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**Chemistry.** — „*On the melting of binary solid mixtures by cooling*”.

By Prof. H. W. BAKHUIS ROOZEBOOM.

(Communicated in the meeting of March 29, 1902).

The phenomena which may occur when mixtures pass from one state of aggregation into another are as a rule of a much more complex nature than those which take place with a single substance. For this reason a number of cases have been discovered in which the succession of the states of aggregation is wholly or partially reversed.

The earliest known instance is met with in the phenomenon of retrograde condensation, where a binary liquid is first formed from vapour by increase of pressure at a constant temperature and then passes again into vapour.

A similar reversion occurs with ternary liquid-mixtures when these on evaporation first deposit a solid substance and then redissolve the same. <sup>1)</sup>

We may also consider in this light my recent communications on saline solutions with two boiling points. <sup>2)</sup> Here, the possibility of a solution commencing to boil by cooling was shown to exist.

I will now mention a case where a binary mixture first solidifies on cooling but then again partly liquefies by further cooling.

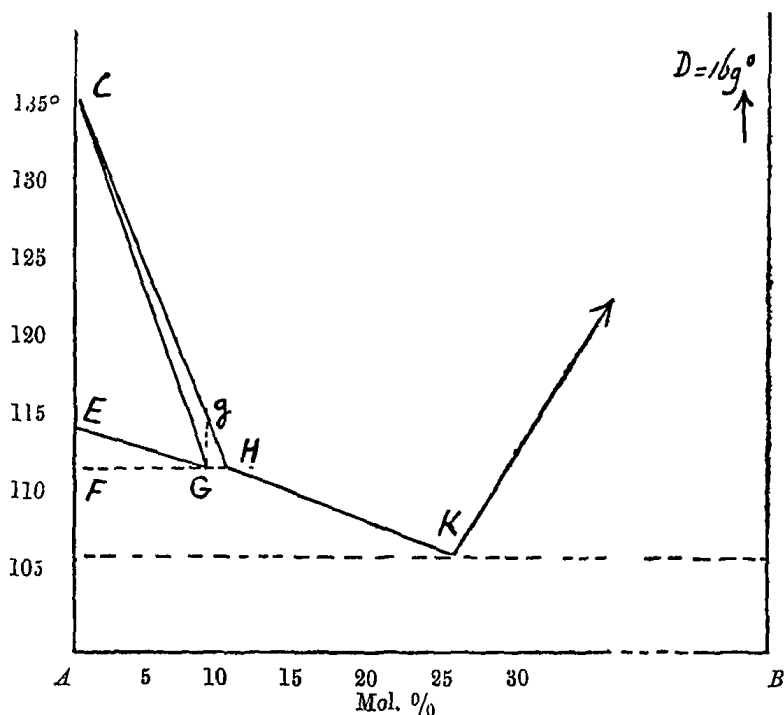
The possibility of such a phenomenon first occurred to me during my theoretical study of the changes of binary solid mixtures. <sup>3)</sup>

Among the large number of types which I then distinguished were found a few instances (l.c. fig. 15 and 20) where mixed crystals, on cooling, undergo a transformation and break up into another solid phase and liquid. For want of some detailed example of transformation of mixed crystals, I did not further investigate these special cases although it seemed to me that one of these might possibly be found during the study of the so-called liquid crystals. A case where mixed crystals occurred in the liquid crystalline condition had been investigated shortly before by SCHENCK who had found such a mixing between azoxyanisol and benzophenone. My surmise has now been completely confirmed and Mr. DE KOCK who is engaged with a dissertation on this subject has had the good fortune to meet with a very striking example in mixtures of azoxyanisol and hydroquinone.

<sup>1)</sup> SCHREINEMAKERS, *Zeit. phys. Chem.* 10.467 and MOHR *ibid.* 27.214. A good many allied examples are found in binary and ternary systems with two or three liquid-layers.

<sup>2)</sup> *Rep. Meeting* 28 Dec. 1901.

<sup>3)</sup> *Zeits. phys. Chem.* 30. 413 (1899).



In the above figure  $AB$  represents the proportions of azoxyanisole ( $A$ ) and hydroquinone ( $B$ ); the vertical axis represents the temperature. Substance  $B$  has a melting point at  $D : 169^\circ$ . Substance  $A$ , however, which is solid below  $E$  (condition  $A_2$ ) passes above  $E = 114^\circ$  into the condition of liquid crystals  $A_1$  which may be recognised by the eye as an apparently turbid liquid which passes at  $C = 135^\circ$  into an isotropic clear yellow liquid.

If the liquid crystals are really looked upon as *crystals* for which there are sound reasons, then  $C$  is the melting point and  $E$  a transition point from  $A_1$  into  $A_2$ .

In the liquid condition  $A$  and  $B$  are completely miscible above  $C$  and  $D$ . Below these temperatures, the mixing-limits for the different concentrations are  $CH$ ,  $HK$  and  $KD$ .

On the line  $DK$  commences the separation of  $B$ , on  $HK$  of solid  $A_2$  ( $K = 106^\circ$  and 25 mol. %), but on the line  $CH$  liquid mixed crystals are deposited. Consequently, to  $CH$  a second line  $CG$  must be added which shows the composition of the adjoining liquid mixed crystals. This line is the key to the important phenomenon which I have in view. The formation of the liquid mixed crystals takes place regularly on cooling any liquid-mixture below  $CH$  and is completed below  $CG$ . The clear liquid has then completely disappeared and has made room for the liquid crystals.

The region in which these mixtures exist does not however extend below the line  $EG$ . For in  $\bar{E}$  the transformation takes place of pure azoxyanisol from  $A_1$  to  $A_2$ . In the mixed crystals this temperature is lowered in an increasing degree with the concentration of hydroquinone; this causes the fall of the line  $EG$ . From the liquid mixed crystals, azoxyanisol is separated in the ordinary solid condition  $A_2$  by cooling below  $EG$ ; the remaining mixed crystals successively move towards the point  $G$ . This, however, is the lowest point of the triangle  $CEG$  within which mixed crystals are possible.

At this temperature,  $111.6^\circ$ , they already exist in presence of solid  $A_2$  and can also exist in presence of the liquid  $H$ . As below the line  $FGE$ , solid  $A_2$  can only exist with liquids  $HK$ , the mixed crystal  $G$  must, on further cooling, be transformed into solid  $A_2$  and liquid  $H$ ; this indeed happens. The phenomenon is the most striking if one starts from a concentration corresponding with  $G$ . The formation of liquid mixed crystals then takes place from  $g$  to  $G$  and on further cooling the transformation: liquid crystal  $G \rightarrow$  solid  $F$  + liquid  $H$  immediately takes place. The liquid again appears, not however  $G$  but  $H$ , therefore of modified concentration and also in a more limited degree because some solid  $A_2$  is deposited at the same time.

The relation of liquid to solid is as  $FG:GH$  and as  $G$  and  $H$  respectively belong to 8.75 and 10 mol. % of hydroquinone the calculation shows that 87 % by weight of the total mass returns to the state of liquid  $H$ . The phenomenon is the more striking because the formation of the liquid crystals from  $g-G$  took place within a small temperature-interval ( $3.5^\circ$ ). The great ease with which mixed crystals undergo change when in the liquid crystalline condition renders it probable that the phenomenon will often present itself with mixtures in which substances of this kind occur.

A condition is, of course, that the line  $EG$  must intersect the line  $CG$ , or expressed in the language of the theory of the dilute solutions, that the depression of the melting point  $C$  by the admixture of the second substance, is sufficiently larger than the depression of the transition point  $E$ . Since, as far as is known, the heat of transformation at  $C$  is many times smaller than that at  $E$  (about 40 times in the case of azoxyanisol), therefore the molecular depression

$$\frac{0.02 T^2}{q}$$

in which  $q$  represents that heat, will be much greater for point  $C$  than for point  $E$ , even when taking into consideration that in the calculation the concentration  $GH$  must be taken in the first and  $FH$

in the second case. The necessary condition for the appearance of the phenomenon will, therefore, easily be satisfied.

The above phenomenon is one of retrograde solidification if we consider the liquid crystalline condition as a solid.

Fortunately another instance has been found recently with mixed crystals which are solid in the ordinary meaning of the word.

With the aid of my theory, HAYCOCK and NEVILLE when interpreting the results of their studies on the solidification phenomena of alloys of copper and tin, have come to the conclusion that a mixture containing 27 atom % of tin which solidifies between  $720^{\circ}$ — $633^{\circ}$  to homogenous mixed crystals, breaks up when the lower temperature is passed into the solid compound  $\text{Cu}_3\text{Sn}$  (25 at. % of Sn) and a liquid containing 42 at % of Sn. Calculation shows that a maximum of 6.5 % by weight may again become liquid below  $633^{\circ}$ . Whether this quantity of liquid metal would be visible between the crystals is perhaps doubtful. As the interpretation in question was only brought to light after the experiments were finished, it could only be proved by a microscopical examination of the completely solidified mass, that at  $633^{\circ}$  a partial liquefaction of the previously solid mixed crystals had taken place.

The theory of phases has here again explained the exact connection and there is no doubt that the liquefaction of binary mixtures by cooling is not an extremely rare phenomenon.

**Geology.** — *"STARING and the coal-question of Southern Limburg."*

By Prof. J. L. C. SCHROEDER VAN DER KOLK.

(Communicated in the meeting of March 29, 1902).

Lately the coal-fields of Southern Limburg have repeatedly been discussed, also in the report of the Royal mining commission, instituted April 17<sup>th</sup> 1899.

The name of STARING is however invariably omitted, and the result of his researches simply laid aside. Therefore I wish to point out, in this paper, the extent of all that was known to STARING, already full forty years ago. I wish to do so, not only from a feeling of justice towards STARING, for much that now seems new to us, was already known to him, but also because to my opinion, his knowledge may be of use to us, even now.

The principal object of this paper is, clearly to bring out STARING'S standard of knowledge, at the time, so I shall almost exclusively make use of his statements. I borrow those statements from: Plate