

Citation:

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formed into black radiation as well when there is a "black grain" in the contracting reflecting enclosure, as in the absence of such a "catalyser". Else we should get into collision with the second law of thermodynamics.¹⁾ If there are N monatomic molecules in a vessel with rough walls, distributed according to MAXWELL'S law, and if this ideal gas is compressed by an infinitely slow shifting of the walls of the vessel, the distribution finally follows again MAXWELL'S law, both when the molecules during the compression can collide, and when they could penetrate perfectly through each other. Probably more examples might be found in which through an "adiabatic influencing" of the separate degrees of freedom a state of equilibrium arises from a state of equilibrium.²⁾ But in general this is not the case, e.g. for molecules consisting of more than one atom or for mon-atomic molecules on which an external field of force acts.³⁾

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

In all our previous communications we have always contemplated the case that the occurring solid substances are ternary compounds. Now we shall assume that a binary compound occurs.

It is evident that we may deduce the saturationcurves under their own vapour-pressure and the boilingpointcurves of a binary compound in the same way as has been done in the previous communications for a ternary compound.

We take a compound composed of B and C , we represent this in fig. 1 by the point F on the side BC of the components-triangle ABC . We now take a definite temperature T and a pressure P in such a way, that no vapour can be formed and the isotherm consists only of the saturationcurve of F . This is represented in fig. 1 by curve pq .

On decrease of P , a gasregion occurs somewhere and also the region $L-G$, which separates gas- and liquidregion from each other.

¹⁾ M. PLANCK, *Wärmestrahlung* II. Aufl. § 71.

²⁾ The two mentioned cases have this in common that the pressure only depends on the total energy of the system, and not on its distribution over the different degrees of freedom.

³⁾ In an analogous way we can see that a canonical ensemble of gases generally does *not* remain canonical after an "adiabatic influencing".

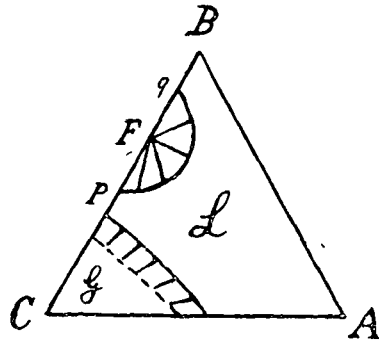


Fig. 1.

in the binary system BC .

I. The equilibrium liquid-gas of the binary system BC shows neither a maximum- nor a minimumpoint of pressure. The pressure of every liquid consisting of B and C is situated, therefore, between the pressure of the pure substances B and C .

II and III. The equilibrium liquid-gas of the binary system BC shows a maximum- or a minimumpoint of pressure.

We take at first the case mentioned sub I; we assume, for fixing the ideas, that the pressure decreases from C to B . The result of this is that every heterogeneous region $L-G$, at every temperature and under every pressure, intersects only once the side BC (fig. 1) and that this region on decrease of P with its liquid-line ahead moves along BC from C to B . Of course it is indifferent, where the gasregion and the region $L-G$ arise, on condition that this does not occur in a point of the side BC (excepted in C itself). Decreasing the pressure, a pressure P_M , occurs, under which the liquidcurve of the region LG and the saturationcurve of F obtain at first a common point; we shall call this point M . P_M , therefore, is the highest pressure, under which the system $F + L + G$ occurs.

When M is situated within the triangle, then, as was formerly deduced, M is a point of contact of the two curves and F , M and the corresponding vapourpoint M_1 are situated on a straight line. The point M then is a point of maximum pressure of the saturationcurve under its own vapourpressure.

When M is situated on the side BC of the triangle, e.g. in the point p of figure 1, the points F , p , and the corresponding vapourpoint on the side BC are, therefore, also situated on a straight line; then usually the two curves do not come in contact with one another. If we imagine in fig. 1 the liquidcurve drawn through p , the two curves will come in contact with one another in p only exceptionally. The pressure P_p is then the highest pressure under which the system

These regions may arise either anywhere within the triangle, or on one of the sides or in one of the angular-points; in fig. 1 we may think them arisen in the angular-point C . Also two or more of these regions may be formed in different points of the triangle and they may come together later in different ways.

We will distinguish now three principal cases according to the phenomena

$F+L+G$ occurs, but the point p is not a point of maximum pressure of the saturationcurve under its own vapourpressure (we will refer to this later).

On further decrease of pressure one or more points of intersection are found, therefore also one or more threephasetriangles; the different diagrams may be easily deduced in the same way as in communication I.

On further decrease of pressure we attain a pressure P_m under which the contemplated curves have for the last time a common point; we call this point m . P_m therefore is the lowest pressure under which the system $F+L+G$ can still occur and the points F , m and the corresponding vapourpoint m_1 are situated again on a straight line. When m is situated within the triangle, it is again a point of contact and also a point of minimum pressure of the saturationcurve under its own vapourpressure. When m is situated on the side BC of the triangle, (we imagine in fig. 1 the liquid curve of the region LG through the point q) the two curves do not come in contact with one another in q , and q is not a point of minimum pressure of the saturation curve under its own vapourpressure. Of course P_q is the lowest pressure under which the system $F+L+G$ may yet occur.

Now we will deduce some saturationcurves under their own vapourpressure.

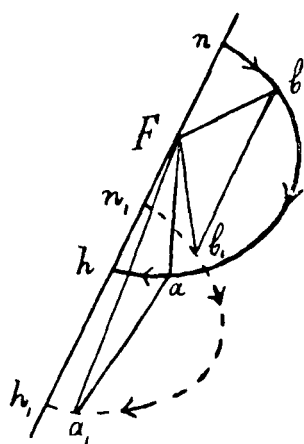


Fig. 2.

$T < T_K$. At first we choose a temperature T lower than the point of maximum sublimation T_K of the binary compound F . In a similar way as we have deduced fig. 11 (I) for the general case, we now find a diagram as is drawn in fig. 2. In this figure however only a part of the componenttriangle ABC is drawn; the line h_1Fn is a part of the side BC . Curve $habn$ is the saturationcurve under its own vapourpressure, $h_1a_1b_1n_1$ the corresponding vapourcurve; we shall call also here both the curves circumphased.

At the deduction of this diagram we have assumed, that on these curves neither a point of maximum- nor a point of minimum pressure occurs; the pressure increases from n to h , without being however in n a minimum and in h a maximum. From the deduction it follows also that the sides solid-liquid and solid-gas of the threephasetriangles must have a position with respect to one another as is drawn in the triangles Faa_1 and Fbb_1 .

Formerly (communication V and VI) we have deduced several rules for the movement of the sides of a threephasetriangle on change of pressure. When a saturationcurve under its own vapourpressure and its corresponding vapourcurve are removed comparatively far from the point F , the formation of vapour from $F + L$ takes place on increase of volume and the formation of liquid from $F + G$ on decrease of volume. The threephasetriangle turns on increase of pressure in such a way that the conjugationline solid-vapour goes ahead; on decrease of pressure it turns in opposite direction. If in fig. 2 we make triangle Faa_1 or Fbb_1 turn towards higher or lower pressures, we see that these movements are in accordance with the previous rules.

Also we may imagine on curve $habn$ a point of maximum pressure M and on curve $h_1a_1b_1n_1$ the corresponding point M_1 ; the points F , M and M_1 are then situated on a straight line. The pressure then increases from h and n towards M . Triangle Faa_1 must then also have another position as is drawn in fig. 2; the line Fa must viz. be situated closer to the side Fh_1 than the line Fa_1 . Therefore, when we take two threephasetriangles, situated on different sides of the line FMM_1 , they turn their sides solid-gas towards each other. We see that this is also in accordance with our previous considerations.

We may also imagine a point of minimum pressure m on curve $habn$ and the corresponding point m_1 on curve $h_1a_1b_1n_1$. Triangle Fbb_1 must then have another position; the line Fb_1 must then be situated closer to the side Fh than the line Fb .

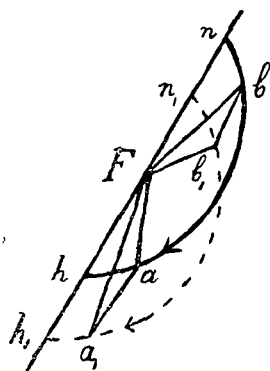


Fig. 3.

$T_K < T < T_F$. We now take a temperature T higher than the point of maximum sublimation T_K , but lower than the minimum-meltingpoint T_F of the substance F . In a similar way as we have deduced for the general case fig. 7 (I), we now find a diagram as fig. 3. Curve $habn$ is circumphased, curve $h_1a_1b_1n_1$, exp phased. Further, it is assumed again that on these curves

neither a point of maximum- nor a point of minimum pressure occurs. Because the points a and a_1 are removed comparatively far from the point F , the above mentioned rule applies again to the moving of triangle Faa_1 on change of pressure; we see that its turning is in accordance with this rule.

It is different with triangle Fbb_1 , its points b and b_1 are to be imagined close to n and n_1 . Let us at first contemplate the equilibrium $F + \text{liquid } n + \text{vapour } n_1$ of the binary system BC .

Because we have in this system a temperature between T_K and T_F , between the three phases the reaction: $F \rightleftharpoons \text{liquid } n + \text{vapour } n_1$ takes place from left to right with increase of volume. We compare now the ternary equilibrium $F + \text{liquid } b + \text{vapour } b_1$, wherein b and b_1 differ but little from n and n_1 , with the previous system. We then see that as well the formation of vapour from $F + \text{liquid } b$ as also the formation of liquid from $F + \text{vapour } b_1$ takes place with increase of volume. According to the rule deduced in communication VI, the sides solid-liquid and solid-vapour of the threephasetriangle must then approach one another on increase of P and separate from one another on decrease of P . We see that the movement of Fbb_1 in fig. 3 is in accordance with this rule.

The occurrence of a point of maximum- or minimumpressure can be easily examined by the reader.

$T_F < T$. We now take a temperature T a little higher than the minimummeltingpoint T_F of the substance F . We then must distinguish two cases, according as the substance expands or contracts on melting. We only take the first case. In a similar way as is deduced for the general case fig. 12 (I), we now find a diagram as fig. 4, wherein the two curves are exphased. Further, it is assumed again that on these curves neither a point of maximum nor a point of

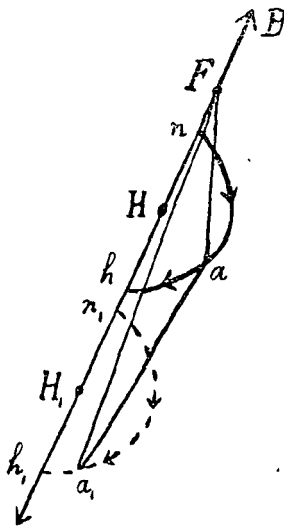


Fig. 4.

minimumpressure occurs. From the deduction of the diagram, it follows that Fa_1 of the threephasetriangle Faa_1 is situated always between Fa and Fh_1 . When the points a and a_1 are situated in the vicinity of n and n_1 , Faa_1 turns, as is clear from the figure, in such a way on decrease of pressure, that the line Fa goes ahead. When a and a_1 are situated however, in the vicinity of h and h_1 , Faa_1 turns on decrease of pressure in such a way that Fa_1 goes ahead. This turning is in accordance with the rules, deduced in communication VI. Let us firstly contemplate the equilibrium $F + L_n + G_{n_1}$ of the binary system BC . Herein the reaction $L_n \rightleftharpoons F + G_{n_1}$ takes place from left to right

with decrease of volume. Let us now take the system $F + L_a + G_{a_1}$ of which the points a and a_1 are situated in the immediate vicinity of n and n_1 . At the formation of vapour from $F + L_a$ the volume will decrease, at the formation of liquid from $F + G_{a_1}$ the volume will increase.

According to the rule, deduced in communication VI Faa_1 , must on increase of pressure turn in such a way that the line Fa goes ahead. This is in accordance with fig. 4.

In the same way it is deduced that triangle Faa_1 , when a and a_1 are situated in the vicinity of h and h_1 , must turn on increase of pressure in such a way that the line Fa_1 goes ahead.

Also, however, curves of quite another form may occur, viz. closed curves; these are, therefore, situated completely within the triangle and they are expahsed. We imagine e.g. in fig 12 (I) the component triangle to be drawn in such a way that the point F is situated on the side BC and that the two curves fall within the triangle. Both the curves then show a point of maximum- and a point of minimum pressure. While a binary compound generally may be in equilibrium, in addition to a series of ternary solutions, yet also with two binary solutions, in the above mentioned case, therefore, it is no more the case; now it may be only in equilibrium with ternary solutions.

Drawing the saturationcurves under their own vapourpressure and their corresponding vapourcurves for different temperatures, we may distinguish two principal types; these are represented in fig. 5 and 6. In both the figures, however, the vapourcurves are omitted. At temperatures below the minimum meltingpoint T_F the saturationcurves under their own vapour pressure are circumphased; at T_F the curve goes through F and above T_F they are expahsed. In fig. 5 they disappear in a point H on the side, in fig. 6 in a point R within the triangle.

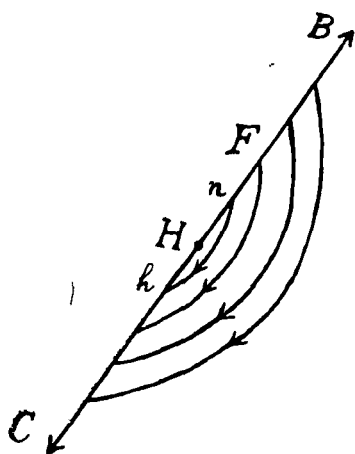


Fig. 5.

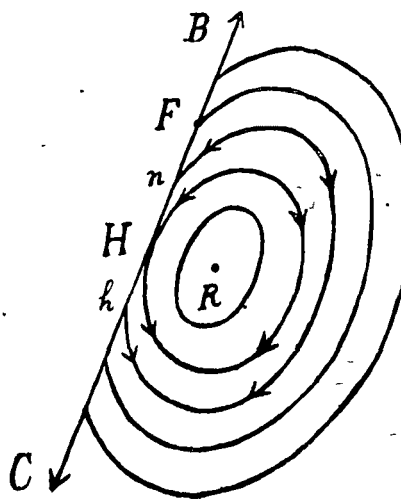


Fig. 6.

At first let us contemplate fig. 5. The arrows indicate the direction in which the pressure increases, therefore, it is assumed that on these curves neither a point of maximum- nor a point of minimum-pressure occurs. When this however is the case, these points form the limit-curve, formerly treated, which is easy to draw in the figure.

The saturationcurves disappear at T_H in the point H ; the corresponding vapourcurves disappear at the same time in the point H_1 , which is not drawn. We see from fig. 5 that T_H is the highest temperature at which, in the binary system BC , the equilibrium $F + L + G$ can still occur. In this case T_H is also the highest temperature at which in the ternary system the equilibrium $F + L + G$ can still occur.

In fig. 6 the saturationcurve of the temperature T_H does not disappear in the point H ; it forms a closed curve, which touches the side of the triangle in a point H . On further increase of temperature it comes completely within the triangle and disappears in a point R . It is evident that these closed curves, and also the not-closed curves, being situated in the vicinity, show a point of maximum- and a point of minimumpressure. In this case, therefore, a limit-curve exists, going through the point R . The curves situated at a greater distance, need not necessarily show this point of maximum and that of minimumpressure.

If it is imagined viz. that these points, on extension of the curves, continue to approach closer to the side BC and that they coincide with this at last; the point of maximumpressure disappears somewhere between H and C , the point of minimumpressure between H and B on the side BC . The limit-curve then terminates in both these points.

Also we see from the figure that the highest temperature (T_R) at which in the ternary system the equilibrium $F + L + G$ may still occur, is higher than T_H .

In figs. 5 and 6 the curves of different temperatures are all drawn in a same plane. Imagining however perpendicular to this plane a temperature axis and the curves to be drawn in space according to their temperature, the saturationsurface of F under its own vapour-pressure arises. In a similar way the corresponding vapoursurface arises.

In the surfaces belonging to fig. 5 the highest points (H and H_1) are situated on the side-plane BCT ; in the surfaces belonging to fig. 6 the highest points (R and R_1) are situated within the prism and not on the sideplane BCT .

Deducing the boilingpointcurves for different pressures we reind again the figures 2, 3, and 4 and figures 5 and 6 deduced from these. The arrows must then be drawn however in opposite direction so that in the figs. 2, 3, and 4 T_h is the lowest and T_n the highest temperature at which the equilibrium $F + L + G$ occurs.

We must still contemplate the cases II and III namely that the vapourpressurecurve of the binary system BC shows a point of maximum, or a point of minimum pressure. After the previous general considerations on the occurrence of ternary points of maximum- and of minimum-pressure, this need not to be considered here.

Now we shall contemplate some points more in detail. When F is a binary compound of the composition $0, \beta, 1-\beta$ (therefore $a=0$)

$$[xr + (y-t)s] dx + [xs + (y-\beta)t] dy = 0. \quad (1)$$

applies to its saturationcurve at a constant T and P .

The liquid curve of the region LG is fixed by:

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = 0. \quad (2)$$

We now imagine in fig. 1 that the liquid curve of the region LG is drawn through the point p or q ; we now contemplate $\frac{dy}{dx}$ in this point p or q for both the curves. Because in this point $x=0$ and $\text{Lim. } xr = RT$ it follows for the saturation curve that:

$$\left(\frac{dy}{dx}\right)_{x=0} = -\frac{RT + (y-\beta)s}{(y-\beta)t} \quad (3)$$

and for the liquid curve of the region LG that:

$$\left(\frac{dy}{dx}\right)_{x=0} = -\frac{\left(\frac{x_1}{x} - 1\right)RT + (y_1-y)s}{(y_1-y)t} \quad (4)$$

From (3) and (4) it follows that the tangents on both the curves in the point p have usually a different position, so that the two curves do not come in contact with one another. When (3) is accidentally equal to (4), the two curves touch one another in p or q . This will be the case when:

$$y_1-y = \left(\frac{x_1}{x} - 1\right)(y-\beta) \quad \text{or} \quad \frac{x_1}{x} = \frac{y_1-\beta}{y-\beta} \quad (5)$$

Later we shall see that in this case their point of contact p or q is then also a point of maximum- or of minimumpressure of a saturationcurve under its own vapour pressure or of a boiling point curve.

In order to find the saturationcurve under its own vapourpressure we put in (8) and (9) (II) $\alpha = 0$. We obtain:

$$[xv + (y - \beta)s] dx + [xs + (y - \beta)t] dy = AdP \quad . \quad . \quad (6)$$

$$[(x_1 - x)r + (y_1 - y)s] dx + [(x_1 - x)s + (y_1 - y)t] dy = CdP \quad . \quad (7)$$

In the terminating point of this curve on the side BC (therefore in the points h and n of figs. 2, 3, and 4), $x = 0$. We find from (6) and (7):

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx} \right)_{x=0} = \frac{y_1 - y - (y - \beta) \left(\frac{x_1}{x} - 1 \right)}{(y_1 - \beta)V + (y - y_1)v + (\beta - y)V_1} \quad . \quad . \quad (8)$$

In order to find the boilingpointcurve we must substitute in (6) and (7) AdP by $-BdT$ and CdP by $-DdT$. We then find:

$$\frac{1}{RT} \cdot \left(\frac{dT}{dx} \right)_{x=0} = - \frac{y_1 - y - (y - \beta) \left(\frac{x_1}{x} - 1 \right)}{(y_1 - \beta)H + (y - y_1)\eta + (\beta - y)H_1} \quad . \quad (9)$$

From (8) it follows that in a terminatingpoint of the saturationcurve under its own vapourpressure on one of the sides (points h and n of fig. 2, 3, and 4) $\frac{dP}{dx}$ has a definite value different from zero so that the pressure is in the terminatingpoint neither a maximum nor a minimum. The same follows from (9) for the temperature in the terminatingpoint of a boilingpointcurve.

In the binary system BC the relation between a change of P and T in the equilibrium $F + L + G$ is fixed by:

$$\left(\frac{dP}{dT} \right)_{x=0} = \frac{(y_1 - \beta)H + (y - y_1)\eta + (\beta - y)H_1}{(y_1 - \beta)V + (y - y_1)v + (\beta - y)V_1} \quad . \quad . \quad (10)$$

From (8), (9), and (10) it now follows that:

$$\left(\frac{dP}{dx} \right)_{x=0} : \left(\frac{dT}{dx} \right)_{x=0} = - \left(\frac{dP}{dT} \right)_{x=0} \quad . \quad . \quad . \quad (11)$$

In order to see the meaning of this we imagine a graphical representation of P and T of the binary equilibrium $F + L + G$. We will call that part of the P, T -curve on which the pressure increases when raising the temperature, the ascending branch, the part on which the pressure decreases when lowering the temperature the descending branch. In the ascending branch $\frac{dP}{dT}$ is positive, in the descending branch it is negative; from (11) it follows, that $\frac{dP}{dx}$ and $\frac{dT}{dx}$ have in the ascending branch the opposite sign and in the descending branch the same sign. We find therefore:

When the binary equilibrium $F + L + G$ is situated in an ascending branch of its P, T -curve, addition of a third substance has an opposite influence on the pressure (at constant temperature) and on the temperature (under constant pressure). When addition of a third substance e. g. increases the pressure (at constant T) it will decrease the boiling point (under a constant pressure).

When the binary equilibrium $F + L + G$ is situated in a descending branch of its P, T curve addition of a third substance has the same influence on the pressure (at constant T) and on the temperature (under constant P). When addition of a third substance increases for instance the pressure (at constant T) it will also increase the boilingpoint (under constant P).

These rules are also true when F is instead of a combination one of the components e.g. B or C .

We will now still examine, in what case the pressure (at constant T) of the binary equilibrium $F + L + G$ is increased or decreased by addition of a third substance. We may express this also in the following way: in what case does the pressure along a saturationcurve under its own vapourpressure from one of its terminatingpoints (h and n in figs. 2, 3, and 4) increase or decrease?

We take for this formula (8), which indicates the relation between the change of pressure dP and the quantity dx of the new substance.

Between the 3 phases of the binary equilibrium $F + L + G$ a reaction may always take place. We let the reaction take place in such a way that 1 quantity of vapour occurs. The occurring change of volume we call ΔV . The denominator of (8) becomes then $(\beta - y) \Delta V$, so that we may write:

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx} \right)_{x=0} = \frac{1}{\Delta V} \cdot \left(\frac{x_1}{x} - \frac{\beta - y_1}{\beta - y} \right) \dots \dots (12)$$

We now take the ternary equilibrium $F + L + G$ wherein L and G contain still only a little of the third substance. The line solid-liquid (Fa or Fb in figs. 2—4) then intersects the X -axis (side CA of the componenttriangle) in a point at the distance S from C . The line solid-gas (Fa_1 or Fb_1 figs. 2—4) intersects this X -axis in a point at the distance S_1 from C . We take S and S_1 positive, when the points of intersection are situated on the right, negative, when they are on the left of C . S and S_1 are fixed by

$$S = \frac{\beta x}{\beta - y} \quad S_1 = \frac{\beta x_1}{\beta - y_1} \dots \dots (13)$$

Substituting $\beta - y$ and $\beta - y_1$ from (13) in (12) we find:

$$\frac{1}{RT} \left(\frac{dP}{dx} \right)_{x=0} = \frac{1}{\Delta V} \cdot \frac{x_1}{x} \left(1 - \frac{S}{S_1} \right) \dots \dots (14)$$

From this relation it follows that the sign of the change of pressure depends on the sign of ΔV . Now ΔV is almost always positive for the binary equilibrium $F + L + G$ and negative only between the points F and H (figs. 5 and 6). Further it follows that the sign of the change of pressure is not fixed by the ratio $x_1 : x$ (the partition of the third substance between gas and liquid), but by the ratio $S : S_1$; therefore this is by the ratio of the parts which the lines Fa and Fa_1 or Fb and Fb_1 cut off from the X -axis. We may consider S and S_1 also as the perspective projections of x and x_1 from the point F on the X -axis. We shall call for that reason S the perspective concentration of the new substance in the liquid, and S_1 that of the new substance in the vapour. These perspective concentrations can be as well positive as negative.

From (14) we can now easily deduce for the addition of a new substance :

1. The formation of vapour in the binary system $F + L + G$ takes place with increase of volume ($\Delta V > 0$).

When in liquid and vapour the new substance has perspective concentrations of opposite sign, the pressure increases.

When in liquid and vapour the new substance has perspective concentrations of the same sign, the pressure increases, when the perspective concentration (apart from the sign) of the new substance is greater in the vapour than in the liquid, the pressure decreases when the reverse is the case.

2. The formation of vapour in the binary system $F + L + G$ takes place with decrease of volume ($\Delta V < 0$).

The changes of pressure take place in opposite direction as sub 1. It may be considered with this, that $\Delta V < 0$ is the case only between T_F and T_H , therefore between the minimum-melting point of F and the point of maximum-temperature of the binary system $F + L + G$.

When we take a threephasetriangle in the vicinity of the side BC , its angle F is either a little greater than 0° (Faa_1 and Fbb_1 in fig. 2) or a little smaller than 180° (Fbb_1 in fig. 3). We will call the threephasetriangle in the first case acute-angled, in the second case obtuse-angled. We may express the previous rules also in the following way:

1. The formation of vapour in the binary system $F + L + G$ takes place with increase of volume ($\Delta V > 0$).

An obtuse-angled threephasetriangle moves on increase of pressure both its sides solid—liquid and solid—gas towards each other and on decrease of pressure away from each other.

An acute-angled threephasetriangle moves on increase of pressure with the side solid—gas ahead, on decrease of pressure with the side solid—liquid ahead.

2. The formation of vapour in the binary system $F + L + G$ takes place with decrease of volume ($\Delta V < 0$).

The triangles move in the opposite direction as sub 1..

We see that the position of the threephasetriangles in the figs. 2—4 are in accordance with these rules.

In a similar way as we have converted (8) into (14), we may deduce from (9):

$$\frac{1}{RT^2} \cdot \left(\frac{dT}{dx} \right)_{x=0} = - \frac{1}{\Delta W} \cdot \frac{x_1}{x} \left(1 - \frac{S}{S_1} \right) \dots (15)$$

ΔW represents here the heat that is required to form 1 quantity of vapour. The same rules as above may be deduced from this, we must then however replace increase of pressure by decrease of T and decrease of pressure by increase of T .

We should have been able to deduce the rules, deduced above, for the movement of the threephase triangles on change of pressure and temperature, from the rules found in Communication V and VI.

As a particular case of the above-discussed we may put the question: what influence has a third substance on the binary equilibrium $F + L + G$ when this is situated in the point of maximum sublimation or in the minimummelting point of the substance F .

In the point of maximum sublimation the binary vapour has the same composition as the substance F ; therefore $y_1 = \beta$. The vapour-saturationcurve under its own vapour-pressure goes through the point F (in this transition-case between the figures 2 and 3 n_1 coincides therefore with F). When we put in (8) and (9) $y_1 = \beta$, we find:

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx} \right)_{x=0} = \frac{1}{V_1 - v} \cdot \frac{x_1}{x} \text{ and } \frac{1}{RT^2} \cdot \left(\frac{dT}{dx} \right)_{x=0} = - \frac{1}{\Delta W} \cdot \frac{x_1}{x} \quad (16)$$

Herein $V_1 - v$ is the increase of volume on sublimation, ΔW the heat of sublimation of the substance F . Therefore, both are positive. From (16) it now follows:

when the equilibrium $F + L + G$ is situated in the point of maximum sublimation of the substance F , addition of a third substance will increase the pressure (T constant) and decrease the temperature (P constant).

In the minimum-melting point the binary liquid has the same composition as the substance F , therefore $y = \beta$. The saturationcurve under its own vapour-pressure goes therefore through point F . (In this transition-case between figs. 3 and 4, n , therefore, coincides with

F). When we put in (8) and (9) $y = 3$, then it follows :

$$\frac{1}{RT} \cdot \left(\frac{dP}{dx} \right)_{x=0} = \frac{1}{V-v} \text{ and } \frac{1}{RT^2} \cdot \left(\frac{dP}{dx} \right)_{x=0} = - \frac{1}{\Delta W}. \quad (17)$$

Herein $V-v$ is the increase of volume on melting, ΔW the heat of melting of the substance F . $V-v$ can be as well positive as negative, ΔW is always positive. From (17) it now follows that :

when the equilibrium $F + L + G$ is situated in the minimum-meltingpoint of the substance F , addition of a third substance will increase the pressure (T constant), when the substance melts with increase of volume ($V > v$) and decrease when the substance melts with decrease of volume ($V < v$). The temperature (P constant) is lowered.

We may express the above-stated also in the following way :

from F the pressure increases along the vapoursaturationcurve under its own vapour-pressure going through F and the temperature decreases along the boilingpointcurve going through F .

From F the pressure increases along the saturationcurve under its own vapourpressure going through F , when F melts with increase of volume and the pressure decreases when F melts with decrease of volume. Along the boilingpointcurve going through F the pressure decreases from F .

Also we should be able to examine what influence has a third substance on the binary equilibrium $F + L + G$, when this is situated in the point of maximum temperature (point H in figs. 5 and 6) or in the point of maximum pressure of its P, T -curve. We refer to this later.

(To be continued).

Physiology. — “*The effect of subcutaneous turpentine-injections on the chemotaxis of remote places.*” By Prof. H. J. HAMBURGER.
After experiments by Dr. J. BUTENHUIS.

(Communicated in the meeting of November 29, 1913).

On a former occasion the attention was drawn to the favourable effect of slight amounts of turpentine on the rapidity of phagocytosis.¹⁾ In a dilution of 1 : 100.000 an increase was found of 24.7 % and even in a dilution of 1 : 500.000 an increase of 16 %.

¹⁾ HAMBURGER, DE HAAN and BUBANOVIC: On the effect of Chloroform, Iodoform and other substances dissoluble in fat, on Phagocytosis. Proceedings of the Meeting of Jan. 28, 1911, p. 913.