TABELLE IV. Die mittlere Kurve.

Phase	v	Phase	v	Phase	v	Phase	v
-90^{d}	$9^{m}.74$	-20^{d}	$13^{m}.27$	$+50^{d}$	$11^{m}.00$	$+120^{d}$	$7^{m}.75$
-80	10.31	-10	13.47	$+60$	9.96	$+130$	8.03
-70	10.88	0	13.53	$+70$	8.92	$+140$	8.42
-60	11.45	$+10$	13.46	$+80$	8.20	$+150$	8.89
-50	11.99	$+20$	13.19	$+90$	7.78	$+160$	9.40
-40	12.50	$+30$	12.72	$+100$	7.60	$+170$	9.97
-30	12.93	$+40$	11.96	$+110$	7.59	—	—

Die Streuung ist wieder grösser beim Maximum, und grösser im aufsteigenden Aste. Das Verhältnis der Streuungen $0^{m}.415$ und $0^{m}.286$ ist 1.45, das Verhältnis der durchschnittlichen Geschwindigkeiten des Lichtwechsels bei Auf- und Abstieg 1.43.

Zusammenfassung.

Aus 764 in den Jahren 1905 bis 1932 (2416847 bis 2426979) angestellten Beobachtungen von *T Ursae Majoris* sind die folgenden Elemente des Lichtwechsels abgeleitet worden:

$$\left.\begin{array}{l}\text{Minimum: } 2421928^{d}\\ \text{Maximum: } 2422033\end{array}\right\} + 255^{d}.6\,E + 9^{d}\,\sin 5^{\circ}\,(E-8)\,; \quad \begin{array}{r} v = 13^{m}.53\\ v = 7\;.58\\ \hline \text{Amplitude} = 5\;.95,\end{array}$$

woraus $\frac{M-m}{P} = 0.411$.

Die mittlere Lichtkurve hat einen volkommen glatten Verlauf.

Utrecht, November 1932.

Chemistry. — *Osmotic systems, in which non-diffusing substances may occur also.* II. *Equilibrium and the change of the permeability of the membrane.* By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of November 26, 1932).

We take the free equilibrium

$$L\,(d+n)_{P}\,|\,L'\,(d+n')_{P'} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

in which d diffusing substances, n non-diffusing ones on the left side and n' non-diffusing ones on the right side of the membrane. If we do not pay attention to the quantities of the liquids L and L', which quantities in this free equilibrium may be varied arbitrarily whenever desired, then (1) has

$$d + n + n' \text{ freedoms} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If we replace the membrane by an other, or when it changes its nature under some influence or other, we may imagine several cases.

We shall say that a membrane becomes less permeable, when it becomes impermeable for one or more of the diffusing substances (and at the same time also remains impermeable for the substances that were already non-diffusing); here also belongs the special case that the membrane becomes impermeable for all substances.

When the reverse takes place, namely that the membrane becomes permeable for one or more of the non-diffusing substances (and at the same time also remains permeable for the substances that were diffusing already) we shall say that it becomes more permeable.

We may also imagine that the membrane changes, without this causing a change in the diffusing and non-diffusing substances; then we shall say that the membrane remains equipermeable.

Of course we may suppose besides that the membrane becomes permeable for one or more of the non-diffusing substances and at the same time impermeable for one or more of the diffusing substances. Then, according to the meaning I have attached to more- and less-permeable, it is neither completely the one, nor completely the other; for this reason I shall call it m.l.-permeable.

All these changes may be a result of the influence of the substances present, of changes of tension in the membrane, of the age, hysteresis etc.; in nature also other factors as e.g. stimuli may be the cause [1]).

We shall first discuss now what influence this change of permeability can have on the number of freedoms of the free equilibrium (1).

1. When the membrane remains equipermeable, so that d, n and n' do not change, the number of freedoms does not change.

2. We now imagine that the membrane becomes less permeable for q diffusing substances. Then only $d-q$ diffusing substances remain, but $n+q$ non-diffusing ones on the left side and $n'+q$ non-diffusing ones on the right side. The number of freedoms is then

$$(d-q) + (n+q) + (n'+q) = d + n + n' + q \quad . \quad . \quad . \quad (3)$$

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[1]) Comp. e.g. J. M. JANSE. The Verslagen 4, 332 (1888); 35, 418 (1926); M. F. E. NICOLAI, Diss. Leiden 1929, in which other literature is found also.

and has increased, therefore, with q. From this it follows e.g.: when the membrane of the equilibrium [1])

$$L(W + X + \bar{Y} + \bar{Z} + \bar{U})_P \,|\, L'(W + X + \bar{Y} + \bar{Z} + \bar{V})_{P'} \quad . \quad (4)$$

becomes impermeable for the substances X, the number of freedoms increases with one.

3. Now we assume that the membrane becomes more permeable for r of the non-diffusing substances, each occurring on the two sides of the membrane.

Then there will be $d + r$ diffusing substances, but only $n - r$ non-diffusing ones will remain on the left side and $n' - r$ non-diffusing ones on the right side of the membrane. The number of freedoms then becomes

$$(d + r) + (n - r) + (n' - r) = d + n + n' - r \quad . \quad . \quad . \quad . \quad (5)$$

and has consequently decreased with r. From this it follows e.g.:

when the membrane of (4) also becomes permeable for $Y(Z)$, the number of freedoms will decrease with one; when it becomes permeable for Y and Z at the same time, it will decrease with two.

4. Now we suppose that the membrane becomes more permeable for s of the non-diffusing substances, occurring only on the left side and for s' of the non-diffusing substances, occurring only on the right side of the membrane.

Then there will be $d + s + s'$ diffusing substances, but only $n - s$ non-diffusing ones will remain on the left side and $n' - s'$ non-diffusing ones on the right side. The number of freedoms then is:

$$(d + s + s') + (n - s) + (n' - s') = d + n + n' \quad . \quad . \quad . \quad (6)$$

and has consequently not changed.

From this it appears that the number of freedoms will not change when the membrane of (4) becomes permeable for U or for V or for both.

5. If we now imagine that the membrane becomes m.l.-permeable, then we can easily find that the number of freedoms will increase with $q - r$, in which q and r have the same meaning as sub 2 and 3. Then the number of freedoms can increase, decrease or remain constant.

From this it follows among other things that the number of freedoms of (4) will not change when the membrane becomes impermeable for X and permeable for Y or Z. The number of freedoms will decrease with one, however, when the membrane becomes impermeable for X and permeable for Y and Z.

In either case it does not matter whether the membrane does become permeable at the same time for U or V or for both, or does not.

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[1]) The dash, placed above a substance, indicates as in the preceding communication, that the membrane is impermeable for that substance.

Above we have until now only paid attention to the change in the number of freedoms; we are now going to discuss also the change, which can occur in the state of an equilibrium. Instead of the free equilibrium I take for this purpose some definite equilibrium or other, so that the quantity of each of the substances present and the pressures P and P' are determined. Then we have a definite $P.Q.$-equilibrium

$$m \times L\,(d+n)_P \,|\, m' \times L'\,(d+n')_{P'} \quad . \; . \; . \; . \; . \quad (7)$$

This equilibrium has no freedom left and only exists in a single, entirely determined state, the quantities m and m' of the two liquids being determined also (comp. L. Comm. I).

For an osmotic system with d diffusing substances to be in equilibrium, it is necessary and sufficient that d equations

$$O\,.\,A = (O\,.\,A)' \quad . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

are satisfied, expressing that each of the d diffusing substances on both sides of the membrane has the same $O.A.$; the $O.A.$'s of the non-diffusing substances do not play a part here; their concentrations, however, as well as those of the diffusing substances, occur in the d equations (8). We now shall distinguish the following cases.

a. We now suppose in the same way as above sub 1, that the membrane remains equipermeable; it is clear that the state of (7) then cannot change.

b. We now assume that in the same way as above sub 2, the membrane becomes less permeable for q of the diffusing substances. As each of the d diffusing substances of (7) has the same $O.A.$ on both sides, it is clear that this must still be the case for the $d-q$ remaining substances; consequently the equilibrium will not have changed.

From *a* and *b* now follows:

A. when a membrane remains equipermeable or becomes less permeable, the state of the equilibrium does not change. Of course this still obtains also when the membrane becomes completely impermeable; then, however, we cannot speak of an equilibrium any longer.

c. We now suppose as above sub 3 that the membrane becomes more permeable for r non-diffusing substances, all occurring on both sides of the membrane. The d diffusing substances, which already had in (7) the same $O.A.$ on both sides, will still have this of course. It would be a coincidence however (to which we shall refer later on) when the r new diffusing substances also had the same $O.A.$ on both sides already in (7). Even if this should not be the case for one of these r, the state of the equilibrium must change.

Let us imagine now that (4) is a Def. $P.Q.$-equilibrium, so that the quantities m and m' which have not been indicated, are determined also. When the membrane now becomes permeable for Y also, (4) will not be in equilibrium any longer; then the substances W, X and Y will begin diffusing in some direction or other, until at last a new equilibrium sets in in an other state; the composition and the quantities m and m' of the two liquids namely will then differ from those in (4).

This same phenomenon will repeat itself, when the membrane becomes permeable for Z besides.

Above we have said that it would be a coincidence when a non-diffusing substance had the same *O.A.* on both sides: in some cases, however, this is no coincidence at all any more.

Let us imagine e.g. that the membrane, as sub *b*, becomes less permeable for q diffusing substances, then it is clear that each of these q now non-diffusing substances, must have the same *O.A.* in the two liquids. When the membrane for some reason would become more permeable for one or more of these q substances, it is clear that the state of the equilibrium would not be changed hereby.

d. Now we suppose in the same way as above, sub 4, that the membrane becomes more permeable for s of the non-diffusing substances occurring only at the left side and for s' of the non-diffusing substances occurring only on the right side of the membrane. Without further explanation it will be clear that (7) now cannot be in equilibrium any longer, so that a new state must set in.

If namely we imagine that the membrane of (4) now also becomes permeable for U, then U will begin to diffuse towards the right; of course this also causes W and X to pass through the membrane in some direction or other, until at last a new equilibrium has set in again. The same phenomenon will repeat itself once more, when the membrane becomes permeable for V too. From c and d now follows:

B. when a membrane becomes more permeable, the state of the equilibrium will change; each of the changes in the permeability is followed by an osmosis until the new state has set in.

Attention should be paid here, however, to the coincidence, discussed sub *c*, when one of the non-diffusing substances occurring on both sides, becomes diffusing.

e. Now we imagine in the same way as above sub 5, that the membrane becomes m.l.-permeable. We now find that for this case the same obtains as has been discussed above in *B*.

When through the change in the permeability of its membrane an equilibrium passes into a new state, it may occur that the liquid on one of the sides of the membrane disappears entirely.

This is certainly the case when the membrane becomes permeable for all substances and the pressures P and P' are different. Previously namely (*E.* Comm. I) we have seen that a system with a membrane permeable for all substances, can be in equilibrium only when the two liquids have the same pressure and composition. Consequently the system cannot reach an equilibrium when the two pressures are different, so that all substances will flow towards that side of the membrane where the pressure is smallest.

Let us take as an other example an equilibrium

$$L(d+\bar{X})_P \,|\, L'(d+\bar{X}+\bar{Y}+\bar{Z})_{P'} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which it depends upon the concentration of the non-diffusing substances whether P will be greater than P' yes or no.

When the membrane now becomes permeable for X, then

$$L_1(d+X)_P \,|\, L'(d+X+\bar{Y}+\bar{Z})_{P'} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

forms, in which the two liquids will have an other composition than in (9). This system, however, can exist only when $P < P'$ (comp. F Comm. I).

If in (9) P should be $< P'$, then (10) is an equilibrium; if, however, in (9) P should be $> P'$, all liquids will diffuse from left to right; then a state

$$\times_P \,|\, L'_2(d+X+\bar{Y}+\bar{Z})_{P'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

forms in which the sign $\times$ indicates that all liquids have disappeared here.

It is clear that a similar state can occur only, when the membrane becomes permeable for all substances of both or of one of the two liquids; in the latter case it is clear also that all liquids can gather only on that side of the membrane where the non-diffusing substances are found.

We now imagine that the membrane M of an equilibrium by z successive changes in its permeability passes into a membrane, which we shall call M_z; the state R of this equilibrium then passes into an other state R_z.

Now one might believe that this state R_z would always be independent of the sequence of these z changes; this is not always the case, however. As a general consideration would lead us too far, I shall make this clear by a simple example only. For this purpose we take the equilibrium

$$L(W+X)_P \,|\, L'(W+X+\bar{Y})_{P'} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

in which P always $< P'$. We now imagine two changes viz. the becoming impermeable for X and the becoming permeable for Y. We now distinguish two cases.

1. The membrane becomes impermeable first for X and afterwards permeable for Y. The first change causes (12) to pass into

$$L(W+\bar{X})_P \,|\, L'(W+\bar{X}+\bar{Y})_{P'} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

in which of course L and L' still have the same composition as in (12). With the second change (13) passes into

$$L_2(W+\bar{X}+Y)_P \,|\, L'_2(W+\bar{X}+Y)_{P'} \quad . \quad . \quad . \quad . \quad (14)$$

in which W and Y are distributed in quite an other way as in (12).

2. The membrane of (12) first becomes permeable for Y and afterwards impermeable for X. The first change makes the membrane permeable

for all substances; because, as we have seen before, $P < P'$, now (12) passes into:

$$L_1 (W + X + Y)_P \,|\, X_{P'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which further remains unchanged, when at the second change the membrane now becomes impermeable for X.

From this it appears that two similar changes in the permeability, but taken in a different sequence, may result in an other state. So we may say:

C. when a given equilibrium [viz. a Def. *P.Q.*-equilibrium] passes through a series of states because of changes in its membrane, its final-state (and also intermediate states) may be dependent of the sequence of these changes.

We now suppose that by the changes in its membrane an equilibrium travels successively through the states

$$R \quad R_1 \quad R_2 \quad R_3 \ldots . R_z \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In each of these states the equilibrium has a definite ζ, which we represent by ζ, ζ_1, ζ_2, ... ζ_z. As the ζ of a system containing a definite quantity of each of the substances, can only decrease or remain constant under constant pressure (and at constant temperature), it follows:

$$\zeta > \zeta_1 > \zeta_2 > \zeta_3 \ldots . > \zeta_z \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

in which, however, also two or more ζ's following each other immediately, may be equal. E.g. ζ_2 can be $= \zeta_3$, but not e.g. $\zeta_2 = \zeta_5$, unless also $\zeta_2 = \zeta_3 = \zeta_4 = \zeta_5$.

From this it follows that indeed two successive states e.g. R_2 and R_3 can be equal, but not e.g. R_2 and R_5, unless R_2, R_3, R_4 and R_5 are equal; for this reason we shall consider them as one state. From these considerations it follows among other things:

D. when by a change in its membrane a given equilibrium has passed through a few states, it is not possible to alter the membrane in such a way that one of the states already passed through, can return once more.

E. when in a series of changes of a given equilibrium a state A preceeds a state B (between which one or more other states may or may not be situated), then in an other series of changes of this same equilibrium this state A never can follow B.

From these considerations other results can still be deduced; I leave this to the reader, however.

If we place one or more membranes against one another, then a new membrane arises, which I shall call a "combination-membrane". If e.g. we imagine

M_1 only permeable for W, X, Y and Z
M_2 ,, ,, ,, W, X and Z
M_3 ,, ,, ,, W, Y and U

and when we bear in mind that a combination is only permeable for those substances, which can diffuse through each of the two membranes, then it is clear that the combination-membrane

$M_1 M_2$	will be permeable only for	W, X and Z
$M_1 M_3$	,, ,, ,, ,, ,,	W and Y
$M_2 M_3$	,, ,, ,, ,, ,,	W

and that the latter is also the case for the combination $M_1 M_2 M_3$.

From this it also appears that the permeability of a membrane by combining it with an other can decrease or remain equal, but that it never can increase.

In the special case that two membranes are equipermeable, their combination also is equipermeable with both.

We now take the two osmotic equilibria

$$A \overset{M_1}{|} B \quad \text{and} \quad A \overset{M_2}{|} C \quad \ldots\ldots \quad (18)$$

in which three arbitrary states, which have been called A, B and C. In the first, in which a membrane M_1, state A is in equilibrium with B; in the second, in which a membrane M_2, state A is in equilibrium with C.

Now it is clear that the osmotic system

$$B \overset{M_1 M_2}{|} C \quad \ldots\ldots \quad (19)$$

in which the combination-membrane $M_1 M_2$, will now be in equilibrium also.

If namely we imagine M_1 permeable for d_1 substances, then each of these d_1 substances must have the same $O.A.$ in states A and B; when M_2 is permeable for d_2 substances, each of these d_2 substances must have the same $O.A.$ in states A and C. From this it follows that every substance which can diffuse as well through M_1 as through M_2 and consequently also through their combination $M_1 M_2$, must also have the same $O.A.$ in B and C, so that (19) is in equilibrium.

As (19) will still remain in equilibrium also, when we substitute the membrane $M_1 M_2$ by an equi- or less permeable membrane, it follows:

F. when each of the states B and C may be in equilibrium with an other state A, the states B and C will also be in osmotic equilibrium, at least, when the membrane is equi- or less permeable than the combination-membrane.

It is clear that we can here understand by "state" any arbitrary phase (liquid, gas or solid substance) and also a system of more phases (e.g. a solution + solid substance or a solution + solid substances + vapour, etc.) at least when these phases are in equilibrium among each other.

As a special case of F we have among other things:

G. when each of the states B and C can be in equilibrium with a state A with the aid of a membrane, permeable for water only, the states B and

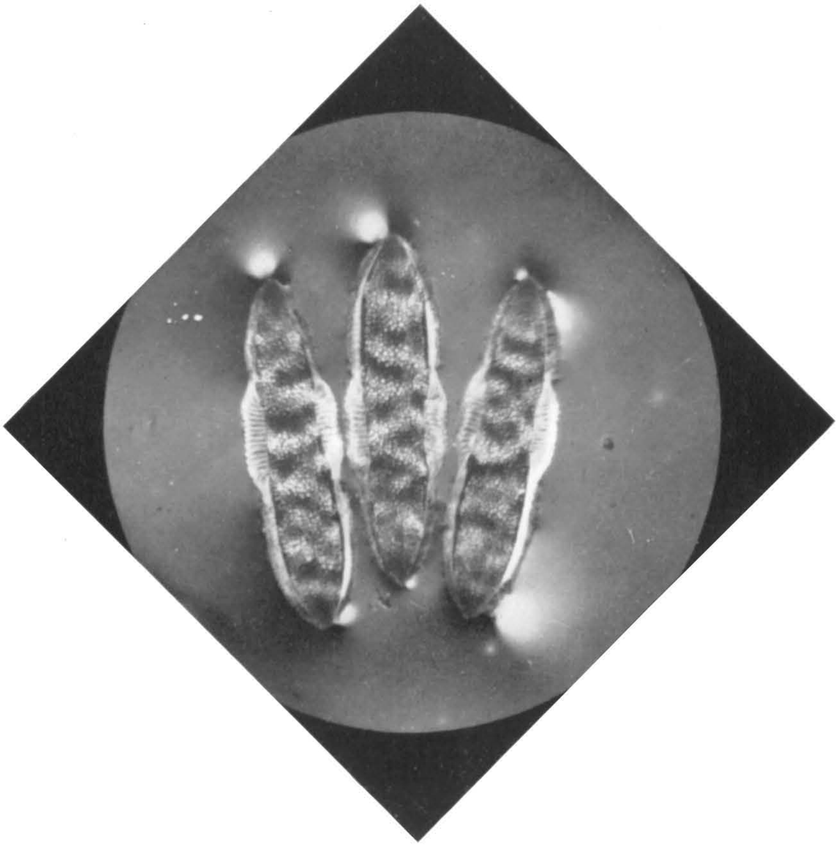

Fig. 5. Three shortwinged eggs. Dorsal surface. Strongly marked oblique bars.

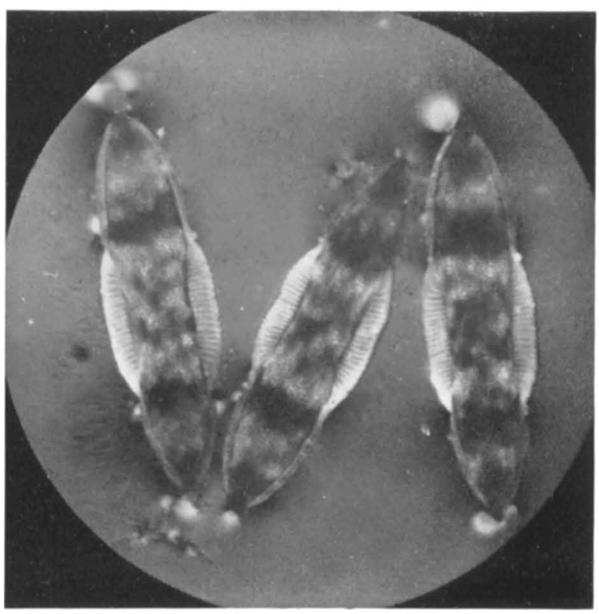

Fig. 6. Three longwinged eggs. Dorsal surface. Transverse bars distinctly marked.

C will be in equilibrium also, at least when this membrane is also permeable for water only.

If we apply the previous considerations to the equilibria

$$L\,(W+X+\bar{Y})_P \mid L'\,(W+X+\bar{Y}+\bar{\bar{Z}})_{P'} \quad . \quad . \quad . \quad . \quad (20)$$

$$L\,(W+X+\bar{Y})_P \mid L''\,(W+X+\bar{\bar{U}})_{P''} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

then it follows that the osmotic system

$$L'\,(W+X+\bar{Y}+\bar{\bar{Z}})_{P'} \mid L''\,(W+X+\bar{\bar{U}})_{P''} \quad . \quad . \quad . \quad (22)$$

will be in equilibrium also. This will still be the case when the membrane is permeable only for one of the two substances W and X: this will no more be the case, however, when the membrane is permeable besides for one or more of the substances Y, Z or U.

We now take the two osmotic equilibria

$$(Water)_P \mid L'\,(W+n')_{P+\pi'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

$$(Water)_P \mid L''\,(W+n'')_{P+\pi''} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

in which the liquids L' and L'' contain n' and n'' non-diffusing substances, which may or may not be different; from this it follows that the osmotic system:

$$L'\,(W+1')_{P+\pi'} \mid L''\,(W+n'')_{P+\pi''} \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

shall also be in equilibrium now. This is no longer the case when the membrane is permeable besides for one or more of the other substances.

The osmotic pressure of liquid L' is π', that of liquid L'' is π''. It now appears from (25) that the two liquids are not in equilibrium under the pressure P, neither when each of the two liquids is found under its own osmotic pressure (π' and π''), but that these pressures must be $P+\pi'$ and $P+\pi''$.

If e.g. we have two diluted liquids L' and L'', so that their osmotic pressure is small (e.g. $\pi'=0.5$ and $\pi''=0.6$ atmosphere) and if we take, as usually is the case in determining osmotic pressure, $P=1$ atmosphere, then the two liquids will be in equilibrium with one another under the pressures 1.5 and 1.6 atmosphere.

(To be continued.)

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