TABELLE VI. Die mittlere Kurve,

Phase	v	Phase	v	Phase	v	Phase	v	Phase	v
$- 100^d$	10.31^m	$- 20^d$	13.19^m	$+ 60^d$	11.10^m	$+ 140^d$	6.66^m	$+ 230$	6.51^m
$- 90$	10.77	$- 10$	13.32	$+ 70$	10.30	$+ 150$	5.56	$+ 240$	7.02
$- 80$	11.21	0	13.35	$+ 80$	9.72	$+ 160$	4.78	$+ 250$	7.52
$- 70$	11.63	$+ 10$	13.31	$+ 90$	9.34	$+ 170$	4.50	$+ 260$	8.03
$- 60$	12.03	$+ 20$	13.16	$+ 100$	9.05	$+ 180$	4.50	$+ 270$	8.53
$- 50$	12.40	$+ 30$	12.92	$+ 110$	8.76	$+ 190$	4.71	$+ 280$	9.02
$- 40$	12.73	$+ 40$	12.50	$+ 120$	8.32	$+ 200$	5.09	$+ 290$	9.50
$- 30$	13.00	$+ 50$	11.87	$+ 130$	7.65	$+ 210$	5.53	$+ 300$	9.98
						$+ 220$	6.01	$+ 310$	10.45

Zusammenfassung.

Aus 962 in den Jahren 1905 bis 1932 (2416836 bis 2426915) angestellten Beobachtungen von χ Cygni sind die folgenden Elemente des Lichtwechsels abgeleitet worden:

$$\text{Maximum: } 2421927^d \left.\begin{matrix} \\ \end{matrix}\right\} + 407^d\, E + 0.165\, E^2; \quad \begin{matrix} v = 13^m.35 \\ v = 4.48 \end{matrix}$$
$$\text{Minimum: } 2422102$$
$$\overline{\text{Amplitude} = 8\,.87.}$$

Der Stern scheint beim Aufstieg eine Verdunkelung von $2^m.91$ zu erleiden, welche einen vollkommen symmetrischen Verlauf hat, und deren Minimum auf 2422055 fällt.

Utrecht, August 1932.

Chemistry. — *Osmotic systems in which non-diffusing substances may occur also.* I. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of October 29, 1932.)

I. *Equilibria.*

We take an osmotic system:

$$L_P \,|\, L'_{P'} \qquad \ldots \ldots \ldots \ldots \quad (1)$$

in which on the left side a liquid L under the pressure P and on the right side a liquid L' under the pressure P'. We now assume that there are d diffusing substances, that liquid L still contains n-and liquid L' still n' non-

diffusing substances : in most cases it does not matter here, as will appear later on, whether one or more of these non-diffusing substances occur together or do not occur together in both liquids.

Now when system (1) has come in equilibrium, either the two liquids will contain the d diffusing substances, no matter whether they were originally present on the two sides of the membrane yes or no. Then liquid L will contain : $d + n$ and liquid $L' : d + n'$ substances. We now represent this equilibrium by

$$L (d + n)_P \,|\, L' (d + n')_{P'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If W is one of the diffusing substances, then with the aid of the ζ-function we can find an equation, expressing that the total ζ of (2) does not change when a small quantity of W passes from the one liquid towards the other. This equation expresses that the substance W has the same thermodynamical potential in the two liquids, or in other words that both liquids (the one under the pressure P and the other under the pressure P') have the same O.W.A. (Osmotic Water Attraction).

As there are d diffusing substances, consequently also d of these equations exist, expressing that every diffusing substance has the same O.A. on both sides of the membrane. From this follows :

A. when an osmotic system is in equilibrium, then every diffusing substance has the same O.A. on the two sides of the membrane and the reverse.

Let us take as an example the equilibria :

$$L (W + \overline{X} + \overline{Y})_P \,|\, L' (W + \overline{X} + \overline{Y})_{P'} \quad . \quad . \quad . \quad . \quad (3)$$

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

$$L (W + X)_P \,|\, L' (W + X + \overline{Y})_{P'} \quad . \quad . \quad . \quad . \quad (5)$$

in which the dash placed above a substance indicates that this substance does not diffuse.

For the equilibria (3) and (4) it then suffices that the two liquids have the same O.W.A. ; in (5), however, the two liquids must have the same O.W.A. and O.X.A.

To enable us to express various results in a simpler way, we shall understand by "state" on the left(right)side of a membrane : the composition and the pressure of the left(right)side liquid.

As liquid L contains $d + n$ substances, its composition is determined by $d + n - 1$ concentrations ; if besides we add to this the pressure P, then it follows that the state on the left side of the membrane depends upon $d + n$ variables. The state on the right side of the membrane is determined by $d + n'$ variables. The entire system (2) contains, therefore: $2d + n + n'$ variables.

As, however, the system is in equilibrium, d relations will exist between these variables:

$$O.A = (O.A)' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

expressing that every diffusing substance must have the same O.A. on both sides; so there are only $2d + n + n' - d = d + n + n'$ free variables left. From this it follows:

B. the osmotic equilibrium

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

has $d + n + n'$ freedoms.

From this it follows that we may say also:

C. the number of freedoms of an osmotic equilibrium is equal to the number of substances, unless every non-diffusing substance, occurring on both sides of the membrane counts for two.

Now we may say also:

D. the osmotic equilibrium (7) can exist with an ∞ number of states on the left and on the right side of the membrane, having together $d + n + n'$ freedoms.

If we apply B or C to (3), (4) and (5), then we find that (3) has five freedoms, (4) four and (5) three, although all these equilibria consist of the same substances.

In the special case that the membrane is permeable for all substances, we have an equilibrium

$$L (d)_P | L' (d)_{P'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

As now $n = 0$ and $n' = 0$, the number of freedoms now will be d.

Each of the states namely, on the left and on the right side of the membrane, has d variables (viz. $d - 1$ concentrations and the pressure).

If we now take a definite state on one of the sides so that d freedoms are left out, then the state on the other side has no freedoms any more. From this it follows: when the state on one of the sides is determined, then the other state is determined also.

If only stable states are considered, then we can deduce with the aid of thermodynamica that we must always have $P = P'$.

If besides only those systems are considered, of which the liquids are mixable in all ratios, then we also find that we must have: $L = L'$.

As we shall here suppose both these conditions present, it follows:

E. when an osmotic system in which a membrane permeable for all substances, is in equilibrium, then the same state will be found on the two sides. Consequently both liquids have the same composition and pressure.

Later on I shall refer to systems in which also dimixtion can occur.

We now take the equilibrium

$$L (d)_P | L' (d + \bar{U})_{P'} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

in which, besides the d diffusing substances, a non-diffusing substance U is also present in liquid L'. As now $n = 0$ and $n' = 1$, this equilibrium will have $d + 1$ freedoms. Now with the aid of thermodynamica we can deduce that we must always have $P < P'$.

If we now take a definite state on the left side, so that the number of freedoms decreases with d, then the right-side state will have one freedom left. Consequently an ∞ number of states can exist on the right side, but in such a way that a definite composition goes with every definite pressure.

If, however, we take a definite state on the right side, so that the number of freedoms decreases with $d + 1$, then the left side will have no freedom left. On the left side, consequently, there will also exist a definite state now, viz. a definite pressure and a definite composition.

From these considerations it follows:

F. the equilibrium

$$L (d)_P | L' (d + \bar{U})_{P'} . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

has $d + 1$ freedoms; the pressure P' is always greater than the pressure P; if we have a definite state on the left side, then an ∞ number of states can occur on the right side, having one freedom (viz. an ∞ number of pressures P' and an ∞ number of compositions of the liquid L', but in such a way, that with every definite pressure P' goes also a definite composition of L'). If we have a definite state on the right side, then also on the left side a definite state will exist.

As a special case of (10) we take

$$L (Water)_P | L' (Water + \bar{U})_{P'} \quad . \quad . \quad . \quad . \quad (11)$$

in which only one diffusing substance, viz. water; what has been said above in F for equilibrium (10) obtains here also. The difference in pressure $P' - P$ is now the osmotic pressure of liquid L' (namely with respect to water under the pressure P).

We now suppose a definite state in the general equilibrium (2) on the left side of the membrane; as the number of freedoms now decreases with $d + n$, there will still remain

$$d + n + n' - (d + n) = n'. \quad . \quad . \quad . \quad . \quad (12)$$

freedoms; so the right-side state has as many freedoms as it has non-diffusing substances. From this it follows:

G. when in the equilibrium

$$L (d + n)_P | L' (d + n')_{P'} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

one of the states has been determined, the other state will still have as many freedoms as it has non-diffusing substances.

We see that the rules E and F only form a special case of the general rule G; an application of this rule to other cases is left to the reader.

In discussing equilibrium (7) we have not made any suggestion as to the quantity of each of the substances present and the two pressures P and P'; for this reason we shall call this equilibrium a free equilibrium.

If, however, we have an equilibrium with two definite pressures P and P', we shall call it a definite pressure- or Def. P-equilibrium.

If we take an equilibrium, containing a definite quantity of each of the substances present, we shall call it a definite quantity- or Def. Q-equilibrium.

If we take an equilibrium, having not only two definite pressures but a definite quantity of each of the substances as well, we shall call it a Def. PQ-equilibrium.

In order to illustrate the difference between these different equilibria, we take the equilibrium:

$$m \times L \, (W + X + \bar{Y} + \bar{Z})_P \mid m' \times L' \, (W + X + \bar{Y} + \bar{U})_{P'} \ . \quad (14)$$

in which m quantities of a liquid L with the composition

$$x \, X + y \, Y + z \, Z + (1 - x - y - z) \, W \ . \ . \ . \ . \quad (15)$$

and m' quantities of a liquid L' with the composition

$$x' \, X + y' \, Y + u' \, U + (1 - x' - y' - u') \, W \ . \ . \ . \quad (16)$$

If besides the two pressures and the six concentrations (x, y, z, x', y' and u') we consider the quantities m and m' of the two liquids as well, then (14) will contain 10 variables.

As (14) is in equilibrium there will always exist between these variables the two relations

$$OWA = (OWA)' \quad \text{and} \quad OXA = (OXA)' \ . \ . \ . \quad (17)$$

expressing that both liquids have the same O.W.A. and the same O.X.A.

If (14) is a free equilibrium, so that it needs only satisfy the two relations (17), it will consequently have $10 - 2 = 8$ freedoms. These two relations, however, do not contain the quantities m and m', so that we may take always them quite arbitrarily; this is indeed obvious, because the being in equilibrium or not in equilibrium of two liquids does not depend upon their quantities.

If, therefore, we only take into consideration the state of the equilibrium (viz. the compositions and pressures of the two liquids), then the quantities m and m' cannot play a part in the free equilibrium. If we omit them

because of this, then $8 - 2 = 6$ freedoms will still remain. As $d = 2$, $n = 2$ and $n' = 2$, this is also in accordance with (7).

If we now give a definite value to both pressures, then (14) becomes a Def. *P*-equilibrium, having $6 - 2 = 4$ freedoms. It is clear that the quantities m and m' now will not play a part either.

This becomes different, however, when (14) is a Def. Q-equilibrium, so that it contains a definite quantity of each substance. We shall assume namely that in total (viz. on the left and on the right side of the membrane together) there are w_0 and x_0 quantities of the substances W and X. From this follow the two equations

$$m \left(1 - x - y - z \right) + m' \left(1 - x' - y' - u' \right) = w_0 \atop m\, x + m'\, x' = x_0 \right\} \quad . \quad . \quad (18)$$

Further we assume that on the left side of the membrane y_0 and z_0 quantities of the non-diffusing substances Y and Z occur; from this then follows:

$$m\, y = y_0 \quad \text{and} \quad m\, z = z_0. \quad . \quad . \quad . \quad . \quad (19)$$

Finally we assume besides that on the right side of the membrane y'_0 and u'_0 quantities of the non-diffusing substances Y and U are present; from this then follows also:

$$m'\, y' = y_0' \quad \text{and} \quad m'\, u' = u_0' \quad . \quad . \quad . \quad . \quad (20)$$

So, as is apparent from (19) and (20) we have assumed that the non-diffusing substance Y, occurring on both sides of the membrane, is also present on both sides in a definite quantity.

We now shall substitute (18) by

$$m + m' = w_0 + x_0 + y_0 + z_0 + y_0' + u_0' \atop m\, x + m'\, x' = x_0 \right\} \quad . \quad . \quad (21)$$

The first of these equations is found by adding up all equations (18)—(20) ; of course we might also have written down this equation, expressing that $m + m'$ is the total quantity of all substances, at once.

So the 10 variables of (14) now must not only satisfy the 2 equations (17), but also the 6 equations (19)—(21). From this it follows that the Def. Q-equilibrium (14) has $10 - 8 = 2$ freedoms.

It appears from the equations (19)—(21) that the quantities m and m' are no longer arbitrary now. At first sight this may perhaps seem a little peculiar, because, as has been said already above, the being in equilibrium or not in equilibrium of two liquids does not depend upon their quantities. It is clear, however, that in a Def. Q-equilibrium we cannot change m and m' without changing the quantities of the substances at the same time.

If in this Def. Q-equilibrium (14) we take two more definite pressures

P and P', so that it becomes a Def. PQ-equilibrium, it will have no freedom left; then the composition and the quantities m and m' of the two liquids will be completely determined.

From this it appears that the state of a Def. PQ-equilibrium is absolutely determined; of course it depends upon the quantities of the substances present, what state will occur. It appears namely from the equations (19)—(21) that the variables m, m', x, y etc. also depend upon the quantities w_0, x_0 etc. Consequently each change in one or more of these quantities results also in a change of the state. Only in the special case that we change w_0, x_0 etc. in the same ratio, m and m' will change only, but the composition of the two liquids will remain the same.

From these considerations it appears among other things also that the state of a Def. PQ-equilibrium is one definite state of the ∞ number the free equilibrium can have.

Now we may also apply these considerations to the general equilibrium

$$m \times L\,(d+n)_P \,|\, m' \times L'\,(d+n')_{P'} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Instead of the two equations (17) we now have the d equations

$$OA = (OA)' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

expressing that each of the d diffusing substances has the same O.A. in both liquids.

Instead of the two equations (18) or (21) we now find d equations, instead of the two equations (19), n equations and instead of the two equations (20) now n' equations.

In a similar way as for (14) we now find:

H. The free equilibrium (22) has $d+n+n'+2$ freedoms; the quantities m and m', however, may always be taken arbitrarily. This equilibrium can exist in an ∞ number of states, having $d+n+n'$ freedoms.

I. The Def. P-equilibrium (22) has $d+n+n'$ freedoms; we may always take the quantities m and m' arbitrarily, however. This equilibrium can exist in an ∞ number of states, having $d+n+n'$-2 freedoms. In the special case that there is only one diffusing and one non-diffusing substance, there is only one state too.

K. The Def. Q-equilibrium (22) has two freedoms; the quantities m and m' are determined now. This equilibrium can exist in an ∞ number of states (with 2 freedoms) which are all included in the ∞ number of states of the free equilibrium.

L. The Def. Q-equilibrium (22) has no freedom left; now the quantities m and m' are also determined. This equilibrium only exists in one absolutely determined state, being one of the ∞ number of states of the free equilibrium.

In the special case that an equilibrium contains diffusing substances only, both liquids must have the same pressure and composition (comp. E). Of course this involves that some of the preceding results must be a little altered ; this is left to the reader.

We now imagine the m quantities of liquid L closed up in a space with a volume V and the m' quantities of liquid L' in a space with a volume V'. We now represent this by :

$$[m \times L (d + n)_P]_V \mid [m' \times L' (d + n')_{P'}]_{V'} \quad . \quad . \quad . \quad . \quad (24)$$

As we now have two variables V and V' more than in (22), (24) will now contain $2d + n + n' + 4$ variables. Between them, however, now always exist the two relations

$$m v = V \quad \text{and} \quad m' v' = V' \quad . \quad . \quad . \quad . \quad . \quad (25)$$

in which v and v' represent the volume of one quantity of the liquids L and L'. As $v(v')$ is a function of the pressure $P(P')$ and the composition of liquid $L(L')$, these relations consequently will contain all the variables of (24).

If we do not make a single suggestion as to the variables, we shall call (24) once more a free equilibrium ; if we take definite volumina V and V', we may call (24) a Def. V-equilibrium ; if we take a definite quantity of each of the substances, then we call (24) a Def. Q-equilibrium ; if we take as well definite volumes as definite quantities of the substances, we may call (24) a Def. VQ-equilibrium.

If, besides considering the equations obtaining for equilibrium (22) we take into consideration the two equations (25) as well, then we find results for the equilibrium (24) corresponding to those above in H—L for the equilibrium (22).

Of course there are some differences indeed, as now that m and m', as appears from (25), are also connected with the volumina V and V'.

A closer consideration of these differences is left to the reader, however.

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(To be continued).