ELECTROMOTIVE FORCE OF SILVER NITRATE CONCENTRATION CELLS.

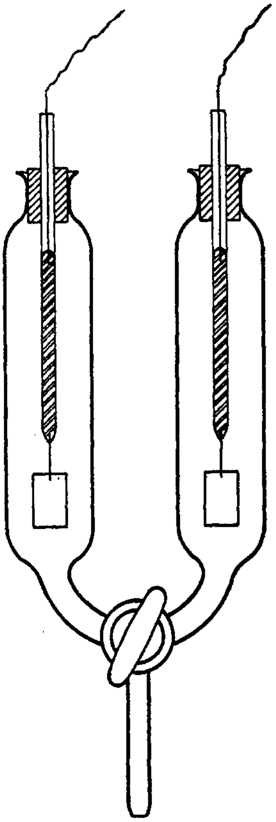
BY JAMES M. BELL AND ALEXANDER L. FEILD.

Received April 3, 1913.

The electromotive forces of concentration cells—two aqueous solutions of silver nitrate between silver electrodes, $Ag/AgNO_3/AgNO_3/Ag$—have been measured by Miesler,[1] by Nernst,[2] by Negbaur,[3] by Cumming and Abegg,[4] and by Cybulski and Dunin-Borkowski[5]. Non-aqueous solutions have been employed in similar measurements by Bodländer and Eberlein,[6] by Neustadt and Abegg,[7] and by Roshdestwensky and Lewis,[8] the non-aqueous solvents being ethylamine, methylamine, methyl alcohol, ethyl alcohol, acetone and pyridine.

The present paper contains results of measurements of the electromotive force in aqueous solutions and in ethyl alcohol solutions over a wider range of concentrations than heretofore used.

The water used in making up the solutions was distilled several times and had a low conductivity. The ethyl alcohol stood several days over quicklime and was then distilled from barium oxide. Baker's analyzed silver nitrate was used, the impurities present being negligible in amount.



The cell is shown in the figure, and consists of a U-tube with outlet tube and three-way stopcock. While the cell was in the thermostat, the outlet tube was capped. The three-way stopcock permitted the removal of either solution, and permitted the separation of the solutions in the limbs of the tube until the measurement was about to be made. The electrodes were of platinum foil about 1 cm. square, welded to platinum wire which was fused through a glass tube containing mercury. Frequently during the course of the experiments, the platinum foil and wire were plated with silver from silver nitrate solutions acidified with nitric acid. When the two solutions were at the same level in the two limbs

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[1] *Monatshefte*, **8**, 193, 365 (1887); *J. Chem. Soc.*, **52**, 1073 (1887); **54**, 13 (1888).

[2] *Z. physik. Chem.*, **4**, 155 (1889).

[3] *Wied. Ann.*, **44**, 737 (18 1).

[4] *Z. Elektrochem.*, **13**, 18 (1907).

[5] *Anz. Akad. Wiss. Kraukau*, **1909**, 660; *Chem. Zentr.*, **1909**, II, 1295.

[6] *Ber.*, **36**, 3945 (1903).

[7] *Z. physik. Chem.*, **69**, 486 (1909).

[8] *J. Chem. Soc.*, **99**, 2138 (1911).

of the U-tube, connection between them was made by opening the stopcock, and the E. M. F. was determined by the ordinary potentiometer method. The galvanometer was sensitive to 0.00005 volt even with a large resistance in the circuit. An electrically heated and electrically controlled thermostat was run at 25° constant to 0.01°. The measurements were irregular until the metal coating of the thermostat tank was grounded.

Measurements of the electromotive force of such combinations were constant within 0.0001 volt for at least 20 minutes after putting the solutions in contact. The table below gives the mean of two values obtained when different solutions and freshly plated electrodes were used. These duplicate measurements differed at most by 0.0003 volt and in the majority of cases by not more than 0.0001 volt.

TABLE I.

	Mols/liter c_1.	Mols/liter c_2.	E.M.F. obs. Millivolts.	$K = \frac{E}{\log_{10} c_1/c_2}$.
(1)	1.0	0.1	47.2	0.0560
(2)	1.0	0.01	103.6	0.0584
(3)	0.3	0.03	53.6	0.0606
(4)	0.3	0.003	113.8	0.0616
(5)	0.1	0.01	56.6[1]	0.0608
(6)	0.03	0.003	60.1	0.0623
(7)	0.01	0.001	60.2[2]	0.0623

These readings show satisfactory agreement among themselves, for the sum of (1) and (5) should equal (2), and the sum of (3) and (6) should equal (4). The differences are 0.0002 and 0.0001 volt respectively.

The Nernst formula for cells of this type is

$$E = \frac{2v}{u+v} \frac{RT}{nF} \log_e \frac{c_1}{c_2}$$

where c_1 and c_2 refer to the concentration of silver ions and not to the concentration of silver nitrate. It is necessary to know the values of u and v, the migration ratios of Ag^+ and NO_3^-. With solutions for which u and v are constant, values proportional to the ionic concentrations are given by the conductivities of the solutions, and these are inversely proportional to the resistances of the solutions. Cumming and Abegg con-

TABLE II.

Concentration.	Resistance.
1.0	3.486
0.3	9.646
0.1	24.25
0.03	73.80
0.01	206.49
0.003	679.32
0.001	1907.0

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[1] Cumming finds 59.0 millivolts.

[2] Cumming finds 61.8 millivolts.

clude "that conductivity seems to be an exact measure of ion concentration." The preceding table contains the results of measurements of the resistances of the above solutions.

Measurements of the migration ratios at each concentration were not made. The table given by Lehfeldt[1] indicates that the migration ratio for silver nitrate is fairly constant up to a concentration of 0.2 mols per liter. Assuming this value to be constant the above equation becomes

$$\frac{E}{\log_{10} c_1/c_2} = \frac{2v}{u+v} \cdot \frac{RT}{nF} \cdot \log_e 10 = K.$$

The values of $K = \frac{E}{\log_{10} c_1/c_2}$ are given in the last column of Table I and with the exception of cells 1 and 2, where normal solutions were used, they are fairly constant. This confirms the results of previous investigations, which show that the Nernst formula holds for dilute solutions of silver nitrate. From the value of K found above the values of u and v may be calculated by substitution of the proper values of the other quantities in the equation

$$K = \frac{RT}{nF} \frac{2v}{u+v} \log_e 10.$$

Taking $K = 0.0623$ the value of v is 0.523 while the observed value, given by Lehfeldt[1] is 0.528.

The table compiled by Lehfeldt indicates that the value of v is less for concentrated solutions and this would make the value of K smaller in proportion. The present results are in harmony with this fact, although it is impossible as yet to calculate the electromotive force between two solutions of silver nitrate of such concentrations that the migration ratio of the two are different.

The following table gives the results of measurements of the electromotive forces of three combinations where ethyl alcohol was used as solvent.

TABLE III.

	Mols/liter c_1.	Mols/liter c_2.	E.M.F. obs. Millivolts.	$K = \frac{E}{\log_{10} c_1/c_2}$.
(1)	0.1	0.01	47.0	0.068
(2)	0.1	0.001	106.6	0.071
(3)	0.01	0.001	59.7	0.074

The experimental values are consistent among themselves as the sum of (1) and (3) is 106.7 against 106.6 for (2).

The relative ionic concentration of silver ions was determined by conductivity measurements the results being given in the next table.

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[1] *Electrochemistry*, p. 256 (1904).

TABLE IV.

Concentration.	Resistance.
0.1	208.5
0.01	1024.0
0.001	6420.0

Again assuming that at all the concentrations employed the values of the migration ratios remain constant, the value of K was determined by the same formula as for aqueous solutions. As these values vary somewhat (see Table III), it seems probable that the migration ratios of Ag^+ and NO_3^- are not constant even for concentrations below 0.1 *N*. Taking $K = 0.074$, the value of v is 0.62.

Summary.

The electromotive forces of concentration cells containing solutions of silver nitrate in water at 25° are in accord with the Nernst formula for dilute solutions. Where higher concentrations were employed the calculated value of the electromotive force is greater than the observed because the migration ratio v is smaller at the higher concentrations. This affects two factors in the Nernst equation, *viz.*, $2v/u + v$ and $\log c_1/c_2$. The latter factor is affected because the ratio of the ion concentrations c_1/c_2 is determined from conductivity measurements and this method of determination is valid only when the migration velocity remains constant. The value of the migration ratio for dilute solutions calculated from the above results agrees closely with the values found by direct experiment.

For ethyl alcohol solutions the migration ratio apparently varies even at concentrations below 0.1 *N*. The value of v calculated from the most dilute solution was 0.62.

UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, N. C.

A STUDY OF THE METALLIC TELLURITES.

BY VICTOR LENHER AND EDWARD WOLESENSKY.

Received March 28, 1913.

Since the early work of Berzelius[1] very little has been contributed to the chemistry of the tellurites. What work has been done has been largely incidental rather than a systematic study.

In our work the tellurites of potassium, sodium, silver, barium, magnesium, cadmium, nickel, cobalt, manganese, lead, and ammonium were studied. In addition to the normal tellurites, the di- and tetratellurites of the alkali metals were also studied. The normal and ditellurites of potassium and sodium were prepared by fusing tellurium dioxide with the calculated quantities of the alkali carbonates. The tetratellurites of

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[1] *Jahresb.*, 1833; *Pogg. Ann.*, 28, 396 (1833); *Kongliga Svenska Vetenskaps Akademiens Handlingar*, 1833, 277; *Pogg. Ann.*, 32, 1-577 (1834); *Ann. chim. phys.*, [2] 58, 225 (1835).