

Citation:

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Let us now take the case generally occurring in which, on a change in pressure in the one direction $F + G$ is converted into $F + L' + G'$, and into $F + G''$ on a change in pressure in the other direction. Hence, on a change of pressure in the one direction liquid is formed, but not when in the other direction.

In the previous communication we have deduced: if $F + L$ is converted into $F + L' + G'$ with increase in volume, the conjugation line solid-liquid will, on lowering the pressure turn towards the vapour point. If $F + L$ is converted into $F + L' + G'$ with contraction of volume, the conjugation line solid-liquid turns in the opposite direction.

In a similar manner we may now deduce: if $F + G$ is converted into $F + L' + G'$ with increase in volume, the conjugation line solid-vapour, on lowering the pressure, turns away from the liquid point, and on increasing the pressure it turns towards the same. If $F + G$ is converted into $F + L' + G'$ with contraction of volume the conjugation line solid-vapour will turn in the opposite direction.

The conversion of $F + L$ into $F + L' + G'$, or as we may also call it the formation of vapour from $F + L$ generally takes place with increase in volume and only on certain conditions with a decrease in the same. The conversion of $F + G$ into $F + L' + G'$, or in other words the formation of vapour from $F + G$ takes place as a rule with decrease in volume and only in definite conditions with an increase of the same.

In the previous communication (V) we have demonstrated that the rule for the rotation of the conjugation line solid-liquid is in conformity with the saturation lines under their own vapour pressure as deduced in communication (I): in the same manner we may now also show that this is the case with the movement of the conjugation line solid-vapour.

Let us imagine in fig. 7 (I) a tangent to be drawn through F on the vapour saturation curve of F under its own vapour pressure, therefore, on curve $M_1 a_1 m_1 b_1$. As on a change in pressure in either direction the new conjugation line solid-vapour falls outside the first three-phase triangle, the system $F + G$, in this particular case, is converted on a change in pressure in the one direction into $F + G'$ and by a change in the other direction into $F + G''$. Hence, no liquid is formed either on an increase or a decrease in pressure. At an infinitesimal change in pressure nothing happens but evaporation of a little solid substance F in, or else a slight deposit of solid F from the vapour G .

On evaporation of F , the volume will as a rule increase; as the

gas then draws nearer to the point F , the pressure along the vapour saturation curve, starting from the point of contact, will decrease towards F and increase in the other direction. This is in agreement with fig. 7 (I) and 12 (I) but not so with fig. 13 (I); from the deduction of this last figure, however, it is more to be expected that the curve $M_1 m_1$ is either circumphased or exp phased, but is then situated at the other side of F like curve Mm .

Let us now consider the case when the vapour saturation curve of F under its own vapour pressure possesses a form like curve amb in fig. 4 (V); the saturation line should then be supposed to lie more towards the right. We may then draw through F tangents to the vapour saturation line with the points of contact R, R', X and X' .

In the point $R' (X')$ now also takes place the above considered conversion of $F + G$ into $F + G'$ and $F + G''$. In the point R , however, the system $F + G$ is converted, on change in pressure, in the one direction, into $F + L' + G'$, and by a change in the other direction into $F + L'' + G''$. Hence, liquid is formed on increase as well as on decrease in pressure. At an infinitesimal change in pressure, only a little solid substance F evaporates into, or else a little of this is deposited from the vapour; hence, when starting from the point of contact, the pressure along the vapour-saturation curve will decrease towards F , but increase in the other direction.

We have noticed above that the rotation-direction of the conjugation line solid-liquid depends on the change in volume when vapour is formed from $F + L$, whereas that of the conjugation line solid-vapour depends on the change in volume when liquid is formed from $F + G$. In the three-phase equilibrium $F + L + G$ we may now suppose four cases to occur.

1. The formation of vapour from $F + L$ takes place with increase, the formation of liquid from $F + G$ with decrease in volume.

2. The formation of vapour from $F + L$ takes place with decrease, the formation of liquid from $F + G$ with increase in volume.

3. The formation of vapour from $F + L$ and that of liquid from $F + G$ both take place with increase in volume.

4. The formation of vapour from $F + L$ and that of liquid from $F + G$ both take place with decrease in volume.

Let us first take the case mentioned sub 1 which is also the one usually occurring; from what has already been communicated it follows that, on increase in pressure, the conjugation line solid-liquid turns towards the vapour point and that the conjugation line solid-vapour turns away from that point.

Hence, on increase of the pressure, the three-phase triangle turns in such a manner that the conjugation line solid-vapour gets in front; on diminution of the pressure the three-phase triangle turns in the opposite direction, but in such a manner that the conjugation line solid-liquid precedes.

On increase in pressure the two three-phase triangles of fig. 3 (I) with their conjugation line solid-vapour in front, will therefore move towards each other; on diminution in pressure they move away from each other, with the conjugation line solid-liquid in front, to be converted, for instance, into fig. 8 (I). If in fig. 11 (I) we suppose each liquid to be united with its correlated vapour and the solid substance F we notice that the three-phase triangle moves in conformity with the above mentioned rule.

It is evident that we must not look upon this rotation of the three-phase triangle as if this turns in its entirety without a change in form; during this rotation not only the length of the conjugation lines solid-liquid and solid-vapour is changed, but also the angle formed by the two lines.

In the case mentioned sub 2 the changes in the volumes have the opposite sign to that mentioned in the case sub 1; the three-phase triangle then of course will turn in the opposite direction namely in such a manner that on increase in pressure the conjugation line solid-vapour gets in front.

A similar case we meet in fig. 12 (I), if in this we take two three-phase triangles, one at each side, and adjacent to the straight line $Fm m_1$; the two triangles turn the conjugation line solid-vapour towards each other. On lowering the pressure the two triangles must move towards each other and on increasing the pressure they must part from each other, which is in conformity with fig. 12 (I).

In the case mentioned sub 3, the two conjugation lines, solid-liquid and solid-vapour, of the three-phase triangle will, on increase in pressure, move towards each other, and on decrease in pressure part from each other; in the case mentioned sub 4 they move in opposite directions.

Let us suppose that the expahsed vapour saturation line of F , in fig. 13 (I) is situated at the other side of F . We now take a liquid close to the point m so that its conjugated vapour is adjacent to the point m_1 . The three-phase triangle then forms in F an angle of nearly 180° . As here occurs the case mentioned sub. 3, the two conjugation lines solid-liquid and solid-vapour must draw nearer each other on increase in pressure. And this is in agreement with fig. 13 (I).

If we take a liquid close to the point M and hence a vapour

adjacent to the point M_1 , the case mentioned sub 4 occurs and the movement of the conjugation lines is in conformity with the rule deduced above. The cases mentioned sub 3 and sub 4 also occur in other figures, for instance also in fig. 12 (I).

In the above considered conversion of $F + L$ we can distinguish three special cases.

1. The case, mentioned above sub A 2 and A 3, which has already been discussed in detail, when no vapour is formed at an infinitesimal change in pressure or in volume.

2. At an infinitesimal change in volume the quantity of the liquid does not alter (its composition, of course, changes).

3. At an infinitesimal change in volume the quantity of solid matter does not change.

In each of these cases one of the sides of the three-phase triangle will occupy a special position. We have already noticed previously that in the case mentioned sub 1 the conjugation line solid-liquid meets the saturation line under its own vapour pressure.

In the case mentioned sub 2, dn in the formula given in the previous communication V (p. 1213) must be taken $= 0$; from that it follows that the tangent drawn in the liquidum point to the saturation line under its own vapour pressure is parallel to the conjugation line solid-vapour.

In the case mentioned sub 3 dn in the said formula must be taken $= 0$; this signifies that the conjugation line liquid-vapour touches in the liquidum point the saturation line under its own vapour pressure.

In the saturation curves deduced previously diverse examples of these cases are to be found.

It is evident that in the system $F + G$, three corresponding cases may be distinguished; these then relate to the direction of the tangent in the vapour point of a vapour saturation line under its own vapour pressure.

We will now consider the case already mentioned in the previous communication sub B, when a phase reaction between the three phases takes place. The three phases are then represented by three points of a straight line and the pressure for the system $F + L + G$ is then a maximum or a minimum.

Let us first take the case mentioned sub B 1 when the reaction $F \rightleftharpoons L + G$ occurs; the point F then falls between the points L and G as, for instance, in fig. 4 (I), if in these figures we suppose a_1 to have coincided with b_1 and α with b . We then obtain fig. 5 (I)

in which the points m_1 , F , and m correspond with the homonymous points in fig. 7 (I).

If now we suppose first that the reaction $F \rightleftharpoons L + G$ proceeds from the left to the right with increase in volume, the system $L + G$ will then appear at lower pressures and the systems $F + L$ and $F + G$ at higher ones. Hence, on lowering the pressure, fig. 5 (I) will be converted into fig. 6 (I) and on increasing the same into fig. 4 (I), which is in agreement with our previous considerations. As, on increase of pressure, fig. 5 (I) is converted into fig. 4 (I) the pressure for the system $F + L + G$ in fig. 5 (I) is consequently a minimum.

If we had assumed that the conversion $F \rightleftharpoons L + G$ took place from the left to the right with decrease in volume, the pressure would be a maximum. Such a change in volume can only occur when the liquid differs but little in composition from F , and when F melts with contraction of volume. If we imagine in fig. 13 (I) the curve $M_1 m_1$ to have shifted so far to the other side of F that M_1 gets situated at the other side of F , this case will occur in the system $F + \text{liquid } M + \text{vapour } M_1$.

Let us now take the case mentioned sub B 2, namely when the reaction $F + L \rightleftharpoons G$ takes place, so that the point G lies between the points F and L . This is, for instance the case in fig. 9 (I). Let us now assume first that the reaction takes place from the left to the right with increase in volume. The system $F + L$ will then appear at a higher, the systems $F + G$ and $L + G$ at a lower pressure. In agreement with our previous considerations fig. 9 (I) will be converted, on increase in pressure, into fig. 8 (I) and on lowering of the pressure into fig. 10 (I). As on increase of pressure fig. 9 (I) is converted into fig. 8 (I) the pressure for the system $F + L + G$ in fig. 9 (I) is a minimum. This is also in harmony with the situation of the points m_1 , m , and F in figs. 11 (I) and 13 (I).

Let us now just take a system $F + L_1 + G_1$ in which L_1 differs but little from L , and G_1 but little from G ; this system will then be represented by a triangle situated in the vicinity of the line $F m m_1$. As the reaction $F + L \rightleftharpoons G$ takes place with increase in volume, the conversion of $F + L_1$ into $F + L'_1 + G'$ in the infinitesimally differing system $F + L_1 + G_1$ will take place with increase in volume and the conversion of $F + G_1$ into $F + L'_1 + G'$, with decrease in the same. We have noticed previously that, in this case the three-phase triangle must turn in such a manner that, on increase in pressure, the conjugation line solid-vapour gets in front and that on reduction of pressure the conjugation line solid-liquid precedes. This also is in

agreement with figs. 8 (I) and 9 (I). On lowering the pressure, the first figure is converted into the second and we notice that in this conversion both three-phase triangles turn in such a manner that the conjugation line solid-liquid gets in front.

In the case now considered when the reaction $F + L \rightleftharpoons G$ takes place from the left to the right with increase in volume, the pressure can also be a maximum; I will elucidate this with a single example.

We take a saturation line of the solid substance F at the pressure P , this is represented in fig. 1 by the curve fgh ; within this saturation line is situated a vapour region encompassed by a heterogeneous region, of which the liquidum line is drawn and the vapour line dotted.

On lowering the pressure the vapour region expands and at a

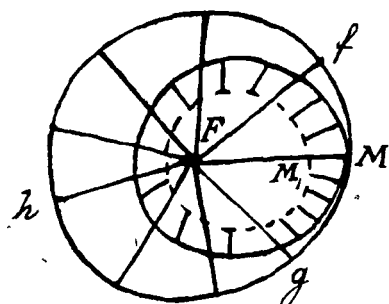


Fig. 1.

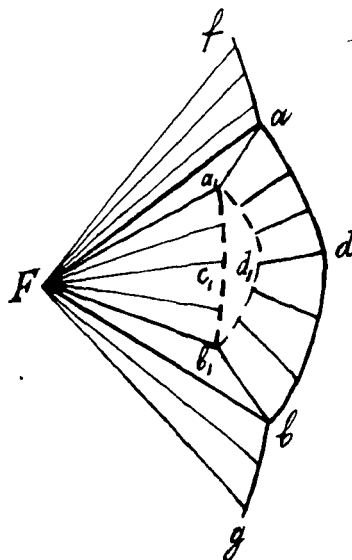


Fig. 2.

certain pressure P_M the saturation line of F and the liquidum line of the heterogeneous region meet each other in M . There is now formed the three-phase equilibrium solid F + liquid M + vapour M_1 , represented by three points of a straight line, whereas the vapour phase M_1 lies between the points F and M . Hence, the reaction is $F + L \rightleftharpoons G$ namely from the left to the right with increase of volume, whilst the pressure P_M is a maximum.

At a pressure somewhat lower than P_M is now formed a diagram as in fig. 2 in which, however, we must imagine the only partially drawn saturation line af and bg of F to be closed. The vapour

saturation line $a_1 c_1 b_1$, the liquidum line $a d b$ and the vapour line $a_1 d_1 b_1$ have been drawn only to the extent where they represent stable conditions.

We have noticed previously that from the system $F + L + G$, which exists at the pressure P_M , are formed, on increase in pressure, the systems $F + G$ and $L + G$; we find this confirmed here also in figs. 1 and 2. We also notice, in agreement with the rule given above that the two three-phase triangles Faa_1 and Fbb_1 turn, on reduction in pressure, in such a manner that the conjugation line solid-liquid gets in front; on increase of pressure the conjugation line solid-gas precedes.

I must leave the consideration of the other cases to the reader.

In our previous considerations we have compared the course of the saturation- and vapour-saturation lines under their own vapour pressure with the change in volume that takes place in the conversion of $F + L$ and of $F + G$ into $F' + L' + G'$. In the same manner we might compare the course of the boiling point-line and the vapour-boiling point line with changes in entropy occurring in these reactions. Instead of increasing, or decreasing the volume of the systems $F + L$ and $F + G$ we must either supply, or withdraw, a little heat to, or from the same.

If we distill a ternary liquid at a constant temperature, then, as is well known, the pressure continuously decreases during the distillation. The liquid and the at each moment distilling vapour proceed along a curve which we distinguish as the distillation curve of the liquid and of the vapour. We obtain, as is well known, clusters of these distillation curves which emanate from one or more definite points (the distillation points) and meet in one or more definite points.

If now at the temperature of distillation a solid substance F' also occurs, this can modify the course of the distillation lines; of course, not the theoretical but the experimental course.

According to whether the initial and terminal points of the distillation curves are situated within or without the saturation line of F' under its own vapour pressure, we may now distinguish several cases, of which we will only take a single one.

Let us choose a temperature below the minimum melting point of the solid substance F' , so that its saturation line under its own vapour pressure is circumphased. In fig. 3 has been drawn a part of this saturation line with the point of maximum pressure M and of minimum pressure m ; the dotted curve $M_1 s_1 a_1 b_1$ is a part of the correlated vapour line.

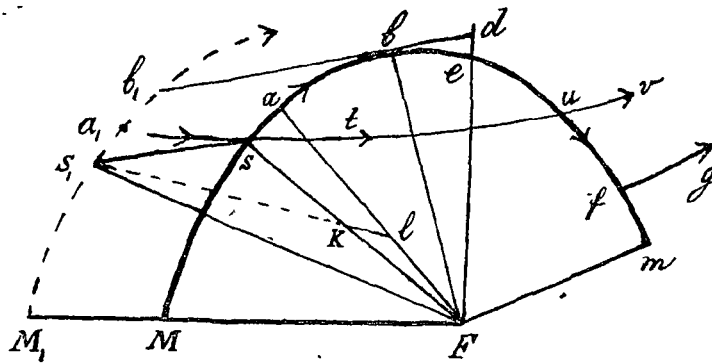


Fig. 3

From the situation of the points M and m it is now evident that the arrows do not, as in the previous figures, indicate here the direction of the increasing pressure, but that of the decreasing one.

Let us now imagine in fig. 3 to be drawn the distillation curve of a liquid and its conjugated vapour curve. It is now evident that if the first does not intersect the saturation line under its own vapour pressure, the second will also not intersect the vapour saturation line and reversedly. We further perceive at once that in this case the distillation curve will suffer no change owing to the appearance of the solid substance.

When, however, the distillation curve, such as the curve $rstuv$ in fig. 3, intersects the saturation line under its own vapour pressure, matters are different; the arrows on this curve $rstuv$ indicate the direction of decreasing pressure, hence also the direction in which the liquid moves during the distillation. It is now evident that with a point of intersection s of the distillation curve of the liquid and the saturation line of F under its own vapour pressure must correspond a point of intersection s_1 of the distillation curve of the vapour and the vapour saturation curve of F under its own vapour pressure. As s_1 represents the vapour which can be in equilibrium with the liquid s , the distillation curve of the liquid must meet the line ss_1 in s .

If no solid F occurred, the liquid r would, on distillation, proceed along the curve $rstuv$; now however, when it has arrived in s something else takes place. For if we withdraw from the liquid s a small quantity of vapour s_1 , the new liquid will be represented by a point of the line aF ; we must then suppose the point a to be situated adjacent to s . The new liquid will now resolve into solid F and the solution a of the saturation line under its own vapour pressure. The liquid, therefore, does not proceed along the distillation curve stu , but moves, with separation of F , along the saturation

line under its own vapour pressure from s towards a . If now we again generate a little vapour which can be in equilibrium with the liquid a , therefore the vapour a_1 , the liquid a moves, with separation of F , along the saturation line under its own vapour pressure in the direction of b .

If, as assumed for the point b in fig. 3, the conjugation line liquid-vapour (the line $b_1 b$) meets the saturation line under its own vapour pressure in the liquidum point b , then, as we have seen previously, the system $F + L$ is converted, at an infinitesimal change in pressure, into $F + L' + G'$ without any solid substance either dissolving or crystallising. If, however, we withdraw a little more vapour, so that the liquid b is converted into d , F is dissolved and d is converted into liquid e . Hence, on distillation the liquid s will traverse a part of the saturation curve of F under its own vapour pressure, first with separation of solid F and afterwards with solution of the same. The point f in which all solid substance has again disappeared will, as a rule, not coincide with the point u of the distillation curve $rstuv$. Starting from the point f , the liquid, on continued distillation, proceeds along a distillation curve fg .

If no solid substance F did occur the liquid r would, on distillation, traverse the distillation curve $rstuv$; as now, however, solid matter F appears, it first proceeds along curve rs , then along curve sbf and finally along curve fg . From the foregoing considerations it follows: if a distillation curve meets the saturation line under its own vapour pressure it proceeds starting from this point of intersection, along a part of the saturation line under its own vapour pressure and abandons it in another point along a distillation line which, with regard to the first one, has shifted.

We may also express this as follows: If during the distillation of a liquid a solid substance F separates, the liquid leaves the distillation curve in order to proceed along a part of the saturation line of F under its own vapour pressure. As soon as, on continued distillation, the solid substance F again disappears, the liquid again proceeds along a distillation curve which, however, does not coincide with the prolongation of the first. The occurrence of the solid substance has, therefore transferred the liquid to another distillation curve.

Although, as stated above, the appearance of a solid substance generally causes the shifting of a distillation line, yet in some cases no shifting can take place so that the liquid after the disappearance of the solid matter traverses the prolongation of the original distillation curve. This will be the case when the vapour contains only

one of the three components, the distillation curves of the liquid then become straight lines, those of vapour and distillate are reduced to a single point.

When a distillation curve of a liquid meets the saturation line of F under its own vapour pressure in the point b , it will not penetrate within the heterogeneous region, but meet this saturation curve in b ; its vapour distillation curve will then also meet the vapour saturation curve.

Among all distillation curves intersecting the saturation line of F under its own vapour pressure there is one that behaves in a particular manner: it is the one that intersects the saturation line in the point M and, therefore, meets the line MM , in M . If we withdraw from the liquid M a little of the vapour M_1 , M will not change its composition, but the reaction: liquid $M \rightarrow$ solid F + vapour M_1 will appear. If now the vapour is continuously distilled off, the liquid M will disappear without change in pressure and only the solid substance F will remain. The distillation curve arriving in M , therefore, terminates in this point without proceeding any further along the saturation curve of F .

What follows next is dependent on the temperature; this, as we have presupposed has been chosen lower than the minimum melting point of F . We now can distinguish two cases.

1. The distillation temperature is higher than the maximum sublimation point of F . The saturation curve and the vapour saturation curve of F under their own vapour pressure then possess a form like in fig. 7 (I), the isothermic-isobaric diagrams are as shown in figs. 1 (I)—6 (I).

After, on distillation, the liquid M has disappeared and only the solid substance F remains, the pressure conforming with fig. 2 (I) will fall to the pressure to which fig. 5 (I) applies. At this pressure, the reaction solid $F \rightleftharpoons$ liquid m + vapour m_1 now occurs. If now the vapour is continually driven off, the solid substance F will disappear and the liquid m will remain, without any change in pressure. On further distillation, the liquid transverses the distillation curve, starting from point m in fig. 3.

The liquid, therefore, proceeds first along a distillation curve terminating, at the pressure P_M in the point M , and then along another one starting from m at the pressure P_m ; at the transfer of the liquid from the one to the other distillation curve, hence, between the pressures P_M and P_m , it is converted into the solid substance F .

2. The distillation temperature is lower than the maximum sublimation

point of F . The saturation- and the vapour-saturation curve of F under their own vapour pressure then have a form as in fig. 11(I), the isothermic-isobaric diagrams as in figs. 1(I), 2(I), 3 (I), 4(I), 8(I), 9(I) and 10(I).

As soon, as on distillation, the liquid M has disappeared and, consequently, only the solid substance F remains, the pressure conforming with fig. 2 (I) will fall. If now, however, the pressure P_m , which now conforms with fig. 3 (I) has been attained, the solid matter F will not be capable of splitting, as in the previous case. On further lowering of the pressure, fig. 10 is formed; hence, the substance F will only appear in the solid condition. On further decrease in pressure the vapour saturation curve of fig. 10 (I) undergoes contraction and finally, at a definite pressure, coincides with the point F . The solid substance F can now be in equilibrium with vapour of the composition F , or in other words: the substance F sublimes.

Hence, the liquid first traverses, at a pressure P_M , a distillation curve terminating in the point M , where it is converted into the solid substance F , which at a further lowering of the pressure sublimes at a definite pressure. The distillation of the liquid is, therefore, finally changed into a sublimation of the solid substance F .

We will now investigate what happens when we distill a liquid saturated with a solid substance F . We take a liquid s (fig. 3) and the solid substance F in such proportion that the complex is represented by point K of the line sF . We now withdraw from this complex K a little vapour s_1 , which can be in equilibrium with this complex; the complex now arrives in l and hence, is resolved into liquid a + solid F . The little straight line Kl is now an element of the curve which the complex K will traverse on distillation; we will call this curve the complex distillation curve. From the deduction of this curve it now follows at once that the tangent drawn in the point K at the complex distillation curve which passes through this point, passes through the point s_1 . Further, it is evident that this applies to all complexes situated on the line Fs . From this follows: in order to find the direction of the tangent to a complex distillation curve in a point (k) we should take the three-phase triangle, whose conjugation line solid-liquid (sF) passes through this point K . The line which connects this point (K) with the vapour point (s_1) of the three-phase triangle is the looked for tangent. We may express this also as follows: in the point of intersection of a complex distillation curve with a conjugation line solid-liquid the tangent to this curve passes through the vapour point correlated to that conjugation line.

From this follows: if we intersect a cluster of complex distillation curves by a conjugation line solid-liquid, the tangents in these points of intersection form a cluster of straight lines which all pass through the vapour point appertaining to that conjugation line. Further, it is evident that the vapour distillation curve representing the vapour distilling over at each moment is the vapour saturation line of F under its own vapour pressure.

We can now demonstrate that a complex distillation curve turns in each point its convex side towards the correlated vapour point and that a definite point will be a point of inflexion if the tangent which passes through this point meets the vapour saturation line of F under its own vapour pressure and if this latter point of contact is not itself a point of inflexion.

If we intersect a cluster of complex distillation curves by a conjugation line solid-liquid, then as we have seen previously, the tangents in these points of intersection all pass through the vapour point correlated to this conjugation line. If now, in the proximity of this vapour point the vapour saturation curve under its own vapour pressure is situated outside the three-phase triangle none of the above mentioned points of intersection will be a point of inflexion.

We can imagine a curve transmitted through the points of inflexion of the complex distillation curve, which we will call the point of inflexion curve; this curve may be found in the following manner. We draw to the point X of the vapour saturation line under its own vapour pressure a tangent; the point of intersection of this tangent with the conjugation line solid-liquid appertaining to the point X we will call S . If now the point X traverses the saturation curve under its own vapour pressure the point S will traverse the looked for point of inflexion curve.

This point of inflexion curve always passes through the points M_1 and m_1 of the vapour saturation curve [Fig. 7 (I), 11 (I), 12 (I)] and if we can draw through F a tangent to this vapour saturation curve also through the point F . For our purpose, only the part of the point of inflexion curve which is situated within the heterogeneous region has any significance, that is in so far as it intersects the conjugation line solid-liquid between the points indicating the solid substance and the liquid.

In the points of intersection of the saturation curve under its own pressure with the point of inflexion curve, the conjugation line liquid-vapour meets the vapour saturation curve.

In the proximity of a maximum or a minimum point of the three-

phase equilibrium $F+L+G$ the three-phase triangle is very narrow and as noticed previously, we can distinguish many cases. From a consideration of these cases appears the following.

We represent, as before, the liquid with the maximum pressure by M the correlated vapour by M_1 , the liquid with the minimum pressure by m and the correlated vapour by m_1 . The complex distillation curves have, in the vicinity of the line $FM(Fm)$ a direction about parallel to this line from F towards $M(m)$ or reversedly so. If, however, the vapour point $M_1(m_1)$ is situated between F and $M(m)$ they proceed from F and $M(m)$ towards the point $M'(m_1)$ or reversedly so, and in the vicinity of this point they inflect in definite direction away from the line $FM(Fm)$ or towards that line.

Let us take the case of a distillation temperature lower than the maximum sublimation point of the solid substance F ; the saturation line of F under its own vapour pressure and the correlated vapour line then possess a form as in fig. 11 (I). In fig. 4 a part $Mdbm$ of this saturation line has been drawn but the correlated vapour line has been omitted. From a consideration of the three-phase triangles we can readily deduce the course of the complex saturation curves; the arrows indicate the direction in which the complex moves on distillation. If these complex distillation curves are intersected by a straight line passing through the point F the tangents and curvatures in these points of intersection must then satisfy the conditions deduced therefor.

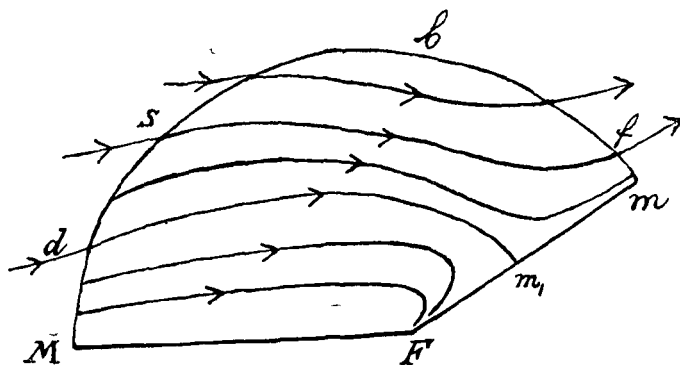


Fig. 4.

If in the vicinity of the line Fm_1m we imagine a three-phase triangle so that the vapour point is adjacent to m_1 and the liquidum point adjacent to m , we notice that a part of the complex distillation curves must proceed towards the point F and another part towards the point m , whilst there is one that, without bending

towards F or m , draws near to the point m_1 . This is represented by dm_1 . The point b of fig. 4 corresponds with the homonymous one of fig. 3; it is, therefore, that point of the saturation line under its own vapour pressure in which the side liquid-gas of the three-phase triangle meets this saturation line. The points d and b divide the branch $Mdbm$ of the saturation line under its own vapour pressure into three parts.

On distilling the liquid d a complex $F + L$ is formed which traverses the complex distillation curve dm_1 ; the pressure therefore falls from P_d to the minimum pressure P_m and the liquid itself traverses the curve dbm . As the pressure gets nearer P_m , the liquid and the solid substance F will be left behind more and more in that proportion in which the vapour m_1 can be formed from them; at the last moments of the distillation we notice the solid matter and the liquid to disappear simultaneously.

Let us now take a liquid c of the branch Md . On distillation of this liquid, a complex $F + L$ is formed which traverses the complex distillation curve proceeding from c towards F . The pressure, therefore, falls from P_c to the minimum pressure P_m and the liquid itself traverses the branch cbm . The nearer the pressure gets to P_m the less liquid will be retained in the complex which finally will practically consist of the solid substance F only.

Let us now take a liquid s of the branch db ; this on distillation forms a complex $F + L$ which traverses the complex distillation curve sf . Hence, the pressure falls from P_s to P_f and the liquid itself proceeds along the curve sbf ; the liquid s is, therefore, converted into the liquid f at first with separation of solid matter which is then again redissolved.

We notice from this that the point d is a point of demarcation and in such a manner that all the liquidum distillation curves which meet the saturation line under its own vapour pressure between d and M do not leave the heterogeneous region, whereas those meeting this curve between d and b abandon that region.

If we take a distillation temperature higher than the maximum sublimation point but lower than the minimum melting point of the substance F the saturation- and vapour-saturation curve under their own vapour pressure will have a form as in fig. 7 (I). All liquidum distillation curves which meet this saturation curve abandon the heterogeneous region. I must leave the consideration of the other cases to the reader.

(To be continued).