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10. Any coincidence of the Q^4 is completed into a quadruple by two *complementary* points. The locus σ of those points which we shall call the *complementary curve* has apparently *quadruple points* in S_k ; for L_k^3 has four coincidences. Of the four coincidences of F^3 , four of the complementary points lie on σ^2 ; with this conic the curve σ has therefore $4 + 5 \times 4 = 24$ points in common. Consequently the *complementary curve* is of order 12.

The curves q^4 , which touch the plane λ in the points of the curve of coincidences γ^6 , intersect λ moreover on the complementary curve σ^{12} ; so they form a surface of order 24, which passes eight times through the curve q^5 .

This surface is intersected by a plane λ' along a curve of order 24 with 5 octuple points S_k . As the curve of coincidences γ^6 lying in λ' has double points in S_k the two curves outside S_k have $24 \times 6 - 5 \times 8 \times 2 = 64$ points in common. Consequently there are 64 curves q^4 , *touching two given planes*.

The surface A^9 belonging to the straight line l intersects an arbitrary plane φ along a curve φ^9 , which has 5 triple points on q^5 . As the curve of coincidences φ^6 lying in φ has 5 nodes on q^5 , it intersects φ^9 moreover in $9 \times 6 - 5 \times 3 \times 2 = 24$ points. From this appears once more that the curves q^4 , which touch a given plane, form a *surface of order 24*. At the same time, the fact that the *complementary curve* is of order 12, is confirmed.

Chemistry. — “*Equilibria in ternary systems*”. XII. By Prof. SCHREINEMAKERS.

We have seen in the previous communication that the saturation-curve under its own vapour-pressure of the temperature T_H (the point of maximum temperature of the binary system $F + L + G$) is either a point [fig. 5 (XI)] or a curve [fig. 6 (XI)]. We shall now examine this case more in detail.

If we calculate $\frac{dy}{dx}$ for this curve in the point H from (6) and (7) (XI), then we find an infinitely great value. The curve going through H in fig. 6 (XI) and the curve disappearing in H of figure 5 (XI) come in contact, therefore, in H with the side BC . Now we take a temperature somewhat lower than T_H . The saturation-curve under its own vapour-pressure terminates then in two points n and h situated on different sides of and very close to H . [n and h in fig. 4—6 (XI) may be imagined very close to H .] As the saturation-curve

under its own vapour-pressure touches BC in H , the tangent in n and the tangent in h to the curve, going through these points, will yet be almost parallel BC .

Because the equilibria $F + \text{liquid } n + \text{vapour } n_1$ and $F + \text{liquid } h + \text{vapour } h_1$ differ but very little from one another, the perspective concentrations S and S_1 (see the previous communication) will be, on addition of a third substance, also approximately equal. Therefore, when in the one equilibrium $S > S_1$, this is also the case in the other. Of course the same applies to $S < S_1$. Now we distinguish, according as the substance expands or contracts on melting, two principal cases.

1. F expands on melting ($V > v$). The point H is then situated with respect to F as in fig. 4—6 (XI) viz. between F and C , but close to F ; ΔV is negative between F and H , positive in the other points of BC . From the situation of n and h with respect to F , it follows that S and S_1 are both positive. We distinguish $S > S_1$ and $S < S_1$.

a. $S > S_1$. As ΔV is positive in h and negative in n , it follows from our previous communication that the pressure decreases from h along the saturationcurve under its own vapour-pressure and it increases from n . In which direction shall this curve now proceed from h ? As the tangent in h coincides almost with BC , the curve must go from h either almost in the direction towards n or almost in opposite direction. We find the first in fig. 5, the second in fig. 6 (XI). In order to determine this direction, it is to be considered that the region $L-G$ shifts on decrease of pressure from h towards n , so that the pressure decreases in this direction. As the pressure along the saturationcurve under its own vapour-pressure must also decrease from h , this curve must therefore, also go from h almost in the direction towards n . It has, therefore, from h a direction as in fig. 5 (XI). As the tangent in n coincides almost with BC , the curve must go from n either almost in the direction towards h or almost in opposite direction. Considering that the region $L-G$ shifts on increase of pressure from n towards h , so that the pressure increases from n towards h and further that the pressure along the saturationcurve under its own vapour-pressure must also increase from n , we see that this curve must go, therefore, also from n almost in the direction towards h .

The saturationcurve under its own vapour-pressure has, therefore, a form as curve hn in fig. 5 (XI); it is situated, therefore, close to the side BC and it disappears at T_H in the point H .

b. $S < S_1$. In a similar way as above we find that the pressure

along the saturationcurve under its own vapour-pressure increases from h and decreases from n . Further we find that this curve must have in the vicinity of n and h a direction as in fig. 6 (XI). As further the pressure in h is greater than in n , therefore on this curve as well a point of maximum- as a point of minimumpressure must be situated. Consequently, we obtain a curve hn , as in fig. 6 (XI), this does not disappear at the temperature T_H , but it forms a curve, touching the side BC in H .

2. F melts with decrease of volume ($V < v$). Now the points H and H_1 are no more situated, as in the previous case, between F and C . From the binary equilibrium $F + L + G$ it follows that H is situated between F and B ; the point H_1 may be imagined as well between F and C as between F and B . In the last case H_1 should be situated between F and H and therefore very close to H ; the region $L-G$ should then be very narrow in the vicinity of the side BC , which is only possible in very exceptional cases. Therefore we consider only the first case: H is situated between F and B , and H_1 between F and C .

If we take two points n and h close to H and the corresponding points n_1 and h_1 close to H_1 then we see that S and S_1 have an opposite sign. If further we keep in mind that ΔV is negative between F and H and positive in the other points of BC , then it follows, in a similar way as above, that curve nh must have a form as in fig. 5 (XI). Therefore, it disappears at T_H in the point H . Consequently, we obtain a diagram as in fig. 5 (XI), but with this difference, that H is situated now between F and B .

Contemplating the boilingpointcurves of F , we obtain diagrams as fig. 5 and 6 (XI), the arrows must then however, indicate in opposite direction. Further we must imagine the point of maximum temperature H to be replaced by the point of maximum pressure Q of the binary equilibrium $F + L + G$. ΔW is negative between F and Q , positive in the other points of BC . From the position of Q and Q_1 with respect to F , it follows that S and S_1 are both positive. We distinguish two cases.

a. $S > S_1$. We find that the boilingpointcurve ln has a form as in fig. 5 (XI); the arrows must, however, indicate in opposite direction. Therefore, this curve disappears under the pressure P_Q in the point Q .

b. $S < S_1$. The boilingpointcurve ln has a form as in fig. 6 (XI); the arrows must, however, indicate in opposite direction. Therefore the curve does not disappear in Q under the pressure P_Q .

If we sum together the results obtained above, we have:

1. F melts with increase of volume. The saturationcurve under its own vapour-pressure disappears, when is raised the temperature in H [fig. 4 (XI)] when the concentration of the new substance is greater in the liquid than in the vapour. It does not disappear in H [fig. 6 (XI)] when the concentration of the new substance is smaller in the liquid than in the vapour.

2. F melts with decrease of volume. The saturationcurve under its own vapour-pressure disappears, when is raised the temperature in H [Fig. 5 (XI)], wherein however H must be situated between F and B]

3. The boilingpointcurve disappears, on increase of P in Q [fig. 5 (XI)], when the concentration of the new substance is greater in the liquid than in the vapour. It does not disappear in Q [fig. 6 (XI)] when the concentration of the new substance is smaller in the liquid than in the vapour. We mean of course, with "concentration" above "perspective concentration".

Now we will deduce in another way the relations in the vicinity of the point H or Q . The saturationcurve under its own vapour-pressure is fixed by the equations (1) (II), when we put therein $\alpha = 0$ and when we keep T constant. As $\frac{\partial Z}{\partial x}, \frac{\partial^2 Z}{\partial x^2}$, etc. become infinitely great for $x = 0$, we shall put

$$Z = U + RTx \log x \dots \dots \dots (1)$$

so that all differential quotients of U with respect to x , remain finite. We put in the same way :

$$Z_1 = U_1 + RTx_1 \log x_1 \dots \dots \dots (2)$$

so that the same applies to U_1 . Then we have :

$$\frac{\partial Z}{\partial x} = \frac{\partial U}{\partial x} + RT(1 + \log x) \quad ; \quad \frac{\partial Z}{\partial y} = \frac{\partial U}{\partial y} \quad ; \quad \frac{\partial Z}{\partial P} = \frac{\partial U}{\partial P} = V \dots (3)$$

and similar relations for Z_1 and U_1 .

The equations 1 (II) then become :

$$x \frac{\partial U}{\partial x} + (y - \beta) \frac{\partial U}{\partial y} + RTx - U + \zeta = 0 \dots \dots (4)$$

$$x_1 \frac{\partial U_1}{\partial x_1} + (y_1 - \beta) \frac{\partial U_1}{\partial y_1} + RTx_1 - U_1 + \zeta = 0 \dots \dots (5)$$

$$\frac{\partial U}{\partial x} + RT(1 + \log x) = \frac{\partial U_1}{\partial x_1} + RT(1 + \log x_1) \dots \dots (6)$$

$$\frac{\partial U}{\partial y} = \frac{\partial U_1}{\partial y_1} \dots \dots \dots (7)$$

In the points H and H_1 of figs. 4—6 (XI), the pressure is equal to P_H , $x = 0$ and $x_1 = 0$; further we put $y = (y)_0$ and $y_1 = (y_1)_0$. For a point in the vicinity of BC on this saturationcurve under its own vapour-pressure, the pressure is $P_H + dP$, $x = \xi$, $x_1 = \xi_1$, $y = (y)_0 + \eta$ and $y_1 = (y_1)_0 + \eta_1$.

In the points H and H_1 themselves the binary equilibrium $F + L + G$ exists; to this applies:

$$-(y - \beta) \frac{\partial U}{\partial y} - U + \xi = 0 \quad \frac{\partial U}{\partial y} = \frac{\partial U_1}{\partial y_1} \quad \dots \quad (8)$$

wherein the pressure is equal to P_H , $y = (y)_0$, $y_1 = (y_1)_0$ and U and U_1 are independent of x and x_1 .

We now take the condition (6), from this it follows:

$$RT \log \frac{x_1}{x} = \frac{\partial U}{\partial x} - \frac{\partial U_1}{\partial x_1} \quad \dots \quad (9)$$

Therefore, we obtain for very small values of x and x_1 :

$$\log \frac{\xi_1}{\xi} = \frac{1}{RT} \text{Lim} \left(\frac{\partial U}{\partial x} - \frac{\partial U_1}{\partial x_1} \right) \quad \dots \quad (10)$$

or

$$\xi_1 = K \xi \quad \dots \quad (11)$$

wherein K is determined in (10).

We now take the condition (7); in this we put the pressure P equal to $P_H + dP$, $x = \xi$, $x_1 = \xi_1$, $y = (y)_0 + \eta$ and $y_1 = (y_1)_0 + \eta_1$.

If we expand both terms of (7) into a series and consider that in the point H (8) is satisfied, then we find:

$$s \xi + t \eta + \frac{\partial V}{\partial y} dP + \frac{1}{2} \frac{\partial s}{\partial x} \cdot \xi^2 + \frac{1}{2} \frac{\partial t}{\partial y} \cdot \eta^2 + \frac{1}{2} \frac{\partial^2 V}{\partial y \partial P} dP^2 + \frac{\partial s}{\partial x \partial y} \xi \eta + \left. \begin{aligned} &+ \frac{\partial^2 V}{\partial x \partial y} \xi dP + \frac{\partial^2 V}{\partial y^2} \cdot \eta dP + \dots []_1 \end{aligned} \right\} \quad (12)$$

Herein $r = \frac{\partial^2 U}{\partial x^2}$, $s = \frac{\partial^2 U}{\partial x \partial y}$, $t = \frac{\partial^2 U}{\partial y^2}$; these values must be kept, as they are in the point H . The second member of (12) is indicated by $[]_1$; this means that we deduce the second member from the first by substituting ξ_1 , η_1 , s_1 , t_1 etc. for ξ , η , s , t etc. Now we expand (4) into a series; if we keep in mind, that in the point H (8) is again satisfied, and that x and x_1 must be put equal to zero, then we find a series, which we write in the following form:

$$RT \cdot \xi + \frac{1}{2} t \eta^2 - (V - v) dP - \frac{1}{2} \left(\frac{\partial V}{\partial P} - \frac{\partial v}{\partial P} \right) dP^2 + R + (y - \beta) L = 0 \quad (13)$$

In R only terms occur, which are infinitely small with respect

to those, which are already written down, viz. ξ^2 , $\xi\eta$, etc. ξdP and ηdP are wanting. L represents the first term of (12). For the sake of simplification (y_0) has been replaced by y .

If we expand (5) into a series, we find:

$$RT \xi_1 + \frac{1}{2} t_1 \eta_1^2 - (V_1 - v) dP - \frac{1}{2} \left(\frac{\partial V_1}{\partial P} - \frac{\partial v}{\partial P} \right) dP^2 + R_1 + (y_1 - \beta) L_1 = 0 \quad (14)$$

Herein R_1 contains only terms, infinitely small with respect to those preceding, L_1 represents the second term of (12); $(y_1)_0$ has been replaced by y_1 .

Now, in the point H the denominator of (8) (XI) is equal to zero, therefore:

$$(y_1 - \beta) V + (y - y_1) v + (\beta - y) V_1 = 0.$$

We write this condition in the form:

$$\frac{V - v}{y - \beta} = \frac{V_1 - v}{y_1 - \beta} = \frac{V_1 - V}{y_1 - y} = \mu \quad \dots \quad (15)$$

Now we have the four relations (11), (12), (13) and (14) between the five variables. If we multiply (13) with $y_1 - \beta$ and (14) with $(y - \beta)$ then follows:

$$\left. \begin{aligned} (y_1 - \beta) \left[RT \xi + \frac{1}{2} t \eta^2 - \frac{1}{2} \left(\frac{\partial V}{\partial P} - \frac{\partial v}{\partial P} \right) dP^2 \right] + \dots = \\ = (y - \beta) \left[RT \xi_1 + \frac{1}{2} t_1 \eta_1^2 - \frac{1}{2} \left(\frac{\partial V_1}{\partial P} - \frac{\partial v}{\partial P} \right) dP^2 \right] + \dots \end{aligned} \right\} \quad (16)$$

These equations may be satisfied when we take ξ and ξ_1 of the order dP^2 and η and η_1 of the order dP . From (12), (13) and (14) then follows:

$$t\eta + \frac{\partial V}{\partial y} dP = t_1\eta_1 + \frac{\partial V_1}{\partial y_1} dP \quad \dots \quad (17)$$

$$t\eta = \left(\mu - \frac{\partial V}{\partial y} \right) dP \quad \dots \quad (18)$$

$$t_1\eta_1 = \left(\mu - \frac{\partial V_1}{\partial y_1} \right) dP \quad \dots \quad (19)$$

These last three equations are, as is seen immediately, dependent on one another. Substituting η from (18) and η_1 from (19) in (16) we find:

$$2 RT \left[(y_1 - \beta) - (y - \beta) \frac{\xi_1}{\xi} \right] \xi = a \cdot dP^2 \quad \dots \quad (20)$$

Herein $\xi_1 : \xi$ is fixed by (11); further is:

$$a = \frac{y-\beta}{t_1} \left(\mu - \frac{\partial V_1}{\partial y_1} \right)^2 - \frac{(y_1-\beta)}{t} \left(\mu - \frac{\partial V}{\partial y} \right)^2 + (y_1-\beta) \frac{\partial V}{\partial P} + (y-y_1) \frac{\partial v}{\partial P} + (\beta-y) \frac{\partial V_1}{\partial P} \quad (21)$$

From (18) now follows:

$$2 RT \left[(y_1 - \beta) - (y - \beta) \frac{\xi_1}{\xi} \right] \xi = \frac{at^2}{\left(\mu - \frac{\partial V}{\partial y} \right)^2} \cdot \eta^2 \quad (22)$$

From (22) it follows that the saturationcurve under its own vapour-pressure under consideration is in the vicinity of the point H [fig. 4—6 (XI)] a parabola, which touches the side BC in H . From (18) and (20) follows the change of ξ and η along this curve at a small change of pressure dP .

We can find the meaning of a (22) in the following way.

We represent the length of Cp or Cq [fig. 1 (XI)] by Y , the length of the part, which is cut off by the liquid curve of the region $L - G$ from CB by y . Then we have:

$$t_0 \frac{dY}{dP} = \frac{V_0 - v}{Y - \beta} - \frac{\partial V_0}{\partial Y}; \quad t \frac{dy}{dP} = \frac{V_1 - V}{y_1 - y} - \frac{\partial V}{\partial y}; \quad t_1 \frac{dy_1}{dP} = \frac{V_1 - V}{y_1 - y} - \frac{\partial V_1}{\partial y_1} \quad (23)$$

Herein t_0 and V_0 refer to the point of intersection of the saturationcurve with BC . Now we put:

$$Y - y = l$$

and we calculate $\frac{dl}{dP}$ and $\frac{d^2l}{dP^2}$. For this it may be considered that

V_0 depends on P and Y , V on P and y and V_1 on P and y_1 . If now the saturationcurve of F and the liquid-curve of the region $L - G$ go both through the point H , then (15) is satisfied; also at the same time V_0 becomes $= V$ and $t_0 = t$. Then we find:

$$\frac{dl}{dP} = 0 \quad \text{and} \quad a = t(y - \beta)(y_1 - y) \frac{d^2l}{dP^2} \quad (24)$$

Substituting this value of a in (20), we find after deduction with the aid of (13) (XI) and (11)

$$2 RT \cdot K \left(1 - \frac{S}{S_1} \right) \xi = t(y - y_1) \frac{d^2l}{dP^2} \cdot dP^2 \quad (25)$$

and

$$2 RT \cdot K \left(1 - \frac{S}{S_1} \right) \xi = \frac{t^3 (y - y_1)}{\left(\mu - \frac{\partial v}{\partial y} \right)^2} \cdot \frac{d^2l}{dP^2} \cdot \eta^2 \quad (26)$$

wherein $t > 0$; that there may be agreement with our figures, we take $y - y_1 > 0$.

We now distinguish two cases.

1. $1 - \frac{S}{S_1}$ and $\frac{d^2l}{dP^2}$ have the same sign. From (26) it follows that ξ is positive, so that the parabola touches BC in H and is further situated within the triangle [fig. 6 (XI)]. This is apparent also yet from (25), as ξ becomes positive as well for dP positive as negative.

2. $1 - \frac{S}{S_1}$ and $\frac{d^2l}{dP^2}$ have an opposite sign. From (26) it follows that ξ is negative. Therefore the parabola touches BC in H , but is further situated outside the triangle. Therefore a similar parabola may be imagined in fig. 5 (XI). Then only its point H represents a liquid, its other points have no meaning.

From our deduction of $\frac{dl}{dP}$ and $\frac{d^2l}{dP^2}$ in the point H , follows:

$$Y - y = \frac{1}{2} \cdot \frac{d^2l}{dF^2} \cdot dF^2.$$

Now, in the point H of fig. 4—6 (XI) $Y - y$, therefore also $\frac{dl^2}{dP^2}$ becomes positive, as well on increase as on decrease of pressure. When, however, the point H is situated on the other side of F , then $Y - y$ and therefore also $\frac{d^2l}{dP^2}$ becomes negative.

We now consider some cases.

1. F melts with increase of volume ($V > v$). $\frac{d^2l}{dP^2} > 0$. S and S_1 positive.

a. $S > S_1$. From (26) follows: the saturationcurve under its own vapourpressure is a parabola, which touches BC in H , but is situated further outside the triangle [fig. 5 (XI)].

b. $S < S_1$. From (26) follows: the saturationcurve under its own vapourpressure is a parabola, which touches BC in H , but is further situated within the triangle. [fig. 6 (XI)].

2. F melts with decrease of volume ($V < v$). $\frac{d^2l}{dP^2} < 0$.

We take again S and S_1 with opposite sign.

As sub 1. a. In fig. 5 (XI) the point H must be imagined on the other side of F , therefore, between F and B and H_1 between F and C .

From (18) it follows that η changes sign with dP , as in the point H the coefficient of dP is negative, η and dP must have the opposite sign. Therefore, the pressure increases in the direction in

which η decreases and reversally. We see that this is in agreement with the direction of the arrows in fig. 5 and 6 (XI).

If it is desired to know the influence of a small change of T on the position of the saturation curve under its own vapour pressure going through H , we must also include terms with dT in the previous expansions into a series. Now $U = Z - RTx \log x$ therefore, $\frac{\partial U}{\partial T} = -H - Rx \log x$, therefore in the point H ($x = 0$) itself $\frac{\partial U}{\partial T} = -H$.

In the right member of (12), therefore, must be added $-\frac{\partial H}{\partial y} dT$ and terms with ξdT and ηdT ; in the left member $-\frac{dH_1}{\partial y_1} dT$.

In (13) must be added $(H - \eta_v) dT$; in (14) $(H_1 - \eta_v) dT$; in order to distinguish the coordinate η , the entropy of the solid substance F is indicated by η_v .

In the first member of (16) must be added: $(y_1 - \beta) (H - \eta_v) dT$; in the second member $(y - \beta) (H_1 - \eta_v)$.

From (13) follows:

$$t\eta = \left(\mu - \frac{dV}{\partial y} \right) dP + \dots$$

from (14)

$$-t_1\eta_1 = \left(\mu - \frac{dV_1}{\partial y_1} \right) dP + \dots$$

As we must substitute these values in (16), it is apparent that we may neglect the other terms. As

$$(\beta - y_1) H + (y_1 - y) \eta_v + (y - \beta) H_1 = (y - \beta) \frac{\Delta W}{T}$$

we obtain:

$$2 RT \left[y_1 - \beta - (y - \beta) \frac{\xi_1}{\xi} \right] \xi = a \cdot dP^2 + (y - \beta) \cdot \frac{\Delta W}{T} \cdot dT$$

or, after deduction:

$$2 RT \cdot K \left(1 - \frac{S}{S_1} \right) \xi = t (y - y_1) \frac{d^2 l}{dP^2} \cdot dP^2 - \frac{\Delta W}{T} dT \quad (27)$$

and:

$$2 RT \cdot K \left(1 - \frac{S}{S_1} \right) \xi = \frac{t^2 (y - y_1)}{\left(\mu - \frac{\partial V}{\partial y} \right)^2} \cdot \frac{d^2 l}{dP^2} \cdot \eta^2 - \frac{\Delta W}{T} \cdot dT \quad (28)$$

From (28) it follows that not only the saturation curve under its

own vapour-pressure, going through H , but also those which are situated in the vicinity of H are parabolas.

In the point H of figs. 5--6 (XI) ΔW is negative, when H is situated on the other side of F , ΔW is positive. From (28) it now follows:

when the curve, touching in H is situated outside the triangle [fig. 5 (XI)], it shifts on decrease of T , within the triangle [curve hn in fig. 5 (XI)]

when the curve, touching in H is situated within the triangle [fig. 6 (XI)], it shifts on increase of T within the triangle [the closed curve in fig. 6 (XI)] and on decrease of T partly outside the triangle. Therefore, curve hn of fig. 6 (XI) must be imagined to be closed by a part hn situated outside the triangle; this part, however, has no physical meaning.

In fig. 1 three curves are drawn through F ; $F'l$ is the liquid-curve of the region $L-G$ at the temperature T_F and under the pressure P_F , therefore at the minimummeltingpoint of F ; $F'K$ is the boilingpointcurve and $F's$ the saturationcurve under its own vapourpressure. The two first curves are but partly drawn. We now construe in F a tangent to each of these curves. With the aid of the formulas from the previous communication, we find:

for the tangent to the liquidcurve ($F'l$) of the region LG :

$$\left(\frac{dy}{dx}\right)_l = - \frac{\left(\frac{x_1}{x} - 1\right) RT + (y_1 - \beta) s}{(y_1 - \beta) t} \dots \dots (29)$$

for the tangent ($F'Z_1$) to the boilingpointcurve ($E'K$):

$$\left(\frac{dy}{dx}\right)_k = - \frac{\left(\frac{x_1}{x} - 1\right) RT + (y_1 - \beta) s - RT \frac{D}{B}}{(y_1 - \beta) t} = \left(\frac{dy}{dx}\right)_l + \frac{D}{B} \cdot \frac{RT}{(y_1 - \beta) t} (30)$$

and for the tangent ($F'Z_2$) to the saturationcurve under its own vapourpressure ($F's$):

$$\left(\frac{dy}{dx}\right)_s = - \frac{\left(\frac{x_1}{x} - 1\right) RT + (y_1 - \beta) s - RT \frac{C}{A}}{(y_1 - \beta) t} = \left(\frac{dy}{dx}\right)_l + \frac{C}{A} \cdot \frac{RT}{(y_1 - \beta) t} (31)$$

Now we take again the most probable case that $BC-AD$ is positive (communication II). That there may be agreement with the figs. 5 and 6 (XI) and fig. 1, we take $V > v$ therefore A positive. As further $y_1 - \beta$ is negative, we can deduce:

$$\left(\frac{dy}{dx}\right)_l > \left(\frac{dy}{dx}\right)_k > \left(\frac{dy}{dx}\right)_s \dots \dots (32)$$

The curves F_l , F_h and F_s must, therefore, be situated with respect to one another as in fig. 1.

When $V < v$, therefore A is negative, then it follows:

$$\left(\frac{dy}{dx}\right)_s > \left(\frac{dy}{dx}\right)_l > \left(\frac{dy}{dx}\right)_k \dots \dots \dots (33)$$

The point H and therefore also the point s , must be imagined, however in this case, also in fig. 1 on the other side of F . In agreement with (33) F_l comes then between the two other curves.

Now we shall consider the solutionpath consisting of a straight line of F under its own vapourpressure or in short the solutionpath of F . We take viz. the system $F + L + G$, but we take care that the quantity of vapour is always very small. On change of T the liquid traces a straight line going through F , which we have called the solution- or cristallisationpath of F . In fig. 1 three similar solutionpaths FZ , FZ_1 , and FZ_2 are drawn.

Let us consider now the binary equilibrium $F + L + G$. In fig. 2 its P, T -curve is represented by EFU , Q is the point of maximum-pressure, H the point of maximum-temperature; F is the minimum-meltingpoint, K the point of maximumsublimation of the compound. aK is the sublimation-, Fd the meltingcurve. Curve EFU touches Fd in F and aK in K . It is apparent from the direction of the meltingcurve that we assume $V > v$ in agreement with fig. 1.

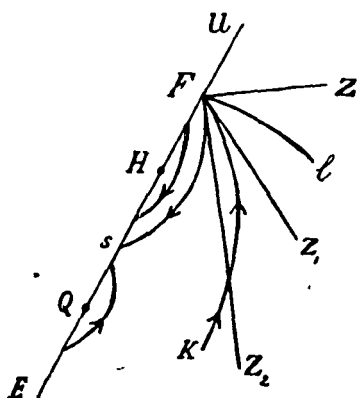


Fig. 1.

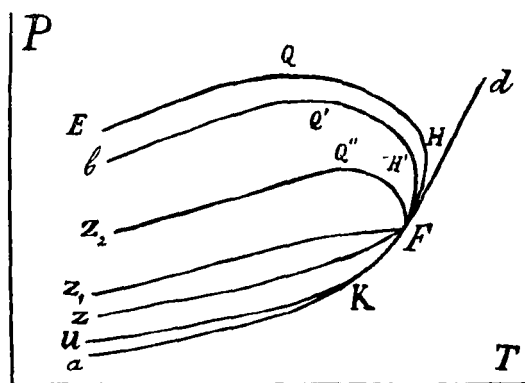


Fig. 2.

When the solutionpath FZ in fig. 1 coincides with FU , its P, T -curve in fig. 2 is, therefore, represented by UKF ; when FZ coincides in fig. 1 with FE , it is represented in fig. 2 by EHF . When the solutionpath FZ in fig. 1 turns from the position FU

towards FE , its corresponding P, T -curve must therefore change from UKF into EHF . Now we shall examine this more in detail.

The saturation curves under their own vapour pressure have, in the vicinity of H either a form as in fig. 5 (XI) or as in fig. 6 (XI); we assume that they have a form as in fig. 5 (XI). In fig. 1 the curve surrounded by F_s , and F_s , itself represent saturation curves under their own vapour pressure; the arrows indicate the direction of increasing pressure.

The boiling point curves have also a position as in fig. 5 (XI); we must consider, however, that H is replaced by the point of maximum pressure Q and that the arrows point in opposite direction. Two of these curves are drawn in fig. 1, one in the vicinity of Q and curve Fk ; the latter is indicated for a part only.

Now we imagine in fig. 1 a solution path between FE and FZ_2 . Imagining in this figure still many other saturation curves under their own vapour pressure to be drawn, then we see that some of these are not intersected by this path, other ones twice, and others again once. Further we see that one of these curves touches this path; we call that point of contact H' .

From this it follows: at first the temperature increases along this solution path from F up to H' and after that it decreases. Further it follows: $T_{H'}$ is lower than T_H .

Imagining yet many other boiling point curves to be drawn in fig. 1, then we see that one of these touches the solution path in a point that we shall call Q' . Now we deduce: the pressure increases along this solution path from F up to Q' and after that it decreases. Further it follows: $P_{Q'}$ is smaller than P_Q .

Now it follows from this all that the P, T -curve belonging to this solution path has a form in fig. 2 as curve bF with a point of maximum pressure in Q' and a point of maximum temperature in H' .

As long as the solution path in fig. 1 is situated between FE and FZ_2 , the P, T -curves retain a form as bF in fig. 2; according as the path, however, approaches closer to FZ_2 , the points Q' and H' come closer to F . When the path coincides with FZ_2 , H' coincides with F and the P, T -curve has a form as Z_2F in fig. 2 with a point of maximum pressure Q'' . The tangent in F stands vertically.

To see this, it must be considered that the line EZ_2 touches in F the saturation curve under its own vapour pressure going through F (F_s in fig. 1). Going from F , along an infinitely small distance, along curve F_s and therefore also along the tangent FZ_2 , the pressure increases while the temperature remains constant. As dP , therefore, is positive, and dT is zero, the P, T -curve therefore, in fig. 2, along

a small distance, must point vertically upwards, so that it has there a vertical tangent. Considering the saturationcurves under their own vapourpressure, we see that FZ_2 intersects only curves of temperatures lower than T_H , so that the temperature decreases along FZ_2 from F .

Considering the boilingpointcurves, we see that the same still applies to these as to a solutionpath, situated between FE and FZ_2 . The pressure, therefore, increases at first from F and after that it decreases. From all this it follows that the P, T -curve has, therefore, a form as curve bF in fig. 2.

Let us now take a solutionpath between FZ_1 and FZ_2 . It is easy to see that the P, T -curve retains a form as FZ_2 in fig. 2, with this difference, however, that the tangent in F stands no longer vertically. The curve proceeds viz. from F immediately towards higher pressures and lower temperatures. According as the solutionpath in fig. 1 comes closer to FZ_1 , in fig. 2 the point of maximumpressure Q'' approaches closer to F . When the solutionpath coincides with FZ_1 , Q'' coincides with F , and in figure 2 the P, T -curve obtains a form as Z_1F with a horizontal tangent in F .

In order to see this, we consider the solutionpath FZ_1 which touches the boilingpointcurve FK in F . (fig. 1). Going from F along an infinitely small distance along curve FK and, therefore, also along the tangent FZ_1 , the temperature decreases, while the pressure remains constant. As dT , therefore, is negative and dP is zero, the P, T -curve must, therefore, from F over a small distance point horizontally towards the left; consequently it has a horizontal tangent in F .

We now take a solutionpath FZ , situated between FU and FZ_1 . It follows from a consideration of the saturationcurves under their own vapourpressure and the boilingpointcurves in the vicinity of F , that pressure and temperature decrease from F . The P, T -curve is represented in fig. 2 by FZ , it proceeds from F towards lower temperatures and pressures.

At the deduction of fig. 2 it is assumed that the saturationcurves under their own vapourpressure and the boilingpointcurves have a form as in fig. 1. Curve Fs and Fk are drawn herein in the vicinity of F , concave towards H . When in F they turn their convex side towards H , then curve Fs will intersect its tangent FZ_2 still in another point and curve FK its tangent FZ_1 . Although then in fig. 2 the tangent in F to Z_1F remains horizontal and the tangent to Z_2F vertical, all curves will obtain a somewhat different form in the vicinity of F (we may also compare the previously

treated P, T diagrams for the case that F is a ternary compound).

After the previous considerations, the reader can easily deduce the P, T diagram for the solutionpaths of F , when the curves are situated as in fig. 6 (XI).

Formerly [5 (IV)] we have deduced for a solutionpath

$$\frac{dP}{dT} = \frac{DM-BN}{CM-AN} \dots \dots \dots (34)$$

now, as $\alpha = 0$, herein is:

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

$$N = x (x_1-x) r + [x (y_1-y) + (x_1-x) (y-\beta)] s + (y_1-y) (y-\beta) t$$

In the point F becomes $x = 0$ and $y = \beta$, therefore $M = 0$ and $N = 0$. Let us now contemplate a solution path and let us call the angle, which it forms with the X -axis, φ . If we imagine for the sake of simplicity that the coordinatesystem is rectangular, then it follows: $\cotg. \varphi = x : (y-\beta)$. We then obtain:

$$\frac{M}{N} = \frac{x r \cotg \varphi + 2 x s + (y-\beta) t}{(x_1-x) r \cotg \varphi + [(y_1-y) \cotg \varphi + x_1-x] s + (y_1-y) t}$$

In the point F becomes $x = 0$ and $y = \beta$ therefore:

$$\frac{M}{N} = \frac{RT}{\left(\frac{x_1}{x} - 1\right) RT + (y_1-\beta) (s + t \tg \varphi)} \dots \dots (35)$$

The question now arises, what P, T curve touches the meltingline Fd in F . For this must, according to (34):

$$\frac{DM-BN}{CM-AN} = \frac{B}{A}$$

therefore, $M : N = 0$. It is apparent from (35) that this is only the case when $\tg \varphi$ is infinitely great, consequently for $\varphi = 90^\circ$ and $\varphi = 270^\circ$. Then the solutionpath coincides either with FE or with FU (fig. 1). Therefore, both the binary solutionpaths EF and UF only touch in F the meltingline Fd ; the ternary paths do not touch this meltingline.

In order that the tangent to the P, T curve of a solutionpath may be vertical in F we have, according to (34) $CM-AN=0$. As $M:N$ is fixed by (35), it follows that this is the case, when

$$\tg \varphi = \frac{\left(\frac{x_1}{x} - 1\right) RT + (y_1-\beta) s - RT \frac{C}{A}}{(y_1-\beta) t}$$

From (31) it follows that in F this solutionpath must touch the saturationcurve under its own vapourpressure going through the

point F [curve Fs fig. 1], the required solutionpath is, therefore, FZ_2 .

If we require a solutionpath, whose x, t curve has a horizontal tangent in F , we must, as follows from (34) put $DM - BN = 0$. From this now follows:

$$tg \varphi = - \frac{\left(\frac{x_1}{x} - 1\right) RT + (y_1 - \beta) s - RT \frac{D}{B}}{(y_1 - \beta) t} \dots \dots (37)$$

From this it follows, in connection with (30) that in F the solutionpath must touch the boilingpointcurve going through the point F [curve Fk in fig. 1]; the wanted solutionpath is, therefore, FZ_1 .

Now it follows from the previous considerations: in the P, T diagram (fig. 2), none of the ternary solutionpaths touches the meltingline Fd in F ; the solutionpath, touching in F in the concentration-diagram (fig. 1) the saturationcurve under its own vapour-pressure going through F , has in the P, T diagram a vertical tangent in F ; the solutionpath, in the concentrationdiagram touching the boiling-pointcurve going through F , has a horizontal tangent in F in the P, T diagram.

It is evident that the above-mentioned rules apply quite generally no matter whether the relations of fig. 5 (XI) or 6 (XI) occur or the curves in F are concave or convex towards H .

In fig. 1 Fk represents the liquidcurve of a region LG , now we imagine a solutionpath, touching curve Fk in F . The direction of this solutionpath is, therefore, fixed by (29). In order to find $\frac{dP}{dT}$ in the point F of this path, we must, therefore, substitute the second term of (29) in (35) for $tg \varphi$. We then find an infinitely great value for (35). From (34) now follows:

$$\frac{dP}{T} = \frac{D}{C} = \frac{H_1 - H + (\beta - y_1) \frac{\partial H}{\partial y}}{V_1 - V + (\beta - y_1) \frac{\partial V}{\partial y}} \dots \dots (38)$$

The latter part of (38) indicates the direction of the P, T -curve of the evaporationline of the liquid F . This line is traced, when we melt the substance F and when we regulate after that the temperature and the pressure in such a way that the liquid remains in equilibrium with an infinitely small quantity of vapour. Therefore the liquid retains the composition F during this. This curve is represented in fig. 3 (III) by Fc . the pressure and the temperature increase from F along this curve.

Consequently we find: the solutionpath, touching in F in the

concentration-diagram the liquid curve of the region $L-G$ (curve F_l in fig. 1) going through F , has in the P, T -diagram the same tangent in F as the evaporationline of the liquid F starting from F .

If we compare the P, T -diagram of the solutionpaths of a binary compound F (fig. 2) with those of a ternary compound F [fig. 4 (IV) and 1 - 3 (V)], then we see very great differences in the vicinity of the point F . We find these differences also in the concentration-diagrams. When viz. in fig. 1. in the point F we construct tangents to the curves F_l , F_k and F_s going through the point F , three different tangents arise. If F is a ternary compound, as e. g. in fig. 1 (IV), then these curves touch one another in F and the three tangents coincide in the line XFY .

All this is based on the following. When F is a binary compound, a new substance must be added, in order to trace a ternary solution-path from F . When, however, F is a ternary compound, we add no new substance in order to trace a solutionpath, from F , but substances, which are already present in the melted F .

(To be continued).

Physics. "An apparatus for the determination of gas isotherms up to about 3000 atms." VAN DER WAALS-fund researches N^o. 5. By Prof. PH. KOHNSTAMM and K. W. WALSTRA. (Communicated by Prof. VAN DER WAALS).

(Communicated in the meeting of December 27, 1913).

As is known the material for testing the theory of the equation of state at very high pressures consists almost exclusively of what AMAGAT has published in his famous papers. It seems desirable for different reasons to extend this material. Quite apart from the desirability to get to know the behaviour of other gases than those examined by AMAGAT — we think in the first place of the mon-atomic gases — AMAGAT's work itself gives rise to different questions, which can only be decided by means of new experiments.

First of all it is known that AMAGAT does not give the direct results of his observations; he only publishes the results of a graphical interpolation between these observations. The question rises how great the deviations are between the interpolated and the real observations, and whether another way of interpolation had been possible. Nor can the probable experimental error of AMAGAT's observations be inferred from his experiments. And it has finally