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The total amount of chemical energy which was set free in germination was therefore always larger than the quantity of energy given off as heat to the surroundings. A part of the free energy which became available in the process of germination was therefore evidently used for other purposes (osmosis etc.) than for heat-evolution only.

This was however doubtful only on the second day, the evolution of heat on that day was not determined; the loss of energy, calculated from the heat of combustion, was however so small in this period that it is very possible that the evolution of heat at that moment was larger. If afterward it should appear that this is really the case, it would be very intelligible. For in the beginning of germination imbibition will principally take place so that in this case evolution of heat is not at all necessarily connected with chemical transformations.

The results of this investigation may therefore be summarized as follows. ·

The loss of energy calculated from the heat of combustion as well as the evolution of heat increase with the duration of germination.

Both are small at the beginning of germination and greatly increase, chiefly on the 3$^{\text{id}}$ day.

The evolution of heat is greatly dependent on the surrounding temperature.

The optimum of heat-evolution is roughly 35°.

The total loss of energy during germination at 20° exceeds the loss of energy by evolution of heat at the same temperature.

Utrecht, 1914.   *Botanical Laboratory.*

Chemistry. — *"Equilibria in ternary systems XV"*. By Prof. F. A. H. Schreinemakers.

(Communicated in the meeting of April 24, 1914).

In our previous considerations on saturationcurves under their own vapourpressure and on boilingpointcurves we have considered the general case that each on the three components is volatile and occurs consequently in the vapour. Now we shall assume that the vapour contains only one or two of the components. Although we may easily deduce all appearances occurring in this case from the general case, we shall yet examine some points more in detail.

The vapour contains only one component.

We assume that of the components A, B, and C the first two are extremely little volatile, so that practically we can say that the vapour consists only of C. This shall e.g. be the case when A and B are two salts and C a solvent, as water, alcohol, benzene, etc.

Theoretically the vapour consists always of $A + B + C$; the quantity of A and B, however, is generally exceedingly small, compared with the quantity of C, so that the vapour consists practically completely of C.

When, however, we consider complexes in the immediate vicinity of the side AB, circumstances change. A complex or a liquid situated on this side has viz. always a vapourpressure, although this is sometimes inmeasurably small; consequently there is also always a vapour, consisting only of $A + B$ without C. When we take a complex in the immediate vicinity of the side AB, the quantity of C in the vapour is, therefore, yet also exceedingly small in comparison with the quantity of $A + B$.

Considering equilibria, not situated in the vicinity of the side AB, we may, therefore, assume that the vapour consists only of C; when, however, these equilibria are situated in the immediate vicinity of the side AB, we must also take into consideration the volatility of A and B and we must consider the vapour as ternary.

Considering only the occurrence of liquid and gas, as we have formerly seen, three regions may occur, viz. the gasregion, the liquid-region and the region $L-G$. This last region is separated from the liquid-region by the liquid-curve and from the vapour-region by the vapourcurve.

As long as the liquid-curve is not situated in the immediate vicinity of AB, this last curve, as a definite vapour of the vapourcurve is in equilibrium with each liquid of the liquid-curve, will be situated in the immediate vicinity of the anglepoint C. Therefore, the gas-region is exceedingly small and is reduced, just as the gascurve, practically to the point C. Consequently we distinguish within the triangle practically only two regions, which are separated by the liquid-curve, viz. the liquid-region and the region $L-G$; the first reaches to the side AB, the last to the anglepoint C. The conjugation-lines liquid-gas come together, therefore, practically all in the point C.

When, however, the liquid-curve comes in the immediate vicinity of the side AB, so that there are liquids which contain only exceedingly little C, then in the corresponding vapours the quantity of A and B will be large with respect to C. The vapour-curve will

then also be situated further from the anglepoint C and closer to the side AB, so that also the vapour region is large. At a sufficient decrease of pressure or increase of temperature, the vapour-region shall even cover the whole components-triangle. Consequently it is absolutely necessary that we must distinguish the three regions, of which the movement, occurrence, and disappearance were already formerly treated.

When the equilibrium $F + L + G$ occurs, we may now deduce this in the same way as it was done formerly for a ternary vapour.

a) The solid substance is a ternary compound or a binary compound, which contains the volatile component C.

For fixing the ideas we shall assume that in the triangle ABC of fig. 1 which is partly drawn, the point C represents water, F an aqueous doublesalt, F' and F'' binary hydrates. In accordance with our previous general deductions we now find the following.

The saturationcurves under their own vapour-pressure are circum- or explased at temperatures below T_s (T_s = minimum meltingpoint of the solid substance under consideration). The corresponding vapour-curves are reduced to the point C. When these substances melt with
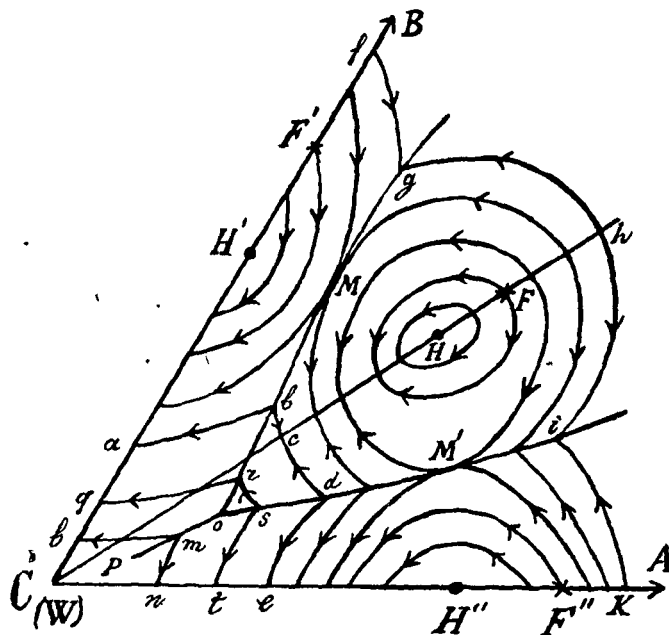

Fig. 1.

increase of volume, the points H, H' and H'' are situated with respect to F, F' and F''' as in fig. 1 ; when they melt with decrease of volume, these points are situated on the other side.

In fig. 1 different saturationcurves are completely or partly drawn, the pressure increases along them in the direction of the arrows. Further it is apparent that along the saturationcurve of F the pressure is maximum or minimum in its points of intersection with the line CF; the point of maximumpressure is situated closest to C. On the curve $b c d i h g$ of fig. 1, which is only partly drawn, c is, therefore, a point of maximum-, h a point of minimumpressure.

The pressure along a saturationcurve of the binary hydrate F' (or F'') is highest in the one and lowest in the other end, without being however in these terminating points maximum or minimum. On the curve $a b g f$ of fig. 1 which is only partly drawn, the pressure in a is the highest and in f the lowest.

This is also in accordance with the rule, formerly deduced, that the pressure is maximum or minimum, when the phases F, L, and G are situated on a straight line, but that this is no more the case when this line coincides with a side of the triangle.

As the vapour has always the composition C here the point of maximum- and that of minimumpressure of the saturationcurve of F are, therefore, always situated on the line CF; the saturationcurves of F' and F''' can, however, not have a point of maximum- or minimum-pressure.

As we may obtain all solutions of the line $C h$ (CB and CA) by adding water to F (F' and F'') or removing water from F (F' and F''), we shall call the solutions of $C h$ (CB and CA) pure solutions of F (F' and F''). Further we call the solutions of CH (CH' and CH'') rich in water and those of $H h$ ($H'B$ and $H''A$) solutions poor in water. Consequently in fig. 1 a, c and e represent pure solutions rich in water and f, h and k pure solutions poor in water. We may express now the above in the following way:

Of all solutions saturated at constant T with a binary or ternary hydrate, the pure solution rich in water has the greatest and the pure solution poor in water the lowest vapourpressure Therefore, the pressure increases along the saturationcurve from the pure solution poor in water towards the pure solution rich in water. When the solid substance is a ternary hydrate, the highest pressure is at the same time a maximum- and the lowest pressure also a minimum pressure.

We see that this is in accordance with the direction of the arrows in fig. 1.

b) The solid substance is the component A or B or a binary compound of A and B; therefore, it does not contain the volatile component C.

In fig. 2 some saturationcurves under their own vapourpressure of A ($a\,k, b\,l, c\,m, o\,n$) and of B ($h\,i, g\,l, f\,m, pn$) are completely or partly drawn. When in one of the binary systems, e.g. in CB, there exists a point of maximumtemperature H', then also there occur saturationcurves as the dotted curve $q\,r$. As long as we consider solutions, not situated in the vicinity of $A\,B$,-the vapour region is represented by point C. When we consider, however, also solutions in the vicinity of $A\,B$, the vapour region expands over the triangle.
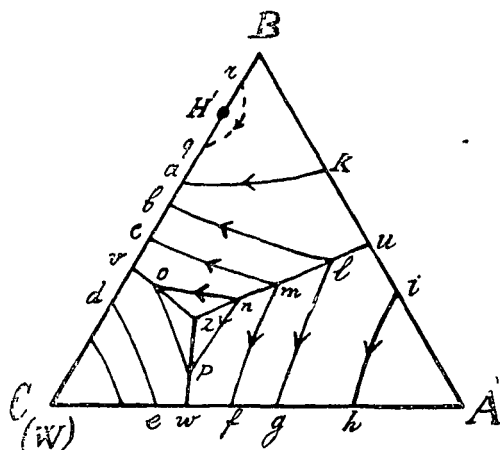

Fig. 2.

Consequently, when we deduce the saturationcurves under their own vapour-pressure, assuming that the vapour is represented by C, we may do this only for solutions, not situated in the vicinity of AB. For points of the curves in the vicinity of AB we take the case, treated already in communication XIII that the vapour is ternary. The same applies, as H' is situated in the vicinity of B, also to the curves in the vicinity of H'.

If follows from the deduction of the saturationcurves that the pressure, e.g. along $a\,k$, continues to decrease from a; only in the vicinity of k, a point of minimumpressure may perhaps be situated. As the pressure in b and consequently also in the minimum possibly occurring is exceedingly small and practically zero, we can say: along the saturationcurve of a component the pressure increases from the solution free from water (k) towards the pure solution (a). The pressure of the solution free from water is practically zero.

Let us now take a binary compound of A and B (for instance an anhydric double-salt); it may be imagined in fig. 2 to be represented by a point F on AB. When we leave out of account saturationcurves in the vicinity of F, we may say that the saturationcurves under their own vapourpressure have two terminatingpoints, both situated on AB. As the pressure is again very small in both the terminatingpoints, it follows: along the saturationcurve of an anhydric double-salt, the pressure increases from each of the solutions free from water towards the pure solution.

c) The solid substance contains the volatile component C only. This is for instance the case when an aqueous solution of two

salts is in equilibrium with ice; the saturation- or icecurve under its own vapourpressure has then, as curve ed in fig. 2, one terminatingpoint on CA and one on CB. We find further: along an icecurve under its own vapourpressure the pressure is the same in all points and it is equal to the pressure of sublimation of the ice.

We may deduce the previous results also in the following way. As the vapour consists only of C, we equate, in order to find the conditions of equilibrium for the system $F + L + G$ in (1) (II) $x_1 = 0$ and $y_1 = 0$. We then find:

$$Z - x\frac{\partial Z}{\partial x} - y\frac{\partial Z}{\partial y} = Z_1 \text{ and } Z_1 + \alpha\frac{\partial Z}{\partial x} + \beta\frac{\partial Z}{\partial y} = \zeta \quad . \quad . \quad . \quad . \quad (1)$$

For the saturationcurve of F under its own vapourpressure we find:

$$(x r + y s)\, dx + (x s + y t)\, dy = - C\, dP \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$(\alpha r + \beta s)\, dx + (\alpha s + \beta t)\, dy = - (A + C)\, dP \quad . \quad . \quad . \quad (3)$$

which relations follow also immediately from 8 (II) and 9 (II). In order that the pressure in a point of this curve should be maximum or minimum, dP must be $= 0$. This can be the case only, when

$$\alpha y = \beta x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This means that the liquid is situated in the point of intersection of the curve with the line CF, consequently, that the liquid is a pure solution of F. Consequently we find: along a saturationcurve under its own vapourpressure of a ternary substance, the pressure is maximum or minimum in the pure solutions.

In order to examine for which of the two pure solutions the pressure is maximum and for which it is minimum, we add to the first part of (2) still the expressions:

$$\frac{1}{2}\left(r + x\frac{\partial r}{\partial x} + y\frac{\partial s}{\partial x}\right)dx^2 + \left(s + x\frac{\partial r}{\partial y} + y\frac{\partial s}{\partial y}\right)dx dy + \frac{1}{2}\left(t + x\frac{\partial s}{\partial y} + y\frac{\partial t}{\partial y}\right)dy^2 + ..$$

and to the first term of (3):

$$\frac{1}{2}\left(\alpha\frac{\partial r}{\partial x} + \beta\frac{\partial s}{\partial x}\right)dx^2 + \left(\alpha\frac{\partial r}{\partial y} + \beta\frac{\partial s}{\partial y}\right)dx dy + \frac{1}{2}\left(\alpha\frac{\partial s}{\partial y} + \beta\frac{\partial t}{\partial y}\right)dy^2 + ...$$

Now we subtract (2) from (3), after that (2) is multiplied by α and (3) by x. Substituting further their values for A and C, we find:

$$\frac{1}{2}\alpha\left(r dx^2 + 2s dx dy + t dy^2\right) = [(x - \alpha) V_1 + \alpha V - xv]dP. \quad . \quad (5)$$

Representing the change of volume, when one quantity of vapour

arises at the reaction between the phases F, L and G, by ΔV_1 (5) passes into:

$$\frac{1}{2} \alpha \left(r dx^2 + 2s dx dy + t dy^2\right) = (x - \alpha) \Delta V_1 \times dP \quad . \quad . \quad . \quad (6)$$

Let us consider now in fig. 1 the pure solutions of F, therefore the solutions of the line Ch. For points between C and F $x - \alpha < 0$, for the other points $x - \alpha > 0$. Considering only the solutions of the line Ch, we can consider the system $F + L + G$ as binary. Imagining a P, T-diagram of this system, H is the point of maximum-temperature. From this it is apparent that ΔV_1 is negative between H and F, positive in the other points of the line Ch. From this it follows:

$(x - \alpha)$ ΔV_1 is negative in points between C and H, therefore for the solutions of F rich in water.

$(x - \alpha)$ ΔV_1 is positive in the other points of this line, therefore, for the solutions of F poor in water.

The same applies also when the point H is situated on the other side of F.

Let us take now a pure solution rich in water of F, for instance solution c of the fig. 1; as the first term of (6) is positive and $(x - \alpha) \Delta V_1$ is negative, it follows: dP is negative. This means that the pressure is a maximum in c.

When we take a pure solution poor in water of F, for instance solution h of figure 1, $(x - \alpha) \Delta V_1$ is positive, therefore, the pressure is a minimum in h.

In accordance with the previous considerations, we find, therefore, that the pressure along the saturationcurve of a ternary compound is a minimum for the pure solution poor in water and a maximum for the pure solution rich in water.

When the solid substance is a binary compound, as F' in fig. 1 or 3, we must equate $\alpha = 0$. (Of course $\beta = 0$ for the compound F''). (2) and (3) pass now into:

$$(xr + ys) dx + (xs + yt) dy = -C dP \quad . \quad . \quad . \quad . \quad (7)$$
$$\beta s dx + \beta t dy = -(A + C) dP , \quad . \quad . \quad . \quad . \quad (8)$$

From this we find:

$$\beta x (rt - s^2) dx = [(xs + yt)(A + C) - \beta C] dP \quad . \quad . \quad . \quad (9)$$

From this it is apparent that dP can never be zero or in other words: on the saturationcurve of a binary hydrate never a point of maximum- or of minimumpressure can occur.

In the terminatingpoint of a saturationcurve on BC $x = 0$; as

$Lim\ r = \dfrac{RT}{x}$, while t and s remain finite, it follows, when we replace also A and C by their values:

$$\beta\,.\,RT\,.\,dx = [(y - \beta)\ V_1 + \beta V - yv]\,dP\,.\quad\ldots\quad(10)$$

Representing by ΔV_1 the change of volume, when one quantity of vapour arises at the reaction between the three phases (F', L and G), (10) passes into:

$$\beta RT\,.\,dx = (y - \beta)\,\Delta V_1\,.\,dP\quad\ldots\ldots\quad(11)$$

For solutions between C and F' is $y - \beta < 0$, between F' and B is $u - \beta > 0$. Imagining a P,T-diagram of the binary system $F' + L + G$, H' is the point of maximum temperature; ΔV_1 is consequently negative between H' and F', positive in the other points of CB. From this it follows: $(y - \beta)\,\Delta V_1$ is negative in points between C and H', therefore, for the solutions rich in water; $(y-\beta)$ ΔV_1 is positive in points between H' and B, therefore for the solutions of F' poor in water.

From (11) it now follows: dP is negative for liquids on CH', positive for liquids on $H'B$. In accordance with our former results consequently we find: along the saturationcurve of a binary hydrate the pressure increases from the pure solution poor in water towards the pure solution rich in water.

When F is one of the components, which are not volatile, e.g. B in fig. 2, then $\alpha = 0$ and $\beta = 1$. From (11) then follows:

$$RT\,.\,dx = (y - 1)\,\Delta V_1\,.\,dP.\quad\ldots\ldots\quad(12)$$

We now imagine a P,T-diagram of the binary system $B + L + G$; this may have either a point of maximumtemperature H' in the vicinity of the point B or not. When a similar point does not exist, ΔV_1 is always positive; when a similar point does exist, ΔV_1 is positive between C and H', negative between H' and B. As we leave, however, here out of account points, situated in the vicinity of B, ΔV_1 is positive. As $y - 1$ is always negative, it follows from (12) that dP is negative. In accordance with our former results we find therefore: along the saturationcurve of a component the pressure decreases from the pure solution towards the solution free from water.

When F is the volatile component, as for instance in the equilibrium $ice + L + G$, then $\alpha = 0$ and $\beta = 0$. The second of the conditions of equilibrium (1) passes now into: $Z = \zeta$. This means that not a whole series of pressures belongs to a given temperature, but only one definite pressure, viz. the pressure of sublimation of the ice. Therefore we find again: along an icecurve under its own

vapour pressure the pressure is the same in all points and equal to the pressure of sublimation of the ice.

Now we shall consider the boilingpointcurves; in general the same applies to them as to the saturationcurves under their own vapourpressure, which we have considered above.

Now we assume that the curves in fig. 1 represent boilingpointcurves; the point H no longer represents a point of maximum temperature, but a point of maximum pressure; consequently it is always situated between C and F. This point of maximumpressure H is always situated closer to C than the point of maximum temperature H; the same applies to the points H' and H'' in the figs. 2 and 3. Wishing to indicate by arrows the direction in which the temperature increases, we must give the opposite direction to the arrows in the figs. 1—3.

We saw before that on the side CB of fig. 2 a point of maximumtemperature H' may either occur or not; on this side, however, always a point of maximumpressure is situated. The same applies to the side CA. We now find the following.

a) of all solutions saturated under constant P with a binary or ternary hydrate, the pure solution rich in water has the lowest — and the pure solution poor in water the highest boilingpoint. Therefore, the boilingpoint increases along the boilingpointcurve from the pure solution rich in water towards the pure solution poor in water. When the solid substance is a ternary hydrate, the highest boilingpoint is at the same time a maximum- and the lowest at the same time a minimumboilingpoint.

b) along the boilingpointcurve of a component or of an anhydric double-salt the boilingpoint increases from the pure solution. When the solid substance is an anhydric double-salt, the boilingpoint of the pure solution is at the same time a minimum.

c), along the curve of the solutions saturated with ice under a constant pressure the boilingpoint is the same in all the points and it is equal to the sublimationpoint of the ice.

The icecurve under its own vapourpressure of the temperature T and the boilingpointcurve of the ice under the pressure P coincide, therefore, when P is the pressure of sublimation of the ice at the temperature T.

The following is amongst others apparent from what precedes. We take a pure solution of a solid substance (component, binary or ternary compound). Through this solution pass a saturationcurve

under its own vapourpressure and a boilingpointcurve. Generally we now have: when the vapour pressure at a constant T decreases (or increases) from the pure solution, the boilingpoint under a constant P will increase (or decrease).

This, however, is no more the case for solutions between the point of maximumpressure and the point of maximumtemperature. The point of maximumpressure is situated viz. closer to the point C than the point of maximumtemperature. When we take a solution between these points, it is a solution rich in water with respect to the saturationcurve under its own vapourpressure, a solution poor in water, however, with respect to the boilingpointcurve. Consequently as well the pressure along the saturationcurve as the temperature along the boilingpointcurve will decrease from this solution.

We may express the foregoing also in the following way: the vapourpressure (at constant T) and the boilingpoint (under constant P) change from a pure solution generally in opposite directions. When, however, the pure solution is situated between the point of maximumpressure and the point of maximumtemperature, then as well the vapourpressure as the boilingpoint decrease from this solution.

Formerly we have already considered the saturationcurve under its own vapourpressure of two solid substances (viz. the equilibrium $F + F' + L + G$); now we shall discuss some points more in detail. It should be kept in mind in this case that all deductions apply also now to points, which are not situated in the vicinity of AB. The deductions discussed already formerly apply to points in the vicinity of this line.

Let us take the solution m of fig. 2 saturated with $A + B$, therefore, the equilibrium $A + B + L_m + G$. As the pressure increases from m towards c and towards f, we may say: the solution saturated with two components has a smaller vapourpressure than the pure solution of each of the components separately.

When we consider the solution p of fig. 2 saturated with $ice + A$ and when we imagine curve np to be extended up to CA, it appears: the solution saturated with $ice + A$ has a greater vapourpressure than the solution saturated with $A + B$ and a smaller vapourpressure than the metastable pure solution of A.

In the previous communication we have already discussed the curves zu, zv, and zw; zu represents the solutions of the equilibrium $A + B + L + G$, zw those of the equilibrium $ice + A + L + G$ and zv these of the equilibrium $ice + B + L + G$, w and v are binary, z is the ternary cryohydric point under its own vapourpressure.

Let us now contemplate the solution m of fig. 3 saturated with the hydrates $F + F'$; it is apparent from the figure that solution m has a smaller vapourpressure than l or n. When we take however
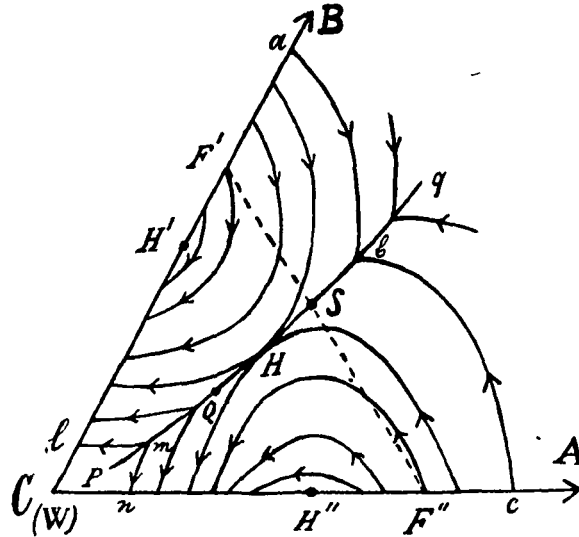

Fig. 3.

the solution b, saturated with these hydrates, this has a larger vapourpressure than the solutions a and c.

Curve pq represents the solutions of the equilibrium $F+F'+L+G$; point H is the point of maximumtemperature of this curve. In accordance with our previous definitions we call the liquids of branch pH rich in water and those of branch Hq poor in water. We then may express what precedes in this way:

the solution saturated with two components or with their hydrates has in the region rich in water always a smaller vapourpressure, in the region poor in water always a greater vapourpressure than the pure solution of each of the substances separately.

Let us now take a liquid saturated with a double salt and one of its limit-substances. [In fig. 1 the series of solutions saturated with F of curve bcd is limited in b by the occurrence of F' and in d by the occurrence of F''. Therefore we shall call F' and F'' the limit-substances of the double-salt F]. Curve po represents the solutions of the equilibrium $F + F' + L + G$, curve og those of the equilibrium $F' + F + L + G$ and curve oi those of the equilibrium $F'' + F + L + G$. M and M' are points of maximumtemperature of these curves. In accordance with previous definitions we call solutions of oM and oM' rich in water and those of Mg and $M'i$ poor in water.

The following is apparent from the direction of the arrows in fig. 1.

a. In the region of the liquids rich in water. When a doublesalt is soluble in water without decomposition, the solution saturated with this double-salt and with one of its limit-substances has a smaller vapourpressure than the pure solution of the doublesalt and also than that of the limit-substance.

When a double-salt is decomposed by water, the solution saturated with this double-salt and one of its limit-substances has a smaller vapour pressure than the pure solution of the limit-substance. The solution saturated with double-salt and with the limit-substance, which is not separated, has a smaller vapour-pressure than the solution, saturated with double-salt and with the limit-substance, which is separated.

b. In the region of the liquids poor in water the opposite takes place.

As a special case a liquid can be saturated with two substances of such a composition, that one of these may be formed from the other
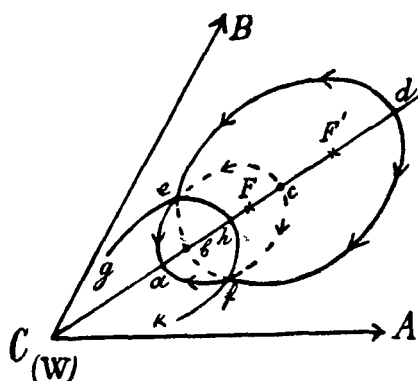

Fig 4.

by addition of water. They are represented then by two points F and F'', which are situated with C on a straight line. In fig. 4 this line CFF'' does not coincide with one side of the triangle. In this figure $a\,e\,c\,f$ is a saturationcurve under its own vapourpressure of F, curve $b\,e\,d\,f$ one of F''; the arrows indicate the direction, in which the pressure increases. Both the curves can be circum- or exphased and they either intersect or they do not. In fig. 4 they intersect in e and f, so that the equilibria $F + F'' + L_e + G$ and $F + F'' + L_f + G$ occur. Now we can prove that the vapour pressure of those two equilibria is the same, therefore $P_e = P_f$. When we remove viz. the liquid from both the equilibria, we retain $F + F'' + G$. As between these three phases the reaction $F \rightleftarrows F'' + G$ is possible, we can consider $F + F'' + G$ as a binary system. We then have two components in three phases, so that the equilibrium is monovariant. At each temperature $F + F'' + G$ has, therefore, only one definite vapourpressure, from which immediately follows:
$P_e = P_f$.

6

Curve $gehfk$ in fig. 4 indicates the solution of the equilibrium $F + F' + L + G$; when in a P, T-diagram we draw the curve $F + F' + G$ (consequently the curve of inversion $F \rightleftarrows F' + G$) and curve $F + F' + L + G$, then they coincide.

In fig. 5 the line CFF' coincides with the side BC of the triangle; we assume viz. that the component B and its hydrate F occur as solid substances; further we have also assumed that the component A occurs as solid substance. The curves bc, fy and ik are saturation-curves under their own vapourpressure of A, ih and ef of B, ab and de of the hydrate F; the arrows indicate again the direction in which the pressure increases.

It is apparent from the figure that vz represents the solutions of the equilibrium $A + F + L + G$, zw those of $A + B + L + G$

Fig 5.

and zu those of $B + F + L + G$. Consequently in z the invariant equilibrium $A + B + F + L + G$ occurs. Curve zu terminates on side BC in the quadruplepoint u with the phases $B + F + L + G$ of the binary system CB. When we remove the liquid L_e from the equilibrium $B + F + L_e + G$ occurring at the temperature T_e and under the pressure P_e, we retain the monovariant binary equilibrium $B + F + G$. When we draw in a P, T-diagram the

curve $B + F + G$ (therefore the curve of inversion $F \rightleftarrows B + G$) and curve $B + F + L + G$, these two curves coincide. We can say, therefore:

the vapourpressure of a solution, saturated with a component and with its hydrate, is equal to the pressure of inversion of the hydrate (the pressure of the reaction $F \rightleftarrows B + G$).

From the direction of the arrow on de it follows that the pressure in e is smaller than in d. We can say, therefore:

the solution saturated with a component and with one of its hydrates has a lower pressure than the pure solution of the hydrate.

The same considerations apply also when two hydrates of a same component occur.

We may summarise the previous results in the following way. Through each solution saturated with two solid substances go two saturationcurves; when we limit ourselves to the stable parts of
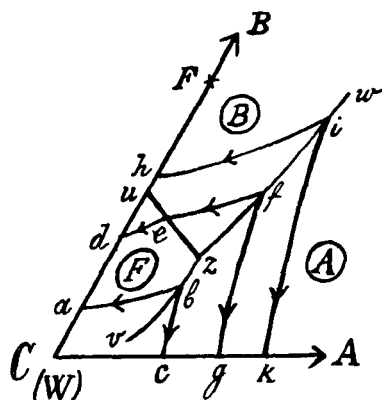
these curves, we may say that two saturationcurves proceed from such a solution. Then we may say :

1. The two solid substances are situated in opposition with respect to the line LG.

a. The solution saturated with these substances is rich in water.

The pressure increases from this solution along the two saturationcurves.

b. The solution saturated with these substances is poor in water. The pressure decreases from this solution along the two saturationcurves.

2. The two solid substances are situated in conjunction with respect to the line LG.

a. The solution saturated with these substances is rich in water.

The pressure decreases from this solution along the saturationcurve of that solid substance which is situated closest to the line LG; the pressure increases along the other saturationcurve.

b. The solution saturated with these substances is poor in water.

The same as sub 2^a.; we must take however the changes of pressure in opposite direction.

3. The two solid substances are situated on a straight line with the vapour.

The pressure increases from the solution saturated with these substances along the saturationcurve of the substance with the largest amount of water, it decreases along the saturationcurve of the substance with the smallest amount of water.

We find examples of 1^a in the equilibria :

$F+F'+L_b+G$ (fig. 1), $F+F'''+L_d+G$ (fig. 1), $A+B+L_m+G$ (figs. 1 and 2), $F'+F'''+L_m+G$ (fig. 3), $A+B+L_b+G$ (fig. 5) and $F+A+L_f+G$ (fig. 5).

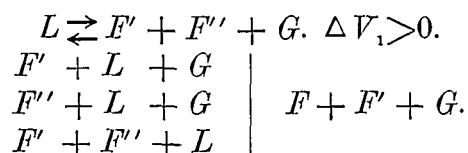We find examples of 1^b in the equilibria: $F+F'+L_g+G$ (fig. 1), $F+F'''+L_i+G$ (fig. 2) and $F'+F'''+L_b+G$ (fig. 3).

An example of 2^a is found in the equilibrium $F+F'+L_i+G$ (fig. 1).

We find examples of 3 in the equilibria: $F+F'+L_e+G$ (fig. 4), $F+F'+L_f+G$ (fig. 4) and $B+F+L_e+G$ (fig. 5).

We may deduce the above-mentioned rules also in the following way. We shall viz., while the temperature remains constant, change the volume of the system $F + F' + L + G$, so that a reaction takes place between the phases and there remains at last a three-phase-equilibrium. As this reaction is determined by the position of the four points with respect to one another, we may immediately distinguish the above-mentioned cases 1, 2, and 3. When we call

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the change of volume, when one quantity of vapour is formed at the reaction, ΔV_1, then ΔV_1 is always positive, except when the liquid is represented by a point of the fourphase-curve between the point of maximumtemperature and the intersectingpoint of this curve with the line FF''. When we now apply the rule: "the equilibria, which arise at increase (decrease) of volume, are stable under lower (higher) pressure", we may easily refind the above-mentioned rules.
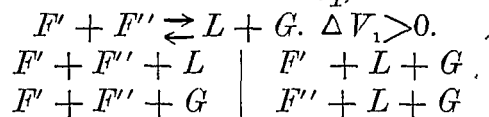
When we take as an example fig. 3 in which the case sub 1 occurs, the equilibrium $F' + F'' + L + G$ is represented by curve pq, which intersects the line $F'F''$ in S; H is the point of maximumtemperature of this curve. Consequently $\Delta V'$ is positive on pH and Sq, negative on HS; the solutions of pH are rich in water, those of Hq poor in water. When we take a liquid rich in water, the reaction is:

$$L \rightleftarrows F' + F'' + G. \quad \Delta V_1 > 0.$$
$$\begin{array}{c|c}
F' + L + G & \\
F'' + L + G & F + F' + G. \\
F' + F'' + L &
\end{array}$$

As the reaction proceeds from left to right with increase of volume ($\Delta V_1 > 0$), the equilibrium to the right of the vertical line occurs on decrease of pressure and the equilibria to the left of the vertical line occur on increase of pressure. Therefore, from each point of branch pQ the equilibria $F' + L + G$ and $F''' + L + G$ proceed towards higher pressures; consequently we find the rule 1^a.

When we take a liquid poor in water, this is situated on HS or on Sq. When it is situated on HS, the above-mentioned reaction applies also, but $\Delta V_1 < 0$. Therefore, from each point of branch HS the equilibria $F' + L + G$ and $F'' + L + G$ proceed towards lower pressures; this is in accordance with rule 1^b.

When we take a solution of branch Sq, the reaction is:

$$F' + F'' \rightleftarrows L + G. \quad \Delta V_1 > 0.$$
$$\begin{array}{c|c}
F' + F'' + L & F' + L + G. \\
F' + F'' + G & F'' + L + G
\end{array}$$

As the reaction proceeds from left to right with increase of volume the equilibria to the right of the line occur with increase of volume.

In accordance with rule 1^b we find, therefore, that the equilibria $F' + L + G$ and $F'' + L + G$ proceed from each point of the branch Sq towards lower pressures.

Now we have deduced the rules 1^a and 1^b assuming that point H is situated on branch pS; we may act in a similar way when point H is situated on branch qS. In a similar way we can also deduce the rules 2 and 3.

Considering, instead of the saturationcurves the boiling point curves, the same applies to these in general. We must then replace on the fourphase-curve the point of maximumtemperature by the point of maximum pressure. In fig. 3 besides the point of maximum-temperature H, also the point of maximum-pressure Q is drawn. We imagine further that the saturationcurves are replaced in the diagrams by boilingpointcurves. We then refind the rules 1, 2, and 3, with this difference, however, that increase of pressure must be replaced by decrease of the boilingpoint and decrease of pressure by increase of the boilingpoint.

From each point of the four-phase curve proceed two saturation-curves and two boilingpointcurves. When this solution is to be considered as rich in water or as poor in water with respect to the saturationcurves, it is also the same with respect to the boiling-pointcurves. Only the solutions between the point of maximum-pressure and the point of maximumtemperature make an exception; these are rich in water when we consider the saturationcurves, poor in water when we consider the boilingpointcurves. Now we find: from a solution saturated with two solid substances the vapour-pressure (along one of the saturationcurves) and the boilingpoint (along the corresponding boilingpointcurve) change generally in opposite direction. When, however, this solution is situated between the point of maximumpressure and the point of maximumtemperature, vapourpressure and boilingpoint change in the same direction.

(To be continued).

Physics. — "_On the thermodynamic potential as a kinetic quantity_". (First part). By Dr. H. HULSHOF. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of April 24, 1914).

In a communication published in These Proc. II p. 389 of Jan. 27 1900.[1]) it has been set forth by me that in the capillary layer the molecular pressure must have a different value in different directions as a direct consequence of the attraction of the particles, whereas the thermic pressure (the sum of the molecular and the

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[1]) I expressly call attention to this date, because some time after, this subject was treated in the same way by a writer who had informed me of his own accord that he was going to publish an article on this subject in the Zeitschrift für phys. Chemie, and that he should of course, cite my paper there, but who has failed to do so.