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

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We consider a liquid L, saturated with the solid substance F and in equilibrium with the vapour G. We allow this liquid to proceed along a straight line which passes through the point F.

If we call dn the quantity of solid substance F that dissolves in the unit of quantity of the liquid, we get:

$$dx = (\alpha - x)\, dn \qquad dy = (\beta - y)\, dn$$

If we substitute these values in (6) (II) and (7) (II)[1]) we have:

$$- M \cdot dn = A dP - B dT \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$- N \cdot dn = C dP - D dT \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where for the sake of brevity:

$$M = (x-\alpha)^2 r + 2(x-\alpha)(y-\beta)s + (y-\beta)^2 t$$

$$N = (x_1 - x)(x-\alpha)r + \{(x-\alpha)(y_1 - y) + (x_1 - x)(y - \beta)\}s + (y_1 - y)(y - \beta)$$

From this follows:

$$dP = \frac{DM - BN}{BC - AD} \cdot dn = \frac{DM - BN}{BC - AD} \cdot \frac{dx}{\alpha - x} \quad . \quad . \quad . \quad (3)$$

$$dT = \frac{CM - AN}{BC - AD} dn = \frac{CM - AN}{BC - AD} \cdot \frac{dx}{\alpha - x} \quad . \quad . \quad . \quad (4)$$

$$\frac{dP}{dT} = \frac{DM - BN}{CM - AN} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As in the previous communication, we assume the very probable case that $BC - AD$ is positive.

If now we call $x = \alpha$ and $y = \beta$ then $M = 0$, $N = 0$ and $\dfrac{M}{\alpha - x} = 0$,

but $\dfrac{N}{\alpha - x}$ does not become 0 as a rule. If we call $tg\varphi = \dfrac{y - \beta}{x - \alpha}$ we get:

$$dP = \frac{B[(x_1 - \alpha)r + (y_1 - \beta)s + \{(x_1 - \alpha)s + (y_1 - \beta)t\} tg\varphi]}{BC - AD} dx \quad (6)$$

and for dT a same form with this difference that in the numerator B has been replaced by A.

To perceive the significance of this we take fig. 1 in which the closed curves indicate the boiling point lines of the solutions saturated with F. The exphased ones, as has been stated previously, have

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[1]) The figures (I), (II), and (III) refer to the former communications.

shifted to that side of F where the vapour region is situated. On increase of pressure, the boiling point line disappears finally in the point M, the correlated vapour line in the point M_1. The point D indicates the vapour which can be in equilibrium with the solid substance F and the liquid F, therefore the vapour which forms at the minimum melting point of the compound F. The line XFY is the tangent in F at the boiling point line passing through F. We have already noticed previously that the lines DFE and XY are conjugated diagonals of the indicatrix in F at the liquidum side of the ζ-plane.

We now lay down through F an arbitrary line ZZ_1 and let a liquid proceed along this line; as according to (6) dP and dT have a definite value differing from nil it follows that in this point neither the pressure nor the temperature is at a maximum or a minimum.

If, however, we choose the line in such a manner that

$$(x_1-\alpha)r + (y_1-\beta)s + \{(x_1-\alpha)s + (y_1-\beta)t\}\, tg\varphi = 0 \quad . \quad . \quad (7)$$

then dP as well as dT is nil. From (13) (1) it follows that (7) is satisfied when the line drawn through F comes into contact in F with the boiling point line passing through this point, therefore when the liquid proceeds along the straight line XFY.

If now we introduce a line element $d\varrho$ positive in the direction away from F and negative in the direction towards F, and if we let φ change from $0°$ to $360°$ we have $dx = \cos\varphi \cdot d\varrho$ so that (6) is converted into:

$$dP = \frac{B[\{(x_1-\alpha)r + (y_1-\beta)s\}\cos\varphi + \{(x_1-\alpha)s + (y_1-\beta)t\}\sin\varphi]}{BC-AD}\, d\varrho. \quad (8)$$

The factor

$$\{(x_1-\alpha)r + (y_1-\beta)s\}\cos\varphi + \{(x_1-\alpha)s + (y_1-\beta)t\}\sin\varphi \quad . \quad .. \quad (9)$$

in the point F is nil towards X as well as towards Y; in all other directions it differs from nil. If to φ is given such a value that the line passes through the point D we notice that the factor (9) is positive. Hence, in the point F the value of (9) is positive in the direction towards D and negative in the direction towards E.

We may now easily deduce that (9) is positive if, starting from F, we move towards that side of the line XFY where the point D is situated; and that (9) is negative when we move from F towards the other side of the line XFY. These positive or negative values are, however, very small if the direction almost coincides with FX or FY so that at some distance a reversal of the sign may perhaps take place. $B = H-\eta$ being positive it follows from (8) that the pressure when starting from F increases towards that

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side of the line XFY where the point D is situated and decreases when starting from F towards the other side of the line XFY.

Hence, if a liquid proceeds along the line FD or FM_1 or FZ the vapour pressure increases starting from F; if it proceeds along the line FZ_1 or FG or FE the vapour pressure decreases from F. Only in the direction of F towards X or towards Y the vapour pressure remains at first unchanged.

It will be easily perceived that these considerations are in harmony with fig. 1. For the closed curves drawn in fig. 1 are the boiling point lines of the solutions saturated with F; each curve, therefore, applies to a definite constant pressure. As the pressure becomes higher, these curves draw nearer to M to finally disappear in this point. Of course, it may happen also that on increase of pressure a curve moves away entirely or partially from M to again draw nearer to M at a further increase of pressure. In the point F this, however, is not the case; we have already demonstrated that the part of the boiling point line passing through F situated in the vicinity of F moves on increase of pressure towards M, and on reduction of pressure away from M.
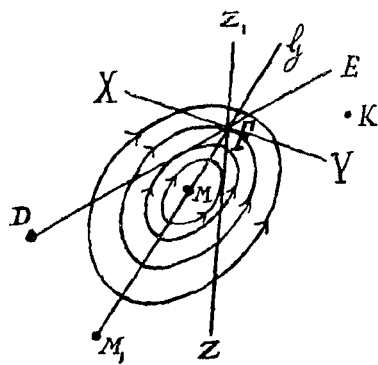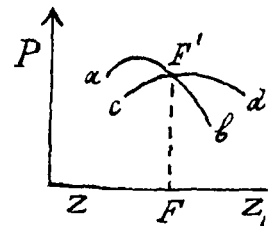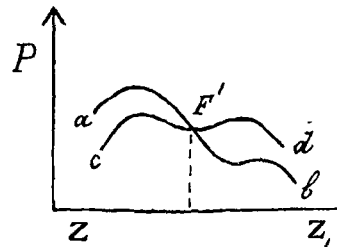

Fig. 1.

Fig. 2.

Fig. 3.

In fig. 2 the line ZFZ_1 represents the same line of fig. 1; the part FZ lies, therefore, at the same side of XFY where the point D is situated; the part FZ_1 lies, therefore, at the other side. Perpendicularly on the line ZZ_1 we place the pressure axis, hence the vapour pressures of the liquids saturated with F of the line ZFZ_1. As

according to our previous considerations the pressure increases from F towards Z and decreases towards Z_1 the vapour pressure curve in F' must have a direction like curve $aF'b$. As the line FZ comes into contact with one of the exphased boiling point lines, the pressure in this point is a maximum; on the curve $aF'b$ of fig. 2 a maximum vapour pressure must, therefore, occur somewhere between a and F'.

If, however, the line ZFZ_1 of fig. 1 is turned in such a manner that it keeps on passing continually through F, the curve $aF'b$ of fig. 2 will change its form although it will of course, also keep on passing through F'. From our previous considerations it follows at once that the direction of the tangent in F' and the position of the point with maximum vapour pressure changes. If ZFZ_1 coincides with XFY we obtain in fig. 2 a curve $cF'd$ with a horizontal tangent in F'.

We have assumed in fig. 1 that the boiling point line passing through F is curved in the point F in the direction towards D; in our previous communication (II) we have noticed, however, that, in the vicinity of F it may be curved in some other direction also. It may then present a form such as curve aFb of fig. 2 (II) in which, however, we must imagine the arrows to point in the opposite direction. We have deduced this form while assuming that the vapour contains one of the three components only. Although in this case, the appearance of such a form is not very likely, the possibility thereof is greater when the vapour contains the three components and when, for instance, in the system LG a maximum temperature occurs. We now imagine through point F of fig. 1 and also at somewhat higher and lower pressures, boiling point lines of this form. Lines proceeding from F towards that side of XFY where the point D is situated will then each again come into contact with a boiling point line, so that a pressure maximum must occur. Lines which proceed from F towards the other side of XFY either do not come into contact with a boiling point line at all, or else they meet two of these, so that there occurs one point with a maximum and one with a minimum vapour pressure. The latter case will occur on lines in the vicinity of FX and FY.

On turning the line ZFZ_1 of fig. 1 we will, therefore, have vapour pressure curves like $aF'b$ of fig. 2, further like $aF'b$ of fig. 3, and if ZFZ_1 coincides with XFY of fig. 1, a vapour pressure curve $cF'd$ of fig. 3.

In order to investigate the change in temperature in the point F on the lines passing through this point we take the formula corresponding with (8):

$$dT = \frac{A[\{(x_1-\alpha)\,r+(y_1-\beta)\,s\}\cos\varphi + \{(x_1-\alpha)\,s + (y_1-\beta)\,t\}\sin\varphi}{BC-AD}\,d\varrho \; . \; (10)$$

in which $A = V - v$ therefore positive or negative.

From this it follows that dT will be *nil* when (9) is *nil*, therefore when the line drawn through F coincides with the tangent XFY in F at the boiling point line passing through this point, or what amounts to the same thing, at the saturation line under its own vapour pressure. We now distinguish two cases.

$V > v$. The saturation lines under their own vapour pressure are now situated as in fig. 14 (I); we now imagine, in this figure, the tangent drawn on to the saturation line under its own pressure, passing through F. As in fig. 1 we will call this XFY. The point corresponding with the point D of fig. 1 is, of course, situated in fig 14 (I) on the vapour line correlated to the saturation line under its own vapour pressure which passes through the point F. Hence it is situated, as in fig. 1 to the left of the line YFX.

If now we move in fig. 14 (I) from F towards that side of the line XFY where the point D is situated, then, as follows from (10), the temperature increases starting from F; when moving towards the other side of the line XFY the temperature decreases from F.

After the previous considerations in regard to Fig. 1 it is evident that this agrees with fig. 14 (I). If in this figure we imagine a line drawn from F towards that side of XFY where the point D is situated this will come into contact with one of the exphased saturation lines under their own vapour pressure. As each of these curves belongs to a definite constant temperature differing, of course, from curve to curve, the temperature in this point of contact is a maximum one. If now in fig. 2 we imagine the pressure axis to be replaced by the temperature axis we again obtain a curve like $aF''b$ with a maximum temperature between a and F'. If in fig. 14 (I) we turn the line passing through F until it coincides with XFY, the curve $aF''b$ of fig. 2 is transformed to curve $cF''d$ of this figure.

Should the case occur that in F the saturation line under its own vapour pressure becomes curved away from D, we obtain curves as in fig. 3 in which we must again imagine the pressure axis to be replaced by the temperature axis.

$V < v$. The saturation lines under their own vapour pressure are no longer situated as in fig. 14 (I); we may, however, easily imagine them from this figure if we suppose the point F to lie on the line MM_1 between M and M_1. From a consideration of this figure it then follows that, starting from F, the temperature decreases towards that side of the line XFY where the point D is situated and

increases towards the other side of this line. At the side turned away from the point D of the line XFY is now also found the temperature maximum. This is also in agreement with (10). $A = V - v$ now being negative it follows that for positive values of (9) and of $d\varphi$, dT from (10) is now negative; this means that the pressure decreases from F towards that side of the line XFY where the point D is situated.

We now take $\dfrac{dP}{dT}$ from (5) and write this in the form:

$$\frac{dP}{dT} = \frac{B - RD}{A - RC} \quad\quad\quad\quad (11)$$

In this:

$$R = \frac{M}{N} = \frac{\{(x-\alpha)r + (y-\beta)s\} \cos\varphi + \{(x-\alpha)s + (y-\beta)t\} \sin\varphi}{\{(x_1-x)r + (y_1-y)s\} \cos\varphi + \{x_1-x)s + (y_1-y)t\} \sin\varphi} \quad (11a)$$

For $x = \alpha$ and $y = \beta$, $R = 0$ unless φ is chosen in such a manner that the denominator also becomes 0, this is the case, when starting from F in fig. 1, one moves along FX or FY. We will first assume that this is not the case.

If one moves from F towards that side of XFY where the point D is situated R will be positive, when moving from F towards the other side R will be negative. We now let a liquid saturated with solid F proceed along the line ZFZ_1, from (11) it now follows that in the point F

$$\frac{dP}{dT} = \frac{B}{A} = \frac{H - \eta}{V - v} \quad\quad\quad\quad (12)$$

$V > v$. In the PT-diagram of fig. 4 aK represents the sublimation,

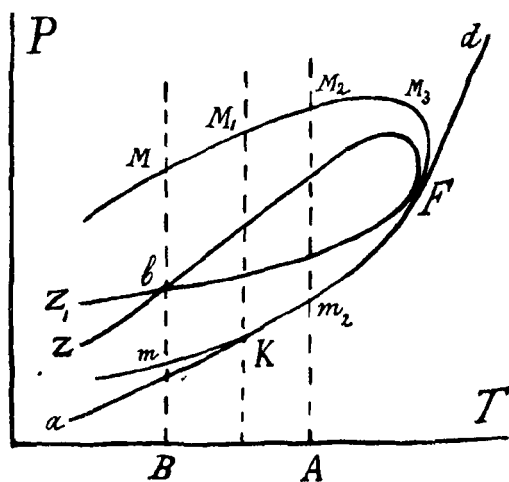Fig. 4.

KF the three-phase and Fd the melting point curve of the compound F; these three curves are therefore the same as the homogeneous-curves of fig. 3 (III). The direction of the melting point curve Fd (fig. 4) is determined by:

$$\frac{dP}{dT} = \frac{H-\eta}{V-v}$$

From (12) it follows that, in point F of fig. 4, the PT curve ZFZ_1 must come into contact with the melting point line Fd. The further course of this PT-curve in the vicinity of the point F may be traced in the following manner:

We proceed in fig. 1 from F towards Z_1, R thus becoming negative. From (11) it now follows that $\frac{dP}{dT}$ remains positive so that the curve must be situated like curve FZ_1 of fig. 4.

If, in fig. 4 we move from F towards Z, R becomes positive. A being small, the denominator of (11) will soon become nil so that curve FZ of fig. 4 must have a vertical tangent in the vicinity of the point F. If in fig. 1 we move further from F towards Z, then $\frac{dP}{dT}$ from (11) will become negative first, and nil afterwards, so that curve FZ of fig. 4 must have a horizontal tangent. As $\frac{dP}{dT}$ afterwards becomes positive, curve FZ is bound to fall at a decreasing temperature.

Proceeding from point Z we find on curve ZFZ_1 first a pressure- and then a temperature maximum, further a point of contact with the melting point line Fd of the compound F at the minimum melting point of the compound and finally a receding branch FZ_1. All this reminds of the P, T-curves deduced by VAN DER WAALS for solid + liquid + gas in binary systems.

To some differences, for instance that the P, T-curves mentioned here do not meet the sublimation line of F in the maximum sublimation point, I will refer later.

In fig. 4 it has been assumed that curve ZFZ_1 exhibits a double point b, namely a point of intersection of the branches FZ and FZ_1. In order to perceive the possibility of a similar double point we take a circumphased boiling point line (fig. 1). On this occurs a point with a maximum and another with a minimum temperature. These points divide the boiling point line into two branches and in such a manner that to each point of the one branch appertains a definite point of the other branch, namely in that sense that both points indicate

solutions of the same temperature and the same vapour pressure, and saturated with F.

Of all straight lines which unite two such correlated points of the two branches one is sure to pass through the point F. If now, we allow the line ZFZ_1 of fig. 1 to coincide with the above mentioned connecting line, we then find two solutions situated at different sides of F, which have the same temperature and the same vapour pressure. The branches FZ and FZ_1 of fig. 4 then must intersect each other at that temperature and pressure.

$V < v$. The melting point line Fd of fig. 4 now proceeds from the point F towards lower temperatures and higher pressures; the point F of curve ZFZ_1 now gets situated between the point with a maximum temperature and that with a maximum vapour pressure.

To each of the solutions of the line ZFZ_1 of fig. 1 saturated with solid F, appertains of course a definite vapour; the points representing these vapours form a curve which we will call the vapour line conjugated with the line ZFZ_1. It is evident that this vapour curve conjugated with ZFZ_1 must pass through the point D of fig. 1. If the line ZFZ_1 is turned, the conjugated vapour curve will also alter its position and form, but still pass through the point D. In fig. 5, the vapour curve conjugated with ZFZ_1 is represented by the dotted curve (fca De).

In fig. 5 it is assumed that the straight line ZFZ_1 and its conjugated vapour curve intersect each other in a; that such a point of intersection can appear is easy to understand. On each of the boiling point lines of fig. 1 occurs a point where the temperature along this curve is a maximum and another point where
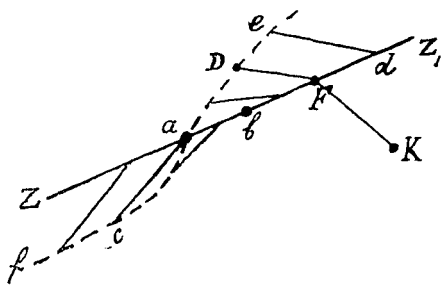

Fig. 5.

it is a minimum. If now we take the vapour phase appertaining to a similar solution, this with the liquid and the point F, will lie on a straight line. We now draw, through a similar liquid b with a maximum or minimum temperature, the line ZFZ_1 (fig. 5); the vapour a which is in equilibrium with this liquid b is then also situated on the line ZFZ, so that the vapour curve fe must intersect the line ZFZ_1 in a. With each liquid of the line bZ_1 is now in equilibrium a vapour of curve ae, such as liquid d with vapour e, liquid F with vapour D, liquid b · with vapour a. With each liquid of line baZ a vapour of curve

acf is in equilibrium. If *c* represents the vapour in equilibrium with the liquid *a*, a vapour between *a* and *c* will be in equilibrium with a liquid between *a* and *b*. If each liquid is united with the vapour with which it is in equilibrium, these conjugation lines not only occupy the strip eaZ_1 and faZ but also a part situated between *ba* and curve *ca* outside this field.

We have taken the point of intersection *a* of ZFZ_1 and the curve *fe* between F and Z; it is evident that it may also be situated at the other side of F.

We now imagine drawn in fig. 5 a set of straight lines passing through F and for each one its conjugated vapour curve; these latter all pass through the point D. Among these there is one that also passes through the point F. At the maximum sublimation point of the compound F the vapour in equilibrium with solid F has the composition F and the liquid which then, of course, is present in an infinitely small quantity only, a composition K (fig. 5). We can observe this also by other means. We imagine then in fig. 1, besides the boiling point lines of the solutions saturated with F, also drawn their appertaining vapour lines; one of these passes through the point F so that at a definite P and T a vapour exists of the same composition as F which can be in equilibrium with solid F and a liquid. This liquid is represented by the point K of the boiling point line of the pressure P, appertaining to the vapour point F. In fig. 1 and 5 this point is represented by K. Hence, the equilibrium solid F + vapour F + liquid K occurs; we are therefore, at the upper sublimation point of the compound F, therefore, in the point K of the sublimation line aK of fig. 4.

If now in fig. 5 we turn the line ZFZ_1, until it passes through the point K, its conjugated vapour curve will pass through the points D and F.

We have noticed above that the straight line ZFZ_1, and its conjugated vapour line can have a point of intersection *a* (fig. 5). As in this case the vapour *a*, the liquid *b* and the solid substance F are situated on a straight line, it follows from (11) that:

$$\frac{dP}{dT} = \frac{(x_1 - x)B - (x - a)D}{(x_1 - x)A - (x - a)C} = \frac{(x_1 - a)H + (a - x)H_1 + (x - x_1)\eta}{(x_1 - a)V + (a - x)V_1 + (x - x_1)v} \quad (13)$$

so that the same relation applies as if the three phases belong to a binary system.

If, on one of the straight lines ZFZ_1, the points *a* and *b* of fig. 5 coincide, the solid substance F is in equilibrium with a liquid and a vapour which both have the same composition. This is the

case if in the ternary system liquid + vapour, a singular point occurs and when the saturation curve of F passes through this point. As in this case $x = x_1$ and $y = y_1$ it follows from (11), as R becomes infinitely large, that :

$$\frac{dP}{dT} = \frac{D}{C} = \frac{H_1 - H}{V_1 - V} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (14)$$

We have noticed above that if the straight line ZFZ_1 passes through point K of fig. 5, its conjugated vapour curve must pass through D and F and that with the liquid K a vapour F is in equilibrium. Hence, we have for the point K $x_1 = a$ and $y_1 = \beta$. As R now becomes — 1 it follows from (11) that :

$$\frac{dP}{dT} = \frac{B + D}{A + C} = \frac{H_1 - \eta}{V_1 - v} \quad \cdot \quad \cdot \quad , \quad \cdot \quad \cdot \quad (15)$$

The above formula also determines the sublimation line aK of the compound F (fig. 4) If, in fig. 5 the straight line ZFZ_1 passes through the point K, the corresponding P,T.-curve in fig. 4 must meet the sublimation curve aK in the point K. We now give in fig. 1 different positions to the straight line ZFZ_1; to each position appertains a definite P, T-curve in fig. 4 so that we can draw in this figure an infinite number of P, T-curves. From our previous considerations it now follows that *all* these (I will refer later to a single exception) meet the melting point line Fd of the compound F in the point F and that *one* only meets the sublimationcurve aK in the point K. The latter takes place when the straight line ZFZ_1, in fig. 1 passes through the point K. All other P, T-curves in fig. 4. proceed above the point K, or in other words: at the upper sublimation temperature T_k. of the compound F the vapour pressure of each system : solid F + liquid + vapour is greater than the vapour pressure of the solid substance F.

Different P, T-curves, besides coming into contact in F with the melting point curve Fd will also meet the three-phase line FK. Although all this is evident from what has been said previously, we will still consider a few of these points in another manner.

On warming the solid compound F, this, as mentioned previously. proceeds along the sublimation curve aK of fig. 4 until the upper sublimation point K is attained ; then the equilibrium: solid F + liquid + vapour is formed which proceeds along the three-phase line KF of fig. 4 until the melting point line Fd has been obtained.

We have already noticed previously that the liquid and vapour continually alter their composition therewith and we may now ask what curves they proceed along in fig. 1.

At the temperature T_K of fig. 4, therefore at the upper sublimation point of the compound F, the vapour has the composition F and the liquid which can be in equilibrium with that vapour the composition K of fig. 1. At the temperature T_F of fig. 4, therefore at the minimum melting point, the vapour has the composition D and the liquid the composition F of fig. 1. Whereas the compound F proceeds in the P,T-diagram of fig. 4 along the three-phase line FK the liquid in fig. 1 proceeds along a curve from K towards F ,and the vapour along a curve from F towards D; we will call these curves the curves KF and FD.

We now imagine drawn in fig. 1 some more boiling point lines of the solutions saturated with F among which also those passing through the point K; on each of these a maximum and a minimum temperature occurs. The curve KF now intersects each of the boiling point lines situated between K and F in the point with the maximum temperature, or in other words the curve KF is the geometrical place of the points with a maximum temperature on the boiling point lines situated between K and F.

The liquid and vapour of the three-phase line KF of fig. 4 being formed from the solid substance F, the three points F, L, and G in fig. 1 must always lie on a straight line.

This means that the temperature along the boiling point line of such a liquid is a maximum or a minimum one.

From a consideration of fig. 1 it follows that here the temperature in this case is a maximum, from which follows at once what has been said above as to the course of the curve KF.

In the same manner we find that the curve FD also intersects each of the vapour lines conjugated with the boiling point lines in the point with the maximum temperature.

In fig. 1 we might also have drawn instead of the boiling point lines the saturation lines of F under their own vapour pressure. We then should have found that the curve KF intersects each of these lines in the point with the minimum vapour pressure.

We now turn the line ZFZ_1 of fig. 1 until it intersects the curve KF of this figure; the corresponding P,T-curve in fig. 4 must then meet the three-phase curve FK in a point. For in the point of intersection of the line ZFZ_1 and the curve KF in fig. 1 the pressure and temperature for both curves is namely the same; as, however, the curve KF passes through the points with maximum temperature of the boiling point lines in fig. 1 and as this is not the case with the line ZFZ_1 a higher temperature (the pressure being equal) is found on curve KF than on the line ZFZ_1. The P,T-curve of the line

ZFZ_1 therefore comes into contact with the three-phase line KF of fig. 4 and is situated further above and to the left of this three-phase line.

In order to deduce something more from the P,T-curves, we take a temperature T_B lower than the minimum melting point of the compound F. The saturation line of F under its own vapour pressure has at this temperature T_B a form as in fig. 7 (I) or 11 (I); the minimum vapour pressure in the point m of this saturation line under its own pressure we call P_m, the maximum pressure P_M. Of all the equilibria of F + liquid + gas appearing at the temperature T_B, the highest vapour pressure is, therefore, P_M and the lowest P_m. If, in fig. 4, we represent both pressures by the points M and m, one P,T-curve passes, through the point M and one through the point m, whereas all the others must intersect the perpendicular line placed in B between M and m. One obtains the P,T-curve passing at T_B through the point M when the moving line ZFZ_1 of fig. 1 coincides with the line FM, and the one passing through the point m when the line ZFZ_1 coincides with the line F_m of fig. 7 (I) or 11 (I). In fig. 4 two P,T-curves must pass through each point between M and m. For if we choose a pressure P between P_M and P_m we notice from fig. 7 (I) and 11 (I) that at the temperature T_B two different systems: solid F + liquid + gas have a vapour pressure P, from which it follows at once, that in fig. 4 two P,T-curves must pass through each point between M and m.

If on the curve $Mamb$ of fig. 7 (I) or 11 (I) we imagine two points of equal pressure connected by a straight line, we notice that there must be a definite pressure P_b at which this conjugation line passes through the point F. If now, the straight line ZFZ of fig. 1 passes through this conjugation line, the corresponding P,T-curve at the temperature T_B and the pressure P_b must exhibit a double point. This curve is represented in fig. 4 by $ZbFbZ_1$. All the other P,T-curves as a rule intersect the line Mm in two points of which one is situated above and the other below the point b.

If the temperature T_B is changed, then in fig. 7 (I) or 11 (I) the saturation line under its own vapour pressure changes its position and form, while P_M, P_m and P_b also change. The points M, m and b in fig. 4 then proceed along a curve; the curve through which the points M and m go, is represented by $MM_1M_2M_3Fm_2Km$; we will call this curve the boundary curve of the system: solid F + liquid + gas.

The equilibrium between solid F, liquid, and gas is determined by (6) II and 7 (II). To the point M and m also applies the relation:

$$\frac{x-a}{x_1-x} = \frac{y-\beta}{y_1-y} \, .$$

From this follows for the boundary curve:

$$\frac{dP}{dT} = \frac{(x_1-x)B-(x_1-a)D}{(x_1-x)A-(x_1-a)C}$$

so that this boundary curve must come into contact with the subli-mation line of the compound in the maximum sublimation point K and with the melting line in the minimum melting point F. Further it is evident that the three-phase line KF of the compound F is a part of the boundary curve.

Hence, all the P,T-curves in fig. 4 are situated in the region encompassed by the boundary curve; through each point of this region pass two P,T-curves and through each point of the boundary line passes a P,T-curve which meets this boundary line in that point.

The boundary curve itself is, therefore, no P,T-curve in that sense that it corresponds with a straight line passing through F, this, however, is the case if only one of the three components of F occurs in the vapour.

The double point b passes in fig. 4 through a curve terminating in the point F. When the saturation curves under their own vapour pressure possess, in the vicinity of the minimum melting point T_F, a form as in fig. 12 (I) no double point of a P,T-curve appears above T_F. The double point curve in fig. 4 then proceeds from F towards lower temperatures.

If, however, the saturation line at T_F under its own vapour pressure has a form such as the curve aFb in fig. 2 (II) the double points are still possible above T_F and at each temperature more than one may appear.

From (11a) it appears that R can become nil only for $x=a$ and $y=\beta$, therefore, in the point F. R, however, may become infinitely great and change its sign in other points of the component triangle. This will be the case when the denominator becomes 0, hence:

$$\{ (x_1-x)\,r + (y_1-y)\,s \} \cos \varphi + \{ (x_1-x)\,s + (y_1-y)\,t \} \sin \varphi = 0 \cdot \quad (16)$$

Let us call the solution for which this is the case, the solution q; (16) then means that the line Fq comes into contact in q with the liquidum line passing through the point q, of the heterogeneous region $L + G$. We may express this also as follows: R becomes infinitely great when the conjugation lines liquid-solid and liquid-gas are conjugated diagonals of the indicatrix in the liquidum point. As $R = \infty$, (11) is converted into:

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

, 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*).

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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: