than predicted by Latimer's method[10] (47.7 for CrI_3; 37.4 for CrI_2) but in view of the approximations involved and the neglect of probable nonideal characteristics they cannot be considered inconsistent with the solution hypothesis.

It is apparent that one may not draw a definite conclusion concerning the character of the solid mixed halide phases at this time. Thermodynamic properties are generally consistent with those one would anticipate for either random or ordered arrangement of halide ions. The relationship between chromium iodide and the iodide mixed halides investigated in this work bears a close resemblance to that observed between $FeBr_3$ and $FeBrCl_2$, formed by bromination of $FeCl_2$.[11]

The difference in entropy between CrI_3 and CrI_2 noted above corresponds fairly well with the estimation method proposed by Latimer.[10] It is also of interest that the change in entropy on thermal dissociation of $CrICl_2$ reverses the downward trend noticed in $CrIBr_2$ as compared with CrI_3. This may possibly be associated with the observation that $CrCl_2$ possesses a different crystal structure than $CrBr_2$ and CrI_2[12] since the structures of the chromium(III) phases are very similar. The difference in entropy between $CrCl_3$ and $CrCl_2$ (3.3 e.u.) is also observed to be small when compared with the difference between CrI_3 and CrI_2 (9.3 e.u.).

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[10] W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

[11] N. W. Gregory, *ibid.*, **73**, 5433 (1951).

[12] L. L. Handy and N. W. Gregory, *J. Chem. Phys.*, **19**, 1314 (1951).

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The Solubility of Silver Chloride and the Formation of Complexes in Chloride Solution[1]

BY J. HAWORTH JONTE AND DON S. MARTIN, JR.

A radioassay technique has been used to determine the concentration of silver in various chloride solutions in contact with silver chloride at temperatures of 15.0, 25.0 and 35.0°. A minimum in silver concentration of about 5×10^{-7} *M* was found at 25° for a chloride activity of 2×10^{-3}. The data have been interpreted in terms of equilibria which involve the species Ag^+, AgCl(aq), $AgCl_2^-$ and AgCl(s). Equilibrium constants and thermodynamic quantities for the reactions involving these species have been calculated.

Introduction

Recently in this Laboratory radioactive assays have been utilized to measure the solubility of some rare earth oxalates.[2] From such experiments it was possible to evaluate equilibrium constants describing precipitation and complex formation. It has not been possible to apply other methods for the study of these equilibria. The present work, in which similar techniques were used to measure silver concentrations in various chloride solutions, was undertaken since some results of the radioassays could be tested directly with the solubility product determined by exceedingly accurate potentiometric means. Chloride concentrations could be adjusted only down to about 5×10^{-5} *M*. Actually, the region was small for which a solubility product law was valid because of the formation of complexes. The existence of chloro complexes of silver is well recognized since the solubility of silver chloride increases in concentrated chloride solutions. Forbes[3a] and Forbes and Cole[3b] have provided extensive quantitative data demonstrating this effect. They measured the concentration of silver in chloride solutions of various concentrations which produced a barely detectable turbidity. The results in this paper include a region of chloride concentration which has not been studied previously.

Experimental

Procedures and precautions for the determination of solubilities by radioactive assays have been included in the description of the measurements with the rare earth oxalates.

The radioactive silver was obtained from the Oak Ridge National Laboratory as a high specific activity sample with 0.088 millicuries/mg. The standard silver solutions were prepared by first electroplating the radioactive silver onto platinum. The weighed deposits were dissolved in a minimum quantity of dilute nitric acid. Small amounts of perchloric acid were added and the solutions repeatedly evaporated nearly to dryness so that the dense fumes of perchloric acid were evident. Finally, the residues were dissolved in the redistilled water and diluted in volumetric flasks. All equilibrium solution counting assays were compared with an evaporated aliquot from one of the standard silver solutions. A specific activity of 5×10^6 counts min.$^{-1}$ (mg. Ag)$^{-1}$ was obtained for first shelf geometry.

Sodium chloride solutions were prepared from reagent grade salt and standardized by conventional procedures.

All water used had been redistilled from alkaline permanganate.

Equilibrium mixtures were prepared by the mixing of standard solutions of silver in perchloric acid and of sodium chloride. The solutions were diluted to 200 ml. and stored in glass stoppered Pyrex flasks. Equilibrium for various mixtures was approached from both directions by first heating or cooling the flasks at least 10° above or below the equilibrium temperature and then shaking them in a thermostat which maintained the desired constant temperature to within ±0.05°. Samples were withdrawn after a period of at least a week in the thermostat and the total silver concentration of the solution determined by radioassays. Assays were repeated at least twice after intervals of several days to verify that concentrations were not changing. Mixtures which had been previously heated and cooled came to the same final concentration. The chloride ion concentration was calculated by subtracting the amount precipitated as silver chloride from that added as sodium chloride in the standard solution. In the most dilute chloride solution about 80% was precipitated; in many of the solutions only

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] (a) C. E. Crouthamel and D. S. Martin, Jr., THIS JOURNAL, **72**, 1382 (1950); (b) **73**, 569 (1951).

[3] (a) G. S. Forbes, *ibid.*, **33**, 1937 (1911); (b) G. S. Forbes and H. I. Cole, *ibid.*, **43**, 2492 (1921).

a negligible fraction of the chloride was precipitated. Chloride was always present in excess. Adsorption of chloride on the precipitates could have amounted to only a negligible fraction of the solution chloride. Perchloric acid concentrations were computed from the measured *p*H of the solution and activity coefficients consistent with the finally calculated ionic strength of the solution. Since the precipitates remained in contact with the solutions for long periods, they were considered well aged.

Assay aliquots were withdrawn by calibrated micropipets from a portion of the solution which had been centrifuged for a short period. The necessity for centrifuging before removing the aliquots deserves emphasis. If the equilibrium solutions were not centrifuged, radioassays were considerably higher. Counting samples were prepared by evaporating the aliquots on copper discs. The centrifuge was mounted in an air thermostat controlled to within ±0.2° of the water-bath in which the solutions were shaken. If the samples were centrifuged at a temperature much below the thermostat, precipitation occurred during the centrifuging. Solubilities were determined at 15.0, 25.0 and 35.0° to permit the estimation of entropies for reactions. Solubilities lower than those at 15° could not be measured conveniently with the available specific activity. The upper limit was fixed by the requirements for the thermostated centrifuging and assaying.

Results and Discussion

The experimental data have been collected in Table I. Chloride ion activities have been calculated from concentrations by using an activity coefficient γ_1, for a singly charged ion. Values of γ_1 are tabulated in reference (2b) as a function of the ionic strength. Activity coefficients of neutral species, γ_0, in this work have been taken equal to unity because of the low concentrations and ionic strengths involved. When the log $M_{\text{Ag-tot}}$ was plotted as a function of the log a_{Cl^-}, the points for each temperature clustered around separate smooth curves. It should be noted that because of variations in activity coefficients, the points should not lie exactly on a smooth curve. An upper limit of about 0.1 *M* was taken for the chloride concentrations since activity coefficients cannot be reliably estimated for higher concentrations. The maximum slope of the smooth curves was less than 1; accordingly there was no indication for the formation of a complex containing more than two chlorides in the concentration region studied. The system could therefore be described by the three independent equilibria.

$$Ag^+ + Cl^- \rightleftarrows AgCl(aq) \qquad (I)$$

$$Ag^+ + 2Cl^- \rightleftarrows AgCl_2^- \qquad (II)$$

$$AgCl(s) \rightleftarrows Ag^+ + Cl^- \qquad (III)$$

TABLE I

DATA FROM SOLUBILITY EXPERIMENTS WITH AgCl

M_{Cl^-} moles/l.	*p*H	$\mu^{1/2}$	$-\log a_{\text{Cl}^-}$	$-\log M_{\text{Ag-tot}}$ moles/l. Obsd.	Calcd.
		For 15°			
5.48×10^{-5}	1.65	0.161	4.33	5.75	5.73
1.11×10^{-4}	2.15	.094	4.00	6.05	6.03
2.01×10^{-4}	1.59	.174	3.76	6.24	6.19
3.74×10^{-4}	1.72	.149	3.49	6.41	6.38
5.50×10^{-4}	2.14	.092	3.30	6.57	6.49
9.65×10^{-4}	1.90	.123	3.07	6.56	6.57
1.10×10^{-3}	2.15	.094	3.00	6.56	6.59
1.26×10^{-3}	1.92	.122	2.95	6.61	6.60
1.59×10^{-3}	2.22	.091	2.84	6.61	6.62
2.75×10^{-3}	2.25	.094	2.60	6.62	6.63
5.50×10^{-3}	2.22	.111	2.31	6.59	6.58
1.10×10^{-2}	2.10	.141	2.02	6.55	6.47
2.75×10^{-2}	5.80	.165	1.63	6.19	6.23
5.50×10^{-2}	2.28	.248	1.35	6.04	6.00
1.10×10^{-1}	2.15	.345	1.07	5.69	5.74
		For 25°			
5.38×10^{-5}	1.45	0.206	4.35	5.27	5.29
5.92×10^{-5}	5.01	.008	4.23	5.48	5.46
1.12×10^{-4}	5.25	.011	3.96	5.69	5.70
2.08×10^{-4}	1.36	.167	3.76	5.78	5.81
3.44×10^{-4}	1.78	.138	3.53	5.99	5.98
5.51×10^{-4}	6.25	.024	3.27	6.16	6.16
9.66×10^{-4}	1.81	.136	3.07	6.16	6.20
1.10×10^{-3}	5.48	.033	2.98	6.28	6.24
1.27×10^{-3}	1.88	.127	2.95	6.22	6.24
1.59×10^{-3}	2.02	.111	2.85	6.25	6.26
2.75×10^{-3}	6.28	.052	2.58	6.31	6.29
5.50×10^{-3}	5.32	.074	2.29	6.24	6.24
1.10×10^{-2}	6.04	.105	2.01	6.18	6.15
2.75×10^{-2}	5.96	.166	1.63	5.96	5.91
5.50×10^{-2}	5.58	.235	1.34	5.71	5.68
1.10×10^{-1}	6.51	.332	1.07	5.42	5.42
		For 35°			
6.42×10^{-5}	1.70	0.153	4.25	5.01	5.03
1.15×10^{-4}	2.12	.092	3.98	5.34	5.30
2.03×10^{-4}	1.67	.158	3.76	5.48	5.46
3.45×10^{-4}	4.10	.021	3.47	5.67	5.70
5.52×10^{-4}	2.30	.077	3.29	5.80	5.78
9.66×10^{-4}	2.12	.097	3.06	5.86	5.89
1.10×10^{-3}	2.08	.081	3.00	5.87	5.92
1.27×10^{-3}	2.00	.112	2.94	5.89	5.93
1.59×10^{-3}	2.30	.085	2.84	6.04	5.96
2.75×10^{-3}	2.15	.103	2.61	5.95	5.98
5.50×10^{-3}	2.28	.107	2.31	5.96	5.95
1.10×10^{-2}	2.30	.129	2.01	5.90	5.86
5.50×10^{-2}	2.45	.243	1.35	5.49	5.41
1.10×10^{-1}	2.32	.341	1.07	5.19	5.15

The three equilibrium constants were defined in this manner.

$$K_1 = \gamma_0 M_{\text{AgCl(aq)}} / \gamma_1 M_{\text{Ag}^+} a_{\text{Cl}^-} \qquad (1)$$

$$K_2 = M_{\text{AgCl}_2^-} / M_{\text{Ag}^+} a_{\text{Cl}^-}^2 \qquad (2)$$

$$K_{\text{sp}} = \gamma_1 M_{\text{Ag}^+} a_{\text{Cl}^-} \qquad (3)$$

The total silver concentration in the equilibrium mixture, which is the quantity measured by the radioassays, is then given by the expression

$$M_{\text{Ag-tot}} = M_{\text{Ag}^+} + M_{\text{AgCl(aq)}} + M_{\text{AgCl}_2^-} \qquad (4)$$

When the quantities of equation 4 are expressed in terms of chloride activity, the expression becomes

$$M_{\text{Ag-tot}} = \frac{K_{\text{sp}} a_{\text{Cl}^-}^{-1}}{\gamma_1} + \frac{K_1 K_{\text{sp}}}{\gamma_0} + \frac{K_2 K_{\text{sp}} a_{\text{Cl}^-}}{\gamma_1} \qquad (5)$$

This equation is of the form

$$M_{\text{Ag-tot}} = \frac{A a_{\text{Cl}^-}^{-1}}{\gamma_1} + \frac{B}{\gamma_0} + \frac{C a_{\text{Cl}^-}}{\gamma_1} \qquad (6)$$

The *A* coefficients, which are the solubility products of silver chloride, were taken from the potentiometric values of Owen.[4] The *B* and *C* coefficients were computed to fit the experimental data. It was found that variations of about 20% in one constant with adjustments of the other one gave dis-

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[4] B. B. Owen, THIS JOURNAL, 60, 2229 (1938).

tinctly poorer fits to the experimental data. The coefficients were adjusted somewhat to give a smoothed variation with temperature. The equilibrium constants corresponding to the coefficients selected are included in Table II. The solubilities calculated for the various equilibrium solutions are included in Table I for a comparison with the experimental values. As a test for the fit of equation 5 with the equilibrium constants of Table II to the experimental data, the quantity, $\sqrt{\Sigma\delta/^{2}N}$, was computed in which δi was ($\log M_{\text{Ag total-obsd.}} - \log M_{\text{Ag-total-calcd.}}$) and the summation was over the N determinations in each set. The values obtained were 0.040 for 15°, 0.025 for 25° and 0.044 for 35°.

Table II

Equilibrium Constants Used for Describing Total Silver Concentrations

Temp., °C.	K_{sp}	$K_1 \times 10^{-3}$	$K_2 \times 10^{-5}$
15	7.02×10^{-11}	2.29	2.16
25	1.77×10^{-10}	2.04	1.76
35	4.15×10^{-10}	1.69	1.39

The necessity for including the B coefficient in equation 6 was evident from the broad minima in the curves which approximated the data. This term represents the contribution of undissociated AgCl(aq) species to the solubility. It is of interest to note that the ionization constant of AgCl(aq) at 25° is: $1/K_1 = 4.9 \times 10^{-4}$. Accordingly, silver chloride should be considered a rather weak electrolyte.

The solubility data of Forbes and Cole[3] extend down to chloride concentrations of 4×10^{-3}. Their chloride concentrations were converted to activities by values of γ_1 consistent with the ionic strengths corresponding to their electrolyte concentrations. The solubilities which they reported were then approximately 35% above the values computed by equation 6. It is to be noted that their method involved measuring the silver concentration at which an opalescence was detected within the interval of one hour after mixing. It is believed that their higher values may result from the fact that they measured concentrations before equilibrium with a crystalline solid phase was established since higher concentrations may exist in contact with finely divided, freshly formed precipitates. Neuman,[5] who measured the solubility of silver chloride in various electrolytes by measuring concentrations at which a Tyndall beam appeared, reported that a 72-hour period was required to ensure no change. His solubilities agreed with potentiometric values to within a few per cent. In the present work solubilities at low chloride activities approached the solubility product values in a satisfying manner.

Thermodynamic quantities for reactions I and II, calculated from the equilibrium constants and their variations with temperature, are included in Table III. Ionic entropies of 17.5 e.u. for Ag^+ and 13.5 e.u. for Cl^- given by Latimer, Pitzer and Smith[6] were employed. Certainly, the accuracy of the entropy changes is not high. However the results indicate that the addition of each chloride in the formation of a complex is accompanied by a small entropy change (an increase of approximately 5 e.u. in each case). It is interesting to compare these with King's[7] results for the addition of chlorides in forming complexes with cadmium. He found a small increase (8.5 e.u.) for the first chloride, a small decrease (−2.5 e.u.) for the second chloride but a large increase (+20.2 e.u.) for the third chloride. It will be necessary to have considerable experimental data on the entropies of complex formation before the features which determine these quantities can be adequately described.

Table III

Values of Standard Heat Content, Free Energy and Entropy Changes for the Reactions (25°)

$$Ag^+ + nCl^- \rightleftarrows AgCl_n^{1-n}$$

Reaction to form	$\Delta H°$, kcal.	$\Delta F°$ kcal.	$\Delta S°$ e.u.	$S°$ (complex), e.u.
AgCl(aq)	−2.7	−4.5	+ 6	37
$AgCl_2^-$	−3.9	−7.2	+11	56

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[5] E. W. Neuman, This Journal, **54**, 2195 (1932).

[6] W. M. Latimer, K. S. Pitzer and W. V. Smith, *ibid.*, **60**, 1829 (1938).

[7] E. L. King, *ibid.*, **71**, 319 (1949).