Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

F.A.H. Schreinemakers, Equilibria in ternary systems. IX, in: KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 385-395

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tellurium, tungsten-blue and many other inorganic colloids by fibrous substances <sup>1</sup>). These phenomena have been usually described as adsorptions, although the name adhesion would be the more correct one. If, however there exists a continuity between colloidal and molecular solutions, this will then also exist between adhesion and adsorption.

Delft, July 1913.

## **Chemistry.** — "Equilibria in ternary systems". IX. By Prof. F. - A. H., Schreinemakers.

We will now consider 'the four-phase equilibrium F + F' + L + Gin connection with the saturation- and vapour saturation-curves of F and of F' under their own vapour pressures.

These saturation-curves under their own vapour pressures may be situated with respect to one another in different ways  $\cdot$  1. they may intersect one another; 2. they may touch one another; 3. the one may be situated outside the other; 4. the one may surround the other.

Let us, in the first instance, consider fig. 2, in which the continuously drawn curves represent the saturation curves, the dotted curves the vapour saturation curves of F and of F' under their own vapour pressures.

At the given temperature, therefore, every liquid of the curve f x y g is saturated with the solid F and in equilibrium with a vapour of the corresponding curve  $f_1g_1$ ; every liquid of the curve f x' y' g is saturated with the solid F' and in equilibrium with a vapour of the corresponding curve  $f_1g_1$ .

Because all these liquids are under their own vapour pressures, the pressure changes will, as we have seen before, move along these curves.

If we now consider f as a point on the saturation curve of F, it is under a pressure P; if, on the other hand, we consider f as a point on the saturation curve of F', it is under a pressure P'. The question now arises: Is P the same as P' or are they different?

Under the pressure P, therefore, the system  $F + L_f + G$  exists, and under the pressure P' the system  $F' + L_f + G'$ . At a definite

Proceedings Royal Acad. Amsterdam. Vol. XVI.

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<sup>&</sup>lt;sup>1</sup>) R. ZSIGMONDY, Verh. d. Ges. D. Naturf. u. Aerzte, 73 Vers. Hamburg 1901, p. 168. L. VANINO, Ber. d. D. Chem. Ges. **35**, 662 (1902).

W. SPRING, Beobachtungen über die Waschwirkung von Seifen, Zeitschr. f. Kolloidchemie 4, 161 (1909).

W. BILTZ. Ber. d. D. Chem. Ges. 37, 1766 (1904).

temperature, however, a definite liquid  $L_f$  cannot be in equilibrium with vapour under two different pressures.

P and P' must therefore be the same. Further it also follows that the vapours G and G' are the same. We call this vapour  $G_{f_1}$ .

The point of intersection of the two saturation curves under their own vapour pressures signifies, therefore, that under a definite pressure the three-phase equilibrium  $F + L_f + G_{f_1}$  can be met with as well as  $F' + L_f + G_{f_1}$ . To every point of intersection f of the saturation curve belongs, therefore, a definite point of intersection  $f_1$  of the vapoursaturation curves under their own vapour pressures. Hence it follows that the point of intersection f represents the liquid L, the corresponding point of intersection  $f_1$  the vapour G of the fourphase equilibrium F + F' + L + G; in other words : f represents the solution saturated with F + F' under its own vapour pressure;  $f_1$  is the corresponding vapour. The same, of course, applies to the points of intersection g and  $g_1$ .

The following equilibria, therefore, exist in fig. 2:

1. A series of solutions saturated with F under their own vapour pressures, with their corresponding vapours; therefore the system F + L + G.

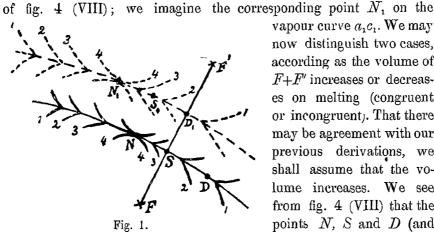
2. A series of solutions saturated with F' under their own vapour pressures, with their corresponding vapours; therefore the system F' + L + G.

3. Two solutions saturated with F + F' under their own vapour pressures with their corresponding vapours; therefore the system F + F' + L + G. The one exists under the pressure  $P_f$  with the liquid f and the vapour  $f_1$ ; the other under the pressure  $P_g$  with the liquid g and the vapour  $g_1$ . Usually  $P_f$  and  $P_g$  are different; only in exceptional cases can they be equal.

For the sake of abbreviation we shall call in future the point of intersection of two saturation curves under their own vapour pressures "the liquid point of intersection", and the point of intersection of two vapour saturation curves under their own vapour pressures "vapour point of intersection".

If we now assume, that in the figs. 1-3 (VIII) the saturation and vapour saturation curves of F and of F' under their own vapour pressures are drawn, then it is evident that the liquid points of intersection fall on the liquid curve ac and the vapour points of intersection on the vapour curve  $a_1c_1$  of the four-phase equilibrium. In fig. 1, corresponding with fig. 1 (VIII) some of these curves are partly drawn. On the liquid curve ac [fig. 1-3 (VIII)] we take a point N, corresponding with the point of maximum temperature N

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vapour curve  $a_1c_1$ . We may now distinguish two cases, according as the volume of F+F' increases or decreases on melting (congruent or incongruent). That there may be agreement with our previous derivations, we shall assume that the volume increases. We see from fig. 4 (VIII) that the points N, S and D (and

consequently also the corresponding points  $N_1$ ,  $S_1$  and  $D_1$ ) must then lie with respect to one another as in fig. 1.

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The liquid curve (fig. 1) has, therefore, its maximum temperature at N, the vapour curve at  $N_1$ . On the liquid curve, therefore, the temperature decreases from N, on the vapour curve from  $N_1$  in both directions.

Let us now take a temperature  $T_1$ , lower than the maximum temperature of sublimation  $T_D$ ; the saturation and vapour saturation curves under their own vapour pressures (which are only partly drawn in the figure) corresponding to this temperature  $T_1$ , are indicated by "1". In fig. 2 we find the complete diagram. From figs. 1 and 1-3 (VIII) it follows, (as is also drawn in fig. 2), that at temperatures lower than the maximum point of sublimation, the two liquid points and also the two vapour points of intersection are situated in opposition with respect to FF'.

We now take a temperature  $T_2$  between the maximum point of sublimation  $T_D$  and the minimum meltingpoint I's. The saturation and vapour saturation curve under their own vapour pressures, corresponding with this temperature  $T_{2}$  and only partly drawn in the figure, are indicated by "2". One of the liquid points of intersection is situated between S and D, the corresponding vapour point of intersection between  $S_1$  and  $D_1$ . We find the complete diagram in fig. 3. The points f and g are situated in opposition,  $f_1$  and  $g_1$  in conjunction with respect to the line FF'. The figs. 2 and 3 differ from one another only as regards the position of the point  $g_1$  with respect to the line FF'. When fig. 2 passes into fig. 3 the point  $g_1$  falls on the line FF'; this is the case at the maximum temperature of sublimation  $T_D$ ; the points g and  $g_1$  of this transition figure agree then with the points D and  $D_1$  of figure 1.

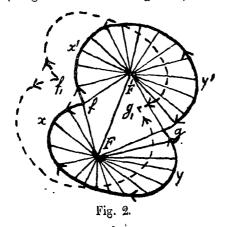
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We now take in fig. 1 a temperature  $T_3$  between the melting point  $T_S$  and the point of maximum temperature  $T_N$ . The saturation and vapour saturation curve under their own vapour pressures, corresponding to this temperature, are partly drawn and indicated by 4. One of the liquid points of intersection is situated between S and N, the corresponding vapour point of intersection between  $S_1$  and  $N_1$ . Fig. 4 indicates the complete diagram. The points f and g as well as the points  $f_1$  and  $g_1$  are situated in conjunction as regards the line FF'. When fig. 3 passes into fig. 4, the point gfalls on the line FF'; this is the case at the minimum melting point  $T_S$ . The points g and  $g_1$  of this transition figure agree with the points S and  $S_1$  of fig. 1.

At the maximum temperature  $T_N$  the two saturation curves touch one another in the point N, the two vapour saturation curves in  $N_1$ . We find the complete diagram in fig. 5. At this temperature, therefore, only one single solution N exists, saturated under its own vapour pressure with F + F'; the corresponding vapour is represented by  $N_1$ . If we raise the temperature still more, the two saturation- as well as the two vapour saturation-curves fall outside each other, and finally disappear. The manner in which this takes place has already been described in communication I.

In deducing diagrams 2—5 we have based our arguments principally on fig. 1, in which the points F, F', S and  $D_1$  are situated as in type 1. As we have seen before, however, that 12 types can be distinguished, we shall now consider from another point of view the appearance of two saturation- and two vapour saturation curves under their own vapour pressures. We shall namely distinguish 7 chief groups with respect to the temperature. We assume again in the first instance that the volume of F + F' increases on melting (congruent and incongruent). The points N, S, and D are situated



with respect to one another as in fig. 4 (VIII) and 1.

I. The temperature is lower than the maximum point of sublimation  $T_D$ . It is easy to see that not only the two liquid points of intersection but also the two vapour-points of intersection are situated in opposition as regards the line FF'.

One of the many diagrams, satisfying these conditions, is drawn in fig. 2. The points F, F', f and g are situated in this figure in such a way that they form the angular points of a quadrilateral, they may, however, also form a triangle, surrounding the point F or F'. The same applies to the points F, F',  $g_1$  and  $f_1$ .

In addition to the above mentioned instances, the different diagrams may yet still differ from one another with respect to the reactions which may take place in either of the two four-phase systems F + F' + L + G. For the system F + F' +liquid g +vapour  $g_1$ , we distinguish the following cases:

a. The point  $g_1$  is situated within the triangle FF'g.

Reaction:  $F + F' + L \rightleftharpoons G$ .

b. The points form a quadrilateral; the line  $Fg_1$  intersects F'g. Reaction:  $F' + L \gtrsim F + G$ .

c. The points form a quadrilateral; the line Fg intersects  $F'g_1$ . Reaction:  $F + L \gtrsim F' + G$ .

d. The point g is situated within the triangle  $FF'g_1$ .

Reaction:  $L \rightleftharpoons F + F' + G$ .

For the system  $F + F' + \text{liquid } f + \text{vapour } f_1$  we may of course distinguish the same cases.

If we consider the above-mentioned reactions in the direction from left to right, vapour is formed, and, therefore, the volume increases. The three-phase equilibria, which are formed, when the reactions take place from left to right, exist therefore at lower temperatures, and those which are formed when the reactions take place from right to left exist, therefore, at higher pressures than the fourphase equilibrium. Hence the following is easily deduced: out of the point of intersection of the two saturation curves under their own vapour pressures, the pressure

1. decreases along both curves, when reaction a

2. increases along the one curve and decreases along the other, when reaction b or c

3. increases along both curves, when reaction d takes place in the four-phase equilibrium.

The same of course applies to both the vapour saturation curves under their own vapour pressures. As follows from the position of the points of intersection in fig. 2, the reaction "a" is there assumed for the equilibrium  $F + F' + \text{liquid } g + \text{vapour } g_1$ , the reaction "d" for the equilibrium  $F + F' + \text{liquid } f + \text{vapour } f_1$ . The pressure changes along the curves in the vicinity of the points of intersection of this figure are in accordance with the previous considerations.

It is evident that yet many other cases are possible, which can be obtained by combining the reactions a-d, two at a time. It should however be kept in mind that in the immediate vicinity of the maximum point of sublimation only the reactions a, b and ccan take place (compare the reaction series  $A_1$ ,  $B_1$  and  $C_1$ ). Reaction d can take place at a greater distance from this point only.

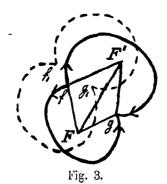
We may also consider the different cases from yet another point of view. For this purpose we take two saturation curves and their corresponding vapour saturation curves. We let these intersect one another in such a way, that the two liquid points of intersection as well as the two vapour points of intersection are situated in opposition with respect to the line FF'.

If we consider stable conditions only, merely a part of each curve will remain. We may now distinguish several cases, according as the points of maximum and minimum pressure are situated on the stable or metastable parts of these curves, and these will be in agreement with what has been said above. It is evident that for each stable or metastable point of maximum or minimum pressure on a saturation curve there exists a stable or metastable point on the corresponding vapour saturation curve.

In fig. 2 the points of maximum pressure are indicated by x and x', the points of minimum pressure on the saturation curves by y and y'. The two curves intersect each other in fig. 2 in such a way that these four points are stable, consequently the corresponding four points (not drawn in the figure) on the vapour saturation curves are also stable.

II. The temperature is equal to the maximum point of sublimation  $T_D$ .

The two liquid points of intersection are situated in opposition with respect to the line FF'; one of the vapour points of intersection is situated on the line FF'. We imagine in fig. 2 or 3 the point  $g_1$  on the line FF'. When a congruent sublimation takes place,  $g_1$  is situated between the other two points, with an incongruent sublimation F or F' is situated there.



III. The temperature is higher than the maximum point. of sublimation  $T_D$ , but lower than the minimum melting point  $T_S$ . The two liquid points of intersection are situated in opposition with respect to the line FF'; the two vapour points of intersection are situated in conjunction with respect to that line. One of the many diagrams satisfying these conditions is drawn in fig. 3. In the equilibrium F+F' + liquid g

+ vapour  $g_1$ , one of the reactions a - d no longer takes place; instead one of the reactions

 $f) F \rightleftharpoons F' + L + G; \quad g) F' \rightleftharpoons F + L + G$ e)  $F+F' \rightleftharpoons L+G;$ takes place.

As follows from the position of the points g and  $g_1$  in fig. 3, the reaction e takes place. Hence it follows that the pressure decreases from g along the two curves.

IV. The temperature is equal to the minimum meltingpoint,  $T_S$ .

The two vapour points are situated in conjunction with respect to the line FF'; one of the liquid points of intersection is situated on the line FF'. We shall call this figure "fig. 3a". When a congruent melting takes place, g is situated between the other two points; when an incongruent melting takes place, F or F' is situated there.

We have seen before that the minimum melting point  $T_S$  of the complex F + F' can be lower than that of one of the two components F or F' taken separately. Imagining in fig. 3a the saturation curve of F to be exphased, then  $T_S$  is lower than the minimum melting point of F; when both the saturation curves in fig. 3a are exphased, then  $T_S$  is lower than the minimum melting point of either of the two compounds F and F'. As the exphased saturation curves are generally not very far removed from F and F', this last mentioned case can only occur when the points F and F' are situated close to each other, that is if they differ only a little in composition.

V. The temperature is higher than the minimum melting point,  $T_S$ , but lower than the point of maximum temperature  $T_N$ .

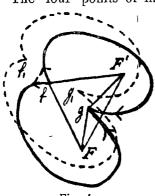


Fig. 4.

The four points of intersection are all situated on the same side of the line FF'. In fig. 4 one of the many possible diagrams is drawn. As long as the point y is still situated in the vicinity of the line FF', reaction a cannot take place in the four-phase equilibrium F + F' +liquid g + vapour  $g_1$ , but instead one of the reactions b-d takes place. As follows from the position of the points g and  $g_1$ in fig. 4, the reaction that takes place is d, therefore:  $L \geq F + F' + G$ .

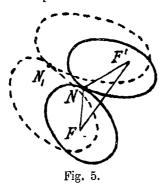
Vapour is formed as the reaction proceeds from left to right. Although in such a case the volume generally increases, in this particular instance the volume, however, decreases. We have namely seen before that this formation of vapour in points between N and S takes place with decrease of volume.

As the three-phase equilibria F + L + G and F' + L + G are formed here, when the reaction proceeds from left to right, both these equilibria exist under pressures lower than those of the four-phase equilibrium. On both saturation curves under their own vapour pressures, the pressure decreases therefore from the point g outwards.

In the system F + F' + L + G the volume increases, of course, with the formation of vapour.

VI. The temperature is equal to the point of maximum temperature  $T_N$ .

The two saturation curves under their own vapour pressures touch one another; the same applies to the two vapour saturation curves. The two points of contact are situated on the same side of the line FF'. In fig. 5 one of the many possible cases has been drawn. As the point N is generally situated in the vicinity of the line FF', consequently in the four-phase equilibrium reaction a does usually not take place, but instead one of the reactions b-dtakes place.



In fig. 5 the curves touch one another externally. It is evident that they may also touch one another internally, or that one or more of the four curves may be exphased.

From our previous considerations it follows that, during a reaction between the four phases of the system F + F' +liquid N + vapour  $N_1$ , the volume remains constant.

While the point of contact between two saturation curves under a constant pressure is situated on the line FF' (the only exceptions being metastable points of contact, which may be situated on the spinodal line, when the liquids separate into two layers), the point of contact of two saturationcurves under their own vapour pressures is always situated outside the line FF'.

VII. The temperature is higher than the point of maximum temperature  $T_N$ .

The two saturation curves under their own vapour pressures neither intersect nor touch each other; the one is situated either outside or completely round about the other. The same, of course applies to the two vapour saturation curves under their own vapour pressures.

For this purpose we have deduced from fig. 1, that, at the maximum temperature  $T_N$  the two saturation curves as well as the two vapour saturationcurves under their own vapour pressures touch

each other, and also that the two points of contact are not situated on the line joining F and F' of the solid phases. This also follows from the equations of these curves.

The saturation curve under its own vapour pressure is, as we have seen before [8 and 9] (II)] fixed by

 $[(x-a) r + (y-\beta) s] dx + [(x-a) s + (y-\beta) t] dy = A \cdot dP \cdot (1)$  $[(x_1-x) r + (y_1-y) s] dx + [(x_1-x) s + (y_1-y) t] dy = C \cdot dP \cdot (2)$ We may write for this, after eliminating <math>dP

 $\{(x-\alpha)\ C-(x_1-x)\ A\ (rdx\ +\ sdy)\ +\ \{(y-\beta)C-(y_1-y)A\}(sdx\ +\ tdy)\ =\ 0\ (3)$ 

For the saturation curve of F' under its own vapour pressure we have :

$$\{(x-\alpha') C - (x_1 - x) A'\} (rdx + sdy) + \{(y-\beta') C - (y_1 - y) A'\} (sdx + tdy) = 0$$
 (4)  
If the two saturation curves under their own vapour pressures  
touch one another, then, for this point of contact,  $\frac{dy}{dx}$  from (3) and  
(4) must necessarily have the same value. This is the case when:

$$\frac{(x-a)\ C-(x_1-x)\ A}{(x-a')\ C-(x_1-x)\ A'} = \frac{(y-\beta)\ C-(y_1-y)\ A}{(y-\beta')\ C-(y_1-y)\ A'} . \quad . \quad . \quad (5)$$

If we substitute herein the values of A, A' and C we find after reduction:

 $n v + n' v' + m V + m_1 V_1 = 0.$  . . . . . (6)

where n, n', m and m, have the same values as in (6) (VIII).

(6) is not satisfied by a point on the line FF'; in this case, namely  $m_1$  becomes = 0, and consequently, we should have to satisfy, at the same time:

As the value of the first part of (7) is, however, dependent on the volumes of the three phases F, F' and L, consequently (7) is usually not satisfied. This also follows from the meaning of the first part of (7); this, namely, represents the change of volume which takes place in the minimum melting point of the complex F + F', and this is, of course, only in highly exceptional cases equivalent to zero.

The first part of (6) represents, as we have seen before, the change of volume which takes place in a reaction in the four-phase system F + F' + L + G. In agreement with previous considerations consequently, we see that two saturation curves under their own vapour pressures touch, if the four-phase reaction takes place without change of volume.

If the condition is calculated that two vapour saturation curves may touch, then a form is obtained, which is deduced from (6) by

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substituting therein  $x_1$ ,  $y_1$  and  $V_1$  for x, y and V, and vice versa. In this way condition (6) is again obtained. From this follows: if two saturation curves under their own vapour pressures touch each other, then their corresponding vapour saturation curves must also touch, and vice versa. This is the case when the four phase reaction takes place without change of volume.

When considering figs. 2—5 we have supposed that in the fourphase systems always a four-phase reaction takes place As a transition instance a three phase reaction may, however, also take place.

If we limit ourselves to such reactions taking place between liquid, vapour and one of the solid bodies, then we have: h)  $F' + L \rightleftharpoons Gi$   $L \gneqq F + Gj$   $F \gneqq L + Gk$   $F' + L \gneqq Gl$   $L \gneqq$ F' + Gm  $F' \gneqq L + G$ .

In the four-phase equilibrium  $F + F' + \text{liquid } g + \text{vapour } g_1$ (figs 2, 3 and 4) reaction h, i or j takes place, if the points F, gand  $g_1$  are situated in a straight line. Reaction h takes place if the point  $g_1$ , reaction i if the point g, and reaction j if the point F is situated between the other two points.

If, however, the three points F, g and  $g_1$  are in a straight line, then the pressure for the system  $F + \text{liquid } g + \text{vapour } g_1$  will be a maximum or minimum, as we have seen before. The point gwill then be the point of maximum or minimum pressure for the saturation curve of F, the point  $g_1$  such a one for the vapoursaturation curve under its own vapour pressure. Consequently in fig. 2 the point g coincides with the point y or the point f with the point x.

The previous considerations may also be expressed thus: when in the equilibrium F + F' + L + G one of the three-phase reactions h-m takes place, a point of maximum or minimum pressure of a saturation curve is situated on the liquid curve of this equilibrium, and a similar point of the vapour saturation curve under its own vapour pressure on the vapour curve of this equilibrium.

In connection with the previously deduced properties (communication VIII) we find, consequently, that if in a four phase equilibrium F + F' + L + G a three-phase reaction takes place between liquid, gas and one of the solid bodies then:

1. the four-phase curve, the limit curve of this compound and the solution path of this compound belonging to this point will touch one another in the P, T-diagram.

2. in the concentration diagram on the liquid curve of the four phase equilibrium a point of maximum or minimum pressure of the saturation curve of the compound will be situated, and on the vapour curve of this equilibrium a similar point of the vapour saturation curve under its own vapour pressure.

If one of the properties mentioned under 1. or 2. appears, then, reasoning backwards, the three-phase reaction, mentioned above, will also take place in the four-phase equilibrium.

Above we have considered only the case that the volume increases at the congruent or incongruent melting of the complex F + F'; corresponding properties make their appearance when the volume decreases. These the reader can easily deduce for himself.

In the same way in which we deduced above the properties or two saturation- and vapour saturation curves under their own vapour pressures, the reader can consider the appearance of two boilingpoint curves and their corresponding vapour curves.

## Astronomy. — "On the constancy of the velocity of light". By Prof. W. DE SITTER.

In my communication to the meeting of February of this year (see these Proceedings, Vol 15, page 1297) I pointed out that the existence of spectroscopic doubles whose motion obeys the laws of KEPLER, is incompatible with the theory of RITZ, while in agreement with that of LORENTZ.

Since then Messrs. P. GUTHNICK<sup>1</sup>) and E. FREUNDLICH<sup>2</sup>) have brought forward the hypothesis that the velocity of light might depend on the velocity of the source in a manner differing from the simple addition postulated by the theory of RITZ. The most simple 'hypothesis would be

 $v = c + \varkappa u$ ,

where v is the velocity of light emitted by a source having the velocity u. The problem then is no longer to decide whether z = 0 or z = 1, intermediate values being excluded, but to assign an upper limit to z.

We have then, using the notations of my former paper

$$\alpha := \varkappa \frac{\triangle}{c^2}.$$

If the true orbit is a circle, then the equation (1) becomes:

$$u = u_0 \cos \frac{2\pi}{T} (t - t_0) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If  $\varkappa$  is very small we find for the equation (2) the following approximate expression

<sup>&</sup>lt;sup>1</sup>) Astronomische Kriterien für die Unabhangigkeit der Fortplanzungsgeschwindigkeit des Lichtes von der Bewegung der Lichtquelle, Astr. Nachr. 4670 (195, 265).

<sup>&</sup>lt;sup>2</sup>) Zur Frage der Konstanz der Lichtgeschwindigkeit, Physik. Zeitschn. 14, 835.