unexpected result—no gold residue remained after filtering. At this high temperature some mercury seemed to escape with the hydrogen when the tubes were sampled. The composition of the amalgams was about 25%, so this run yielded only a rough indication of the solubility. Series M-9 bumped very definitely during the evaporation of the mercury, so the analyses were not carried to completion; series M-10 was run to replace series M-9. The two series SU and SN were made, by another worker in this Laboratory, in essentially the same air-bath used by Weiner, and are included for the sake of completeness.

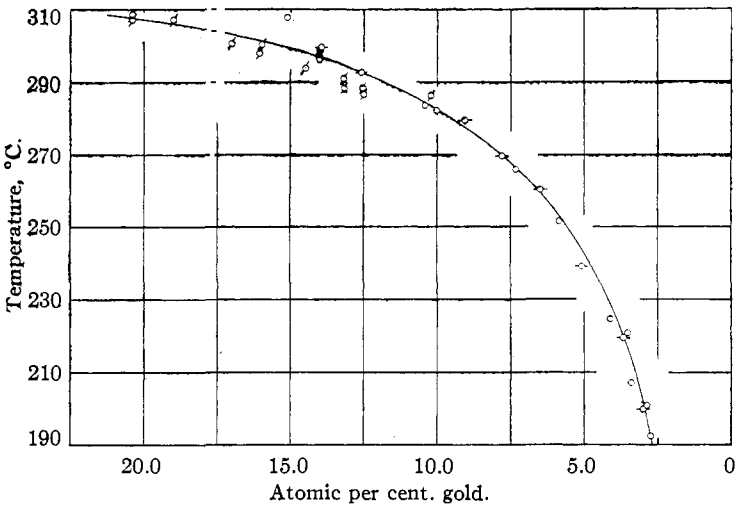

Fig. 1.—Solubility of gold in mercury: ◔, Fitzsimmons; -O-, Weiner; ◑, Anderson (where two or three determinations gave values which could not be distinguished on a plot of this size, this has been indicated by several cross bars); ○, author.

Discussion of Results

In Fig. 1 the results are plotted as atomic per cent. solubility *versus* temperature in °C. All of the data obtained in this interval of temperature in this Laboratory have been included in the plot;[3] the agreement in the various researches is seen to be quite satisfactory considering the different types of tubes, thermostats and thermometers used. A full discussion of the work of others as well as the nature of the solid phase is reserved for the fifth paper referred to.

The writer wishes to express his thanks and appreciation to Professor Sunier for the help which made this work possible.

(3) The data of Anderson are found in the fifth paper of this series [*J. Phys. Chem.*, **36**, 2145 (1932)]. The data of Parravano, Britton and McBain and Plaksin have been plotted in Fig. 4 of the last paper and Fig. 4 of the fifth paper. Complete references are found in the fifth paper.

Summary

About seventy determinations of the solubility of gold in mercury have been made, in the temperature interval 190 to 300°, with a modified solubility tube and an oil-bath. These determinations are in good agreement with an equal number of determinations made under different conditions in this Laboratory. No maximum in the solubility curve, in this interval of temperature, has been found.

ROCHESTER, NEW YORK RECEIVED FEBRUARY 28, 1938

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE NEBRASKA STATE TEACHERS COLLEGE]

The Direct Current Conductances of Potassium Chloride Solutions[1]

BY LYLE V. ANDREWS AND WILLIAM E. MARTIN

A large number of determinations of the conductances of potassium chloride solutions have already been made using the conventional alternating current method, but no direct current measurements have been made except those of Newbery[2] and Eastman,[3] who measured the conductance of 1 normal solutions only.

We believe that a quantity as important as the conductance of electrolytes should be measured by as many methods as possible, and are presenting a direct current method which is different from any in the literature.

Apparatus, Materials and Experimental Procedure.—The cell and connections are shown in Fig. 1. Broken lines numbered 1 represent connections for method 1, and broken lines numbered 2 represent connections for method 2. The two electrodes of the cell were made up alike and consisted of a layer of mercury covered with a paste

(1) Presented at the Midwest Regional meeting of the American Chemical Society in Omaha, May, 1937.
(2) Newbery, *J. Chem. Soc.*, **113**, 701 (1918).
(3) Eastman, THIS JOURNAL, **42**, 1648 (1920).

of mercurous chloride. The cell was filled with the solution to be measured and was flushed with fresh solution at various times during the measurements. The resistances R, P and Q were all calibrated with a Leeds and Northrup Wheatstone bridge, and the fall of potential over each resistance was measured with a Leeds and Northrup potentiometer. E_Q, the fall of potential over Q, ranged from 1–1.5 volts and E_R, the fall over R, ranged from 0.01–0.015 volt. The small current through the cell produced some polarization. The small back electromotive force due to polarization reached a constant value after a few minutes and remained so for hours. The polarization was corrected by opening the battery circuit and measuring the fall of potential over R, caused by the polarization current set up by the back electromotive force. This small potential, E'_R, was never more than 0.05% of E_R. Method 1 was used for the more concentrated solutions, and method 2 for the more dilute solutions, and also for the solvent. Both methods were used for some of the solutions, and the results of these two methods agreed within a few hundredths of one per cent.

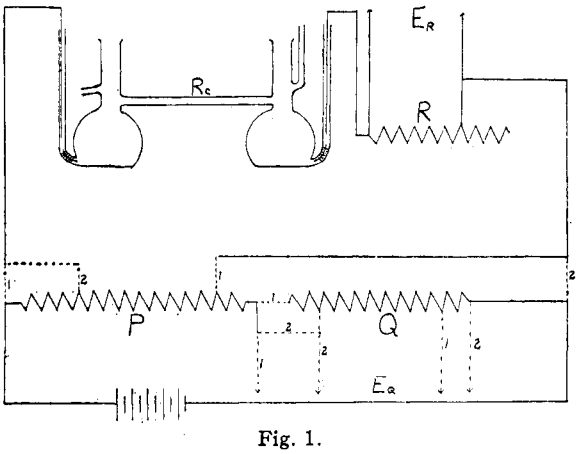

Fig. 1.

The resistance of the cell, R_C, was calculated by the formula

$$R_C = \frac{RPE_Q}{Q(E_R + E'_R)} - (R + P)$$

for method 1, and

$$R_C = \frac{R(P+Q)E_Q}{Q(E_R + E'_R)} - R - \frac{E'_R}{E_R + E'_R}(P + Q)$$

for method 2. The term $\frac{E'_R}{E_R + E'_R}(P + Q)$ is less than 0.004% of R_C, and was neglected. At least nine trials of R_C were made for each concentration, with R, P and Q being varied between wide limits. The individual trials of R_C agreed within a few hundredths of one per cent.

The temperature of the bath was kept at 25.00 ± 0.01°.

Distilled water was redistilled from alkaline permanganate in an all Pyrex still, and had a specific conductance of about 10^{-6} ohm^{-1}. All samples had about the same conductance. Part of the water used in making up each solution was kept under the same conditions as the solution, and was measured as soon as the resistance measurements of the solution were finished.

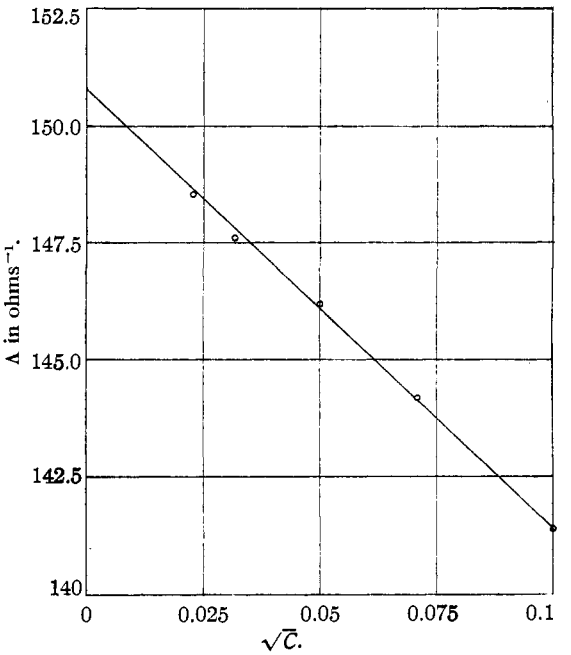

Fig. 2.

One of the best grades of potassium chloride was recrystallized from redistilled water and dried at 150°. One of the best grades of mercurous chloride was washed several times with the solution to be measured, and then placed in the cell. Redistilled mercury was used in all measurements.

The solutions to be measured were prepared from a solution containing 7.4612 g. of potassium chloride per liter at 25.0°. Weighed portions of this solution were made up to volume in volumetric flasks at 25.0°. All weighings are corrected to vacuum.

The cell constant was determined from the resistance of the 0.01 N solutions, and the specific conductance of a 0.01 demal solution as determined by Jones and Bradshaw.[4] Using their value for a 0.01 D solution, we obtain 141.37 ohm^{-1} for the equivalent conductance of a 0.01

(4) Jones and Bradshaw, THIS JOURNAL, 55, 1780 (1933).

N solution, which contains 0.74552 g. of potassium chloride per liter at 25.0°. This agrees closely with the value, 141.32 ohm^{-1}, as given by Shedlovsky.[5] The results are shown in Table I.

TABLE I

CONCENTRATIONS AND CONDUCTANCES OF SOLUTIONS

Gram formula weights per liter	Resistance of cell in ohms, corrected for resistance of water	Λ in ohms^{-1}	Λ_0 in ohms^{-1}
0.010001	1.0001×10^5	141.37	150.78
.0049986	1.9617×10^5	144.18	150.84
.0025050	3.8731×10^5	146.18	150.89
.0009937	9.6385×10^5	147.62	150.58
.0005130	1.8552×10^6	148.57	150.70

The last column gives the conductances at zero concentration, calculated from the Onsager equation, $\Lambda_0 = \frac{\Lambda + 59.79\sqrt{C}}{1 - 0.2274\sqrt{C}}$. In Fig. 2, the solid line represents the theoretical results. One point is the value 141.37 ohms^{-1} for the 0.01 N solution and another is the value for Λ_0 calculated by the Onsager equation from the 0.01 N value for Λ. The circles represent our experimental results, which show a general variation of ±0.06%. Using a Leeds and Northrup type K potentiometer, more accurately calibrated resistances and weight normal solutions, it should be possible to make measurements to ±0.01%.

(5) Shedlovsky, THIS JOURNAL, **54**, 1411 (1932).

Summary

The equivalent conductances of potassium chloride solutions have been measured from 0.01 to 0.0005 N.

A new method of measuring conductances has been presented and is upheld by results of sufficient accuracy to substantiate it.

CHADRON, NEBRASKA RECEIVED DECEMBER 4, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE OF THE COLLEGE OF THE CITY OF NEW YORK]

The Liquidus Surface of the System Sodium, Lithium and Calcium Nitrates

BY ALEXANDER LEHRMAN AND DAVID BRESLOW

The liquidus surface of the ternary system sodium, lithium and calcium nitrates was explored as part of an investigation of the liquidus of the quaternary system potassium, sodium, lithium and calcium nitrates. As was explained in a previous paper[1] it is hoped that this quaternary system will yield a salt bath melting below 100°.

One of the binaries involved here (lithium nitrate–calcium nitrate) has been determined by the apparatus and methods used in the work being reported.[1] A check of the other two binary systems involved (sodium nitrate–calcium nitrate and sodium nitrate–lithium nitrate) by means of time–temperature cooling curves showed eutectic temperatures which differed from those reported in the literature. The liquidus curves of these two binary systems were therefore redetermined. While the melting point of lithium nitrate obtained by us agrees with values previously reported, the melting point of sodium nitrate obtained differs somewhat from previously reported values. Calcium nitrate decomposes before melting and therefore its melting point cannot be directly measured.

(1) Lehrman, *et al.*, THIS JOURNAL, **59**, 179 (1937).

Experimental

Materials.—The salts used in the binary and ternary systems were prepared as described in a previous paper.[1]

Temperature Measurements.—Temperatures were measured with a copper–constantan thermocouple of No. 24 wire in conjunction with a Leeds and Northrup potentiometer indicator, the cold junction being cracked ice. The couple was protected from the molten nitrates by a shield of narrow Pyrex tubing sealed at one end. It was standardized by determining the e. m. f.'s at the boiling point of water, the melting point of U. S. Bureau of Standards tin (231.9°) and the melting point of purified potassium nitrate (333.0°) and plotting the deviations from the standard table of Adams.[2] The deviation curve was a straight line.

Method.—The mixtures, about 20 g. each, were weighed by difference into 2.5 × 20-cm. Pyrex test-tubes, the salt with the highest melting point being the first in the tube. The weights were taken to the nearest centigram.

Two methods were used to obtain the initial crystallization temperatures. The first was that of obtaining time–temperature cooling curves in the manner and in the apparatus described by Lehrman, Selditch and Skell.[3] This method worked well for the pure salts and for those mixtures in the binary systems where lithium or sodium nitrate was the first solid to crystallize. Due, however,

(2) Pyrometric Practice, U. S. Bureau of Standards Technological Paper No. 170, p. 309.

(3) Lehrman, Selditch and Skell, THIS JOURNAL, **58**, 1612 (1936).