

Citation:

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8. The diffraction tells us something of the size of the crystals and by this means possibly of the temperature at which they have been formed: "with falling temperature the size of the crystals diminishes"¹⁾. In that way the halo-colours, which have been too much neglected, may possibly contribute to a better knowledge of the higher atmosphere.

VI. Conclusions.

The above investigation seems to me to justify the following conclusions:

1. The simple refraction-theory cannot explain the halo-phenomena completely, in particular as regards the great variety of the colours.

2. The diffraction-theory gives a simple explanation of the colours which appear and allows special conclusions to be drawn regarding the influence of the size and the shape of the crystals. It alone gives the ordinary circle its correct place of 22° .

3. The rings which have been observed in the neighbourhood of 22° are secondary diffraction-rings: their radii are not constant.

4. The diffraction-theory will probably be able to afford a better insight into the formation of the circumzenithic arc.

5. It is necessary that the colours be accurately recorded by each observer in order to permit a further testing of the theory and a complete deduction of the origin of the observed phenomenon.

Chemistry. — "*In-, mono- and divariant equilibria*". XVI. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of March 31, 1917).

The regions in the P,T-diagram.

In communication VIII we have already briefly discussed those regions; now we shall consider them more in detail. When the equilibrium

$$E = F_1 + F_2 + \dots + F_n \dots \dots \dots (1)$$

consists of n components, then it is generally divariant; consequently it is generally represented in the P,T -diagram by a region. We shall consider this region E in its whole extensity, viz. without taking into consideration that some parts may become metastable by the occurrence of other phases.

With a definite equilibrium E we may distinguish:

¹⁾ PERNTER, l. c. p. 289.

1. the total composition of E .
2. the composition of each of the phases, of which the equilibrium E consists.

We shall say that two equilibria have the same phases-composition when the phases of both equilibria have the same composition.

We now take a definite point x of the region E (consequently the equilibrium E under P_x and at T_x). Then the equilibrium E has either only one definite phase-composition E_x , or two phase-compositions E_x and E'_x or three viz. E_x , E'_x and E''_x etc. We may express this by saying that either one, or two or more equilibria E belong to the point x of the region E .

When only one single equilibrium E_x belongs to each point x of the region E , then we call the region one-leafed; when in a part of the region two equilibria (E_x and E'_x) belong to each point x , then we call that part two-leafed etc.

As the equilibrium E_x , which belongs to a definite point of the region E , may be as well stable as unstable, the region E may consist, besides of stable, yet also of unstable leaves.

When the point x traces the region E of the P, T -diagram or in other words, when we give to the equilibrium E all possible phase-compositions, then equilibria may occur, which show something particular.

1. The equilibrium E of n components in n phases passes into an equilibrium E_0 of $n-1$ components in n phases. [The index 0 indicates that the quantity of one of the components has become zero].

2. Between the n phases of the equilibrium E a phase-reaction

$$\lambda_1 F_1 + \lambda_2 F_2 + \dots + \lambda_n F_n = 0 \quad (2)$$
 may occur. We call this equilibrium E_R . [The index R indicates that a reaction may occur].

3. Critical phenomena occur between two phases; we call this equilibrium E_K .

The first case occurs when the quantity of one of the components e.g. K_1 may become zero in all phases. It is evident that the phases with constant composition are not allowed to contain this component K_1 , therefore.

The equilibrium E_0 contains $n-1$ components in n phases and is, therefore, monovariant; consequently it is represented in the P, T -diagram by a curve, which we shall call curve E_0 . This curve E_0 is, therefore, nothing else but a monovariant curve of a system with $n-1$ components. Consequently it is defined by:

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V} \dots \dots \dots (3)$$

Herein ΔH represents the increase of entropy and ΔV the increase of volume with the reaction, which may occur in the equilibrium E_0 .

As on curve E_0 the quantity of one of the components becomes zero, the region E must terminate (or begin) in curve E_0 ; for this reason we call E_0 the limit-line of the region E . We shall refer to this later. In fig. 1 ab and cd are the limit-lines of a region $abcd$; on curve ab one of the components is missing e.g. K_1 , on curve cd an other component e.g. K_2 is missing in the equilibrium E . When we go, starting from a point h of a limit-line towards a point l or m within the region, then the equilibrium E_0 passes into the equilibrium E .

Let us take now the second case, viz. that an equilibrium E_R occurs. The equilibrium E_R consists of n components in n phases, between which the phase-reaction (2) may occur. E_R is, therefore, a monovariant equilibrium and it may be represented by a curve in the P, T -diagram. It is defined by (3) in which ΔH and ΔV relate now to reaction (2). In order to examine the position of the region in the vicinity of this curve, we use the property: when in a system of n components in n phases a phases-reaction may occur, then at constant T the pressure and under constant P the temperature is maximum or minimum¹⁾.

Let ef be in fig. 2 a curve E_R . When we trace the region along a horizontal line (P constant) then in the point of intersection of this line with ef the temperature must be maximum or minimum. Let g be this point of intersection and let us assume that T_g is a maximum, then consequently the region must be situated at the left of curve ef . At $T_g + dT$ ($dT > 0$) then viz. no equilibrium E exists, at $T_g - dT$ two different equilibria E exist, however; consequently the region is two-leaved in the vicinity of curve E_R . In fig. 2 the one leaf of the region is dotted, the other leaf is striped. When we trace the region along a vertical line, then the pressure on ef is a minimum.

Consequently curve E_R is also a limit-line of the region E , but in connection with the property of the region in the vicinity of this curve, we call it "turning line" of the region E .

Also on the turning-line E_R the concentration of one of the components may become zero at a definite T (and corresponding P);

¹⁾ F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOM. III¹. 285.

then we obtain an equilibrium $E_{R,0}$, which belongs as well to the turning-line E_R as to the limit-line E_0 . Turning-line and limit line touch one another in the point $E_{R,0}$.

In the case mentioned under 3 critical phenomena appear between 2 phases. This is the case when in the equilibrium E two liquids L_1 and L_2 get the same composition or when a liquid and a gas become identical. Then we obtain an equilibrium E_K of n components in n phases, of which 2 phases are in critical condition. This equilibrium E_K is represented in the P, T -diagram by a curve E_K which we call the critical curve of the region. In the vicinity of this curve E_K the region is one-leafed.

Consequently it is apparent from the previous that a bivariant region is one-leafed in the vicinity of a limit-line or critical-line, in the vicinity of a turning-line it is two-leafed. We shall refer to this later.

One- and two-leafed regions.

A one-leafed region may be limited by limit-lines and critical lines, but it may also be unlimited. When the equilibrium E contains e. g. only phases of invariable composition, then neither limit-line, nor critical line, nor turning-line exists. Consequently the region E is unlimited. [Of course a part of this region becomes metastable at higher T , because another phase is formed e. g. a liquid by melting or transformation of solids. When we leave out of consideration however the occurrence of other phases, then the region extends itself unlimited]. The region may also be unlimited when in the equilibrium, besides invariable phases also variable phases occur, which do not contain all components [e. g. mixed crystals or a gas].

We take an equilibrium $E = L + G$ of a binary system with the components A and B , which occur both in the vapour G . Then the region E has two limit-lines E_0 . When in L and G the component A is missing, then we have the limit-line $E_{A=0}$, when B is missing, then we have the limit-line $E_{B=0}$. Consequently curve $E_{A=0}$ is the boiling-point-line of the substance B , curve $E_{B=0}$ that of the substance A .

When L and G have always different composition, then the region $E = L + G$ has no turning-line; then it may be represented by fig. 1 in which ab and cd are the limit-lines. When L and G may get the same composition, so that a reaction $L \rightleftharpoons G$ may occur, then also a turning-line E_R exists. Then the region may be repre-

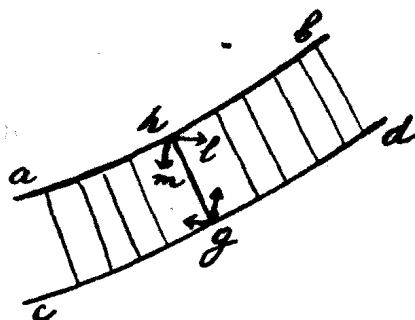


Fig. 1.

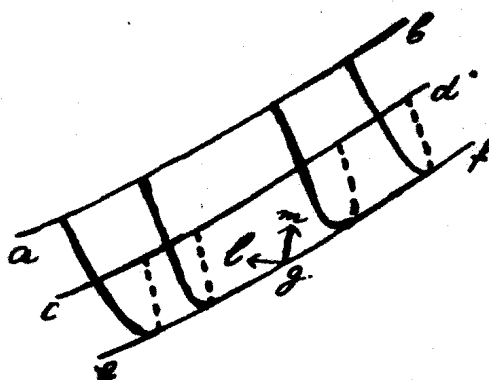


Fig. 2.

sented by fig. 2, in which ab and cd are the limit-lines and ef the turning-line.

The same is true for an equilibrium $E = M + L$ or $M + G$ of a binary system $A + B$ [M represents mixed crystals].

The region E exists in fig. 2 of two leaves, viz. $aefb$ and $cefd$. On the one leaf the liquid contains more A , on the other leaf more B than the vapour.

Let us assume that in the binary system $A + B$ a compound F occurs. The region $E = F + L$ has then no limit-line E_0 , but a turning-line E_R ; this is the melting-line of the compound F . The region $E = F + L$ is, therefore two-leaved, in the one leaf are situated the liquids, which contain a surplus of A with respect to F , in the other leaf are situated the liquids, which contain a surplus of B .

The region $E = F + G$ of the binary equilibrium $A + B$ has also no limit-line, but a turning-line E_R ; this is the sublimation-curve of the compound F .

We take a ternary system with the three volatile components A , B , and C , in which occurs a binary compound F of B and C . We now take the equilibrium $E = F + L + G$, in which consequently G contains also the 3 components. [Compare also "Equilibria in ternary systems XI"; in fig. 6 of this communication the arrow in the vicinity of point F on the curve going through the point F has to point in the other direction].

This region E has a limit-line $E_{A=0}$; consequently this represents the equilibrium $F + L + G$ of the binary system $B + C$ and it is indicated in fig. 3 by curve acd ; it has in b a maximum of pressure and in c a maximum-temperature.

When no equilibrium E_R occurs, then the region E is one-leaved and consequently it must be situated in fig. 3 within curve $abcd$.

[Therefore, it does not extend itself, as is drawn in fig. 3 over af].

When an equilibrium E_R exists [this is the case when the 3 phases in the concentration-diagram are situated on a straight line] then also a turning-line E_R exists, this is represented in fig. 3 by ef . This point of contact f represents the equilibrium $E_{R_A=}$.

The region E is now two-leafed, afe is the one, dcf is the other leaf.

When we consider the equilibrium $E = F + L + G$ at a constant T , lower than T_f , then the pressure on the turning-line ef is a maximum; when the turning-line was represented by gh , then the pressure would be a minimum.

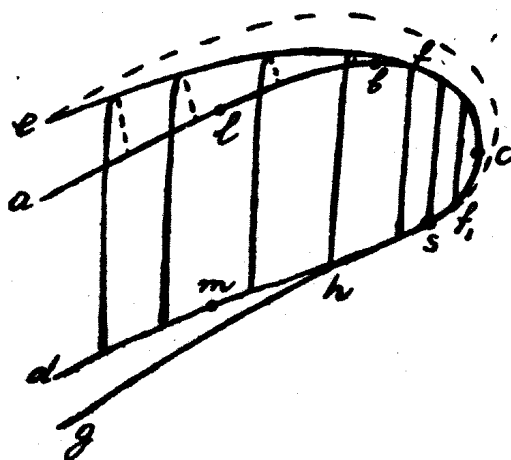


Fig. 3.

On curve acd is situated in the vicinity of c a solution s , which has the same composition as the compound F . When F melts with increase of volume, then s is situated on branch dc , as in fig. 3.

It is apparent from formula 17 of the communication on "Equilibria in ternary systems XI": when we enter at constant T starting from the point s the region $E = F + L + G$, then the pressure must increase.

Hence it follows, that the point of contact h of curve gh must always be situated on branch ds and that of curve ef always on branch as . In the latter case the point of contact may, therefore, also be situated between s and c e.g. in f_1 ; then we get a limit-curve like ef_1 . The equilibrium $E = F + L + G$ then still exists at temperatures above T_c , the highest temperature at which the equilibrium $E_{A=0}$ may occur.

Let us now consider the equilibrium $E = B + L + G$ of the

ternary system $A + B + C$. [Compare also "Equilibria in ternary systems XIII" February 1914]. The region E has then two limit-lines $E_{A=0}$ and $E_{C=0}$. The first represents the monovariant equilibrium $B + L + G$ of the binary system $B + C$; the second the same monovariant equilibrium of the binary system $A + B$. Each of those curves may either have a point of maximum-pressure or not, so that we may distinguish three cases. When in the equilibrium E does not occur an equilibrium E_R , then the region E is situated completely within the limit-lines and it is, therefore, one-leaved; when an equilibrium E_R occurs, then also a turning-line exists and the region is, therefore, two-leaved.

Two limit-lines ab and cd may intersect one another in a point s (fig. 4); this means that the two equilibria E_0 have the same pressure P_s at the temperature T_s . In this case there is always a limit-curve ef (fig. 4), which may be situated as well above as below the point s . The turning-line ef may touch the curves cs and sb in fig. 4.

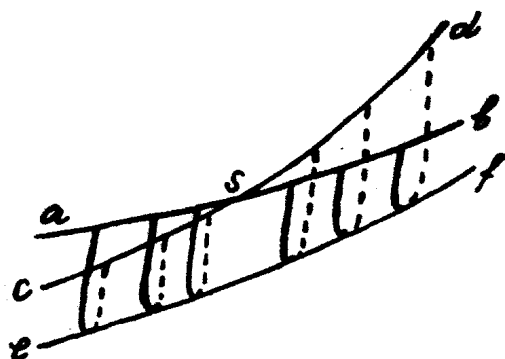


Fig. 4.

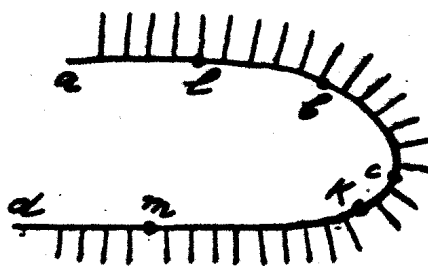


Fig. 5.

Let us now consider the equilibrium $E = L_1 + L_2 + G$, in which L_1 and L_2 represent two liquid-phases. [In a similar way we may also discuss the equilibria $L_1 + L_2 + F$, $M_1 + M_2 + L$ and $M_1 + M_2 + G$, etc., in which M_1 and M_2 represent mixed crystals]. When in the equilibrium $E = L_1 + L_2 + G$ the two liquids become identical, then a critical equilibrium exists: $E_K = L_K + G$. Curve E_K may have a form, like curve acd ¹⁾ in fig. 3. When in the equilibrium E_K the quantity of one of the components e.g. of A , approaches to zero, then curve E_K has a terminating-point $E_{K.A=0}$.

When acd represents in fig. 3 the critical curve E_K , then the region $E = L_1 + L_2 + G$ is situated either completely within curve

¹⁾ Compare also F. A. H. SCHREINEMAKERS, Archives Néerl. Serie II. VI. 170 (1901).

acd or it is partly two-leafed with the turning-line ef or gh . Also in fig. 5 a critical curve E_K is represented by acd ; the region E is situated here, however, completely outside the critical curve and it may have a turning-line also in this case.

We take in figs. 3 and 5 two points l and m on a vertical line; consequently we have $T_l = T_m$. At the temperature $T_l = T_m$ two equilibria E_K exist, therefore, the one [$E'_K = L'_K + G$] under the pressure P_l , the other [$E''_K = L''_K + G$] under the pressure P_m .

The critical liquids L'_K and L''_K may now belong either or not to the same region of un-mixing under its own vapour-pressure of the temperature $T_l = T_m$. When they belong to the same region of un-mixing, then the region E is situated as in fig. 3; when they belong to different regions of un-mixing, then the region E is situated as in fig. 5; in both cases either a turning-line may occur or not.

We might think that in point c of figs. 3 or 5 two critical liquids get the same composition, so that L_c should be a critical liquid of the 2nd order. This is, however, not the case in the point c , but in another point K of the curve; this is drawn in fig. 5 on branch dc . Curve acd touches in this point a curve KK_1 (not drawn in the figure); the points of this curve KK_1 represent critical liquids of the 2nd order. Of all those liquids only the liquid K can be in equilibrium with vapour.

More-leafed regions.

Besides one- and two-leafed regions, of which we have considered above some examples, also more-leafed regions may occur. This may take place e.g. when in the region E occur two turning-lines. We shall consider a definite case for fixing the ideas. For this we take the equilibrium $E = B + L + G$ of a ternary system with the three volatile components A , B , and C . This equilibrium E has two limit-lines $E_{A=0}$ and $E_{C=0}$; these are represented in the concentration-diagram (fig. 6) by the sides BC and BA of the triangle ABC , in the P, T -diagram (fig. 7) by the curves $aeil$ and $dhkn$. When we imagine in fig. 7 those two curves to be prolonged towards higher T , then both curves terminate in a point B , which represents the P and T of the melting-point under its own vapour-pressure of the substance B . Above we have already said that these curves may have a maximum of pressure or not.

The equilibrium $E = B + L + G$ consists at a temperature T_0 of a series of solutions, which are saturated with solid B and a series of corresponding vapours. This series of solutions forms the saturation

curve under its own vapour-pressure of B , the corresponding vapours form the vapour-saturation-curve. [Compare also: Equilibria in ternary systems XIII, February 1914]. In fig. 6 curve $abcd$ represents a saturation-curve of B under its own vapour-pressure, the corresponding vapour-saturation-curve has not been drawn. Now we assume that on curve ad occurs a point of minimum-pressure b and a point of maximum-pressure c ; then the pressure increases along ad in the direction of the little arrows.

Now we imagine in the P, T -diagram (fig. 7) a vertical line, which corresponds with the temperature T_a . It appears from fig. 6 that the points a, b, c and d must be situated in the P, T -diagram with respect to one another as in fig. 7; of course those four points must be situated on the same vertical line; for the sake of clearness a small deviation from the true position has been allowed in fig. 7.

In accordance with fig. 6, therefore also in fig. 7 at the temperature T_a the pressure first decreases starting from a as far as in b ,

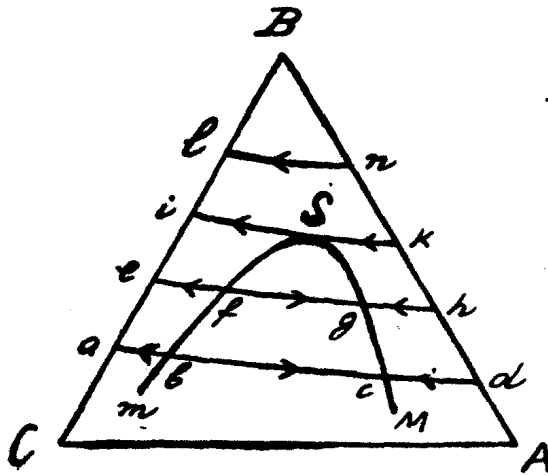


Fig. 6.

afterwards it increases starting from b up to c and further it decreases again starting from c as far as in d . The points b and c are drawn in fig. 7 within both the limit-lines; it is apparent, however, that b might be situated also below curve dn and that c might be situated also above curve al .

Now we take a temperature T_e ; the saturation-curve under its own vapour-pressure

is represented in fig. 6 by curve eh ; it has a point of minimum-pressure in f , or point of maximum-pressure in g . We find the corresponding points in fig. 7. Now we assume that on increase of T the point of minimum- and the point of maximum pressure of the saturation-curve under its own vapour-pressure come nearer to each other and that they coincide at T_i in the point S . Then the pressure increases along curve iSK (figs. 6 and 7) starting from K towards i . In the P, T -diagram the points i, S and K must then be situated with respect to one another, as in fig. 7; it is evident that the point S must be situated between the points i and K .

At temperatures above T_i , e.g. at T_l , the saturation-curves under

