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reaction is the smaller, notwithstanding the fact that according to the researches of MENSCHUTKIN and CARRARA, methylalcohol itself accelerates similar reactions to a greater extent than ethylalcohol. It appears to us therefore that it follows from this case, as in the case of the reaction of o-dinitrobenzene and alcoholate, that reactions taking place in solvents other than water depend on circumstances which are as yet unknown, in addition to the degree of dissociation into ions.

From our earlier research we had concluded that the sodium dissolved in a 50 % mixture of alcohol and water is present mainly as alcoholate. The same conclusion may be drawn from an experiment in which a solution of 5 grams of Na in $1/2$ litre of a 50 % mixture of alcohol and water was warmed to 25° for 8 days with 32 grams (1 mol.) of ethyliodide. By means of several fractional distillations about 11.5 grams of ethylether were obtained, the theoretical quantity being 15.5 grams. Considering the unavoidable losses it may therefore be said that by far the greater part of the iodide was converted into ether.

It is still necessary to examine reactions such as those here studied, in mixtures of alcohol and water containing a large proportion of water, since in these there cannot be much alcoholate.

The details of this research will shortly be published in the "Recueil des travaux chimiques."

Chemistry. — Mr. Prof. H. W. BAKHUIS ROOZEBOOM speaks on: „An example of the conversion of mixed crystals into a compound".

(Read in the meeting of June 24th 1899.)

In the meeting of the 25th February 1897, page 376, I gave an explanation of the solidification of mixtures of optical isomers, when the solidification results in the formation (1) of a conglomerate (2) of mixed crystals, (3) of a racemic compound.

In a more complete paper, Zeitschr. phys. Chemie 28, 512, I have further developed the theory of the phenomena which must occur when these three types pass into each other when the solid mass is further cooled.

As one of the most interesting cases, Mr. ADRIANI, has at my request, studied an example of the conversion of mixed crystals into a compound below a certain temperature.

The example was camphoroxime. Mr. ADRIANI prepared the

d-oxime; we owe the *l*-oxime to the kindness of Prof. BECKMANN of Leipzig.

1. The melting points of the pure oximes and of mixtures of them were first determined. Both melt at 118°.8; the inactive mixture, containing 50% *d*- and 50% *l*-oxime melts at exactly the same temperature as also a number of mixtures containing excess of *d*- or *l*-oxime. No difference could be discovered within the limits of attainable accuracy. The accuracy here is not more than 0°.1, because it is very difficult to determine the melting-point exactly, owing to the small difference in the refractive indices of the solid and liquid. Very satisfactory results were obtained finally by using very thin walled tubes in which a thin cylindrical ring of the solid mass was placed just above the lower end. The solid mass is, in all proportions, microscopically homogeneous and regular. FORSTER and POPE's view (Journ. Chem. Soc. 71.1049) that we are here concerned with mixed crystals is confirmed by the discovery of one melting-point line alone.

At the same time the existence of mixed crystals of optical isomers, the probability of which was pointed out by KIPPING and POPE, is confirmed.
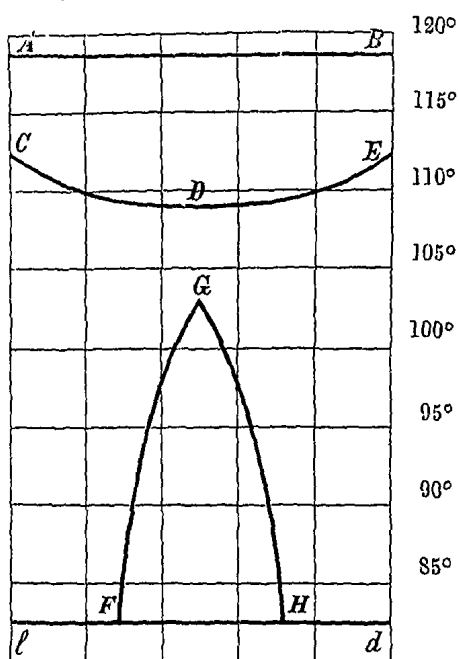
In the figure, the horizontal line *A B* represents the melting point line. The view that the melting points of all the mixtures would be the same is thus confirmed in this case. I have already pointed out that this is possible in no other series of mixed crystals than those containing optical isomers.

A consequence of the horizontal melting-point line is that each mixture solidifies to a homogeneous mass. The melting point line therefore represents the compositions both of the liquid and of the solid phase.

2. According to POPE the two isomers, as well as mixed crystals containing them, undergo a change from regular to monosymmetric crystals shortly after they have solidified.

The temperatures at which this change took place were however unknown. They were therefore determined.

Change from regular to monosymmetric crystals.

$$100\% \quad d \text{ or } l \quad 112°.6$$

$$90\% \quad \text{\textit{n}} \quad \text{\textit{n}} \quad \text{\textit{n}} \quad 110°.6$$

$$70\% \quad \text{\textit{n}} \quad \text{\textit{n}} \quad \text{\textit{n}} \quad 109°.7$$

$$50\% \quad \text{\textit{n}} \quad \text{\textit{n}} \quad \text{\textit{n}} \quad 109°.4$$

These values are shown by the line *CDE*, which is completely symmetrical and has a minimum of temperature at the transition point of the inactive mixture. Since here again only one curve is obtained for all the transition temperatures we must conclude that the regular mixed crystals change into monosymmetric mixed crystals.

When the change takes place with falling temperature it may be much delayed; in the other direction however it is very sharp. With the microscope it may be observed clearly, with the thermometer with great difficulty, and very distinctly by means of the dilatometer. With the non-racemic mixed-crystals it is possible that the transition takes place through some interval of temperature. In any case this is very small.

3. A further change takes place in the monosymmetric mixed crystals when they are cooled still more. POPE has observed this, only in the inactive mixtures, and ascribed it to the formation of a racemic compound (which may be obtained from a solution of the inactive mixture at the ordinary temperature). In that case the conversion of the mixed crystals into the compound should theoretically occur in other mixtures also but at lower temperatures.

This has been shown to be the case.

Conversion of mixed crystals into a compound.

$$50\% \quad d \text{ or } l \quad 103°$$

$$60\% \quad \text{\textit{n}} \quad \text{\textit{n}} \quad \text{\textit{n}} \quad 97°$$

$$70\% \quad \text{\textit{n}} \quad \text{\textit{n}} \quad \text{\textit{n}} \quad 86°$$

These points are indicated by the line *FGH* which has a maximum at 50 %.

The change occurs less readily the greater the excess of d or l which is present and proceeds very slowly. At 75 % it could not be observed even at the ordinary temperature.

The monosymmetric crystals change to a granular mass; when excess of d or l is present this is of course only partial.

The transition temperature in this case could not be detected by means of the thermometer or of the dilatometer but only by means of the microscope and then only when the temperature was rising. With 50 % the change is complete at the maximum temperature; with the other mixtures the change is gradual; the line FGH represents the temperatures at which the racemic compound in a given mixture has just disappeared. All points between the two branches represent conglomerates of the compound with mixed crystals.

The course of the conversion of mixed-crystals into a compound, deduced by me on theoretical grounds, is therefore completely confirmed by this first example.

Chemistry. — „*On the Enantiotropy of Tin*". By Dr. Ernst Cohen and Dr. C. van Eyk (Communicated by Prof. H. W. Bakhuis Roozeboom).

(Read in the meeting of June 24th 1899).

1. That pure tin falls into a grey powder when exposed to great cold is a phenomenon with which the tin traders of Russia especially have been long familiar. The phenomenon is, in that country, so common that a special name has been given to the tin powder which may be translated as *tin which may be scattered*.

The phenomenon has been very frequently referred to in scientific literature; the first description of it is due to Erdmann[1] in 1851. He is followed by Fritsche[2], Lewald[3], Rammelsberg[4], Oudemans[5], Walz[6], Petri[7], Schertel[8], Rammelsberg[9],

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[1] Journ. f. pract. Chemie 52, 428 (1851).

[2] B. B. 2, 112 en 540 (1869), Mém. de l'Académie de Pétersbourg, VII Série N° 5 (1870).

[3] Dinglers polytechn. Journal 196, 369. (1870).

[4] B. B. 3, 724 (1870). Zeitschrift für Chemie 1870. 733.

[5] Processen-Verbaal der Kon. Akad. v. Wetenschappen te Amst., vergad. 28 Oct. 1871.

[6] Wagner's Jahresbericht 1873, 207 uit: Deutsche Industriezeitung 1872, 468.

[7] Wildemanns Ann. (2) 2, 304. (1877).

[8] Journ. für pract. Chemie 19, 322 (1879).

[9] Berl. Akad. Ber. 1880, 225.