

*Citation:*

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In the investigation of the liver of a new-born calf were found, per kilo, 31 mgs. of copper and 81.1 mgs. of zinc.

From the results obtained the following conclusions may be drawn :

1. Arsenic is not a normal constituent of the human liver.
2. Copper and zinc appear to occur regularly in the human liver.
3. They are already deposited in the liver during the foetal stage and, as regards copper, even in a larger quantity than in the following period.
4. Otherwise, there seems to exist no relation between the copper and zinc content of the liver and the age, sex, occupation and place of residence.

5. The figures given by LEHMANN for the copper content are comparatively low. His maximum figure of 5 mg. per kilogram of liver is, as a rule, exceeded in Holland.

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**Chemistry.** — “*Equilibria in ternary systems. II*”. By Prof. SCHRINEMAKERS.

(Communicated in the meeting of November 30, 1912).

In the previous communication we have observed the changes when at a constant temperature there is a change of pressure, and from this deduced the saturation lines of a solid substance  $F$  under their own vapour pressure. We will now briefly consider the case that, at a constant pressure, there is a change in temperature. At a constant temperature a reduction of pressure causes an expansion of the gas region and a contraction of the liquidum region; under a constant pressure the same happens on elevating the temperature.

A system that exhibits at a constant temperature a maximum vapour pressure (minimum), has at a constant pressure a minimum boiling point (maximum).

At a constant temperature, the influence of the pressure on the situation and form of the saturation line of  $F$  is generally small unless at temperatures close to the melting point of  $F$ , at a constant pressure the influence of the temperature is usually much greater and the movement of the line, therefore, much more rapid. Yet, as a rule, the liquidum line will move more rapidly than the saturation line unless indeed the latter is on the point of disappearing.

At a constant temperature, the saturation line of  $F$  may disappear on increasing or reducing the pressure; this depends on whether, on melting, an increase or a decrease of the volume takes place. Under

a constant pressure it disappears at an elevation of temperature only.

From all this it follows that most of the diagrams described above which occur at a constant temperature on reduction of pressure will also, as a rule, form at a constant pressure by an elevation of temperature. At a constant temperature, the liquid and the gas of the three-phase equilibrium  $F + L + G$  each proceed along an isothermic-polybaric curve which we have called the saturation line of  $F$  under its own vapour pressure and the vapour line appertaining thereto.

Under a constant pressure, the liquid and the gas of the three-phase equilibrium  $F + L + G$  each proceed along a polythermic-isobaric curve. As these solutions saturated with  $F$  can, at a given pressure, be in equilibrium with vapour and consequently boil at that temperature we will call these lines the boiling point line of the solutions saturated with  $F$  and the vapour line appertaining thereto.

The saturation line of  $F$  under its own pressure may be circumphased [fig. 7 (I) and 11 (I)]<sup>1)</sup> as well as exp phased [fig. 12 (I) and 13 (I)]. The same applies to the boiling point line of the solutions saturated with  $F$ , with this difference, however, that fig. 13 (I) does not occur. The saturation line of  $F$  under its own vapour pressure exhibits a pressure maximum and minimum; the boiling point line of the solutions saturated with  $F$  a temperature maximum and minimum. These are, however, so situated that the arrows of the figs. 7 (I), 11 (I) and 12 (I) should point in the opposite direction.

We will refer later to these curves in various respects.

We can also unite these boiling point lines with their correlated vapour lines for different pressures, in a same plane. We then obtain a diagram analogous to fig. 14 (I) in which the arrows, however, must point in the opposite direction. If the pressure axis is taken perpendicularly to the plane of drawing, the spaceal representation gives two planes, namely the boiling point plane of the solutions saturated with  $F$  and the correlated vapour plane.

We will now consider still in another way the saturation lines under their own pressure and the boiling point lines of the liquids saturated with a solid substance.

We assume that a solid substance  $F$  of the composition  $\alpha, \beta$ , and

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<sup>1)</sup> The number (I) placed behind a figure signifies that a figure from the first communication is intended.

$1-\alpha-\beta$  is in equilibrium with a liquid  $L$  of the composition  $x, y$  and  $1-x-y$  and with a vapour  $L$  of the composition  $x_1, y_1$  and  $1-x_1-y_1$ . We call the volumes of these phases  $v, V$ , and  $V_1$ , their entropies  $\eta, H$ , and  $H_1$ , their thermodynamic potentials  $\zeta, Z$  and  $Z_1$ .

As equilibrium conditions we find

$$\left. \begin{aligned} Z - (x-\alpha) \frac{\partial Z}{\partial x} - (y-\beta) \frac{\partial Z}{\partial y} &= \zeta \\ Z_1 - (x_1-\alpha) \frac{\partial Z_1}{\partial x_1} - (y_1-\beta) \frac{\partial Z_1}{\partial y_1} &= \zeta \\ \frac{\partial Z}{\partial x} &= \frac{\partial Z_1}{\partial x_1} \quad \text{en} \quad \frac{\partial Z}{\partial y} = \frac{\partial Z_1}{\partial y_1} \end{aligned} \right\} \dots \dots \dots (1)$$

From this we find:

$$[(x-\alpha)r + (y-\beta)s] dx + [(x-\alpha)s + (y-\beta)t] dy = AdP - BdT \quad (2)$$

$$[(x_1-\alpha)r_1 + (y_1-\beta)s_1] dx_1 + [(x_1-\alpha)s_1 + (y_1-\beta)t_1] dy_1 = A_1dP - B_1dT \quad (3)$$

$$r dx + s dy = r_1 dx_1 + s_1 dy_1 + \left( \frac{\partial V_1}{\partial x_1} - \frac{\partial V}{\partial x} \right) dP - \left( \frac{\partial H_1}{\partial x_1} - \frac{\partial H}{\partial x} \right) dT \quad (4)$$

$$s dx + t dy = s_1 dx_1 + t_1 dy_1 + \left( \frac{\partial V_1}{\partial y_1} - \frac{\partial V}{\partial y} \right) dP - \left( \frac{\partial H_1}{\partial y_1} - \frac{\partial H}{\partial y} \right) dT \quad (5)$$

If we only want a relation between  $dx, dy, dP$ , and  $dT$  then from the previous equations we deduce:

$$-[(x-\alpha)r + (y-\beta)s] dx + [(y-\alpha)s + (y-\beta)t] dy = AdP - BdT \quad (6)$$

$$[(x_1-\alpha)r_1 + (y_1-\beta)s_1] dx_1 + [(x_1-\alpha)s_1 + (y_1-\beta)t_1] dy_1 = CdP - DdT \quad (7)$$

In this:

$$A = V - v + (x-\alpha) \frac{\partial V}{\partial x} + (y-\beta) \frac{\partial V}{\partial y} \quad B = H - \eta + (x-\alpha) \frac{\partial H}{\partial x} + (y-\beta) \frac{\partial H}{\partial y}$$

$$C = V_1 - V + (x-x_1) \frac{\partial V}{\partial x} + (y-y_1) \frac{\partial V}{\partial y} \quad D = H_1 - H + (x-x_1) \frac{\partial H}{\partial x} + (y-y_1) \frac{\partial H}{\partial y}$$

In order to obtain the saturation line of the solid substance  $F$  under its own vapour pressure we call in (6) and (7)  $dT = 0$ ; we then obtain:

$$[(x-\alpha)r + (y-\beta)s] dx + [(x-\alpha)s + (y-\beta)t] dy = AdP \quad (8)$$

$$[(x_1-\alpha)r_1 + (y_1-\beta)s_1] dx_1 + [(x_1-\alpha)s_1 + (y_1-\beta)t_1] dy_1 = CdP \quad (9)$$

The correlated vapour line is obtained by interchanging in these relations the *quantities* relating to vapour and liquid. In order that the pressure in a point of the saturation line under its own pressure may become maximum or minimum  $dP$  in (8) and (9) must be  $= 0$ . Hence:

$$[(x - \alpha) r + (y - \beta) s] dx + [(x - \alpha) s + (y - \beta) t] dy = 0. \quad (10)$$

$$[(x_1 - \alpha) r + (y_1 - \beta) s] dx + [(x_1 - \alpha) s + (y_1 - \beta) t] dy = 0. \quad (11)$$

This means that in this point the saturation line under its own vapour pressure comes into contact with the isothermic-isobaric saturation line of  $F$  (10) and with the liquidum line of the heterogeneous region  $LG$  (11).

We can satisfy (10) and (11) by:

$$\frac{y - \beta}{x - \alpha} = \frac{y_1 - \beta}{x_1 - \alpha} \dots \dots \dots (12)$$

This means that the three points representing the solid substance  $F$ , the liquid and the vapour are situated on a straight line. Hence, we find that on a saturation line of a solid substance  $F$  under its own vapour pressure, the pressure is maximum or minimum when the three phases ( $F$ ,  $L$ , and  $G$ ) are represented by points of a straight line, or in other words, when between the three phases a phase reaction is possible.

If we imagine before us the equation of the correlating vapour line we notice that when the pressure in a point of the saturation line under its own vapour pressure is at its maximum or minimum, this must also be the case in the corresponding point of the correlated vapour line. It then also follows that the correlated vapour line, the vapour saturation line of  $F$  and the vapour line of the heterogeneous region  $LG$  meet in this point.

The previous remarks apply, of course, also to the boiling point line of the solutions saturated with  $F$ ; in (6) and (7)  $dP$  must then be supposed  $\doteq 0$ .

Hence we conclude:

When solid matter, liquid and gas have such a composition that between them a phase reaction is possible (the three figurating points then lie on a straight line) then, on the saturation line of the saturated solutions under its own pressure, the pressure is at its maximum or minimum; on the boiling point line this will be the case with the temperature. The same applies to the vapour lines appertaining to these curves. In each of these maximum or minimum points the three curves come into contact with each other.

The properties found above have been already deduced by another way in the first communication.

We will now investigate the saturation line of  $F$  under its own vapour pressure in the vicinity of point  $F$ . First of all, it is evident that one line may pass through point  $F$ .

For if in (8) we call  $x = \alpha$  and  $y = \beta$  it follows that  $dP = 0$ ; (9) is converted into:

$$[(x_1 - \alpha)r + (y_1 - \beta)s] dx + [(x_1 - \alpha)s + (y_1 - \beta)t] dy = 0. \quad (13)$$

We thus find a definite value for  $\frac{dy}{dx}$ ; at the same time it appears from (13) that in point  $F$  the saturation line under its own vapour pressure and the liquidum line of the heterogeneous region  $LG$  meet each other. It further appears from (13) that the tangent to the saturation line in  $F$  under its own vapour pressure and the line which connects the points  $F$  with the vapour phase are conjugated diagonals of the indicatrix in point  $F$ . (The same applies, of course to the boiling point line of the saturated solutions).

If accidentally, not only the liquid but also the vapour still has the composition  $F$ , therefore, when not only  $x = \alpha$  and  $y = \beta$ , but also  $x_1 = \alpha$  and  $y_1 = \beta$ , then  $\frac{dy}{dx}$  becomes indefinite.

In this case, however a maximum or minimum vapour pressure appears in the ternary system  $LG$ ; we will refer to this later.

From (6) and (7) we deduce for  $x = \alpha$  and  $y = \beta$ :

$$\frac{(BC - AD) dT}{A} = \{(x_1 - \alpha)r + (y_1 - \beta)s\} dx + \{(x_1 - \alpha)s + (y_1 - \beta)t\} dy \quad (14)$$

This relation determines the change in temperature  $dT$  around point  $F$ ; this is always differing from 0 unless one chooses  $dx$  and  $dy$  in such a manner that the second member of (14) becomes nil. According to (13) this signifies that, starting from  $F$ , one moves over the tangent to the liquidum line of the heterogeneous region  $LG$ .

We now choose  $dx$  and  $dy$  along the line which connects the point  $F$  with the vapour phase; for this we put:

$$dx = (x_1 - \alpha) d\lambda \quad \text{and} \quad dy = (y_1 - \beta) d\lambda \quad \dots \quad (15)$$

We then obtain from (14)

$$(BC - AD) dT = (V - v) \{(x_1 - \alpha)^2 r + 2(x_1 - \alpha)(y_1 - \beta)s + (y_1 - \beta)^2 t\} d\lambda \quad (16)$$

In this we have replaced  $A$  by the value  $V - v$ , which  $A$  obtains for  $x = \alpha$  and  $y = \beta$ .

Let us investigate the sign of:

$$K = BC - AD = (H - \eta) C - (V - v) D.$$

Now,  $C$  is the increase in volume when a quantity of vapour is generated from an indefinitely large quantity of liquid;  $D$  is the increase in entropy in this reaction. Hence so long we are not too close to temperatures at which critical phenomena occur between liquid and vapour,  $C$  is as a rule large in regard to  $(V - v)$ ;  $H - \eta$  and  $D$  are quantities of about the same kind. If now  $V < v$ , then  $K$  is for certain positive; if, however,  $V > v$ , then  $K$  is, as a rule,

also still positive on account of the small value of  $V - v$  in regard to  $C$ . We will, therefore, in future always put  $K$  positive; should it become negative the necessary alterations can readily be introduced.

We now distinguish two cases.

- a.  $V > v$ ,  $dT$  and  $d\lambda$  have the same sign;
- b.  $V < v$ ,  $dT$  and  $d\lambda$  have the opposite sign.

Now, it follows from (15) that  $d\lambda > 0$  signifies that one is moving from point  $F$  towards the vapour phase. From this we conclude:

The part of a saturation line passing through the point  $F$  of the substance  $F$  under its own vapour pressure and situated in the vicinity of  $F$  moves at an increase of temperature:

- a. if  $V > v$ , towards the vapour phase appertaining to point  $F$ .
- b. als  $V < v$ , away from the vapour phase appertaining to point  $F$ .

From (6) and (7) instead of (16) we can deduce also:

$$K dP = (H - \eta) \{ (x_1 - \alpha)^2 r + 2(x_1 - \alpha)(y_1 - \beta)s + (y_1 - \beta)^2 t \} d\lambda. \quad (17)$$

From this we conclude:

The part of a boiling point line of the saturated solutions of  $F$  situated in the vicinity of  $F$  moves, on increase of pressure, always more towards the vapour phase appertaining to point  $F$ .

In order to get a better knowledge of the saturation line of  $F$  under its own vapour pressure which passes through the point  $F$  and of the boiling point line of the saturated solutions of  $F$  we will also introduce in our formulae terms with  $dx^2$ ,  $dx dy$ , and  $dy^2$ . In order to simplify the calculations a little we will assume provisionally that the vapour consists of one component only.

We, therefore call in our previous formulae  $x_1 = 0$  and  $y_1 = 0$ . Our equilibrium conditions (1) then are converted into:

$$Z - x \frac{\partial Z}{\partial x} - y \frac{\partial Z}{\partial y} = Z_1 \dots \dots \dots (18)$$

$$Z_1 + \alpha \frac{\partial Z}{\partial x} + \beta \frac{\partial Z}{\partial y} = \zeta \dots \dots \dots (19)$$

We now write for (18),  $T$  being kept constant:

$$\begin{aligned} (xr + ys) dx + (xs + yt) dy + \frac{1}{2} \left( r + x \frac{\partial r}{\partial x} + y \frac{\partial r}{\partial y} \right) dx^2 + \\ + \left( s + x \frac{\partial s}{\partial x} + y \frac{\partial s}{\partial y} \right) dx dy + \frac{1}{2} \left( t + x \frac{\partial t}{\partial x} + y \frac{\partial t}{\partial y} \right) dy^2 \dots = \\ = \left( v - V_1 - x \frac{\partial V}{\partial x} - y \frac{\partial V}{\partial y} \right) dP + \dots \dots \dots (20) \end{aligned}$$

From (19) follows:

$$\begin{aligned}
 & (\alpha r + \beta s) dx + (\alpha s + \beta t) dy + \frac{1}{2} \left( \alpha \frac{\partial r}{\partial x} + \beta \frac{\partial s}{\partial x} \right) dx^2 + \\
 & \quad + \left( \alpha \frac{\partial s}{\partial x} + \beta \frac{\partial t}{\partial x} \right) dx dy + \frac{1}{2} \left( \alpha \frac{\partial s}{\partial y} + \beta \frac{\partial t}{\partial y} \right) dy^2 + \dots \\
 & = \left( v - V_1 - \alpha \frac{\partial V}{\partial x} - \beta \frac{\partial V}{\partial y} \right) dP + \dots \dots \dots (21)
 \end{aligned}$$

Let us now deduce (21) from (20) after having substituted in (20)  $x = \alpha$  and  $y = \beta$ : we find:

$$\frac{1}{2} r \cdot dx^2 + s dx dy + \frac{1}{2} t dy^2 + \dots = A dP + \dots \dots (22)$$

in which the coefficients of  $dP \cdot dx$  and  $dP \cdot dy$  are nil, whereas for the sake of brevity we write the coefficient of  $dP$  in (21) —  $(A + C)$ .  $A$  and  $C$  then have herein the same values as in our former equations. Then, however, we assume  $x = \alpha$ ,  $y = \beta$ ,  $x_1 = 0$ , and  $y_1 = 0$ .

From (22) follows  $dP$  of the order  $dx^2$  and  $dy^2$ , here from (21) at first approximation:

$$(\alpha r + \beta s) dx + (\alpha s + \beta t) dy = 0 \dots \dots (23)$$

In connection with (13) it appears from this that the liquidum line passing through point  $F$  and the saturation line of  $F$  under its own vapour pressure come into contact with each other.

If we eliminate  $dP$  from (21) and (22) we obtain:

$$\begin{aligned}
 & (\alpha r + \beta s) dx + (\alpha s + \beta t) dy + \frac{1}{2} \left( \alpha \frac{\partial r}{\partial x} + \beta \frac{\partial s}{\partial x} + r + \lambda r \right) dx^2 + \\
 & + \left( \alpha \frac{\partial s}{\partial x} + \beta \frac{\partial t}{\partial x} + s + \lambda s \right) dx dy + \frac{1}{2} \left( \alpha \frac{\partial s}{\partial y} + \beta \frac{\partial t}{\partial y} + t + \lambda t \right) dy^2 = 0 (24)
 \end{aligned}$$

in which  $\lambda = \frac{C}{A}$ .

For the liquidum line passing through point  $F$  we find:

$$\begin{aligned}
 & (\alpha r + \beta s) dx + (\alpha s + \beta t) dy + \frac{1}{2} \left( \alpha \frac{\partial r}{\partial x} + \beta \frac{\partial s}{\partial x} + r \right) dx^2 \\
 & + \left( \alpha \frac{\partial s}{\partial x} + \beta \frac{\partial t}{\partial x} + s \right) dx dy + \frac{1}{2} \left( \alpha \frac{\partial s}{\partial y} + \beta \frac{\partial t}{\partial y} + t \right) dy^2 = 0 \dots (25)
 \end{aligned}$$

For the sake of brevity we write (24) and (25) as follows:

$$aX + bY + \frac{1}{2} (c + \lambda r) X^2 + (d + \lambda s) XY + \frac{1}{2} (e + \lambda t) Y^2 = 0 \dots (26)$$

$$aX + bY + \frac{1}{2} cX^2 + dXY + \frac{1}{2} eY^2 = 0 \dots \dots (27)$$

Equation (26) now relates to the saturation line, under its own pressure, passing through  $F$ , (27) on the liquidum line of the heterogeneous region  $LG$  passing through  $F$ .



Now the curvature of (27) is given by:

$$\frac{2abd - a^2e - b^2c}{(a^2 + b^2)^{3/2}} \dots \dots \dots (28)$$

that of curve (26) by:

$$\frac{2abd - a^2e - b^2c - \lambda(a^2t + b^2r - 2abs)}{(a^2 + b^2)^{3/2}} \dots \dots \dots (29)$$

As (28) and (29) have the same denominator we, in order to compare the curvatures of both curves, only want the numerators. For the sake of brevity we write:

$$2abd - a^2e - b^2c = Q \dots \dots \dots (30)$$

and

$$2abd - a^2e - b^2c - \lambda(a^2t + b^2r - 2abs) = Q - \lambda S \dots (31)$$

If, by means of the known values of  $a$  and  $b$  we calculate the value of  $S$  we find:

$$S = (rt - s^2)(a^2r + 2\alpha\beta s + \beta^2t)$$

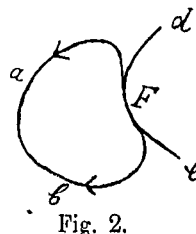
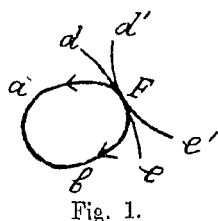
hence,  $S$  is always positive.

In order to find the direction of the curvature we calculate the coordinates  $\xi$  and  $\eta$  of the centre of the curved circle and ascertain at which side of the tangent this centre is situated. Therefore, we call the origin of the coordinate system the point which in this case represents the vapour,  $O$ . We now find the following: the liquidum line is curved in the point  $F$  towards  $O$  when  $Q < 0$ ; it is curved in  $F$  away from  $O$  if  $Q > 0$ .

A consideration of  $Q$  shows that this can be positive as well as negative; hence, the liquidum line can be curved in  $F$ , away from  $O$  as well as towards  $O$ .

In order to find the saturation line under its own vapour pressure we will consider two cases.

Owing to the small value of  $V - v$ ,  $\lambda$  will generally have a large positive value. In Fig. 1, wherein for the moment we disregard the curve  $d'F'e'$ , the liquidum line is represented by  $dFe$ ; the point  $O$  is supposed to be somewhere to the left of this curve  $dFe$  so that this is curved towards  $O$ ;  $Q$  is consequently negative.



From this it follows at once that  $Q - \lambda S$  is also negative and that the saturation line under its own vapour pressure, namely the curve  $Fab$ , must possess a curvature stronger than that of the liquidum line. It further follows from our previous considerations that they must intersect also the line  $OF$  somewhere between  $O$  and  $F$  so that they must exhibit a form as indicated schematically in fig. 1. The change in pressure along this curve is determined in  $F$  by (22)', from which it follows, that, starting from  $F$ ,  $dP$  is positive whether towards  $a$  or towards  $b$ . The pressure in  $F$  is, therefore a minimum one and increases in the direction of the arrows. The solution with maximum vapour pressure is, of course, in this case situated on the intersecting point of this curve with the line  $OF$ .

We will now disregard the liquidum line  $dFe$  of fig. 1 and suppose it to be replaced by  $d'Fe'$  which is curved in another direction:  $Q$  is, therefore, positive so that  $Q - \lambda S$  can be positive as well as negative. If the liquidum line is not curved too strongly  $Q - \lambda S$  will be negative and the saturation line under its own vapour pressure again exhibits a form like the curve  $aFb$  of Fig. 1. If however the liquidum line is curved very strongly and  $\lambda$  is not too large, then  $Q - \lambda S$  can also become positive, so that both curves in  $F$  are bent in the same direction. This has been assumed in Fig. 2 wherein  $dFe$  represents the liquidum line and  $aFb$  the saturation line under its own vapour pressure. As in this case,  $Q$  is larger than  $Q - \lambda S$  it follows, as assumed in Fig. 2, that in the vicinity of  $F$  the curve  $dFe$  must be bent more strongly than the curve  $aFb$ .

$V < v$ .  $\lambda$  has, therefore, generally a large negative value. In the same way as above we find that Figs. 3 and 4 can now appear. The saturation line under its own vapour pressure is again represented by  $aFb$ , the liquidum line by  $dFe$ . In Fig. 3 are united two cases,

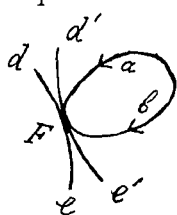


Fig. 3

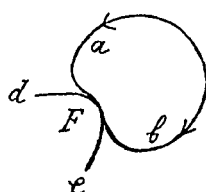


Fig. 4.

namely a liquidum line  $dFe$  curved towards  $O$  and another  $d'Fe'$  curved in the opposite direction. We must remember also that the line  $OF$  must intersect the saturation line somewhere in a point situated at the other side of  $F$  than the point  $O$ .  $A$  now being negative, it further follows from (22) that the pressure of  $A$  must now decrease towards  $a$  as well as towards  $b$ ; hence, the arrows

again indicate the direction in which the vapour pressure increases.

The previous considerations relate to the saturation line under its own vapour pressure; in a similar manner we may likewise investigate the boiling point line of the saturated solutions. We must then

in (26) replace  $\lambda$  by  $\mu$  in which  $\mu = \frac{D}{B} = \frac{-D}{H-\eta}$ .

Instead of  $Q-\lambda S$  we must then consider  $Q-\mu S$ .  $\mu$  is now always positive and as regards absolute value smaller than  $\lambda$ . Further we must replace  $AdP$  in (22) by  $BdT$ . As, moreover, the line  $OF$  must intersect the boiling point line of the saturated solutions in a point between  $O$  and  $F$ , we re-find the cases represented in figs. 1 and 2 in which  $aFb$  now represents the boiling point line of the saturated solutions. If, however, the arrows must indicate the direction of an increasing temperature one must imagine them to point in the opposite direction.

If we compare the values of  $Q-\lambda S$  and  $Q-\mu S$  in regard to each other, we may search for the different situations of the saturation line under its own pressure, and for the boiling point line of the saturated solutions in regard to each other, in the vicinity of point  $F$ . I will, however, not go in for this now; I will, however, refer to it when discussing the value of  $\frac{dP}{dT}$  in the vicinity of the point  $F$ .

Whether all conceivable combinations are actually possible is difficult to predict. Perhaps a solution might be found by introducing the condition of equilibrium of VAN DER WAAALS and expressing the different quantities in the  $a$  and  $b$  of VAN DER WAAALS, which must then be considered as functions of  $x$  and  $y$ .

We will now deduce the vapour saturation lines under their own pressure and the boiling point lines of the saturated solutions yet in another manner.

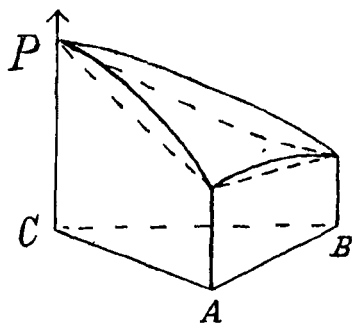


Fig. 5.

In order to find the saturation line, under its own pressure, of a definite temperature  $T$  we take the vapour- and the liquidum surface of this temperature  $T$ ; we then obtain fig. 5 in which the pressure axis is taken perpendicularly to the component triangle  $ABC$ . The liquidum surface is represented by the drawn, the vapour plane by the dotted lines. If the vapour contains only two of the components the vapour side reduces itself to a curve situated in one of the border planes; if it contains but one single component it reduces itself to a single point. Like in our former considerations, we further assume, provisionally, that in the liquidum side occurs neither a maximum, minimum, nor a stationary point.

We further take, at the assumed temperature  $T$  and an arbitrary pressure  $P$ , a saturation line of the solid substance  $F$ . If we alter the pressure,  $T$  remaining constant, this saturation line changes its form. If, to the component triangle, we place perpendicularly the  $P$ -axis and if on this we place the different saturation lines we get an isothermic-polybaric saturation surface of  $F$ . This surface may lie as in fig. 6 or 7; the component triangle has been omitted from both figures. the arrows point in the direction of increasing pressure. That both cases are possible is evident from what follows:

$V > v$ . At the assumed temperature  $T$  the substance  $F$  will melt at a definite pressure. Because the substance melts with increase of volume the saturation line of  $F$  will appear on elevation of

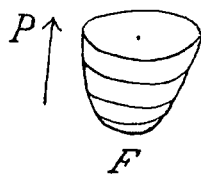


Fig. 6.

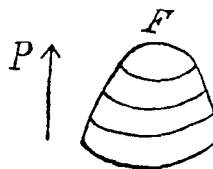


Fig. 7.

pressure, so that we obtain a surface like in fig. 6, namely with the convex side directed downwards.

$V < v$ . At the assumed temperature  $T$  the solid substance  $F$  will also melt at a definite pressure. Because on melting there is now a decrease of volume, the saturation line of  $F$  will now appear on reduction of pressure. We thus obtain a surface like in fig. 7, namely with the concave side directed downwards.

The surfaces of figs. 5, 6, and 7 are isothermic-polybaric; they, therefore, apply only to a definite temperature; if this is changed those surface alter their form and situation. On elevation of temperature the liquidum and vapour surfaces of fig. 5 shift upwards likewise the surface of fig. 6. On elevation of temperature, the surface of fig. 7

moves, however, downwards; as  $V$  is smaller than  $v$  the correlated melting pressure will fall on increase of the melting temperature of  $F$ .

As a small change in the melting point usually causes a very great change in pressure both surfaces of figs. 6 and 7 will generally move much more rapidly than the vapour and liquidum side of fig. 5.

$V > v$ . We now suppose the saturation line of fig. 6 to be introduced also in fig. 5, to begin with we assume the point  $F$  of the saturation surface to be far below the liquidum side. All points of the section of both surfaces now represent liquids saturated with solid  $F$  and in equilibrium with vapour, consequently the system  $F + L + G$ . As the points of the section all appertain to the same temperature, this section is therefore the previously recorded saturation line of the solid substance  $F$  under its own vapour pressure. If we project this section on the component triangle we obtain a curve surrounding point  $F$  like the drawn curves in fig. 7 (I) or fig. 11 (I). It is also evident that the pressure must increase in the direction of the arrows of these figures. We now again imagine in fig. 5 the section of liquidum surface and saturation surface; with each point of this section corresponds a definite point of the vapour surface. On the vapour surface is situated, therefore, a curve indicating the vapours in equilibrium with the solutions saturated with  $F$ ; this curve is the vapour line appertaining to the saturation line under its own vapour pressure. If this curve is projected on the component triangle we obtain a curve surrounding point  $F$  such as the dotted curve of figs. 7 (I) or 11 (I).

If the temperature is increased the liquidum, gas, and saturation surfaces of  $F$  move upwards; as the latter surface, however, moves more rapidly than the first, there occurs a temperature where  $F$  falls on the liquidum surface so that the solid substance  $F$  is in equilibrium with a liquid of the same composition and with a vapour. Like VAN DER WAALS in the binary systems, we may call this temperature the minimum melting point of  $F$ .

As the plane of contact *introduced* in  $F$  at the saturation surface is horizontal, the saturation surface must intersect the liquidum surface. We notice that this section proceeds from  $F$  towards the direction of the vapour surface. If we project this curve on the component triangle we obtain the curve  $aFb$  of figs. 1 or 2. The curves  $de$  or  $d'e'$  of these figures are the sections of the plane of contact in  $F$  at the saturation surface with the liquidum side; they are consequently the liquidum lines of the heterogeneous region  $LG$  at this minimum melting point of the substance  $F$ .

From a consideration of fig. 5 it immediately follows that the vapour lines appertaining to the curves  $aFb$  of figs. 8 and 2 are expased and may, or may not, intersect the saturation line.

If we still increase the temperature a little, the point  $F$  gets above the liquidum surface and the saturation line of  $F$  under its own pressure becomes expased. We then obtain fig. 12 (I) in which the vapour line may, or may not, intersect the saturation curve under its own vapour pressure.

If we increase the temperature still a little more, the saturation and the liquidum surface come into contact in a point; it is evident that on the saturation surface of  $F$  this point does not coincide with  $F$ , but is shifted towards the gas surface. We now have the highest temperature at which the system  $F + L + G$  exists. In fig. 12 (I) both lines contract to a point; both points lie with  $F$  on a straight line.

$V < v$ . We now imagine the saturation surface of fig. 7 to have been introduced in fig. 5 and in such a manner that the point  $F$  is situated above the liquidum surface. The section is then again a saturation line of the substance  $F$  under its own vapour pressure, which surrounds the point  $F$ . In projection we, therefore, again obtain fig. 7(I) or 11(I) with an expased or circumphased correlated vapour line which has shifted towards the side of the vapour surface.

On increasing the temperature the liquidum and vapour surface shift in an upward direction but the saturation surface of  $F$  shifts, however, downwards. At a definite temperature, the minimum melting point temperature of  $F$  (point  $F$ ) arrives at the liquidum side and it is now evident that the saturation line under its own vapour pressure has shifted, starting from  $F$ , from the gas surface. In projection we thus obtain the curves  $aFb$  of fig. 3 or 4. The correlated vapour line has, of course, shifted towards the side of the gas surface and may be either expased or circumphased.

What will happen at a further increase of temperature will now be readily understood.

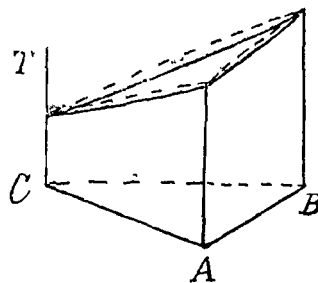


Fig. 8.

In order to find the boiling point line of the solutions saturated with  $F$ , for a definite pressure  $P$ , we take the vapour surface and the liquidum surface for this pressure  $P$ ; we then obtain fig. 8 in which the temperature axis is taken perpendicularly to the component triangle  $ABC$ . The liquidum surface is represented by the drawn, the vapour surface by the dotted lines. In

order to act in accordance with our determined assumption that  $C$  is the component with the highest vapour pressure the boiling point of  $C$  has been taken lower than that of  $A$  and  $B$ .

We now also take a polythermic-isobaric saturation surface of  $F$ . At the assumed pressure  $P$ , there exists, for an entire series of temperatures, at each temperature a definite saturation line of  $F$ . If these are put on a temperature axis, the polythermic-isobaric saturation surface is formed which we can represent by fig. 7 in which however, we must imagine  $P$  to be replaced by  $T$ ; we will call this figure fig. 7a.

The figs. 7a and 8 apply only to one definite pressure; if this is altered they change their situation and form. On increase of pressure both surfaces of fig. 8 move upwards; the saturation surface of the figure 7a can move upwards as well as downwards. This depends on whether on melting, there is an increase or decrease of volume. As however, a change in pressure causes, as a rule, a comparatively small change in the melting point of a substance, the movement of the saturation surface of the substance  $F$  will be slower than that of the two surfaces in fig. 8.

We now imagine the saturation surface of the fig. 7a to be introduced in fig. 8 and in such a manner that the point  $F$  lies above the liquidum side. The section is then the boiling point line of the solutions saturated with  $F$ ; the correlated vapour line has, as seen from the figure, shifted towards the vapour surface. A projection on the component triangle gives a circumphased boiling point line of the solutions saturated with  $F$  and a circumphased and an exp phased vapour line. We thus again obtain the figures 7 (I) or 11 (I) in which however, the arrows, indicating the direction of increasing temperatures, must be supposed to point in the opposite direction.

On further increase in pressure, the point  $F$  first arrives at the liquidum surface, then the liquidum surface comes into contact with the saturation surface of  $F$  from which follow the previously described boiling point lines of the saturated solutions and their correlated vapour lines.

In place of the saturation surface of  $F$  we could also have considered the vapour saturation surface of  $F$  and its movement in regard to the vapour surface of the system  $L G$ . We will refer later to the vapour saturation surfaces of a solid substance, in connection with another investigation.

We have already stated above that the vapour surface; when the vapour contains two components only, reduces itself to a vapour curve, and to a point when the vapour contains only one component.

This causes that many of the properties already mentioned may be deduced and expressed in a much more simple manner. I will refer to this later when discussing the vapour pressures and boiling points of aqueous solutions saturated with salts and double salts, which in some cases have been determined experimentally.

(To be continued).

**Chemistry.** — “*Equilibria in ternary systems.*” III. By Prof. SCHRÖENEMAKERS.

(Communicated in the meeting of Dec. 28, 1912).

In the previous communications <sup>1)</sup> we have assumed that in the system liquid-vapour occurs neither a maximum or minimum, nor a stationary point; we have also limited ourselves to the appearance of two three-phase triangles.

We will now discuss first the case that in the ternary system occurs a point with a minimum vapour pressure.

Let us imagine that in fig. 1 (1) the liquidum line  $de$  and the vapour line  $d_1e_1$  of the heterogeneous region  $LG$  surround the saturation line of  $F$ , so that we get a diagram as in fig. 1. The saturation line of  $F$  is here surrounded by the liquidum region  $L$ , this by the heterogeneous region  $LG$  and this in turn by the vapour region. All liquids saturated with  $F$  therefore occur at the stated  $P$  and  $T$  in a stable condition.

On reduction of pressure, the liquidum region contracts so as to disappear simultaneously with the heterogeneous region  $LG$  in a point. This point represents for the stated temperature, the liquid and the vapour which, at the minimum pressure of the system liquid

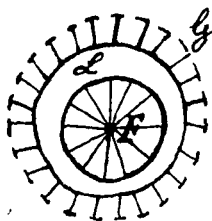


Fig. 1.

+ gas can be in equilibrium with each other. This point may occur without as well as within the saturation line of  $F$ . As at lower temperatures the region  $FL$  is generally large, but small at temperatures in the vicinity of the melting point of  $F$ , the said point will appear, at high temperatures, usually without, and at lower temperatures as well within as without the saturation line of  $F$ .

We now first consider the case where the point with a minimum vapour pressure falls outside the saturation line of  $F$ , or in other words that the liquidum and the heterogeneous region disappear in a point outside the saturation line of  $F$ .

<sup>1)</sup> These Proc. p. 700 and 853.