junction potential of the cell might not be negligible[5b] and where the increased solubility of silver halides in excess halide would necessitate a knowledge of the association constants of AgX and X^-.

The specific Helmholtz free energies of formation ΔA of CdX^+ and CdX_2 (where X is bromide or iodide) were evaluated using the equations of the quasi-lattice model[9,10] (asymmetric approximation) with the coördination number $Z = 6$. Since the equations of the model were derived for ions of the same charge, they might not be expected to apply to a mixture of singly charged and multiply charged ions. It is seen from the values of ΔA in Table II that the variation with temperature although very small is somewhat larger than in the case of singly charged ions.[11] The decrease of ΔA with increasing temperature is in the same direction as was observed for the association of silver ions with sulfate ions in molten KNO_3.[12] The "specific entropy of association"[9] $\left(-\left(\frac{\partial \Delta A}{\partial T}\right)\right)$ may be characteristic of a change in the internal degrees of freedom of the ions involved in the association, although the effect in this case is almost within the experimental uncertainty. The relatively small variation of ΔA with temperature indicates that the quasi-lattice model may be useful for predicting the temperature coefficients of the association constants of singly charged ions with multiply charged ions as well as with other singly charged ions.

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[CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY,[3] OAK RIDGE, TENNESSEE, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MAINE, ORONO, MAINE]

Thermodynamic Association Constants of Silver Ions with Bromide or Iodide Ions in Molten Potassium Nitrate and their Comparison with the Quasi-lattice Theory

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Electromotive force measurements in dilute solutions of Ag^+ and Br^- in molten KNO_3 at 403, 438, 452, 474 and 500° and Ag^+ and I^- in molten KNO_3 at 402° were used to evaluate the association constants K_1, K_2 and K_{12} for the formation of AgX, AgX_2^- and Ag_2X^+, respectively, where X = Br or I. The comparison of the values of K_1 in the bromide containing system with the theoretical calculations based on the quasi-lattice model demonstrated that the temperature coefficients of the K_1 are correctly predicted by the theory for any reasonable choice of the coördination number using values of the "specific bond free energies" ΔA_1, which are independent of temperature. For $Z = 5$ average values of ΔA_1, ΔA_2 and ΔA_{12} are 7.14, 7.0 and 6.7 kcal./mole, respectively. The values of the "specific bond free energies" for the formation of the ion pairs Ag^+–Cl^-, Ag^+–Br^- and Ag^+–I^- in KNO_3 for $Z = 5$ are 5.8_8, 7.1_4 and 9.3_8 kcal./mole, respectively, and are consistent with the relative but not absolute values of the predictions of Flood, Førland and Grjotheim.

Introduction

Measurements of the activity coefficients of $AgNO_3$ in molten KNO_3 in dilute solutions of Ag^+ and Br^- ions at five temperatures ranging from 403 to 500° and of Ag^+ and I^- at 402° are described in this paper. In previous papers the comparison with calculations based on the quasi-lattice model[4–6] of similar measurements in dilute solutions of Ag^+ and Cl^- in pure KNO_3,[7,8] pure $NaNO$[9] and in equimolar $NaNO_3$–KNO_3[10] mixtures demonstrated that the temperature coefficient of the association constant K_1 for the formation of the ion pair Ag^+–Cl^- is correctly predicted by the expression derived from the theoretical calculations

$$K_1 = Z\left(\exp\left(-\Delta A_1/RT\right) - 1\right) \qquad (1)$$

where Z is a coördination number and ΔA_1 is the "specific bond free energy" and was constant.[11] ΔA_1 was about 1 kcal. more negative in the solvent KNO_3 than in $NaNO_3$ and the value of ΔA_1 in the equimolar $NaNO_3$–KNO_3 mixture appeared to be the average of the values of ΔA_1 in the pure nitrates.

The purpose of this paper is to demonstrate that equation 1 gives a correct prediction of the temperature coefficient of K_1 in the bromide containing system. We shall show further that the generalized calculations[6] based on the quasi-lattice model, within experimental error, lead to a correct prediction of the temperature coefficients for the as-

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[3] Operated for the United States Atomic Energy Commission by Union Carbide Corporation.

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[11] In systems in which the change of the entropy of the internal degrees of freedom of the ions involved in the association process is small $d\Delta A_i/dT \cong 0$ and $\Delta A_i \cong \Delta E_i$.

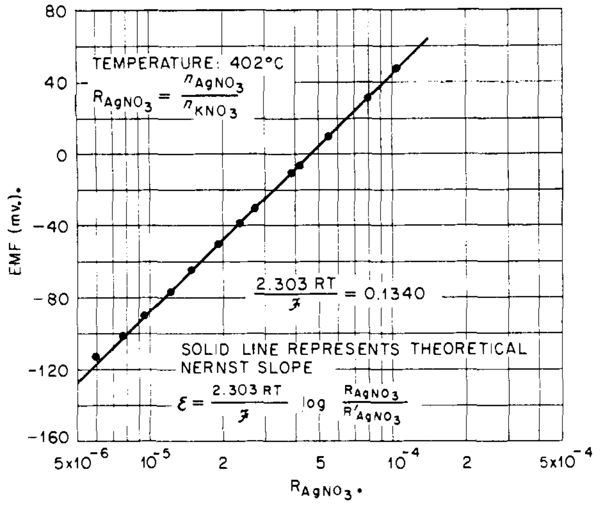

Fig. 1.—E.m.f. of the concentration cell

$$\begin{array}{c} Ag\,|\,AgNO_3(R_{AgNO_3})\,||\,AgNO_3(R_{Ag\text{-}NO_3})\,|\,Ag \\ \quad KNO_3 \qquad\qquad\qquad KNO_3 \end{array}$$

Plotted against the mole ratio of silver nitrate in the right hand half cell in the absence of bromide or iodide ions.

sociation constants K_2 and K_{12} for the formation respectively of $AgBr_2^-$ and Ag_2Br^+ from the ion pair Ag^+–Br^- if the "specific bond free energies" ΔA_i are assumed to be independent of temperature. Lastly we will illustrate the differences in the values of K_1 and the values of ΔA_1 for the association of Ag^+ with Cl^-, Br^- and I^- in molten KNO_3.

Experimental

Reagent grade KBr and KI from Baker and Adamson were heated in a dry atmosphere to remove water and used as solute. Otherwise, the materials, apparatus and procedure were essentially the same as previously described.[7,8,10]

Results

Electromotive force measurements were made of the concentration cell

$$Ag \left| \begin{array}{l} KNO_3 \\ AgNO_3 \end{array} \right| \begin{array}{l} KNO_3 \\ AgNO_3 \\ KX \end{array} \right| Ag$$

where X is Br^- or I^-.

As described previously the activity coefficients γ_{AgNO_3} of $AgNO_3$ may be calculated from the relation

$$\Delta E = \frac{2.303\ RT}{F} \log \gamma_{AgNO_3}$$

where ΔE is the change of e.m.f. upon the addition of KBr or KI to the right hand electrode compartment at a constant concentration of $AgNO_3$ and at concentrations of Ag^+ and Br^- or I^- ions too low to precipitate AgBr or AgI. In Table I are given values of ΔE obtained in this system at several concentrations of $AgNO_3$ and KBr at 403, 438, 452, 474 and 500°.

The reproducibility of the measurements was not as good as in the chloride containing systems. Many duplicate series of measurements were made to check the reliability and reproducibility. Four somewhat low sets of measurements were rejected out of the total of 31 sets measured. Only one set of measurements (438°) was rejected without making at least three sets of measurements at the given temperature and concentration of $AgNO_3$. The rejected set of measurements at 438° was rejected because it was inconsistent with data at other temperatures. Because of the low solubility of AgI, the measurements in the iodide containing systems were of necessity made at very low concentrations of Ag^+ and I^- or at concentrations of KI in sufficient excess to keep AgI in solution. Figure 1 is a plot of e.m.f. *vs.* log R_{AgNO_3}, where R_{AgNO_3} is the mole ratio of $AgNO_3$, at 402° as obtained in the concentration cell

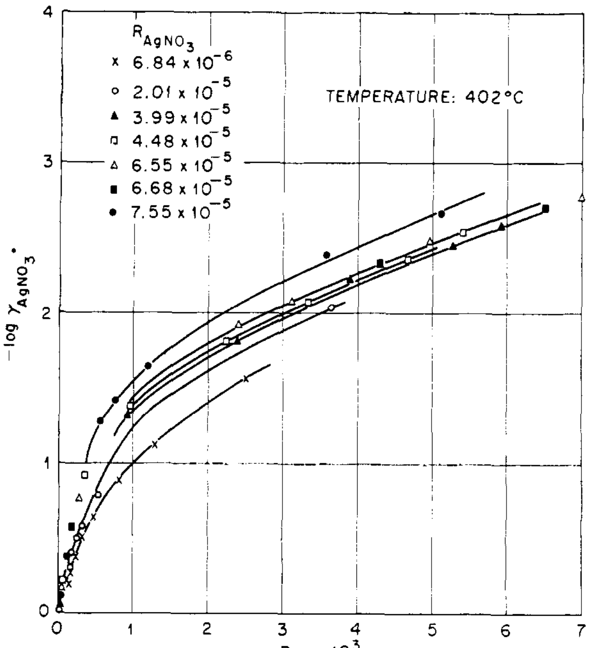

Fig. 2.—Negative logarithm of the activity coefficient of silver nitrate in molten potassium nitrate as a function of the mole ratio of potassium iodide at several fixed mole ratios of silver nitrate.

$$Ag \left| \begin{array}{l} AgNO_3\ (R_{AgNO_3}) \\ KNO_3 \end{array} \right|\ \left| \begin{array}{l} AgNO_3\ (R_{AgNO_3}) \\ KNO_3 \end{array} \right| Ag$$

for low concentrations of $AgNO_3$. The points fall on the line of the Nernst equation slope down to concentrations below 10^{-5}. This indicates that the electrode may be used to measure activities of $AgNO_3$ at these low concentrations. The e.m.f. changes upon the addition of iodide at fixed concentrations of $AgNO_3$ are given in Table I at the low concentrations of KI. The activity coefficients of $AgNO_3$ are plotted in Fig. 2 at the higher concentrations of KI.

Evaluation of K_1, K_{12} and K_2.—The method of evaluating K_1, K_2 and K_{12} has been described previously.[12] In the bromide system large scale plots of $-\log \gamma_{AgNO_3}$ (or of ΔE) were made as a function of the mole ratio of KBr(R_{KBr}) at several fixed concentrations of $AgNO_3$(R_{AgNO_3}). The limiting slopes of these plots were obtained graphically at $R_{KBr} = 0$ and are plotted as a function of R_{AgNO_3} at five temperatures in Fig. 3a. The intercepts of the plots in Fig. 3a at $R_{AgNO_3} = 0$ are equal

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TABLE I

E.M.F. CHANGE OF HALF CELLS CONTAINING SOLUTIONS OF $AgNO_3$ IN KNO_3 UPON THE ADDITION OF KBr OR KI

T = 403°

$R_{\mathrm{AgNO_3}} = 0.315 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.635 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.091 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.071	3.6	0.199	8.5	0.040	1.5
.141	6.8	.426[a]	23.3[a]	.104	3.7
.289	14.0	.741	31.3	.149	5.1
.500	23.5	.912	39.2	.242	8.3
.745	34.1			.319	10.7
1.057	47.1			.419	14.1
1.630	68.0			.481	16.2
1.916	77.7			.576	19.5
2.390	92.1				
2.624	98.7				

T = 438°

$R_{\mathrm{AgNO_3}} = 0.315 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.085 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.032	1.5	0.194	5.9
.317	12.8	0.656	20.2
.540	21.7		
.864	33.4		
1.429	52.5		
1.767	62.7		
2.044	70.4		

T = 452°

$R_{\mathrm{AgNO_3}} - 0.319 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.319 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.596	23.9	0.689	27.0
1.065	40.7	1.167	43.7
1.450	53.5	2.149	74.0
1.936	68.2		
2.595	86.2		
3.051	97.6		

$R_{\mathrm{AgNO_3}} = 0.630 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.643 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.634 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.180	6.6	0.445	15.5	0.523	18.6
.422	14.9	0.780	27.3	0.961	33.2
.786	27.1	1.271	43.0	1.382	46.2
1.173	39.4	1.650	54.5	1.917	62.2
1.554	51.2	2.026	65.3	2.465	77.1
2.006	64.1	2.372	74.9	2.942	89.3
2.610	79.6	2.794	85.4		
2.980	88.9				

$R_{\mathrm{AgNO_3}} = 1.084 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.089 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.423 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.555	16.0				
1.072	30.7	0.341	9.6	0.474	12.2
1.486	41.8	0.830	23.3	1.114	29.3
2.015	56.6	1.468	40.5	1.459	39.4
2.400	66.6	1.805	50.2		
2.900	78.9	2.085	57.4		
3.380	90.4				
4.126	109.8				

T = 474°

$R_{\mathrm{AgNO_3}} = 0.374 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.656 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.655 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.412	14.5	0.430	14.4	0.470	15.1
0.833	28.8	0.796	25.7	0.798	25.3
1.455	47.9	1.162	36.3	1.352	41.3
1.765	56.9	1.466	45.0	1.791	53.3
2.179	68.0	1.935	57.6	2.380	68.5
2.554	77.1	2.520	72.5	2.899	81.1
3.097	90.1	2.904	81.5		
3.511	98.9				

$R_{\mathrm{AgNO_3}} = 1.086 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.420 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.418 \times 10^{-3}$	
$K_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.389	11.2	0.581	14.3	0.404	10.0
1.110	30.9	0.937	23.8	0.867	20.9
1.541	42.1	1.404	35.5	1.284	30.9
1.919	51.7	1.851	46.9	1.710	42.1
2.263	59.6	2.318	59.5	2.158	53.9
2.689	70.3	2.711	69.9	2.829	69.7
3.080	79.5				

T = 500°

$R_{\mathrm{AgNO_3}} = 0.330 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.329 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.331 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.467	15.5	0.417	14.1	0.352	11.0
0.912	29.3	0.878	29.5	0.826	27.0
1.434	44.3	1.367	44.2	1.099	35.6
1.948	58.2	2.046	62.4	1.644	51.8
2.441	69.8	2.512	73.4	2.024	61.9
2.831	79.0			2.461	72.7
				2.924	83.2
				3.347	92.4

$R_{\mathrm{AgNO_3}} = 0.331 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.632 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 0.634 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.550	17.8	0.401	12.1	0.360	10.5
1.059	33.1	0.842	24.0	0.821	23.6
1.555	46.9	1.199	34.3	1.386	38.4
1.961	57.0	1.525	42.9	1.878	50.9
2.581	71.7	1.919	52.7		
2.897	78.6	2.424	64.3		
3.285	86.9	2.817	72.9		
3.656	94.3	3.286	82.8		

$R_{\mathrm{AgNO_3}} = 1.086 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.417 \times 10^{-3}$		$R_{\mathrm{AgNO_3}} = 1.416 \times 10^{-3}$	
$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)	$R_{\mathrm{KBr}} \times 10^3$	ΔE (mv.)
0.352	8.8	0.356	8.7	0.794	19.7
0.954	24.2	0.812	19.6	1.472	35.3
1.549	38.3	1.123	26.6	1.930	45.3
2.035	49.3	1.442	33.8	2.335	54.6
2.492	59.2	1.836	42.7	2.735	62.9
2.949	68.8	2.218	51.0	3.030	69.3
3.268	75.4	2.675	61.0		
		3.361	75.7		

T = 402°

$R_{\mathrm{AgNO_3}} = 6.84 \times 10^{-6}$		$R_{\mathrm{AgNO_3}} = 2.01 \times 10^{-5}$		$R_{\mathrm{AgNO_3}} = 3.12 \times 10^{-5}$	
$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)	$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)	$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)
0	0	0	0	0.43	1.5
0.48	1.4	0.32	2.0	1.68	5.9
1.0	3.0	0.80	4.5	4.10	13.8
2.0	7.1	2.21	7.0	10.91	34.0
3.6	11.6	3.59	12.0		
7.3	20.4	5.25	17.0		
		7.01	23.0		
		9.48	31.0		

$R_{\mathrm{AgNO_3}} = 3.82 \times 10^{-5}$		$R_{\mathrm{AgNO_3}} \approx 3.84 \times 10^{-5}$		$R_{\mathrm{AgNO_3}} = 3.99 \times 10^{-5}$	
$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)	$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)	$R_{\mathrm{KI}} \times 10^5$	ΔE (mv.)
0	0	0	0	0	0
0.85	2.9	0.60	2.0	2.43	8.6
1.81	6.9	1.43	5.8	7.67	28.0
2.69	10.0	2.85	11.1	27.9	100
4.14	15.1	5.12	18.0		

6.17	24.0	10.3	32.4
12.9	46.5	14.0	48.9

$R_{AgNO_3} = 4.48 \times 10^{-5}$		$R_{AgNO_3} = 6.68 \times 10^{-5}$		$R_{AgNO_3} = 7.55 \times 10^{-5}$	
$R_{KI} \times 10^5$	ΔE (mv.)	$R_{KI} \times 10^5$	ΔE (mv.)	$R_{KI} \times 10^6$	ΔE (mv.)
0	0	0	0	0	0
2.33	8.4	0.53	1.7	0.81	2.5
4.36	16.8	1.84	6.1	1.39	4.0
6.75	26.1	2.74	9.2	2.70	9.0
11.88	50.6	3.56	11.6	3.79	12.3
				4.39	12.8
				5.41	16.0

$R_{AgNO_3} = 8.36 \times 10^{-5}$	
$R_{KI} \times 10^5$	ΔE (mv.)
0	0
0.92	4.0
1.18	4.4
1.91	7.8
2.37	8.0
2.72	8.9

[a] Data point not used in calculations.

to $(-K_1/2.303)$ and the limiting slopes are equal to $[(K_1^2 - 2K_1K_{12})/2.303]$ since

$$\lim_{\substack{R_{KBr}=0 \\ R_{AgNO_3}=0}} \left(\frac{\partial \log \gamma_{AgNO_3}}{\partial R_{KBr}}\right) = -(K_1/2.303) \qquad (2)$$

and

$$\lim_{\substack{R_{KBr}=0 \\ R_{AgNO_3}=0}} \left(\frac{\partial^2 \log \gamma_{AgNO_3}}{\partial R_{KBr} \partial R_{AgNO_3}}\right) = \frac{(K_1^2 - 2K_1K_{12})}{2.303} \qquad (3)$$

Values of K_1 and K_{12} obtained in this manner are listed in Table II. K_2 was evaluated by a least squares fit of the experimental data (at fixed concentrations of $AgNO_3$) to the equation

$$-\log \gamma_{AgNO_3} = AR_{KBr} + BR^2_{KBr} \qquad (4)$$

The limit of a plot of B *vs.* R_{AgNO_3} at $R_{AgNO_3} = 0$ is

$$\lim_{R_{AgNO_3}=0} B = \frac{(K_1K_2 - {}^1/_2K_1^2)}{2.303} = B_0 \qquad (5)$$

and was evaluated from the plots given in Fig. 3b. Values of K_2 calculated from this limit are given in Table II. It should be emphasized that since K_2 and K_{12} are relatively large, relatively large uncertainties in the limit of the derivative in equation 3 or in the limit of B in equation 5 lead to relatively small uncertainties in K_2 or K_{12}. Values of K_1 calculated from lim A $R_{AgNO_3} = 0$ differed by less than the estimated experimental error from the values evaluated graphically and given in Table II.

From the data in Table I the values of the limiting slopes

$$\left[\left(\frac{\partial \Delta E}{\partial R_{KI}}\right)_{R_{AgNO_3}}\right]_{R_{KI} = 0}$$

at 402° were evaluated graphically and are plotted in Fig. 4. Values of K_1 and K_{12} in Table II were evaluated from the plot in Fig. 4. The linearity of log γ_{AgNO_3} within experimental precision to relatively large values of $-\log \gamma_{AgNO_3}$ (0.2) indicated that $K_2 \cong {}^1/_2K_1$. K_1, K_2 and K_{12} and derived values of ΔA_i are given in Table II.

Comparison with Theory.—The generalized calculations based on the quasi lattice model lead to the relation for K_1 given in equation 1 and for K_2 and K_{12} for non-directional "bonding"[6]

$$K_2 = \frac{(Z-1)}{2}\left(\beta_2 - 1 + \frac{\beta_2 - \beta_1}{\beta_1 - 1}\right) \qquad (6a)$$

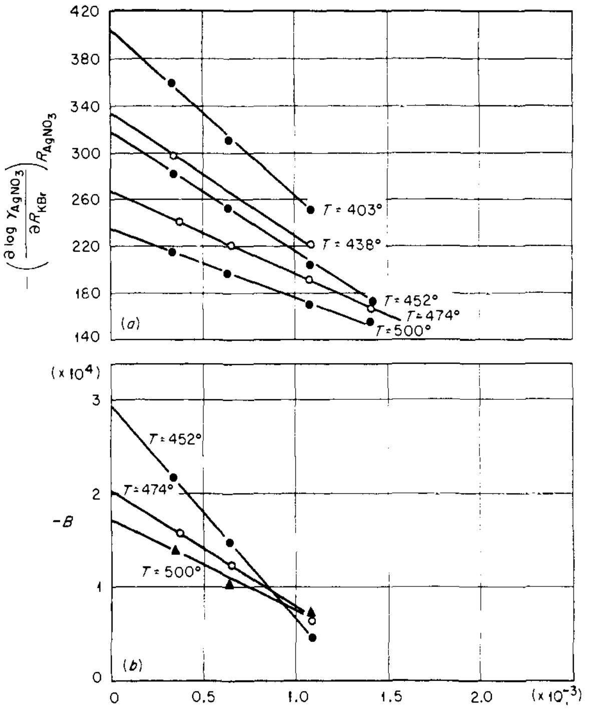

Fig. 3.—(a) Extrapolation of the limiting slopes, $-\left(\frac{\partial \log \gamma_{AgNO_3}}{\partial R_{KBr}}\right)_{R_{AgNO_3}}$ evaluated at zero mole ratio of potassium bromide, to infinite dilution of silver nitrate to obtain the stepwise association constants for AgBr and Ag_2Br^+ in molten potassium nitrate. (b) Extrapolation of the coefficients B to infinite dilution of silver nitrate to obtain the stepwise association constant for $AgBr_2^-$ in molten potassium nitrate.

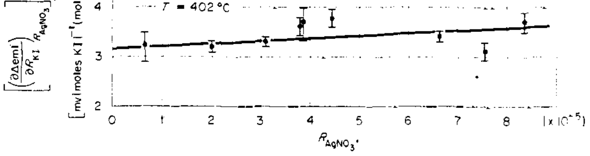

Fig. 4.—Extrapolation of the limiting slopes, $\left(\frac{\partial \Delta emf}{\partial R_{KI}}\right)_{R_{AgNO_3}}$ evaluated at zero mole ratio of potassium iodide, to infinite dilution of silver nitrate to obtain the stepwise association constants for AgI and Ag_2I^+ in molten potassium nitrate.

$$K_{12} = \frac{(Z-1)}{2}\left(\beta_{12} - 1 + \frac{\beta_{12} - \beta_1}{\beta_1 - 1}\right) \qquad (6b)$$

where $\beta_1 = \exp(-\Delta A_i/RT)$, where ΔA_i are "specific bond free energies" and Z is a coördination number. Values of ΔA_1, ΔA_2 and ΔA_{12} calculated from the association constants are listed in Table II using assumed values of Z of 4, 5 and 6 which should cover the entire range of possible values of the coördination number. For any given value of Z, the values of ΔA_1, ΔA_2 and ΔA_{12} within the estimated error appear to be constant over the entire range of temperatures. This indicates that equations 1, 6a and 6b, with values ΔA_i independent of temperature, lead to a correct

TABLE II

CALCULATED VALUES OF K_1, K_2 AND K_{12} AND DERIVED VALUES OF ΔA_1, ΔA_2 AND ΔA_{12}

		$AgNO_3$–KBr–KNO_3					$AgNO_3$–KI–KNO_3
		T, °K.					
		676°	711°	725°	747°	773°	675°
K_1 (mole/mole KNO_3)$^{-1}$		932	768	728	617	540	5420
K_2 (mole/mole KNO_3)$^{-1}$		370[a]	285[a]	273	228	195	2700
K_{12} (mole/mole KNO_3)$^{-1}$		293	230	208	174	145	3555
$Z = 4$	ΔA_1 (kcal./mole)	7.32	7.43	7.50	7.48	7.54	9.68
	ΔA_2 (kcal./mole)	7.4	7.4	7.50	7.47	7.5	10.1
	ΔA_{12} (kcal./mole)	7.08	7.12	7.12	7.08	7.04	10.4
$Z = 5$	ΔA_1 (kcal./mole)	7.01	7.12	7.18	7.16	7.21	9.38
	ΔA_2 (kcal./mole)	7.0	7.0	7.10	7.04	7.1	9.7
	ΔA_{12} (kcal./mole)	6.70	6.72	6.70	6.64	6.61	10.0
$Z = 6$	ΔA_1 (kcal./mole)	6.78	6.86	6.93	6.87	6.93	9.13
	ΔA_2 (kcal./mole)	6.7	6.7	6.77	6.72	6.7	9.4
	ΔA_{12} (kcal./mole)	6.40	6.40	6.38	6.33	6.28	9.8
Estimated % error in K_1		8	5	3	3	4	5
K_2		12	10	7	7	12	25
K_{12}		10	8	7	7	9	12

[a] Estimated from data at one concentration of $AgNO_3$ (0.315×10^{-3}).

and potentially useful prediction of the temperature coefficients, not only of K_1, but also of K_2 and K_{12}.[6,11]

A comparison of the values of K_1 at 402° (403°) for the formation of the ion pairs AgCl, AgBr and AgI is given in column 2 of Table III. Values of ΔA_1 for $Z = 5$, for example, averaged over measured temperature ranges are given in column 3. Flood, Førland and Grjotheim[13] and Førland[14] postulate that ΔF^0 or ΔH^0, the free energy or heat change for the reciprocal reaction

$$KX\,(liq) + AgNO_3\,(liq) \rightleftarrows AgX\,(liq) + KNO_3\,(liq)$$

should be a measure of ΔA. Their expression is $Z\Delta A_1 \cong \Delta H_0$ (or $Z\Delta A_1 \cong \Delta F^0$). Because data are not available to calculate all the values of ΔH^0 or ΔF^0 the value of ΔH_{solid} for the reaction of the solids at 298° given in column 4 of Table III was substituted.[15] These values of ΔH_{solid} at 298° probably differ less than two or three kcal./mole from ΔH^0. In the last column are given values of $\Delta H_{solid}/\Delta A_1$. These are smaller than any reasonable value of Z, but the relative constancy of this quantity is an indication that ΔH^0 or ΔH_{solid} is a fairly good measure of the relative values of ΔA_1 in a particular solvent. Since ΔH^0 or ΔH_{solid} for these substances may be related mainly to differences in the van der Waals and in part to differences in the coulombic contributions to the lattice energies of the four salts in the reciprocal reaction, ΔA_1 and the tendency to association may be related to van der Waals and coulombic forces.[16] Since the relative contributions of these types of interactions to ΔH_{solid} and to ΔA_1 probably differ depending on the particular system, only semiquantitative correlations may be made between the two. In a subsequent paper, the comparison of measurements in the $AgNO_3$–NaBr–$NaNO_3$ system with measurements in $AgNO_3$–KBr–KNO_3, $AgNO_3$–NaCl–$NaNO_3$ and $AgNO_3$–KCl–KNO_3 will be used to provide a clue to the types of forces involved.

TABLE III

COMPARISON OF K_1, ΔA_1 AND ΔH_{Solid}

Ion pair	K_1 (402°)	$-\Delta A_1$ ($Z = 5$)	$-\Delta H_{Solid}$	$\Delta H_{Solid}/\Delta A_1$
AgCl	396	5.88	14.6	2.5
AgBr	932	7.14	18.5	2.6
AgI	5420	9.38	25.0	2.7

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