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$$\frac{dP}{dT} = \frac{D}{C} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (17)$$

, in which D and C have another value than in (14).

Equation (16) is, of course, also satisfied $x = x_1$ and $y = y_1$, hence by a singular point of the system liquid + gas. In this case, D and C and consequently $\frac{dP}{dT}$ obtain the same value as in (14). We now imagine also the P,T-curve of the singular point drawn in fig. 4; we may then easily demonstrate that $\frac{dP}{dT}$ is determined for this curve by (14).

If now, on one of the straight lines ZFZ_1 of fig. 1 a singular point occurs, so that in the equilibrium of solid F + liquid + vapour the two latter ones have the same composition, its P,T-curve must meet the P,T-curve of the singular point in fig. 4.

Such a case occurs when at a definite P and T a singular point appears or disappears on the saturation line of F, so that the saturation line and the correlated vapour line meet each other in that point.

With the aid of the previous formulae we might be able to investigate more accurately the course of the P,T-lines if we expressed the quantities r, s, t etc. by means of the equation of state of Van der Waals, in which a and b must then be considered as functions of x and y.

(*To be continued*).

Chemistry. — "*Equilibria in ternary systems.*" V. By Prof. F. A. H. Schreinemakers.

(Communicated in the meeting of February 22, 1913).

In the previous communication we have disregarded the case when the straight line ZFZ_1 of fig. 1 (IV) coincides with the line XFY of this figure. If a liquid moves from the point F of this figure towards X or towards Y then, as follows from (11^a) (IV) both the numerator and denominator of R are $= 0$.

The value of $\frac{dP}{dT}$ from (11) (IV) then becomes indefinite so that we will consider this case separately. In order to simplify the calculations we again limit ourselves to the case when the vapour contains one component only so that we may put x_1 and $y_1 = 0$.

Our conditions of equilibrium are given in this case by (18) (II) (19) (II). We now write these:

$$x\frac{\partial Z}{\partial x} + y\frac{\partial Z}{\partial y} - Z + Z_1 = 0$$

$$(x-a)\frac{\partial Z}{\partial x} + (y-\beta)\frac{\partial Z}{\partial y} - Z + \zeta = 0 \qquad \qquad \dots \dots (1)$$

If we develop these with regard to x, y, P and T and call $x = a$ and $y = \beta$ we find, if we keep to the same notation as in communication (II):

$$adx + bdy + \tfrac{1}{2}cdx^2 + ddxdy + \tfrac{1}{2}edy^2 + \dots .$$

$$= -CdP + DdT + \dots \dots \dots \dots \dots \dots \dots (2)$$

$$\tfrac{1}{2}rdx^2 + sdxdy + \tfrac{1}{2}tdy^2 + \dots = AdP - BdT + \dots \dots (3)$$

In equation (3) are wanting the terms $dx\,dP$, $dy\,dP$, $dx\,dT$ and $dy\,dT$. A, B, C and D have herein the same significance as in communication II; therein, however we must now call $x = a$, $y = \beta$, $x_1 = 0$ and $y_1 = 0$.

We now allow the liquid, saturated with F and in equilibrium with vapour, to proceed along the line ZFZ, in fig. 1 (IV). For this we call $dy = tg\,\varphi . dx$; from (2) and (3) now follows:

$$(a + b\,tg\,\varphi)\,dx + \tfrac{1}{2}(c + 2d\,tg\,\varphi + e\,tg^2\,\varphi)dx^2 + \dots .$$

$$= -CdP + DdT + \dots . \qquad \dots \dots \dots \dots (4)$$

$$\tfrac{1}{2}(r + 2s\,tg\,\varphi + t\,tg^2\,\varphi)\,dx^2 + \dots = AdP - BdT + \dots \dots (5)$$

We now allow the straight line ZFZ_1 in fig. 1 (IV) to coincide with the line XFY of this figure. As XFY is the tangent in the point F at the liquidum line of the heterogeneous region passing through F, this is determined by:

$$(ar + \beta s)dx + (as + \beta y)dy = adx + bdy = 0.$$

Hence, if in fig. 1 (IV) the line ZFZ_1 coincides with the line XFY, $a + b\,tg\,\varphi = 0$.

If we substitute this value of $tg\,\varphi$ in (4) and (5) we get:

$$-\frac{1}{2b^2} Q\ dx^2 + \dots = -CdP + DdT + \dots \qquad \dots \dots (6)$$

$$\frac{1}{2b^2} S . dx^2 + \dots = AdP - BdT + \dots \qquad \dots \dots (7)$$

In this Q and S have the same value as in communication (II), namely:

$$Q = 2abd - a^2e - b^2c$$

$$S = a^2t + b^2r - 2abs = (rt - s^2)(a^2r + 2a\beta s + \beta^2t)$$

At first, we may limit ourselves to terms recorded in (6) and (7); from this we find:

$$- \frac{dP}{dT} = \frac{B}{A} \frac{Q - \mu S}{Q - \lambda S} \cdot \quad \cdots \cdots \quad (8)$$

in which μ and λ have the same significance as in communication (II), namely

$$\lambda = \frac{C}{A} \text{ and } \mu = \frac{D}{B}$$

and further:

$$dP = \frac{B}{2b^2} \cdot \frac{Q - \mu S}{BC - AD} \, dx^2 \quad dT = \frac{A}{2b^2} \cdot \frac{Q - \lambda S}{BC - AD} \cdot dx^2 \quad \cdots \quad (9)$$

wherein, as in the previous occasion, we take $BC - AD > 0$.

Let us first take a P, x-diagram such as in fig. 2 (IV) and 3 (IV). As $B = H - \eta$ is always positive, dP has the same sign as $Q - \mu S$. In communication (II) we have seen that $Q - \mu S$ is negative when the boiling point line, of the solutions saturated with F passing through F is curved in the point F towards O. The point O here represents the component occurring in the vapour. The boiling point line then has a form like the curve aFb in fig. 1 (II). dP now being negative, the P, x-curve must have a form like $cF'd$ in fig. 2 (IV).

If the boiling point line of the solutions saturated with F is curved in the point F away from the point O so that it presents a form like curve aFb in fig. 2 (II), $Q - \mu S$ will be positive. From the value of dP from (9) it now follows that the P, x-curve must have a form like curve $cF'd$ of fig. 3 (IV).

In order to find the T, x-curve in the vicinity of the point F we must distinguish two cases.

$V > v$ or $A > 0$. If $Q - \lambda S$ is negative, the saturation curve of F under its own vapour pressure is curved in the vicinity of F towards O and, therefore, has a form like curve aFb in fig. 1 (II); dT is now negative and the T, x-curve has a form like curve $cF'd$ in fig. 2 (IV). If $Q - \lambda S$ is positive the saturation line of F under its own vapour pressure will have a form like aFb in fig. 2 (II); dT from (9) is now positive and the T, x-curve has a form like $cF'd$ in fig. 3 (IV).

$V < v$ or $A < 0$. If $Q - \lambda S$ is negative the saturation curve of F under its own vapour pressure will have a form like curve aFb in fig. 4 (II); dT from (9) is now positive and the T, x-curve, has consequently a form like curve $cF'd$ in fig. 3 (IV). If $Q - \lambda S$ is positive the saturation curve of F under its own vapour pressure will have a form like curve aFb in fig. 3 (II); dT from (9) is now negative so that the T, x-curve has a form like curve $cF'd$ of fig. 2 (IV).

79

From the value of $\dfrac{dP}{dT}$ from (8) it follows that this is not equal to $\dfrac{B}{A}$; the P,T-curve corresponding with the straight line XFY of fig. 1 (IV) will, therefore. not meet, in fig. 4 (IV), the melting point line Fd in F. Whereas, as we have stated previously, all the P,T-curves in fig. 4 (IV) meet the melting point line of F in the point F - this is no longer the case when the straight line ZFZ_1 in fig. I (IV) coincides with XFY.

In order to determine this P,T-curve in the vicinity of F more closely we eliminate dx^2 from (6) and (7); we then get:

$$a_1\, dx^3 + \ldots = (AQ - CS)\, dP - (BQ - DS)\, dT + b_1\, dx dP + c_1\, dx dT + \ldots \ldots \quad (10)$$

In this equation, as dP and dT are according to (9) of the order dx^2, $dx dP$, and $dx dT$ are of the order dx^3; the terms omitted are all of the order dx^4 and higher. We now substitute in (10) the value of dx which we can deduce from (7) namely:

$$dx + \ldots = a_2\, \sqrt{AdP - BdT} + \ldots \ldots \quad (11)$$

so that (10) is converted into

$$a_3\, (AdP - BdT)^{3/2} = (AQ - CS)\, dP - (BQ - DS)\, dT +$$
$$+ a_2\, (Adp - BdT)^{1/2}\, (b_1\, dP + c_1\, dT) \quad \ldots \quad (12)$$

in which the terms omitted are of an order higher than dx^3. For (12) we write:

$$(AQ - CS)\, dP - (BQ - DS)\, dT = (b_2\, dP + c_2\, dT)\,(A\, dP - B\, dT)^{1/2} \quad . \quad (13)$$

or:

$$(a_4\, Y - b_4\, X)^2 = (b_2\, Y + c_2\, X)^2\,(AY - BX). \quad . \quad . \quad (14)$$

In order to investigate (14) we take a straight line $a_4\, Y - b_4\, X = d$, in which d is infinitely small so that this line is situated parallel to, and in the immediate vicinity of, the tangent in the point F. Its points of intersection with (14) are given by:

$$a_4\, Y - b_4\, X = d \quad \text{and} \quad (b_2\, Y + c_2\, X)^2\,(AY - BX) = d^2.$$

This is satisfied by:

$$Y = a_5 \cdot d^{2/3} \quad \text{and} \quad X = b_5\, d^{2/3} \quad \ldots \ldots \quad (15)$$

hence: $a_4 a_5 - b_4 b_5 = 0$ and $(b_2 a_5 + c_2 b_5)^2\,(Aa_5 - Bb_5) = 1$

or :

$$\frac{b_5^3}{a_4^3}\,(Ab_4 - Ba_4)\,(b_2 b_4 + c_2 a_4)^2 = 1 \cdot \ldots \ldots \quad (16)$$

$$\frac{a_5^3}{b_4^3}\,(Ab_4 - Ba_4)\,(b_2 b_4 + c_2 a_4)^2 = 1 \cdot \ldots \ldots \quad (17)$$

As X and Y do not change their sign when d does so, it follows

that the P,T-curve has in point F a cusp so that we find at both sides of the tangent in F a branch of this curve. Now $a_4 = A(Q - \lambda S$

$b_4 = B(Q - \mu S)$

$$Ab_4 - Ba_4 = (BC - AD) S$$

so that $Ab_4 - Ba_4$ is positive. From (16) and (17) it now follows that b_5 and $A(Q - \lambda S)$ have the same sign, and the same applies to a_5 and $B(Q - \mu S)$.

In connection with (15) follows:

$$dT \text{ of } X \text{ has the same sign as } A(Q - \lambda S) \quad . \quad . \quad (18)$$

$$dP \text{ „ } Y \text{ „ } \text{ „ } \text{ „ } \text{ „ } \text{ „ } B(Q - \mu S) \quad . \quad . \quad (19)$$

what agrees with (9).

We will now consider some cases.

$V > v$ hence $A > 0$ and $\lambda > 0$; $Q - \lambda S < 0$; $Q - \mu S < 0$.
From

$$\frac{dP}{dT} = \frac{A}{B} \cdot \frac{Q - \mu S}{Q - \lambda S} = \frac{A}{B} \left[1 + \frac{(\lambda - \mu) S}{Q - \lambda S} \right] \quad . \quad . \quad . \quad (20)$$

it follows that $\dfrac{dP}{dT}$ is smaller than $\dfrac{B}{A}$. (From our assumption $BC - AD > 0$ follows namely $\lambda - \mu > 0$): If in fig. 1 the line $d_1 F d$ represents the tangent at the point F of the not drawn melting point line, the P,T-curve XFY will, in its turning point F, have a tangent like the dotted line in fig. 1 passing through F. From (18) and (19) and also from (9) it follows that dP and dT are negative, so that the curve XFY in fig. 1 must proceed from F towards lower temperatures
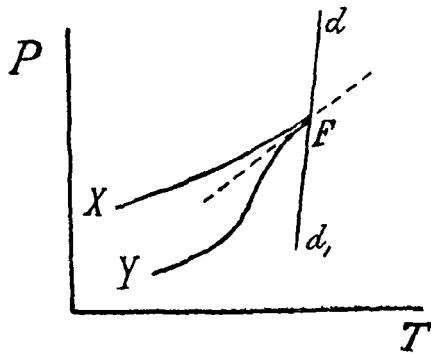

Fig. 1.

and pressures. The latter may be found also by other means. For this we take the minimum melting point of the compound F, therefore the temperature T_F of fig. 1; as $Q - \lambda S < 0$, the saturation line of F under its own vapour pressure has at this temperature a form like curve aFb in fig. 1 (II) in which we must also imagine the tangent XFY to be drawn. As this tangent has only one point in common with the saturation curve, namely the point of contact F, a vertical line passing in fig. 1 through the point F may intersect the curve XFY in the point F only.

We now take a temperature T' somewhat lower than T_F; if

now in fig. 1 (II) we also imagine to be drawn the saturation line under its own vapour pressure of this temperature T', we notice that this intersects the line XFY in two points. In fig. 1, therefore, a vertical line corresponding with the temperature T' must intersect the curve XFY in two points.

If we take a temperature T'' somewhat higher than T_F we find that the vertical line corresponding with this temperature does not intersect the curve XFY in fig. 1.

We now take the boiling point line of the compound F of the pressure P_F, that of a somewhat lower pressure P' and that of a somewhat higher pressure P''. As $Q - \mu S < 0$ it follows that that of the pressure P_F has a form like curve aFb of fig. 1 (II) in which, however, we must imagine the arrows to point in the opposite direction. From a consideration of these boiling point lines it follows that in fig. 1 curve XFY is intersected by a horizontal line corresponding with the pressure P_F in F only, and in two points by a horizontal line corresponding with the somewhat lower pressure P'.

$V > v$ therefore $A > 0$ and $\lambda > 0$; $Q - \lambda S < 0$; $Q - \mu S > 0$.

From (8) it follows that $\dfrac{dP}{dT}$ is negative, from (9) and also from (18) and (19) that dT is negative and dP positive. In fig. 2 d_1Fd again represents the tangent at the point F of the not drawn melting point line; the dotted line passing through the point F is the tangent in the cusp F of curve XFY.

The fact that the curve XFY proceeds from F towards lower temperatures and higher pressures may be deduced also in the following manner. From a consideration of the saturation lines under their own
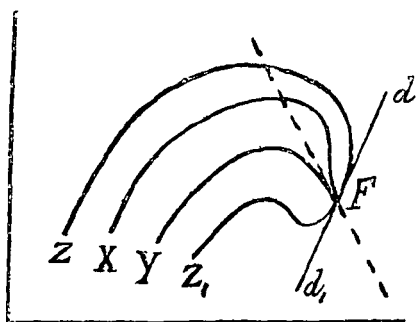

Fig. 2.

vapour pressure of the temperature T_F, the somewhat lower temperature T'', and the somewhat higher temperature T''', it follows that curve XFY in fig. 2 is intersected by the vertical line corresponding with the temperature T_F in F only and in two points by the vertical line corresponding with the somewhat lower temperature T'.

As $Q - \mu S > 0$, the boiling point line of the solutions saturated with F has, at the pressure P_F a form like curve aFb of fig. 2 (II) in which, however, the arrows must be imagined to point in the opposite direction. If we imagine in this figure the tangent XFY,

notice that the latter, besides the point of contact F, has another

points of intersection in common with curve aFb, which both

rtain to a lower temperature than T_F. The horizontal line in fig. 2

esponding with the pressure P_F must therefore intersect the curve

Y, besides in F, also in two other points to the left of point

the one point of intersection must lie on the branch XF, the

r on the branch YF.

now we-take the boiling point line of a somewhat lower pres-

P', this will be intersected in fig. 2 (II) in two points by the

XFY. Hence, the horizontal line in fig. 2 corresponding with

pressure P' must intersect curve XFY in two points.

he boiling point line of a somewhat higher pressure P'' is inter-

ed by the line XFY in four points, of which two lie on the

XF and two on the part YF of this line. The horizontal line

esponding with this pressure P'' in fig. 2 intersects therefore

h of the branches XF and YF in two points.

f in fig. 2 (II) we take a straight line ZFZ_1 whose direction

ers but little from the tangent XFY this will intersect the boiling

at line of the pressure P_F not only in F but also in three other

nts namely two on FZ_1 and another on FZ. The horizontal line

fig. 2 corresponding with the pressure P_F, therefore, intersects

curve ZFZ_1 in F and further the branch ZF in one and the

nch Z_1F in two points. Hence, on branch Z_1F must occur a

nt with a maximum and another with a minimum vapour pressure

$V > v$ therefore $A > 0$ and $\lambda > 0$; $Q - \lambda S > 0$; $Q - \mu S > 0$.

From (20) follows: $\dfrac{dP}{dT}$ positive and greater than $\dfrac{B}{A}$; from (9) and

) from (18) and (19) follows dP and dT positive. The curve XFY

st therefore have a form as drawn in fig. 3 wherein d_1Fd again

resents the tangent in the point F at the omitted melting point

; the dotted line passing through F represents the tangent in the
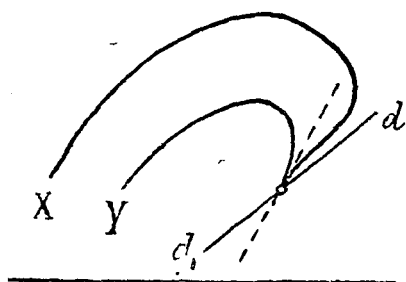
p F at curve XFY.

Fig. 3.

The fact that curve XFY in fig. 3 must proceed from F towards higher temperatures and pressures is again evident from a consideration of the saturation line of the temperature T_F under its own vapour pressure, and of the boiling point line of the solutions saturated with F of the pressure P_F. For both curves have in this case a form

like in fig. 2 (II) so that the tangent XFY besides meeting the curve aFb in the point F, also intersects this in two other points. In harmony with fig. 3 we find that the vertical line corresponding with the temperature T_F must intersect the curve XYF in two points above F, and the horizontal line corresponding with the pressure P_F must intersect this curve in two points at the left of F.

From a consideration of the straight lines whose direction differs but little from the tangent XFY it follows that their P,T-curves in fig. 3 must exhibit on the one branch proceeding from F, a point with a maximum temperature and one with a maximum pressure, and on the other branch, besides two similar points, also one with a minimum temperature and a minimum pressure.

The deduction and further consideration of the other cases I must leave to the reader.

We can also determine the course of the saturation lines under their own vapour pressure and of the boiling point lines of the solutions saturated with solid matter, which has been discussed in the previous communications, in a different manner.

For the stability requires that if we convert a system, at a constant temperature, into another having a smaller volume the pressure must increase; if converted into one with a greater volume the pressure must decrease.

We may also perceive this in the following manner. At the pressure P exists the system S which is converted at the pressure $P + dP$ into the system S'. We represent the ζ of the system S, at the pressures P and $P + dP$ by ζ_P and ζ_{P+dP}, that of the system S' by ζ'_P and ζ'_{P+dP}.

As at the pressure P the system S is the stable one, it follows that $\zeta_P < \zeta'_P$.

As at the pressure $P + dP$ S' is the stable one it follows that $\zeta'_{P+dP} < \zeta_{P+dP}$. If we represent the volumes of S and S' at the pressure P by V and V' the latter condition can also be expressed by :

$$\zeta'_P + V'dP < \zeta_P + VdP.$$

From this now follows in connection with the first condition :

$$V'dP < VdP$$

hence, $V' < V$ if dP is positive and $V' > V$ if dP is negative.

The volume V'' of the system S', is, at the pressure $P + dP$, like $V' + \dfrac{dV'}{dP}dP$, in which $\dfrac{dV'}{dP}$ is negative; from this now follows :

$V' < V$ if dP is positive and $V'' > V$ if dP is negative.

Hence, if we compare two systems S and S' which are converted into each other, at a constant temperature, by a small alteration in pressure, it follows from the foregoing that:

If S exists at a higher pressure than S', the volume of S is smaller, if S exists at a lower pressure than S', the volume of S is greater than that of S'. And reversally :

if S has a smaller volume than S' it exists at a higher, if it has a greater volume than S' it exists at a lower pressure than S'.

We may express this also a follows :

a system S is converted by increase in pressure into a system with a smaller and on reduction in pressure into a system with a greater volume. And reversally : ·

if a system S is converted into another with a smaller volume, the pressure must increase, and if converted into one with a greater volume the pressure must decrease. We may then compare the volumina of the two systems either both under their own pressure or both under the pressure of the system S, or both under the pressure of the system S'.

It is evident that a similar consideration applies to two systems S and S' which, at a constant pressure, are converted into each other by a small change in temperature. For the case in question, the equilibrium : solid + liquid + gas we may also deduce the above rules in a different manner. For this, we take at the temperature T and the pressure P a complex consisting of n quantities $F + m$ quantities $L, + q$ quantities G. We now allow a reaction to take place between these phases at a constant T and P wherein

$(n + dn)$ quantity $F + (m + dm)$ quantity $L' + (q + dq)$ quantity G' is formed and in which L' and G' differ but infinitesimally from L and G.

The increase in volume Δ in this reaction is then determined by :

$$v dn + V dm + V_1 dq + m \frac{\partial V}{\partial x} dx + m \frac{\partial V}{\partial y} dy + q \frac{\partial V_1}{\partial x_1} dx_1 + q \frac{\partial V_1}{\partial y_1} dy_1.$$

As the total quantity of each of the three components remains unchanged in this reaction we have:

$$\alpha dn + x dm + x_1 dq + m dx + q dx_1 = 0$$
$$\beta dn + y dm + y_1 dq + m dy + q dy_1 = 0$$
$$dn + dm + dq = 0.$$

After elimination of dn, dm, and dq we find :

$$m \{(y_1 - \beta) A + (\beta - y)(A + C)\} dx - m \{(x_1 - \alpha) A + (\alpha - x)(A + C)\} dy$$
$$-q \{(y - \beta) A_1 + (\beta - y)(A_1 + C_1)\} dx_1 + q \{(x - \alpha) A + (\alpha - x_1)(A_1 + C_1)\} dy_1$$
$$= \{(x_1 - \alpha)(y - \beta) - (x - \alpha)(y_1 - \beta)\} \Delta$$

which for the sake of brevity we write :

$$m A_y dx - m A_x dy - q A_{y_1} dx_1 + q A_{x_1} dy_1 = E . \Delta$$

We will choose the new system $F + L' + G'$ in such a manner that it is in equilibrium at the temperature T and the pressure $P + dP$. Then, as follows from our previous communications, dx, dy, dx_1 and dy_1 are determined by:

$$[(x - \alpha) r + (y - \beta) s] dx + [(x - \alpha) s + (y - \beta) t] dy = A dP$$

$$[(x_1 - \alpha) r + (y_1 - \beta) s] dx + [(x_1 - \alpha) s + (y_1 - \beta) t] dy = (A + C) dP$$

and two corresponding equations which determine dx_1 and dy_1.

From this we find:

$$E (rt - s^2) dx = - (sA_x + tA_y) dP \qquad E (rt - s^2) dy = (rA_x + sA_y) dP$$

$$E (r_1 t_1 - s_1^2) dx_1 = (s_1 A_{x_1} + t_1 A_{y_1}) dP \quad E (r_1 t_1 - s_1^2) dy_1 = - (r_1 A_{x_1} + s_1 A_{y_1}) dP.$$

After substitution we find:

$$m \frac{rA^2_x + 2sA_xA_y + tA^2_y}{rt - s^2} + q \frac{r_1 A^2_{x_1} + 2s_1 A_{x_1} A_{y_1} + t_1 A^2_{y_1}}{r_1 t_1 - s_1^2} = - E^2 \frac{\Delta}{dP}$$

so that Δ and dP must have the opposite sign.

In the above relation Δ represents the change in volume if both systems are compared at the same pressure P; if, when the new system is taken at the pressure $P + dP$, the change in volume is represented by Δ', we get:

$$\Delta' = \Delta + \frac{dV_t}{dP} \cdot dP$$

in which V_t represents the total volume of the new system at the pressure P. From this follows that Δ' and Δ have always the same sign and Δ' and dP always the opposite one.

Let us now consider the system $F + L + G$ at a constant temperature, namely the saturation line of F under its own vapour pressure and its conjugated vapour line. These are respresented in fig. 7 (I), 11 (I), 12 (I) and 13 (I) by the curves $Mamb$ and $M_1 a_1 m_1 b_1$.

We now take the system $S = F + L + G$ which is stable at the pressure P and the system $S' = F + L' + G'$ which is stable at the pressure P'. If now the volume of S' is smaller than that of S, P' will be greater than P; if the volume of S' is greater than that of S, P' will be smaller.

Reversally, if P' is greater than P the volume of S' is smaller than that of S; if P' is smaller than P the volume of S' will be greater.

All this applies, as we have noticed previously, if S and S' can be converted into each other and when P and P' differ but little.

We now omit from the system S the vapour so that we retain $F + L$ only. We now can distinguish two chief cases, depending on whether a phase reaction is possible, or impossible, between the three phases of the system $F + L + G$.

A. No phase reaction is possible The three phases form the apexes of a three phase triangle such as, for instance, Faa_1, in fig. 4 (I). We may further distinguish three other cases, namely

1. $F + L$ is converted by a change of pressure in the one direction into $F + L' + G'$ and by a change of pressure in the other direction, into $F + L''$. Hence on change of pressure in the one direction vapour is formed, but not when in the other direction.

2. $F + L$ is converted by a change of pressure in the one direction into $F + L' + G'$, and by a change of pressure in the other direction into $F + L'' + G''$. Hence, vapour is formed on increase as well as on decrease of pressure.

3. $F + L$ is converted by a change of pressure in the one direction into $F + L'$ and by a change in the other direction into $F + L''$. Hence, no vapour is formed either on increase or on reduction of pressure. The case cited in 1 is the one generally occurring, those mentioned in 2 and 3 only occur exceptionally.

B. A phase reaction is possible. The three phases are now represented by three points situated on a straight line. The system $F + L$ can then be converted by a change in volume unaccompanied by a change of pressure, into the system $F + L + G$. So long as these three phases are adjacent, neither the pressure nor the composition of liquid or vapour is altered by a change in volume; all that happens is a reaction between the three phases. As regards this reaction, we can now distinguish three cases:

1. $F \rightleftarrows L + G$.

In the graphic representation, the point F is situated between the points L and G. On a change in volume in the one direction solid matter is deposited; when in the other direction this disappears.

2. $F + L \rightleftarrows G$.

In the graphic representation the point G is now situated between the points F and L. On change in volume in the one direction, gas is formed; when a change takes place in the other direction the gas disappears.

3. $F + G \rightleftarrows L$.

In the graphic representation the point L is now situated between the points F and G. On change in volume in the one direction, liquid is formed, when in the other direction this disappears. If, in one of the reactions sub *A* and *B* vapour is formed, the volume will as a rule become larger and if vapour disappears it will become smaller. The reverse, however, may also occur as will be perceived in the following manner. In order to convert $F + L$ into $F + L' + G'$ we first of all form from L a little of the vapour G'; the liquid L

,is hereby converted into a somewhat different liquid L''. Now, so-as to convert L'' into L' either solid F must dissolve in L'' or crystallise from the same. If now this solution or crystallisation of F is accompanied by a great decrease in volume, this may exceed the increase of volume occurring in the generation of the vapour; the system $F + L$ is then converted with decrease in volume into $F + L' + G'$.

Such a conversion may be particularly expected in points of the saturation line under its own vapour pressure which are adjacent to the point F. The liquid then differs but little in composition from the solid substance F so that in order to slightly alter the composition of the liquid large quantities of solid substance must either dissolve or else crystallise out. Moreover, if in this case the solid substance F melts with increase in volume, the latter will increase on addition of F and decrease on the separation of the same. If F melts with decrease in volume, the volume will decrease on addition of F and increase when this substance is deposited.

Hence, in the case of points of the saturation line of F under its own vapour pressure situated in the vicinity of F, the system $F + L$ can be converted with decrease in volume into $F + L' + G'$:

1. if in that conversion solid matter separates and if this melts with increase of volume $(V > v)$.

2. if in that conversion solid matter dissolves and if this melts with decrease of volume $(V < v)$.

We may now apply the above considerations in different ways. If, for instance, we take the change in volume along the saturation line under its own vapour pressure as known, we may determine the change in pressure; if the value of the latter is known we may determine the change in volume. We now merely wish to demonstrate that these views support our previous considerations. We first take the case when all the points of the saturation line under its own vapour pressure are removed comparatively far from the point F, so that the two-phase complex $F + L$ is converted with increase in volume into the three-phase equilibrium $F + L' + G'$.

We represent the equilibrium $F + L + G$ by the three-phase triangle Faa_1 of fig. 3 (1) or 4 (1); the two-phase complex $F + L$ is then represented by a point of the line Fa.

As, according to our assumption the system $F + L$ which exists at the pressure P, is converted with increase in volume into the three-phase equilibrium $F + L' + G'$ existing at the pressure P', the new pressure P' must be smaller than P.

From a consideration of fig. 3 (I) or 4 (I) it follows at once that the new liquid L' must be situated in such a way that the new

conjugation line FL' is situated at the other side of Fa than the point a_1. From all this it follows that, on reduction in pressure, the conjugation line solid-liquid turns away from the vapour point, and that on increase in pressure it turns towards the same.

We notice at once that this is in conformity with the change in pressure along the saturation line under its own vapour pressure in fig. 7 (I) and 11 (I).

For if we allow the conjugation line solid-liquid to turn away from m towards M or along maM or along mbM, it always turns towards the vapour point while the pressure increases. We now take the case when the saturation line of F under its own vapour pressure is situated, in part, adjacent to the point F. We now distinguish two cases depending on whether the substance F melts with increase or decrease in volume.

$V > v$. The substance melts with increase in volume. For these points of the saturation line under its own vapour pressure which are removed far from the point F, $F+L$ will be converted into $F+L'+G'$ with increase of volume; for points in the vicinity of F, $F+L$ may pass into $F + L' + G'$ with decrease in volume, provided that, as stated above, much solid matter is deposited in this conversion.

We have already seen above in what direction the conjugation line solid-liquid turns when $F + L$ is converted with increase in volume into $F + L'.+ G'$; we may now readily deduce that this conjugation line will turn in the opposite direction if that conversion takes place with decrease in volume. Hence, we find the following: we take from the three-phase equilibrium $F + L + G$ the two-phase complex $F + L$; if $F + L$ is converted into $F + L' + G'$ with increase of volume the conjugation line solid-liquid on reduction of pressure turns away from the vapour point; at an increased pressure it turns towards the vapour point.

If $F + L$ is converted into $F + L' + G'$ with decrease in volume the conjugation line solid-liquid turns in the opposite direction.

Let us now consider the saturation line of fig. 12 (I) under its own vapour pressure of which a part is adjacent to the point F and which, as we have seen before, applies to the case when the substance F expands on melting ($V > v$). We draw through F two tangents at this curve Mm; we will call these points of contact R and R'.

As seen from the figure, the conjugation line solid-liquid now moves, on increase in pressure, on the branch RMR' towards the vapour point; on the branch RmR', however, it moves away from the vapour point. In connection with the above, it now follows that the conversion of $F + L$ into $F + L' + G'$ is accompanied

on .the branch RMR' with an increase and on branch RmR' with a decrease in volume.

In the points of contact themselves where both branches amalgamate, the case sub A 3 now occurs. Let us take the two-phase complex $F +$ liquid R. We now see that, on increase as well as on reduction in pressure, the conjugation line F-liquid R gets outside the new three-phase triangle so that no vapour can be formed.

Let us now see what happens in a similar point of contact R if the pressure changes but infinitesimally. At this infinitesimal change of pressure, the liquid then moves at an infinitesimal rate along the tangent FR either towards or away from F. The only thing what happens is that in the liquid a little F is dissolved, or else crystallised from the same, without any vapour being formed.

If now a substance F melts with increase in volume and, therefore, in this case also dissolves with increase in volume, it will crystallise out on increase in pressure and get dissolved on reduction of the same. This also is in harmony with the change in pressure along the saturation line under its own vapour pressure in the point R of fig. 12 (I): on elevation of the pressure the liquid moves, starting from R, from the point F; this signifies that solid matter is being deposited. On reduction of pressure the liquid moves from R towards the point F; this means that solid matter is being dissolved.

The fact that in a point of contact R no vapour takes part in the reaction may be also demonstrated in the following manner. We again take at the pressure P a system S consisting of:

n quantities $F + m$ quantities $L + q$ quantities G;

at the pressure $P + dP$ is formed thereof the system S' consisting of:

$(n + dn)$ quantities $F + (m + dm)$ quantities $L' + (q + dq)$ quantities G'

From the three relations already employed for this and which indicate that the quantity of each of the three components remains the same in this conversion we can deduce:

$$Edn = - m \{(y_1 - y)dx - (x_1 - x)dy\} - q \{(y_1 - y)dx_1 - (x_1 - x)dy_1\}$$

$$Edq = m \{(\beta - y)dx - (\alpha - x)dy\} + q \{(\beta - y)dx_1 - (\alpha - x)dy_1\}$$

$$Edm = m \{(y_1 - \beta)dx - (x_1 - \alpha)dy\} + q \{(y_1 - \beta)dx_1 - (x_1 - \alpha)dy_1\}$$

in which all the letters have again the same meaning as before.

If now we proceed at the pressure P from the system $F + L$ we must call $q = 0$; we then obtain:

$$Edn = - m \{(y_1 - y)dx - (x_1 - x)dy\}$$

$$Edq = m \{(\beta - y)dx - (\alpha - x)dy\}$$

$$Edm = m \{(y_1 - \beta)dx - (x_1 - \alpha)dy\}.$$

Hence, as a rule dn, dm and dq are not 0; if, however, we can draw through the point x,y of the saturation curve under its own vapour pressure a tangent passing through the point F we find

$$\frac{dy}{dx} = \frac{\beta - y}{a - x}$$

hence $dq = 0$, whereas dn and dm differ from nil. It means that no vapour takes part in the reaction so that the system $F + L$ is converted into another system $F + L'$ devoid of vapour.

We have noticed previously that the saturation line of the substance F under its own vapour pressure which passes through the point F can have a form like the curve Fab of fig. 2 (II). At a somewhat lower temperature this curve still possesses about this

form but it becomes circumphased. In fig. 4 a part of this curve has been drawn. So long as the point F is situated sufficiently close to this curve we can draw through F four tangents at this curve with the points of contact R, R', X and X'. Let us now imagine in fig. 4 the saturation line under its own vapour pressure to be shifted further towards the left and also its correlated vapour line to be drawn.
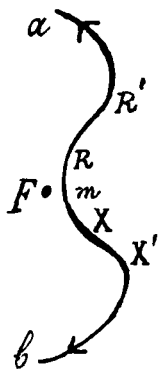
We now allow a conjugation line solid-liquid to turn from m in such a direction that the pressure increases. Let us now proceed from m towards a. On

Fig. 4. the branch mR, the conjugation line F-liquid turns towards the vapour point, from R to R' away from the vapour point and from R' to a and further on it again turns towards the vapour point. The same applies to the branch $mXX'b$ on which, in the points X and X', the direction of the rotation of the conjugation line gets reversed. The conversion of $F + L$ into $F + L' + G'$ then takes place on branch mR and mX (and mX) with increase in volume, on branch RR' (and XX') with decrease in volume and on branch $R'a$ (and $X'b$) again with increase in volume. In the point of contact R now appears the case sub A 2 and in the point of contact R' the case cited sub A 3. Let us take for instance the two-phase complex $F +$ liquid R. We now notice that on increase as well as on decrease in pressure the conjugation line F-liquid R gets situated within the new three-phase triangle so that $F +$ liquid R is converted into $F + L' + G'$.

On an infinitesimal change in pressure, nothing takes place in the points R and R' but a solution, or a crystallisation of solid matter. As F melts with increase in volume and in this case also dissolve

with increase in volume, crystallisation will occur at an increased and solution at a reduced pressure. This is, moreover, in conformity with the change in pressure in the points R and R' along the saturation line under its own vapour pressure.

The same considerations as the above-cited may be also applied to the case when the substance F melts with decrease in volume.

(*To be continued*).

Chemistry. — "*The dynamic Allotropy of sulphur.*" (Fifth commu-
nication.) [1] By Dr. H. R. KRUYT. (Communicated by Prof.
P. VAN ROMBURGH.)

(Communicated in the meeting of January 25, 1913).

As point 5 of the résumé of my third paper on the above subject I wrote in 1909:

"Es wurden neue Untersuchungen über den Einfluss des S_μ auf den Umwandlungspunt $S_{ih} \rightleftarrows S_{mon}$ in Aussicht gestellt".

In connection therewith I wrote [2] in July 1911 :

"Dr. VAN KLOOSTER of Groningen has this year started that investigation and although the provisional result is only of a qualitative character as yet it may be taken for granted . . . ."

Nevertheless, Messrs. SMITS and DE LEEUW published, in these Proceedings (XIV, p. 461), an investigation concerning this question.

In the Zeitschr. f. Electrochemie [3] I communicated, in connection with some other questions regarding sulphur, that the above investigation had been continued and brought to a close, also to what conclusions it had led and that a detailed communication would soon appear; recently it appeared as the fourth communication in this series

Meanwhile, Dr. DE LEEUW (Proc. XV p. 584) has contradicted the above cited conclusions and condemned the still unpublished investigations in advance.

Although I should have every reason not to take any notice of that paper, two reasons in particular have induced me to repeat and extend

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[1] For the previous communications see Zeitschr. f. physik. Chem. viz. I : **64**, 513 (1908); II : **65**, 486 (1909); III : **67**, 321 (1909) and IV; **81**, 726 (1913).

[2] Chem. Weekbl. **8**, 643 (1911).

[3] Z. f. Elektrochemie **18**, 581 (1912).