COLLOIDAL SOLID SOLUTIONS.

By D. McIntosh and R. Edson.

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When a salt solution is reduced gradually in temperature, ice or salt separates until the cryohydric temperature is reached. If the cooling be continued, the precipitation of salt and ice together takes place regularly until the material is changed to a solid. But if the solution be suddenly chilled by liquid air or solid carbon dioxide, the whole mass is quickly frozen without apparent segregation of salt or ice. We propose, in this preliminary paper, to describe some of the properties of these frozen solutions, to which we have given the name of colloidal solid solutions; and we hope in the future, to study their conducting power, their transference ratios and other properties with some care.

The solutions were prepared by plunging a copper tube containing the liquids (and the platinized electrodes when conduction experiments were intended) into a refrigerant, such as carbonic acid and ether. When the solution had reached the temperature of the bath, the tube was removed and dipped for an instant into warm water. The frozen block was pulled out, placed in a test tube, and examined at a convenient temperature.

This frozen material naturally resembled ice, but is more opaque and not so hard. It may be ground to any degree of fineness in a cooled mortar. When examined with a microscope, it appears perfectly homogeneous, and shows no evidence of the formation of ice or salt crystals, so that the particles may be colloidal in size. Analyses of sections from various parts of the solution showed the same composition. If the solid be allowed to melt undisturbed, the salt—except in the case of very strong solutions—dissolves completely. These solutions may be described as "reversible" in comparison with the cryohydrates.

Frozen solutions of this type conduct electricity slightly at low temperatures. When a direct current is employed, the electrodes polarize, and the salt is decomposed as in an aqueous solution. With a 20% solution of potassium iodide at —80°, iodine showed itself instantly when 110 volts were applied. Alkali, of course, was produced during electrolysis.

The resistance of these solutions is large, but decreases rapidly as the temperature rises. A change of 30° may alter the resistance several thousandfold.

When one of these solutions is finely powdered, it gives on melting the exact temperature at which the original liquid would be in equilibrium with pure ice, so that they can be used to maintain any desired temperature. One needs only to prepare a solution freezing at the temperature desired. The solution is then chilled quickly in the manner described. When powdered, it melts exactly at its freezing point, and in a Dewar flask, may be used to maintain a very constant temperature.

It is possible in this way, to prepare constant temperature baths to —40°, using a solution of hydrochloric acid. For lower temperatures, organic liquids might be employed. Mixtures of salts might be used, too, to give constant melting points at high temperatures; but here the choice of materials is so large that this would be of little value.

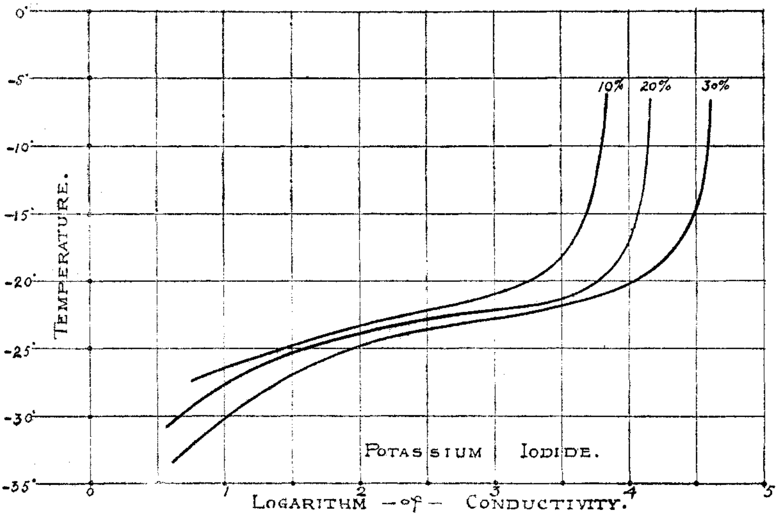

Fig. 1.

We have measured the conductivities at various temperatures of 10, 20, and 30% solutions of potassium iodide in water, and the results are shown in the curves (Fig. 1) where the logarithms of the conductivities

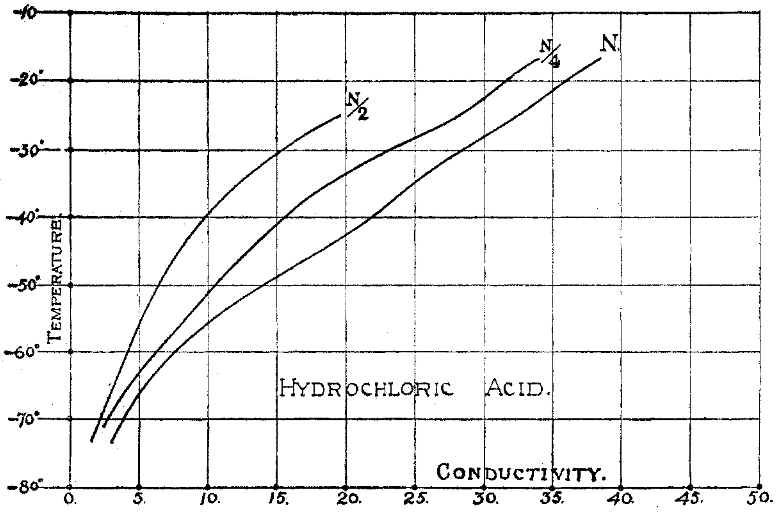

Fig. 2.

are plotted, in order that the results may be shown. A bath of ether and carbon dioxide was used, and with an automatic device it was possible to maintain the temperature within 0.3° of any temperature desired. These frozen solutions are poor conductors of heat, and the temperature must be held constant for at least thirty minutes before measurements can safely be made.

From the actual figures, the conduction is seen to increase most rapidly at about —21°, and as this is the cryohydric temperature for a solution of potassium iodide in water, it seems that even with rapid cooling a certain amount of segregation takes place.

In Fig. 2 the relative conductivities of *N*, 0.5 *N* and 0.25 *N* hydrochloric acid solutions are shown. These values are plotted directly, the last values being multiplied by 10. The conducting power increases fairly regularly with the temperature, so that there is no evidence of segregation. This is to be anticipated, since the cryohydric temperature for hydrochloric acid and water is far below the temperatures employed. The conductivities of the acid solutions are much greater than those of salt solutions of the same strength.

Until the experiments described here were undertaken, we were unaware that these solutions had been studied. Professor W. D. Bancroft has kindly given us a number of references to articles by Weimarn. We have been unable to consult the originals but the abstracts in the *Centralblatt* do not seem to bear directly on our work.

McGILL UNIVERSITY.

CRYOSCOPIC MEASUREMENTS AT LOW TEMPERATURES.

BY H. S. REID AND D. McINTOSH.

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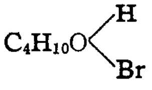
It has been shown that organic substances containing oxygen, when dissolved in liquefied hydrobromic acid, unite with the solvent forming definite salts melting far above the melting point of either constituent.[1] Ether, for example, gives the compound $C_4H_{10}O.HBr$ melting at —46°, while ether and hydrobromic acid melt at —120° and —86°, respectively. To explain the formation of these salts it has been assumed that the oxygen at the low temperature acts as a tetravalent element, yielding with hydrobromic acid such compounds as  $C_4H_{10}O\langle^{H}_{Br}$ or $C_4H_{10}O = BrH$.

The first of these formulae seems the more probable; for, in a study of the transport numbers,[2] it was found that the ether, or other organic body,

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[1] Archibald and McIntosh, *J. Chem. Soc.*, **85**, 919 (1904); McIntosh, THIS JOURNAL, **33**, 71 (1911); Maass and McIntosh, *Ibid.*, **34**, 1273 (1912).

[2] Steele, McIntosh and Archibald, *Phil. Trans.*, (*A*) **205**, 99 (1905).