

Citation:

F.A.H. Schreinemakers, Equilibria in ternary systems. XIV, in:
KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 1136-1152

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

(Communicated in the meeting of March 28, 1914).

After the previous discussion of the saturationcurves under their own vapourpressure and of the boilingpointcurves of a component, we must yet deduce its solutionpaths under its own vapour-pressure. As, however, we discussed already formerly those of binary and ternary compounds the reader may easily deduce those of a component.

In the previous communications VII—X we have discussed the fourphase-equilibrium $F + F' + L + G$; for this we have assumed that F and F' are both ternary compounds. It is, however, easily seen. that these considerations apply also to binary and unary substances, provided that F and F' contain together the three components; the line FF' is then situated, perhaps its extremities excepted, completely within the componentstriangle. Then the liquid contains also the three components, so that the quantity of none of them can approach to zero in it. When F and F' contain together only two components, the line FF' coincides with one of the sides of the componentstriangle. The quantity of one of the components may then approach to zero in the liquid and in the vapour, so that we must contemplate this case separately.

When we take e. g. the ternary equilibrium $B + C + L + G$, it is evident that the quantity of A can become equal to zero in the liquid and in the vapour. If the liquid and the vapour, in which the quantity of one of the components becomes equal to zero, is represented by L_0 and G_0 , then the binary equilibrium $B + C + L_0 + G_0$ arises. Herein L_0 is the eutectical liquid under its own vapour-pressure of the binary system $B + C$; G_0 is the corresponding vapour; the corresponding temperature and pressure we call T_0 and P_0 . The ternary equilibrium $B + C + L + G$ terminates, therefore, when the quantity of A becomes zero, at the temperature T_0 and under the pressure P_0 in the binary eutectical point with the phases $B + C + L_0 + G_0$.

Reversally we may also say that by addition of A the fourphase-equilibrium $B + C + L + G$ proceeds from the binary eutectical point with the phases $B + C + L_0 + G_0$.

When we take a eutectical point $B + C + L_0$ under a constant pressure, so that no vapour occurs, the threephaseequilibrium $B + C + L$ is formed on addition of A and the eutectical temperature is always lowered. From this naturally the question follows:

what influence has the addition of a new substance A on the temperature T_0 and the pressure P_0 of the eutectical point under its own vapourpressure with the phases $B + C + L_0 + G_0$.

We may put this question also more generally; for this we replace the eutectical point with the phases $B + C + L_0 + G_0$ by a quadruplepoint with the phases $F + F' + L_0 + G_0$; F and F' are then either the components B and C or binary compounds of B and C .

When we take a constant pressure so high, that the vapour disappears, and when we add the substance A to the equilibrium $F + F' + L_0$ then the temperature is lowered. We may express this also in the following way: the common meltingpoint or point of inversion of two substances is lowered under a constant pressure by addition of a third substance¹⁾.

We now must put the question what influence has the addition of a new substance A on the temperature T_0 and on the pressure P_0 of the quadruplepoint with the phases $F + F' + L_0 + G_0$.

Firstly we shall consider the general case treated in communication VIII more in detail. Instead of the equations (2), (3), and (4) (VIII) we write:

$$[(x - \alpha)r + (y - \beta)s] dx + [(x - \alpha)s + (y - \beta)t] dy = AdP - BdT \quad (1)$$

$$[(x_1 - \alpha)r + (y_1 - \beta)s] dx + [(x_1 - \alpha)s + (y_1 - \beta)t] dy = (A + C) dP - (B + D) dT \quad (2)$$

$$[(\alpha' - \alpha)r + (\beta' - \beta)s] dx + [(\alpha' - \alpha)s + (\beta' - \beta)t] dy = (A - A') dP - (B - B') dT \quad (3)$$

We find from (1) and (3), eliminating dy :

$$E(rt - s^2) dx = \left\{ \begin{aligned} & [(\alpha' - \alpha)A + (x - \alpha)A']s + \{(\beta' - y)A + (y - \beta)A'\}t \} dP \\ & - [(\alpha' - \alpha)B + (x - \alpha)B']s + \{(\beta' - y)B + (y - \beta)B'\}t \} dT \end{aligned} \right\} \quad (4)$$

We find from (2) and (3):

$$E_1 (rt - s^2) dx = \left\{ \begin{aligned} & [(\alpha' - \alpha_1)A + (\alpha_1 - \alpha)A' + (\alpha' - \alpha)C]s + \{(\beta' - y_1)A + (y - \beta)A' + (\beta' - \beta)C\}t \} dP \\ & - [(\alpha' - \alpha_1)B + (\alpha_1 - \alpha)B' + (\alpha' - \alpha)D]s + \{(\beta' - y_1)B + (y - \beta)B' + (\beta' - \beta)D\}t \} dT \end{aligned} \right\} \quad (5)$$

Herein E is equal to:

$$\begin{aligned} (\alpha' - \alpha)(\beta - y) + (x - \alpha)(\beta' - y) &= (\beta' - \beta)(x - \alpha) + (\alpha' - \alpha)(\beta - y) = \\ &= (\beta' - \beta)(x - \alpha') + (\alpha' - \alpha)(\beta' - y). \end{aligned}$$

We find E_1 by substituting in E x_1 and y_1 for x and y . For the sake of abbreviation we put the following:

¹⁾ F. A. H. SCHREINEMAKERS. Heterog. Gleichgewichte III.

$$\left. \begin{aligned} (\alpha' - \alpha) V + (x - \alpha') v + (\alpha - x) v' + E \frac{\partial V}{\partial y} &= (\alpha' - \alpha) V_y \\ (\beta' - \beta) V + (y - \beta') v + (\beta - y) v' - E \frac{\partial V}{\partial x} &= (\beta' - \beta) V_x \\ (\alpha' - \alpha) H + (x - \alpha') \eta + (\alpha - x) \eta' + E \frac{\partial H}{\partial y} &= (\alpha' - \alpha) H_y \\ (\beta' - \beta) H + (y - \beta') \eta + (\beta - y) \eta' - E \frac{\partial H}{\partial x} &= (\beta' - \beta) H_x \end{aligned} \right\} \quad (6)$$

When we replace E, V, H, x and y by E_1, V_1, H_1, x_1 and y_1 ($\frac{\partial V}{\partial y}, \frac{\partial V}{\partial x}$ etc. rest unchanged) we obtain the corresponding quantities V_{1y}, V_{1x}, H_{1y} and H_{1x} .

The following relations exist between these eight quantities, as we may easily deduce.

$$\left. \begin{aligned} E_1 V_y - E V_{1y} &= E_1 V_x - E V_{1x} \\ E_1 H_y - E H_{1y} &= E_1 H_x - E H_{1x} \end{aligned} \right\} \dots \dots \dots (7)$$

We find another relation by eliminating E_1 and E from both these equations.

Substituting in (4) and (5) their values for A, B etc., we find with the aid of (6):

$$\left. \begin{aligned} E(rt - s^2) dx &= [(\alpha' - \alpha) V_y \cdot s + (\beta' - \beta) V_x \cdot t] dP \\ &\quad - [(\alpha' - \alpha) H_y \cdot s + (\beta' - \beta) H_x \cdot t] dT \end{aligned} \right\} \quad (8)$$

$$\left. \begin{aligned} E_1(rt - s^2) dx &= [(\alpha' - \alpha) V_{1y} \cdot s + (\beta' - \beta) V_{1x} \cdot t] dP \\ &\quad - [(\alpha' - \alpha) H_{1y} \cdot s + (\beta' - \beta) H_{1x} \cdot t] dT \end{aligned} \right\} \quad (9)$$

Eliminating dx from (8) and (9) we find, when we make use of the relations (7):

$$\frac{dP}{dT} = \frac{H_{1y} - \frac{E_1}{E} H_y \cdot H_{1x} - \frac{E_1}{E} H_x}{V_{1y} - \frac{E_1}{E} V_y \cdot V_{1x} - \frac{E_1}{E} V_x} \dots \dots \dots (10)$$

Herein H_y, H_x etc. have the meaning indicated in (6), from (10) it follows however, that this is also true when the term, in which E or E_1 occurs, is omitted in each of the eight relations (6).

Further we may deduce from (8) and (9):

$$\frac{dP}{dx} = \frac{(rt - s^2) E \left(H_{1x} - \frac{E_1}{E} H_x \right)}{(\alpha' - \alpha)(V_y H_{1y} - V_{1y} H_y) s + (\beta' - \beta)(V_x H_{1x} - V_{1x} H_x) t} \quad (11)$$

$$\frac{dT}{dx} = \frac{(rt - s^2) E \left(V_{1x} - \frac{E_1}{E} V_x \right)}{N} \dots \dots \dots (12)$$

In (12) N indicates the same denominator as in (11).

Let us now consider the case that both the solid substances of the equilibrium $F + F' + L + G$ are binary compounds of B and C . We must then put $a = 0$ and $a' = 0$. As E becomes $= (\beta' - \beta) x$ and $E_1 = (\beta' - \beta) x_1$, it follows from (10), (11) and (12):

$$\frac{dP}{dT} = \frac{H_{1,x} - \frac{x_1}{x} H_x}{V_{1,x} - \frac{x_1}{x} V_x} \dots \dots \dots (13)$$

$$\frac{dP}{dx} = \frac{(rt - s^2)x \left(H_{1,x} - \frac{x_1}{x} H_x \right)}{(V_x H_{1,x} - V_{1,x} H_x)t} \dots \dots \dots (14)$$

$$\frac{dT}{dx} = \frac{(rt - s^2)x \left(V_{1,x} - \frac{x_1}{x} V_x \right)}{(V_x H_{1,x} - V_{1,x} H_x)t} \dots \dots \dots (15)$$

Let us now consider the terminating point of the ternary equilibrium $F + F' + L + G$ in the quadruplepoint $F + F' + L_0 + G_0$. For this we make in the previous equations x and x_1 approach to zero. As $\lim rx = RT$ it follows:

$$\frac{dP}{dT} = \frac{H_{1,x} - \left(\frac{x_1}{x} \right)_0 H_x}{V_{1,x} - \left(\frac{x_1}{x} \right)_0 V_x} \dots \dots \dots (16)$$

$$\frac{dP}{dx} = \frac{RT \left[H_{1,x} - \left(\frac{x_1}{x} \right)_0 H_x \right]}{V_x H_{1,x} - V_{1,x} H_x} \quad \frac{dT}{dx} = \frac{RT \left[V_{1,x} - \left(\frac{x_1}{x} \right)_0 V_x \right]}{V_x H_{1,x} - V_{1,x} H_x} \quad (17)$$

Herein $\left(\frac{x_1}{x} \right)_0$ is the value which $\frac{x_1}{x}$ assumes for $x = 0$ and $x_1 = 0$.

Further is:

$$(\beta' - \beta) V + (y - \beta') v + (\beta - y) v' = (\beta' - \beta) V_x \quad (18)$$

$$(\beta' - \beta) V_1 + (y_1 - \beta') v + (\beta - y_1) v' = (\beta' - \beta) V_{1,x} \quad (19)$$

$$(\beta' - \beta) H + (y - \beta') \eta + (\beta - y) \eta' = (\beta' - \beta) H_x \quad (20)$$

$$(\beta' - \beta) H_1 + (y_1 - \beta') \eta + (\beta - y_1) \eta' = (\beta' - \beta) H_{1,x} \quad (21)$$

wherein to all quantities (y, y_1, V, V_1 , etc.) we must give the values, which they have in the quadruplepoint $F + F' + L_0 + G_0$. Herein L_0 has the composition: y quantities of $B + (1 - y)$ quant. of C ; G_0 has the composition: y_1 quant. of $B + (1 - y_1)$ quant. of C .

Between the three phases F, F' and L_0 always may occur the reaction:

$(\beta' - \beta)$ quant. of $L_0 + (y - \beta')$ quant. of $F + (\beta - y)$ quant. of $F' = 0$ (22), in which always one of the coefficients is negative. This reaction represents, according to the sign of the coefficients:

1. a congruent melting or solidification of $F + F'$ viz. the reaction $F + F' \rightleftharpoons L_0$.

2. an incongruent melting or solidification of $F + F'$ viz. the reaction $F \rightleftharpoons F' + L_0$ or $F' \rightleftharpoons F + L_0$.

Consequently the incongruent melting or solidification of $F + F'$ means: the inversion of F in F' or reversally, by the side of liquid and vapour.

From (18) and (20) it follows that V_x represents the change of volume and H_x the change of entropy, when one quantity of vapour is formed at this reaction. Therefore, V_x is the increase of volume, H_x the increase of entropy at the congruent or incongruent melting of $F + F'$.

Between the three phases F , F' and G_0 the reaction:

$(\beta' - \beta)$ quant. of $G_0 + (y_1 - \beta')$ quant. of $F + (\beta - y)$ quant. of $F' = 0$ (23) may take place. From (19) and (21) it follows that V_{1x} represents the increase of volume, H_{1x} the increase of entropy when one quantity of vapour is formed at the reaction (23). V_{1x} is, therefore, the increase of volume, H_{1x} the increase of entropy at the congruent or incongruent sublimation of $F + F'$.

If we call W_x the (congruent or incongruent) heat of melting, and W_{1x} the (congruent or incongruent) heat of sublimation of $F + F'$, then $H_x = \frac{W_x}{T}$ and $H_{1x} = \frac{W_{1x}}{T}$. Further we put for the sake of abbreviation

$$V_{1x} \cdot W_x - V_x \cdot W_{1x} = K \quad . \quad . \quad . \quad . \quad . \quad (24)$$

When V_x , the change of volume on melting of $F + F'$ is positive, K is certainly positive; when, however V_x is negative, this form will nevertheless still be also positive, by reason of the great value of V_{1x} with respect to V_x . For this we shall assume K positive.

When we put further:

$$\Delta V = V_{1x} - \left(\frac{x_1}{x}\right)_0 V_x \quad \text{and} \quad \Delta W = W_{1x} - \left(\frac{x_1}{x}\right)_0 W_x \quad . \quad (25)$$

it follows:

$$T \frac{dP}{dT} = \frac{\Delta W}{\Delta V} \quad ; \quad \frac{dP}{dx} = -\frac{RT}{K} \cdot \Delta W \quad ; \quad \frac{dT}{dx} = -\frac{RT^2}{K} \Delta V \quad . \quad (26)$$

$\left(\frac{x_1}{x}\right)_0$ is the ratio of the quantity of A in the vapour to that in the liquid when we add a little A to the binary equilibrium $F + F' +$

+ $L_0 + G_0$, we may call this ratio the limitratio of A in $F + F' + L_0 + G_0$.

Considering the cases $\left(\frac{x_1}{x}\right) < 1$ and $\left(\frac{x_1}{x}\right) > 1$ in connection with the values of V_{1x} , V_x , W_{1x} and W_x (V_x can also be negative) it follows:

The P, T curve of the ternary equilibrium $F + F' + L + G$ ends in the quadruplepoint $F + F' + L_0 + G_0$; it is a curve ascendant with the temperature, when the limitratio of A is smaller or only a little larger than 1; it may have a point of maximum pressure when the limitratio of A is much greater than 1; it may have, besides the point of maximum pressure, also a point of maximum temperature, when the limitratio of A is very large (e. g. larger than 10000) and when the volume increases at the congruent or incongruent melting of $F + F'$.

We may express the previous also in the following way:

The congruent or incongruent meltingpoint of two substances ($F + F'$) is always lowered by addition of a new substance, when we take the pressure constant; generally this is also the case when this addition takes place under its own vapourpressure. In the latter case the temperature may however, before it decreases, yet first rise a little. This can take place however only in the case that the limitratio $\left(\frac{x_1}{x}\right)_0$ of the new substance in $F + F' + L_0 + G_0$ is very large and when the volume increases at the formation of liquid from $F + F'$.

The vapourpressure of the congruent or incongruent meltingpoint, can by addition of the new substance according to the value of $\left(\frac{x_1}{x}\right)_0$, either decrease immediately or, before it decreases, firstly increase. This latter is certainly the case when the temperature increases also firstly, but it may also take place then, when the temperature decreases immediately.

Let us now consider the case that $\left(\frac{x_1}{x}\right)_0$ is exceedingly small or approaches to zero. This will be the case when the quantity of A is exceedingly small in the vapour, therefore, e. g. when A is a salt, very little or not volatile. From (25) and (26) then follows:

$$T \frac{dP}{dT} = \frac{W_{1x}}{V_{1x}} ; \quad \frac{dP}{dx} = -\frac{RT}{K} W_{1x} ; \quad \frac{dT}{dx} = -\frac{RT^2}{K} V_{1x} . \quad (27)$$

As W_{1x} represents the (congruent or incongruent) heat of subli-

mation and V_{1x} the increase of volume at the (congruent or incongruent) sublimation of $F + F'$, W_{1x} and V_{1x} are both positive. Therefore, the equilibrium $F + F' + L + G$ proceeds from the quadruplepoint immediately towards lower temperatures and pressures. Let us imagine a P, T -diagram with the quadruplepoint $F + F' + L_0 + G_0$. Four triplecurves proceed from this point viz. the (congruent or incongruent) binary meltingcurve $F + F' + L_0$, the (congruent or incongruent) binary sublimationcurve $F + F' + G_0$ and further the two binary solutioncurves under their own vapour-pressure, viz. the curves $F + L_0 + G_0$ and $F' + L_0 + G_0$. When we draw in this P, T -diagram also the curve for the ternary equilibrium $F + F' + L + G$, this touches, according to (27) the binary sublimationcurve $F + F' + G_0$ in the quadruplepoint.

An example of this case will be found when we add a third substance, which is not volatile, to the equilibrium: $ICl + ICl_3 + L_0 + G_0$ occurring at $T_0 = 22,7^\circ$ and under $P_0 = 42$ m.m., in which G_0 contains the two components I_2 and Cl_2 . The same shall also be the case when we add a substance, which is not volatile, e.g. $NaCl$ or $NaN O_3$ to the equilibrium $Na_2SO_4 \cdot 10H_2O + Na_2SO_4 + L_0 + G_0$ wherein G_0 consists only of water-vapour.

Let us now consider the case that $\left(\frac{a_1}{x}\right)_0$ is very large; as limit-case we shall assume $\left(\frac{a_1}{x}\right)_0$ infinitely large. From (25) and (26) then follows:

$$T \frac{dP}{dT} = \frac{W_x}{V_x} \dots \dots \dots (28)$$

As W_x represents the heat, required for the congruent or incongruent melting of $F + F'$, and V_x the increase of volume at this reaction, W_x is positive, while V_x may be as well positive as negative. Imagining in a P, T -diagram the quadruplepoint $F + F' + L_0 + G_0$ and the binary (congruent or incongruent) meltingcurve $F + F' + L_0$, proceeding from this point the curve of the ternary equilibrium $F + F' + L + G$ will touch this binary meltingcurve in the quadruplepoint.

In the quadruplepoint $F + F' + L_0 + G_0$ always between the phases L_0 , G_0 and F the reaction:

$$(y_1 - \beta) \text{ quant. of } L_0 + (\beta - y) \text{ quant. of } G_0 + (y - y_1) \text{ quant. of } F = 0 \quad (29)$$

may occur. The changes of entropy and of volume at this reaction are:

$$(y_1 - \beta) H + (\beta - y) H_1 + (y - y_1) \eta \dots \dots \dots (30)$$

$$(y_1 - \beta) V + (\beta - y) V_1 + (y - y_1) v \dots \dots \dots (31)$$

It follows from the values of V_2 , $V_{1,x}$, H_1 , and $H_{1,x}$ [(18)—(21)] that we may also write for (30) and (31):

$$(\beta-y) H_{1,x} - (\beta-y_1) H_x \dots \dots \dots (32)$$

and

$$(\beta-y) V_{1,x} - (\beta-y_1) V_x \dots \dots \dots (33)$$

(30) and therefore also (32) represent the increase of entropy, when at the reaction between L_0 , G_0 , and F in all $\beta-y$ quantities of vapour are formed; (31) and (33) represent the change of volume at this reaction. From this it follows: when between the phases L_0 , G_0 , and F a reaction takes place, so that one quantity of vapour is formed, the increase of entropy is:

$$H_{1,x} - \frac{\beta-y_1}{\beta-y} H_1 \dots \dots \dots (34)$$

consequently the heat which is to be added

$$W_{1,x} - \frac{\beta-y_1}{\beta-y} W_x \dots \dots \dots (35)$$

and the increase of volume:

$$V_{1,x} - \frac{\beta-y_1}{\beta-y} V_x \dots \dots \dots (36)$$

Let us now imagine in a P, T -diagram the quadruplepoint $F + F' + L_0 + G_0$ and the binary solutioncurve of F under its own vapourpressure, proceeding from this point, therefore, the curve $F + L_0 + G_0$, its direction in the quadruplepoint is fixed by

$$T \frac{dP}{dT} = \frac{W_{1,x} - \frac{\beta-y_1}{\beta-y} W_x}{V_{1,x} - \frac{\beta-y_1}{\beta-y} V_x} \dots \dots \dots (37)$$

We imagine also in this P, T -diagram to be drawn the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this quadruplepoint $F + F' + L_0 + G_0$. Its direction is fixed in this point by (25) and (26). When accidentally:

$$\left(\frac{x_1}{x}\right)_0 = \frac{\beta-y_1}{\beta-y} \dots \dots \dots (38)$$

both the curves will touch one another in the quadruplepoint.

The meaning of (38) is the following. We imagine in the concentration-diagram on the side BC the liquid of the quadruplepoint q . Through this point q runs a saturationcurve under its own vapourpressure and a boilingpointcurve of F . The meaning of (38) is that the point of maximum or minimum pressure or temperature falls exactly in q .

In the same way we find that in a P, T -diagram the binary solutioncurve under its own vapourpressure of F' proceeding from the quadruplepoint, therefore, curve $F' + L_0 + G_0$, and the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this point touch one another when

$$\left(\frac{v_1}{x}\right)_0 = \frac{\beta' - y_1}{\beta' - y} \dots \dots \dots (39)$$

We can summarise the previous results in the following way. We imagine a P, T -diagram with the quadruplepoint $F + F' + L_0 + G_0$, the four triplecurves proceeding from this point and the curve of the ternary equilibrium $F + F' + L + G$ proceeding from this point. This last curve touches in the quadruplepoint:

the binary (congruent or incongruent) meltingcurve of $F + F'$ (curve $F + F' + L_0$) when $\left(\frac{v_1}{x}\right)_0 = \infty$

the binary (congruent or incongruent) sublimationcurve of $F + F'$ (curve $F + F' + G_0$) when $\left(\frac{v_1}{x}\right)_0 = 0$

the binary solutioncurve under its own vapourpressure of F (curve $F + L_0 + G_0$) when (38) is satisfied

the binary solutioncurve under its own vapourpressure of F' (curve $F' + L_0 + G_0$) when (39) is satisfied.

The above considerations apply of course also to the ternary cryohydric curves under their own vapourpressure. As in a binary cryohydric point under its own vapourpressure the equilibrium $F + Ice + L_0 + G_0$ occurs and as from this point the ternary cryohydric curve $F + Ice + L + G$ proceeds, we have to replace only F' by Ice in our previous considerations. Then we must equate β' to 0 in (18)–(21), (25) and (26); we then may summarise our previous results in the following way:

The cryohydric point of a substance is always lowered by addition of a new substance when we keep the pressure constant; generally this is also the case when this addition takes place under its own vapourpressure. In the latter case the temperature, however, may also firstly increase a little, before it decreases; this may take place however only then, when the limitratio $\left(\frac{v_1}{x}\right)_0$ of the new substance in $F + Ice + L_0 + G_0$ is very large and when the volume increases at the formation of liquid from $F + Ice$.

The vapourpressure of the cryohydric point, may, according to the value of $\left(\frac{v_1}{x}\right)_0$ by addition of a new substance either decrease im-

mediately or, before it decreases, first increase. This latter is certainly the case when the temperature also increases a little at first, but it may also take place then when the temperature decreases immediately.

We have assumed in all our previous considerations of the equilibrium $F + F' + L + G$ that the four phases have a different composition; now we shall consider the case that two of these phases have the same composition. This will amongst others be the case when F and F' are modifications of the same solid substance or also when F or F' is one of the components and when the vapour consists only of this component. This latter is e. g. the case for the cryohydric curve under its own vapourpressure $F + Ice + L + G$ when of the three components only the water is volatile and the gasphase contains consequently only watervapour.

Let us first consider the latter case; we take, therefore, the cryohydric curve under its own vapourpressure $F + Ice + L + G$ and we preassume that the gas contains only watervapour. The results, therefore, of course remain also valid, when we replace the ice by another component. Now we must equate in our previous considerations $\alpha' = 0$, $\beta' = 0$, $x_1 = 0$ and $y_1 = 0$; from this follows: $E = \alpha y - \beta x$ and $E_1 = 0$, from (6) follows $V_{1x} = V_1 - v'$ and $H_{1x} = H_1 - \eta'$. Now it follows from (10):

$$\frac{dP}{dT} = \frac{H_{1x}}{V_{1x}} = \frac{H_1 - \eta'}{V_1 - v'} \dots \dots \dots (40)$$

Herein H_1 and V_1 represent the entropy and the volume of the gas, therefore of the watervapour; η' and v' are the entropy and the volume of the ice. From this follows, therefore, that $\frac{dP}{dT}$ is the same for the ternary equilibrium $F + Ice + L + G$ and for the unary equilibrium $Ice + \text{watervapour}$. This is evident, also without calculation; removing viz. from the ternary equilibrium $F + Ice + L + G$ the solid substance F and the liquid L , we retain, as G consists only of watervapour, the unary equilibrium $ice + \text{watervapour}$.

If we imagine the sublimationcurve of the ice and the cryohydric curve $F + ice + L + G$ to be drawn in a P, T -diagram the two curves must, therefore, coincide. As the first curve is experimentally known, we know, therefore, also the curve $F + ice + L + G$.

A cryohydric curve under constant pressure (consequently the equilibrium $F + ice + L$) has in the concentrationdiagram the point of maximumtemperature in its point of intersection with the line, which joins the two solid phases F and ice . This is also the case

with the cryohydric curve under its own vapour pressure. In the point of intersection of this curve with the line $F-ice$ is viz. $ay = \beta x$, therefore $E = 0$. From (11) and (12) it follows therefore, that $dP = 0$ and $dT = 0$. In this point of intersection pressure and temperature are, therefore, either maximum or minimum. In order to examine more in detail whether a maximum or a minimum occurs, we assume the conditions of equilibrium for the system $F + ice + L + G$.

These are:

$$\left. \begin{aligned} x \frac{\partial Z}{\partial x} + y \frac{\partial Z}{\partial y} - Z + \zeta &= 0 \\ \alpha \frac{\partial Z}{\partial x} + \beta \frac{\partial Z}{\partial y} + \zeta' - \zeta &= 0 \text{ and } Z_1 - \zeta' = 0 \end{aligned} \right\} \dots (41)$$

Now it follows from the first of these conditions:

$$\left. \begin{aligned} (xr + ys) dx + (xs + yt) dy + \left(x \frac{\partial V}{\partial x} + y \frac{\partial V}{\partial y} - V + v' \right) dP \\ - \left(x \frac{\partial H}{\partial x} + y \frac{\partial H}{\partial y} - H + \eta' \right) dT + \frac{1}{2} \left(r + x \frac{\partial r}{\partial x} + y \frac{\partial s}{\partial y} \right) dx^2 + \\ + \left(s + x \frac{\partial r}{\partial y} + y \frac{\partial s}{\partial y} \right) dx dy + \frac{1}{2} \left(t + x \frac{\partial s}{\partial y} + y \frac{\partial t}{\partial y} \right) dy^2 + R = 0 \end{aligned} \right\} (42)$$

From the second it follows:

$$\left. \begin{aligned} (\alpha r + \beta s) dx + (\alpha s + \beta t) dy + \left(\alpha \frac{\partial V}{\partial x} + \beta \frac{\partial V}{\partial y} + v' - v \right) dP \\ - \left(\alpha \frac{\partial H}{\partial x} + \beta \frac{\partial H}{\partial y} + \eta' - \eta \right) dT + \frac{1}{2} \left(\alpha \frac{\partial r}{\partial x} + \beta \frac{\partial s}{\partial y} \right) dx^2 \\ + \left(\alpha \frac{\partial r}{\partial y} + \beta \frac{\partial s}{\partial y} \right) dx dy + \frac{1}{2} \left(\alpha \frac{\partial s}{\partial y} + \beta \frac{\partial t}{\partial y} \right) dy^2 + R' = 0 \end{aligned} \right\} (43)$$

Herein R and R' contain terms with $dP dx$, $dT dx$ etc., which we may neglect as will appear later. From the third condition follows:

$$(V_1 - v') dP - (H_1 - \eta') dT = 0 \quad \dots (44)$$

wherein the terms of higher order can also be neglected. As in the point of intersection of the curve with the line $F-Ice$ $ay = \beta x$, so we may substitute in (43) $\alpha = \lambda x$ and $\beta = \lambda y$.

When we subtract (42) from (43) after having multiplied (42) by λ , we find:

$$\left. \begin{aligned} \{ \lambda(V - v') + v' - v \} dP - \{ \lambda(H - \eta') + \eta' - \eta \} dT \\ = \frac{1}{2} \lambda (r dx^2 + 2s dx dy + t dy^2) + R'' \end{aligned} \right\} \dots (45)$$

Let us substitute the value of dy from (43) into (45); it is apparent from (45) that it is sufficient that:

$$(\alpha s + \beta t) dy = -(\alpha r + \beta s) dx$$

and that we may neglect the terms with dP , dT etc. We may

write then for the second term of (45). $\frac{1}{2} \lambda Q \cdot dx^2$, wherein Q is positive. From (6) it follows that we may write V_x and H_x for the coefficient of dP and dT ; (45) passes into:

$$V_x \cdot dP - H_x \cdot dT = \frac{1}{2} \cdot \frac{\alpha}{x} \cdot Q \cdot dx^2 \dots (46)$$

From (44) and (46) follows:

$$2x [H_x(V_1' - v') - V_x(H_1 - \eta')] dP = - \alpha(H_1 - \eta') Q dx^2 \dots (47)$$

$$2x [H_x(V_1 - v') - V_x(H_1 - \eta')] dT = - \alpha(V_1 - v') Q dx^2 \dots (48)$$

As $V_1 - v' = V_{1x}$ and $H_1 - \eta' = H_{1x}$, we see from (24) that the coefficients of dP and dT in (47) and (48) are positive. Therefore, dP and dT are zero at first approximation, at second approximation negative so that pressure and temperature are maximum.

We may summarise the previous results in the following way: in a P, T -diagram the sublimationcurve of the ice and the cryohydric curve under its own vapourpressure ($F + ice + L + G$) coincide. The cryohydric curve under a constant pressure has its maximum-temperature in the pure solutionpoint of F ; the cryohydric curve under its own vapourpressure has in this point its maximum-temperature and -pressure.

When F is a binary compound, we must in the previous considerations not only put $\alpha' = 0$, $\beta' = 0$, $x_1 = 0$ and $y_1 = 0$, but also $\alpha = 0$. From this follows: $E = -\beta x$, $E_1 = 0$, $V_{1x} = V_1 - v'$ and $H_{1x} = H_1 - \eta'$. From (10) again it follows that:

$$\frac{dP}{dT} = \frac{H_1 - \eta'}{V_1 - v'} \dots (49)$$

so that in a P, T -diagram again the sublimationcurve of the ice and the cryohydric curve $F + Ice + L + G$ coincide.

Considering the cryohydric curve in the vicinity of the binary cryohydric point $F + ice + L_0 + G_0$, it follows from (25) and (26):

$$\frac{dP}{dx} = - \frac{RT}{K} W_{1x} = - \frac{RT^2}{K} H_{1x}' = - \frac{RT^2}{K} (H_1 - \eta') \dots (50)$$

$$\frac{dT}{dx} = - \frac{RT^2}{K} V_{1x} = - \frac{RT^2}{K} (V_1 - v') \dots (51)$$

From the binary cryohydric point, therefore, pressure and temperature decrease along the cryohydric curve.

We can also obtain these results by substituting $Z = U + RT \cdot x \log x$ in the three equations (41).

Now we shall suppose that F and F' are modifications of a same substance, so that $F + F' + L + G$ represents the modificationcurve

under its own vapourpressure and its corresponding vapourcurve. We put in the formulae (2)—(4) (VIII) $\alpha' = \alpha$ and $\beta' = \beta$. We then may write these:

$$(x - \alpha)r + (y - \beta)s] dv + [(x - \alpha)s + (y - \beta)t] dy = AdP - BdT. \quad (52)$$

$$\left. \begin{aligned} [(x_1 - \alpha)r + (y_1 - \beta)s] dv + [(x_1 - \alpha)s + (y_1 - \beta)t] dy \\ = (A + C) dP - (B + D)dT \end{aligned} \right\} \quad (53)$$

$$(v' - v) dP - (\eta' - \eta) dT = 0 \quad \dots \quad (54)$$

Let us first take the substance F . The P, T -diagram of this substance was already discussed formerly and is drawn in fig. 3 (III) and 4 (IV). In fig. 1 arK represents the sublimationcurve, Fd the meltingcurve and KF a part of the limitcurve $mKFM$ of the substance F . We find also in fig. 1 the P, T -diagram of the substance F' ; herein $a'rK'$ is the sublimationcurve, $F'd'$ the melting curve and $K'F'$ a part of the limitcurve $m'K'F'M'$ of the substance F' .

The two sublimationcurves touch one another in r ; consequently in r the equilibrium $F + F' + G$ occurs, wherein G has the composition $F = F'$. Therefore from r also a curve rh proceeds, which represents the equilibrium $F + F'$. This curve may proceed from r as well towards higher as towards lower temperatures; in fig. 1 the first case has been assumed. It is apparent from the position of the different curves that we have assumed $v' > v, \eta' > \eta, V > v$ and $V' > v'$.

From (54) it follows that $\frac{dP}{dT}$ for the equilibrium $F + F' + L + G$ and $F + F'$ is, the same. This is also apparent without more explanation; when we remove viz. the liquid and the gas from

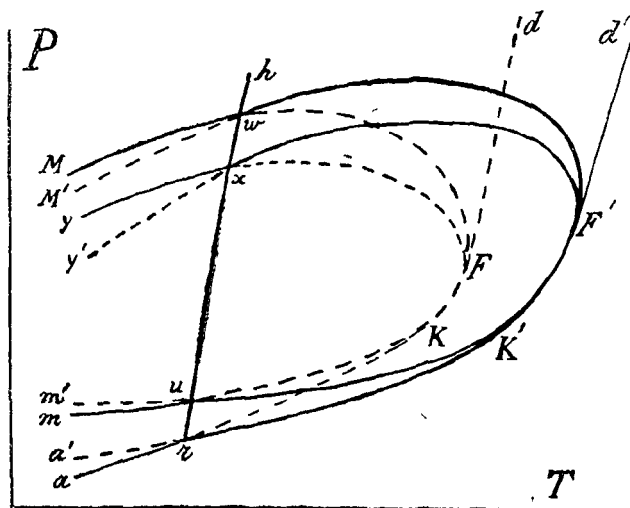


Fig. 1.

$F + F' + L + G$, then $F + F'$ remains. Therefore, in fig. 1 curve $F + F' + L + G$ must coincide with rh ; it will, however, only partly cover this curve. It is represented in fig. 1 by uw , wherein u and w are the points of intersection of $mKFM$ and $m'K'F'M'$.

In order to see this we take any point x of the curve $F + F' + L + G$. When we remove F' and when we keep further the quantity of vapour always exceedingly small, the liquid L of the remaining equilibrium $F + L + G$ traces at change of temperature a solutionpath of F under its own vapourpressure. The P, T -curve of this path is represented in fig. 1 by yxF . When we remove F and when we keep again the quantity of vapour exceedingly small, the liquid L traces a solutionpath of F' on change of temperature; this is indicated in fig. 1 by $y'xF'$.

Only the part yx of the first solutionpath, only the part xF' of the second represent stable conditions. Restricting ourselves to stable conditions, we may say therefore from each point of the modificationcurve $F + F' + L + G$ one solutionpath of F proceeds towards lower temperatures, and one of F' towards higher temperatures. From this it follows that the one extremity of the modificationcurve must be situated in u , and the other in w .

In order to deduce the modificationcurve and its corresponding vapourcurve in the concentrationdiagram, we may act in a similar way as e.g. at the deduction of the saturationcurves under their own vapourpressure. When we take a definite T and P and when at this T and under this P a saturationcurve of F exists, this is circumphased; the same applies to that of F' . When at the assumed T and P the modification F is the stable one, its saturationcurve surrounds that of F' , when F' is the stable form, the saturationcurve of F' surrounds that of F .

The two saturationcurves can never intersect each other, they can completely coincide. This is the case when we choose P and T in such a way that they are in accordance with a point of curve rh in fig. 1, so that the two modifications F and F' may exist by the side of one another. Then these two coinciding curves form the modificationcurve under a constant P and at a constant T ; it represents the liquid L of the equilibrium $F + F' + L$.

Now we change not only the T or the P , but both together and in such a way that they are always in accordance with a point of the curve rh in fig. 1; also we consider the vapourregion and the heterogeneous region $L-G$. Then we find easily that the modificationcurve under its own vapourpressure and its corresponding vapourcurve are circumphased.

It follows amongst others from the formulas (52)—(54) that this modificationcurve cannot go through the point $F = F'$; when we put herein $x = \alpha$ and $y = \beta$, it follows that

$$\frac{H - \eta}{V - v} = \frac{H - \eta'}{V - v'} = \frac{\eta' - \eta}{v' - v} \dots \dots \dots (55)$$

must be satisfied.

This means that the curves $Fd, F'd'$ and rh of fig. 1 touch one another in one point. Now it is apparent that these curves may intersect one another in one point. When viz. two of these curves intersect one another, necessarily the third goes also through this point of intersection, only very accidentally they can, however, touch one another. In the same way we find that also the corresponding vapourcurve cannot go through the point $F = F'$. From (52)—(54) it follows that dP and dT become zero at the same time and that this is the case when

$$\frac{y - \beta}{x - \alpha} = \frac{y_1 - \beta}{x_1 - \alpha} \dots \dots \dots (56)$$

This means that the solid substance ($F = F'$), the liquid and the vapour are situated on a straight line. It is evident that on each closed modificationcurve two such points u and w occur and on the corresponding vapourcurve two corresponding points u_1 and w_1 . Pressure and temperature of the equilibrium $F + F' + L_u + G_{u_1}$ are in accordance with point u of fig. 1, pressure and temperature of the equilibrium $F + F' + L_w + G_{w_1}$, with the point w of fig. 1.

From (54) it follows that the pressure can as well increase as decrease at increase of temperature, therefore we may distinguish two cases.

- 1) P - and T -maximum coincide and also P - and T -minimum.
- 2) P -maximum and T -minimum coincide and also P -minimum and T -maximum.

The case sub 1 occurs when the pressure increases at increase of temperature; curve rh is then situated as in fig. 1. The case sub 2 occurs when the pressure decreases at increase of temperature, curve rh proceeds then in fig. 1 from r towards lower temperatures.

Now we shall assume that F' and consequently also F is a binary compound of B and C ; to the P, T diagram again then fig. 1 applies, in which now however the solutionpaths no longer touch the melting-curve in F or F' .

In the concentrationdiagram the modificationcurve $F + F' + L + G$ ends in two points on the side BC , the same applies to its corresponding vapourcurve.

Let us assume that point F in fig. 3 (XI) represents the two modifications F and F' and that $h a b n$ is the modificationcurve and $h_1 a_1 b_1 n_1$ the vapourcurve.

Therefore, in the binary system two temperatures and pressures of inversion occur, viz. in the points h and n . Considering the equilibria under a constant pressure, $T_h = T_n$; under their own vapour pressure, however T_h and T_n as well as P_h and P_n are different. The points h and n of fig. 3 (XI) resemble viz. u and w of fig. 1. Although solid substance, liquid and gas of the equilibrium $F + F' + L_h + G_h$ and $F + F' + L_n + G_n$ are represented by points of a straight line, yet in h and n $dP = 0$ and $dT = 0$ is not the case. In order to see this, we substitute in (52)–(54) $\alpha = 0$; from this we find:

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx} \right)_{x=0} = \frac{x_1}{x} \cdot \left(1 - \frac{s}{s_1} \right) \frac{\eta' - \eta}{(\eta' - \eta) \Delta V - (v' - v) \Delta H} \quad (57)$$

$$\frac{1}{RT} \cdot \left(\frac{dT}{dx} \right)_{x=0} = \frac{x_1}{x} \left(1 - \frac{s}{s_1} \right) \frac{v' - v}{(\eta' - \eta) \Delta V - (v' - v) \Delta H} \quad (58)$$

so that dP and dT in h and n are not zero. ΔV is the increase of volume and ΔH is the increase of entropy when between F , L , and G of the equilibrium $F + F' + L_n + G_n$ or $F + F' + L_h + G_h$ a reaction takes place, at which one volume of vapour is formed. [We may also replace in (57) and (58) ΔV and ΔH by $\Delta V'$ and $\Delta H'$, which indicate then the same increases when the phases F' , L , and G react]. When in fig. 3 (XI) h and n are situated not too close to F , or in other words, when the temperatures of inversion T_h and T_n are situated not too close to the meltingpoint T_F , ΔV is > 0 and large with respect to $v' - v$, the denominator of (57) and (58) is then generally positive.

That there may be accordance with fig. 1, we take first $v' > v$. In fig 3 in the vicinity of h and h_1 (see $\Delta F a a_1$) $s > s_1$; in the vicinity of n and n_1 (see $\Delta F b b_1$) $s < s_1$. From (57) and (58) now follows: P and T increase along the modificationcurve from n towards h . When we take $v' < v$ then it follows: T increases from h towards n , P from n towards h .

At last we may still consider the case, that F' and consequently also F is one of the components, e.g. B . The reader can easily draw himself the P, T -diagram, which is now simpler than in fig. 1. In the concentrationdiagram the modificationcurve ends then in two points, the one on BC and the other on BA . If we determine the modificationcurve under a constant pressure, T is the same in each point of this curve; in this case T and P will change however again

along the curve from point to point and either in the same or in opposite direction.

When we determine, therefore, e.g. the temperature of inversion and pressure of inversion of rhombic in monoclinic sulfur, or of two modifications of KNO_3 etc. in a mixture of two solvents and under its own vapour pressure, this T and P of inversion change with the composition of the solvent. These changes are, however, very small, as it follows from the previous considerations.

(To be continued.)

Mathematics. — “On the singular solutions of ordinary and partial differential equations of the first order”. By Prof. H.K. DE VRIES and G. SCHAAKE.

(Communicated in the meeting of March 28, 1914).

INTRODUCTION. If the complete integral of a partial differential equation of the first order with two independent variables, $F(x, y, z, p, q) = 0$ is represented by $f(x, y, z, c_1, c_2) = 0$, and if the result of the elimination of c_1 and c_2 from the three equations

$$f = 0 \quad , \quad \frac{\partial f}{\partial c_1} = 0 \quad , \quad \frac{\partial f}{\partial c_2} = 0$$

is called for the sake of brevity $E = 0$, the following peculiar phenomena may arise. If the general solution $f(x, y, c) = 0$, of an ordinary differential equation of the first order $F(x, y, p) = 0$, possesses a nodal locus, it belongs generally speaking to the result of elimination of c from the two equations

$$f = 0 \quad , \quad \frac{\partial f}{\partial c} = 0 ;$$

and only in *one* particular case it does not belong to it; with the partial equations it is just the reverse, at least if in this case the locus of the nodes consists of one or more *curves*; if there is a nodal *surface*, it does belong in general to $E = 0$, though there is a possibility that it does not.

It is a matter of course that all possible cases may be arrived at by a purely analytical method; but it appears that considerations derived from polydimensional geometry throw a vivid light on those various analytical possibilities and so to say increase the differences and render them more essential; to prove this is the aim of the following paragraphs.

§ 1. Let in the first place be given an ordinary differential equation of the 1st order

$$F(x, y, p) = 0,$$