

*Citation:*

F.A.H. Schreinemakers, Equilibria in ternary systems. XIII, in:  
KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 841-857

the apex of the young rolled-up leaves. This is the only one of the three factors which becomes separately visible. When it is present heterozygotically, segregation takes place in the proportion of 3 with and 1 without, for example, from  $R\ 4-2$  (green)  $\times$  3 I obtained 46 large plants, of which 35 had the narrow red edge and 11 were without it. In the same way out of 35 specimens from  $R\ 13-1-1$  (green) 27 had it and 8 were without it.

In  $F_2$  of the crosses this segregation is also seen. Of 125 "green" examples of  $(R\ 4-7) \times (G\ 11-5)$   $R\ 1$  I obtained only 51 in bloom, the others died by the continuous rain. With segregation in the proportion of 27:37 (see the table)  $37-16 = 21$  plants must occur, which show the narrow red edge, as against 16 real "green" ones. Calculated according to the proportion the number of those with the narrow red edge is 28.94 and of "green" ones 22.05. The figures found were 30 and 21, certainly a sufficient agreement. It is perhaps not unnecessary to add that the 6 specimens which remained from the 16 "green" ones from  $(R\ 4-7) \times (G\ 11-5)$   $R\ 6$ , were really "green", without the narrow red edge on the leaves.

New crossings of the same two forms but of different origin have in the meantime been made, as also the crossing of  $R\ 13-4-3$  with *Canna glauca*, which differ in at least ten characters and probably in still more. The whole  $F_1$  generation is however up to the present only one specimen, of which the fertility is still doubtful. The leaf shape is intermediate between that of the parents; the leaves have still something of the wax-like appearance of the mother and the red edge of the father.

Medan (Sumatra), January 1914.

**Chemistry.** — "*Equilibria in ternary systems.*" XIII. By Prof. F. A. H. SCHREINEMAKERS.

Now we consider the case, that the substance  $F$  is one of the components; it is evident that we can deduce then the saturation-curves under their own vapourpressure and the boilingpointcurves in the same way as is done in the previous communications for a ternary and a binary compound.

We take the component  $B$  as solid substance and now we choose a  $T$  and  $P$  in such a way, that no vapour is formed and the isotherm consists only of the saturationcurve  $rs$  of fig. 1. On decrease of pressure anywhere a gasregion and the region  $LG$  occur. These regions may arise in different points; in fig. 1 the region  $LG$ , the

liquidcurve of which is indicated by  $ed$ , may be imagined arisen in  $C$ . Also two or more of these regions can be formed in different points of the triangle and they can later disappear and come together in different ways.

We may now distinguish several principal cases, according to the appearances in the binary systems  $BC$  and  $BA$ .

I. Neither in the binary system  $BC$  nor in the binary system  $BA$  the equilibrium liquid—gas shows a point of maximum- or of minimum pressure.

II. In the binary system  $BC$  or in the binary system  $AB$  or in both these systems the equilibrium liquid—gas shows a point of maximum- or minimum pressure. We only consider the first case, so that a region  $LG$  intersects only once as well the side  $BC$  as the side  $BA$ . We may distinguish the following cases:

1°. on decrease of pressure or increase of  $T$  the region  $LG$  shifts with its liquidline ahead along  $CB$  from  $C$  to  $B$ , and along  $AB$  from  $A$  to  $B$ .

2°. On decrease of pressure or increase of  $T$  the region  $LG$  shifts with its liquidcurve ahead along  $BC$  from  $B$  to  $C$ , and along  $BA$  from  $B$  to  $A$ . Consequently the movement is opposite to that sub 1°.

3°. On decrease of pressure or increase of  $T$  the region  $LG$  shifts with its liquidcurve ahead firstly along  $CB$  from  $C$  to  $B$ , and after this along  $BA$  from  $B$  to  $A$  or reversally from  $A$  along  $B$  to  $C$ .

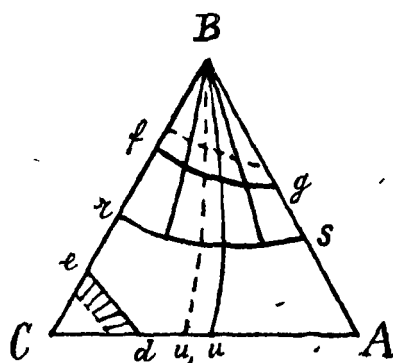


Fig. 1.

the gasregion arises in  $A$  or in a point of  $CA$  or anywhere within the triangle. This case may yet also be imagined, when different gas regions arise, e.g. in  $A$  and  $C$ , which coincide afterwards.

In the case sub 2° it is to be imagined, that the gasregion arises in  $B$  on decrease of pressure;  $fg$  (fig. 1) may then represent the

In the case mentioned sub 1°. it is to be imagined e.g., that the gasregion arises on decrease of pressure in  $C$  (fig. 1), expands then across the triangle, and attains at last the point  $B$ . The one extremity of the region  $LG$  shifts then on decrease of pressure with its liquid line ahead from  $C$  to  $B$ , the other firstly from  $C$  to  $A$  and subsequently from  $A$  to  $B$ . This case may also be imagined when



When however  $y_1:y$  becomes greater than  $(H_1-\eta):(H-\eta)$ , while it remains smaller than  $(V_1-v):(V-v)$ , only  $\Delta W_y$  can become  $=0$  and consequently only a point of maximum pressure occurs.

In order that  $\Delta V_y$  may also become  $=0$ ,  $V-v > 0$  and as  $V_1-v$  is ordinarily ten thousand times as great as  $V-v$ ,  $y_1:y$  must obtain a very great value. As  $\Delta W_y$  and  $\Delta V_y$  may become  $=0$ , the  $P, T$ -curve has then a point of maximum pressure and of maximum temperature. Therefore we find: the  $P, T$ -curve of the binary equilibrium  $B+L+G$  is a curve ascending with the temperature, when the solvent is less volatile or only a little more volatile than the solid substance; it may show a point of maximum pressure when the solvent is much more volatile than the solid substance; it may have, besides a point of maximum pressure, also a point of maximum temperature, when the solvent is a thousand times more volatile than the solid substance and this melts with increase of volume.<sup>1)</sup>

Let us now consider the saturationcurves under their own vapour-pressure of  $B$ . For this we take firstly the case sub 1. We now choose the  $P$  and  $T$  in such a way, that the saturationcurve of  $B$  is represented by  $rs$  and the liquidcurve of the region  $LG$  by  $ed$  in fig. 1. On decrease of pressure  $ed$  approaches to  $rs$ . We assume that the first common point arises by the coincidence of  $r$  and  $s$ . This point is represented in fig. 2 by  $h$ . In the same way as for the case that the solid substance is a binary compound we can prove, that  $ed$  and  $rs$  do not touch one another in  $h$  and that although  $P_h$  is the highest pressure, under which the system  $F+L+G$  occurs, the point  $h$  is yet not a point of maximum pressure of the saturationcurve under its own vapourpressure. The vapour corresponding with  $h$  is indicated in fig. 2 by  $h_1$ .

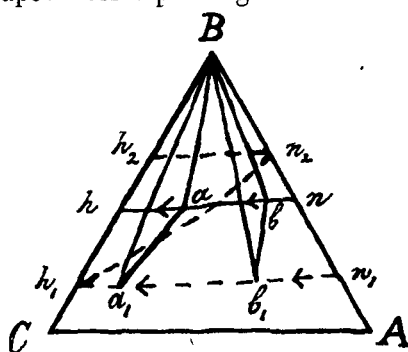


Fig. 2.

Lowering the pressure still more, the intersecting point of  $ed$  and  $rs$  of fig. 1, shifts within the triangle; in fig. 2 a similar intersecting point is represented by  $a$  and the corresponding vapour point by  $a_1$ . From the manner in which the three phase triangle arises, it follows, that this must turn its side solid-gas ( $Ba_1$ ) towards  $BC$ .

When on further decrease of pressure the curves  $ed$  and  $rs$  of

<sup>1)</sup> See also PH. KOHNSTAMM; these communications 15, (1907).

fig. 1 continue to intersect one another only in one point, under a pressure  $P_n$  the points  $s$  and  $d$  of fig. 1 coincide in a point  $n$  of fig. 2; curve  $ed$  is then situated completely within the sector  $Brs$ . Now the saturationcurve under its own vapourpressure is represented in fig. 2 by  $hn$  and the corresponding vapourcurve by  $h_1n_1$ ; the pressure increases in the direction of the arrows, therefore from  $n$  towards  $h$ . Consequently  $P_h$  is the highest and  $P_n$  the lowest pressure, under which the equilibrium  $F + L + G$  occurs,  $h$  not being however a point of maximum- and  $n$  a point of minimum pressure of the curve. Further we see, that on change of pressure, the turning of the threephase triangles  $Baa_1$  and  $Bbb_1$  is in accordance with the rules formerly deduced.

We have assumed when deducing the above, that the curves  $ed$  and  $rs$  of fig. 1 intersect one another only in one point under every pressure. It is also possible, however, to imagine that after the formation of the first point of intersection, a second arises by the coincidence of  $d$  and  $s$  (fig. 1). The liquidcurve of the region  $LG$  proceeds then in fig. 1 from  $s$  firstly outside and afterwards within the sector  $Brs$ . On further decrease of pressure the two points of intersection shift towards one another and coincide under a pressure  $P_m$  in a point  $m$  not drawn in the figure; the corresponding vapourpoint  $m_1$  is then situated on a straight line with  $m$  and  $B$ . The pressure  $P_m$  is the lowest pressure under which the equilibrium  $B + L + G$  may yet occur;  $m$  and  $m_1$  are points of minimum pressure of the curves  $hn$  and  $h_1n_1$ .

It is evident from the manner in which arises the threephase triangle  $Bbb_1$  in the vicinity of  $BA$  that this now must have another position than in fig. 2; its conjugation line solid-gas therefore  $Bb_1$  must be situated between  $Bb$  and  $BA$ . Two three-phase triangles situated on both sides of the point of minimum pressure turn therefore towards one another their sides solid-liquid.

In the two previous cases we have assumed, that the first common point of  $ed$  and  $rs$  arises by the coincidence of  $e$  and  $r$ . We now assume, that both the curves touch one another in a point  $M$  situated within the triangle; the corresponding vapour point  $M_1$  is then situated on a straight line with  $M$  and  $B$ . The pressure  $P_M$  is the lowest pressure under which the equilibrium  $B + L + G$  occurs.

On decrease of pressure two points of intersection of  $ed$  and  $rs$  now arise; the one disappears, when  $r$  and  $e$ , the other when  $d$  and  $s$  coincide. We then obtain again a saturationcurve under its own vapourpressure as  $hn$  and a corresponding vapourcurve as  $h_1n_1$  in fig. 2; the points,  $M$  and  $M_1$ , which are not drawn, are

points of maximum pressure. It is evident, that in this case we must imagine in fig. 2 the side  $Ba$  of the three phase triangle  $Baa_1$  between  $Ba_1$  and  $BC$ .

When we consider in a similar way as above also the cases sub 2° and 3°, we find:

the saturation curves under their own vapour pressure have a terminating point on  $BC$  and one on  $BA$  (curve  $hn$  in fig. 2). On this curve either a point of maximum or of minimum pressure occurs or there occurs none. The corresponding vapour curve is situated with respect to  $hn$  in the case sub 1° as  $h_1n_1$ , in the case sub 2° as  $h_2n_2$  and in the case sub 3° as  $h_1n_2$  (or  $h_2n_1$ ).

Previously we have seen, that the saturation curves under their own vapour pressure of a ternary and a binary substance  $F$  become exphased at temperatures above the minimum melting point of  $F$ . At the deduction of these curves for the binary compound  $F$  we have seen, that the point of maximum temperature of the binary system  $F+L+G$  takes a prominent position and that these curves occur in the vicinity of this point [point  $H$  in fig. 4—6 (XI)]. The same applies also to the saturation curves under their own vapour pressure of the component  $B$ ; we shall not discuss these here more in detail as similar appearances occur in the case of the boiling point curve.

Let us now consider the boiling point curves of the component  $B$ ; firstly we take these curves under pressures lower than the pressure in the minimum melting point of  $B$ ; we then find: the boiling point curves have a terminating point on  $BC$  and one on  $BA$  (curve  $hn$  in fig. 2); on this curve, either a point of maximum- or minimum temperature occurs or there is none. The corresponding vapour curve is situated with respect to  $hn$ , in the case sub 1° as  $h_1n_1$ , in the case 2° as  $h_2n_2$  and in the case sub 3° as  $h_1n_2$  (or  $h_2n_1$ ). If it is desired that in fig. 2 the three phase triangles  $Baa_1$  and  $Bbb_1$  retain their position, the arrows must indicate in opposite direction and the temperature increases, therefore, from  $h$  towards  $n$ .

It follows from the previous deductions, in what direction the three phase triangles solid-liquid-gas turn on change of pressure (at constant  $T$ ), or on change of temperature (under constant  $P$ ). From this also follows the influence of a third substance on the pressure (at constant  $T$ ) or on the temperature (under constant  $P$ ) of the binary equilibrium  $B+L+G$ .

We may also deduce these results in the following way. We

represent the quantity of  $A$  of a phase by  $x$  (or  $x_1$ ), the quantity of  $C$  by  $y$  (or  $y_1$ ), and the quantity of  $B$  by  $1-x-y$  (or  $1-x_1-y_1$ ). We put, therefore, the origin of our coordinatesystem in the angle point  $B$ , the  $X$ -axis along the side  $BA$ , and the  $Y$ -axis along the side  $BC$  of the triangle. To the saturationcurve under its own vapourpressure of  $B$  then applies:

$$(xr + ys) dx + (xs + yt) dy = AdP. \quad (3)$$

$$[(x_1 - x)r + (y_1 - y)s] dx + [(x_1 - x)s + (y_1 - y)t] dy = CdP \quad (4)$$

In order to have the boilingpoint curves, we must replace in (3)  $AdP$  by  $-BdT$  and  $CdP$  by  $-DdT$ .

In the terminating point of both these curves on the side  $BC$ ,  $x = 0$ . We then find:

$$\frac{1}{RT} \cdot \left( \frac{dP}{dx} \right)_{x=0} = \frac{\frac{x_1}{x} - \frac{y_1}{y}}{\Delta V_y} \quad \text{and} \quad \frac{1}{RT^2} \cdot \left( \frac{dT}{dx} \right)_{x=0} = \frac{\frac{y_1}{y} - \frac{x_1}{x}}{\Delta W_y}. \quad (5)$$

In the terminating point of both these curves on the side  $BA$ ,  $y = 0$ . We then find:

$$\frac{1}{RT} \cdot \left( \frac{dP}{dy} \right)_{y=0} = \frac{\frac{y_1}{y} - \frac{x_1}{x}}{\Delta V_x} \quad \text{and} \quad \frac{1}{RT^2} \cdot \left( \frac{dT}{dy} \right)_{y=0} = \frac{\frac{x_1}{x} - \frac{y_1}{y}}{\Delta W_x}. \quad (6)$$

Herein is:

$$\begin{aligned} \Delta V_x &= V_1 - v - \frac{x_1}{x}(V - v) & \Delta V_y &= V_1 - v - \frac{y_1}{y}(V - v) \\ \frac{\Delta W_x}{T} &= H_1 - \eta - \frac{x_1}{x}(H - \eta) & \frac{\Delta W_y}{T} &= H_1 - \eta - \frac{y_1}{y}(H - \eta). \end{aligned}$$

From this it is easily found, that the relation 11 (XI) and the rules deduced from this apply also on the addition of a third substance to the binary equilibrium  $B + L + G$ .

We may in the same way as in the previous communication introduce also in (5) and (6) the perspective concentrations  $S$  and  $S_1$  of the new substance. Then  $S$  is the part cut off by the line  $B$ -liquid,  $S_1$  the part cut off by the line  $B$ -vapour from the side  $CA$  (fig. 2). When the binary equilibrium  $B + L + G$  is situated on  $BC$  ( $x = 0$ ), so that  $A$  is the new substance, these parts must of course been measured from  $C$ ; when the binary equilibrium is situated on  $BA$  ( $y = 0$ ), so that  $C$  is the new substance, they must be measured from  $A$ .

When the binary equilibrium  $B + L + G$  is situated on the side  $BC$  ( $x = 0$ ), we find



$$S = \frac{x}{x+y} \quad \text{and} \quad S_1 = \frac{x_1}{x_1+y_1}$$

Substituting from this the values of  $y$  and  $y_1$ , in (5), we find:

$$\left. \begin{aligned} \frac{1}{RT} \cdot \left( \frac{dP}{dx} \right)_{x=0} &= \frac{1}{\Delta V_y} \cdot \frac{x_1}{x} \cdot \left( 1 - \frac{S}{S_1} \right) \\ \frac{1}{RT^2} \cdot \left( \frac{dT}{dx} \right)_{x=0} &= - \frac{1}{\Delta W_y} \cdot \frac{x_1}{x} \cdot \left( 1 - \frac{S}{S_1} \right) \end{aligned} \right\} \dots \dots (7)$$

As  $S$  and  $S_1$  are very small we have equated,  $(1-S_1) : (1-S) = 1$ .

When the binary equilibrium  $B + L + G$  is situated on the side  $BA$  ( $y=0$ ) we find from (6)

$$\left. \begin{aligned} \frac{1}{RT} \cdot \left( \frac{dP}{dy} \right)_{y=0} &= \frac{1}{\Delta V_x} \cdot \frac{y_1}{y} \cdot \left( 1 - \frac{S}{S_1} \right) \\ \frac{1}{RT^2} \cdot \left( \frac{dT}{dy} \right)_{y=0} &= - \frac{1}{W \Delta x} \cdot \frac{y_1}{y} \cdot \left( 1 - \frac{S}{S_1} \right) \end{aligned} \right\} \dots \dots (8)$$

We see that (7) and (8) are in accordance with (14) and (15) (XI); we may deduce from this for the addition of a new substance to the binary equilibrium  $B + L + G$  the same rules as was done in communication XI for the equilibrium  $F + L + G$ . It is however to be considered with this that now  $S$  and  $S_1$  are positive. We see that the position of the threephase triangles in fig. 2 is in accordance with these rules.

In communication XII we have deduced in different ways form and position of the saturationcurves under their own vapourpressure in the vicinity of the point of maximum temperature and of the boilingpoint curves in the vicinity of the point of maximum pressure of the binary equilibrium  $F + L + G$ .

All this applies also when the solid substance is one of the components. We must keep in mind that in the binary system  $B + L + G$  there occurs not always a maximum of pressure and temperature, which is indeed the case in the binary system  $F + L + G$ . For that reason we shall express these rules now in the following way.

Let in fig. 5 and 6 (XI)  $H$  be a point of maximum temperature of the binary equilibrium  $B + L + G$ . The saturationcurve under its own vapourpressure of  $B$  disappears on increase of  $T$  in  $H$  [fig. 5 (XI)], when the concentration of the new substance in the liquid is greater than in the vapour; it does not disappear in  $H$  [fig. 6 (XI)], when the concentration of the new substance is smaller in the liquid than in the vapour.

If we imagine in fig. 5 and 6 (XI)  $H$  to be replaced by the

point of maximum pressure  $Q$  of the equilibrium  $B + L + G$  and the arrows in opposite direction, then we have: on increase of  $P$  the boilingpoint curve disappears in  $Q$  [fig. 5 (XI)], when the concentration of the new substance is greater in the liquid than in the vapour; it does not disappear in  $Q$  [fig. 6 (XI)], when the concentration of the new substance is smaller in the liquid than in the vapour.

Of course we have meant above with concentration the perspective concentration.

From the meaning of the perspective concentrations  $S$  and  $S_1$  of a new substance, it follows immediately:

for equilibria in the vicinity of the side  $BC$  ( $x = 0$ ):

when  $S > S_1$  then also  $y_1 : y > x_1 : x$  and reversally,

when  $S < S_1$  „ „ „  $y_1 : y < x_1 : x$  „ „

for equilibria in the vicinity of the side  $BA$  ( $y = 0$ ):

when  $S > S_1$  then also  $x_1 : x > y_1 : y$  and reversally,

when  $S < S_1$  „ „ „  $x_1 : x > y_1 : y$  „ „

On increase of pressure the boilingpointcurve  $ln$  of fig. 2 changes its position and form in order to disappear at last. This may take place in different ways which we shall consider now. We have seen at the deduction of the boilingpointcurves of the binary compound  $F$ , that the point of maximum pressure  $Q$  of the binary system  $F + L + G$  takes a prominent position, it is evident that this is also the case with the boilingpoint curves of the substance  $B$ .

We saw before that we may distinguish the three cases mentioned sub 1°, 2°, and 3° with regard to the movement of the region  $LG$  on decrease of  $P$  or increase of  $T$ . In the case mentioned sub 1° as well the solvent  $C$  as  $A$  is more volatile than the solid substance  $B$ . Therefore a point of maximum pressure of the binary equilibrium  $B + L + G$  can be situated either on  $BC$  or not; the same applies to the side  $BA$ .

In the case sub 2° both the solvents  $A$  and  $C$  are less volatile than the substance  $B$ ; therefore neither on  $BA$  nor on  $BC$  can a point of maximum pressure be situated.

In the case mentioned sub 3°  $C$  is more volatile.  $A$  however less volatile than the substance  $B$ ; therefore on  $BC$  either a point of maximum pressure occurs or it does not; this is however not possible on  $BA$ .

With regard to the occurrence of a point of maximum pressure in both the binary systems  $B + L + G$ , we may, therefore, distinguish three cases:

- a. no point of maximum pressure occurs.
- b. one „ „ „ „ „
- c. two points „ „ „ „ occur.

In the case sub *a* the pressure of the binary equilibrium  $B+L+G$  increases from *C* along *CB* and from *A* along *AB* up to *B* (fig. 2). On increase of pressure the points *h* and *n* shift therefore towards *B*; under  $P_B$  (the pressure of the minimum meltingpoint of *B*) the boilingpointcurve disappears in *B*.

In the case sub *b* one of the binary equilibria  $B+L+G$  has a maximum pressure, represented in fig. 3 by the point *Q*. Consequently the pressure increases from *C* along *BC* up to *Q* and from *A* firstly along *AB* and afterwards along *BC* up to *Q*. Under pressures lower than  $P_B$  the boilingpointcurves have therefore one extremity on *AB*

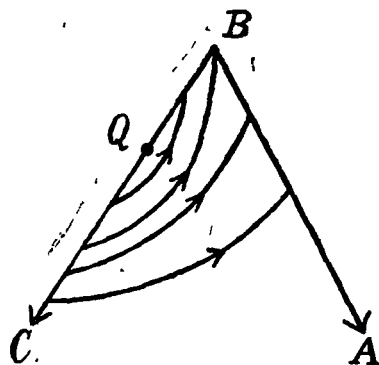


Fig. 3.

and one on *BC* between *C* and *Q*; under pressures between  $P_B$  and  $P_Q$  the one terminating point is situated on *BQ* and the other on *CQ*. In the vicinity of the point *Q* the boilingpointcurves may have two kinds of form. In fig. 3 we have assumed that they disappear in *Q* on increase of pressure. In the other case, which the reader may draw easily himself, there is one touching the side *BC* in *Q* and they disappear in a point within the triangle. A part of these curves has then necessarily a point of maximum- and one of minimum temperature.

From the position of the boiling point curves in the vicinity of the point *Q* it follows that  $S > S_1$  and therefore also  $y_1 : y > x_1 : x$  is assumed or in words: if we add to the binary equilibrium  $B+L+G$  situated on the side *BC* ( $x=0$ ) the substance *A*, its perspective concentration is greater in the liquid than in the vapour. If we consider that  $\Delta W_y$  is positive between *Q* and *C*, and negative between *Q* and *W*, then it follows from (5) or (7), that on the boiling point curves in the vicinity of *Q* the temperature must increase in the direction of the arrows.

In the case sub *c* both the binary equilibria  $B+L+G$  have a point of maximum pressure, represented in fig. 4—6 by the points *Q* and *Q'*. We distinguish three types:

1. in the vicinity of the one point of maximum pressure [*Q* fig. 4]  $S > S_1$ ; in the vicinity of the other [*Q'* fig. 4]  $S < S_1$ .
2. in the vicinity of both the points *Q* and *Q'*,  $S < S_1$  (fig. 5).
3. in the vicinity of both the points *Q* and *Q'*  $S > S_1$  (fig. 6).

In each of these diagrams the pressure increases therefore along *BC* from *B* and *C* to *Q* and along *BA* from *B* and *A* to *Q'*

Under pressures lower than  $P_B$ , the boiling point curve consists therefore of one single branch with the one extremity on  $CQ$  and the other on  $AQ'$ ; on this curve either a point of maximum (fig. 6) or a point of minimum temperature (fig. 5) occurs or neither of these points (fig. 4).

Under the pressure  $P_B$  now also the point  $B$  itself occurs,  $P_B$  is viz. the pressure of the minimum melting point or in this case as  $B$  is one of the components, therefore also the pressure in the triplepoint of the substance  $B$ ; under this pressure exists the unary equilibrium solid  $B + \text{liquid } B + \text{vapour } B$ . Consequently the boilingpointcurve of the pressure  $P_B$  consists of a branch with

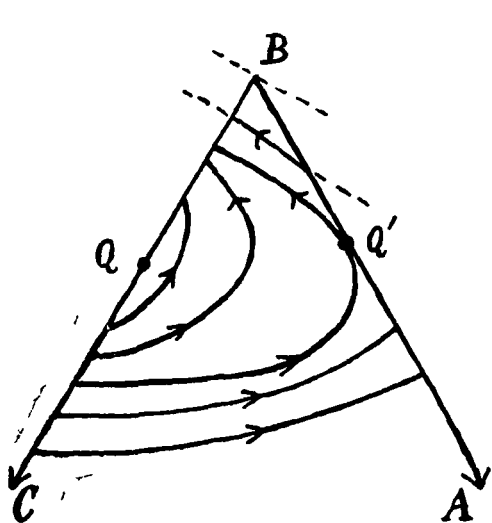


Fig. 4.

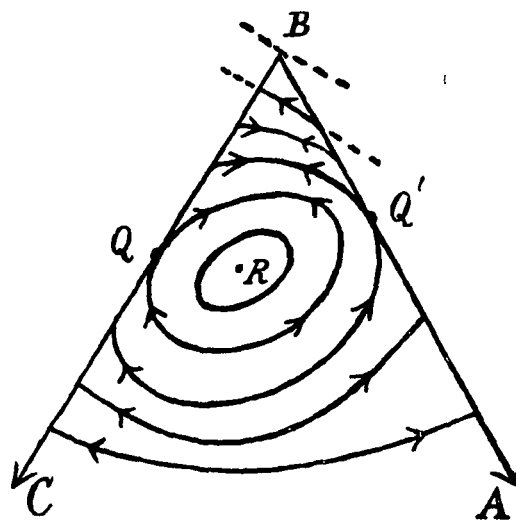


Fig. 5.

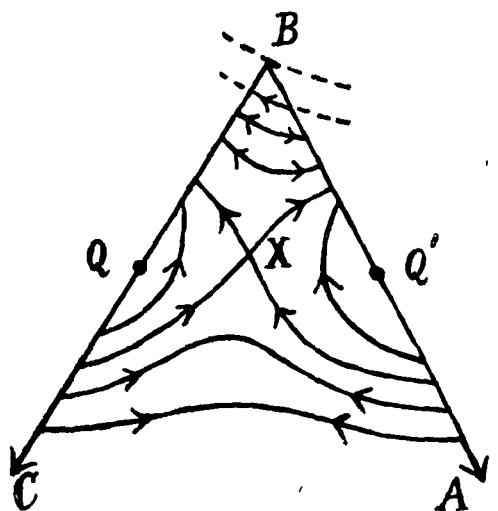


Fig. 6.

the one extremity on  $CQ$  and the other on  $AQ'$  and of the isolated point  $B$  (fig. 4—6).

On further increase of  $P$  boilingpointcurves now arise, consisting of two branches separated from one another. In the vicinity of  $B$  a new branch is viz. formed with the one end on  $BQ$  and the other on  $BQ'$  (fig. 4—6). On further increase of  $P$  both the branches shift towards one another and under a definite pressure  $P_X$  both the branches come together in a point  $X$ . This point  $X$  is situated 1°. on one of the sides  $BA$  or  $BC$ , 2°. within the triangle; in the first case  $X$  coincides with  $Q$  or  $Q'$ . In fig. 4 and 5 the two branches come together in  $Q'$ , in fig. 6 in a point  $X$  within the triangle.

In fig. 4 and 5 the boilingpointcurve of the pressure  $P_Q$  forms, therefore, a single branch. From our previous considerations it follows that this is curved as a parabola in  $Q'$  and touches the side  $BA$  in this point. The temperature must increase in the direction of the arrows along this curve in the vicinity of  $Q'$ .

On further increase of pressure the boilingpointcurve shifts from point  $Q'$  (fig. 4 and 5) into the triangle and we may distinguish two cases. Either it disappears in the point  $Q$  on the side  $BC$  (fig. 4) or it touches the side  $BC$  in the point  $Q$  (fig. 5). In the latter case it shifts on further increase of pressure from the point  $Q$  into the triangle, so that a closed curve arises, which disappears in  $R$  somewhere within the triangle.

In fig. 6 the point  $X$  in which the two branches of the boilingpointcurve come together, is situated within the triangle. Here we have a case as was treated formerly in communication  $X$  (fig. 5). On further increase of pressure again two branches are formed, separated from one another, which are situated now quite different than at first and on which the points of maximum pressure are wanting. On further increase of pressure the one disappears in  $Q$  and the other in  $Q'$ .

Besides the diagrams drawn in figs. 4-6, several others may be imagined. For instance we may assume that the two branches of the boilingpointcurve do not disappear in  $Q$  and  $Q'$  as in fig. 6, but that they touch in these points the sides of the triangle. The boilingpointcurves then consist of two branches separated from one another, which are both closed, and of which the one disappears in a point between  $Q$  and  $X$  and the other in a point between  $Q'$  and  $X$ .

We may consider now more in detail the boilingpointcurves in the vicinity of the point  $B$ ; as in this point  $x$  becomes  $= 0$  and  $y = 0$ , we put:

$$Z = U + RT(x \log x + y \log y) \text{ and } Z_1 = U_1 + RT(x_1 \log x_1 + y_1 \log y_1)$$

We then find for the equilibrium  $B + L + G$  in the vicinity of the point  $B$  when we put  $x = \xi$ ,  $x_1 = \xi_1$ ,  $y = \eta$ ,  $y_1 = \eta_1$ ,  $P = P_B + dP$  and  $T = T_B + dT$ :

$$\left. \begin{aligned} \xi_1 &= K\xi, \quad \eta_1 = K_1\eta \\ RT\xi + RT\eta - (V-v)dP + (H-\eta_b)dT &= 0 \\ RT\xi_1 + RT\eta_1 - (V_1-v)dP + (H_1-\eta_b)dT &= 0 \end{aligned} \right\} \quad (9)$$

Herein, in order to distinguish the coordinate  $\eta$ , the entropy of the solid substance  $B$  is represented by  $\eta_b$ .

In order to examine the influence of the pressure on the position of the boilingpointcurves, we eliminate from (9)  $dT$ . We then obtain:

$$\xi \Delta W_x + \eta \Delta W_y = -\frac{BC-AD}{R} dP \quad (10)$$

wherein  $BC - AD > 0$ . (See Comm. II).

When we put in (10)  $dP = 0$ , we obtain:

$$\xi \Delta W_x + \eta \Delta W_y = 0 \quad (11)$$

the boilingpointcurve going through the point  $B$ .

At first we take  $\Delta W_x$  and  $\Delta W_y$  negative, so that the case treated sub *c* occurs (fig. 4—6). From (11) it follows that  $\xi$  and  $\eta$  have the opposite sign; the boilingpointcurve of the pressure  $P_B$  is situated, therefore, excepted in the point  $B$  itself, completely outside the triangle.

In figs 4—6 a similar curve going through the point  $B$  is dotted and a curve situated in the vicinity of  $B$  is extended outside the triangle; these parts situated outside the triangle have of course no meaning for us. The direction of the boilingpointcurve going through the point  $B$ , is fixed by  $\Delta W_x$  and  $\Delta W_y$ ; if accidentally  $\frac{x_1}{x} = \frac{y_1}{y}$ , therefore, also  $\Delta W_x = \Delta W_y$ , then this curve runs parallel to  $AC$ .

We now take a pressure somewhat higher than  $P_B$ , therefore  $dP$  positive; the second term of (10) is, therefore, negative. From this it follows that the curve cuts off a positive part  $\eta$  from the  $Y$ -axis ( $BC$ ) and a positive part  $\xi$  from the  $X$ -axis ( $BA$ ), the curve is situated, therefore, partly within the triangle as in figs 4—6 the curve in the vicinity of  $B$ , partly drawn and partly dotted. In accordance with what was treated sub *c* (figs. 4—6) we find, therefore, that the boilingpoint curve shifts on increase of  $P$  from the point  $B$  into the triangle.

In the same way it is apparent from (10) that under a pressure, somewhat lower than  $P_B$ , therefore for  $dP$  negative, the curve cuts off a

negative part  $\eta$  from the  $Y$ -axis and also a negative part  $\xi$  from the  $X$ -axis. The boilingpointcurve is, therefore, situated completely outside the triangle. Considering only the stable parts, therefore the parts of these curves situated within the triangle, we can say:

On decrease of  $P$  the boilingpointcurve disappears in  $B$ ;

On increase of  $P$  it arises in  $B$  and shifts from this point into the triangle.

The direction of the boilingpointcurve in the vicinity of  $B$  is determined according to (10) by  $\Delta W_x$  and  $\Delta W_y$ . If we put  $\frac{y_1}{y} > \frac{x_1}{x}$  then it follows in absolute value  $\Delta W_y > \Delta W_x$ . If we call the part, which the curve cuts off from the  $X$ -axis ( $BA$ )  $\xi_0$  and the part which it cuts off from the  $Y$ -axis ( $BC$ )  $\eta_0$ , then follows from (10)  $\xi_0 > \eta_0$ .

$\frac{y_1}{y}$  is the ratio of the quantity of  $C$  in the vapour and in the liquid, when we add a little  $C$  to the unary system solid  $B$  + liquid  $B$  + vapour  $B$ ; we shall call this ratio the limit-ratio of  $C$  in the equilibrium solid  $B$  + liquid  $B$  + vapour  $B$ . The same applies to  $\frac{x_1}{x}$  on addition of  $A$ . We may now express what precedes in such a way: when in the equilibrium solid  $B$  + liquid  $B$  + vapour  $B$  the limit ratio of  $C$  is greater than that of  $A$ , the boilingpointcurve cuts off a smaller part from the side  $BC$  than from the side  $BA$ .

The above-mentioned rule applies only when  $\Delta W_x$  and  $\Delta W_y$  are both negative, therefore, when the  $P, T$ -curve of each of the two binary systems  $B + L + G$  proceeds from  $B$  towards higher pressures.

In figs. 4—6 in  $B$  is assumed  $\frac{y_1}{y} > \frac{x_1}{x}$  in accordance with this the boilingpointcurve, situated in the vicinity of  $B$  cuts off from  $BC$  a smaller part than from  $BA$ .

When we take  $\Delta W_x$  and  $\Delta W_y$  positive, we have the case sub  $a$ . From (10) and (11) it follows that the boilingpointcurves in the vicinity of  $B$  have the same position as in the case sub  $c$ ; on change of  $P$  they move, however, in opposite direction. On decrease of  $P$  they shift viz. from  $B$  into the triangle and on increase of  $P$  they disappear in  $B$ .

When we take also here  $\frac{y_1}{y} > \frac{x_1}{x}$ , it follows that  $\Delta W_y < \Delta W_x$ ; we now find: when in the equilibrium solid  $B$  + liquid  $B$  + vapour  $B$  the

limit-ratio of  $C$  is greater than that of  $A$ , the boilingpointcurve cuts off a greater part from the side  $BC$  than from the side  $BA$ .

In the end  $\Delta W_x$  and  $\Delta W_y$  may have an opposite sign, so that the case sub  $b$  occurs. That there may be accordance with fig. 3, we take  $\Delta W_x > 0$  and  $\Delta W_y < 0$ . From (11) it now follows that  $\xi$  and  $\eta$  have the same sign, so that the boilingpointcurve going through  $B$  must be situated within the triangle. We see that this is in accordance with fig. 3.

If the pressure is a little raised, so that  $dP$  is positive, it follows from (10) that the boilingpointcurve cuts off a positive part  $\eta$  from the  $Y$ -axis ( $BC$ ) and a negative part  $\xi$  from the  $X$ -axis ( $BA$ ). If the pressure is lowered, so that  $dP$  is negative, then we find that the curve cuts off a negative part  $\eta$  from the  $Y$ -axis ( $BC$ ) and a positive part  $\xi$  from the  $X$ -axis ( $BA$ ). If we imagine in fig. 3 some boilingpointcurves still to be drawn in the vicinity of that going through  $B$  and these extended outside the triangle as the sides  $AB$  and  $CB$ , then we see that all this is in accordance with the previous results. Considering only the parts of the curves, situated within the triangle, it follows: the terminatingpoint of the boilingpointcurve going through the point  $B$  shifts on decrease of  $P$  from  $B$  on the side  $BA$  and on increase of  $P$  from  $B$  on the side  $BC$ .

Now we shall still examine how the temperature changes along a boilingpointcurve in the vicinity of the point  $B$ . For this we choose a boilingpointcurve of a definite pressure  $P_B + dP$ , so that we must assign a definite constant value to  $dP$  in (9). We then find:

$$\Delta W_y \cdot dT = RT^2 \left( \frac{y_1}{y} - \frac{x_1}{x} \right) \xi + T \cdot \Delta V_y \cdot dP \quad (12)$$

$$\Delta W_x \cdot dT = RT^2 \left( \frac{x_1}{x} - \frac{y_1}{y} \right) \eta + T \cdot \Delta V_x \cdot dP \quad (13)$$

As in (9) the temperature is put equal to  $T_B + dT$ ,  $dT$  is, therefore calculated from the point  $B$ . Desiring to proceed from the terminatingpoint of the boilingpointcurve on the  $Y$ -axis ( $BC$ ), we put  $dT = dT'_y + dT_y$ ; herein  $dT'_y$  is the change of  $T$ , wanted to come from the point  $B$  in the terminatingpoint of the boilingpointcurve on the  $Y$ -axis and  $dT$  the change of temperature from this terminatingpoint along the curve. We now have:  $\Delta W_y \cdot dT'_y = T \cdot \Delta V_y \cdot dP$ . Substituting in (12)  $dT = dT'_y + dT_y$ , we obtain:

$$\Delta W_y \cdot dT_y = RT^2 \left( \frac{y_1}{y} - \frac{x_1}{x} \right) \xi \quad (14)$$

When we represent the change of temperature along the boiling-



pointcurve from its terminatingpoint on the  $X$ -axis ( $BA$ ) by  $dT_x$ , we find from (13):

$$\Delta W_x \cdot dT_x = RT^2 \left( \frac{x_1}{x} - \frac{y_1}{y} \right) \eta \quad (15)$$

Let us firstly consider fig. 3, in the vicinity of the point  $B$  of this figure is  $\Delta W_y < 0$  and  $\Delta W_x > 0$ , therefore  $\frac{y_1}{y} > \frac{x_1}{x}$ . From (14) and (15) it now follows that  $dT_y$  and  $dT_x$  are both negative. This means that on a boilingpointcurve, situated in the vicinity of  $B$ , the temperature decreases from the terminatingpoint situated in the vicinity of  $B$ . This is in accordance with fig. 3.

In fig. 4—6 we will assume  $\frac{y_1}{y} > \frac{x_1}{x}$  in order to remain in accordance with the direction of the boilingpointcurves, situated in the vicinity of  $B$ . As  $\Delta W_y$  and  $\Delta W_x$  are both negative, it follows from (14) and (15) that  $dT_y < 0$  and  $dT_x > 0$ . On a boilingpointcurve situated in the vicinity of  $B$  the pressure, therefore, increases from the terminatingpoint on  $BA$  ( $dT_x > 0$ ) and it decreases from the terminatingpoint on  $BC$  ( $dT_y < 0$ ). In conjunction with the length of the parts, cut off by the curves from the sides  $BA$  and  $BC$ , we may express this also in the following way: along a boilingpointcurve situated in the vicinity of  $B$  the temperature increases in that direction, in which this curve comes nearer to  $B$  (fig. 4—6).

In the case sub  $a$   $\Delta W_x$  and  $\Delta W_y$  are both positive, we now find the same rule as above for the change of temperature along a boilingpointcurve situated in the vicinity of  $B$ .

We may give a short résumé of some of the previous results in the following way. For this we assume that in the equilibrium solid  $B$  + liquid  $B$  + vapour  $B$  the limit-ratio of  $C$  is greater than that of  $A$ .

a) The two binary  $P, T$ -curves proceed from the point  $B$  towards lower pressures; consequently no point of maximum pressure occurs [ $\Delta W_x > 0$  and  $\Delta W_y > 0$ ; case sub  $a$ ]. A boilingpointcurve situated in the vicinity of  $B$  cuts off from the side  $BC$  a greater part than from the side  $BA$ . The curve comes on decrease of  $P$  within the triangle.

b) One of the two binary  $P, T$ -curves proceeds from  $B$  towards lower pressures and one towards higher pressures, consequently one point of maximum pressure occurs [ $\Delta W_x > 0$  and  $\Delta W_y < 0$ ; case sub  $b$ , fig. 3]. The boilingpointcurve cuts off under pressures, somewhat higher than  $P_B$ , a part from  $BC$ , under pressures, somewhat lower

than  $P_B$ , a part from  $BA$  The curve remains, therefore, within the triangle as well on increase as on decrease of  $P$ .

c) Both the binary  $P, T$ -curves proceed from the point  $B$  towards higher pressures; consequently two points of maximum pressure occur [ $W_x < 0, \Delta W_y < 0$ ; case sub  $c$ ; fig. 4—6]. A boiling point curve situated in the vicinity of  $B$  cuts off from the side  $BC$  a smaller part than from the side  $BA$ . The curve comes, on increase of  $P$ , within the triangle.

In each of the cases, mentioned sub  $a, b, c$ , the temperature along a boiling point curve situated in the vicinity of  $B$ , increases in that direction in which this curve comes nearer to  $B$  (figs. 3—6).

(To be continued).

**Chemistry.** — “*Studies in the Field of Silicate-Chemistry: I. On Compounds of Lithiumoxide and Silica.* By Prof. Dr. F. M. JAEGER and Dr. H. S. VAN KLOOSTER. (Communicated by Prof. P. VAN ROMBURGH)

§ 1. In connection with a series of investigations going on in this laboratory, on natural and synthetical lithiumaluminumsilicates, it seemed to us of importance once more to take up the study of the binary system: lithiumoxide-silica, by means of the equipment and methods, which are now at our disposal; only in this way it seemed to us possible, to obtain thermal data, which are reliable and reducible to the nitrogen gas thermometer. At the same time we hoped to get information on the origin of in some respects rather strongly deviating results of earlier investigators, who have occupied themselves also with the study of these lithiumsilicates.

The two-componentsystem  $\text{Li}_2\text{O}—\text{SiO}_2$ , has already several times been an object of research; thus some time ago by one of us<sup>1)</sup>, using the method, already so often successfully employed upon metal-alloys, of the crystallization phenomena on cooling, which will show themselves in such binary mixtures of varying composition. Later it was studied in the same way by ENDELL and RIEKE<sup>2)</sup>, who of course in general also came to the same results, but who were not able finally to answer the question, if a third compound, the lithiumsilicate, could separate from molten mixtures, like the ortho-, or meta-silicate.

<sup>1)</sup> H. S. VAN KLOOSTER, Dissertatie Groningen (1910); Zeits. f. anorg. Chemie **69**, 136 (1910).

<sup>2)</sup> K. ENDELL und R. RIEKE, Sprechsaal, **44**. No 46 (1910); **45**. No 6 (1911).