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distinct discontinuity as was found at 4°.19 K in the electrical conductivity, although the thermal conductivity becomes much larger, when the temperature decreases. As there do not exist direct determinations for solid mercury, we only can make a rough estimation with the aid of WIEDEMANN and FRANZ's law.

At the melting point, the electrical conductivity of liquid mercury amounts to $1.10.\,10^4$ cm. Ω^{-1} and of solid mercury to about five times as much, thus to $5.50.\,10^4$ cm^{-1} Ω^{-1}. From this we find by comparison e.g. with lead about 0.075 for the thermal conductivity. The values here obtained in liquid helium are 3.5 and 5.5 times as large.

Chemistry. *"Equilibria in ternary systems"*. XVII. By Prof. SCHREINEMAKERS.

(Communicated in the meeting of Oct. 31, 1914).

Now we will consider the case, mentioned sub 3 (XVI), viz: the solid substance is a binary compound of a volatile- and a non-volatile component. A similar case occurs for instance in the system Na_2SO_4 + water + alcohol, when the solid phase is $Na_2SO_4.\,10\,H_2O$, or in the system $FeCl_3 + HCl + H_2O$, when the solid phase is one of the hydrates of ferric chloride, for instance $Fe_2Cl_6.\,12\,H_2O$.

For fixing the ideas we shall assume that of the three components A, B, and C (fig. 1) only A and C are volatile, so that all vapours consist either of A or of C or of $A + C$.

In fig. 1 $CA\,de$ represents a heterogeneous region $L—G$; ed is the liquid curve, CA the corresponding straight vapour-line. The liquid d, therefore, can be in equilibrium with the vapour A, the liquid e with the vapour C and each liquid of curve ed with a definite vapour of AC.

Previously (XVI) we have seen that this heterogeneous region $L—G$ can arise in different ways on decrease of pressure, viz. either in one of the anglepoints A and C or in a point of AC; also two heterogeneous regions may occur, the one in A and the other in C, which come together on further decrease of pressure somewhere in a point of AC.

In fig. 1 we may imagine that the region $L—G$ has arisen in these different ways; curve ed may of course also turn its convex side towards AC. Besides this heterogeneous region $L—G$ we also find in fig. 1 the saturationcurve under constant pressure of the binary

51

- 2 -

substance F, represented by pq [we leave the curve rs, drawn in the figure out of consideration for the present].
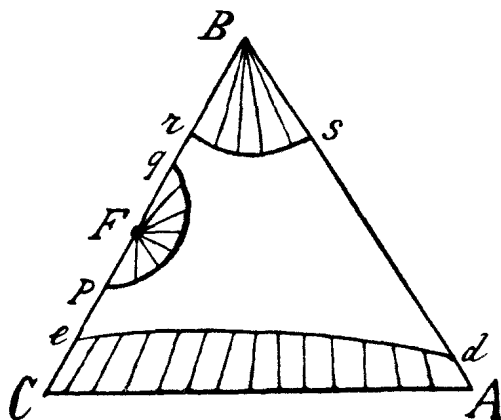

Fig. 1.

In the same way as we have acted in the general case [fig. 11 (1)] or in the peculiar case (XI), we may deduce also now the different diagrams.

$T < T_F$. At first we take a temperature T lower than the minimummeltingpoint T_F of the binary compound F. Now we find a diagram just as fig. 2 for the saturationcurve under its own vapourpressure of F and the corresponding straight vapour-line. In this figure, in which the component-triangle is only partly drawn, hgn is the saturationcurve under its own vapourpressure; we find the corresponding straight vapour line Cg_1 on side CA.

When we assume, as is supposed at the deduction of fig. 2, that neither a point of maximum-pressure, nor a point of minimum-pressure occurs, the pressure increases from n towards h; consequently it is lowest in n and highest in h, without being, however, a minimum in n or a maximum in h. It follows from the deduction that the sides solid-gas and solid-liquid of the threephasetriangles must be situated with respect to one another and to the side CB just as is drawn in fig. 2.

It is apparent from the figure that the binary liquids h and n can be in equilibrium with the unary vapour C and that the ternary liquids a, c and b can be in equilibrium with the binary vapours a_1, c_1 and b_1. It is apparent that somewhere between the liquids c and b a liquid g must be situated, the corresponding vapour g_1 of which represents the extreme point of the straight vapour line Cg_1.

When a liquid follows curve hn, first from h towards g and afterwards from g towards n, the corresponding vapour g_1 follows conse-

quently 'first Cy_1 from C towards g_1 and afterwards again this same line, but in opposite direction, consequently from g_1 towards C.
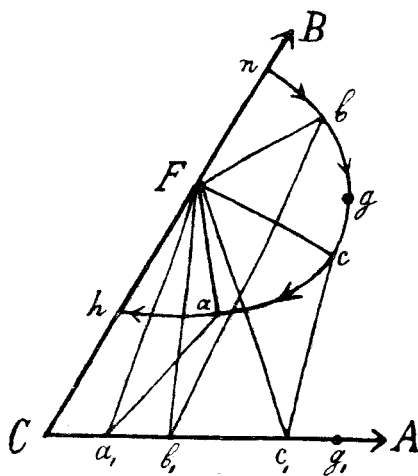

Fig. 2.

Each vapour of this straight vapour line Cy_1 can, therefore, be in equilibrium with two different liquids, the one of branch hy and the other of branch gn.

We may express this also in the following way: when we have an equilibrium $F + L + G$, then there exists under another pressure, also an equilibrium $F + L_1 + G_1$, in which L and L_1 have a different composition; G and G_1, however, have the same composition.

It is apparent from the deduction of fig. 2 that in curve hn also a point of maximumpressure can occur. This case is drawn in fig. 3; hn represents again the saturationcurve under its own vapourpressure and Cy_1 represents the corresponding straight vapourline; M is the point of maximumpressure, M_1 the corresponding vapour. The points M_1, M, and F must of course be situated on a straight line.

While under the pressure P_M there occurs only one equilibrium, viz. $F + L_M + G_{M_1}$, under each pressure, somewhat lower than P_M there exist two equilibria, for instance $F + L_a + G_{a_1}$ and $F + L_c + G_{c_1}$; we can imagine these to be represented by the threephasetriangles Faa_1 and Fcc_1, when we imagine both triangles in the vicinity of the line FMM_1. It follows from the deduction of the diagram that both these triangles turn their sides solid-gas towards one another, consequently also towards the line FMM_1.

Suppose, we want the curves ed and pg to move in fig. 1 with respect to one another in such a way that a point of minimumpressure occurs on the saturationcurve under its own vapourpressure,

51*

then we see that this is impossible. Yet we can imagine a saturation-curve with a point of maximum- and a point of minimumpressure.
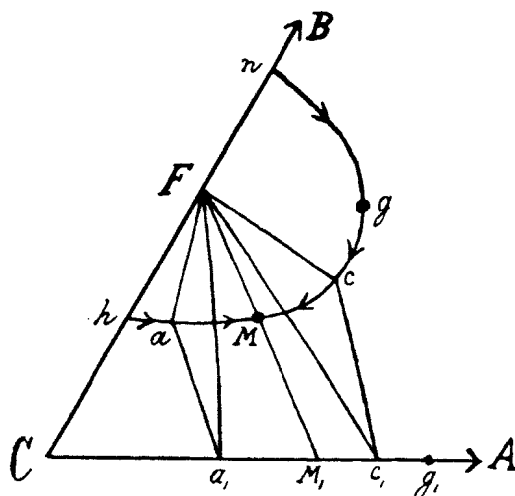

Fig. 3.

When we trace curve hn starting from n, we arrive first in the point of maximum- afterwards in the point of minimumpressure. We will refer to this later.

$T_F < T$. Now we take a temperature T a little above the minimum meltingpoint T_F of the solid substance F. Then we must distinguish two cases, according as the solid substance expands or contracts on melting. We take the first case only.

Then we find a diagram like fig. 4 (XI); herein, however, the same as in figs. 2 and 3, we must imagine that the vapourcurve $h_1 a_1 n_1$ is replaced by a straight vapourline Cg_1 on side CA. We will refer later to the possibility of the occurrence of a point of maximum- and a point of minimumpressure.

We can, however, also get curves of a form as curve hn and the curves situated inside this in fig. 6 (XI); these curves show as well a point of maximum- as a point of minimumpressure.

When we draw the saturationcurves under their own vapour-pressure for different temperatures, we can distinguish two principal types; we can imagine those to be represented by figs. 5 (XI) and 6 (XI). At temperatures below T_F these curves are circumphased, above T_F they are exphased. In fig. 5 (XI) they disappear in a point H on side BC, in fig. 6 (XI) in a point R within the triangle. The corresponding straight vapourlines disappear in fig. 5 (XI) at T_H in the point C; in figure 6 (XI) they disappear at T_R in a point R_1, the intersecting point of the line FR with the side CA.

Now we will consider some points more in detail. In order to get the conditions of equilibrium for the system $F + L + G$, when F is a binary compound of B and C and when the vapour consists only of A and C, we must equate $a = 0$ and $y_1 = 0$. The conditions (1) (II) pass then into:

$$Z - x\frac{\partial Z}{\partial x} - (y - \beta)\frac{\partial Z}{\partial y} = \zeta \qquad \left.\begin{array}{l} \dfrac{\partial Z}{\partial x} = \dfrac{\partial Z_1}{\partial x_1} \\[2mm] \end{array}\right\} \quad \cdots \quad (1)$$

$$Z_1 - x_1\frac{\partial Z_1}{\partial x_1} + \beta\frac{\partial Z}{\partial y} = \zeta$$

Now we put:

$$Z = U + RTx \log x \quad \text{and} \quad Z_1 = U_1 + RTx_1 \log x_1 \quad \cdots \quad (2)$$

Hence the conditions (1) pass into:

$$x\frac{\partial U}{\partial x} + (y - \beta)\frac{\partial U}{\partial y} + RTx - U + \zeta = 0 \quad \cdots \quad (3)$$

$$x_1\frac{\partial U_1}{\partial x_1} - \beta\frac{\partial U}{\partial y} + RTx_1 - U_1 + \zeta = 0 \quad \cdots \quad (4)$$

$$\frac{\partial U}{\partial x} + RT \log x = \frac{\partial U_1}{\partial x_1} + RT \log x_1 \quad \cdots \quad (5)$$

When we keep the temperature constant, we may deduce from (3)—(5):

$$[xr + (y - \beta)s + RT] dx + [xs + (y - \beta)t] dy = A\,dP \quad (6)$$

$$\left[x_1 r - \beta s + \frac{x_1}{x}RT\right] dx + [x_1 s - \beta t] dy = (A + C)dP \quad (7)$$

$$\left(r + \frac{RT}{x}\right) dx + sdy - \left(r_1 + \frac{RT}{x_1}\right) dx_1 = \left(\frac{\partial V_1}{\partial x_1} - \frac{\partial V}{\partial x}\right) dP \quad (8)$$

Here we must equate of course in A and C $a = 0$ and $y_1 = 0$. In order to let the pressure be a maximum or a minimum, dP must be $= 0$. From (6) and (7) it follows that then must be satisfied:

$$x\,\beta + x_1(y - \beta) = 0. \quad \cdots \cdots \quad (9)$$

This means that the point of maximum- or of minimumpressure M (x, y) and the corresponding vapourpoint M_1 (x_1, y_1) are situated with F on a straight line (fig. 3).

In order to examine the change of pressure along a saturation-curve under its own vapourpressure in its ends h and n (figs. 2 and 3) we equate in (6) and (7) $x = 0$ and $x_1 = 0$. Then we find:

$$[(y - \beta)s + RT] dx + (y - \beta) tdy = \left[V - v + (\beta - y)\frac{\partial V}{\partial y}\right] dP \quad (10)$$

$$\left[-\beta s + \frac{x_1}{x}RT\right] dx - \beta tdy = \left[V_1 - v + \beta\frac{\partial V}{\partial y}\right] dP \quad (11)$$

The ratio $x_1 : x$ has a definite value herein, as it follows from (5). When we eliminate dy from (10) and (11), then we find:

$$\left[\beta + (y-\beta)\frac{x_1}{x} \right] RTdx = [\beta V + (y-\beta) V_1 - yv] dP. \quad . \quad (12)$$

The quantities in the coefficient of dP relate all to the binary equilibrium $F + L + G$. When we call ΔV_1 the change of volume, when between the three phases of this binary equilibrium a reaction takes place, at which the unity of quantity of vapour arises, then is:

$$(y-\beta) \Delta V_1 = \beta V + (y-\beta) V_1 - yv \quad . \quad . \quad . \quad . \quad (13)$$

Consequently we may write for (12):

$$dP = \left(\frac{x_1}{x} + \frac{\beta}{y-\beta} \right) \frac{RT}{\Delta V_1} \cdot dx \quad . \quad . \quad . \quad . \quad (14)$$

Now we introduce again, as in (XI) the perspective concentrations of the substance A in liquid and gas; it is evident that the perspective concentration S_1 is equal to the real concentration x, of A in the vapour; we find for the perspective concentration of A in the liquid:

$$S = \frac{\beta x}{\beta - y} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

so that we can write for (14):

$$\left(\frac{dP}{dx} \right)_{x=0} = \frac{x_1}{x} \left(1 - \frac{S}{x_1} \right) \frac{RT}{\Delta V_1} \quad . \quad . \quad . \quad . \quad (16)$$

When the vapour contains the three components, then, as we have seen previously (14) (XI) is true; when we replace herein S_1 by x_1, this passes into (16).

It follows from (16) that the sign of the change of pressure in the ends h and n of a saturationcurve under its own vapourpressure, depends on the sign of ΔV_1. Now ΔV_1 is almost always positive for the binary equilibrium $F+L+G$ and it is only negative between the points F and H [fig. 5 (XI) and fig. 6 (XI)]. Consequently ΔV_1 is positive in the points h and n of figs. 2 and 3, also in the point h of fig. 5 (XI) and 6 (XI); ΔV_1 is negative in the point n of the two last figures. Further it follows that the sign of the change of pressure is not determined by the ratio $x_1 : x$ (the partition of the third substance between gas and liquid) but by the ratio $S : x_1$ (the perspective partition of the third substance between gas and liquid).

Let us take now a liquid of the saturationcurve under its own vapourpressure in the vicinity of the point h of fig. 2, for this we imagine triangle Faa_1 in the vicinity of the side BC. From the position of Fa and Fa_1 with respect to one another, follows

$S > x_1$. As ΔV_1 is positive in h, it follows from (16) that the pressure must decrease on addition of a third substance. We see that this is in accordance with the direction of the arrow in the vicinity of h.

In the vicinity of point h of fig. 3 is $x_1 > S$ as follows from the position of triangle Faa_1. As ΔV_1 is positive, it follows from (16) that the pressure must increase on addition of a third substance. This is in accordance with the direction of the arrow in the vicinity of h.

In the vicinity of point n of the figs. 2 and 3 S is negative (we imagine for instance in fig. 2 triangle Fbb_1 in the vicinity of side BC); as ΔV_1 is positive, it follows from (16) that in both figures the pressure must increase, starting from n.

Consequently we find: in a terminatingpoint of a saturationcurve under its own vapourpressure, situated between C and H, the pressure decreases on addition of a third substance, when the threephasetriangle turns its side solid-gas towards BC (fig. 2) and the pressure increases when the threephasetriangle turns its side solid-liquid towards BC.

As, therefore, at temperatures lower than T_F (figs. 2 and 3) the pressure always increases, starting from n, and increases or decreases starting from h, we find the following. When we trace curve nh, the pressure increases continually starting from n towards h (fig. 2), or we come starting from n first in a point of maximumpressure, after which the pressure decreases as far as in h (fig. 3) or we come, starting from n first in a point of maximum- and afterwards in a point of minimumpressure, after which the pressure increases up to h.

As in point h of fig. 5 (XI) the pressure decreases starting from h, consequent it is assumed here, that the threephasetriangle turns its 'side solid-gas towards BC. (Cf. fig. 2 and fig. 4 (XI); in this last figure we imagine however curve h_1n_1 on side CA). In the point h of fig. 6 (XI) is assumed that the threephasetriangle turns its side solid-liquid towards BC.

Let us consider now the terminatingpoint n of the saturationcurve in fig. 5 (XI) and fig. 6 (XI). As n is situated between F and H, ΔV_1 is negative, when the threephasetriangle turns its side solid-gas towards BC, then is $S > x_1$ and it follows from (16) that the pressure increases on addition of a third substance. We then have the case of fig. 5 (XI). When, however, the threephasetriangle turns its side solid-liquid towards BC, then $S < x_1$ and it follows from (16) that the pressure decreases on addition of a third substance. We then have the case represented in fig. 6 (XI).

When we consider the saturationcurve going through the point F in fig. 5 (XI) and fig. 6 (XI), then for this point $y = \beta$, consequently, according to (15) $S = \infty$. From (13) follows also $\Delta V_1 = \infty$. Therefore we take (12); from this follows for $y = \beta$

$$\left(\frac{dP}{dx}\right)_{x=0} = \frac{RT}{V-v} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As fig. 5 (XI) and fig. 6 (XI) are drawn for $V > v$, the pressure must increase starting from F along the saturationcurve going through F.

As the pressure increases starting from F along the saturation-curves under their own vapourpressure of fig. 6 (XI) and decreases starting from a point n, situated in the vicinity of H, somewhere between F and n must consequently be situated a point, starting from which the pressure neither increases nor decreases. This point is, therefore, the point of maximum- or of minimumpressure of a saturationcurve, and is not situated within the componenttriangle, but accidentally it falls on side BC. It follows from the figure that this point is a point of minimumpressure; we shall call this the point m.

The limitcurve (viz. the geometrical position of the points of maximum- and minimumpressure) goes consequently through the points m and R; it represents from m to R points of minimum-pressure; starting from R further within the triangle, it represents points of maximumpressure. This latter branch can end anywhere between H and C on side BC.

The terminatingpoint of a limitcurve on side BC can be situated between F and C, but cannot be situated between F and B. A similar terminatingpoint is viz. a point of maximum- or a point of minimum-pressure of the saturationcurve, going through this point. Consequently in this point along this saturationcurve $dP = 0$; from (16) it follows that then must be satisfied :

$$S = x_1 \quad \text{or} \quad \beta x + (y-\beta) x_1 = 0 \quad . \quad . \quad . \quad . \quad (18)$$

Herein x and x_1 are infinitely small; their limit-ratio is determined by (5). As x and x_1 are both positive, it follows from (18) : $y < \beta$. The terminatingpoint of a limitcurve must, therefore, be situated between F and C (fig. 6) and it cannot be situated between F and B. In accordance with this we found above that one of the ends of the limitcurve is situated in fig. 6 (XI) between n and F.

Now we must still consider the case mentioned sub 4 (XIV), viz. that the solid substance is one of the components. A similar case

occurs for instance in the systems: $Z +$ water $+$ alcohol, wherein Z represents an anhydric single, salt, which is not-volatile.

For fixing the ideas we assume that B is the component, which is not-volatile (fig. 1), so that A and C represent the volatile components.

Now we imagine in fig. 1 curve pq to be omitted, so that the curves ed and rs rest only, ed is the liquidcurve of the region $L-G$, rs is the saturationcurve under a constant pressure of the substance B.

We can, in order to obtain the different diagrams, act in the same way as we did before in the general case, or as in communication XIII. For this we consider the movement of the curves ed and rs with respect to one another on decrease of pressure.

As we assume that B is not volatile, these considerations are not true, therefore, for points situated in the vicinity of B. Equilibria situated in the immediate vicinity of B have viz. also always the substance B in their vapour, so that the considerations of communication XIII apply to these.

When we decrease the pressure, the liquidcurve ed (fig. 1) shifts further into the triangle towards the point B, so that under a definite pressure the curves ed and rs meet one another. Now we distinguish three cases.

1. We assume that the curves ed and rs meet one another first in a point on one of the sides of the triangle; when this takes place on side BC, then consequently the points e and r coincide in fig. 1, while the two curves have no other point in common further. On further decrease of P, this intersecting point shifts within the triangle and it disappears at last on the side AB, when in fig. 1 the points s and d coincide. Curve ed is situated then inside the sector Brs and curve rs inside the region $CedA$.

From this follows that the saturationcurve of B under its own vapourpressure can be represented by curve $habn$ in fig. 4, in which the arrows indicate the direction, in which the vapourpressure increases. The corresponding vapourcurve is the side CA; the liquid h viz. is in equilibrium with the vapour C, liquid n with the vapour A and with each liquid (a and b) of hn a definite vapour (a_1 and b_1) of CA is in equilibrium. It follows from the deduction that the threephase-triangles (Baa_1, Bbb_1,) turn their sides solid-gas towards the point h and their sides solid-liquid towards the point n.

This fig. 4 is a peculiar case of fig. 2 (XIII); when we suppose viz. that the substance B does not occur in the vapour, curve $h_1a_1b_1n_1$ of fig. 2 (XIII) must coincide with the side CA of the triangle and fig. 4 arises.
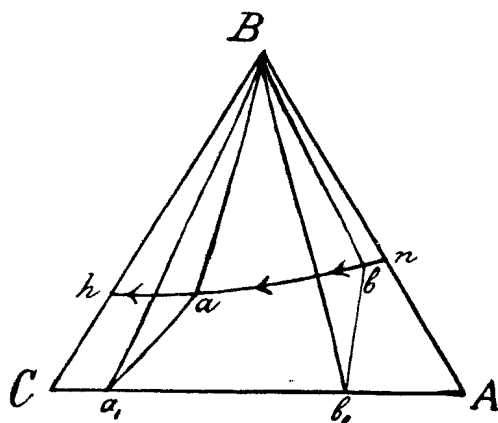
Fig. 4.

2. Now we assume again that the curves ed and rs (fig. 1) meet one another first in a point of the side BC; this point of intersection shifts then on further decrease of P into the triangle. Under a definite pressure we want a second point of intersection to be formed by the coincidence of d and s (fig. 1). The two points of
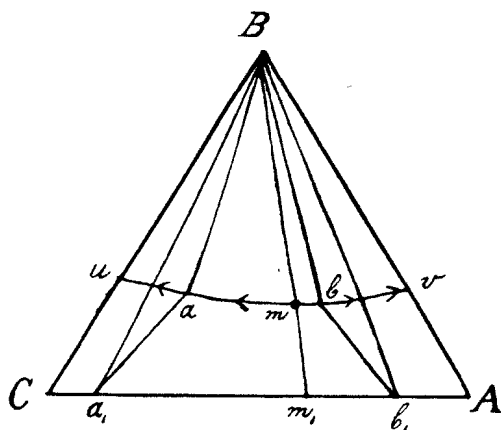

Fig. 5.

intersection approach one another on further decrease of pressure, in order to coincide at last in a point m. It is evident that m is a point of minimumpressure of the saturationcurve under its own vapourpressure; it is represented in fig. 5 by curve $uambv$, the corresponding vapourcurve is the side CA. It is evident that the vapour m_1, which can be in equilibrium with the liquid m, is situated on the line Bm.

3rd. We can assume also that the curves ed and rs (fig. 1) meet on decrease of pressure first in a point M, which is situated within the triangle. On further decrease of pressure then two points of

intersection arise; the one disappears on BC by the coincidence of e and r, the other on BA by the coincidence of d and s (fig. 1). It is evident that M is then the point of maximum-pressure of the saturationcurve of B under its own vapourpressure, the corresponding vapourpoint M_1 is situated of course on the line BM.

One can understand the occurring diagram with the aid of fig. 5 ; herein we have to give an opposite direction to the arrows and we have to replace the points of minimumpressure m and m_1 by the points of maximumpressure M and M_1 ; further the triangles Baa_1 and Bbb_1 are to be drawn, in such a way that they turn their sides solid—gas towards the line BMM_1.

We shall consider some points in another way now. In order to find the conditions of equilibrium for the equilibrium $B + L + G$, when the vapour consists of A and C only, we equate in the relations (1)—(8) $\beta = 1$; in the general values of A and C (II) we put $\alpha = 0$, $\beta = 1$ and $y_1 = 0$. The condition for the occurrence of a point of maximum- or of minimumpressure $(dP = 0)$ becomes then :

$$x = (1 - y) x_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

This relation also follows from (9), when we put $\beta = 1$. This means : the point of maximum- or of minimumpressure of the saturationcurve of B under its own vapourpressure and the corresponding vapourpoint are situated with point B on a straight line (fig. 5).

In order to determine the change of pressure along a saturationcurve under its own vapourpressure in its ends on the sides BC and BA (figs. 4 and 5) we put in (16) $\beta = 1$. We then find

$$\left(\frac{dP}{dx}\right)_{x=0} = \frac{x_1}{x}\left(1 - \frac{S}{x_1}\right)\frac{RT}{\Delta V_1} \quad . \quad . \quad . \quad . \quad (20)$$

In this S and ΔV_1 are determined by (13) and (15), when we put herein $\beta = 1$. Consequently S is always positive. When we apply (20) to the figures (4) and (5), then we see that the change of pressure is in accordance with the position of the sides solid-gas and solid-liquid of the threephasetriangles.

Now we have treated the case that either the binary compound F (figs. 2 and 3) or the component B (figs. 4 and 5) occurs as solid phase. When F and B occur both as solid phases, then the two saturationcurves under their own vapourpressure can either intersect one another or not. We only consider the case, drawn in fig. 6, that the two curves intersect one another in a point; the vapour, being in equilibrium with the liquid s, is represented by s_1 $(s_2$ or $s_3)$.

A similar case may occur for instance in the system $Na_2SO_4 +$ water $+$ alcohol, then curve cs is the saturationcurve under its own

vapourpressure of $Na_2SO_4 . 10 H_2O$ (F), sa the saturationcurve of the anhydric Na_2SO_4 (B). Then there exists a series of solutions, saturated under their own vapourpressure with $Na_2SO_4 . 10 H_2O$ (curve cs) and one series saturated with Na_2SO_4 (curve sa); the equilibrium $Na_2SO_4 . 10 H_2O + Na_2SO_4 + L_s + G_s$ occurs only under a definite pressure P_s. The solution L_s has then a definite composition s and the vapour, which consists only of water and alcohol has a definite composition s_1.

In the binary system $Na_2SO_4 +$ water, the equilibrium $Na_2SO_4 . 10 H_2O + Na_2SO_4 +$ vapour exists only under one definite pressure; we shall call this pressure P_0. In the ternary system $Na_2SO_4 +$ water $+$ alcohol the equilibrium $Na_2SO_4 . 10 H_2O + Na_2SO_4 + L_s + G_s$ exists also only under a definite vapourpressure P_s. This pressure P_s is influenced
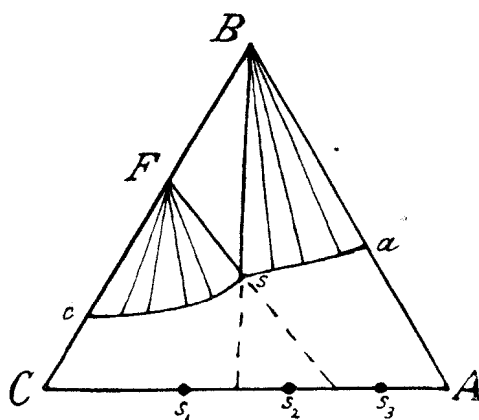

Fig. 6.

by the watervapour and the alcohol-vapour together; now we may show that the partialpressure of the watervapour herein is also equal to P_0 and that the pressure of the alcohol vapour is consequently $P_s - P_0$.

In order to show this, we consider the general case that in the system $A + B + C$ (figs. 1—6) the substances A and C are volatile and that a compound F of B and C occurs.

The binary equilibrium $B + F + G_0$, wherein the vapour consists of C only, occurs under a single pressure P_0 only.

The ternary equilibrium $B + F + G$, wherein consequently the vapour consists of A and C, can occur at a whole series of vapourpressures.

When we represent the ζ of B and F by ζ and ζ_1, then the condition of equilibrium is true:

$$\zeta_1 - \beta\zeta = (1-\beta)\left(Z_1 - x_1 \frac{\partial Z_1}{\partial x_1}\right) \quad \ldots \ldots \quad (21)$$

Hence follows:

$$\left[v_1 - \beta v - (1 - \beta)\left(V_1 - x_1 \frac{\partial V_1}{\partial x_1} \right) \right] dP + (1 - \beta) x_1 r_1 dx_1 = 0. \quad (22)$$

When we assume that the gas-laws hold for the vapour G, then:

$$\frac{\partial V_1}{\partial x_1} = 0 \quad \text{and} \quad r_1 = \frac{RT}{x_1(1-x_1)} \quad \cdots \cdots \quad (23)$$

From (22) now follows:

$$[(1 - \beta) V_1 - v_1 + \beta v] dP = \frac{1-\beta}{1-x_1} RT \cdot dx_1 \quad \cdots \quad (24)$$

The coefficient of dP represents the change of volume when 1 Mol. F is decomposed into β Mol $B + (1 - \beta)$ quantities of G; this is very nearly $(1 - \beta) V_1$. As at the same time $PV_1 = RT$, we can write for (24);

$$(1 - x_1) dP = P dx_1 \quad \cdots \cdots \cdots \quad (25)$$

From this follows:

$$P = \frac{P_0}{1-x_1}. \quad \cdots \cdots \cdots \quad (26)$$

When we call the partial pressures of A and C in the vapour P_A and P_C, then $P_A = x_1 P$ and $P_C = (1 - x_1) P$; from (26) now follows:

$$P_A = \frac{x_1}{1-x_1} P_0 \quad \text{and} \quad P_C = P_0 \quad \cdots \cdots \quad (27)$$

This means that in the ternary equilibrium $B + F + G$ the partial pressure P_C of the substance C is equal to the vapourpressure of the binary equilibrium $B + F + G_0$.

When we bear in mind now that in a system the pressure and the composition of the vapour do not change, when we add to this system still a liquid, which is in equilibrium with all phases of this system, then follows:

In the ternary equilibria $B + F + G$ and $B + F + L_s + G_s$ the partialpressure of the substance C in the vapour is equal to the vapourpressure of the binary equilibrium $B + F + G_0$.

The first equilibrium (viz. $B + F + G$) exists at a whole series of pressures; both the others occur under a definite pressure only.

The binary equilibrium $Na_2SO \cdot 10 H_2O + Na_2SO_4 +$ watervapour has at 25° a vapourpressure of 18.1 m.m. when we add alcohol, then, when the gas laws hold in the vapour, in the equilibrium $Na_2SO_4 \cdot 10H_2O + Na_2SO_4 + G$ and $Na_2SO_4 \cdot 10H_2O + Na_2SO_4 + L + G$ the partialpressure of the watervapour will also be equal to 18.1 m.m.

Now we will put the question, whether we can also deduce some-

thing about the change of pressure starting from s along the curves sa and sc (fig. 6). In communication V we have deduced the following rule. When the equilibrium solid $+ L$ can be converted with increase of volume into solid $+ L' + G'$ (in which L' differs extremely little from L) then of a threephasetriangle solid—liquid—gas the side solid—liquid turns on increase of pressure towards the vapourpoint and it turns away from the vapourpoint on decrease of pressure.

When we assume now that s (fig. 6) is not situated in the vicinity of B or F (the equilibrium $B + L$ and $F + L$ converts itself into $B + L' + G'$ and $F + L' + G'$ with increase of volume) we can apply the above-mentioned rule. We distinguish now according as the vapour is represented by s_1, s_2 or s_3, three cases.

1. The vapour is represented by s_1.

First we consider the threephasetriangle Fss_1. When the side Fs turns towards c, then consequently it turns towards its vapourpoint s_1; the vapourpressure increases, therefore, starting from s along sc towards c.

Let us consider now the threephasetriangle Bss_1. When the side Bs turns towards a, it turns, therefore, away from its vapourpoint s_1; consequently the vapourpressure decreases starting from s along sa towards a.

Consequently we find that the vapourpressure starting from s increases along sc and that it decreases along sa. It is evident that this is only true for points in the vicinity of s; the occurrence at a greater distance of s of a point of maximumpressure on sc and a point of minimumpressure on sa, is viz. not excluded.

2. The vapour is represented by s_2.

It follows from a consideration of the threephasetriangles Fss_2 and Bss_2 that the vapourpressure starting from s increases as well along sc as along sa.

3. The vapour is represented by s_3.

It follows from a consideration of threephasetriangles Fss_3 and Bss_3 that the vapourpressure starting from s decreases along sc and increases along sa.

We can obtain the previous results also in the following way. Between the four phases of the equilibrium $B + F + L_s +$ vapour $(s_1, s_2$ or $s_3)$ a phasereaction occurs on change of volume. We choose this reaction in such a direction that vapour is formed, we call the change of volume ΔV.

The point s (fig. 6) is a point of the quadruplecurve $B + F + + L + G$; ΔV is positive for each point of this curve. When, however, a point of maximumtemperature H occurs on this curve,

then ΔV is negative between this point H and the terminatingpoint of the curve on side BC. It is apparent from the position of the curves sc and sa (fig. 6) that point s is chosen on that part of the quadruplecurve, where ΔV is positive. We distinguish now again the same three cases as above.

1st. The vapour is represented by s_1.

It is apparent from the position of the points F, B, s and s_1 with respect to one another that the fourphase-reaction:

$$F + L_s \rightleftarrows B + G_{s_1} \; (\Delta V > 0)$$

$F + L + G$ (Curve sc) $B + L + G$ (Curve sa)

$F + B + L$ $F + B + G$
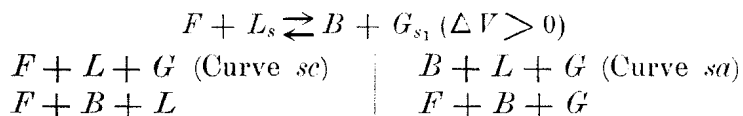
takes place; it proceeds from left to right with increase of volume Hence it follows that the equilibria written at the right of the vertical line occur under lower pressures, the equilibria at the left occur under higher pressures. In accordance with the above we find, therefore, that starting from s (fig. 6) the pressure increases along sc (equilibrium $F + L + G$) and decreases along sa (equilibrium $B + L + G$).

2nd and 3rd. Also in these cases we find agreement with the previous considerations.

When a point of maximumtemperature H occurs on the quadruplecurve $B + F + L + G$, then two points of intersection s occur at temperatures a little below T_H. When we consider now a point of intersection s between H and the terminatingpoint of the quadruplecurve on side BC, then ΔV is negative. This involves that above in 1st—3rd increase of P is replaced by decrease of P and reversally. We find also the same when we consider the threephase-triangles solid-liquid-vapour. *To be continued.*)

Chemistry. — *"On the quaternary system: $KCl-CuCl_2-BaCl_2-H_2O$."* By Prof. Schreinemakers and Miss W. C. de Baat.

(Communicated in the meeting of October 31, 1914).

In a previous communication [1]) we have already discussed the equilibria occurring in this system at 40° and at 60°; the results of the analysis on which these considerations are based, we have hitherto not yet communicated. Now we will communicate the results of the analysis; all the points, curves etc. quoted in this communication apply to the two figures of the previous communication (l. c.). We want to draw the attention to the fact that fig. 1 represents the equilibria at 40° and fig. 2 the equilibria at 60°.

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[1]) These Communications (1912; 326.