

Citation:

F.A.H. Schreinemakers & Deuss, J.J.B., On the system: Water - Alcohol - Manganous sulphate, in: KNAW, Proceedings, 14 II, 1911-1912, Amsterdam, 1912, pp. 924-927

are older, they are also thicker and the marking on the cell-wall is more distinct. Moreover the growth in thickness of some parts of the cell-wall sometimes shows abnormalities, so that it may happen that younger parts have thicker walls than older ones and give a stronger cellulose-reaction (sometimes in *Closterium Ehrenbergii*). When all this is taken into account, it is clear that the cell-wall in *Closterium* even in one and the same species shows an enormous diversity, especially with respect to the number and position of the transverse lines or the length of the parts of the cell-wall and the thickness of the cell-wall in different parts. For this reason I cannot agree with HAUPTFLEISCH that the arrangement of the transverse lines in different species is so constant that they can serve for the systematic classification of the genus *Closterium*.

Chemistry. — “*On the system: Water — Alcohol — Manganous sulphate.*” By Prof. F. A. H. SCHREINEMAKERS and Dr. J. J. B. DEUSS.

(Communicated in the meeting of January 27, 1912).

The equilibria occurring in this system are represented in fig. 1; the points *W* and *A* indicate the components water and alcohol, the third apex of the components-triangle which is not drawn here therefore represents the $MnSO_4$. The temperature axis is taken perpendicular to the plane of the components-triangle.

The curve *hl* situated in the side plane $MnSO_4 - A - T$ of the prism is the solubility line of the anhydrous $MnSO_4$ in absolute alcohol; as this salt is practically insoluble in absolute alcohol the curve *hl* must lie in very close proximity to the axis *AT* of the prism.

The equilibria occurring in the binary system: water — $MnSO_4$

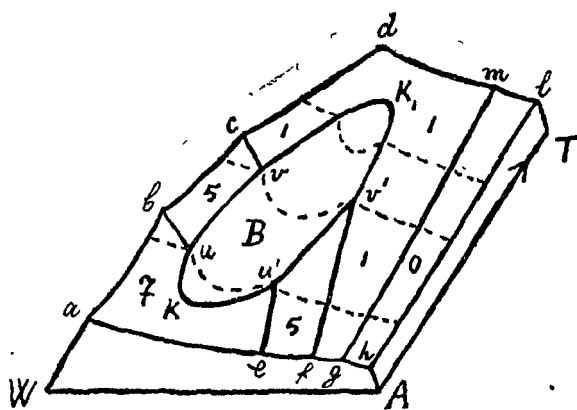


Fig. 1.

have been investigated by F. G. COTTRELL¹⁾; these equilibria, so far as they are required in the ternary system are represented in fig. 1 by the curves ab , bc , and cd situated in the side plane $MnSO_4 - W - T$.

The curve ab indicates the solutions saturated with $MnSO_4 \cdot 7 H_2O$, the curve bc those saturated with $MnSO_4 \cdot 5 H_2O$ and the curve cd the solutions saturated with $MnSO_4 \cdot H_2O$.

The equilibria occurring in the ternary system are represented by the surfaces situated within the prism, their intersecting lines and intersecting points:

$abuku'e$	is the saturation surface of the	$MnSO_4 \cdot 7 H_2O$
$efv'u'$ and $bcvu$	„ „ „ „ „ „	$MnSO_4 \cdot 5 H_2O$
$fgmcdok_1v'$	„ „ „ „ „ „	$MnSO_4 \cdot H_2O$
$ghln$	„ „ „ „ „ „	$MnSO_4$.
$kwk_1v'u'$	„ „ binodal surface.	

In order to facilitate the survey, the figures 7, 5, 1 and 0 are drawn on the saturation surfaces, and the letter B on the binodal surface. For the sake of brevity we will call the salts in future Mn_7 , Mn_5 , Mn_1 and Mn_0 .

The saturation surface of the Mn_5 consists of two parts separated from each other; the one to the left indicates the saturated solutions of Mn_5 rich in water, the one to the right those rich in alcohol.

The binodal surface B should be imagined to be divided into two parts by the critical line KK_1 ; with each solution L_1 of the one part, a definite solution L_2 of the other part can be in equilibrium. The binodal surface therefore represents the two-layer systems $L_1 + L_2$.

The intersecting lines of the saturation surfaces of a solid substance form the saturation lines representing the solutions saturated with two salts.

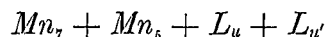
eu' and ub	is the saturation line of	$Mn_7 + Mn_5$
fv' and vc	„ „ „ „ „ „	$Mn_5 + Mn_1$
gm	„ „ „ „ „ „	$Mn_1 + Mn_0$.

The intersecting lines of the binodal surface with the saturation surfaces of the solid substance represent the conjugated liquid-pairs which are saturated with a solid salt. Because as seen in fig. 1 the binodal surface intersects each of the saturation surfaces of Mn_7 , Mn_5 and Mn_1 in two curves, it follows that one series of liquid-pairs is saturated with Mn_7 , another series with Mn_5 and a third series with Mn_1 . In fig. 1 are represented:

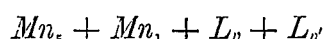
¹⁾ F. G. COTTRELL, Journ. Phys. Chem. 4 637 (1900).

the liquid-pairs saturated with Mn_7 by Ku and Ku'
 „ „ „ „ „ Mn_5 „ „ uv „ „ $u'v'$
 „ „ „ „ „ Mn_1 „ „ vK_1 „ „ $v'K_1$

Each of the points u and u' is the intersecting point of the binodal surface with the saturation surfaces of Mn_7 and Mn_5 . These points therefore represent a liquid pair $L_u + L_{u'}$ saturated at the temperature $T_u = T_{u'}$ with $Mn_7 + Mn_5$ or, in other words, the system:

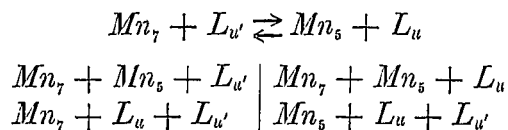


The same is true for the points v and v' which at $T_v = T_{v'}$ represent the two liquids of the equilibrium:



The saturation line of $Mn_7 + Mn_5$ consists (experimentally) of the two parts eu' and ub ; as, however $T_u = T_{u'}$, the complex $Mn_5 + Mn_7 + L$, traverses an uninterrupted temperature series; the solution however, changes its composition abruptly, at $T_u = T_{u'}$, from L_u into $L_{u'}$, or reversedly so. The same is true for the complex $Mn_5 + Mn_1 + L$ in the points v and v' .

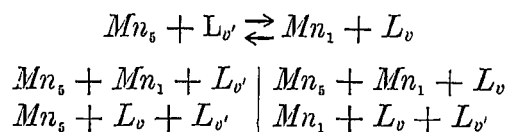
From the composition of the solutions L_u and $L_{u'}$ it follows that at $T_u = T_{u'}$ the reaction:



occurs.

From this reaction it follows that from $T_u = T_{u'}$ one saturation line of $Mn_7 + Mn_5$ must proceed to a lower, and another one to a higher temperature. Further, it follows that the liquid-pairs saturated with Mn_7 occur below and those saturated with Mn_5 above $T_u = T_{u'}$.

From the composition of the solutions L_v and $L_{v'}$ it follows that at $T_v = T_{v'}$ the reaction:



occurs. The situation of the curves proceeding in fig. 1 from the points v and v' is in accordance with this reaction.

From the figure it follows that the dissociation region, if we only consider stable conditions, extends from $T_k = 5.3$ to $T_{k_1} = 43.5^\circ$. Between T_k and T_{k_1} a separation into two liquids in the stable condition is possible, below T_k and above T_{k_1} , this is, however, no

longer the case and, as has been confirmed experimentally, only a separation in the metastable condition can take place.

In general the mixtures: water + alcohol + salt, in which the separation only takes place in ternary solutions, exhibit a minimum critical mixing temperature. That is to say that below this critical temperature no dissociation into two liquids can take place; above this temperature, however, decomposition may occur.

For instance, in water-alcohol mixtures KNO_3 can cause dissociation only above 79.5° , NH_4NO_3 only above 67.6° , $(NH_4)_2SO_4$ only above 8° , and Na_2CO_3 only above 27.7° .

Similar systems with a maximum critical temperature, namely with a temperature above which no separation can any longer occur have to our knowledge not yet been found. In the system water-alcohol- $MnSO_4$, however, now investigated by us, not only a minimum critical temperature T_k , but also a maximal critical temperature T_{k_1} seems to exist.

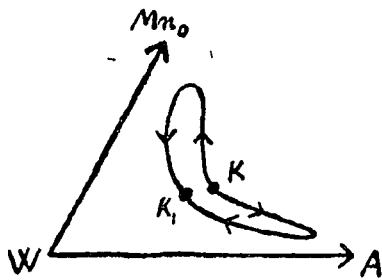


Fig. 2.

If we project the special curve $kuvk_1v'u'$ on the plane of the components-triangle $W-A-MnO$, we obtain something as in fig. 2. The triangle, however, has only been drawn partially in this figure. The projection of the special curve consists of two conjugated branches which form a closed curve of a peculiar form; the arrows indicate the direction in which the temperature increases.

Each of the branches kk_1 must, of course, exhibit a discontinuity in two points corresponding with the temperatures T_u and T_v .

If we intersect the spacial representation by planes perpendicular to the temperature axis, we obtain the isotherms; these have been determined at 50° , 35° , 30° and 25° . A few points of the isotherm of 0° have also been determined.

The isotherm at 50° can be represented schematically by the curves dm and ml and the isotherm of 0° by the curves ae , ef , fg and gh . A few other isotherms are represented in fig. 1 by the dotted curves.