Chemistry. — *"Equilibria in systems, in which phases separated by a semi-permeable membrane"*. XIII. By F. A. H. SCHREINEMAKERS.

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The isotonic curves in ternary systems, in which dimixtion into two or three liquids occurs.

Till now we only have discussed the isotonic curves in systems, in which all liquids are mixible with one another in all proportions; we now assume that dimixtion into two or three liquids can occur also.

The sides of the components-triangle are not drawn in order not to enlarge the figure too much; only the angle-point W which represents the diffusing substance W (water or an other component), is indicated. The terminating-points of the isotonic curves, which are indicated in the figure by dotted curves, are situated on the side of the components-triangle, starting from point W.

As known, the region of dimixtion of a ternary system at constant temperature and under a constant pressure, is encircled by the binodal-curve; its points represent conjugated or coexisting liquids, viz. liquids which can be in equilibrium with one another two by two [1]). Those binodal-curves are represented in the figures by fully drawn curves. The critical points α and β divide the binodal-curve into two branches; with every liquid of the one branch a definite liquid of the other branch can be in equilibrium; some of those conjugated liquids are united in the figures by straight lines, the conjugation-lines. Consequently we find indicated in those figures the equilibria

$$L_{a_1} + L_{a_2} \qquad L_{b_1} + L_{b_2} \qquad L_{c_1} + L_{c_2}.$$

With regard to the extension of the region of dimixtion, we may distinguish two principal cases [2]).

A. The region of dimixtion is situated totally within the components-triangle, consequently dimixtion occurs in ternary liquids only, but not in the binary liquids.

B. The region of dimixtion extends itself as far as one of the sides, consequently dimixtion occurs also in one or more of the binary systems.

Although the case mentioned sub *A* experimentally seems to occur as

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[1]) For a treatment in detail of ternary equilibria with two and three liquids, compare F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM; Drittes Heft. Zweiter Teil.

[2]) Comp. f.i. the figs. 1—6, l. c.

exception only [1]), yet we will take this as a starting-point at the consideration of the isotonic curves. We may apply viz. the results also to the cases, mentioned sub B, some changes excepted, which occur in the vicinity of the sides of the components-triangle and which we shall indicate further.

In this communication we shall only indicate and describe several properties; in a following communication we shall deduce them with the aid of thermodynamical considerations and we shall enlighten them more in detail.

Let us take two conjugated liquids f.i. L_{b_1} and L_{b_2} (figs. 1—3). As both liquids are in equilibrium with one another, they are isotonic with respect to each of the three components, of which they consist. Consequently both liquids have the same $O.W.A.$ (osmotic water-attraction). Therefore, both liquids belong to the same isotonic curve; they are found in fig. 1 on the isotonic curve 5, in fig. 2 on curve 3 and in fig. 3 on curve 4. Of course the same is true for other conjugated liquids.

As regards the position of the point W with respect to the conjugation-lines of the binodal-curve, we can distinguish two cases. In figs. 2 and 3 one conjugation-line viz $m_1 m_2$ goes through the point W; in fig. 1 this is not the case. Further we shall see that this difference has a great influence on the proceeding of the isotonic curves.

I. None of the conjugation-lines goes through point W (fig. 1).

If we take isotonic curves in the vicinity of the point W, then they are straight lines; at further distance from the point W they are curved (Curve 1 and 2 of fig. 1). Dependent on the increase of the $O.W.A.$ of the liquids of the curves these curves are situated further from the point W and, therefore, they approach more the region of dimixtion till they touch it at last (curve 3). The point of contact coincides with the critical pont α of the binodal-curve, as we shall see later. Consequently all liquids of curve 3 have the same $O.W.A.$ as the critical liquid α.

If we take an isotonic curve with still greater $O.W.A.$, f.i. curve 4, then this curve intersects the binodal-curve in the two conjugated points a_1 and a_2. Then, if we consider stable liquids only, the isotonic curve consists of two branches, separated from one another, united by the conjugation-line $a_1 a_2$. As each point of the line $a_1 a_2$ represents a complex of the two liquids a_1 and a_2, therefore, each point of this line represents also a complex with the same $O.W.A.$ as that of the liquids of curve 4. If we represent an arbitrary liquid of curve 4 by L, then consequently the osmotic equilibrium

$$L \mid L_{a_1} + L_{a_2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

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[1]) We find an example in the system: water, phenol and aceton. F. A. H. SCHREINEMAKERS, Zeitschr. f. Phys. Chem. **33**, 84 (1900).

exists, in which equilibrium two liquids occur at one of the sides of the membrane.

An isotonic curve with still greater *O.W.A.*, f.i. curve 5 (fig. 1), intersects the binodal-curve in the conjugated points b_1 and b_2; curve 6

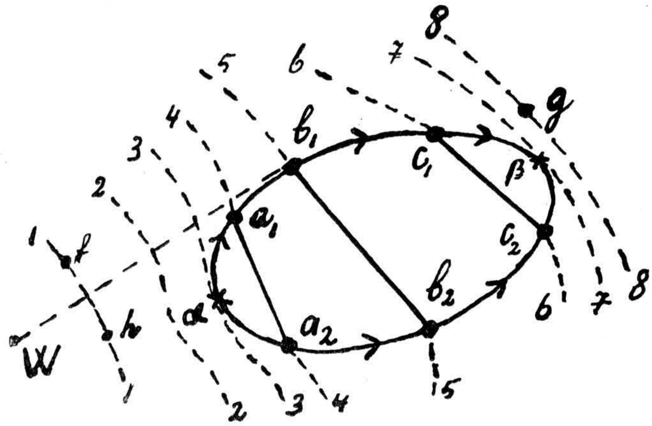

Fig. 1.

intersects them in the points c_1 and c_2 etc. At last we get again, as is represented by curve 7, an isotonic curve, touching the binodal-curve; this point of contact coincides with the critical point β. Isotonic curves with still greater *O.W.A.*, f.i. curve 8, are situated again totally outside the field of dimixtion.

Hence follows that the *O.W.A.* of the liquids of the binodal-curve increases on each of the two branches in the direction of the arrows viz. from the critical point α towards the critical point β. Consequently the *O.W.A.* of the liquids of the binodal-curve is a minimum for the critical liquid α and a maximum for the critical liquid β.

The conjugation-line $b_1 b_2$ divides fig. 1 into two parts; in the one part is situated the point W. If we start from the point b_1 along the binodal-curve towards that part of the plane, in which point W is situated (consequently from b_1 towards α), then we shall say that we go along the binodal-curve towards point W. If, however, we go from b_1 along the binodal-curve towards the other part of the plane (consequently from b_1 towards the point β), then we shall say that we move away from the point W along the binodal-curve.

Consequently we move away along the binodal-curve from point W, if we proceed along this curve:

in fig. 1 starting from α towards β;

in fig. 2 starting from the points m_1 and m_2 towards α and β;

in fig. 3 starting from the points α and β towards m_1 and m_2;

those directions are indicated in the figure by arrows.

In a following communication we shall deduce the property:

the $O.W.A.$ of the liquids of a binodal-curve increases in that direction, in which we move away from the point W along the binodalcurve.

If we apply this to fig. 1 then we find, in accordance with above, that the $O.W.A.$ must increase along the binodal-curve in the direction of the arrows, viz. from α towards β.

II. One of the conjugation-lines goes through point W (figs. 2 and 3).

In the figs. 2 and 3 the binodal-curves are drawn in such a way that the conjugation-line $m_1 m_2$ goes through the point W. In order to indicate more easily the proceeding of the isotonic curves, we have given to the binodal-curves another form than in fig. 1; this has no influence on the results of the considerations. We now distinguish the two cases, represented by the figures 2 and 3.

A. If we go in fig. 2 along the binodal-curve in the direction of the arrows, therefore, from m_1 or m_2 towards α or β, then we move away from the point W. In accordance with the rule, mentioned above, on the change of the $O.W.A.$ of the liquids of a binodal-curve, the $O.W.A.$ must increase, therefore, in the direction of the arrows; consequently it is a minimum for the liquids m_1 and m_2 and a maximum for the critical liquids α and β.

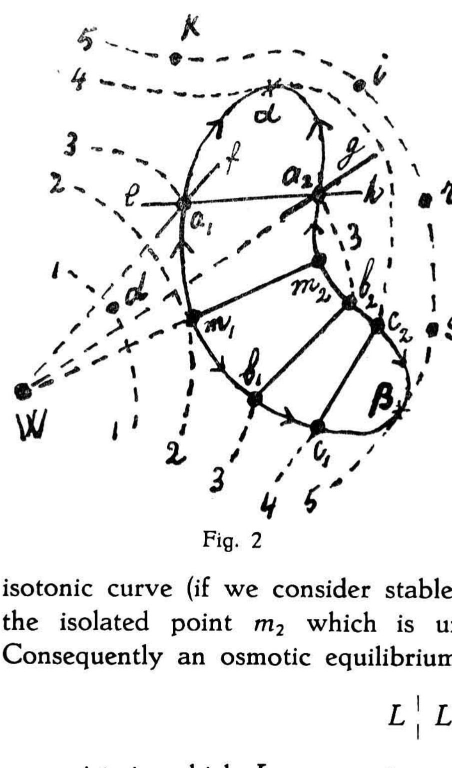

Fig. 2

The isotonic curve 1 is situated in fig. 2 totally outside the region of dimixtion; dependent on the increase of the $O.\ W.\ A.$, they approach this region till they touch it at last (curve 2). It now follows from the above. which we shall deduce later also in another way, that this point of contact coincides with m_1. As liquid m_2 has the same $O.W.A.$ as m_1 and consequently also as all liquids of curve 2, the isotonic curve (if we consider stable states only) consists of a curve and the isolated point m_2 which is united with m_1 by a conjugation-line. Consequently an osmotic equilibrium:

$$L \mid L_{m_1} + L_{m_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

can exist, in which L represents an arbitrary liquid of curve 2.

Isotonic curves with larger $O.W.A.$ consist of three branches, separated from one another. If we take f.i. curve 3 (fig. 2) then those branches are united by the conjugation-lines $a_1\, a_2$ and $b_1\, b_2$. The systems $L_{a_1} + L_{a_2}$

and $L_{b_1} + L_{b_2}$ have the same $O.W.A.$ as all liquids of curve 3; we may have, therefore the osmotic equilibria:

$$L \mid L_{a_1} + L_{a_2} \qquad L \mid L_{b_1} + L_{b_2} \qquad L_{a_1} + L_{a_2} \mid L_{b_1} + L_{b_2} \quad . \quad . \quad (3)$$

in which L represents an arbitrary liquid of curve 3. In the last one of those equilibria two liquids occur on both sides of the membrane.

Isotonic curves with larger $O.W.A.$ approach more the points α and β. If we assume that the $O.W.A.$ of the critical liquid α is smaller than that of the critical liquid β, then we can represent the isotonic curve, going through point α, by curve 4. This curve touches the binodal-curve in α and intersects it in the points c_1 and c_2. Consequently we now may have an osmotic equilibrium:

$$L_\alpha \mid L_{c_1} + L_{c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

in which at the one side of the membrane a critical liquid and at the other side two liquids.

An isotonic curve with the same $O.W.A.$ as liquid β touches the binodal-curve in β (curve 5) and is situated further totally outside the region of dimixtion.

B. In order to proceed in fig. 3 along the binodal-curve in such a way that we move away from the point W, we have to go in the direction of the arrows, viz. starting from α and β towards m_1 and m_2. Consequently the $O.W.A.$ of the liquids must increase also in the direction of the arrows; it is a minimum, therefore, in the critical points and a maximum in m_1 and m_2.

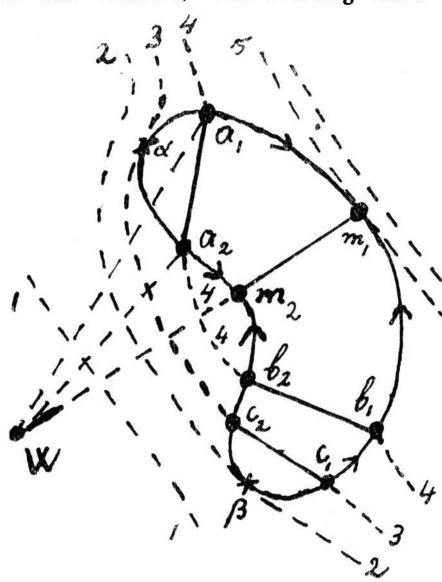

Fig. 3.

The isotonic curve 1 is situated in fig. 3 still totally outside the region of dimixtion; curves with larger $O.W.A.$ approach this region, in order to touch it at last. Of course the point of contact must be a liquid, the $O.W.A.$ of which is a minimum, therefore one of the critical liquids α or β. If the $O.W.A.$ of β is smaller than that of α, then we may represent the isotonic curve by curve 2. The isotonic curve with an $O.W.A.$ equal to that of the liquid α is represented by curve 3; isotonic curves with still greater $O.W.A.$ (as f.i. curve 4) consist of three parts, separated from one another, united with one another by two conjugation-lines ($a_1\ a_2$ and $b_1\ b_2$).

The isotonic curve with an $O.W.A.$ equal to that of the liquid m_1 is represented by curve 5, which touches the binodal-curve in m_1, and the isolated point m_2.

The osmotic equilibria, mentioned above sub (2) and (3) can occur also now; then in (2) L represents a liquid of curve 5 (fig. 3) and in (3) a liquid of curve 4 (fig. 3).

We can briefly summarize the previous considerations.

I. The $O.W.A.$ of the liquids of a binodal-curve increases in that direction in which we move away from the point W.

Hence follows:

II. None of the conjugation-lines of the binodal-curve goes through the point W (fig. 1).

The $O.W.A.$ of the liquids of the binodal-curve is a minimum in the one — and a maximum in the other critical point.

III. One of the conjugation-lines goes through point W (figs. 2 and 3).

A. The $O.W.A.$ of the liquids of the binodal-curve is a minimum in the points, situated on the conjugation-line going through W and a maximum in the critical points (fig. 2).

B. The $O.W.A.$ of the liquids of the binodal-curve is a minimum in the critical points and a maximum in the points, situated on the conjugation-line going through point W (fig. 3).

IV. In each of the critical points and in the points which are situated on the conjugation-lines going through point W, an isotonic curve touches the binodal-curve. Consequently we find in fig. 1 two isotonic curves touching the binodal-curve and in figs. 2 and 3 three of such curves.

If the region of dimixtion extends itself as far as into one or two of the sides of the components-triangle, then in the figures one or both critical points disappear. With the aid of the above-mentioned properties I—IV, of which we may apply always I, yet we can project then the schematical diagrams and define the direction in which increases the $O.W.A.$ of the liquids along the binodal-curve.

However, the following is to be observed with respect to the conjugation-lines going through the point W. The conjugation-lines of the figs. 1—3 unite ternary liquids; for this reason we call them ternary conjugation-lines. If, however, the binary curve terminates in the points p_1 and p_2 on one of the sides of the components-triangle, then $p_1 p_2$ is a binary conjugation-line, which always goes through the point W. The property, mentioned in IV, that in the points, which are situated on a conjugation-line, going through point W, an isotonic curve touches the binodal-curve, is true only for ternary conjugation-lines ($m_1 m_2$ in figs. 2 and 3), but not for binary ones. In the latter case the common point viz. is not a point of contact, but a point of intersection. We shall refer to this at the discussion of the special cases.

We have drawn the isotonic curves 4, 5 and 6 in fig. 1, as if they terminate in the region of dimixtion; this is, however, not the case. If we take f.i. curve 4, then this does not finish in a_1 and a_2, but it goes through the region of dimixtion from a_1 towards a_2; this part, situated within the region of dimixtion, however, represents only metastable and unstable liquids, which, however, have all the same $O.W.A.$ as the other liquids of curve 4. If, however, we limit ourselves, as we have done above, to stable states, then the isotonic curve consists of two separated branches, united by the conjugation-line $a_1\, a_2$.

Of course the same is valid for the isotonic curves of the other figures. If we take f.i. curve 3 of fig. 2, then this does not terminate in a_1 and a_2 and in b_1 and b_2. We now may distinguish two cases:

1. Curve 3 consists of a single continuous curve, which passes through the region of dimixtion from a_1 towards a_2 and from b_2 towards b_1.

2. Curve 3 consists of two separated parts. The branch coming in a_1 passes viz. through the region of dimixtion from a_1 towards b_1. The other branch, on which are situated the points a_2 and b_2, forms a closed curve, which is situated partly outside and partly within the region of dimixtion. In a following communication we will discuss a single case more in detail. [1])

In communication III we have discussed the property:

the saturation-curve of a solid substance and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or within the supplement-angle. If the saturation-curve touches one of the legs of this angle, then the isotonic curve touches the other leg.

As we will show later, for the equilibria treated now, is valid:

the binodal-curve and an isotonic curve are situated in the vicinity of their point of intersection either both within the conjugation-angle or both within the supplement-angle. If the binodal-curve touches one of the legs of that angle, then the isotonic curve touches the other leg.

Let us take in fig. 2 the point of intersection a_1. As liquid a_1 can be in equilibrium with liquid a_2, and as the diffusing substance is represented by point W, angle $W\, a_1\, a_2$ (and its opposite-angle $e\, a_1\, f$) is the conjugation-angle in a_1. As the binodal-curve is situated in the vicinity of a_1 within the conjugation-angle, curve 3 must be situated also within this angle.

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[1]) In order to imagine oneself properly the position of this curve, compare F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOSEBOOM. Drittes Heft, Zweiter Teil. Fig. 135—139 pg. 330—332. In those figures a part of the binodal-curve is drawn, recognizable by its conjugation-lines. If we imagine the diffusing substance to be represented by point V, then the curve, indicated by the figures I, II and III, can represent an isotonic curve. The dotted parts of this curve represent the metastable and unstable states.

In point a_2 (fig. 2) angle $W a_2 a_1$ (and its opposite angle $g a_2 h$) is the conjugation-angle; the two other angles (viz. $a_1 a_2 g$ and $W a_2 h$) form, therefore, the supplement-angle. As the binodal-curve is situated in the vicinity of a_2 within the supplement-angle, curve 3 must be situated also within this angle.

In fig. 1 a tangent is drawn from W, which touches the binodal-curve in b_1. As the binodal-curve touches, therefore, the leg $b_1 W$ of the conjugation-angle, curve 5 must touch in b_1 the other leg, viz. the conjugation-line $b_1 b_2$.

From the property above-mentioned of binodal-curve, isotonic curve and conjugation-angle follows:

An isotonic curve, which touches the binodal-curve in a critical point, is curved in the same direction as the binodal-curve in the vicinity of this point.

This is seen in fig. 1 with the curves 3 and 7; in fig. 2 with the curves 4 and 5; in fig. 3 with the curves 2 and 3. Of course this will be still also the case with isotonic curves, which are situated on some distance of the critical points, as f.i. with curve 2 in fig. 1, etc.

We imagine two conjugated liquids q_1 and q_2. We unite the points q_1 and q_2 with the point W, which represents the diffusing substance, so that the angle $q_1 W q_2$ arises. If we limit ourselves to stable states, then from each of the points q_1 and q_2 a branch of the isotonic curve starts. We now can show:

the stable branches of an isotonic W-curve, starting from two conjugated points q_1 en q_2, are situated always outside the region of the angle $q_1 W q_2$.

If we take f.i. the points a_1 and a_2 (fig. 1—3) then we see that the branches starting from those points, are situated outside the region of the angle $a_1 W a_2$. The same is valid in points b_1 and b_2, c_1 and c_2, etc.

With the aid of those and other properties discussed above, we are able to deduce already at once schematically the position and proceeding of the isotonic curves, if the position of the binodal-curve and its conjugation-lines is known.

Of the many phenomena, which may occur in osmotic systems with a region of dimixtion, we only will discuss some briefly. Let us take f.i. the osmotic system:

$$L_d \mid\!\rightarrow L \qquad \text{fig. 2} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

in which L represents a liquid of the isotonic curve 5. Consequently L has a greater $O.W.A.$ than L_d, so that the water diffuses in the direction of the arrow viz. from L_d towards L. We now assume that the quantities of L_d and L are taken in such a way that an osmotic equilibrium of curve 3 arises. As the line Wd intersects the line $a_1 a_2$ viz. the conjugation-line of the isotonic curve 3, L_d passes, therefore into a complex of the liquids a_1 and a_2. It depends on its position on curve 5, which shall arise from liquid L. If L represents the liquid K, then (5) passes into the osmotic equilibrium:

$$L_{a_1} + L_{a_2} \mid L'_K \qquad \text{fig. 2} \; . \; . \; . \; . \; . \; . \; . \; . \quad (6)$$

in which L'_K is represented by the point of intersection of the line WK with curve 3. If we take in (5) for L the liquid i, then arises

$$L_{a_1} + L_{a_2} \mid L_{a_1} + L_{a_2} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

therefore, an osmotic system, in which appear the same liquids at both sides of the membrane. If we take in (5) for L the liquid r, then arises the osmotic equilibrium:

$$L_{a_1} + L_{a_2} \mid L'_r \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

in which L'_r is represented by the point of intersection of the line Wr with the branch of curve 3, situated between a_2 and b_2. If we take in (5) for L the liquid s or the critical liquid β, then arises the osmotic equilibrium:

$$L_{a_1} + L_{a_2} \mid L_{b_1} + L_{b_2} \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

in which two liquids are found on both sides of the membrane.

In following communications we shall discuss more in detail the phenomena, occurring on the similar osmotic equilibria setting in.

(To be continued).