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at infinity of the  $x$ -axis and having the parabola  $\mathcal{P}_1$  as directrix (i.e. enveloping the parabola  $\mathcal{P}_1$ ). The parameter (of the perpendicular transverse section) of this cylinder is the reciprocal value of the weight  $g_x$  of the variable  $x$ .

The equipotential lines in  $z=0$  are the homothetic ellipses  $[p_i V_i^2] = \text{const.}$  Such an ellipse is the locus of the points of equal  $\epsilon$ .

When the (rigorous) equation of condition is:  $x = \text{const.}$  the parabola  $\mathcal{P}_1$  is parallel to the plane  $x=0$ . The tangent cylinder is then infinitely narrow; its parameter is 0, the weight of  $x$  is infinite.

**Chemistry.** — “*Equilibria in ternary systems.* XVI By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of May 30, 1914).

Now we shall consider the case that the vapour contains two components

We assume that of the components  $A$ ,  $B$ , and  $C$  only the component  $B$  is exceedingly little volatile, so that practically we may say that the vapour consists only of  $A$  and  $C$ . This is for instance the case when  $B$  is a salt, which is not volatile, and when  $A$  and  $C$  are solvents, as water, alcohol, etc

Theoretically the vapour consists only of  $A + B + C$ , herein the quantity of  $B$  is however exceedingly small in comparison with the quantity of  $A$  and  $C$ . so that the vapour consists practically totally of  $A$  and  $C$ .

When, however, we consider complexes in the immediate vicinity of the point  $B$ , the relations become otherwise. The solid or liquid substance has viz. always a vapour-pressure, although this is sometimes immeasurably small, therefore, a vapour exists however, which consists only of  $B$ , without  $A$  and  $C$ . When we now take a liquid or a complex in the immediate vicinity of point  $B$ , the quantity of  $B$  in the vapour is then still also large and is not to be neglected in comparison with that of  $A$  and  $C$ .

Consequently, when we consider equilibria, not situated in the vicinity of point  $B$ , then we may assume that the vapour consists only of  $A$  and  $C$ , when these equilibria are situated, however, in the immediate vicinity of point  $B$ , we must also take into consideration the volatility of  $B$  and we must consider the vapour as ternary.

When we consider only the occurrence of liquid and gas, then, as we have formerly seen, three regions may occur, viz. the gas-region, the liquid-region and the region  $L-G$ . This last region is

separated by the liquid-curve from the liquid-region and by the vapour-curve from the vapour-region. As long as the liquid-curve is not situated in the vicinity of point  $B$ , the corresponding vapour-curve will be situated in the immediate vicinity of the side  $AC$ . Consequently the vapour-region is exceedingly small and is reduced just as the vapour-curve, practically to a part of — or to the whole side  $AC$ . Therefore we shall call this vapour-curve the straight vapour-line of the region  $L - G$  in the following. Consequently we distinguish within the triangle practically only two regions, which are separated by the liquid-curve, viz. the liquid-region and the region  $L - G$ ; the first reaches to the point  $B$ , the latter to the side  $AC$ . The conjugation-lines liquid-gas end, therefore, all practically on the side  $AC$ .

When the liquid-curve comes, however, in the immediate vicinity of point  $B$ , so that there are liquids, which contain only exceedingly little  $A$  and  $C$ , then the quantity of  $B$  in the corresponding vapours will no more be negligible with respect to  $A$  and  $C$ . The vapour-curve will then also be situated further from the side  $AC$ , so that also the vapour-region becomes larger. At sufficient decrease of pressure or increase of temperature the vapour-region will cover even the entire component-triangle. In that case we must, therefore, certainly distinguish between the three regions, of which the movement, occurrence and disappearance have been treated already previously.

In order to deduce the equilibrium  $F + L + G$ , we may act now in the same way as we did before for a ternary vapour. We distinguish the following cases.

1. The solid substance is a ternary compound.
2. The solid substance is a binary compound of two volatile components.
3. The solid substance is a binary compound of one volatile and one non-volatile component.
4. The solid substance is one of the components.

1. We consider firstly the case sub 1, viz. that the solid substance is a ternary compound; this is for instance the case with the compound  $\text{Fe}_2\text{Cl}_6 \cdot 2\text{HCl} \cdot 12\text{H}_2\text{O}$ .

Now we imagine for instance in fig. 7, 11, 12, or 13 (I) the component-triangle  $ABC$  to be drawn in such a way that the point  $H'$  is situated within this triangle. Curve  $Mm$  can then again represent the saturation-curve under its own vapour-pressure of  $F$ ,

the corresponding vapourcurve  $M_1m_1$  is then, however, no more a curve situated within the triangle  $ABC$ , but it becomes a straight line, which is situated on one of the sides of the triangle. We shall call this line the straight vapourline of the compound  $F$ . When  $A$  and  $C$  are the two volatile components, then this straight vapourline is situated on the side  $AC$ . As not a single liquid of curve  $Mm$  can be in equilibrium with a vapour, which consists of pure  $A$  or of pure  $C$ , the points  $A$  and  $C$  can never be situated on the straight vapourline. From this follows: the straight vapourline of the ternary compound  $F$  covers only partly the side  $AC$  and in such a way that it covers neither  $A$  nor  $B$ .

2. The solid substance is a binary compound, of two volatile components. We take a binary compound  $F$  of  $B$  and  $C$  (fig. 1) so that  $B$  and  $C$  now represent the two volatile components and  $A$  the non-volatile component.

In order to deduce the saturationcurve under its own vapour-pressure we may act again in the same way as we did before for the general case. For this we take a definite temperature  $T$  and a pressure  $P$  in such a way that no vapour can be formed and the isotherm consists only of the saturationcurve of  $F$ . This is represented in fig. 1 by  $pq$ .

At decrease of  $P$  the region  $L-G$  occurs; such a region is represented in fig. 1 by  $Cdee_1$  with the liquid-curve  $de$  and the straight vapourline  $Ce_1$ . The liquid  $e$  is in equilibrium with the vapour  $e_1$ , the liquid  $d$  with the vapour  $C$  and with each liquid of curve  $ed$  a definite vapour of the straight vapourline  $Ce_1$  is in equilibrium.

We may distinguish three cases with respect to the occurrence of this region  $L-G$ .

a. In the equilibrium  $L-G$  of the binary system  $BC$  a point of maximum-pressure occurs. The heterogeneous region  $L-G$  arises in a point of the side  $BC$ .

b. In the equilibrium  $L-G$  of the binary system  $BC$  a point of minimum-pressure occurs; one heterogeneous region arises in  $B$  and one in  $C$ , which come together at decrease of  $P$  in a point of  $BC$ .

c. In the equilibrium  $L-G$  of the binary system  $BC$  neither a point of maximum- nor a point of minimum-pressure occurs; the heterogeneous region arises in  $B$  or in  $C$ .

Here we consider only the last case and we assume in this case that  $C$  is more volatile than  $B$ ; after this the reader can easily

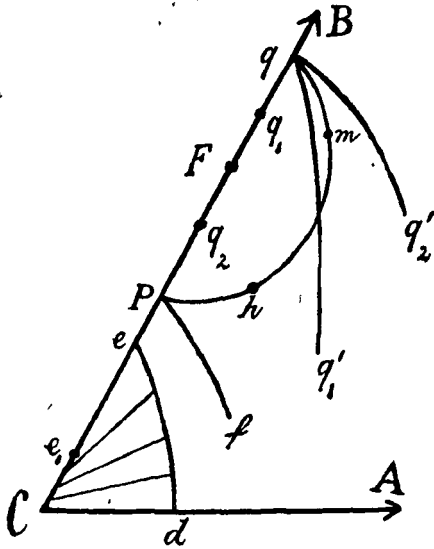


Fig. 1.

deduce the two other cases. At decrease of  $P$  the heterogeneous region arises, therefore, in the angular point  $C$  (fig. 1) and it expands, while curve  $pq$  changes of course its form and position, over the triangle. Under a definite pressure the terminating point  $e$  of the liquid-curve coincides with the terminating point  $p$  of the saturation curve, under a definite other pressure  $e$  coincides with  $q$ .

When  $e$  coincides with  $q$ , we may imagine in fig. 1 that the liquid-curve is represented by  $qq'_2$  or by  $qq'_1$ ; in the latter case it intersects the curve  $qp$ , in the first

case it is situated outside this curve. When  $e$  coincides with  $p$ , we may imagine that the liquid-curve is represented either by  $pf$  (fig. 1) or by a curve, not drawn in the figure, which intersects  $pq$ . Now we shall examine which of these cases may occur.

To the equilibrium between a ternary liquid  $x, y, 1-x-y$ , and a binary vapour  $y_1, 1-y_1$  the conditions are true:

$$Z - x \frac{\partial Z}{\partial x} - (y - y_1) \frac{\partial Z}{\partial y} = Z_1 \text{ and } \frac{\partial Z}{\partial y} = \frac{\partial Z_1}{\partial y_1} \dots \dots (1)$$

Let us firstly consider the region  $L-G$  in the immediate vicinity of the point  $C$ . As  $x, y$ , and  $y_1$  are then infinitely small, we put:

$$Z = U + RTx \log x + RTy \log y \text{ and } Z_1 = U_1 + RTy_1 \log y_1$$

The two conditions (1) pass then into:

$$U - x \frac{\partial U}{\partial x} - y \frac{\partial U}{\partial y} - U_1 + y_1 \frac{\partial U_1}{\partial y_1} - RT(x + y - y_1) = 0 \dots (2)$$

$$\frac{\partial U}{\partial y} + RT \log y = \frac{\partial U_1}{\partial y_1} + RT \log y_1 \dots \dots (3)$$

Under a pressure  $P_C$  the region  $L-G$  in fig. 1 consists only of the point  $C$ , and, therefore,  $x = 0, y = 0$  and  $y_1 = 0$ ; then the unary equilibrium: liquid  $C +$  vapour  $C$  occurs. This is fixed by  $Z = Z_1$  or  $U = U_1$ , wherein  $x = 0, y = 0$  and  $y_1 = 0$ .

Let in fig. 1 the region  $Clee_1$  make its appearance under a pressure  $P_C + dP$ ; the points  $e_1, e$ , and  $d$  are then situated in the imme-

vicinity of  $C$ , now we equate  $x = \xi$ ,  $y = \eta$  and  $y_1 = \eta_1$ . From follows:

$$\eta_1 = K\eta \dots \dots \dots (4)$$

wherein  $K$  is a constant fixed by (3). When we assume, as in fig. 1, that  $C$  is more volatile than  $B$ , the point  $e_1$  is situated between  $C$  and  $e$  and  $K$  is, therefore, smaller than 1.

Now we equate in (1)  $P = P_C + dP$ ,  $x = \xi$ ,  $y = \eta$  and  $y_1 = \eta_1$ ; at the point  $C$   $U = U_1$  is satisfied, it follows, that:

$$-RT[\xi + \eta - \eta_1] + [V - V_1] dP = 0$$

$$\xi + (1-K)\eta = -\frac{V_1 - V}{RT} dP \dots \dots \dots (5)$$

in the immediate vicinity of the angular point  $C$  (fig. 1) curve  $ed$  is, therefore, a straight small line. We find from (5) for the length of parts  $Cd$  and  $Ce$ :

$$Cd = -\frac{V_1 - V}{RT} dP \text{ and } Ce = -\frac{V_1 - V}{RT(1-K)} dP \dots \dots (6)$$

As  $V_1 - V > 0$  and  $1 - K > 0$ , it follows from (6) that  $Cd$  and  $Ce$  are positive, when  $dP$  is negative. At decrease of pressure curve  $cd$  therefore, within the triangle. From (6) follows:  $Cd : Ce = (1 - K)$ ; as  $K = \eta_1 : \eta = Ce_1 : Ce$ , we find:  $Cd = ee_1$ .

In order to examine the liquidcurves going through the points  $d$  and  $e_1$  (fig. 1) in the vicinity of these points, we put in (1):

$$Z = U + RTx \log x \dots \dots \dots (7)$$

then find:

$$U - x \frac{\partial U}{\partial x} - (y - y_1) \frac{\partial U}{\partial y} - RTx - Z_1 = 0 \text{ and } \frac{\partial U}{\partial y} = \frac{\partial Z_1}{\partial y_1} \dots (8)$$

for the liquidcurve of the region  $L-G$  we find from this:

$$[xr + (y - y_1)s + RT] dx + [xs + (y - y_1)t] dy = 0 \dots (9)$$

for the direction of this liquidcurve in its end on the side  $BC$  (before  $x = 0$ ) we find:

$$\frac{dy}{dx} = -\frac{(y - y_1)s + RT}{(y - y_1)t} \dots \dots \dots (10)$$

then we call  $\varphi$  the angle, which this tangent forms with the side  $BC$  (taken in the direction from  $B$  towards  $C$ ), we have, when we imagine the componenttriangle rectangular in  $C$ :

$$\text{tg } \varphi = \frac{(y - y_1)t}{(y - y_1)s + RT} \dots \dots \dots (11)$$

For the saturationcurve under a constant pressure of  $F$ , consequently for curve  $pq$ , we find:

$$Z - x \frac{\partial Z}{\partial x} + (\beta - y) \frac{\partial Z}{\partial y} - \zeta = 0 \quad \dots \quad (12)$$

or after substitution of the value of  $Z$  from (7):

$$[xr + (y - \beta) s + RT] dx + [xs + (y - \beta) t] dy = 0 \quad \dots \quad (13)$$

When we call  $\psi$  the angle which forms the tangent in  $p$  or  $q$  with the side  $BC$  (taken in the direction from  $B$  towards  $C$ ), we find:

$$\operatorname{tg} \psi = \frac{(y - \beta) t}{(y - \beta) s + RT} \quad \dots \quad (14)$$

Let us now consider these two tangents in the point  $p$  of fig. 1. In this point  $y - \beta < 0$  and  $y - y_1 > 0$ .

The denominators of (11) and (14) have, therefore, either opposite sign or they are both positive, so that we may distinguish three cases. In each of these cases we find  $\varphi < \psi$ ; the liquidcurve of the region  $L-G$  and the saturationcurve of  $F$  under a constant pressure are, therefore, situated in the vicinity of point  $p$  with respect to one another in the same way as the curves  $pf$  and  $pq$  in fig. 1.

Curve  $pf$  can also no more intersect curve  $pq$  in its further course; we may see this also in the following way.

At decrease of  $P$  the two curves must touch one another under a definite pressure  $P_h$  somewhere in a point  $h$  within the component-triangle; therefore imagining the liquidcurve of this pressure  $P_h$  to be represented by  $ed$  (fig. 1), we must imagine  $ed$  to be drawn in such a way that it touches  $pq$  in  $h$ . For this point  $h \frac{dy}{dx}$  from (9)

must be equal to  $\frac{dy}{dx}$  from (13); then holds:

$$\frac{xr + (y - y_1) s + RT}{xs + (y - y_1) t} = \frac{xr + (y - \beta) s + RT}{xs + (y - \beta) t} \quad \dots \quad (15)$$

or

$$y_1 = \beta \quad \dots \quad (16)$$

As  $y_1$  indicates the vapour conjugated with liquid  $h$ , (16) means: the liquid-curve of the region  $L-G$  and the saturationcurve under a constant pressure of  $F$  touch one another in a point  $h$ , when the vapour belonging to this liquid  $h$  is represented by the point  $F$ .

As all vapours belonging to curve  $ed$  (fig. 1) are represented by

$Ce_1$ , and consequently no vapour exists of the composition  $F$ , the curves  $ed$  and  $pq$ , therefore, cannot touch one another.

Let us now consider the tangents to the liquid-curve and to the saturationcurve under a constant pressure in the point  $q$  (fig. 1); as the vapour, belonging to this liquid, may be represented either by a point  $q_1$  situated between  $q$  and  $F$  or by a point  $q_2$  between  $F$  and  $C$ , we must distinguish two cases.

When the vapour is represented by  $q_1$ , then we have  $y - \beta > 0$  and  $y - y_1 > 0$ . As  $y - \beta > y - y_1$ , the denominators of (11) and (14) have either the same sign or the denominator of (11) is positive, while that of (14) is negative. In each of these three cases we find  $\varphi < \psi$ ; the liquid-curve of the region  $L-G$  and the saturationcurve under a constant pressure of  $F$  are, therefore, situated in the vicinity of point  $q$  with respect to one another as the curves  $qp$  and  $qq'_1$ .

When the vapour corresponding with liquid  $q$  is represented by  $q_2$ , then  $y - \beta < 0$  and  $y - y_1 > 0$ , in absolute value  $(y - \beta)s$  is always smaller than  $(y - y_1)s$ . The denominators of (11) and (14) have, therefore, either the same sign or the denominator of (11) is negative, while that of (14) is positive. In each of these three cases we find  $\varphi > \psi$ ; the liquid-curve of the region  $L-G$  and the saturationcurve under a constant pressure of  $F$  are, therefore, situated in the vicinity of point  $q$  with respect to one another as the curves  $qp$  and  $qq'_2$ .

With the aid of the preceding considerations we may easily deduce now the saturationcurves under their own vapour-pressure of  $F$ ; for this we shall assume that the solid substance melts with increase of volume. We distinguish three cases.

1. The temperature is lower than the point of maximum-sublimation  $T_K$  of the binary substance  $F$ .

In a similar way as we have deduced the general case fig. 11 (I) we now find with the aid of fig. 1 for the saturationcurve under its own vapourpressure a diagram as is drawn in fig. 2; in this figure a part only of the componenttriangle is drawn. Curve  $hacmbn$  is the saturationcurve under its own vapourpressure,  $h_1a_1c_1F_1b_1n_1$  is the corresponding straight vapourline. In this figure are indicated the equilibria:  $F + L_h + G_{h_1}$ ,  $F + L_a + G_{a_1}$ ,  $F + L_c + G_{c_1}$ ,  $F + L_m + G_{E_1}$ ,  $F + L_b + G_{b_1}$  and  $F + L_n + G_{n_1}$ ;  $L_h$  and  $L_n$  are binary liquids. As we have assumed that the temperature is lower than the point of maximum-sublimation  $T_k$  of the solid



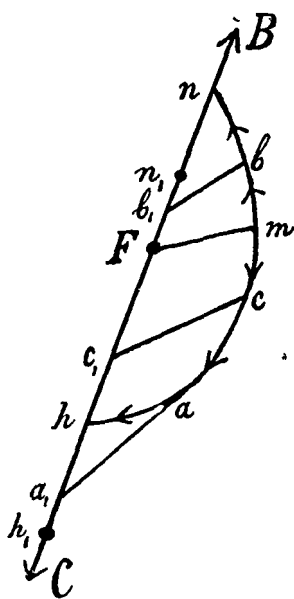


Fig. 2

substance  $F$ , the vapour  $n_1$  must be situated between  $F$  and  $n$ . Consequently we have here the case that the vapour, corresponding in fig. 1 with the liquid  $q$ , is represented by  $q_1$ ; the liquid-curve of the region  $L-G$  going through the point  $q$  can, therefore, be represented by  $qq_1'$  (fig. 1). It follows from this position of  $qq_1'$  that on further decrease of pressure the liquidcurve of the region  $L-G$  must touch curve  $pq$  in a point  $m$  (fig. 1); in fig. 2 this point of contact is also represented by  $m$ . Previously we have seen that the vapour corresponding with such a point of contact has the composition  $F$ ; in fig. 2  $m$  and  $F$  are joined for this reason by a conjugation-line.

It follows from this deduction that the pressure is a minimum in the point  $m$  of fig. 2 and increases from  $m$  in the direction of the arrows, consequently towards  $n$  and  $h$ . Further it is evident that the vapourpressure in  $h$  is higher than in  $n$ .

2. The temperature is higher than the point of maximum sublimation  $T_K$  and lower than the minimum-meltingpoint  $T_F$  of the substance  $F$ .

In a similar way as we have deduced the general case fig. 7 (I), we now find with the aid of fig. 1 a diagram as fig. 3. Curve  $h a c b n$  is the saturationcurve under its own vapour-pressure,  $h_1 a_1 c_1 b_1 n_1$  is the corresponding straight vapour-line. As we have assumed that the temperature is higher than  $T_K$  but lower than  $T_F$ ,  $F$  must, as in fig. 3, be situated between  $n$  and  $n_1$ . Therefore, here we have the case that the vapour, corresponding in fig. 1 with the liquid  $q$ , is represented by  $q_2$ ; the liquid-curve of the region  $L-G$  going through the point  $q$  may, therefore, be represented by  $qq_2'$  (fig. 1). It follows from this position of  $qq_2'$  that on further decrease of pressure the liquid-curve of the region  $L-G$  no more intersects curve  $pq$ .

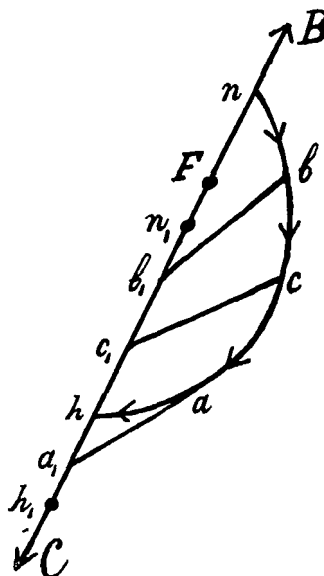


Fig. 3.

From this deduction it follows that the pressure increases along curve  $hn$  in the direction of the arrows, therefore, from  $n$  towards  $h$  and that on this curve  $hn$  neither a point of maximum- nor a point of minimum pressure occurs.

3. The temperature is higher than the minimum-meltingpoint  $T_F$  and lower than the point of maximum-temperature  $T_H$  of the binary equilibrium  $F + L + G$ .

In a similar way as we have deduced the general case fig. 12 (I) we now find for the saturationcurve under its own vapour-pressure an expanded curve, in fig. 4 a similar curve is represented by the curve  $hn$  indicated by 5; the pressure increases in the direction of the arrow, consequently from  $n$  towards  $h$ .

In fig. 4 the saturationcurves under their own vapour-pressure of  $F$  are drawn for several temperatures ( $T_1 - T_5$ ). When we take  $T_1$  and  $T_2$  lower than  $T_K$ , then a point of minimum-pressure must occur on the curves, indicated by 1 and 2. When we take  $T_4$  between  $T_K$  and  $T_F$  and  $T_5$  between  $T_K$  and  $T_H$ , then the saturationcurves under their own vapour-pressure have a position as the curves  $hn$  indicated by 4 and 5, on which no point of minimum pressure occurs. At  $T_H$  the saturationcurve disappears in a point  $H$  and the corresponding straight vapourline in a point  $H_1$  (not drawn in the figure).

On the saturationcurve of the temperatures  $T_1$  and  $T_2$  we find a point of minimum-pressure  $m$ , this point has disappeared on the saturationcurve of the temperature  $T_4$ ; between these two temperatures we consequently find a temperature  $T_3$ , at which the point  $m$  coincides with the terminating point  $n$  of the saturationcurve under its own vapour-pressure. As the vapour belonging to a point of minimum-pressure has always the composition  $F$ , this case occurs when the liquid  $n$  can be in equilibrium with a vapour  $F$ . As then the binary equilibrium  $F + L + \text{vapour } F$  can occur this temperature  $T_3$

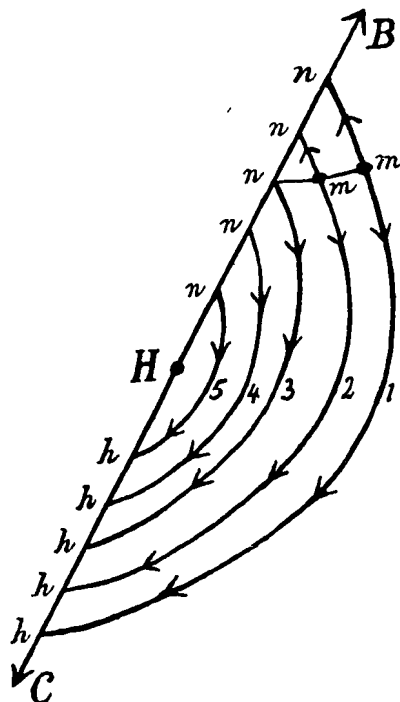


Fig. 4.

consequently is the maximum temperature of sublimation  $T_K$  of the substance  $F$ .

Now we will deduce in another way the saturation curves under their own vapour pressure of  $F$ . The conditions of equilibrium are:

$$Z - x \frac{\partial Z}{\partial x} - (y - t) \frac{\partial Z}{\partial y} = \zeta \quad Z_1 - (y_1 - t) \frac{\partial Z_1}{\partial y_1} = \zeta \quad \frac{\partial Z}{\partial y} = \frac{\partial Z_1}{\partial y_1} \quad (17)$$

These conditions follow also from the equations 1 (II) when we equate herein  $\alpha = 0$  and  $x_1 = 0$  and when we consider  $Z_1$  as independent of  $x_1$ . We put

$$Z = U + RTx \log x \quad . \quad . \quad . \quad (18)$$

The three conditions (17) pass then into:

$$U - x \frac{\partial U}{\partial x} - (y - t) \frac{\partial U}{\partial y} - RTx - \zeta = 0 \quad . \quad . \quad . \quad (19)$$

$$Z_1 - (y_1 - t) \frac{\partial Z_1}{\partial y_1} - \zeta = 0 \quad . \quad . \quad . \quad (20)$$

$$\frac{\partial U}{\partial y} - \frac{\partial Z_1}{\partial y_1} = 0 \quad . \quad . \quad . \quad (21)$$

From this follows

$$\begin{aligned} [xr + (y - t)s + RT] dx + [xs + (y - t)t] dy = \\ = \left[ V - x \frac{\partial V}{\partial x} - (y - t) \frac{\partial V}{\partial y} - v \right] dP \quad . \quad . \quad . \quad (22) \end{aligned}$$

$$(y_1 - t) t_1 dy_1 = \left[ V_1 - (y_1 - t) \frac{\partial V_1}{\partial y_1} - v \right] dP \quad . \quad . \quad . \quad (23)$$

$$sdx + tdy - t_1 dy_1 = \left( \frac{\partial V_1}{\partial y_1} - \frac{\partial V}{\partial y} \right) dP \quad . \quad . \quad . \quad (24)$$

With the aid of (23) we may also write for (24):

$$(y_1 - t) sdx + (y_1 - t) t dy = \left[ V_1 - (y_1 - t) \frac{\partial V}{\partial y} - v \right] dP \quad (25)$$

so that for the relation between  $dx$ ,  $dy$ ,  $dy_1$ , and  $dP$  we shall consider the equations (22), (23), and (25).

In order to examine if a point of maximum- or of minimum-pressure is possible on the saturation curve under its own vapour pressure, we take (23). From this follows  $dP = 0$  when

$$y_1 = t \quad . \quad . \quad . \quad (26)$$

In order to examine if the pressure for this point is a maximum or a minimum, we develop (20) further into a series; when we equate herein  $y_1 = t$ , we find:

$$(V_1 - v) dP = \frac{1}{2} t_1 dy_1^2 . . . . . (27)$$

As  $V_1 - v$  and  $t_1$  are both positive, it is apparent that the pressure is a minimum. In accordance with our previous considerations (see fig. 2) we find therefore: on the saturationcurve under its own vapourpressure of the solid substance  $F$  the pressure is a minimum in a point  $m$ , when the vapour corresponding with this liquid has the composition  $F$ .

In order to examine the change of pressure along the saturationcurve in the vicinity of its extreme ends  $h$  and  $n$  (fig. 2, 3, and 4) we equate  $x = 0$ ; from (22) and (25) we then obtain:

$$[(y - \beta) s + RT] dx + (y - \beta) t dy = [V - (y - \beta) \frac{\partial V}{\partial y} - v] dP . . (28)$$

$$(y_1 - \beta') s dx + (y_1 - \beta) t dy = [V_1 - (y_1 - \beta') \frac{\partial V}{\partial y} - v] dP . . (29)$$

From this follows:

$$(y_1 - \beta') RT dx = [(y_1 - \beta') V + (\beta - y) V_1 + (y - y_1) v] dP . (30)$$

When  $\Delta V_1$  is the change of volume, which occurs when between the three phases of the binary equilibrium  $F + L + G$  a reaction occurs, in which one quantity of vapour arises, then we may write for (30):

$$dP = - \frac{\beta - y_1}{\beta - y} \cdot \frac{RT}{\Delta V_1} \cdot dx . . . . . (31)$$

Now  $\Delta V_1$  is always positive in the binary system  $F + L + G$ , except between the minimum-melting point  $T_F$  and the point of maximumtemperature  $T_H$ , where  $\Delta V_1$  is negative. In fig. 4  $\Delta V_1$  is consequently negative for liquids between  $F$  and  $H$ , positive for all other liquids on the side  $BC$ .

$\beta - y$  is positive, when the liquid is situated between  $F$  and  $C$ , negative when the liquid is situated between  $F$  and  $B$  (figs. 2—4).

$\beta' - y_1$  is positive, when the vapour is situated between  $F$  and  $C$ , negative when the vapour is situated between  $F$  and  $B$  (figs. 2—4).

In the points  $h$  of figs. 2—4 is  $\Delta V_1 > 0$ ,  $\beta' - y > 0$  and  $\beta - y_1 > 0$ ; from (31) follows therefore  $dP < 0$ . From each of the points  $h$  the pressure must, therefore, decrease along the saturationcurves, we see that this is in accordance with the direction of the arrows in the vicinity of the points  $h$  (figs. 2—4).

In the point  $n$  of fig. 2 is  $\Delta V_1 > 0$ ,  $\beta' - y < 0$  and  $\beta - y_1 < 0$ ; from (31) follows, therefore  $dP < 0$ . Consequently we find that

the pressure in fig. 2 must decrease from  $n$  along the saturation-curve, which is in accordance with fig. 2.

In the point  $n$  of figure 3 is  $\Delta V_1 > 0$ ,  $\beta - y < 0$  and  $\beta - y_1 > 0$ ; from (31) follows, therefore  $dP > 0$ . Consequently the pressure must increase from the point  $n$  in fig. 3 along the saturationcurve, which is in accordance with fig. 3.

In the point  $n$  of curve 5 in fig. 4 is  $\Delta V_1 < 0$ ,  $\beta - y > 0$  and  $\beta - y_1 > 0$ ; from (31) follows, therefore  $dP > 0$ . Consequently the pressure must increase from  $n$  along curve 5, which is in accordance with the direction of the arrows.

We may summarise the above-mentioned results also in the following way: when to the binary equilibrium  $F+L+G$  (in which  $F$  is a compound of two volatile components) at a constant temperature we add a substance, which is not volatile, then the pressure increases when the binary equilibrium is between the point of maximum-sublimation  $T_K$  and the point of maximum temperature  $T_H$ ; in all other cases the pressure decreases.

In the consideration of the general case, that the vapour contains the three components (XI and XII) we have deduced that the saturationcurves under their own vapourpressure can disappear in two ways at increase of pressure.

1. The saturationcurve of the temperature  $T_H$  disappears in the point  $H$  on the side  $BC$  [fig. 5 (XI)].

2. The saturationcurve of the temperature  $T_H$  touches the side  $BC$  in the point  $H$  and is further situated within the triangle; at further increase of  $T$  it forms a closed curve situated within the triangle, which disappears at  $T_R$  in a point within the triangle [fig. 6 (XI)].

In the case now under consideration, that the vapour consists only of  $B$  and  $C$ , only the case 1 occurs; this has already been discussed above and is represented in fig. 4. It follows already immediately from the following that the case 2 cannot occur. On a closed saturationcurve under its own vapourpressure a point of maximum- and a point of minimumpressure occurs. On the curves now under consideration only, as we saw before, a point of minimumpressure can occur, so that closed saturationcurves are impossible.

We may deduce this also in the following way and we may prove at the same time these curves, just as in the general case, to be parabolas in the vicinity of  $H$ .

When we consider the binary equilibrium  $F + \text{liquid } H + \text{vapour}$ , then  $x = 0$ ; we equate  $y = y_0$ ,  $y_1 = y_{1,0}$  and the pressure  $= P_H$ . To this equilibrium applies:

$$\left. \begin{aligned} U - (y_0 - \beta) \frac{\partial U}{\partial y} - \xi = 0 \quad Z_1 - (y_{1.0} - \beta) \frac{\partial Z_1}{\partial y_1} - \xi = 0 \\ \frac{\partial U}{\partial y} = \frac{\partial Z_1}{\partial y_1} \end{aligned} \right\} \quad (32)$$

further we have:

$$(y_{1.0} - \beta) V + (\beta - y_0) V_1 + [y_0 - y_{1.0}] v = 0 \quad \dots \quad (33)$$

which condition we may also write:

$$\frac{V - v}{y_0 - \beta} = \frac{V_1 - v}{y_{1.0} - \beta} = \frac{V_1 - V}{y_{1.0} - y_0} = \mu \quad \dots \quad (34)$$

For a ternary equilibrium  $F + L + G$ , the liquid of which is situated in the vicinity of point  $H$ , the pressure is equal to  $P_H + \pi$ ,  $x = \xi$ ,  $y = y_0 + \eta$  and  $y_1 = y_{1.0} + \eta_1$ .

The three equations (17) pass, then, when we use the conditions (22) into:

$$RT\xi + [v - V]\pi + \frac{1}{2}r\xi^2 + \frac{1}{2}t\eta^2 + \frac{1}{2}\left(\frac{\partial v}{\partial P} - \frac{\partial V}{\partial P}\right)\pi^2 + s\xi\eta + \dots + (y - \beta)L = 0 \quad (35)$$

$$[v - V_1]\pi + \frac{1}{2}t_1\eta_1^2 + \frac{1}{2}\left(\frac{\partial v}{\partial P} - \frac{\partial V_1}{\partial P}\right)\pi^2 + \dots + (y_1 - \beta)L_1 = 0 \quad (36)$$

$$L = L_1 \quad \dots \quad (37)$$

Herein is:

$$\left. \begin{aligned} L = s\xi + t\eta + \frac{\partial V}{\partial y}\pi + \frac{1}{2}\frac{\partial s}{\partial x}\xi^2 + \frac{1}{2}\frac{\partial t}{\partial y}\eta^2 + \frac{1}{2}\frac{\partial^2 V}{\partial y\partial P}\pi^2 + \\ + \frac{\partial s}{\partial y}\xi\eta + \frac{\partial^2 V}{\partial x\partial y}\xi\pi + \frac{\partial^2 V}{\partial y^2}\eta\pi + \dots \end{aligned} \right\} \quad (38)$$

$$L_1 = t_1\eta_1 + \frac{\partial V_1}{\partial y_1}\pi + \frac{1}{2}\frac{\partial t_1}{\partial y_1}\eta_1^2 + \frac{1}{2}\frac{\partial^2 V_1}{\partial y_1\partial P}\pi^2 + \frac{\partial^2 V_1}{\partial y_1^2}\eta_1\pi + \dots \quad (39)$$

In (35) and (36)  $y_0$  and  $y_{1.0}$  are replaced by  $y$  and  $y_1$ ; we shall do the same in the following equations. When we multiply (35) by  $y_1 - \beta$  and (36) by  $y - \beta$ , then it follows with the aid of (37) that:

$$\begin{aligned} (y_1 - \beta)RT\xi + \frac{1}{2}(y_1 - \beta)r\xi^2 + \frac{1}{2}(y_1 - \beta)t\eta^2 - \frac{1}{2}(y - \beta)t_1\eta_1^2 \\ + \frac{1}{2}\left[(\beta - y_1)\frac{dV}{dP} + (y - \beta)\frac{\partial V_1}{\partial P} + (y_1 - y)\frac{\partial v}{\partial P}\right]\pi^2 + (y_1 - \beta)s\xi\eta = 0. \end{aligned} \quad (40)$$

From (36), (37), and (40) it follows that this can be satisfied by:  $\eta_1$  of the order  $\pi$ ,  $\eta$  of the order  $\pi$  and  $\xi$  of the order  $\pi^2$ .

From (35), (36) and (37) then follows:

$$t\eta = \left(\mu - \frac{\partial V}{\partial y}\right)\pi \quad \text{and} \quad t_1\eta_1 = \left(\mu - \frac{\partial V_1}{\partial y_1}\right)\pi \quad \dots \quad (41)$$

Substituting these values in (40) we find:

$$2 (y_1 - \beta) RT \xi = a \pi^2 \dots \dots \dots (42)$$

wherein  $a$  has the same value as in (21) (XII).

From this it follows with the aid of the first relation (41) that:

$$2 (y_1 - \beta) RT \xi = \frac{a t^2}{\left(\mu - \frac{\partial V}{\partial y}\right)^2} \eta^2 \dots \dots \dots (43)$$

In the same way as in (XII) we find that we may write for this:

$$2 RT \xi = \frac{t^3 (y - \beta) (y_1 - y) \frac{d^2 l}{dP^2}}{(y_1 - \beta) \left(\mu - \frac{\partial V}{\partial y}\right)^2} \eta^2 \dots \dots \dots (44)$$

wherein  $\frac{d^2 l}{dP^2}$  is fixed by (24) (XII). From this it follows that the curve going in fig. 4 through the point  $H$  is parabolically curved in this point and touches the side  $BC$  in this point.

As in this point  $y - \beta < 0$ ,  $y_1 - y < 0$ ,  $y_1 - \beta < 0$  and  $\frac{d^2 l}{dP^2} > 0$ ,  $\xi$  is always negative. From this it follows that this parabola has only the point  $H$  in common with the triangle and is further situated completely outside the triangle. Consequently only the point  $H$  represents a liquid; its other points have no meaning.

(To be continued).

**Chemistry.** — “*The system Ammonia-water*”. By Prof. A. SMITS and S. POSTMA. (Communicated by Prof. J. D. v. D. WAALS).

(Communicated in the meeting of May 30, 1914).

After the preliminary communication <sup>1)</sup> on this subject the investigation of the system  $\text{NH}_3\text{-H}_2\text{O}$  has been continued in different directions, and it has now been completed.

The continued research was directed in the first place to the accurate determination of the meltingpoint lines, corresponding with the pressure of one atmosphere. These determinations, which were now carried out by means of a gauged resistance thermo-

<sup>1)</sup> These Proc. XII, p. 186.