

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

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Influence of the pressure on osmotic systems and on the osmotic pressure.

An osmotic equilibrium, in which d diffusing substances, and in which occur at the one side of the membrane n_1 components in r_1 phases and at the other side n_2 components in r_2 phases, has, as we have seen in Communication VII, at constant temperature

$$n_1 + n_2 - (r_1 + r_2) + 2 - d$$

licences. Consequently an osmotic equilibrium with one diffusing substance has:

$$n_1 + n_2 - (r_1 + r_2) + 1$$

licences. As at constant temperature the equilibrium at the one side of the membrane has $n_1 - r_1 + 1$ licences and that at the other side has $n_2 - r_2 + 1$ licences, we can also say, therefore, that the number of licences at constant temperature is one smaller than the sum of the licences of the two systems.

We now take a system E , the composition of which we further keep constant; under given pressure the phases of this system are completely defined; they have viz. such composition that the total ζ of the system under that given P (and T) is a minimum. The system E is invariant under given pressure, therefore, so that it has one licence, if the pressure can change also.

If we take now an osmotic equilibrium:

$$(E_1)_{P_1} \mid (E_2)_{P_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which both systems have a constant composition, then this has, in accordance with the membrane-phase-rule above-mentioned: $1 + 1 - 1 = 1$ licence. If we put still one condition, f.i. that the pressure must be equal on both sides of the membrane, so that we get the osmotic equilibrium:

$$(E_1)_P \mid (E_2)_P \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

then this has no more licence, therefore; it can only exist under a definite pressure P .

As system (1) has one licence only, P_1 and P_2 are dependent on one another; consequently we can choose only one of those pressures

arbitrarily. With every definite pressure P_1 at the one side of the membrane, a definite other pressure P_2 at the other side is corresponding, therefore; if P_1 increases with a definite value dP_1 , then P_2 must increase with a definite other value dP_2 . Between those increments a relation exists, which we can find as follows. If (1) passes into the osmotic equilibrium:

$$(E_1)_{P_1+dP_1} \mid (E_2)_{P_2+dP_2} \dots \dots \dots (3)$$

then the *O.W.A.* of both systems increases with:

$$d\xi_1 = -\Delta V_{E_1} \cdot dP_1 \quad d\xi_2 = -\Delta V_{E_2} \cdot dP_2 \dots \dots (4)$$

As, however, the *O.W.A.* must remain the same on both sides of the membrane, it follows:

$$\Delta V_{E_1} \cdot dP_1 = \Delta V_{E_2} \cdot dP_2 \quad \frac{dP_2}{dP_1} = \frac{\Delta V_{E_1}}{\Delta V_{E_2}} \dots \dots (5)$$

If ΔV_{E_1} and ΔV_{E_2} have the same (opposite) sign, then we must, in order to keep both systems in osmotic equilibrium with one another, change the pressure on both sides of the membrane in the same (opposite) direction.

If we draw in a system of coordinates the pressure P_1 on one of the axes and on the other axis the corresponding pressure P_2 , then we have a $P_1 P_2$ curve, the direction of which is defined in every point by (5). If in a point $\Delta V_{E_1} = 0$, then the curve is in this point parallel to the P -axis; with a small change in pressure of system E_1 we must keep constant then the pressure of the system E_2 .

If we draw in this diagram a straight line, which makes equal angles with the two axes, then the points of intersection of this line with the $P_1 P_2$ curve represent the pressure P , under which the osmotic equilibrium (2) exists.

In the special case that E_1 and E_2 represent two gases or vapours, which follow the gas-laws, (5) passes into:

$$\frac{dP_2}{dP_1} = \frac{V_1}{V_2} = \frac{P_2}{P_1} \dots \dots \dots (6)$$

in which V_1 and V_2 represent the molecular volumina of those gases; hence follows:

$$P_2 = C P_1 \dots \dots \dots (7)$$

in which C is a constant. In order to keep both gases in osmotic equilibrium with one another, we have to change therefore, the two pressures in such a way, that their ratio remains constant. Then the $P_1 P_2$ curve is a straight line.

If we have chosen the composition of the two vapours in such a way, that they have the same *O.W.A.* under a certain pressure P_0 , then they have it also under every other pressure. Then the constant C in (7) is 1; the equilibrium (2) then exists not only under a single P ,

but under all pressures P . This is the case when both vapours have a same amount of water.

We now take the osmotic equilibrium :

$$(water)_{P_0} \mid E_P \dots \dots \dots (8)$$

in which at the left of the membrane pure water in liquid state under the pressure P_0 and at the right of the membrane an arbitrary system E under the pressure P . As $\pi = P - P_0$ represents the osmotic pressure of the system E with respect to water under the pressure P_0 , we shall write for (8):

$$(water)_{P_0} \mid E_{P_0+\pi} \dots \dots \dots (9)$$

If we represent the molecular volume of the water under the pressure P_0 by v_0 , then follows from (4):

$$d\xi_0 = -v_0 \cdot dP_0 \dots (10^a) \quad d\xi = -\Delta V_E \cdot dP \dots (10^b)$$

Consequently we find for the osmotic equilibrium (8):

$$v_0 dP_0 = \Delta V_E \cdot dP \quad dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \dots (11)$$

As $d\pi = dP - dP_0$ follows from (11):

$$d\pi = \left(\frac{v_0}{\Delta V_E} - 1 \right) dP_0 \dots \dots \dots (12)$$

The osmotic pressure of an arbitrary system E is dependent, therefore, on the pressure P_0 under which the water is; (12) defines the change $d\pi$ of the osmotic pressure at a small change dP_0 of the pressure of the water. In formula (13) of Communication I we have deduced already this formula (12) in a somewhat other form for the special case that the system E consists only of one binary liquid.

If we replace in (8) and (9) the water by water-vapour, then we get the osmotic equilibrium :

$$(watervapour)_{P_0} \mid E_P \quad (watervapour)_{P_0} \mid E_{P_0+\pi} \dots \dots (13)$$

in which π now represents the osmotic pressure of the system E with respect to watervapour of the pressure P_0 . The change of the *O.W.A.*, of the osmotic pressure, etc. is also defined by (10)–(12). However, in this we have to replace the volume v_0 of the water by the volume V_0 of the vapour.

In order to apply the previous considerations to a definite system E we must know, therefore, ΔV_E . If we take for E one of the equilibria :

$$\left. \begin{array}{ll} (Y + L_w)_P & \text{fig. 1. III} \\ (X + Y + L_c)_P & \text{fig. 1. V} \end{array} \right\} \begin{array}{ll} (Y + L_a)_P & \text{fig. 1. III} \\ (Y + H + L_d)_P & \text{fig. 2. V} \end{array} \quad (14)$$

etc. which we have discussed in the previous communication, then ΔV_E is defined for those systems by the formula's (10^a), (27), (35) or (38) of the previous communication. As we have formerly seen, it depends on the values of the volumina, concentrations etc. whether ΔV_E will be under a definite pressure positive, negative or casually zero. As the magnitudes which define ΔV_E are dependent on the pressure, ΔV_E , therefore, is also a function of the pressure; consequently it is possible that ΔV_E changes its sign with change of pressure.

If we substitute the values, above-mentioned, of ΔV_E in (10^a)—(12) then the change of the O.W.A. and that of the osmotic pressure of the systems (14) is defined.

We now take the osmotic equilibrium (8) or (9) in which E represents an arbitrary system f.i. one of the systems (14). As v_0 is positive, three cases can occur, viz. under the considered pressures is ΔV_E :

- I. positive and larger than v_0 ;
- II. positive and smaller than v_0 ;
- III. negative.

Further we have their mutual combinations and transitions between I and II and between II and III; a transition between I and III is only possible through the medium of II.

In order to represent graphically the further deductions, we take two axes; on the one we draw the pressure P_0 of the water, on the other the osmotic pressure π of the system E belonging to this pressure P_0 . As to every pressure P_0 belongs an osmotic pressure π , we get, therefore, a $P_0\pi$ -curve, as f.i. curve $aegk$ in fig. 1. If the water has f.i. the

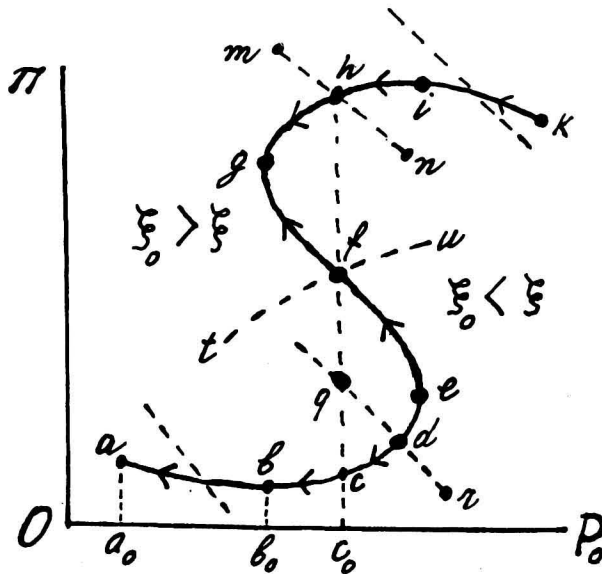


Fig. 1.

pressure $P_0 = O a_0$, then system E has an osmotic pressure $\pi = a_0 a$ and consequently a total pressure $P = O a_0 + a_0 a$.

We now shall consider more in detail the cases, above-mentioned.

I. If we change the pressure of the water with dP_0 then the changes dP and $d\pi$ of the total and osmotic pressure of the system E are defined by:

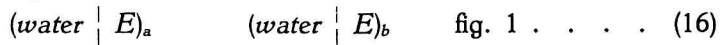
$$dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \quad . \quad . \quad (15^a) \qquad d\pi = - \left(1 - \frac{v_0}{\Delta V_E} \right) dP_0 \quad . \quad . \quad (15^b)$$

in which the term between parentheses is positive and smaller than 1. If we raise the pressure P_0 of the water, then it appears that the total pressure P of the system E becomes larger also, but that its osmotic pressure becomes smaller. Further it is apparent that as well the increase of the total pressure as the decrease of the osmotic pressure, is smaller than the change of pressure which we give to the water. Consequently we get a $P_0\pi$ -curve as branch ab or ik (fig. 1) the first of which is convex to the abscis and the second concave to the abscis.

In fig. 1 are drawn some dotted lines, which make an angle of 45° with the P_0 -axis (in the following viz. we indicate only the angles, smaller than 90°). It follows from (15^b) that the tangent in every point of branches ab and ik makes with the P_0 -axis an angle smaller than 45° . If we go along branch ab from a towards b , then this is situated, therefore, firstly below and afterwards above the dotted line, which is drawn through a point of this branch; the same is valid for the branch ik .

As in an osmotic equilibrium the *O.W.A.* is the same on both sides of the membrane, we can call this the *O.W.A.* of this equilibrium. The change of this *O.W.A.*, when an osmotic equilibrium goes along branch ab or ik , is defined by (10^a) or (10^b). It follows from (10^a) that the *O.W.A.* increases with decreasing values of P_0 ; consequently the arrows on ab and ik indicate the direction, in which the *O.W.A.* increases.

If we represent the osmotic equilibria, which are indicated by the points a and b by:



then is in the first equilibrium:

- the pressure P_0 of the water smaller,
- the osmotic pressure π of system E larger,
- the total pressure P of the system E smaller,
- and the *O.W.A.* larger than in the second equilibrium.

II. In the case, mentioned sub II the coefficient of dP_0 in the two equations:

$$dP = \frac{v_0}{\Delta V_E} \cdot dP_0 \quad . \quad . \quad (17^a) \qquad d\pi = \left(\frac{v_0}{\Delta V_E} - 1 \right) dP_0 \quad . \quad . \quad (17^b)$$

is positive; in (17^a) this coefficient is larger than 1, in (17^b) this can be as well larger as smaller than 1. If we raise the pressure P_0 of the water, then the total and the osmotic pressure of the system increases, therefore. The change dP of the total pressure is larger, the change $d\pi$ of the osmotic pressure can be greater also, but also smaller than the change dP_0 , which we give to the pressure of the water.

Consequently in a $P_0\pi$ -diagram we get a curve, as branch be or gi in fig. 1. The angle, which makes a tangent to those branches with the P_0 -axis can be as well larger as smaller than 45° .

With the aid of (10^a) we find again, that the *O.W.A.* increases along those branches in the direction of the arrows.

III. We now put $\Delta V_E = -\Delta$, so that Δ is positive. The change of the total and of the osmotic pressure are defined by:

$$dP = -\frac{v_0}{\Delta} \cdot dP_0 \quad d\pi = -\left(\frac{v_0}{\Delta} + 1\right) dP_0 \quad . . . \quad (18)$$

in which the term between parentheses is positive and larger than 1. Just as in the case, discussed sub I, the osmotic pressure decreases with increasing values of P_0 ; in contradiction with I, however, this decrease now is larger than the increase of pressure dP_0 which we give to the water; also the total pressure P of the system E decreases with increasing values of P_0 .

Hence follows that now we get a $P_0\pi$ -curve, as branch eg which has a falling direction at increasing values of P_0 just as ab and ik . In contradiction with the branches ab and ik the tangent in every point of this curve eg makes, however, an angle, which is greater than 45° .

It follows from (10^a) that the *O.W.A.* increases along this branch eg in the direction of the arrows.

IV. With the transition of I into II becomes $\Delta V_E = v_0$; we then get at first approximation:

$$dP = dP_0 \quad d\pi = 0 \quad \quad (19)$$

In point b , where the branches ab and eb pass into one another, and in the point i , where this is the case with the branches gi and ki , the tangent is horizontal, therefore. Consequently a small change in pressure dP_0 of the water at first approximation has no influence on the osmotic pressure of the system E ; this is a minimum then (point b) or a maximum (point i).

In order to examine this more in detail, we take in (10^a) and (10^b) still terms of the second order; then we get:

$$d\xi_0 = -v_0 dP_0 + a_0 dP_0^2 \quad d\xi = -\Delta V_E dP + a dP^2 \quad . \quad (20)$$

As those changes of the *O.W.A.* on both sides of the membrane must be equal, follows:

$$-v_0 dP_0 + a_0 dP_0^2 = -\Delta V_E dP + a dP^2 \quad . . . \quad (21)$$

If we put in this $\Delta V_E = v_0$ and $dP = dP_0 + d\pi$ then follows:

$$d\pi = \frac{\alpha - \alpha_0}{v_0} \cdot dP_0^2 \dots \dots \dots (22)$$

in which the terms, which are infinitely small with respect to those, already written, are omitted. Hence is apparent that the osmotic pressure for $\alpha > \alpha_0$ is a minimum and for $\alpha < \alpha_0$ a maximum; also it appears that the curve is parabolic in the vicinity of b and i .

The change of the *O.W.A.* has nothing particular in those points b and i .

V. With the transition of II into III becomes $\Delta V_E = 0$; then follows from (11) and (12)

$$dP = \infty \quad d\pi = \infty \quad \dots \dots \dots (23)$$

so that the tangent in the points e and g is vertical. As $\Delta V_E = 0$, we write for (20) and (21):

$$\left. \begin{aligned} d\xi_0 &= -v_0 dP_0 & d\xi &= \beta \cdot dP^2 \\ -v_0 dP_0 &= \beta \cdot dP^2 \end{aligned} \right\} \dots \dots \dots (24)$$

If we put $dP = dP_0 + d\pi$ then we find:

$$d\xi_0 = d\xi = \beta \cdot d\pi^2 \quad \dots \quad (25^a) \quad d\pi = \pm \sqrt{-\frac{v_0}{\beta} \cdot dP_0} \quad (25^b)$$

in which the terms, which are infinitely small with respect to those, already written, are omitted. We now distinguish two cases.

If β is negative, then we can satisfy (25^b) only by positive values of dP_0 ; with every positive increase of dP_0 then are corresponding a same increase and decrease of the osmotic pressure. Then the curve is situated as in point g , viz. at the right side of the vertical tangent going through this point. In accordance with the arrows follows from (25^a), that the *O.W.A.* decreases along this curve starting from point g in both directions.

The osmotic equilibrium has, therefore, in point g a minimum-pressure of the water, while the osmotic pressure is maximum.

If β is positive, then we can only satisfy (25^b) by negative values of dP_0 ; then the curve is situated as in point e , viz. at the left of the vertical tangent going through this point.

Consequently the osmotic equilibrium gets in the point e a maximum-pressure of the water, while its osmotic pressure is a minimum.

Further it appears from (25^b) that the curve is parabolic in the vicinity of the points e and g .

The vertical line $c_0 h$ intersects the $P_0 \pi$ -curves in three points, which represent the osmotic equilibria:

$$(water \mid E)_c \quad (water \mid E)_f \quad (water \mid E)_h \quad \text{fig. 1.} \quad \dots \quad (26)$$

as, although their osmotic pressures are different, those equilibria yet exist under the same pressure $P_0 = O c_0$ of the water, they have, therefore, also the same *O.W.A.* In general it follows from this: osmotic equilibria, which are situated in the $P_0 \pi$ -diagram on a same vertical line have the same *O.W.A.*

It is apparent from the previous considerations that every osmotic equilibrium has a definite $P_0\pi$ -curve, and that it depends on the ΔV_E of the system E , how many and which branches of the curve drawn in fig. 1 will occur.

If we change the pressure P of an equilibrium E of definite composition, then this can pass into a new system E' under a definite pressure P_s either by the occurrence of one or more new phases or by the disappearance of one or more of the present phases. This pressure P_s is dependent on the composition of the system E . Let us take f.i. the system:

$$E = (Y + L)_P (27)$$

When the solubility of the solid substance Y increases with increase of pressure, then the quantity of the solid substance in this system will decrease, therefore; under a definite pressure P_s the solid substance totally disappears and a new system E' arises, which only consists of a liquid L of definite composition. In this special case the pressure P_s is greater, according as the total concentration of the substance Y in (27) being greater. If we have f.i. the system:

$$E = (X + Y + L)_P (28)$$

in which at increase of pressure the solubility of X as well as of Y increases, then two new systems can arise from this. The first arises when under a pressure P_s one of the solid phases disappears; the second when under a higher pressure P'_s also the other solid substance disappears and consequently only the liquid remains.

If the system E passes into a new system E' under a pressure P_s , then the osmotic equilibrium

$$(water)_{P_0} \mid E_{P=P_0+\pi} (29)$$

passes in a definite point s of its $P_0\pi$ -curve into the new osmotic equilibrium:

$$(water)_{P_0} \mid E'_{P=P_0+\pi} (30)$$

then there are two $P_0\pi$ -curves, which go both through the point s . If we imagine the first to be represented by curve ak of fig. 1, then the second can be indicated by the dotted curve tfu , when $P_s = P_f$. It depends on the ΔV_E of the new system, of how many and of which branches this curve tfu will consist and which angle it makes in f with the first curve.

We take in fig. 1 a point q which is not situated on the $P_0\pi$ -curve, this point represents an osmotic system (q) viz.:

$$(q) = (water \mid E)_q \quad \text{fig. 1} (31)$$

in which the water has a pressure $P_0 = Oc_0$ and E a pressure $P = Oc_0 + c_0q$. As, however, q is not situated on the curve of equilibrium (31) is not

an osmotic equilibrium, so that water must diffuse from the one side of the membrane towards the other. In order to define the direction of this diffusion, we have to compare the *O. W. A.* of the water with that of the system *E*; we represent the first by $\xi_0(q)$ and the second by $\xi(q)$.

As the water has the same pressure $P_0 = Oc_0$ as well in the osmotic system (*q*) as in the osmotic equilibrium (*c*), the *O. W. A.* of the water is also the same, therefore, in both systems; consequently we have $\xi(q) = \xi_0(c)$. As, however, *c* is an osmotic equilibrium, so that the *O. W. A.* is equal on both sides of the membrane, we have also, therefore, $\xi_0(c) = \xi(c)$; consequently we have:

$$\xi_0(q) = \xi_0(c) = \xi(c) \dots \dots \dots (32)$$

We now compare the osmotic system (*q*) with the osmotic equilibrium (*d*). As the line *q d* makes an angle of 45° with the P_0 -axis is:

$$Oc_0 + c_0 q = Od_0 + d_0 d \dots \dots \dots (33)$$

This means that *E* has the same pressure *P* and consequently also the same *O. W. A.*, as well in the osmotic system (*q*) as in the osmotic equilibrium (*d*). Consequently we have:

$$\xi(q) = \xi(d) = \xi_0(d) \dots \dots \dots (34)$$

It is apparent from the direction of the arrows in fig. 1 that $\xi_0(c) = \xi(c)$ is greater than $\xi_0(d) = \xi(d)$. It now follows from (32) and (33):

$$\xi_0(q) > \xi(q) \dots \dots \dots (35)$$

This means that in the osmotic system (*q*) the *O. W. A.* of the water is larger than that of the system *E*. Instead of (31) we write, therefore:

$$(water \overset{\leftarrow}{\mid} E)_q \quad \text{fig. 1} \dots \dots \dots (36)$$

in which the arrow indicates the direction, in which the water diffuses. We find the same for the osmotic systems (*m*) and (*t*).

In the same way as above we find that the water in the osmotic system:

$$(water \overset{\rightarrow}{\mid} E)_r \quad \text{fig. 1} \dots \dots \dots (37)$$

must diffuse in the direction of the arrow; this is valid also for the osmotic systems (*n*) and (*u*).

In order to define more in detail the different behaviour of the systems (*q*) and (*r*) we place ourselves in fig. 1 in the point *O* and we consider the lines, which make an angle of 45° with the P_0 -axis. Then *q* is situated on the line *q d r* at the left of the point *d* and *r* is at the right; on the line *m h n* is situated *m* at the left and *n* at the right of the point *h*; etc. Therefore the $P_0 \pi$ -curve divides the diagram into two parts, of which we shall say that the one is situated at the left and the other at the right side of this curve.

We can summarise the previous results in the following way.

If the osmotic system

$$(water)_{P_0} \overset{\leftarrow}{\mid} E_P \quad \text{fig. 1} \dots \dots \dots (38)$$

is represented in the diagram:

1. by a point of the $P_0 \pi$ -curve, then is $\xi_0 = \xi$; then it is an osmotic equilibrium with the osmotic pressure $\pi = P - P_0$.

2. by a point at the right side of the $P_0 \pi$ -curve, then is $\xi_0 < \xi$; then it is not an osmotic equilibrium but an osmotic system, in which the water diffuses towards the system E .

3. by a point at the left of the $P_0 \pi$ -curve, then is $\xi_0 > \xi$; then the water diffuses away from system E .

We are able to deduce this in the following way also. We imagine anywhere in fig. 1 on the $P_0 \pi$ -curve a point s , through which we draw a horizontal line; on this line we take a point s' in the vicinity of s . Then the point s represents an osmotic equilibrium:

$$(s) = (\text{water})_{P_0} \mid E_P \dots \dots \dots (39)$$

and the point s' an osmotic system:

$$(s') = (\text{water})_{P_0 + dP_0} \mid E_{P + dP_0} \dots \dots \dots (40)$$

the latter arises from the first by changing the pressure on both sides of the membrane with the same amount dP_0 . It now follows from (10^a) and (10^b):

$$\xi_0(s') = \xi_0(s) - v_0 dP_0 \quad \xi(s') = \xi(s) - \Delta V_E \cdot dP_0 \dots \dots (41)$$

As (39) is an osmotic equilibrium, $\xi_0(s)$ viz. the *O. W. A.* of the water is equal to $\xi(s)$ viz. the *O. W. A.* of system E ; consequently it follows from (41):

$$\xi_0(s') - \xi(s') = (\Delta V_E - v_0) \cdot dP_0 \dots \dots \dots (42)$$

We now imagine the point s' in the region which is situated at the right side of the $P_0 \pi$ -curve (viz. at the right, according to the definition given above); we distinguish two cases.

a. Point s is situated on one of the branches *b e*, *e g* or *g i*, so that $\Delta V_E < v_0$. In order to come from s in the point s' we have to take dP_0 positive, therefore. It now follows from (42):

$$\xi_0(s') < \xi(s') \dots \dots \dots (43)$$

b. Point s is situated on one of the branches *a b* or *i k*, so that $\Delta V_E > v_0$. In order to come from s in s' we have to take now dP_0 negative; hence follows again (43).

As, therefore, (43) is valid for every point s' which is situated at the right side of the $P_0 \pi$ -curve, the rule mentioned above sub 2. follows from this.

If we take point s' at the left side of the curve, then we find, just as above:

$$\xi_0(s') > \xi(s') \dots \dots \dots (44)$$

from which follows the rule mentioned above sub 3.

(To be continued).