NOTES

The Conductance of Potassium Ferrocyanide Solutions

By Cecil W. Davies

In a recent issue of this Journal[1] Grinnell Jones and Jelen have reported measurements of the conductance of potassium ferrocyanide solutions. They used their data to test various conductance equations, but the results were disappointing: this is illustrated by the various Λ_0 (molar conductance) values obtained, from which the authors could conclude no more than that the value of this constant is between 742 and 783.

The lower figure 742 is obtained by applying the Kohlrausch square root rule to the figures at the lowest concentrations. Jones and Jelen consider that there is strong reason for believing that this method gives too low a result, since otherwise the conductance curve must show a change in curvature at dilutions too great to be studied experimentally. There are however salts in water which are known to show just such a change in curvature since otherwise the experimental data cannot be reconciled with the known mobilities of the constituent ions at infinite dilution; magnesium sulfate is an example which is discussed and illustrated (Fig. 4) in one of Onsager's papers.[2] With this and many other salts of multivalent ions, a reasonable interpretation of the conductance curve is found in the hypothesis of ion-association, and it is therefore interesting to re-examine the data for potassium ferrocyanide with this possibility in mind. The simplest test of incomplete dissociation is probably that suggested in a paper published since Jones and Jelen's contribution appeared.[3] It is assumed that Onsager's equation, $\Lambda_0 = \Lambda + ac^{1/2}$ represents the behavior of a completely dissociated salt at extreme dilutions, and values of $(\Lambda + ac^{1/2})$, or Shedlovsky's Λ_0', are calculated from the data. For a completely dissociated salt the values should increase with increasing concentration, owing to the higher terms neglected in the limiting equation, and this is what is found for many 1-1-valent and 1-2-valent salts and for lanthanum chloride.[4] But for an incompletely dissociated salt (the dissociation constant of which does not lie above a certain maximum value) the calculated values at first decrease with rising concentration, eventually passing through a minimum. This is the behavior shown by magnesium sulfate and by other salts for which independent methods have indicated incomplete dissociation. That the same is true of potassium ferrocyanide will be seen by reference to Fig. 2 of Jones and Jelen's paper, and unless Onsager's equation is quite inapplicable to the ions of this salt we must conclude that the first stage association, $K^- + Fe(CN)_6^{----} \rightleftarrows KFe(CN)_6^{---}$ proceeds to an appreciable extent in dilute solutions. Exact treatment of the dissociation equilibrium is impossible, but an approximate value for Λ_0, and an idea of the magnitude of the dissociation constant can be obtained as follows.

Onsager's limiting equation cannot be expected to hold for a salt containing a quadrivalent ion at even the highest attainable dilutions, but we can make use of Onsager's rule that when $\Lambda_0 - \Lambda$ is 10% of Λ_0 the limiting equation gives calculated conductances approximately 1% too low, and we can combine this with the known fact that the range of the Onsager equation can be extended somewhat by adding a further term involving the first power of the concentration. This leads (using $\Lambda_0 = 735$ as a first approximation) to the equation: $\Lambda_x = \Lambda_0 - 3535C^{1/2} + 18{,}000C$, where Λ_x should represent the sum of the ionic mobilities in the more dilute solutions. Λ_0 is now found by Onsager's method of plotting $(\Lambda + 3535C^{1/2} - 18{,}000C)$ against the concentration; this gives a line which is only slightly curved, and leads to the extrapolated value: $\Lambda_0 = 736$. Using this value, and assuming that the process $K^+ + Fe(CN)_6^{----} \longrightarrow KFe(CN)_6^{---}$ leads to a reduction of 25% in conducting power, the extent of association can be calculated, and thence a value of the dissociation constant from the equation

$$\log K = \log \frac{(K^-)(Fe(CN)_6^{----})}{(KFe(CN)_6^{---})} - 4\sqrt{\mu}$$

The values obtained for Jones and Jelen's three most dilute solutions are: $K = 0.0061$, 0.0055, 0.0052. Of the approximations employed in

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(1) Jones and Jelen, This Journal, **58**, 2561 (1936).

(2) Onsager, *Trans. Faraday Soc.*, **23**, 341 (1927).

(3) Robinson and Davies, *J. Chem. Soc.*, 574 (1937).

(4) Jones and Bickford, This Journal, **56**, 606 (1934).

deriving these values the most hazardous is the use of the equation: $\Lambda_x = \Lambda_0 - 3535C^{1/2} + 18{,}000C$; if the third term on the right-hand side of this equation is omitted the value $K = 0.008$ is obtained, but this must necessarily be too high.

If 73.5 is accepted as the mobility of the potassium ion,[5] that of the ferrocyanide ion now becomes 110.3. The use of this figure leads to the value 0.035 for the constant A of Falkenhagen and Vernon's theoretical viscosity equation, and greatly improves the agreement between this equation and the experimental results of Jones and Stauffer[6] for the viscosity of potassium ferrocyanide solutions at 25°.

[5] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[6] Jones and Stauffer, *ibid.*, **58**, 2558 (1936).

BATTERSEA POLYTECHNIC
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The Preparation of Azomethane

BY FRANCIS P. JAHN

For some time azomethane has been prepared by workers in this and other laboratories by the oxidation of symmetrical dimethylhydrazine dihydrochloride by means of neutral potassium chromate in aqueous solution.[1] This method was first suggested by Thiele.[2] The method does not give good yields; moreover, according to the writer's experience the product is quite impure.

In an effort to find a more satisfactory method, a procedure based on the work of Diels and Koll was developed.[3] These workers found that oxidation of dimethylhydrazine dihydrochloride in aqueous sodium acetate solution by cupric chloride resulted in the precipitation of an addition compound of azomethane and cuprous chloride. This writer found that azomethane could be prepared satisfactorily by the heating of the dried precipitate.

The addition compound is prepared according to the directions given by Diels and Koll;[3] it may be recrystallized as they suggest but this is not necessary. Drying in a vacuum desiccator is very slow. The operation may be carried out more rapidly by placing the damp precipitate in a glass flask connected by means of a ground glass joint to a high vacuum system and pumping until the flask and contents have attained constant weight. The system includes a purification train arranged as described by Ramsperger,[1a] except that barium oxide is used in the drying tubes with soda lime and calcium chloride, and ordinary stopcocks are used in place of mercury cut-offs. During a drying period one of the traps was cooled with liquid air but no condensate formed; this indicates that the azomethane pressure above the compound at room temperature is negligible.

After completion of the drying the flask is heated from 125–140° by means of an oil-bath. One trap is cooled with solid carbon dioxide–toluene; one following is surrounded with liquid air. The heating is carried out with shaking until the precipitate has become entirely gray. It is found that the dry-ice trap contains practically all the liquid. The loss in weight of the flask during the heating is very close to the theoretical, assuming that the decomposition proceeds according to the equation

$$CH_3—N=N—CH_3 \cdot Cu_2Cl_2 \longrightarrow Cu_2Cl_2 + CH_3—N=N—CH_3$$

The yield of the addition compound from the dimethylhydrazine dihydrochloride is about 70%. Inasmuch as the preparation of the hydrazine derivative is a tedious process,[4] it would seem that the increased yield possible more than compensates for the additional operations as compared with the method of Thiele.

Explosion of Azomethane

Explosions of liquid azomethane have been attributed by other workers[1b] to the bubbling of the gas through mercury in manometers. On the other hand, explosions have not occurred in this Laboratory when azomethane was subjected repeatedly to these conditions by Burton and Davis and the writer. On the basis of his own experience the writer tends toward another explanation.

Some of a three-months old preparation of dimethylhydrazine dihydrochloride which had been preserved in a vacuum desiccator over calcium chloride was oxidized by the method described above. The recovery of addition product was only 29%. Upon heating, only a small amount of azomethane was condensed by liquid air. A large quantitity of a liquid of much lower vola-

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[1] (a) Ramsperger, THIS JOURNAL, **49**, 912 (1927); (b) Allen and O. K. Rice, *ibid.*, **57**, 310 (1935); (c) Rice and Sickman, *J. Chem. Phys.*, **4**, 242 (1936); (d) Burton, Davis and H. A. Taylor, THIS JOURNAL, **59**, 1038 (1937).

[2] J. Thiele, *Ber.*, **42**, 2579 (1909).

[3] Diels and Koll, *Ann.*, **443**, 262 (1925).

[4] Hatt, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Vol. XVI, 1936, p. 18.