The Conductance of Dilute Solutions of Potassium Ferrocyanide

By Elijah Swift, Jr.

One of the most important problems in the study of the conductance of solutions is the selection of a reliable method for the extrapolation of the measured values to obtain the limiting conductance. This extrapolation has been made by the use of numerous empirical equations, such as the Jones and Dole equation,[1] which fit the data over a wide range, or by the use of the Onsager equation (or one of its modifications),[2] a limiting equation applicable only to dilute solutions. These two methods do not always yield concordant results, the disagreement being more marked in the case of the higher valence type salts.

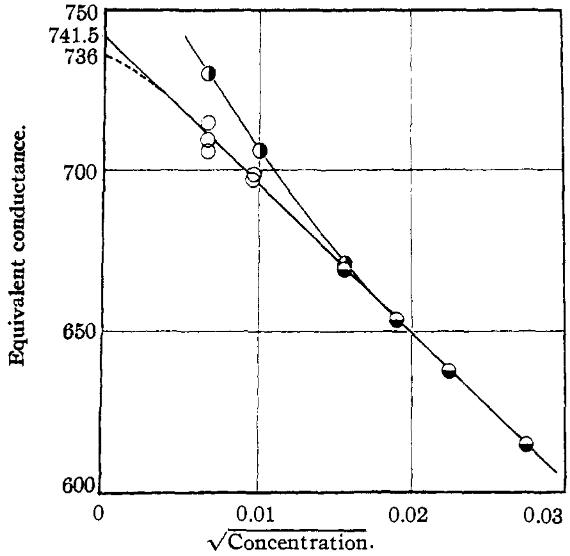

Fig. 1.—◒, Jones and Jelen, experimental points; ◑, calculated by Jones and Dole equation; ○, Swift, experimental points; - - - Davies' extrapolation.

Jones and Jelen[3] found in the case of potassium ferrocyanide that the Jones and Dole equation best fitting all their data up to saturation yields a value of 783 for the limiting conductance. If the equivalent conductance calculated by this equation is plotted against the square root of the concentration, the curve obtained has a positive curvature throughout. Because of this upward curvature, Jones and Jelen state that the value obtained by straight line extrapolation of their data (742) is probably too low. On the other hand, they believe that the extrapolation by means of the Jones and Dole equation gives too high a value.

Davies[4] has proposed a modification of the Onsager equation which makes allowance for the effect of partial association of the ions, and which requires a negative curvature at extreme dilution. (Figure 1.) Applying this equation to the data of Jones and Jelen, he obtained a value of 736 for the limiting conductance.

It was the purpose of this research to extend the measurements of Jones and Jelen to greater dilution in order to determine the direction of the limiting curvature and hence to evaluate the limiting conductance more exactly.

Measurements of the conductivity were made at 25° using the same technique as employed by Jones and Jelen and observing their precautions. Considerable difficulty was experienced at these low concentrations from a continuous change in the resistance of the solutions during measurement, which was perhaps due to an unknown reaction of the material in the cell. This uncertainty amounted to as much as 0.5% of the measured resistance and was corrected for by extrapolation of the measured values to obtain a hypothetical value at the time of dissolving the salt. With the best conductivity water available, which ranged from 0.2–0.6 × 10^{-6} in specific conductance, the water correction amounted to 1–2% and so offered considerable opportunity for error. The results which are tabulated below are also shown in the figure. Measurements were made at concentrations below those given in the table, but the results were so discordant that they are not included.

Table I

c	$\sqrt{c}$	Λ
0.000093715	0.00968	697.9
.000091442	.00956	697.4
.000044078	.00664	706
.000044054	.00664	707
.000044083	.00664	710
.000044100	.00664	715
.000044097	.00664	714

The results for each of the two groups of concentrations gave on averaging: for c = 0.00009216, Λ = 697.7, and for c = 0.00004408, Λ = 710.4. The best straight line that could be drawn through these two points and Jones and

---

[1] Grinnell Jones and M. Dole, This Journal, **52**, 2245 (1930).

[2] L. Onsager, *Trans. Faraday Soc.*, **23**, 341 (1927); T. Shedlovsky, This Journal, **54**, 1405 (1932).

[3] Grinnell Jones and F. C. Jelen, *ibid.*, **58**, 2561 (1936).

[4] C. W. Davies, *ibid.*, **59**, 1760 (1937).

Jelen's four lowest points, which cover the range 0.00025 to 0.00075 molar, was found by the method of least squares. The equation for this line is $\Lambda = 741.56 - 4621\sqrt{c}$, and there is no evidence of curvature from it within the experimental error up to 0.00075 molar.

Jones and Jelen stated that there was no experimental evidence or theoretical warrant for a change in the direction of curvature at the lowest concentrations. These measurements indicate that the curve straightens out in the most dilute solutions as is the case with lower valence type salts, and that the Jones and Dole equation gives too high a value of the limiting conductance due to the upward curvature it imposes on the extrapolated line. On the other hand, no evidence is found for the negative curvature postulated by Davies, although it is not necessarily excluded at still lower concentrations.

The author wishes to thank Professor Grinnell Jones for aid and advice during the course of this research.

MALLINCKRODT CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.
RECEIVED JANUARY 24, 1938

A Calcium Chloride Compound of α-*l*-Sorbose

BY ROY L. WHISTLER AND R. M. HIXON

Calcium chloride is known to form crystalline addition compounds with several sugars.[1-5] All of these compounds undergo mutarotation; the rotatory changes in most cases follow closely the changes exhibited by the pure sugar components. The preparation of a calcium chloride compound of *l*-sorbose was undertaken in the hope of obtaining a compound containing sorbose in either the alpha or beta stereoisomeric forms. Should such a compound be obtained its acetylation might yield a convenient method for preparing the corresponding sorbose acetate.

The compound produced showed a rapid but small upward mutarotation thus resembling the rotatory changes exhibited by pure sorbose.[6] The observed initial rotation was that calculated assuming the sugar component to be unaltered structurally and to possess the same specific rotation as pure sorbose. On acetylating the addition compound by the general procedures for acetylation, the keto sorbose pentaacetate was obtained. Hence, the property of sorbose to form preferentially an open chain pentaacetate is also exhibited by the calcium chloride addition compound. Acetylation using the special method[7] designed to give sorbose tetraacetate produced this tetraacetate in good yield. These facts indicate that the calcium chloride addition compound does not stabilize sorbose in a new form.

Experimental

Twenty grams of *l*-sorbose was dissolved in 25 cc. of warm water and 18 g. of calcium chloride slowly added with stirring. After effecting complete solution by stirring and heating on a hot-plate, the solution was placed in a desiccator over phosphorus pentoxide. In three weeks the solution had turned to a thick mush of crystals. These were stirred with absolute alcohol, filtered and washed free from sirup with absolute alcohol; yield 15 g. The crystals melted at 159° (corr.) and were stable in air. Recrystallization by dissolving in water and slow concentration of the sirup in a desiccator produced fine crystals melting at 159° (corr). Dissolved in water (*c*, 4.4) the rotation two minutes after solution was $[\alpha]^{26}\text{D}$ −24.2°. In fifteen minutes the value became constant at $[\alpha]^{26}\text{D}$ −23.9°.

Anal. Calcd. for $C_6H_{12}O_6 \cdot CaCl_2 \cdot 2H_2O$: Ca, 12.25; Cl, 21.72; α, 2.30. Found: Ca, 12.26; Cl, 21.77; α, 2.30.

The addition product can be prepared in a shorter time by adding three volumes of absolute alcohol to the prepared calcium chloride–sorbose sirup, described above, and then ether in small quantities until crystallization occurs.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA
RECEIVED FEBRUARY 2, 1938

---

(1) Dale, THIS JOURNAL, **51**, 2788 (1929).
(2) Isbell, *Bur. Standards J. Research*, **5**, 741 (1930).
(3) Dale, THIS JOURNAL, **56**, 932 (1934).
(4) Austin and Walsh, *ibid.*, **56**, 934 (1934).
(5) Hann and Hudson, *ibid.*, **59**, 2075 (1937).
(6) Pigman and Isbell, *Bur. Standards J. Research*, **19**, 443 (1937).
(7) Arragon, *Compt. rend.*, **198**, 1508 (1934).