

Citation:

F.A.H. Schreinemakers, In mono- and divariant equilibria. XIV., in:
KNAW, Proceedings, 19 II, 1917, Amsterdam, 1917, pp. 927-932

will immediately overburden cells¹). Only if care is taken that this does not happen benzaldehyde can be used as nutriment.

As follows from the above this is the case when we use very slight concentrations of benzaldehyde. Amygdalin which is among the substances that do not cause overburdening phenomena can be converted *in* cells into glucose, benzaldehyde and HCN without any slackening influence on the growth²).

In the communications mentioned we have demonstrated that generally speaking it is not the nature of the substance absorbed but in the first instance the quantity, that causes overburdening of cells and the accompanying retarding of growth. In this way we have at the same time a specific for bringing narcotic substances into the organism without any harm to the latter.

For this purpose the narcotic substance should be combined with one or more other chemical compounds, so that a complex chemical compound results, which can not overburden cells, but from which the desired active substance may be formed *within* the cell.

Dordrecht, December 1916.

Chemistry. — “*In-, mono- and divariant equilibria.*” XIV. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated in the meeting of January 27, 1917).

22. The occurrence of three indifferent phases; the equilibrium M is constant singular.

In the previous communications we have discussed the occurrence of two indifferent phases; now we shall briefly consider the occurrence of three indifferent phases.

Again we take the two reaction-equations:

$$a_1 F_1 + \dots + a_p F_p + a_{p+1} F_{p+1} + \dots = 0 \quad (1)$$

and

$$\mu_1 a_1 F_1 + \dots + \mu_p a_p F_p + \mu_{p+1} a_{p+1} F_{p+1} + \dots = 0 \quad (2)$$

in which a_1 and μ_1 are positive and at the same time:

$$\mu_1 > \dots > \mu_p > \mu_{p+1} > \mu_{p+2} > \dots \quad (3)$$

When we put:

¹) J. BÖESEKEN and H. J. WATERMAN, These Proceedings, January 24, 1912 p. 608; H. J. WATERMAN, Dissertation Delft, 1913.

²) When at the same moment any conversion into the just mentioned substances occurs too outside the cell of course retarding of growth will all the same be stated.

$$\mu_p = \mu_{p+1} = \mu_{p+2} = \mu$$

then (2) passes into:

$$\mu_1 a_1 F_1 + \dots + \mu a_p F_p + \mu a_{p+1} F_{p+1} + \mu a_{p+2} F_{p+2} + \dots = 0 \quad (4)$$

In order to find the reaction between the phases of the equilibrium (F_p), we have to eliminate F_p from (1) and (4); with this not only F_p disappears, but also F_{p+1} and F_{p+2} . Consequently we do not get a reaction between $n+1$ phases, but between the $n-1$ phases

$$F_1 F_2 \dots F_{p-1} F_{p+3} \dots F_{n+2}.$$

For the reaction between the phases of the equilibria (F_{p+1}) and (F_{p+2}) we find the same relation between those $n-1$ phases. In each of the other reaction-equations for the monovariant equilibria, however, $n+1$ phases occur.

The phases F_p , F_{p+1} and F_{p+2} are, therefore, the indifferent phases, the $n-1$ other phases are the singular ones.

We now have four singular equilibria, viz.:

$$(M) = F_1 + \dots + F_{p-1} + F_{p+3} + \dots + F_{n+2}$$

$$(F_p) = (M) + F_{p+1} + F_{p+2}$$

$$(F_{p+1}) = (M) + F_p + F_{p+2}$$

and

$$(F_{p+2}) = (M) + F_p + F_{p+1}.$$

The three indifferent phases may have in (1) the same sign or not. (In the first case $+++$ or $---$, in the second case, $++-$, $--+$, $+--$, $-++$, $+-+$ or $-+-$). Just as in Comm. X we are able to show now: when in a reaction-equation two indifferent phases have the same (or opposite) sign, then they have also in all other reaction-equations the same (or opposite) sign.

Just as in Comm. X we are able to show: when the three indifferent phases have the same sign, then the singular equilibrium M is transformable, when they have not the same sign, then the equilibrium (M) is not transformable.

In the same way as in Comm. X it now follows:

1. The three indifferent phases have the same sign or in other words: the singular equilibrium M is transformable. Curve (M) is monodirectionable; the four singular curves coincide in the same direction.

2. The three indifferent phases have not the same sign or in other words the singular equilibrium M is not transformable. Curve (M) is bidirectionable; of the 3 other singular curves, 2 cur-

ves (viz. those, which have the same sign) coincide with the one direction of the (M)-curve, the third curve coincides with the other direction of the (M)-curve.

With the aid of those rules we may deduce again, just as in Comm. X, the main-types of the P, T -diagrams; we leave this, however, to the reader and we shall consider more in detail one single example only.

We take a ternary system with the components W ($W =$ water), A and B . Let occur in the invariant point the equilibrium:



in which L_q represents the liquid q (fig. 1) and G represents the vapour. When G consists of water vapour only, then in the equilibrium (5) also the reaction $Ice \rightleftharpoons G$ may occur; A , B and L_q are then the indifferent phases, Ice and G the singular phases. Then we have the singular curves:

$$(M) = Ice + G \text{ [Curve (M) in fig. 3]}$$

$$(A) = B + Ice + L + G \text{ [} qb \text{ in fig. 1; } qb = (A) \text{ in fig. 3]}$$

$$(B) = A + Ice + L + G \text{ [} qa \text{ in fig. 1; } qa = (B) \text{ in fig. 3]}$$

$$(L) = A + B + Ice + G \text{ [Curve (L) in fig. 3]}$$

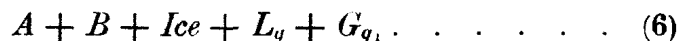
and further the curves

$$(Ice) = A + B + L + G \text{ [} qc \text{ in fig. 1; (I) in fig. 3]}$$

$$(G) = A + B + Ice + L \text{ [Curve (G) in fig. 3]}$$

With the aid of the previous considerations we may deduce the type of P, T -diagram; first, however, we shall do this in another way.

Let us consider viz. the case that the vapour G does not consist of water only, but that it contains also a little of the components A and B . Then we have the equilibrium:



in which G_{q_1} represents the vapour q_1 (fig. 1). The point q_1 is situated in the vicinity of the point W . The five phases of equilibrium (6) now form a type of concentration-diagram as in fig. 5 (II), consequently the type of P, T -diagram must be as in fig. 6 (II). [We have to bear in mind that the figs. 4 (II) and 6 (II) have to be changed inter se]. As q_1 is situated in fig. 1 in the vicinity of W , the line qq_1 intersects either WB and AB or WA and BA . It is apparent from fig. 6 (II) that the curves (I), (A) and (B) must form now a three-curvical bundle, as in fig. 2. When we assume that the line qq_1 intersects the lines WB and AB , then curve (B) must be situated between the curves (A) and (I). We now easily see (amongst others yet also from the diagonal succession of the curves)

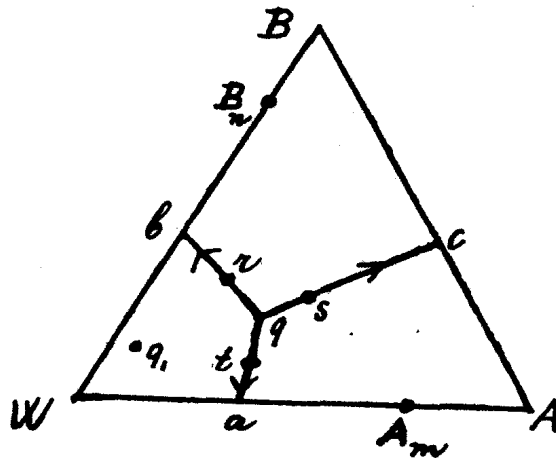


Fig. 1.

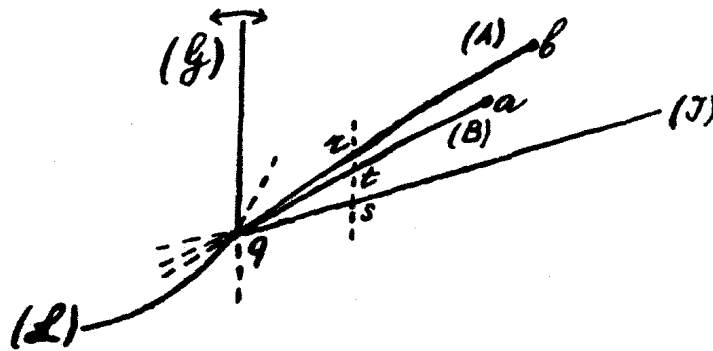


Fig. 2.

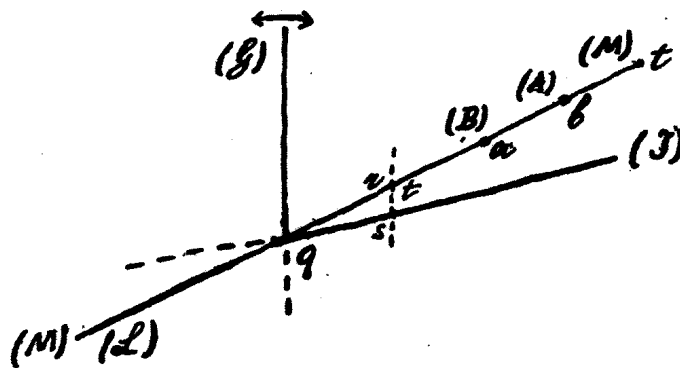


Fig. 3.

that we obtain a P, T -diagram, as is drawn in fig. 2. [The points a and b are the finishing points of the curves (B) and (A) and they are in accordance with the points a and b of fig. 1; the finishing-point c of curve (I) has not been drawn in fig. 2).

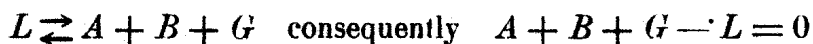
It appears from fig. 2 that at the same temperature the vapour-tension of $(A) = B + ice + L + G$ is larger than that of $(B) =$

$A + ice + L + G$ and this is larger again than that of $(Ice) = A + B + L + G$; this follows from the assumption that the line qq_1 intersects the line WB . [This also appears in the following way. We take in fig. 1 the 3 points r, s and t in such a way, that $T_r = T_s = T_t$ and further 3 points r_1, s_1 and t_1 (those are not drawn in fig. 3), which represent the vapours belonging to r, s and t . Then rs is the saturation-curve under its own vapour-pressure of B , $r_1 s_1$ is the corresponding vapoursaturationcurve. From the change in pressure along this curve it follows $P_r > P_s$. When we also consider the other curves, then we find $P_r > P_t > P_s$].

When we now consider the case that the vapour Gq_1 in (6) contains watervapour only, then equilibrium (6) passes into (5). Then in fig. 1 q_1 coincides with W , so that the singular equilibrium $(M) = Ice + G$ occurs. As A, B and L now become indifferent phases, $(A), (B)$ and (L) become, therefore, singular curves, which consequently have to coincide. It appears from fig. 2 that this coincidence may take place only in such a way that the stable parts of (A) and (B) coincide and that (L) coincides with the metastable parts of (A) and (B) . Then we obtain fig. 3, in which the (M) -curve is therefore bidirectionable.

The position of the curves in fig. 3 is in accordance with the rules, which we have deduced in the general considerations. As we are not able to transform the singular equilibrium $(M) = Ice + G$ into the invariant equilibrium (5), (M) is, therefore, not transformable, so that (M) must be bidirectionable.

When we take a reaction, in which occur the 3 indifferent phases A, B and L , e.g.



then it appears that the 3 indifferent phases have not the same sign. Hence it follows again that curve (M) must be bidirectionable. As A and B have the same sign, the curves (A) and (B) have to coincide in the one direction — and the curve (L) in the other direction with the (M) -curve. All this is in accordance with fig. 3, which we might have found reversally also from those data.

We may deduce fig. 3 yet in another way, which we shall indicate briefly. We draw firstly in a P, T -diagram the curve $(M) = Ice + G$; this terminates in the triplepoint t (fig. 3) of the pure water. The curves $(A) = B + Ice + L + G = (M) + B + L$ and $(B) = A + Ice + L + G = (M) + A + L$ go starting from q towards higher T and they have to coincide with the (M) -curve.

Curve $(L) = A + B + Ice + G = (M) + A + B$ has to coincide also with the (M) -curve, but it goes, starting from q towards lower temperatures.

Curve $(I) = A + B + L + G$ goes starting from q , also towards higher temperatures, but it must be situated below the curves (A) and (B) . In order to show this latter we take again the three points r , s and t in fig. 1. As the vapour-pressure increases, starting from s , along the isotherms rs and ts , the curves (A) and (B) must be situated, therefore, in fig. 3 above curve (I) .

Those considerations are also valid when we replace the components A and B by their hydrates A_m and B_n , provided that solution η is situated within the triangle WA_mB_n and not too close to the line A_mB_n . When this is really the case, then we are able to define the directions of the curves in the same way as e.g. in Comm. XIII.

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(*To be continued.*)

Physics. — "*On the equation of state of water and of ammonia*"

By G. HOLST. Supplement N^o. 41 f' to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of January 27, 1917).

In an investigation published some time ago on the equation of state of methylchloride and ammonia¹⁾, it was shown that the sign of the coefficient C of KAMERLINGH ONNES'S²⁾ equation of state

$$pv = RT \left(1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^4} + \frac{E}{v^6} + \frac{F}{v^8} \right)$$

was different for the two substances; for ammonia it was negative; for methyl chloride, as for other normal substances, C was found to be positive. At that time I ventured the hypothesis C would be found negative for other associating³⁾ substances. Following this idea I have calculated B and C for water vapour, starting from the data given by M. JACOB⁴⁾ in tables 7 and 8 of his paper on

¹⁾ G. HOLST. Comm. Leiden No. 144.

²⁾ See for instance H. KAMERLINGH ONNES and W. H. KEESOM. *Enc. d. Math. Wiss. Art. V* 10 p. 728. also Comm. Leiden Suppl. 23.

³⁾ *Comp. Enc. p. 722*, where it is pointed out that besides the associating (polymerized) substances, others occur (deviating substances) which show similar deviations as the first.

⁴⁾ M. JACOB. *Zeitschr. Ver. D. Ing.* 1912 p. 1980.