented by series a of table 1 or 2. Then the P, T-diagram consists of the bundles of curves A + T, R, B, S and C. [Confer e.g. figs 1, 2 and 3].

When in (23) all values of  $\mu$  are positive, so that the phase  $F_p$  is missing, then series b in table 2 represents the series of signs of the isovolumetrical reaction. When  $F_{p'}$  is the  $(n+2)^{\text{th}}$  phase, therefore the last phase of the subgroup T, then in series b of table 2 the last phase obtains the opposite sign; when  $F_p$  is the  $((n+1)^{\text{th}})$  phase, then in series b of table 2 the two last phases obtain the opposite sign, etc.

When  $F_p$  is e.g. the first phase of group S, then in series b of table 1 all phases of groups S, C, and T get the opposite sign. When  $F_p$  is situated within the group B so that this group is divided into two sub-groups  $B_a$  and  $B_b$ , then the series of signs is represented by series b of table 1. When  $F_p$  is the phase  $A_a$ , then in series b of table 2, all phases, except the first one, get the opposite sign.

It is evident that this change of signs in series b has no influence on the series, which indicate the signs of  $\Delta P$ ; the series which define the signs of  $\Delta T$  undergo however similar changes.

Let us now take for the isentropical reaction  $\Delta V < 0$  and for the isovolumetrical reaction  $\Delta \eta > 0$ . When the phase  $F_p$  is missing, then we find, as we have seen above, for the signs of  $\Delta P$  and  $\Delta T$ the series *i* and *k* of table 2 and for the *P*,*T*-diagram fig. 3.

We divide this diagram into four quadrants by two lines which go through the invariant point. We imagine the one-line parallel to the *P*-axis, the other parallel to the *T*-axis. Those four quadrants are indicated in fig. 3 by the encircled figures 1, 2, 3 and 4. Consequently in fig. 3 all curves are situated within the quadrants 1 and 3. : When  $F_p$  is the last phase of group T, then the last sign of series k (table 2) changes. The last curve of group T no more goes then towards lower, but towards higher temperatures, it does go however still towards lower pressures. The corresponding curve of the sub-group T, consequently the curve, which is situated the closest to  $(A_1)$ , turns therefore, in fig. 3 within the second quadrant. The more the phase  $F_p$  goes towards the left, the more curves of the sub-group Tturn within the second quadrant, when  $F_p$  coincides with the first phase of group T, then in fig. 3 this whole sub-group T takes its place within the second quadrant.

As soon as the phase  $F_p$  comes within the group C, a part of bundle C turns within the fourth quadrant, when  $F_p$  coincides with the first phase of group C, then the whole bundle C is situated within the fourth quadrant.

At further movement of the phase  $F_{\rho}$  first some and at last all curves of bundle S come within the second quadrant, afterwards some and at last all curves of bundle B within the fourth quadrant; afterwards some and at last all curves of R within the second quadrant. When  $F_{\rho}$  coincides with  $A_s$ , then curve  $(A_s)$  goes towards the fourth quadrant, and when  $F_{\rho}$  coincides at last with  $A_s$ , then also curve  $(A_s)$  goes within this quadrant,

The displacement of  $F_{\nu}$  from right to left involves, therefore, that the P, T-diagram changes; the curves turn viz. from the third quadrant towards the second and from the first quadrant towards the fourth quadrant. Only the curve  $(A_1)$  remains in the first quadrant. In all there arise, therefore, n+2 different P, T-diagrams, which belong all, however, to the same type.

Consequently it is apparent from the previous considerations. the series of signs of reaction (21) defines the P, T-diagramtype; viz. the number of bundles of curves and their order of succession; the number of curves and their order of succession in each bundle. It defines also which curves go in the same direction of pressure starting from the invariant point. This series of signs does not define, however, the partition of the bundles over the different quadrants and therefore also not which of the n + 2 different P, T-diagrams, belonging to the type, will occur. In order to define this, we have to know also the series of signs of reaction (22).

In our previous considerations we might have taken instead of the `series of signs of the isentropical reaction' also that 'of the isovolumetrical reaction. This is as we have shown in communication VI for an arbitrary pair of reaction-equations, however the same as that of the isentropical reaction. It causes, therefore, which stands to reason, the same P, T-diagramtype.

The only difference is, that the isentropical reaction still defines at the same time which curves go in the same direction of pressure, and the isovolumetrical reaction defines which curves go in the same direction of temperature.

14. Another deduction of the P, T-diagram types.

In previous communications we have already deduced in different ways the P, T-diagram types. A new deduction follows from the previous considerations in chapter (13).

Using the properties 1 and 2 we found:

the series of signs of the isentropical reaction defines the P, Tdiagram type and 'besides which curves go in the same direction of pressure;

the series of signs of the isovolumetrical reaction defines the P, T-diagramtype and besides which curves go in the same direction of temperature.

Hence we may deduce now, that the series of signs of each other reaction, which occurs between the phases of the invariant point, defines also the P, T-diagramtype.

In order to show this we take the arbitrary reactions:

 $l_1F_1 + l_2F_2 + \ldots + l_{n+2}F_{n+2} = 0$  . . . (24)

 $m_1F_1 + m_2F_2 + \ldots + m_{n+2}F_{n+2} = 0$  . . . (25)

Herein  $l_1$  and  $m_1$  are positive, both are written in such order of succession, that we have :

$$\frac{l_1}{m_1} > \frac{l_2}{m_2} > \dots > \frac{l_{n+2}}{m_{n+2}}$$

In each of those reactions a definite change in volume and entropy occurs; we may, therefore, deduce from them the isentropical and isovolumetrical reaction, as is shown in the previous chapter. We write them:

$$a_1F_1 + a_2F_2 + \ldots + a_{n+2}F_{n+2} = 0 \quad \Delta V \ ; \ 0 \ \ldots \ (26)$$

$$\mu_1 a_1 F_1 + \mu_2 a_2 F_2 + \ldots + \mu_{n+2} a_{n+2} F_{n+2} = 0 \quad 0 \; ; \; \Delta \eta \; . \quad (27)$$

In communication VI we have seen that all pairs of reactionequations, which we can deduce from a given pair, have the same series of signs; (24) has, therefore, the same series of signs as (26). As the P, T-diagramtype is defined by the series of signs of (26), it is, therefore, also defined by the series of signs of (24).

Consequently we find, in accordance with our deductions in the previous communications:

the series of signs of each reaction between the phases of the invariant point defines the P, T-diagram type, viz. the number of bundles of curves and their order of succession, the number of curves and their order of succession in every bundle.

This series of signs does not define, however, which curves go in the same direction of pressure (temperature); this is only the case with the series of signs of the isentropical (isovolumetrical) reaction.

Leiden, Inorg. Chem. Lab. (To be continued).

Physics. — "A Test of the Dispersion Theory of Solar Phenomena, derived from Measurements by Adams and St. John on the Displacements of Fraunhofer Lines in the Spectra of the Sun's Limb and of Sun-spots". By Prof. W. H. JULIUS.

(Communicated in the meeting of February 28, 1914, and published in: Versl. Afd. Natuurk. XXII, p. 1243-1265).

This paper was not inserted in "fliese Proceedings, because its principal contents had already been communicated by the writer in the following English publications: "Note on'the General Shift of the FRACNHOFER Lines towards the Red, and on the Distortion of the Lines in the Spectrum of Eccentrically Located Sun-spots", The Observatory, Vol. 37, p. 252, 1914, and: "Radial Motion in Sunspots?", The Astrophysical Journal, Vol. 40, p. 1, 1914. — A French translation of the whole paper will appear in the Archives néerlandaises, 1916.

**Physics.** — "Anomalous Dispersion and Fraunhofer Lines. Reply to Objections". By Prof. W. H. JULIUS.

(Communicated in the meetings of October 30 and November 27, 1915 Cf.: Versl. Afd. Natuurk. XXIV, p. 678 and 865).

This paper has also been published in extenso in the Astrophysical Journal, Vol. 43, p. 43, 1916; and will therefore not appear in these Proceedings.