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

After having deduced in the previous communication the diagrams for a constant temperature (the saturation- and vapoursaturation-curves under their own vapourpressure), and for a constant pressure (the boilingpointcurves and their corresponding vapourcurves), we will deduce now the diagrams for a constant temperature and pressure. We may act for this in the same way as in communication I. For this we imagine for instance in figure 1 (I) besides the saturationcurve of the compound F also one of the compound F' . Both these saturationcurves may then be situated either outside each other or they may intersect each other, or the one may surround the other. We imagine both curves situated completely in the liquid-region.

Because the heterogeneous region shifts on decrease of pressure in such direction that the liquidregion becomes smaller and the vapour-region becomes greater, under a certain pressure the liquid-curve ed of the heterogeneous region will touch one of the saturationcurves. When it touches that of F , we obtain figure 2 (I) wherein the saturationcurve of F' is to be imagined. This is then still completely situated in the liquidregion and may be situated with respect to that of F in the abovementioned ways. Of all the solutions saturated with F or with F' at this pressure, therefore, only one exists, namely saturated with F , that can be in equilibrium with vapour.

On further decrease of pressure figure 3 (I) now arises; herein we imagine the second saturationcurve, still completely in the liquid-region, and whether or not intersecting that of F . Of all solutions saturated with F or with F' at this pressure now two liquids exist, saturated with F (a and b) which may be in equilibrium with vapour (a_1 and b_1). On further decrease of pressure very many cases may now occur. At first we assume that both the saturation-curves are situated completely outside each other and rest also outside each other in the contemplated pressure-interval. On decrease of pressure the heterogeneous region shifts over the saturationcurve of F , attains at a certain pressure the saturationcurve of F' , and on further decrease of pressure shifts also over this.

We may distinguish for this two principal cases:

1. the saturationcurve of F is situated already completely outside the liquidregion before the liquidcurve ed of the heterogeneous region touches the saturationcurve of F' ;
2. the saturationcurve of F' is situated still partly in the liquid-

region, when the liquidcurve ed of the heterogeneous region touches the saturationcurve of F' .

In the latter case, therefore, there is a series of pressures under which at the same time two liquids saturated with F and two with F' may be in equilibrium with vapour. Solutions saturated with $F + F'$ do not exist.

When both the liquidcurves intersect each other numberless cases are to be distinguished, of which we shall only discuss a few. Imagining for instance in fig. 3 (I) that the vapoursaturation curve of F' is also drawn, then we can obtain a diagram as fig. 1. The liquidline $d-e$ of the heterogeneous region intersects the saturation-

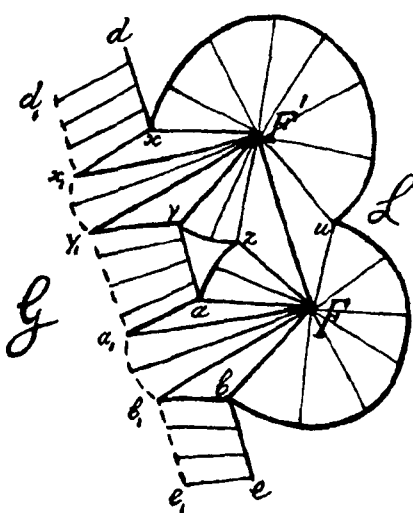


Fig. 1.

The liquids of branch dx may be in equilibrium with the vapours of d_1x_1 ; the liquids of ya with the vapours of y_1a_1 , the liquids of be with the vapours of b_1e_1 . The solid phase F can exist together with the vapours of branch a_1b_1 ; the solid phase F' together with the vapours of branch x_1y_1 .

Further there are four liquids saturated with a solid phase which may be at the same time in equilibrium with a vapour. Therefore, there exist four threephasecomplexes: solid + liquid + vapour, nl. F + liquid a + vapour a_1 , F + liquid b + vapour b_1 , F' + liquid x + vapour x_1 , and F' + liquid y + vapour y_1 . Besides the great liquidregion, indicated by L we find also in the figure the small liquidregion $az y$.

On decrease of pressure figure 1 may pass now into figure 2. The points a , y , and z of figure 1 coincide in figure 2 in the point f , the points a_1 and y_1 of fig. 1 coincide in fig. 2 in the point f_1 .

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The metastable part bx of curve de must therefore go through point f and the metastable part x_1b_1 of curve d_1e_1 must go through the point f_1 . Fig. 2 may also be imagined to have arisen from fig. 1 in that the threephasetriangles $FF'z$, Faa_1 and Fyy_1 move until they touch along one side.

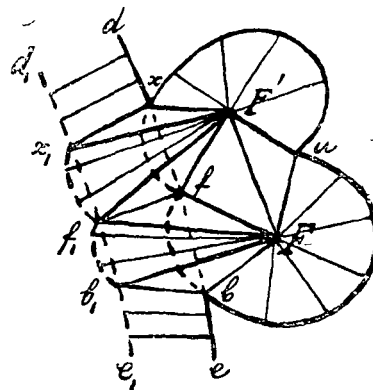


Fig. 2.

Of the two solutions u and f , saturated with $F + F'$, the latter may be in equilibrium with the vapour f_1 ; at the temperature and under the pressure to which fig. 2 applies, therefore, the fourphaseequilibrium $F + F' + \text{liquid } f + \text{vapour } f_1$ occurs.

If the pressure decreases still more, a diagram occurs which we shall call figure 2a. We obtain this figure 2a when we leave the point f in fig. 2 out of account. The two saturationcurves and curve de then go no more through one point; nor the two vapoursaturationcurves and curve d_1e_1 . Only one solution now exists, nl. u , saturated with $F + F'$; the other is metastable and replaced by the vapour f_1 , which may be in equilibrium with the complex $F + F'$. The fourphaseequilibrium occurring in fig. 2 has vanished of course also in fig. 2a.

We shall now contemplate the diagram, occurring at the minimum-melting point of the complex $F + F'$, one of the many possible diagrams is drawn in fig. 3, wherein also are indicated the metastable parts of the two saturationcurves and of the liquid- and vapour-curve of the heterogeneous region.

Fig. 3 can be imagined to have arisen from fig. 2 in the following way. We change the temperature and the pressure in such a way, that we retain a diagram as fig. 2; the fourphase equilibrium $F + F' + \text{liquid } f + \text{vapour } f_1$ therefore remains, although f and f_1 change of course their composition. A similar change of pressure and temperature is always possible when we change these in accordance with the P, T -curve of the fourphase equilibrium $F + F' + L + G$. We take this change now in such

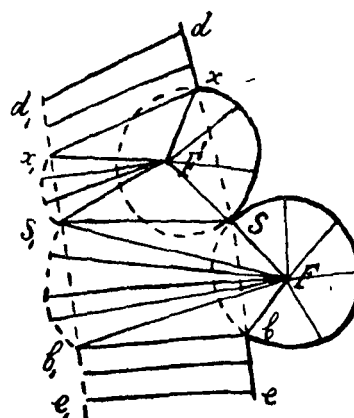


Fig. 3.

direction that the liquidcurve ed of the heterogeneous region, and therefore also the point f in fig. 2 shifts towards the line FF' . At a definite temperature and pressure the points u and f coincide then on the line FF' and fig. 3 may arise; herein however f is replaced by S and f_1 by S_1 . Therefore the fourphaseequilibrium $F + F' + \text{liquid } S + \text{vapour } S_1$ occurs, wherein the liquid S is represented by a point on the line FF' . The pressure and temperature to which fig. 3 applies, agree therefore with the minimum meltingpoint of the complex $F + F'$.

From the situation of S with respect to F and F' it follows that in fig. 3 a congruent melting of the complex $F + F'$ is assumed. With an incongruent melting either F or F' should be situated between the two other points.

Because the point S is situated on the line FF' , the two saturationcurves must touch each other in S . We now imagine in S the common tangent of the two saturationcurves and also the tangent to curve ed to be drawn. For the sake of simplicity we shall call the first the tangent S and the second the tangent de .

Now, as is known, the tangent S and the line FF' are conjugated diameters of the indicatrix in S ; the same applies to the tangent ed and the line SS_1 . Because the indicatrix in S is an ellipse, on the turning of a diameter its conjugated one moves in the same direction; the lines SS_1 , FF' and the two tangents must therefore be situated with respect to each other as in fig. 3. The point S_1 must therefore in fig. 3 be situated on the same side of the tangent S as the point F' , when however F' is situated within the liquid region and F outside that region, then S_1 is situated on the same side of tangent S as the point F . Also in the case, that the points F and F' are situated both at the same time either within or outside the liquidregion, the situation of S_1 , with respect to the tangent S is easy to indicate.

Besides the cases treated above, there are still numberless others which the reader can easily deduce for himself. For that reason we shall only still contemplate some points more in detail.

We take at a definite P and T the two solid phases F' and F'' ; perpendicular to the concentration diagram we draw the ξ of these substances; we shall call these points (F') and (F'') .

When the point (F') is situated below the liquid- and the vapour leaf of the ξ surface, then the compound F' occurs in solid state. We can then construct two cones, which have both their apexes in (F') and of which the one touches the liquidleaf and the other the vapourleaf

of the ξ surface. As well a saturation- as a vapoursaturationcurve of the compound F exists therefore. When we contemplate the two curves with respect to each other, then either one completely or a part of both is metastable.

When the point (F) is situated below the liquid- but above the vapourleaf of the ξ surface, the compound F only exists in vapour-form. Then not a vapoursaturationcurve exists, but a metastable saturationcurve of F , therefore a series of metastable solutions, saturated with F .

When the point (F) is situated below the vapour-, but above the liquidleaf of the ξ surface, the compound F exists only in liquid state. Then not a saturation-, but a metastable vapoursaturation curve of F exists, therefore a series of metastable vapours in equilibrium with F .

When the point (F) is situated above both the leaves of the ξ surface, then the compound F occurs in liquid or in vapour-state, according as below the point (F) the liquid- or the vapourleaf is situated the lowest. Then neither a saturation- nor a vapoursaturationcurve of F exists.

The four above mentioned cases apply of course also to the compound F' .

We now take a pressure and a temperature at which F and F' are both solid. The points (F) and (F') are then situated below both the leaves of the ξ surface and each of the compounds has then a saturation- and a vapoursaturationcurve.

We distinguish now four cases:

1. the line $(F)(F')$ intersects both the leaves of the ξ surface.

We cannot construct through the line $(F)(F')$ a plane of contact on one of the leaves of the ξ surface; the two saturationcurves, therefore, do not intersect each other, nor the two vapoursaturationcurves. The two saturationcurves may now be situated completely outside each other, or the one may surround the other; the same applies to both the vapoursaturationcurves. Therefore neither a liquid nor a vapour exists in equilibrium with $F + F'$.

2. The line $(F)(F')$ intersects the liquidsurface, but is situated below the vapourleaf of the ξ surface.

Because we cannot construct through the line $(F)(F')$ a plane of contact on the liquidleaf, the two saturationcurves do not intersect each other, so that the one is situated outside the other, or the one surrounds the other.

We can (however) quite well construct two planes of contact on the vapourleaf through the line $(F)(F')$. The two vapoursaturationcurves, therefore, intersect each other in two points.

There exists therefore no liquid saturated with $F + F'$. Two vapours exist however, each of which may be in equilibrium with $F + F'$.

3. The line $(F)(F')$ intersects the vapourleaf, but is situated below the liquidleaf of the ζ surface.

It is evident, that now the two saturationcurves intersect each other in two points, while the two vapoursaturationcurves are situated outside each other or the one surrounds the other. Therefore two solutions exist, saturated with $F + F'$, but not a vapour which can be in equilibrium with $F + F'$.

The equilibria existing in the three cases treated above may become completely or partly metastable, by the occurrence of the heterogeneous region LG . Also it is evident, that in the previous cases not yet a fourphaseequilibrium $F + F' + L + G$ can exist.

4. the line $(F)(F')$ is situated below the two leaves of the ζ surface.

We can now construct through the line $(F)(F')$ two planes of contact on each of the two leaves of the ζ surface. The two saturationcurves therefore, intersect each other in two points, situated on both sides of the line FF' . The same applies to the two vapoursaturationcurves. Therefore two solutions exist, saturated with $F + F'$ and two vapours, saturated with $F + F'$.

In fig. 1, z and u are the points of intersection of the two saturationcurves; the points of intersection of the two vapoursaturationcurves α_1 b_1 and x_1 y_1 have not been drawn; we shall call these z_1 and u_1 ; we imagine z_1 on the same side of the line FF' as the point z , and u_1 on the same side as u . Under this pressure and at the temperature to which fig. 1 applies, the systems $F + F' + \text{liquid } z$, $F + F' + \text{liquid } u$, $F + F' + \text{vapour } z_1$, and $F + F' + \text{vapour } u_1$ occur. Of these four threephaseequilibria of fig. 1, only the two first however are stable.

Now let us contemplate a point of intersection of two saturationcurves and the point of intersection of the two vapoursaturationcurves situated on the same side of the line FF' (therefore in fig. 1 the points z and z_1 , or u and u_1). If we imagine that through the line $(F)(F')$ the two planes of contact on both the leaves of the ζ surface are constructed, then the one point of contact is usually always situated above the other surface. Because the projections of the two points of contact of these surfaces represent the above mentioned points of intersection, only one of both these points of intersection will represent a stable phase.

Therefore, if we have a stable solution saturated with $F + F'$, then the vapour saturated with $F + F'$, being situated on the same

side of the line FF' , is metastable. Reversally, if we have a stable vapour saturated with $F' + F''$, then the liquid saturated with $F + F'$, situated on the same side of the line FF' is metastable. Only in the case that a fourphase equilibrium $F + F' + L + G$ occurs, this liquid and vapour are stable at the same time.

Let us now consider the occurrence of this system $F + F' + L + G$. For the occurrence of this fourphaseequilibrium it is not sufficient that the two threephaseequilibria $F + F' + L$ and $F + F' + G$ exist. In addition it is also necessary for this, that the liquid L of the one, and the vapour G of the other threephase system shall be in equilibrium with each other. The liquid curve ed of the heterogeneous region LG then must go through the point of intersection of the two saturationcurves and also the vapourcurve e_1d_1 of the heterogeneous region must go through the point of intersection of the two vapoursaturationcurves. Because this is not the case in fig. 1, no fourphaseequilibrium can occur, at the temperature and under the pressure to which fig. 1 applies. In fig. 2 however, this is indeed the case. Therein curve ed goes through the point of intersection f of the saturationcurves and also curve e_1d_1 goes through the point of intersection f_1 of the vapoursaturationcurves. At the temperature and under the pressure, to which this figure applies, therefore the system $F + F' + \text{liquid } f + \text{vapour } f_1$ can occur. This is also the case in fig. 3 wherein the fourphase equilibrium $F + F' + \text{liquid } S + \text{vapour } S_1$ occurs.

Now we shall consider more in detail yet two points, nl. the situation with respect to each other of the four points F , F' , f and f_1 and also that of the three curves going through the points f and f_1 .

In the previous communications the first point has already been treated here and there. We have seen there that the four points can be situated with respect to each other in seven different ways, so that between the four phases of the system $F + F' + L + G$ one of the seven fourphasereactions: $F + F' + L \rightleftharpoons G$, $F + F' + G \rightleftharpoons L$, $F + L \rightleftharpoons F' + G$, $F' + L \rightleftharpoons F + G$, $F + F' \rightleftharpoons L + G$, $F \rightleftharpoons F' + L + G$ and $F' \rightleftharpoons F + L + G$ occurs.

In the particular case that three of the four points are situated by chance on a straight line, (fig. 3) a threephasereaction occurs.

Let us contemplate now the three curves, going through the points f and f_1 . With the aid of the indicatrix theorem, we can deduce the rule¹⁾:

When two equilibriumcurves (P and T constant) intersect each

¹⁾ F. A. H. SCHREINMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. III² 116.

other, their metastable prolongations are situated in the vicinity of the point of intersection, both within or both outside the corresponding threephaseangle.

Whether the two curves themselves with respect to the other phases are already metastable or not, does of course not effect the validity of this rule.

When two equilibriumcurves intersect each other in a point X , the phase X , (liquid, gas, mixed crystal) may be in equilibrium with two other phases which we shall call M and N (liquid, gas, mixed crystal etc.). The lines XM and XN form four angles; we shall now call the angle XMN therefore, the angle being one of the angles of the three-phaseangle, and its opposite angle, the threephaseangle of the point X .

We can express now the abovementioned rule also in this way:

When two equilibriumcurves (P and T constant) intersect each other, both curves are situated in the vicinity of the point of intersection, either within or outside the threephaseangle of the point of intersection.

In the figures 1, 2, and 3 we see, that the position of the curves in the vicinity of their points of intersection is in agreement with this rule.

Let us take for instance the point of intersection x in fig. 1 or 2. In this point x the curves dx and ux intersect each other and therefore the equilibrium $F' + \text{liquid } x + \text{vapour } x_1$ occurs. The threephaseangle of the point x therefore is $\angle x_1 x F'$ and its opposite angle. The curves dx and ux are drawn in fig. 1 and 2 within this angle, in fig. 3 (herein ux is replaced by Su) outside this angle.

Let us now take a point of intersection of three curves as for instance the point f in fig. 2. Taking these curves two and two, we have three pairs of curves; the abovementioned rule is applicable to each of these pairs.

If we contemplate the pair of curves dfe and uxf , the equilibrium $F' + \text{liquid } f + \text{vapour } f_1$ occurs in f . The threephaseangle of the point f is therefore $\angle f_1 f F'$ and its opposite angle. The curves dfe and uxf are both drawn within this angle.

If we contemplate the pair of curves dfe and ubf , then in f occurs the equilibrium $F + \text{liquid } f + \text{vapour } f_1$; the threephaseangle of the point f is therefore $\angle f_1 f F$ and its opposite angle. The curves dfe and ubf are both drawn within this angle.

If we contemplate the pair of curves uxf and ubf , then in f occurs the equilibrium $F + F' + \text{liquid } f$, the threephaseangle of

the point f is now FfF' and its opposite angle. The curves uuf and ubf are both drawn within this angle.

Similar contemplations apply also to the three curves which intersect each other in the point f_1 .

A relation exists also between the position of the curves in the point f and in the point f_1 . This however we shall not discuss any further here.

In all our previous considerations we have always contemplated saturationcurves under their own vapourpressure and boiling pointcurves of a simple form, nl. curves existing only of a single branch. Under definite circumstances however also curves of a more composite form may occur. Here we shall briefly treat such a boilingpointcurve.

We take a ternary mixture, wherein the system $L-G$ has a ternary point of minimum pressure, therefore also a ternary point of maximum temperature.

We suppose now that at a definite P and T the relations of fig. 1 (III) occur. Herein we find a closed region $L-G$ and within the liquid region the saturation line of the compound F . We keep the pressure constant and raise the temperature; the liquid-region then becomes smaller or in other words:

The liquid curve of the region $L-G$ contracts. Further we assume that heat is required for dissolving F , so that the saturationcurve of F contracts also.

If the saturationcurve of F contracts more rapidly than the liquid curve of the region $L-G$, then no points of intersection arise and therefore under the assumed pressure also no boilingpointcurve of F exists.

When the liquidcurve of the region $L-G$ contracts more rapidly than the saturationcurve of F , at a definite temperature T_m contact takes place. We imagine in fig. 1 (III) that the curves are shifted in such a way, that anywhere on the left side of F a point of contact m arises. If the temperature rises still more, now two points of intersection arise, which move away from each other and shift towards the right. Now different cases may occur of which we have already treated some in communication (III). We assume that on a further increase of T the two points of intersection coincide anywhere on the right side of F in a point M .

We may now obtain a diagram as fig. 4. While at the temperature T_m the saturationcurve of F is surrounded by the liquidcurve of the region $L-G$, at the temperature T_M (fig. 4) it is just the

reverse. In fig. 4 the point F is situated within the region $L-G$; of course it may also be situated in the liquid- or gasregion.

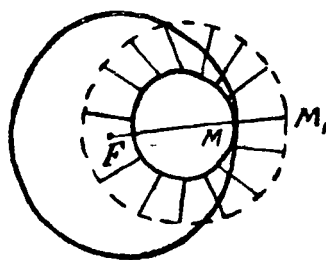


Fig. 4.

Further in fig. 4 the vapourcurve of the region $L-G$ intersects the saturation curve of F ; however, it may also surround this curve so that the saturationcurve is situated completely within the region $L-G$. We shall confine ourselves

in the following to the case drawn in fig. 4.

When on further increase of T the liquid curve of the region $L-G$ contracts now still more rapidly than the saturationcurve of F , no new points of intersection make their appearance. We have then obtained a boilingpointcurve of a simple form with a minimum boilingpoint in m and a maximum boilingpoint in M . It surrounds the point F and is itself surrounded by its corresponding vapourcurve.

We will assume however that the saturationcurve of F and the liquidcurve of the region $L-G$ move in the point M of fig. 4 with the same rapidity (further we shall see under what conditions such a case is possible). While at a temperature somewhat lower than T_M the saturationcurve of F moves in the vicinity of M more slowly than the liquid curve of the region $L-G$, at a temperature somewhat higher than T_M this is just the reverse.

Consequently on increase of T above T_M in the vicinity of the point M , two points of intersection occur (again), which shift towards the left on further increase of T and finally coincide in a point Q . At this temperature T_Q the saturationcurve of F and the liquid curve of the region $L-G$ touch one another again therefore in a point Q . However the two curves are situated now completely outside each other. The liquidregion therefore is now situated completely outside the saturationcurve of F and not as at the temperature T_M (fig. 4) within this

curve. On further increase of T points of intersection occur no more.

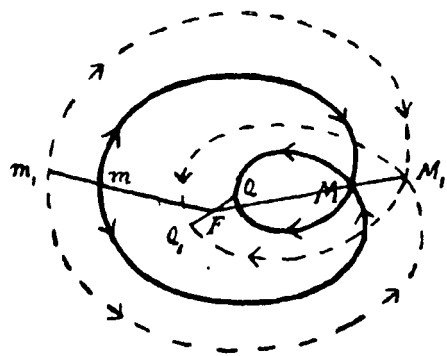


Fig. 5.

The boilingpointcurve will now have a form as curve mMQ in fig. 5: it shows a double point in M . The temperature increases in the direction of the arrows, it is a minimum in m , a maximum in

Q . The corresponding vapour-curve $m_1 M_1 Q_1$ is dotted. In fig 5 the part $M_1 Q_1 M_1$ is drawn circumphased. Of course it may be also expahsed.

If we determine the boilingpointcurve of F under a pressure somewhat different from that, to which fig 5 applies, the boilingpointcurve will suffer also a small change of form. The double point M disappears and either two branches separated from each other occur, of which the one surrounds the other, or one single curve is formed which is very concave and which has two parts which are curved sharply towards each other. The same applies to the corresponding vapour-curve. When in a system boilingpointcurves as deduced above occur, some of our previous deductions must be changed to a certain extent and they must be completed, this however is left to the reader.

Now we may still determine under what conditions the liquidcurve of the region $L-G$ and the saturationcurve of F will move with the same rapidity in the point M of fig. 4.

To the saturationcurve of F applies:

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

To the liquidcurve of the region $L-G$:

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = -Ddt \quad (2)$$

(For the significance of B and D see communication (II)).

We now take any point M of the saturationcurve of F . We call l the length of the line FM . The saturationcurve of the temperature $T + dT$ will intersect the line FM in a point M' in the vicinity of M . We put $MM' = dl$ and we take dl positive in the direction from M towards F . We then have:

$$\frac{dx}{\alpha-x} = \frac{dy}{\beta-y} = \frac{dl}{l} \quad (3)$$

If we substitute these values of dx and dy in (1), it follows that:

$$dl = \frac{B l dT}{(\alpha-x)^2 r + 2(\alpha-x)(\beta-y)s + (\beta-y)^2 t} \quad (4)$$

or:

$$dl = \frac{B}{lK \cos^2 \varphi} dt \quad (5)$$

wherein:

$$K = r + 2 \frac{\beta-y}{\alpha-x} s + \left(\frac{\beta-y}{\alpha-x} \right)^2 t \quad \text{and} \quad (\alpha-x)^2 = l^2 \cos^2 \varphi.$$

Therefore φ is the angle which the line FM forms with the X-axis. We now take any point M of the liquidcurve of the region $L-G$.

We put l_1 the length of the conjugationline MM_1 which joins the liquid M with its corresponding vapour M_1 . The liquidline of the temperature $T + dT$ will now intersect this conjugationline in a point M' in the vicinity of M . We represent MM' by dl_1 ; we take dl_1 positive in the direction from M towards M_1 . We then find from (2)

$$dl_1 = - \frac{D}{l_1 K_1 \cos^2 \varphi_1} dT \quad . \quad . \quad . \quad . \quad . \quad (6)$$

wherein :

$$K_1 = r + 2 \frac{y_1 - y}{x_1 - x} s + \left(\frac{y_1 - y}{x_1 - x} \right)^2 t \text{ and } (x_1 - x)^2 = l_1^2 \cos^2 \varphi_1.$$

φ_1 therefore is the angle which forms the conjugationline MM_1 with the X -axis.

We now suppose 1st that the saturationcurve of F and the liquidcurve of the region $L-G$ go through a same point M ;

2^d that the two curves touch each other in that point.

From 1st it follows that r , s and t have the same value in K and K_1 and that B and D apply to the same liquid.

From 2nd it follows, as is easily deduced, from the equations of the two curves, (P and T constant) that:

$$\frac{\beta - y}{\alpha - x} = \frac{y_1 - y}{x_1 - x}$$

and therefore also $\varphi = \varphi_1$. The meaning of this is that the lines FM and MM_1 coincide. This follows as we saw already before, also immediately from the indicatrix theorem. From this now it follows that we may substitute l , k and φ in (6) for l_1 , k_1 and φ_1 . We then obtain:

$$dl = - \frac{D}{l K \cos^2 \varphi} dT \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Now D is positive; if we assume further that heat is to be supplied for dissolving solid F , then B is also positive. From this it follows that dl and dl_1 always have an opposite sign. In order that the liquidcurve of the region $L-G$ and the saturationcurve of F may move in the same direction, when T is changed, the point M must therefore be situated between the points F and M_1 . This is then also in agreement with fig. 4.

From (5) and (7) it follows, that the two curves will move with the same rapidity as

$$\frac{B}{l} = \frac{D}{l_1} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

We may find this condition also in the following way. The boilingpointcurve of F is fixed by :

$$[(\alpha-x)r + (\beta-y)s] dx + [(\alpha-x)s + (\beta-y)t] dy = B dT \quad (9)$$

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = -D dT \quad (10)$$

From this follows

$$(Pr + Qs) dx + (Ps + Qt) dy = 0 \quad (11)$$

wherein

$$P = (\alpha-x)D + (x_1-x)B \text{ and } Q = (\beta-y)D + (y_1-y)B.$$

In order that the point of the curve under consideration may be an isolated or a double point, the coefficient of dx and dy must be $= 0$. Therefore $P = 0$ and $Q = 0$ or

$$(\alpha-x)D + (x_1-x)B = 0 \text{ and } (\beta-y)D + (y_1-y)B = 0 \quad (12)$$

If B and D are not $= 0$, then

$$\frac{\beta-y}{\alpha-x} = \frac{y_1-y}{x_1-x}$$

follows, which we have also found for this. This means, that the considered point, its corresponding vapour and the point F are situated on a straight line. Further it follows that the liquidcurve of the region $L-G$ and the saturationcurve of F touch each other in the contemplated point. If we substitute for B and D their values in (12), then we find :

$$(\beta-x)H_1 + (x-x_1)\eta + (x_1-\alpha)H = 0 \quad (13)$$

or

$$(\beta-y)H_1 + (y-y_1)\eta + (y_1-\beta)H = 0 \quad (14)$$

The first part of (13) and (14) represents the change of entropy when a reaction takes place between the three phases F , L , and G . From this it follows therefore, that the contemplated point of the boilingpointcurve will be an isolated or a double point, when an isentropic reaction takes place between the three phases F , L and G ; in other words, when no heat must be supplied or removed. In (8) the same is expressed in quite an other form as in (13) and (14). In order to examine whether the contemplated point is an isolated or a double point, we must calculate terms of higher order, namely $A dx^2 + B dx dy + C dy^2$.

Because the fixing of A , B , and C gives cause for extensive calculations, we will leave that aside.

To be continued.