[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

The Determination of the Solubility of Silver Chloride by an Electrometric Titration Method

BY ALFRED S. BROWN[1] AND D. A. MACINNES

There has been a revived interest in the precise determination of the equilibrium concentrations of slightly soluble salts due to the importance of the results of such measurements in connection with the interionic attraction theory of solutions of electrolytes. For instance, Brönsted and La Mer[2] demonstrated, by means of measurements on slightly soluble complex salts, the substantial correctness of the limiting law of the Debye–Hückel theory for electrolytes of various valence types. The method used in their research was the direct analysis of the equilibrium solutions. Solubility measurements have also been made by Popoff and Neuman[3] and by Neuman[4] by a method which consisted in progressively increasing the concentrations of the components until the first trace of a solid phase appeared. Although the potentiometric method for the determination of the solubilities of slightly soluble salts is responsible for a great part of the published data, it has not been much used in recent years. This is probably due to the fact that the galvanic cells that have been used in the method involve uncertain liquid junction potentials. Theoretical and experimental studies have, however, been made on the method by Lange and Swartz,[5] Hahn and Klockmann,[6] and by Cavanagh.[7]

It is the purpose of this paper to describe a modification of the potentiometric method in which the uncertainty due to the liquid junction is reduced to a minimum. The procedure adopted, and applied to the determination of the solubility of silver chloride in certain salt solutions, was to set up concentration cells of the type

$$\mathrm{Ag, AgCl, \underset{C_1}{AgNO_3}, \underset{C_2}{KNO_3}} \mid \mathrm{\underset{C_3}{AgNO_3}, \underset{C_4}{KNO_3}, AgCl, Ag} \qquad \text{(A)}$$

The solution on one side of the liquid junction was kept constant and, together with the electrode, served as a reference half cell, whereas the composition of the solution in the other half cell was progressively changed by the addition of increments of potassium chloride solution. This was, of course, an electrometric titration. Since the solutions in the two half cells initially had the same composition, and the titration changed this composition but little, the liquid junction started with a zero potential and took a series of low values (which could be readily estimated) as the titration progressed.

Theory

During the titration of silver nitrate with potassium chloride under the condition of constant ionic strength we have the relation

$$[\mathrm{Ag^+}]\,[\mathrm{Cl^-}] = L \qquad (1)$$

in which the brackets represent concentrations and L the stoichiometric solubility product. The condition of electrical neutrality requires

$$[\mathrm{Ag^+}] + [\mathrm{K^+}] = [\mathrm{Cl^-}] + [\mathrm{NO_3^-}] \qquad (2)$$

Since $[\mathrm{K^+} - \mathrm{NO_3^-}]$ is a measure of the extent of titration we have, using equation (2)

$$[\mathrm{Cl^-}] - [\mathrm{Ag^+}] = (n - n_e)p/V \qquad (3)$$

in which n is the number of increments of potassium chloride solution each containing p equivalents, V the *constant* volume of solution to which they are added, and n_e is the value of n at the equivalent point. Since the reference electrode contained the initial solution and the liquid junction potential is negligible (as will be shown later), the potential of a cell of type A is

$$E = \frac{RT}{F}\log\frac{[\mathrm{Ag^+}]}{[\mathrm{Ag^+}]_i} = \frac{RT}{F}\log y \qquad (4)$$

in which the subscript i refers to the reference electrode, and $y = [\mathrm{Ag^+}]/[\mathrm{Ag^+}]_i$. Since $n = 0$ at the beginning of the titration

$$[\mathrm{Cl^-}]_i - [\mathrm{Ag^+}]_i = -n_e p/V \qquad (5)$$

The data obtained during a titration may be expressed as a linear equation by eliminating $[\mathrm{Cl^-}]$ between (1) and (3), expressing $[\mathrm{Ag^+}]$ by means of $y[\mathrm{Ag^+}]_i$, introducing equation (5), and solving for $n/(1 - y)$. This yields

$$\frac{n}{1-y} = n_e + \frac{VL}{p[\mathrm{Ag^+}]_i}\,\frac{1+y}{y} \qquad (6)$$

Thus if the theory of the operation of the cell A is correct, a plot of $n/(1 - y)$ against $(1 + y)/y$ should be a straight line with an intercept at n_e.

---

[1] National Research Fellow.

[2] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[3] Popoff and Neuman, *J. Phys. Chem.*, **34**, 1853 (1930).

[4] Neuman, THIS JOURNAL, **54**, 2195 (1932).

[5] Lange and Schwartz, *Z. physik. Chem.*, **129**, 111 (1927).

[6] Hahn and Klockmann, *ibid.*, **146**, 373 (1930).

[7] Cavanagh, *J. Chem. Soc.*, 843, 855 (1928).

The value of the solubility, $\sqrt{L}$, may be computed from the equation

$$\sqrt{L} = (p/V)\sqrt{S(S + n_e)} \qquad (7)$$

This expression is obtained from equations (1), (5) and (6), and S is the slope of the line representing equation (6). We are indebted to a referee for suggesting a method for shortening our original derivation.

The Apparatus and Manipulation

The cell, the glass portions of which are made of Pyrex, is shown diagrammatically in Fig. 1. It consists of cylindrical vessel A, which surrounds another cylindrical vessel B. A passage connecting the two vessels is arranged at D. This passage can be closed by means of the plunger P which has been carefully ground into the connection D at its lower end. A pair of silver-silver chloride electrodes E is inserted as shown into the vessel B and another pair E′ into the annular space of vessel A. The distinctive feature of a titration carried out with this cell is that the same solution is placed initially in vessels A and B. Before commencing a titration the passage between the vessels is closed at D, and increments of the titrating fluid are then added through the opening O to the vessel A. Stirring is carried out by passing a current of nitrogen through tube T. The vessel B and the electrodes thus serve as a reference half cell, the ground joint furnishing sufficient electrical conductivity, and is the seat of a very small and computable liquid junction potential. With this procedure it is evidently necessary to know the proportion of the fluid contained in vessel A. This proportion was accurately determined as a function of the total volume of fluid in the cell by filling the cell with water to a series of levels, finding the total weight of water, and then, after closing the passage D, withdrawing the water from B, drying with a current of air, and reweighing. The inner vessel B holds about one-ninth of the total volume. Leakage through the ground joint is found to be inappreciable.

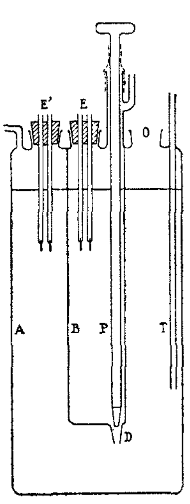

Fig. 1.

The experiments were greatly facilitated by the use of a micro-pipet illustrated in Fig. 2. With this instrument equal increments, known to about 0.02%, were added progressively to the solution in vessel A. This micro-pipet is a simplification of one described by Krogh and Keyes[8] and can be made from easily available materials. The syringe proper is of the B. and D. tuberculin type. The piston D fits smoothly into the barrel C. The needle, N. No. 24 gage, together with the hub. are made of stainless steel. The yoke Y, which provides a guide and one limit to the motion of the piston D, is fastened to the cylinder by means of the split collar L, which is made of Bakelite. Finally, a brass spring, S, which is fastened to the piston D with cement, rests against the yoke Y and keeps the piston from turning. Although there was no evidence of reaction between the stainless steel and the potassium chloride solution contained in the pipet, the precaution was taken of washing out the latter carefully each time it was used. The micro-pipet as described was calibrated by filling with water and delivering the contents just under the surface of water contained in a weighing bottle. A quite remarkable reproducibility was observed. Nine determinations gave 0.41324 cc. as the volume of the pipet with a maximum deviation from the mean of 0.02%.

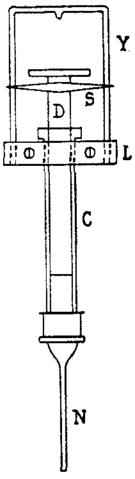

Fig. 2.

The Electrodes.—Silver–silver chloride electrodes were used in this investigation, since they were found to be far more reproducible than silver electrodes. The preparation and behavior of the electrodes used are described in a recent paper from this Laboratory.[9] Four electrodes were used in each titration, two each in the inside and the outside chambers of the vessel shown in Fig. 1.

The potentials were measured with a Leeds and Northrup Type K potentiometer, which had been carefully calibrated. The potentiometer was surrounded by a case which protected it from corrosion and from excessive humidity, and also furnished electrostatic shielding. The leads from the potentiometer terminated in mercury cups suspended in the thermostat. Enameled copper wires, the ends of which had been scraped and amalgamated, connected the electrodes with the mercury cups. These wires were grounded before being placed in position in order to remove the electrostatic charges which they occasionally acquired during handling. The measurements were made in a well-stirred oil thermostat maintained at 25 ± 0.02°. The mercury thermometer used was calibrated against a platinum resistance thermometer which had been calibrated at the ice, steam and boiling sulfur points by Dr. Shedlovsky of this Laboratory.

The manipulation during an experiment was as follows. About 350 g. of potassium nitrate solution of the required strength was weighed into the cell. This solution may be regarded as the "solvent medium." Sufficient silver nitrate was then added to make the solution about 0.0001 normal in silver. The electrodes were put into position and two or three titer increments (deliveries of the micro-pipet) of potassium chloride solution were added. The contents of the cell were then mixed. and the connection between the inner and outer portions of the cell was closed by lowering the plunger P. The cell was then allowed to stand overnight to permit attainment of equilibrium between the precipitated silver chloride and the solution and between the solution and the electrodes. During the rest of the titration. increments of the potassium chloride solution were added to the outer portion, A, of the solution, and the potentials between electrodes E and E′ were measured.

The Results

After the addition of each increment of potas-

---

[8] Krogh and Keyes. *J. Chem. Soc.*, 2436 (1931).

[9] A. S. Brown, THIS JOURNAL, 56, 646 (1934).

sium chloride solution from the micro-buret, the potential between the electrodes E and E′ was measured at intervals of thirty minutes. These potentials showed progressive changes (usually increases) of the order of several hundredths of a millivolt per hour. For that reason the results of the potential measurements are given in Table I in two columns. The first column of the results for a titration gives the number of titer increments, n, the second column the potential reading, E_{2h}, in millivolts, obtained at the end of two hours after the addition of a given titer increment. The potential values given in the third column, E, were obtained by a linear extrapolation to the time of addition of the titer increment. The last column contains the volume, $V + \Delta V$, of the solution in the annular space A of Fig. 1, at the time the corresponding potential measurements were made. The reason for the slow changes in the potential readings will be discussed later in this paper.

TABLE I

RESULTS OF THE TITRATIONS

Solvent medium 0.028557 N KNO_3. Total concentration 0.028592. Titer increment, p, 4.8440 × 10^{-6} equivalent of KCl.

n	E_{2h}, mv.	E, mv.	$V + \Delta V$, liters
	Titration No. 1		
0	0	0	0.32673
1	− .6711	− .6678	.32716
2	−15.098	−15.037	.32760
3	−25.596	−25.479	.32801
4	−37.499	−37.374	.32842
5	−48.755	−48.668	.32884
6	−57.983	−57.897	.32925
	Titration No. 2		
0	0	0	0.33859
1	− 6.602	− .6582	.33900
2	−14.819	−14.777	.33942
3	−24.999	−24.967	.33983
4	−36.533	−36.435	.34024
5	−47,444	−47.327	.34065
6	−56.456	−56.394	.34107
	Titration No. 3		
0	0	0	0.29912
1	− 5.603	− 5.613	.29953
2	−12.506	−12.501	.29995
3	−21.317	−21.307	.30036
4	−32.773	−32.753	.30077
5	−45.728	−45.673	.30118
6	−57.751	−57.691	.30160
7	−67.321	−67.286	.30201
	Titration No. 4		
0	0	0	0.31889
1	− 5.564	− 5.599	.31930
2	−12.415	−12.425	.31971
3	−21.126	−21.029	.32013
4	−31.927	−31.910	.32054
5	−44.168	−44.068	.32095
6	−55.650	−55.620	.32137
7	−64.758	−64.705	.32178

The Corrections to the Observed Data

Before discussing the results in the light of equation (6), it is necessary to bring the data in accord with the conditions postulated in deriving that equation. This involves consideration of corrections for (a) the liquid junction potential, (b) the volume change during a titration and (c) changes of ionic strength. These will be discussed in the order given.

(a) **The Liquid Junction Potential.**—The potential at the liquid junction between two solutions, I and II, containing only univalent ions, may be obtained from the thermodynamic expression

$$E_l = \frac{RT}{F}\int_{1}^{11} \Sigma\, z_i t_i d \ln a_i \qquad (8)$$

in which t_i and a_i are the transference numbers and activities of the ions of type i, and $z_i = +1$ for positive ions and -1 for negative ions. The other terms have their usual significance. The summation includes all the ion types in the solutions and the integration involves a knowledge, real or assumed, of the way the ion concentrations vary from solution I to II. Assuming that in solutions with the same total ion concentration the activities are proportional to the concentrations, equation (8) takes the form

$$E_l = \frac{RT}{F}\int_{1}^{\mathrm{II}} \Sigma\, z_i t_i d \ln C_i \qquad (9)$$

in which C_i is the concentration of ion species i. Starting with this equation and assuming a "mixture" type of boundary Henderson[10] has obtained the equation

$$E_l = \frac{RT}{F}\frac{(U_1 - V_1) - (U_2 - V_2)}{(U_1 + V_1) - (U_2 + V_2)} \log \frac{U_1 + V_1}{U_2 + V_2} \qquad (10)$$

Here $U_1 = \Sigma C_1^+\Lambda_1^+$ and $V_1 = \Sigma C_1^-\Lambda_1^-$, C_1^+ and Λ_1^+ being the concentration and equivalent conductance of a positive ion in solution I and C_1^- and Λ_1^- being the corresponding quantities for a negative ion in the same solution. U_2 and V_2 are obtained in a similar manner for solution II on the other side of the boundary. However, if the solutions on the two sides of the boundary have nearly the same conductance, as is true with the case in hand, the equation becomes difficult to

---

[10] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).

work with, and if they have the same conductance, *i. e.*, $U_1 + V_1 = U_2 + V_2$ it becomes indeterminate. The indeterminate expression can be evaluated by setting $(U_1 + V_1) = (U_2 + V_2) + h$, expanding the logarithm and retaining only the first term. This yields

$$E_1 = \frac{RT}{F}\,\frac{U_1 - V_1 - U_2 + V_2}{U_2 + V_2} \qquad (11)$$

which is convenient for computation and more than sufficiently accurate for our purpose.

Equation (11) can also be obtained more directly as follows. Since for the condition of constant conductance throughout the boundary the transference number t_i of ion species i is given by

$$t_i = \frac{C_i \Lambda_i}{(U_2 + V_2)} = \text{const.} \times C_i$$

then from equation (9)

$$E_1 = \frac{RT}{F}\int_{\text{I}}^{\text{II}} \Sigma\, z_i \frac{\Lambda_i}{(U_2 + V_2)}\,\mathrm{d}C_i = \frac{RT}{F}\,\Sigma\, z_i \frac{\Lambda_i\,(C_{i\text{I}} - C_{i\text{II}})}{(U_2 + V_2)} \qquad (12)$$

in which $C_{i\text{I}}$ and $C_{i\text{II}}$ are, respectively, the concentrations of ion species i in solutions I and II. Recalling the definitions of U_1 and V_1, etc., given in the previous paragraph it can be seen that equation (12) is identical with equation (11).

Since, for substitution into equation (11), it is necessary to know the compositions of the solutions in contact at the liquid junction, it was necessary to make a preliminary computation with the e. m. f. data to obtain the silver and chloride ion concentrations. This information is also useful in connection with the volume correction, which is discussed in the following section. The preliminary computation was made as follows. A sufficiently exact estimate of the end-point of the titration was made by plotting values of the number of increments of titer, n, against second differences of the e. m. f. measurements and the corresponding potential of the cell at the endpoint was obtained by linear interpolation. The silver-ion concentration at the end-point $[Ag_e^+]$ being known, roughly at least, from computations using the uncorrected data, the concentration of that ion $[Ag^+]$ at other points in the titration can be estimated from the simple relation $\Delta E = RT/F \log [Ag^+]/[Ag_e^+]$, in which ΔE is the difference between the measured potential and that at the end-point. The corresponding chloride-ion concentrations can be obtained from a preliminary value of the solubility product. The concentrations of the other ions were obtained from the composition of the original solution.

The computed liquid junction potentials for a typical titration are given in column 3 of Table II. It will be seen that they are about of the order of the experimental error. Since, however, the value of the method described in this paper depends largely upon the smallness of this liquid junction its computation has been fully described. Also, it is evident that the magnitude of these potentials makes it unnecessary to decide whether the junction is really of the "mixture" type as assumed in the computation, rather than of the "free diffusion" or "constrained diffusion" type.

(b) The Volume Correction.—Equation (6) was obtained on the assumption that no volume change occurs during the titration. That condition cannot, of course, be realized experimentally. However, by means of an equation to be derived below, the measured electromotive force values can be corrected so as to correspond to those which would be obtained during a titration in which a constant volume is maintained. The derivation is as follows.

If V is the original volume of the solution to be titrated and ΔV the volume of the added titrating solution, the correction desired involves the effect on the e. m. f. of the removal of the ΔV of solvent. Since these ions are in equilibrium with solid silver chloride, there will be a precipitation, during the solvent removal, of an amount that will be denoted by δ, of each of these ions, and a slight shift of the equilibrium concentrations of silver and chloride ions.

Letting m represent the number of moles of each ion constituent present in solution we have the concentrations

$$[Ag^+]' = \frac{m_{Ag}}{V + \Delta V},\ [Cl^-]' = \frac{m_{Cl}}{V + \Delta V},\ [Ag^+] = \frac{m_{Ag} - \delta}{V},\ [Cl^-] = \frac{m_{Cl} - \delta}{V},\ [\delta] = \frac{\delta}{V + \Delta V} \qquad (13)$$

in which primes indicate concentrations at the volumes $V + \Delta V$ and the unprimed concentrations at the constant volume V. Since from equation (1), $[Ag^+][Cl^-] = [Ag^+]'[Cl^-]' = L$ the equation

$$[\delta]\,([Ag^+]' + [Cl^-]') - [\delta]^2 = L(1 - r^2) \qquad (14)$$

in which $r = V/(V + \Delta V)$, may be obtained. Neglecting the small term $[\delta]^2$, we have

$$[\delta] = \frac{[Ag^+]'\,(1 - r^2)}{1 + [Ag^+]'/[Cl^-]'} \qquad (15)$$

The potential E' of the cell as measured is given by

$$E' = \frac{RT}{F} \log \frac{[\mathrm{Ag}^+]'}{[\mathrm{Ag}^+]_i} \qquad (16)$$

From this equation and equations (13) and (15) we may obtain the difference between E, of equation (4) (the potential of the cell at constant volume), and E', in the form

$$E - E' = \frac{RT}{F} \log \frac{[\mathrm{Ag}^+]}{[\mathrm{Ag}^+]'} = \frac{RT}{F} \log \frac{1}{r}\left(1 - \frac{(1 - r^2)}{1 + [\mathrm{Ag}^+]'/[\mathrm{Cl}^-]'}\right) \qquad (17)$$

This is a small but significant correction, since a plot of equation (6) with y values computed from the uncorrected potentials E' shows a slight curvature, whereas a similar plot from E values is a straight line. It will be observed that computation of the value of this term involves the concentrations $[\mathrm{Ag}^+]'$ and $[\mathrm{Cl}^-]'$. Quite sufficiently accurate values of these concentrations were, however, obtained as described in the section on liquid junction potentials, the error involved being of the order of a few thousandths of a millivolt, which is also the order of the error incurred by neglecting the term $[\delta]^2$.

(c) The Constancy of the Ionic Strength.—The introduction of titrating solution and the precipitation of silver chloride both tend to produce a progressive change of the ionic strength during an experiment. Since this is of the order of 0.02% the effect has been neglected in the computations.

Computations and Discussion

A summary of the results of the computations made with the data obtained during titration No. 2 is given in Table II. The figures given in this table are included to show for a typical case the magnitude of the corrections for liquid junction and for dilution with the titrating fluid, and also to indicate the agreement of the e. m. f. data, thus corrected, with equation (6) derived earlier in this paper. This agreement is shown by a comparison of observed values of $n/(1 - y)$, defined by that equation, with the computed values. It will be seen that the agreement is very satisfactory, the average deviation being 0.066%. That the corrected results can be represented by an expression of the form of equation (6) is also shown by means of Fig. 3 in which values of $n/(1 - y)$ are plotted as ordinates against the observed values of $(1 + y)/y$. The resulting plot is a straight line, as required by the theory. As explained earlier in this paper the solubility, $\sqrt{L}$, can be computed from the slope of this line, S, and the intercept n_e, by means of equation (7). For the data given in Table II the least squares computation yielded 0.2986 for the slope S and 3.738 for the intercept n_e. With the aid of the titer increment p = 4.8440 × 10^{-6}, and the volume V = 0.33859, to which all the measurements were corrected, the value $\sqrt{L}$ = 1.571 × 10^{-5} for the solubility of silver chloride was obtained.

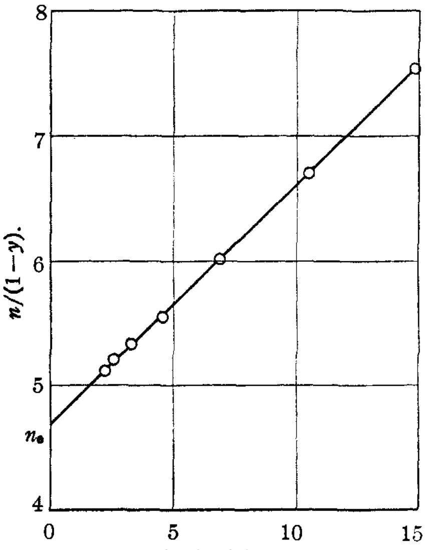

Fig. 3.

The results for the four titrations are summarized in Table III. Computations have been

TABLE II

SUMMARY OF COMPUTATIONS USING DATA FROM TITRATION NO. 2

Titer increments n	Potentials in millivolts Obsd.	Liquid junction corrn.	Diln. corrn.	Corrd.	$(1 + y)/y$	$n/(1 - y)$ Obsd.	$n/(1 - y)$ Calcd.	Deviation, %
1	− 6.602	−0.001	+0.024	− 6.579	2.2919	4.4254	4.4223	+0.070
2	−14.819	− .002	+ .038	−14.783	2.7781	4.5705	4.5675	+ .066
3	−24.999	− .002	+ .028	−24.973	3.6439	4.8249	4.8260	− .023
4	−36.533	− .003	− .017	−36.553	5.1499	5.2699	5.2757	− .110
5	−47.444	− .003	− .079	−47.526	7.3617	5.9325	5.9361	− .061
6	−56.456	− .003	− .135	−56.594	10.0551	6.7449	6.7404	+ .067

made with both sets of e. m. f. data included in Table I. These are the results of measurements taken two hours after the addition of each increment, and those obtained by linear extrapolation to the time of addition. The corresponding solubilities are given in columns 3 and 5 of Table III, and the observed percentage decreases of solubility in the two-hour interval are listed in the last column. The average percentage deviations of the observed data from the values computed by equation (6), as described in the previous paragraph, are given in columns 4 and 6. All the computations were made with the aid of the least square method.

TABLE III

SUMMARY OF THE RESULTS OF THE DETERMINATION OF THE SOLUBILITY OF SILVER CHLORIDE AT AN IONIC STRENGTH OF 0.0286 (25°)

Titration	Ionic strength (average)	Soly. 2-hour data $\times 10^5$	Av. devn., %	Soly. extrapolated data $\times 10^5$	Av. devn., %	Time effect, %
1	0.028589	1.570	0.03	1.571	0.04	0.1
2	.028591	1.571	.07	1.573	.08	.1
3	.028597	1.566	.13	1.568	.15	.1
4	.028591	1.564	.12	1.567	.14	.2
Average	.028593	1.568	.09	1.570	.10	.1

Closely agreeing values of the solubility of silver chloride are obtained from the four sets of data, indicating that potentiometric titrations such as are described in this article may be used to determine accurate values of the solubilities of certain slightly soluble salts. There is, however, a small, but unmistakable, decrease with time (about 0.06% per hour) of the solubility obtained in this manner.

There are at least three ways in which the observed change of solubility with time can be explained. These are (a) an adsorption of silver ion by the precipitated silver chloride, (b) supersaturation with silver chloride and (c) actually greater solubility of the freshly precipitated chloride, due to small grain size. Since adsorption effects, involving small amounts of substance, are quite rapid, the first explanation appears improbable, as the slow drift of potentials observed may persist for many hours. It does not seem possible to decide between the other interpretations with certainty, particularly as both effects may be present at the same time. However, the experimental conditions are favorable for the formation of fine particles, which are well known to have greater solubilities than have larger particles. This has been shown by W. Ostwald,[11] Hulett[12] and others. In the experiments described in this paper comparisons were made between solutions containing freshly formed particles of the same age.

Time was not available for extending the experiments to other concentrations of the potassium nitrate, and to other solvent salts. We hope that there will be an opportunity for such work in the near future. However, with the aid of Neuman's recent work limiting values for the solubility of silver chloride may be computed. With another method for determining solubilities this author has measured activity coefficients of silver chloride in solvent media consisting of various salt solutions, among them potassium nitrate. Interpolating from his data for the activity coefficient f corresponding to an ionic strength of 0.02859 yields 0.8356, and since

$$Lf^2 = L_0$$

in which $\sqrt{L}$ is the measured solubility, $\sqrt{L_0}$ is the solubility at zero ionic strength. Using our average value of $\sqrt{L} = 1.570 \times 10^{-5}$ from Table III this yields $\sqrt{L_0} = 1.312 \times 10^{-5}$. To obtain the solubility, $\sqrt{L_{H_2O}}$, of silver chloride in pure water, we will again make use of an activity coefficient, 0.9985, obtained by Neuman for silver chloride at the corresponding ionic strength. This gives us a value of 1.314×10^{-5}, which is slightly higher than the value, 1.273×10^{-5}, obtained by Neuman. It seems possible that this author's lower value may refer to a more stable form of chloride than ours. His method, it will be recalled, consisted in increasing the concentrations of silver and chloride ions until a permanent turbidity remained. On the other hand, our result agrees excellently with the figure 1.304×10^{-5} given in the "International Critical Tables," obtained from the conductance measurements of Kohlrausch[13] by a short interpolation from his results at other temperatures.

Summary

A method is described for carrying out electrometric precipitation titrations in which the uncertainty due to liquid junction potentials is reduced to a minimum.

A new theoretical treatment of the data obtained during such titrations is discussed. The

---

[11] Ostwald, *Z. physik. Chem.*, **34**, 503 (1900).
[12] Hulett, *ibid.*, **37**, 385 (1901); **47**, 357 (1904).
[13] Kohlrausch, *ibid.*, **64**, 129 (1908).

results may be represented upon a linear plot, the parameters of the line being the titer increment at the equivalence point and a function of the solubility of the precipitated salt.

Accurate values of the solubility of silver chloride in a dilute potassium nitrate solution have been measured.

NEW YORK, N. Y. RECEIVED JANUARY 17, 1935

[CONTRIBUTION FROM THE T. JEFFERSON COOLIDGE, JR.. MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

A Comparison of Copper Extracted from the Blood of the Horseshoe Crab (Limulus Polyphemus) with Common Copper

BY GREGORY PAUL BAXTER AND JOSEPH SMITH THOMAS

Through the kindness of President J. B. Conant[1] a sample of copper obtained from hemocyanin contained in the blood of the horseshoe crab (*limulus polyphemus*) was furnished us in order to determine whether biological separation of the isotopes of copper occurs when this organism absorbs copper from sea water. Since the total quantity of copper ultimately available for the purpose was only 1.5 g., it seemed unlikely that a definitive determination of the atomic weight of this copper could be carried out. We decided therefore to analyze and compare similar samples of copper salt prepared from common and crab copper, using the electrolytic determination of copper in copper sulfate for the purpose. So far as our results indicate, there is no difference between the two samples of copper.

Purification of Materials

Commercial copper rod was purified by electrolytic transport with low current density through a slightly acid solution of copper sulfate prepared from the original copper. The anode mud when tested spectroscopically showed tin, with traces of antimony, silver and gold. No impurities could be detected in either the electrolyte or the copper deposit. Nevertheless the product was subjected to two repetitions of the electrolytic purification. In these, except for a trace of tin in the second electrolysis, even the anode mud seemed to be free from impurities. Copper sulfate was prepared from the purified copper by solution in redistilled sulfuric and nitric acids in platinum and freed from nitric acid by repeated evaporation and solution. After digestion with a small amount of pure copper metal the solution was filtered through platinum sponge and evaporated to crystallization.

The crab copper was received in the form of various inorganic and organic compounds. The organic compounds were destroyed with nitric acid and sulfuric acid, and the excess acids expelled. The inorganic compounds also were converted to sulfate and after combination the copper was electrolytically precipitated on a platinum crucible. The total quantity of copper was less than one gram, and seasonal limitations made it impossible to collect the limulus at the time. We were fortunate enough, however, to secure from Professor A. C. Redfield of the Harvard Biological Institute seven liters of blood containing something over 0.5 g. of copper. From the blood the pigment was precipitated by adding sodium hydroxide to ten per cent. concentration and boiling according to the procedure of Conant and Humphrey. The precipitate was centrifugally settled and partially washed and then the organic material was destroyed by hot sulfuric and nitric acids. After volatilization of most of the excess sulfuric acid the copper was electrolytically deposited. At this point we had 1.50 g. of metallic copper.

The electrolytic deposits were next dissolved in nitric acid and the nitrate was converted to sulfate by evaporation with a slight excess of sulfuric acid. After solution and filtration the copper was again deposited electrolytically. In this case the electrolyte was evaporated to dryness and a small residue was found spectroscopically to contain calcium, magnesium, manganese, tin and silver. The first two are contained in the blood. The tin and silver were puzzling at first but probably were introduced, the former from tin foil covering the stoppers of the specimen tubes when received, the latter from the silver spatulas in common use in organic laboratories. The source of the manganese is uncertain but may be the sodium hydroxide.

Further purification consisted chiefly of seven additional electrolytic depositions, although in the intermediate stages the silver was eliminated as iodide and bromide and the tin by evaporation of the nitric acid solution of the copper. The appearance of the copper improved as the purification proceeded, the final deposit being perfectly bright and free from spots. Furthermore, after this copper had been converted to sulfate and crystallized, no impurities whatever could be detected spectroscopically in the mother liquor. The final weight of purified copper was 1.43 g.

Both the common copper sulfate and that from the crab were further purified by crystallization. Common A was crystallized three times, Common B five times and Common C six times. Because of the small quantity of crab copper it was necessary after each analysis to repurify all the material by conversion to sulfate. Crab A was crystallized three times as sulfate, Crab B four times and Crab C, D and E five times. The arc spectra of samples Common B and C and Crab B seemed to be identical and showed no evidence of impurity.

---

(1) Conant and Humphrey, *Proc. Nat. Acad. Sci.*, **16**, 543 (1930).