Huygens Institute - Royal Netherlands Academy of Arts and Sciences (KNAW)

Citation:

Bakhuis Roozeboom, H.W., The Nature of inactive Carvoxime, in:
KNAW, Proceedings, 2, 1899-1900, Amsterdam, 1900, pp. 160-162

This PDF was made on 24 September 2010, from the 'Digital Library' of the Dutch History of Science Web Center (www.dwc.knaw.nl) > 'Digital Library > Proceedings of the Royal Netherlands Academy of Arts and Sciences (KNAW), http://www.digitallibrary.nl'

place at 160°, the addition of sodium nitrate depresses this temperature.

The limiting mixed crystal of the series which is rich in silver undergoes the change at 138°.

Below 138° only rhombic crystals, containing much silver, and rhombohedral crystals, containing much sodium, are capable of existence.

No transformation has been observed in the latter down to — 50°.

The limits of composition of the two kinds of crystals become more and more restricted as the temperature falls below 138°, so that at 15° they are 0—1,6 % (in molecules) $NaNO_3$ and 64.4—100 % $NaNO_3$.

The compositions of the coexisting limiting crystals were determined by allowing them to deposit beside each other from suitable solutions.

The transformation of the rhombohedral into rhombic crystals on the lines *FH* and *FG* was determined by means of an air dilatometer.

Chemistry. — By Prof. H. W. BAKHUIS ROOZEBOOM: "*The Nature of inactive Carvoxime.*"

In continuation of the investigations of Mr. ADRIANI on the phenomena of fusion and solidification of mixtures of optical antipodes, carvoxime has been examined. Samples of the *d*- and *l*-oximes were prepared for us through the kindness of Prof. GOLDSCHMIDT of Heidelberg.

Up to the present time the inactive carvoxime has been regarded as a racemic compound. This view rested on the facts that the melting point is higher than that of the active substances and that the density is greater (1.126 against 1.108).

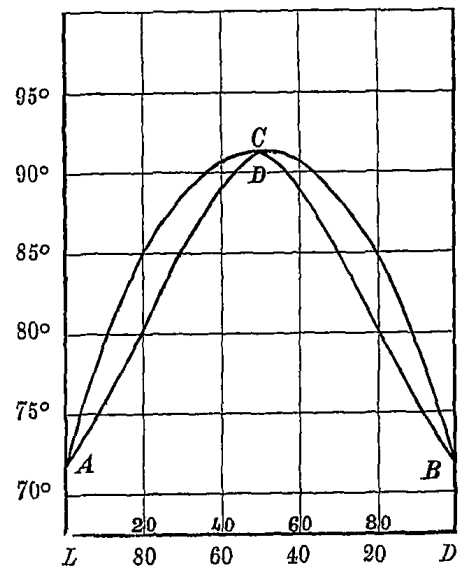
The investigation of the melting and solidifying points gave the following results.

Composition of the fused mass.	Commencement of solidification.	End of solidification.
100 % *d* of *l*	72°	72°
99 " "	72°4	—
98 " "	73°0	—
95 " "	75°4	73°
90 " "	79°0	75°
80 " "	84°6	80°
75 " "	86°4	82°
70 " "	88°2	85°
60 " "	90°4	—
50 " "	91°4	91°.4

The results of these determinations are reproduced in the accompanying figure. The line *ACB* represents the beginning, *ADB* the end of the solidification. To begin with, it is to be remarked that, setting out from the end points, the first line *at once* rises on addition of the active compound of opposite sign.

There is therefore only one meltingpoint line and, consequently, the solid mass must consist of mixed crystals, and the inactive substance (50 pCt. *d* of *l*) is not a racemic compound but a pseudo-racemic mixed crystal.

It were however conceivable that from *A* or *B* a small fall occurs, which escapes observation, because the rise begins at a very small concentration of the second oxime. If this were the case the inactive oxime would really be a racemic compound. The matter can, however, be readily decided. If it is a racemic compound the solidification of *all* mixtures, from 0 to 50 pCt. *d* or *l*, must terminate at the temperature of the eutectic point, which exists where the short falling lines from *A* and *B* meet the line of the racemic compound.



In our case therefore the solidification of all mixtures between 0 and 50 pCt. would have terminated just below 72°.

The final solidifying points, which were susceptible of very accurate observation, lie however on the line *ADB* and change continuously with the concentration.

For some concentrations the end point was determined by observing the course of the cooling as a function of the time in a bath at constant temperature. By this means the time, and therefore also the temperature, at which the solidification is complete may be observed with great accuracy.

The curve *ADB* confirms the view that mixed crystals are formed on solidification at all concentrations.

Thirdly it is supported by the analysis of crystals which were deposited from a fused mixture containing 20 pCt. of *l*-oxime. If the line *ACB* were the melting point line of a racemic compound, this compound would be deposited from the fused mass; if mixed

crystals are formed they must have the composition given by the point on the line *DB*, which lies on the horizontal line drawn through the point on *CB* which corresponds to 20 pCt. of *l*-oxime.

The solid mass, weighing 0.69 gram, which was deposited from 7 grams of liquid, containing 21.7 pCt. of *l*-oxime, was found to contain 32 pCt. The composition of the solid was determined by polarisation and corrected for the adhering mother liquor. The quantity of the latter was determined by adding some $CH Br_3$ and determining the bromine in the liquid and in the drained crystals. The result agrees very well with the position of the line *DB* determined from the final solidification points.

Not only do we obtain thus a continuous series of mixed crystals on solidification, but we have here the first example of such a series with a maximum meltingpoint, which naturally lies at 50 pCt. In agreement with the theory the composition of the fused mass and of the mixed crystals is the same at this point and the interval of solidification therefore vanishes.

The opinion, which I expressed, that even in the case of mixed crystals of optical isomers the equality of melting points, looked for by KIPPING and POPE, does not necessarily exist, is confirmed by this example.

It is worthy of attention that the rule, that racemic compounds with a higher density than their active components also have a higher meltingpoint, appears to be applicable also to mixed crystals; always providing that the difference in density observed at the ordinary temperature still exists near the melting points. Probably this will remain, at least qualitatively, unchanged.

The possibility still exists that carvoxime forms mixed crystals on solidification, which change at lower temperatures wholly or partially into a racemic compound.

Between 10° and 90° however no indication of such a change could be found by means of the dilatometer with an inactive mixture.

That at lower temperatures the inactive oxime, obtained from solutions for example, is a mixed crystal and not a compound is supported by the great crystallographic similarity between the inactive and active crystals which BEYER has observed (Zeits. Krystall. 18, 296, 1890).

The density rule of RETGERS would, therefore, not hold good for this kind of mixed crystals.