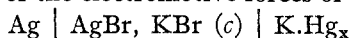


chloride, bromide and iodide ions. These results indicate further that the differences observed in the activity of the various uni-univalent halides, when at the same concentration, are due primarily to differences in the activity of the cations.

Summary.

1. Measurements of the electromotive forces of the cells



have been made.

2. The free-energy decrease and the decrease in heat content attending the reaction in these cells have been calculated.

3. The free energy decrease attending the transfer of one mole of potassium bromide from various concentrations (c) to $0.10 M$ have been computed.

4. The electromotive forces of concentration cells with ion transference and without ion transference have been measured. From these values the transference numbers of the potassium ion have been calculated.

5. The free-energy decrease and the heat-content decrease accompanying the transfer of one mole of potassium bromide from concentration c_1 to concentration c_2 have been computed.

6. The activity coefficients of the bromide ion have been calculated and a comparison made of the activity coefficients of the chloride and bromide ions. For all concentrations up to $0.5 M$ the activity coefficients of these two ions are practically equal.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD COLLEGE AND OF SIMMONS COLLEGE.]

THE SOLUBILITY OF SILVER CHLORIDE IN DILUTE CHLORIDE SOLUTIONS AND THE EXISTENCE OF COMPLEX ARGENTICHLORIDE IONS. II.¹

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In a previous paper by one of us,² where earlier work on this subject was discussed, the solubility of silver chloride in concentrated chloride solutions was proved proportional to integral powers of chloride concentration. From these results was inferred the existence of the complex ion AgCl_4^{\equiv} in the higher concentrations, and of AgCl_3^{\equiv} in the range from $1.5 N$ down to $0.5 N$. Below that point, however, the constant indicating the latter ion increased, which suggested that the ion AgCl_2^- might predominate at the lowest concentrations.

¹ This work was performed in 1915, at Simmons College.

² See Forbes, *THIS JOURNAL*, **33**, 1937 (1911).

The present paper records an effort to investigate solutions less than normal in chloride, which necessitated the measurement of solubility to 0.05 mg. per liter.

Sodium and potassium chlorides were precipitated by hydrogen chloride, washed, dried and ignited. Other salts were recrystallized from redistilled water, and made up into concentrated stock solutions. Silver nitrate solution, 0.001 *N*, was similarly prepared. Portions of the stock solutions were weighed from weight burets and analyzed with the customary precautions, including careful standardization of weights. The greatest variation between duplicate analyses was 6 parts in 10,000.

An 800cc. deep-form beaker was weighed clean and dry with a glass stirrer. The desired amount of solid salt or of stock solution was weighed out, and the volume made up to about 500 cc. with redistilled water carefully protected from dust. The beaker was brought to 25.0° in a thermostat electrically regulated to 0.05°. It was then placed in a blackened wooden box with a comparison beaker containing a similar solution. On the other side of the glass partition was placed a 300-watt tungsten lamp. Black rings at the tops and bottoms of the beakers excluded annoying reflections. If both beakers were equally free from opalescence, a quantity of 0.001 *N* silver nitrate known from preliminary experiments to be just insufficient to cause opalescence was run into the first beaker with vigorous stirring. After an hour at 25°, which had been proved enough to develop opalescence if it was to appear at all, the beaker was carefully wiped, and once more examined in the modified nephelometer, to prove the continued absence of precipitate. Two drops of the silver solution, or 5 in the most concentrated solutions, were added, with vigorous stirring, and the beaker returned to the thermostat for another hour, after which it was again examined and so on. It appeared improbable that supersaturation would greatly exceed the last addition of silver nitrate, about 6×10^{-8} mole in 500 cc. in this case.³ When opalescence appeared, the total weight of the solution was at once determined, also its density by pycnometer. The concentrations in the solution at the end-point could then be calculated without uncertainty due to evaporation or change in volume on mixing. The results appear in Tables II to IV.

The total silver present at the end-point may be classified as follows: (a) silver ion, (b) dissolved molecules of silver chloride, supersaturated or unsaturated, (c) precipitated silver chloride, and colloid in dispersion not too high to be seen under the given light conditions, (d) silver chloride in complex ions and molecules, and possibly adsorption complexes of colloidal silver chloride too highly dispersed to be visible under the given light conditions.

Assuming the solubility product to be 2×10^{-10} , the $(\text{Ag}^+) = 2 \times 10^{-10} / (\text{Cl}^-)$. As this correction is in all the cases less than 3×10^{-8} mole in 500 cc. it will be neglected for the moment.

³ Compare Ref. 2, p. 1939.

The working hypothesis was now tried that the silver chloride in the conditions (b) and (c), under the constant experimental conditions, made up a constant total which may be expressed as b . Let us also postulate

TABLE I.
EVALUATION OF b FOR SODIUM CHLORIDE.

Let $b = \text{AgCl}$ as Dissolved Molecules + Colloidal + Precipitated.

$$k_1 = \frac{\text{total silver}_1 - b}{\text{total chloride}_1} = \frac{\text{total silver}_2 - b}{\text{total chloride}_2}$$

Total chloride.	Total silver.	b .	Total chloride.	Total silver.	b .
3.86	0.00072	0.00058	17.58	0.00131	0.00077
9.24	0.00091		36.54	0.00189	
17.58	0.00131	0.00047	88.44	0.00361	0.00068

Average = 0.00063

that (complex silver) = (total silver - b). If it be further assumed that the complex radical in dilute solutions is AgCl_2 , then $(\text{AgCl}_2) = k_1$ (total chloride). Combining, (total silver - b) = k_1 (total chloride). The two unknowns, b and k_1 may now be evaluated by solving at any two concentrations, but pairs of concentrations below 0.1 N , where b is not small in comparison with total silver, and where the complex is sharply defined, promise the best results. Table I shows 4 values of b thus determined for sodium chloride with an average of 0.00063, while 5 similar pairs with hydrochloric acid yielded 0.00061. The closeness of the agreement, though in the main accidental, does yet in some measure justify the assumption made.

The total silver present in complex form, and the values of k_1 are given in Tables II to IV. The value of k_1 varies without definite trend up to 0.1 N , after which it tends to increase rapidly, while k_2 , calculated on the assumption that the complex radical is AgCl_3 , approaches constancy as shown in the previous paper. Table IV, in which total chloride is constant, shows substantially the same effects of the positive radical

TABLE II.
SILVER CHLORIDE IN SODIUM CHLORIDE SOLUTIONS.
Concentrations in Milli-equivalents per liter.
 $b = 0.00063$.

Total NaCl.	Total silver.	Total complex.	$k_1 \times 10^4$.	$k_2 \times 10^7$.
3.86	0.00072	0.00009	0.23
9.24	0.00091	0.00028	0.30
17.58	0.00131	0.00068	0.39
36.54	0.00189	0.00126	0.35
88.44	0.00361	0.00298	0.34	3.84
355.6	0.0174	0.0168	0.47	1.32
511.2	0.0280	0.0274	0.54	1.06
974.7	0.0806	0.0801	0.82	0.84

on k_1 which were noted at higher concentrations. Where b was not evaluated, it was taken as the mean of 0.00063 and 0.00061. The value of k_1 for hydrochloric acid, which seems to be exceptional, is much higher than its neighbors in Table III.

TABLE III.
SILVER CHLORIDE IN HYDROCHLORIC ACID SOLUTIONS.
Concentrations in Milli-equivalents per Liter.
 $b=0.00061$.

Total HCl.	Total silver.	Total complex.	$k_1 \times 10^4$.	$k_2 \times 10^7$.
4.78	0.00075	0.00014	0.29
9.38	0.00084	0.00023	0.25
17.8	0.00125	0.00064	0.36
34.1	0.00219	0.00158	0.46
74.1	0.00361	0.00300	0.41
91.4	0.00426	0.00365	0.40	4.38
316.7	0.01403	0.01342	0.42	1.32
681.8	0.0448	0.0442	0.64	0.94
779.7	0.0559	0.0553	0.71	0.91
925.8	0.0719	0.0713	0.77	0.83

TABLE IV.
VALUES OF k_1 IN 0.35 N CHLORIDE SOLUTIONS.
Concentrations in Milli-equivalents per Liter.

Chloride taken.	Total chloride.	Total silver.	b .	Total complex.	$k_1 \times 10^4$.
HCl	34.1	0.00219	0.00061	0.00158	0.44
NaCl	36.5	0.00189	0.00063	0.00126	0.35
NH ₄ Cl	37.4	0.00162	0.00062	0.00100	0.27
KCl	36.7	0.00172	0.00062	0.00110	0.30
RbCl	37.7	0.00181	0.00062	0.00119	0.32
CaCl ₂ /2	38.6	0.00175	0.00062	0.00113	0.29
SrCl ₂ /2	36.9	0.00172	0.00062	0.00110	0.30
BaCl ₂ /2	37.5	0.00157	0.00062	0.00095	0.25

The effects of sodium nitrate, nitric acid, and alum, are shown in Table V. The metathetical action of sodium nitrate is always obvious,⁴ though

TABLE V.
OTHER ELECTROLYTES ADDED TO SODIUM CHLORIDE.
Concentrations in Milli-equivalents per Liter.

Total NaCl.	Added electrolyte.	Conc. added.	Total silver.	Difference fr. pure NaCl.
4.26	0.00077
4.37	NaNO ₃	45	0.00102	+0.00025
4.37	HNO ₃	200	0.00099	+0.00022
36.54	0.00189
36.53	NaNO ₃	360	0.00220	+0.00031
35.41	HNO ₃	200	0.00160	-0.00029
37.83	Alum	6	0.00189	±0.00000

⁴ Richards and Wells, *Carnegie Inst. Pub.*, 28, 29 (1905).

one of the results with nitric acid, doubtless erroneously, indicates a decrease in solubility. A trace of alum is without effect, which suggests that colloid formation is relatively unimportant under the given conditions.

The "activity" conception of G. N. Lewis and others was duly considered before presenting these results. In the previous paper it was shown that complex formation in hydrochloric acid at higher concentrations, at least, is always less than in sodium chloride. The activity of hydrochloric acid, however, always exceeds that of sodium chloride, and at 5 *N* it is 5 times as great.⁵ The quantitative application of the activity principle must therefore be postponed. In the present work, also, it was found that *b* and *k* were more constant if total chloride concentrations were used without correction for either ionization or activity coefficient. Possibly chloride molecules, as well as chloride ions, operate to form complexes. At first sight, this seems inconsistent with the observation in the previous paper that the feebly ionized zinc chloride shows but little tendency to form the argentichloride complex. But here self-complex formation, as $\text{ZnCl}_2 + 2\text{Cl}^- = \text{ZnCl}_4^{2-}$ is no doubt considerable.

In very dilute solutions, the total concentration of silver in "true solution" exclusive of the constant *b* should equal the sum of silver ion and of argentichloride ion per liter, *i. e.*, $2 + 10^{-10}/(\text{MCl}) + k_1(\text{MCl})$. By "true solution" is meant one optically clear under the light conditions described above, and one doubtless filterable without loss through a filter paper or Gooch crucible. Differentiating total silver with respect to chloride concentration, we find that the condition under which the derivative becomes zero is $(\text{MCl})^2 = 2 \times 10^{-10}/k_1$. Using 0.34×10^{-4} as the average value of k_1 the minimum total concentration of silver in true solution should be found at 0.0025 *N*, instead of at 0.01 *N*, as predicted in the previous paper under the assumption that the complex radical AgCl_2 persisted in the most dilute solutions. At 0.0025 *N*, $2 \times 10^{-10}/(\text{MCl}) = 8 \times 10^{-8}$ and $k(\text{MCl}) = 8 \times 10^{-8}$, by a curious coincidence. The total silver concentration exclusive of the constant *b* is therefore 1.6×10^{-8} mole, or 0.000025 gram per liter. According to the present work, no chloride solution can contain less than this amount of silver chloride per liter in true solution, if just a bare trace of freshly precipitated silver chloride is present.

At first sight, the results of this paper might seem in preposterous disagreement with those of Richards and Wells, who found a solubility of 0.000003 g. per liter⁶ in a solution containing perhaps an excess of 0.1 equivalent of chloride per liter. It should be emphasized, however, that these determinations were made in filtrates from large precipitates of silver chloride, whose enormous surfaces may have occluded or adsorbed the com-

⁵ Lewis and Randall, *THIS JOURNAL*, **43**, 1117, 1123 (1921).

⁶ Richards and Wells, *Ref. 4*, p. 30.

plex most obstinately. Indeed, these authors suggest that even glass might adsorb sufficient silver chloride to account for losses observed on standing.⁷ Another possibility is that chloride solutions, in the absence of much adsorbing solid, peptize silver chloride in a strictly reproducible fashion.⁸ If so, the degree of dispersion must be very high. The possibility that more than one form of silver chloride with different solubilities may exist, is not excluded. The behavior of silver chloride is so variable under changing conditions that even the above noted difference is not disconcerting, though it invites further investigation.

Summary.

To various chloride solutions less than 0.1 *N* in concentration, 0.001 *N* silver nitrate solution was added to incipient precipitation, at 25°. The total silver was invariably given by the sum: $2 \times 10^{-10}/(\text{MCl}) + 3.4 \times 10^{-5}(\text{MCl}) + b$, where 2×10^{-10} is the solubility product, 3.4×10^{-5} a constant possibly connected with a complex of the type AgCl_2 , and *b* apparently is the constant sum of silver chloride in precipitate, in dispersion, and in dissolved molecules. The great difference between this observed total and the minute silver content of filtrates from large precipitates of silver chloride is discussed.

Silver chloride should be most insoluble, at 25°, in 0.0025 *N* chloride solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY.]

THE USE OF THE WATER INTERFEROMETER AS A PRESSURE GAGE.¹

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Nitrogen-filled glass manometers have been used in this laboratory for many years for the measurement of osmotic pressure, although there are certain objections to their use for this purpose; and since it was desired to measure pressures greater than they could withstand (about 100 atmospheres) it was necessary to devise a suitable manometer for this purpose. Frazer and Myrick² by use of a resistance pressure gage were able to measure osmotic pressure of concentrated sucrose solutions with approximately the same sensitivity at all pressures, but here also,

⁷ Richard and Wells, Ref. 4, p. 29.

⁸ See Homochemical Compounds, V. Veimarn, *Kolloid Z.*, **28**, 97 (1921).

¹ This work was assisted by grants from the Carnegie Institution of Washington, and was carried out at the suggestion of J. C. W. Frazer.

² Frazer and Myrick, *THIS JOURNAL*, **38**, 1907 (1916).