[Contribution from the Department of Chemistry, University of Pittsburgh]

Activity Coefficients in Concentrated Aqueous KCl–KBr Solutions at 25°[1,2]

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Activity coefficients of KCl and KBr in the KCl–KBr–H_2O system have been measured using the isopiestic method at total molalities extending from 2 *m* to saturation. It is found that for each salt at constant total molality the logarithm of the activity coefficient of the salt varies linearly with the molality of the salt. It is also found that for a series of ternary solutions at constant water activity there is a linear variation of the total molality with x_1 (or x_2) where x_1 is the mole fraction of the salt which is KCl and $x_2 = 1 - x_1$. This latter finding greatly simplifies the evaluation from isopiestic measurements of activity coefficients in this ternary system.

The free energies of formation of KCl–KBr solid solutions from the component salts can be evaluated from the solubilities of (a) the two salts and (b) the solid solutions in water if the activity coefficients of the two solutes at saturation (in the two binary and the various ternary systems) are known.[3] The determination of activity coefficients, the results of which are presented in this paper, were begun with this objective in mind. The activity coefficients are, however, of some interest in themselves because of their relevance to the general problem of the thermodynamic behavior of mixed electrolytes in water at high concentrations. For this reason they are being presented here apart from their specific application to the study of the aforementioned solid solutions.

Experimental

Method Employed.—Starting with the Gibbs–Duhem relationship, McKay and Perring developed[4] an expression which proves to be particularly convenient for aqueous solutions containing two solutes. Let us use the subscripts 1, 2 and w to refer to solutes 1 and 2 and the solvent, respectively, and the subscript R to denote a reference solute of known activity coefficient in a binary aqueous solution having the same water vapor pressure as the ternary system. This equality of vapor pressures is the experimental situation which occurs in an isopiestic experiment involving a reference binary solution and the ternary system under investigation. The McKay–Perring equation for a pair of 1-1 electrolytes in water becomes

$$0.036 \ln \frac{m\gamma_1}{M_R\Gamma_R} = \int_0^{\ln a_w} \left[-\frac{1}{m^2}\frac{\partial m}{\partial \ln x_2} - \frac{1}{m} + \frac{1}{M_R} \right]_{a_w} (d \ln a_w)_{x_1} \quad (1)$$

where

m = total molality = $m_1 + m_2$
γ_1 = mean activity coefficient of solute 1 in the ternary system
M_R = molality of a binary ref. soln. of such concn. that its water activity (a_w) equals the water activity of the ternary soln.
Γ_R = activity coefficient of ref. soln.
x_1 = m_1/m and $x_2 = m_2/m$ by definition

The quantity in brackets behind the integral sign requires a knowledge of the variation of total molality (m) with x_2 at constant water activity. The integral therefore is very conveniently evaluated by measurements using the isopiestic technique. McKay and Perring, of course, developed their equation with this in mind.

In practice one establishes isopiestic equilibrium between the reference solution and several ternary systems. The water activity is constant so that one plots *m versus* ln x_2 to evaluate the quantity in brackets. From the known activity of water in the reference solution one can evaluate the integral for a certain value of x_1 and this together with Γ_R, which is known, enables one to obtain γ_1. γ_2 is obtained in a similar way by replacing γ_1 and m_1 by γ_2 and m_2, respectively, in the above equation. Very considerable simplification of the McKay–Perring equation was posssible for most of the concentrations studied, as will be referred to below.

Apparatus and Experimental Method.—The apparatus used was of conventional design, with two vacuum desiccators in a thermostat attached to a rocking mechanism. Each desiccator contained a copper block on which four silver cups were placed, one for reference solution and the other three for mixtures of varying composition.

As seen from equation 1, the basic measurement involved the variation of total molality with mole fraction of one component at constant water activity. Matters were arranged so that concentrations of the two reference solutions were as nearly the same as possible. Then after equilibrium was attained, the desiccator with the more dilute reference solution was gently evacuated until its concentration slightly exceeded the other reference solution. That desiccator was then returned to the thermostat for equilibrium to be re-established. From these data one could obtain by simple interpolation six molalities (seven when one of the salts in the ternary system was used as the reference solution) at constant water activity. For total molalities up to 4.75 *m* KCl was used as reference; from 4.75 to 5.65 *m* both KBr and NaCl were used; above 5.65 *m* NaCl served as reference.

The salts used were reagent grade, further purified by appropriate means and analyzed gravimetrically in triplicate for halide. All the analyses gave results within 0.06% of theoretical halide percentage. Between weighings the salts were kept in an evacuated desiccator over $CaCl_2$ and were heated in a muffle furnace at 450° for 3 to 5 hours every 2 or 3 weeks.

The times necessary for equilibrium were established in preliminary experiments by noting the time required for equilibration between four KCl solutions which initially differed by as much as 0.5 in molality. The times required were found to be 48, 72 and 84 hours for molalities greater than 4, 3 to 4 and 2 to 3, respectively. These times, which were used in the later experiments, are maximal since in the actual experiments concentrations were initially adjusted to within 0.1 in molality of the final concentration.

Experimental Results and Treatment of Data

Upon examining the data resulting from a large number of determinations in the molality range from 2 to 5.9, it was found that the variation of total molality with m_1 (molality of KCl) or m_2 (molality of KBr) was in all cases linear within the experimental error of 0.1%. In the range 2 to 4.8 *m*, where either KCl or KBr could be used as reference, the bracketed factor appearing behind the integral sign of equation 1 could therefore be simplified as

$$\left[-\frac{1}{m^2}\frac{\partial m}{\partial \ln x_2} - \frac{1}{m} + \frac{1}{M_1} \right]_{a_w} = \frac{S^2 x_2^2}{m^2 M_1} \quad (2)$$

$$\left[-\frac{1}{m^2}\frac{\partial m}{\partial \ln x_1} - \frac{1}{m} + \frac{1}{M_2} \right]_{a_w} = \frac{S^2 x_1^2}{m^2 M_2} \quad (3)$$

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[1] From a thesis submitted by W. H. McCoy to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[2] This work was supported by a grant from the Research Corporation.

[3] To be published in This Journal.

[4] H. A. C. McKay and J. K. Perring, *Trans. Faraday Soc.*, **49**, 163 (1953).

where

$$S = -\left(\frac{\partial m}{\partial x_2}\right)_{a_w} = \left(\frac{\partial m}{\partial x_1}\right)_{a_w} = \text{constant} \quad (4)$$

Furthermore, upon evaluating the integrals for concentrations extending to 4.8 m graphically, it is found that their magnitudes never exceed 2×10^{-5}. They can therefore be set equal to zero with negligible error introduced into γ_1 and γ_2 from which it follows that

$$\gamma_1 = \frac{M_1\Gamma_1}{m} \text{ and } \gamma_2 = \frac{M_2\Gamma_2}{m} \quad (5)$$

The behavior of the integral in equation 1 near the lower limit of integration merits some comment. Experimental data extended only to $\ln a_w = -0.071$, corresponding to a total molality of roughly 2. Between total molalities of 2 and 0.2 ($\ln a_w$ increasing from -0.071 to -0.007) one assumes that the relation given in (4) is a valid approximation. That this is so can be shown as follows. The characteristic feature of the isopiestic method in this case is that ϕm is a constant where ϕ is the osmotic coefficient. If Harned's rule holds (equations 6 and 7 in the next section) with $\alpha_{12} = -\alpha_{21}$ for the ternary systems at total molalities less than 0.2, ϕ varies linearly with x_1 at constant total molality. $m\phi$ is also linearly dependent on x_1 in this case since m is a constant. Consider, for example, KCl and KBr solutions at 0.2 m. For KCl $m\phi$ is 0.1826 and for KBr $m\phi$ is 0.1832. This means that for aqueous KBr to be in isopiestic equilibrium with 0.2 m KCl, its concentration must be roughly 0.3% less than 0.2 m. If one now considers an equimolal mixture between 0.1832 and 0.1826 and if ϕ varies linearly with x_1, the value is 0.1829. Hence, for it to be in equilibrium with 0.2 m KCl, its concentration must be less than 0.2 by roughly 0.15%. From such reasoning as this, it can be concluded that in the isopiestic measurements m in the ternary system is always between the values for the limiting cases when $x_1 = 0$ or 1 and, hence, $(\partial m/\partial x_1)_{a_w}$ is approximately equal to $m_{x_1 = 1} - m_{x_1 = 0} = S$. Thus, even if the linearity of m *vs.* x_1 does not hold below 0.2 m, equations 2 and 3 are still valid as approximations. One therefore computes S from the isopiestic molalities of aqueous KCl and KBr solutions determined by Robinson[5] and reproduced in Table I. Columns 1 and 2 give the molalities of KCl and KBr which coexist in equilibrium, and S in column 3 is $m_{x_1 = 1} - m_{x_1 = 0}$. S, of course approaches zero as the water activity approaches unity, and it can be shown that the numerator of the bracketed quantity is a stronger function of concentration than the denominator. Therefore, the integrand vanishes as $\ln a_w$ approaches zero, and the extrapolations can be made with confidence.

TABLE I

ISOPIESTIC MOLALITIES OF KCl AND KBr AT 25°[a]

m_{KBr}	m_{KCl}	S[b]	m_{KCl}	m_{KBr}	S[b]
0.2108	0.2104	0.0004	1.071	1.059	0.012
.3751	.3730	.0021	1.486	1.467	.019
.5570	.5535	.0035	1.517	1.496	.021
.5913	.5873	.0040	1.806	1.786	.020
.8442	.8362	.0080	1.863	1.835	.028

[a] Data by R. A. Robinson, reference 5. [b] For definition of S see equation 4 in text.

To obtain γ_1 above 4.8 m and γ_1 and γ_2 values above 5.65 m where aqueous NaCl was the reference solution, it was necessary to integrate equation 1 graphically. However, in this case the lower limit was not pure water but was instead a solution of arbitrarily selected concentration m' in the range between 2 and 4.8. The McKay–Perring equation in this case is

$$0.036\left(\ln\frac{m\gamma_1}{M_R\Gamma_R} - \ln\frac{m'\gamma'_1}{M'_R\Gamma'_R}\right) = \int_{\ln a'_w}^{\ln a_w}\left[-\frac{1}{m^2}\frac{m}{\ln x_2} - \frac{1}{m} + \frac{1}{M_R}\right]_{a_w} d\ln a_w \quad (1')$$

M'_R and Γ'_R refer, of course, to the NaCl which is in equilibrium with the ternary solution of concentration m'. γ'_1 was obtained from the earlier calculations when aqueous KCl was employed as the reference electrolyte.

Except for the water activities and activity coefficients of KBr solutions more concentrated than 5 M, all data for the reference salt solutions were taken from the compilation by Robinson and Stokes.[6] As they provide no data for KBr solutions above 5 M, it was necessary to determine activities of water and activity coefficients between this composition and saturation (5.736 M). This was done by isopiestic measurements with NaCl as the standard. The results are summarized in Table II.

TABLE II

ISOPIESTIC MOLALITIES OF AQUEOUS NaCl AND KBr AND ACTIVITY COEFFICIENTS OF KBr AT 25°

NaCl, M	KBr, M	a_w	Γ_2[a]
4.639	5.279	0.823	0.631
4.782	5.477	.817	.634
4.982	5.736 (satd.)	.808	.638

[a] Γ_2 = activity coefficient of KBr.

All isopiestic results for the ternary systems are summarized in Table III. In the first three columns are listed molalities of the three reference

TABLE III

SUMMARY OF ISOPIESTIC RESULTS FOR THE KCl–KBr–H_2O SYSTEM AT 25°

Ref. molalities KCl	KBr	NaCl	a_w	S[b]
2.090	(2.050)[a]		0.932	0.040
3.029	(2.973)		.903	.056
3.476	(3.418)		.888	.058
3.885	(3.818)		.873	.067
4.156	(4.092)		.865	.064
4.549	(4.482)		.852	.067
4.795	(4.723)	4.178	.843	.072
	5.073	4.476	.830	.070
	5.144		.828	.070
	5.231	4.606	.8245	.070
	5.437	4.778	.817	.070
	5.529		.8145	.070
	5.600	4.892	.812	.075
		4.987	.808	.071
		5.065	.804	.082

[a] Values in parentheses obtained by extrapolation (see text). [b] For definition of S see equation 4 in text.

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(5) R. A. Robinson, *Trans. Faraday Soc.*, **35**, 1217 (1939).

(6) R. A. Robinson and R. H. Stokes, *ibid.*, **45**, 612 (1949).

solutions. The KBr concentrations in parentheses were obtained by extrapolation of curves of *m vs.* x_1. These extrapolated values are in good agreement with the KBr molalities computed from the KCl–KBr isopiestic ratios measured in connection with this work which in turn are in excellent agreement with the KCl–KBr isopiestic ratios reported by Robinson.[5]

Numerical values for the measured activity coefficients in the ternary system are not given. They may be computed as needed from the equations given in the next section and the data given in Table IV. If one assumes the data for the reference solutions to be exact, the uncertainties in the γ's so computed are ±0.001.

Table IV

Data Relevant to the Additivity Rules

m	α_{12}	$-\alpha_{21}$	$-\log\gamma_{(0)1}$	$-\log\gamma_{(0)2}$
0.2	0.0060	0.0075	0.1427	0.1430
.4	.0048	.0065	.1746	.1746
.6	.0057	.0045	.1931	.1925
.8	.0044	.0053	.2055	.2055
1.0	.0043	.0043	.2147	.2140
1.5	.0034	.0049	.2292	.2292
2.0	.0036	.0038	.2347	.2347
2.5	.0033	.0035	.2366	.2358
3.0	.0028	.0027	.2366	.2336
3.5	.0023	.0021	.2343	.2299
4.0	.0019	.0021	.2314	.2248
4.5	.0018	.0016	.2262	.2175
5.0	.0015	.0014	.2196	(.2103)[a]
5.5	.0015	.0017	.2133	(.2056)

[a] Values in parentheses are extrapolated.

Discussion of Results

If one plots $\log\gamma_1$ in an aqueous solution containing two electrolytes as solutes against m_1, the contribution of 1 to the total molality, a straight line of zero slope is obtained if (1) the total molality m is constant and (2) m is sufficiently small so that the ionic strength principle is obeyed. At higher concentrations where (2) is no longer valid, one still observed[7] linearity but the slope is no longer zero. Following Harned's nomenclature,[8] one writes

$$\log\gamma_1 = \log\gamma_{(0)1} + \alpha_{12}m_1 \qquad (6)$$

and

$$\log\gamma_2 = \log_{(0)2} + \alpha_{21}m_2 \qquad (7)$$

Brönsted's theory of specific ionic interaction leads[9] to the result that $\alpha_{12} = -\alpha_{21}$. Guggenheim's treatment of mixed electrolytes leads[10] to the further restriction that $\log\gamma_{(0)1} = \log\gamma_{(0)2}$. The data reported in the paper may be examined in the light of Harned's rule (equations 6 and 7) and the more restricted versions due to Brönsted and Guggenheim.

For the KCl–KBr system it is found that the Brönsted theory is valid within the experimental error for total molalities from 2.0 to 5.5. If the reasonable assumption of the linearity of the slopes of *m vs.* x_2 down to 0.21 *m* is made, the Guggenheim simplification is applicable from 0.21 to 2.0 *m*.

Guggenheim's[10] treatment of the theory of specific ionic interaction leads to the relation $\log f_{2(0)}/f_{1(0)} = BC$, where the f's are rational activity coefficients in binary solutions of (2) and (1), c is the molar concentration and B is a constant. This equation is analogous to the empirical relationship proposed by Åkerlof and Thomas,[11] to wit

$$\log\frac{\gamma_{2(0)}}{\gamma_{1(0)}} = B_{21}m \qquad (8)$$

where $\gamma_{2(0)}$ and $\gamma_{1(0)}$ refer to the pure binary solutions of molality m, and B_{21} is independent of m. If it is assumed that $\log\gamma_{2(0)}/\gamma_{1(0)} = B_{21}m$ for the KCl–KBr system and that $\alpha_{12} = -\alpha_{21}$, it follows[12] that $B_{21} = 2|\alpha|$; hence, slopes of $\log\gamma$, ϕ *vs.* m, and ϕ for each salt may be calculated. Although in point of fact B_{21} turns out to be a weak function of m above 0.6 molal, there is rather good agreement between the calculated and measured values of α up to 2.5 *m*. Comparison is made in Table V.

Table V

Comparison of the Measured α Values with Those Calculated from the Åkerlof–Thomas Expression[a,b]

m	B_{21}	$\alpha_{\text{calc.}}$	$\alpha_{\text{meas.}}$
0.2	0.0121	0.0060	0.0067
.4	.0114	.0057	.0056
.6	.0101	.0051	.0051
.8	.0096	.0048	.0048
1.0	.0092	.0046	.0043
1.5	.0084	.0042	.0041
2.0	.0076	.0038	.0037
2.5	.0072	.0036	.0034
3.0	.0066	.0033	.0027
3.5	.0060	.0030	.0022
4.0	.0058	.0029	.0020
4.5	.0054	.0027	.0017

[a] For definitions of α and B see text. [b] $\alpha_{\text{meas.}}$ is taken to be the average of the magnitudes of α_{12} and α_{21}.

Returning now to the observed fact that m varies linearly with x_1 in the isopiestic work, it is of interest to know what the exact conditions are under which this will occur. One wishes to know what conditions the solution must meet beyond those specified by equations 6 and 7. Any solutions whose activity coefficients obey those equations has osmotic coefficients which vary[13] with x_1 at constant total molality as

$$\phi_{x1} = \phi_0 - 2.303\alpha_{21}mx_1 + \frac{2.303}{2}(\alpha_{12} + \alpha_{21})mx_1^2 \qquad (9)$$

ϕ_0 is the osmotic coefficient of pure component 2 at a molality m. Thus, if this quantity is called $(\phi_2^0)_m$

$$\phi_0 = (\phi_2^0)_m \qquad (10)$$

Denote by m_0 the isopiestic molality of pure 2, that is, the value when $x_1 = 0$. Then if $(\phi_2^0)_{m_0}$ is the corresponding osmotic coefficient

$$m_0(\phi_2^0)_{m_0} = m\phi_{x_1} \qquad (11)$$

or

$$m\phi_{x1} = m_0(\phi_2^0)_{m_0} = m(\phi_2^0)_m - 2.303\alpha_{21}m^2x_1 + \frac{2.303}{2}(\alpha_{12} + \alpha_{21})m^2x_1^2 \qquad (12)$$

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(7) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, Chapter 14.

(8) Ref. 7, p. 459.

(9) J. N. Brönsted, This Journal, **42**, 761 (1920); **44**, 877 (1922); **44**, 938 (1922); **45**, 2898 (1923).

(10) E. A. Guggenheim, *Phil. Mag.*, [7] **19**, 588 (1935).

(11) G. Åkerlof and H. C. Thomas, This Journal, **56**, 593 (1934).

(12) Reference 7, p. 463.

(13) Reference 7, p. 462.

Now rearranging, one obtains

$$Ax_1^2 + Bx_1 = \left[\frac{1}{m^2}\left\{\frac{m(\phi_2^0)_m - m_0(\phi_2^0)_{m_0}}{m - m_0}\right\}\right](m - m_0) \qquad (13)$$

where $A = -(2.303/2)(\alpha_{12} + \alpha_{21})$ and $B = +2.303\ \alpha_{21}$. If A, B and the quantity in brackets, which may be called C, are weak functions of the total molality m, then x_1 is linear with m. A is zero for the KCl–KBr system and in general is very small, varying but little with m. Hence, it is necessary that α_{12} and C be independent of m for equation 4 to hold. It is readily apparent from Table V and plots of the osmotic coefficients of KCl and KBr against the cube of molality that these conditions are met in the KCl–KBr case, not exactly but sufficiently well that one would not expect the x_1–m plots to be perceptibly non-linear.

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The Solubility of Silver Iodate in Iodate Solutions. Iodato Complexes of Silver*

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Solubilities of silver iodate at 25.0, 35.0 and 50.0° have been measured by means of a radioassay technique in aqueous solutions with various low concentrations of lithium iodate and with solutions having a constant ionic strength of 1.00 M. Solubility product constants obtained for these temperatures were $(3.0 \pm 0.15) \times 10^{-8}$, $(6.3 \pm 0.3) \times 10^{-8}$ and $(17.4 \pm 1.0) \times 10^{-8}$, respectively. In addition to the normal equilibrium solubility product relationship, two complexing equilibria were needed to describe the behavior at higher iodate concentrations: $Ag^+ + IO_3^- \leftrightarrows AgIO_3(aq.)$, for which $\Delta F^\circ_{35^\circ} = -1.13 \pm 0.18$ kcal./mole, $\Delta H^\circ_{35^\circ} = 5.1 \pm 4.5$ kcal./mole; $Ag^+ + 2IO_3^- \leftrightarrows Ag(IO_3)_2^-$, for which $\Delta F^\circ_{35^\circ} = -2.53 \pm 0.04$ kcal./mole, $\Delta H^\circ_{35^\circ} = -5.20 + 0.79$ kcal./mole.

Introduction

A radiosilver assay procedure has been utilized to determine the solubility of silver iodate in aqueous solutions of lithium iodate. The method has also been applied to solutions for which ionic strengths were adjusted at 1.00 M by means of lithium perchlorate. This work was undertaken when it was noted that significant deviation from the solubility product existed in moderately dilute solutions of lithium iodate. Possibilities for the existence of iodato-silver complexing phenomena were indicated.

Ricci and Amron[1] studied the silver iodate–lithium iodate–water system and concluded that the isotherm for this system was of the simplest type with no evidence of compound formation or solid solution, and qualitative tests for silver in the solutions containing silver iodate and the dissolved salt were negative. Shchigol,[2] employing a conventional iodometric procedure for analyses of equilibrium solution phases, reported the solubility of silver iodate at 20–22° in aqueous solutions for three concentrations of potassium iodate. He considered that silver was present in the equilibrium solution phases only in the form of Ag^+ and $Ag(IO_3)_2^-$ ions and reported an instability constant of 2.22×10^{-6} for the diiodatoargentate species. It was of interest to obtain a more quantitative description by use of an effective radioassay method.

Experimental

Materials.—All water used in this work was prepared by redistilling distilled water from alkali permanganate solutions. Its specific conductance was found to be 2.5×10^{-6} mho cm.$^{-1}$.

Lithium perchlorate was obtained in reagent grade from the G. Frederick Smith Chemical Company. Solutions of lithium perchlorate were filtered before being used in order to remove any insoluble matter which was present.

Lithium iodate was prepared by adding a stoichiometric amount of iodic acid to an aqueous solution of lithium carbonate. The salt was crystallized after carbon dioxide formed in the reaction had been driven off by heating. The product was filtered, recrystallized twice from water, refiltered, washed, dried at 120° for 24 hours and stored in a desiccator over anhydrous magnesium perchlorate. Analyses of the salt for total iodate content were consistent with the theoretical composition.

Platinum used in the plating procedure was 1 mil sheet stock supplied by the American Platinum Works.

Silver^{110m} was the tracer employed. It was obtained from the Oak Ridge National Laboratory in 1.4 ml. of 2 N nitric acid and was reported to have a radiochemical purity in excess of 98%. Stock solutions containing radioactive silver were prepared by adding aliquots of this solution to dilute nitric acid solutions containing definite amounts of inactive silver nitrate. These solutions were subsequently scavenged with iron hydroxide and evaporated to dryness with an excess of nitric acid. The radioactive silver was precipitated as the chloride from the dilute nitric acid, filtered from the solution and dissolved with concentrated ammonia. The silver was subsequently electroplated on a platinum gauze cathode according to a method proposed by Slomin.[3] Following this operation, the silver was dissolved from the electrode with 10 N nitric acid and the entire purification cycle was repeated. The remainder of the procedure involved a gravimetric determination of the silver on the electrode, dissolution in 10 N nitric acid, fuming with perchloric acid and dilution in a volumetric flask.

Tagged silver iodate was prepared by adding solutions of lithium iodate to aliquots of the stock solutions of silver tracer after these had been partially neutralized with lithium hydroxide. The wet masses of crystals which formed were washed repeatedly with many small portions of warm water, and finally they were washed, slurried and transferred to the equilibrium flasks with the aid of many small portions of the solution phase with which they were to be equilibrated.

Primary standards and other chemicals used for this work were all of reagent grade according to ACS specifications.

Apparatus.—Mixtures were equilibrated in thermostated water baths in which temperatures were constant to ±0.1°.

Pyrex erlenmeyer flasks were used to contain the mixtures. Some were of red variety glass and others were wrapped with a black plastic adhesive tape to exclude light. When in use,

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* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[1] J. E. Ricci and I. Amron, THIS JOURNAL, **73**, 3614 (1951).

[2] M. B. Shchigol, *Zhur. Obshchei Khim.*, **22**, 728 (1952).

[3] G. W. Slomin, "Rapid Quantitative Electrolytic Methods of Analysis," 7th ed., E. H. Sargent Co., Chicago, Ill., 1954.