

Enthalpies of Precipitation of Silver Halides; Entropy of the Aqueous Silver Ion

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The enthalpies of precipitation of silver halides and the enthalpies of solution of AgNO_3 , KCl , and KBr in H_2O were measured in an adiabatic solution calorimeter.

From the enthalpy measurements of $\text{KCl}(\text{c})$ and $\text{KBr}(\text{c})$ in $\text{AgNO}_3(\text{aq})$, and of $\text{AgNO}_3(\text{c})$ in $\text{KCl}(\text{aq})$, in $\text{KBr}(\text{aq})$, and in $\text{KI}(\text{aq})$, we calculated (in $\text{kJ} \cdot \text{mol}^{-1}$) -65.724 , -84.826 , and -111.124 for ΔH° pptn(298.15 K) for the averages of the chloride, bromide, and iodide reactions, respectively.

A reevaluation of the data for the enthalpy of solution of $\text{AgNO}_3(\text{c})$ has resulted in our selected best value,

$$\begin{aligned}\Delta H^\circ(\infty)(298.15 \text{ K}) &= 22.730 + 0.084 \text{ kJ} \cdot \text{mol}^{-1} \\ &= 5.433 \pm 0.020 \text{ kcal} \cdot \text{mol}^{-1}\end{aligned}$$

A table of enthalpies of dilution of $\text{AgNO}_3(\text{aq})$ is also given.

The average standard entropy for the aqueous silver ion at 298.15 K is found to be

$$\begin{aligned}S^\circ[\text{Ag}^+(\text{aq})] &= 73.42 \pm 0.20 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &= 17.55 \pm 0.05 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}.\end{aligned}$$

Key words: AgBr ; AgCl ; AgI ; AgNO_3 ; enthalpy of dilution; enthalpy of precipitation; enthalpy of solution; entropy; heat of reaction; KBr ; KCl ; solution calorimetry; thermochemistry.

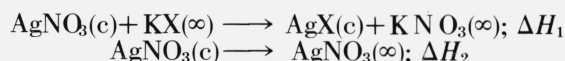
1. Introduction

The thermodynamic properties of the silver halides, AgCl , AgBr , and AgI , are extremely important quantities in determining the properties of many other substances. In conjunction with metallic silver they form electrochemical half-cells of high reproducibility. These half-cells have been combined with many other electrodes to yield thermodynamic data of high precision for a number of chemical reactions. In particular, these electrodes have been combined with the corresponding half-cells containing the aqueous halogen acids and salts to determine the activities of the acids and salts at various temperatures [1];¹ these acids are in turn the keystones for the establishment of a self-consistent set of tables of enthalpies and Gibbs energies of formation [2]. However, the final verification of electrochemical data must come from other sources. To quote from Harned and Owen [3]:

“... Cell reactions, no matter how simple and obvious, must be treated as hypothetical until it can be shown that thermodynamic quantities calculated from

the electromotive force, ΔF , ΔH , equilibrium constants, etc., have been checked by other evidence.”

In the course of our reevaluation of the thermodynamic data on silver and silver compounds, we compared the electrochemical data on the silver-silver halide systems for the reaction $\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightarrow \text{AgX}(\text{c})$ [$\text{X} \equiv \text{Cl}^-$, Br^- , I^-] with the available calorimetric measurements for the reactions. For this comparison we reextrapolated the EMF measurements of Owen and Brinkley [4] using more recent values [45] for the various fundamental constants and converting to absolute electrical units. These results were then combined with the cell data for the silver-silver halide electrodes [1] to calculate the enthalpies of the precipitation reactions. The summary comparison is shown in table 1. Because of the scatter in the various calorimetric measurements we decided to redetermine the enthalpies of precipitation of the three silver halides and establish more precisely the thermodynamic validity of the EMF data for these systems. The reaction scheme used is as follows:



¹ Figures in brackets indicate literature references at the end of this paper.

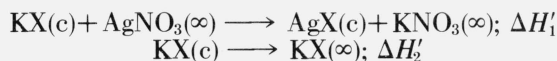
TABLE 1. Comparison of data for the enthalpy of precipitation of the silver halides obtained from various methods

Authors and year	Method	$-\Delta H^\circ(298.15 \text{ K})^a$	Reference
$\text{kJ} \cdot \text{mol}^{-1}$			
$\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}(\text{c})$:			
Lange and Fuoss (1927).....	Calorimetric.....	65.710	[5]
Thomsen (1883).....	do.....	64.98	[6]
Owen and Brinkley (1938) ^b	EMF.....	65.64 $\bar{2}$	[4]
Gledhill and Malan (1954).....	Solubility.....	66.78	[13]
$\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}(\text{c})$:			
Berthelot (1881).....	Calorimetric.....	84.1	[7]
Gellner and Skinner (1949).....	do.....	84.9	[8]
Roth (1944).....	do.....	90.58	[9]
Thomsen (1883).....	do.....	82.84	[6]
Owen and Brinkley (1938) ^b	EMF.....	84.655	[4]
Gledhill and Malan (1954).....	Solubility.....	85.56	[13]
$\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}(\text{c})$:			
Gellner and Skinner (1949).....	Calorimetric.....	109.9	[8]
Berthelot (1875).....	do.....	110.96	[10]
Berthelot (1881).....	do.....	110.08	[7]
Lange and Shibata (1930).....	do.....	111.50	[11]
Yatsimirskii and Skutov (1954).....	do.....	105.18	[12]
Thomsen (1883).....	do.....	109.37	[6]
Owen and Brinkley (1938) ^b	EMF.....	111.01	[4]

^a All calorimetric experimental data have been converted to conditions of infinite dilution at 298.15 K using necessary data from Parker [14]; 1 calorie = 4.1840 joules.

^b Recalculated; see text.

In addition, for both chloride and bromide, we used the reciprocal scheme:



2. Apparatus and Procedures

The vacuum-jacketed adiabatic solution calorimeter used in this work has been described in detail [15]. All parts of the calorimeter in contact with the calorimetric solutions are of platinum-iridium alloys or polytetrafluoroethylene (PTFE). The platinum sample holder shown in figure 1 has three interchangeable cylinders; the largest cylinder (volume, 2.7 cm³) was used for the crystalline potassium halide samples and a smaller cylinder (volume, 1.9 cm³), for the crystalline silver nitrate samples. The calorimetric solutions were approximately 300 cm³ in volume.

The calorimeter temperatures were measured with a 25- Ω platinum resistance thermometer on which one kelvin is 0.10104 Ω at 298.15 K, or with a quartz-oscillator thermometer calibrated by comparison with the platinum resistance thermometer (see [15] for calibration data on these thermometers). The last certified calibrations on the standard resistors and the standard cell were made in June and July 1969, respectively. Dial corrections are based on our calibra-

tions of the six-dial potentiometer in January 1969, and of the G-3 Mueller-type resistance bridge, in November 1970. The previous history of this equipment indicates that no significant drift occurred subsequent to these calibrations.

For the experiments reported in sections 3, 4, and 5, the analytical reagent grade (ACS certified) salts, KCl, KBr, KI, and AgNO₃ were used for the crystalline samples and for the aqueous solutions. The reagents were not dried nor further purified. The weight loss on drying the AgNO₃ indicated less than 0.01 percent moisture content.

The 1969 atomic weights [16] were used to calculate the following molar masses: AgNO₃, 169.8729; KCl, 74.555; KBr, 119.006; KI, 166.0065; and H₂O, 18.0154. For energy conversions, 1 thermochemical calorie = 4.1840 joules.

To obtain the buoyancy factors for calculating the mass of the crystalline samples, the following densities (in g · cm⁻³) were used: KCl, 1.988; KBr, 2.75; and AgNO₃, 4.352 [17a]. For the average conditions in this laboratory, the density of air was 0.00118 g · cm⁻³. The densities (in g · cm⁻³) at 296 K of the aqueous solutions of the salts were taken [17b] as follows: KCl (0.75 wt. %), 1.0013; KBr (1.19 wt. %), 1.0061; KI (1.67 wt. %), 1.0100; AgNO₃ Stock Soln. No. 1 (2.55 wt. %), 1.0194; and AgNO₃ Stock Soln. No. 2 (2.48 wt. %) and AgNO₃ Stock Soln. No. 3 (2.49 wt. %), 1.0188. Each stock solution was initially 2 dm³ in volume and was stored in polyethylene bottles in a dark cabinet when not in use.

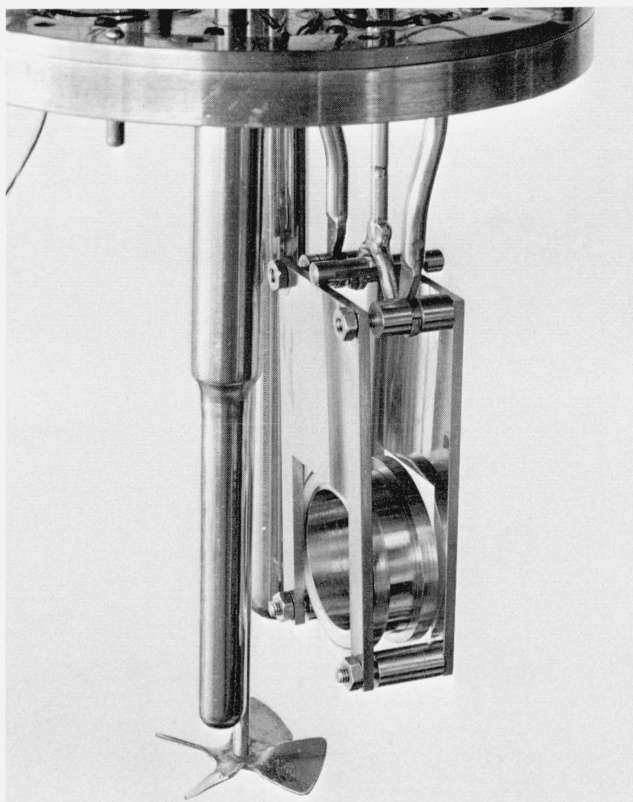


FIGURE 1. Platinum parts inside the vessel of the adiabatic solution calorimeter.

From left, the thermometer well, the stirrer, the heater well (rear), and the sample holder. The sample is contained in the cylinder which initially is at the top and sealed between the two flat plates by the PTFE o-rings. The plates are held together by the "trigger" bar (at top) until the initiation of reaction when the trigger bar releases the front plate, allowing the cylinder to drop to the position shown here.

In each experiment, the chemical reaction was preceded by an electrical calibration of the initial system and followed by an electrical calibration of the final system. Details of procedures and calculations for electrical calibrations and temperature measurements have been described [15].

3. Enthalpies of Solution of the Reagent Salts in H₂O

The enthalpies of solution in H₂O were measured for each of the salts used as crystalline samples in the experiments reported in sections 4 and 5. The data are given in table 2.

In the table, the Expt. No. is the serial number of experiments measured in this calorimeter, ΔR_c is the corrected temperature rise during the chemical reaction period, \overline{EEE} is the mean of the electrical energy equivalents for the initial and final systems (the average difference between the values for the initial and final systems was 0.1% and the maximum difference, 0.35%), Q_r is the product of ΔR_c and \overline{EEE} , and \bar{T} reaction is the mean temperature of

reaction. The corrected temperature rise, ΔR_c , is calculated as the difference between the final and initial temperatures, obtained by solving the linear least-squares-fitted equations of the final and initial rating periods for the temperatures at the time of initiating the reaction. The stirring energy represents the difference between the total and the corrected temperature rise (see [15] for details about the stirring energy). The uncertainty in the stirring energy is about 5 percent or less of the stirring energy.

The heat of the chemical reaction, Q_s , is obtained by subtracting the precisely-measured "Electrical energy added" during the endothermic chemical reaction from Q_r . The isothermal enthalpy of reaction, $\Delta H_r(T)$, at the temperature of reaction (defined as the mean temperature of reaction) is $-Q_s/(\text{mass of solute})$. The temperature of reaction for all of these measurements was near 298.15 K. The concentrations of the final solutions were varied by using differing amounts of solute. Corrections, given in column 12, were made to the enthalpy of reaction using the heat capacity and dilution data from the review by Parker [14] to obtain the enthalpy of solution at 298.15 K and infinite dilution, $\Delta H^\circ(\infty)$, except for AgNO₃, where the dilution data obtained in this work (see table 3 and sec. 4) were used. The differences in concentration of the solute had little if any effect on the values obtained for $\Delta H^\circ(\infty)$.

In Expt. No. 570, the rate of electrical heating during the chemical reaction was not sufficient to compensate for the heat absorbed by the chemical reaction when the sample holder was opened. Consequently, an abnormal temperature difference between the calorimeter vessel and the adiabatic shield occurred. A correction of -0.06 J (see [15] for the method of calculating the correction) was applied to the net heat evolved during the chemical reaction period, Q_r .

In Expt. No. 582 the calorimeter was sealed by replacing the usual polytetrafluoroethylene o-ring bearing for the stirrer with a heavily lubricated nitrile o-ring and sealing the vent tube with the weighted platinum rod as described in [18]. This was to test the effect on the enthalpy of solution of the unvented calorimeter as compared to the usual vented calorimeter. It was found in our work with Standard Reference Material No. 724a, tris(hydroxymethyl)aminomethane, in 0.1 N HCl solution [18] that the enthalpy values obtained with the unvented (closed) calorimeter were about 3 percent more exothermic than those obtained with the calorimeter which was vented or open to the atmosphere. On the other hand no venting effect was found in the reactions of H₂SO₄ · 8 H₂O with 0.02 and 0.08 N NaOH solutions [15], nor in the endothermic reaction of TRIS in NaOH(aq) [18]. In the present work, the enthalpy of solution in Expt. No. 582 using the unvented calorimeter is in satisfactory agreement with those in Expt. Nos. 570 and 571 in which the calorimeter was vented to the atmosphere. This is further evidence that the venting effect is characteristic of the reaction of SRM 724a in HCl(aq), and not a peculiarity of this calorimeter.

TABLE 2. Data for the calorimetric measurements of ΔH_{soln} in H_2O for the solute reagents used in the precipitation reactions

Expt. No.	Mass of solute	Mole ratio solute H_2O :	\overline{EEE}	Stirring ^a energy	ΔRc	\bar{T} reaction	Qr	Electrical energy added	Qs	$\Delta Hr(T)$	Correction	$\Delta H^\circ(\infty)$ (298.15 K)	
	<i>g</i>		$J \cdot \Omega^{-1}$	Ω	Ω	K	J	J	J	$J \cdot g^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kcal \cdot mol^{-1}$
Solute: KCl(c)													
570	2.23251	560.7	17,166.3	0.001494	0.021240	298.121	^b 364.55	889.304	-524.75	235.05	-0.339	17.185	4.107
571	1.32476	945.0	17,173.3	.001066	.052533	297.950	902.16	1213.292	-311.13	234.86	-.300	17.210	4.113
582	2.21843	564.3	17,163.0	.001696	.041378	297.899	710.17	1233.850	-523.68	236.06	-.339 (Mean)	17.260 17.218	4.125 4.115
Solute: KBr(c)													
572	2.38555	837.7	17,172.6	0.001442	0.047350	298.256	813.12	1214.322	-401.20	168.18	-0.255	19.759	4.722
573	4.69414	425.7	17,161.3	.001462	.024852	298.084	426.49	1218.319	-791.83	168.68	-.290 (Mean)	19.784 19.772	4.728 4.725
Solute: AgNO_3 (c)													
574	2.55356	1117.0	17,182.3	0.001023	0.050921	298.238	874.94	1216.506	-341.57	133.76	-0.003	22.719	5.430
575	5.00255	570.1	17,187.7	.001417	.031904	297.932	548.36	1216.424	-668.06	133.54	+.047	22.732	5.433
			$J \cdot K^{-1}$	K	K								
^c 730	1.08990	2616.7	1,732.60	0.01108	0.13472	298.115	233.41	379.622	-146.21	134.15	-0.085	22.703	5.426
^c 737	0.56601	5038.1	1,731.54	.01472	.17311	298.373	299.75	375.687	-75.94	134.17	-.071	22.721	5.430
^c 739	0.28578	9979.1	1,733.53	.00623	.06395	298.174	110.85	149.280	-38.43	134.46	-.104	22.737	5.434
												22.727	5.432
(Graphical limit, see text)													

^a The stirring rate in all experiments was 550 rpm except Expt. Nos. 730 and 737 (450 rpm) and No. 739 (250 rpm).

^b A correction of -0.06 J was applied because of the large departure of the shield temperature from the vessel temperature. (See text, sec. 3).

^c The calorimeter temperature was measured with a quartz-oscillator thermometer.

TABLE 3. Apparent relative molal heat content of $\text{AgNO}_3 \cdot n \text{H}_2\text{O}(\text{aq})$ at 298.15 K

<i>m</i>	<i>n</i>	ϕ_L or $-\Delta H_{\text{diln}}$		
		This work		Parker [14]
<i>molality</i>		$\text{J} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$	$\text{cal} \cdot \text{mol}^{-1}$
5.551×10^{-4}	100,000	46	11	9
1.110×10^{-3}	50,000	64	15	12
2.775×10^{-3}	20,000	89	21	17
5.551×10^{-3}	10,000	105	25	19
1.110×10^{-2}	5,000	102	24	21
1.388×10^{-2}	4,000	97	23	21
1.850×10^{-2}	3,000	86	21	20
2.775×10^{-2}	2,000	64	15	16
3.700×10^{-2}	1,500	42	10	12
5.551×10^{-2}	1,000	-3	-1	2
6.938×10^{-2}	800	-35	-8	-6
9.251×10^{-2}	600	-76	-18	-20
1.110×10^{-1}	500	-112	-27	-32

Parker's "best" values [14] for $\Delta H^\circ(\infty)$ (in $\text{kJ} \cdot \text{mol}^{-1}$) are 17.22 ± 0.04 for $\text{KCl}(\text{c})$, 19.87 ± 0.08 for $\text{KBr}(\text{c})$, and 22.59 ± 0.21 for $\text{AgNO}_3(\text{c})$. Our mean value given in table 2 for KCl is in excellent agreement with Parker's value. Our mean value for KBr differs by about 0.5 percent from Parker's selected value but is within 0.02 percent of the recent results of Tsvetkov and Rabinovich [19]. The uncertainty in Parker's "best" value for AgNO_3 is relatively large, and the mean of our measured values falls near the upper limit of the uncertainty.

4. Enthalpies of Solution and Dilution of AgNO_3

The measurements on the enthalpy of solution of $\text{AgNO}_3(\text{c})$ given in table 2 were extrapolated to infinite dilution using the relation [20]

$$\Delta H - \phi_L = \Delta H^\circ(\infty) = \Delta H - 2879m^{1/2} \times \rho + f(m)$$

where

$$\rho = (1 + m^{1/2})^{-1} - (1/m^{3/2})$$

$$[1 + m^{1/2} - (1/(1 + m^{1/2})) - 2 \ln(1 + m^{1/2})].$$

A plot of $\Delta H - 2879m^{1/2}\rho$ ($= \Delta H'$) against the molality, m , yielded a curve linear below $m = 0.05$ with the intercept, $\Delta H^\circ(\infty) = 22.727 \pm 0.029 \text{ kJ} \cdot \text{mol}^{-1}$ ($5.432 \pm 0.007 \text{ kcal} \cdot \text{mol}^{-1}$). From this value of $\Delta H^\circ(\infty)$, values of ϕ_L were calculated for each measured concentration and a smooth curve plotted versus $m^{1/2}$. Values of ϕ_L were interpolated from the curve and are given in table 3 for various values of m . We estimate the uncertainty in ϕ_L to be about $\pm 10 \text{ J} \cdot \text{mol}^{-1}$ ($\pm 2 \text{ cal} \cdot \text{mol}^{-1}$). Corresponding values estimated by Parker [14] are also shown in the table. Parker's values were obtained from very limited data and the present work indicates that her estimates were only slightly in error.

A summary of earlier calorimetric measurements of the enthalpy of solution of $\text{AgNO}_3(\text{c})$ (corrected to

TABLE 4. Enthalpy of solution of AgNO_3 in H_2O at 298.15 K

Investigator	$\Delta H^\circ(\infty)$		Reference
	$\text{kJ} \cdot \text{mol}^{-1}$	$\text{kcal} \cdot \text{mol}^{-1}$	
Thomsen (1883).....	22.51 ± 0.21	5.38 ± 0.05	[6]
Roth (1944).....	22.573 ± 0.21	5.395 ± 0.050	[9]
Lange and Martin (1937).....	22.907	5.475	[21]
Smith, Brown, and Pitzer (1937).....	22.468 ± 0.21	5.370 ± 0.050	[22]
Graham and Hepler (1958).....	22.740 ± 0.17	5.435 ± 0.040	[23]
Shidlovskii and Voskre- senski (1963).....	22.38	5.35	[24]
This work.....	22.727 ± 0.084	5.432 ± 0.020	
Selected Value.....	22.730 ± 0.084	5.433 ± 0.020	

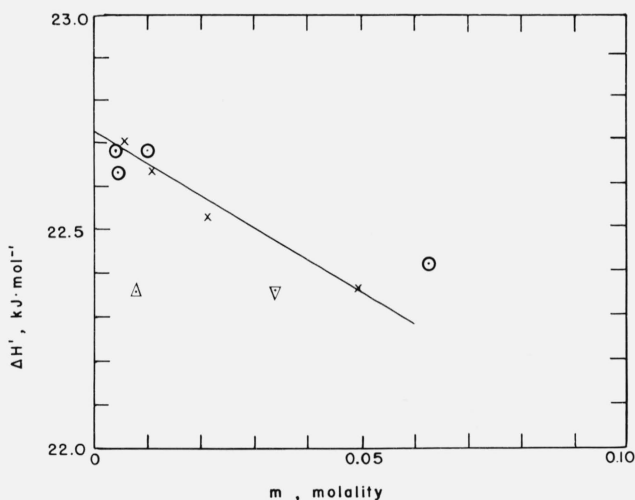


FIGURE 2. Extrapolation of heat of solution measurements on AgNO_3 in the dilute range below 0.05 molal) to infinite dilution at 298.15 K.

○ Graham and Hepler [23]; △ Smith, Brown, and Pitzer [22]; ▽ Roth [9]; X This work. (See sec. 4.)

infinite dilution) is given in table 4. We have combined our dilute solution measurements with those of Graham and Hepler [23] and extrapolated the combined set of data as described above to obtain a selected best value of $\Delta H^\circ(\infty) = 22.730 \pm 0.042 \text{ kJ} \cdot \text{mol}^{-1}$ or $5.433 \pm 0.010 \text{ kcal} \cdot \text{mol}^{-1}$ (see fig. 2).

5. Silver Halide Precipitation Experiments

The enthalpies of reaction were measured for five reactions in which the silver halide precipitates were formed: $\text{KCl}(\text{c})$ in $0.15 \text{ N AgNO}_3(\text{aq})$, reaction I; $\text{AgNO}_3(\text{c})$ in $0.1 \text{ N KCl}(\text{aq})$, reaction II; $\text{KBr}(\text{c})$ in $0.15 \text{ N AgNO}_3(\text{aq})$, reaction III; $\text{AgNO}_3(\text{c})$ in $0.1 \text{ N KBr}(\text{aq})$, reaction IV; and $\text{AgNO}_3(\text{c})$ in $0.1 \text{ N KI}(\text{aq})$, reaction V. The reaction which would complete the set, $\text{KI}(\text{c})$, in $\text{AgNO}_3(\text{aq})$, was not measured because of time limita-

tions. The results of the five reactions measured here were sufficient to produce the desired information. The fluoride reactions were not included because of large uncertainties in the related data.

The data for the 21 silver halide precipitation experiments are given in tables 5 and 6. Explanations of Expt. No., ΔR_c , EEE , Q_r , T reaction, and Stirring energy are given in section 3 and [15]. In these tables and the discussions, solute refers to the crystalline samples of KCl, KBr, and $AgNO_3$, and solvent salt refers to the KCl, KBr, or $AgNO_3$ dissolved in the initial aqueous calorimetric solutions. In each group of reactions, there is one experiment in which the mass of solute was approximately half that used in the other experiments. The variations in the concentration of the solute had a negligible effect on the enthalpy of reaction in this range.

In preliminary experiments (not given in the tables) we encountered some of the difficulties to be expected in this type of reaction. Upon initiating the reaction, there was the expected rapid increase in the calorimeter temperature; after 15 min, the slope of the time-

temperature curve was about ten times that preceding the reaction; after three hours, the slope was about three times that of the initial rating period for the reaction, indicating that heat was still being evolved but at a slowly decreasing rate. Upon opening the calorimeter vessel, we found (in addition to the expected flocculent precipitates, white $AgCl$ and yellow $AgBr$) at the bottom of the vessel a solid mass of material (which assumed the shape of the vessel) covered by a thin sheet of material which had a paper-like consistency when dried. Apparently the samples, of higher density than the solutions, had fallen to the bottom of the vessel. The precipitates formed a protective layer over the unreacted sample and inhibited access of the solution to the crystalline sample. In Expt. No. 568 (reaction I, tables 5 and 6) the stirring rate was increased from 350 rpm to 550 rpm and after 50 min the slope of the time-temperature curve was approximately equal to that of the rating period preceding the reaction. All of the product was the flocculent, white $AgCl$ with no evidence of the incomplete reaction. The stirring rate of 550 rpm was used in all experiments given in table 6.

TABLE 5. Data for the silver halide precipitation experiments

Expt. No.	Reaction period	Solvent composition			Solute	Mole ratios		
		Conc.	Salt	H ₂ O		H ₂ O:solute	Solvent:solute	H ₂ O:solvent salt
	<i>min</i>	<i>wt %</i>	<i>mol</i>	<i>mol</i>	<i>mol</i>			
Reaction I: KCl(c) in 0.15N $AgNO_3$ (aq)								
568	50	2.55	0.04695	16.906	0.029933	565	1.57	360
581	50	2.55	.04697	16.906	.029840	567	1.57	360
605	25	2.49	.04576	16.916	.029109	581	1.57	370
606	170	2.49	.04575	16.916	.029208	579	1.57	370
607	> 30, < 95	2.49	.04576	16.917	.027368	618	1.67	370
608	25	2.49	.04575	16.916	.014717	1542	3.11	370
Reaction II: $AgNO_3$ (c) in 0.1N KCl(aq)								
576	15	0.75	0.03031	16.666	0.015088	1104	2.01	550
577	20	0.75	.03031	16.667	.029455	566	1.03	550
610	20	0.75	.03031	16.668	.023224	718	1.30	550
Reaction III: KBr(c) in 0.15N $AgNO_3$ (aq)								
569	15	2.55	0.04696	16.903	0.039752	425	1.18	360
601	15	2.48	.04569	16.918	.020192	838	2.26	370
604	165	2.49	.04574	16.916	.039782	425	1.15	370
609	> 45, < 75	2.48	.04569	16.917	.033619	503	1.36	370
Reaction IV: $AgNO_3$ (c) in 0.1N KBr(aq)								
578	15	1.19	0.03025	16.591	0.014998	1106	2.02	548
579	20	1.19	.03024	16.590	.029396	564	1.03	549
580	70	1.19	.03025	16.591	.029491	563	1.03	548
Reaction V: $AgNO_3$ (c) in 0.1N KI(aq)								
596	20	1.67	0.03040	16.513	0.023597	700	1.29	543
597	20	1.67	.03040	16.513	.015137	1091	2.01	543
598	20	1.67	.03040	16.513	.023668	698	1.28	543
599	20	1.67	.03040	16.512	.023666	698	1.28	543
600	20	1.67	.03040	16.512	.023471	704	1.30	543

TABLE 6. Calorimetric data for the silver halide precipitation experiments

Expt. No.	Stirring energy	ΔR_c	\overline{EEE}	Q_r	Mass of solute	\bar{T} reaction	$-\Delta H_r(T)$		ΔC_p	$-\Delta H_r(298.15 \text{ K})$	
		Ω	Ω	$J \cdot \Omega^{-1}$			J	g		K	$J \cdot g^{-1}$
Reaction I: KCl(c) in AgNO ₃ (aq)											
568	0.002368	0.084251	17,265.7	1454.65	2.23165	298.056	651.83	48.597	-19.5	48.599	11.615
581	.002628	.083919	17,336.4	1454.85	2.22464	308.518	653.97	48.757		48.555	11.605
605	.001748	.081933	17,337.7	1420.54	2.17024	308.552	654.55	48.800		48.597	11.615
606	.007200	.082146	17,267.8	1418.49	2.17762	298.147	651.40	48.565		48.565	11.607
607	.004361	.077058	17,339.4	1336.14	2.04045	308.489	654.83	48.821		48.619	11.620
608	.001622	.041431	17,264.3	715.28	1.09727	298.438	651.87	48.600		48.594	11.614
										Mean = 48.588	11.613
										sdm = ± 0.010	± 0.002
Reaction II: AgNO ₃ (c) in KCl(aq)											
576	0.001448	0.038460	17,068.8	656.48	2.56312	298.389	256.13	43.510	+21.8	43.515	10.400
577	.001739	.075132	17,085.2	1283.64	5.00369	297.448	256.54	43.579		43.564	10.412
610	.001756	.058692	17,140.8	1006.02	3.94511	308.424	255.00	43.318		43.542	10.407
										Mean = 43.540	10.406
										sdm = ± 0.014	± 0.003
Reaction III: KBr(c) in AgNO ₃ (aq)											
569	0.001553	0.149914	17,276.1	2589.92	4.73088	298.171	547.45	65.150	-13.0	65.150	15.571
601	.001593	.076239	17,268.5	1316.54	2.40302	298.218	547.87	65.200		65.199	15.583
604	.005978	.150107	17,267.6	2591.98	4.73452	297.849	547.46	65.151		65.155	15.572
609	.003698	.126733	17,324.2	2195.55	4.00098	308.785	548.75	65.304		65.166	15.575
										Mean = 65.168	15.575
										sdm = ± 0.011	± 0.003
Reaction IV: AgNO ₃ (c) in KBr(aq)											
578	0.001682	0.055171	17,011.4	938.54	2.54781	297.993	368.37	62.576	+63.	62.566	14.954
579	.003097	.108010	17,026.8	1839.07	4.99368	297.772	368.28	62.561		62.537	14.947
580	.005479	.106780	17,094.4	1825.34	5.00979	308.638	364.36	61.895		62.556	14.951
										Mean = 62.553	14.951
										sdm = ± 0.008	± 0.002
Reaction V: AgNO ₃ (c) in KI(aq)											
596	0.002112	0.122965	17,031.3	2094.26	4.00853	308.673	522.45	88.750	+9.6	88.851	21.236
597	.001929	.079234	16,957.6	1343.62	2.57140	298.640	522.52	88.762		88.767	21.216
598	.001894	.123197	17,028.9	2097.91	4.02068	308.772	521.78	88.636		88.738	21.209
599	.001895	.123855	16,965.1	2101.22	4.02032	297.877	522.65	88.784		88.781	21.219
600	.001638	.122122	17,033.4	2080.16	3.98710	308.740	521.72	88.626		88.728	21.206
										Mean = 88.773	21.217
										sdm = ± 0.022	± 0.005

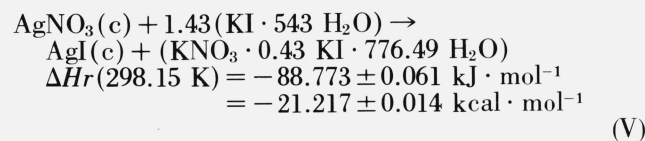
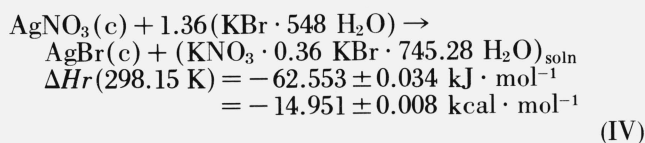
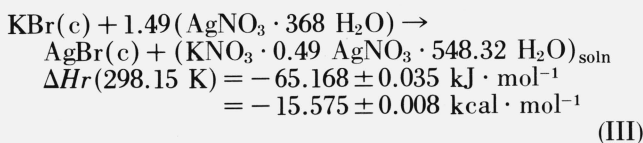
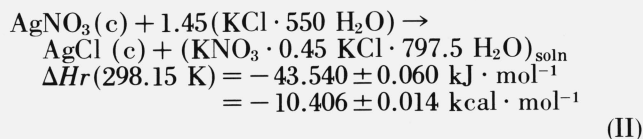
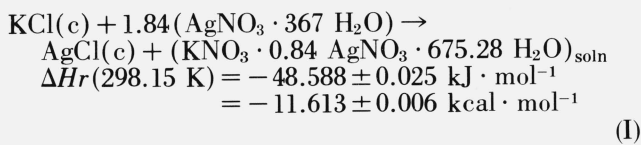
It may be seen in table 5 that there were occasional experiments (Nos. 580, 604, 606, and 609) where the reaction periods were longer than others in the group. We assume that this was caused by the way in which the sample holder (see fig. 1) opened. Initially the cylinder containing the sample is at the top, between the two flat plates. When the trigger is released to start the reaction, the cylinder falls to the lower crossbars. As the cylinder falls, if it tilts toward the stirrer, most of the sample will be quickly dispersed in the solution; however, if the cylinder tilts away from the stirrer, much of the sample falls to the bottom and is covered by the precipitate formed. This limits access of the solution to the sample. In all of the experiments listed in tables 5 and 6, the reactions were complete, as evidenced by the essentially equal slopes

in the initial and final rating periods and by the absence of products of incomplete reaction such as were found in the first experiments described earlier in this section.

In table 6, the isothermal enthalpy of reaction at the temperature of reaction is $\Delta H_r(T) = -Q_r/(\text{mass of solute})$. In each group of reactions, one or more enthalpy measurements were made at 309 K in order to obtain a value of ΔC_p for the reaction. The enthalpy values at 298.15 K were calculated using the values of ΔC_p given in the table for each reaction. The mean $\Delta H_r(298.15 \text{ K})$ and the standard deviations of the mean are given for each group of experiments.

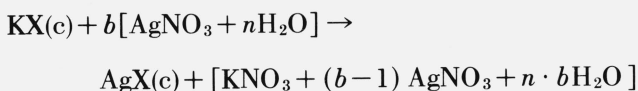
The average reactions for the five groups of experiments are represented by the following equations

(with uncertainties as the experimental imprecision at the 95 percent confidence level):

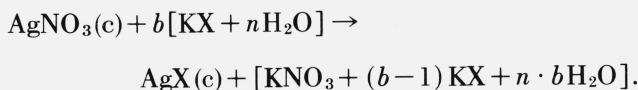


Correction for enthalpy of mixing.

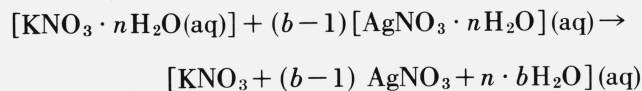
The quantity, $\Delta H_r(298.15 \text{ K})$, given in table 6 represents the enthalpy change for the generalized reaction:



or



For the systems in which Ag^+ ion is in excess the enthalpy of mixing reaction,



was calculated from the measurement of Karapet'yants, Vlasenko, and Solov'eva [25]. Their data were fitted to a function of the form

$$\Delta H_{\text{mix}} = X(1-X)m^2R\text{Th}_0$$

in which X is the mole fraction of AgNO_3 in the solute

mixture, m is the molality of the solution, and ΔH_{mix} is the enthalpy of mixing per kilogram of solvent [26]. For $m=0.15$ we obtained the equation

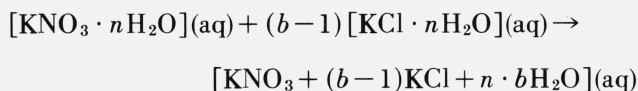
$$\Delta H_{\text{mix}} = -3.95X(1-X), \text{J} \cdot (\text{kgH}_2\text{O})^{-1}.$$

The enthalpy of mixing per mole of solute was then computed from the equation

$$\Delta H_{\text{mix}} = -\frac{b-1}{b} \times \frac{n}{55.51} \times 3.95, \text{J} \cdot \text{mol}^{-1}.$$

For the $\text{KCl}(c) - \text{AgNO}_3(\text{aq})$ reactions, the correction to $\Delta H_r(-\Delta H_{\text{mix}})$ is $9 \text{ J} \cdot \text{mol}^{-1}$ except for Expt. No. 608 in which the correction is $18 \text{ J} \cdot \text{mol}^{-1}$; the average correction is $10 \text{ J} \cdot \text{mol}^{-1}$ ($2.4 \text{ cal} \cdot \text{mol}^{-1}$). For the $\text{KBr}(c) - \text{AgNO}_3(\text{aq})$ the corrections range from 3 to $15 \text{ J} \cdot \text{mol}^{-1}$, the average correction being $8 \text{ J} \cdot \text{mol}^{-1}$ ($1.9 \text{ cal} \cdot \text{mol}^{-1}$).

The enthalpy of mixing reaction



was calculated from the data given in Wu, Smith, and Young [26] and Wood and Smith [27] for the $\text{KCl} - \text{KNO}_3$ system to be less than $1 \text{ J} \cdot \text{mol}^{-1}$ and was omitted. The correction was also assumed to be negligible for the $\text{KBr} - \text{KNO}_3$ and $\text{KI} - \text{KNO}_3$ systems.

6. Enthalpies of Precipitation of the Silver Halides

The measured enthalpies for the five silver halide precipitation reactions (from table 6) and the thermodynamic quantities derived from them are given in table 7. The values of ϕ_l are taken from Parker [14], and the quantity, $q(\text{demix})$, represents the correction for demixing the final solutions as described in section 5. The values for the enthalpies of solution of the solute salts are taken from table 2.

All of the values for ΔH° pptn given in table 7 are in good agreement with those obtained from EMF measurements (see table 1). Our mean value for the chloride reactions, $-65.724 \text{ kJ} \cdot \text{mol}^{-1}$, is in good agreement with the value of Lange and Fuoss; for the bromide reactions our mean value, $-84.826 \text{ kJ} \cdot \text{mol}^{-1}$, agrees with those of Gellner and Skinner, and Berthelot; and for the iodide reaction our value, $-111.125 \text{ kJ} \cdot \text{mol}^{-1}$ agrees best with that of Berthelot's first work.

7. Gibbs Energies of Precipitation of the Silver Halides

The available solubility data on the silver halides are presented in table 8 as the common logarithm of the solubility product. We have also calculated the values of $\log K_s$ for each silver halide from the appropriate values of the standard electrode potentials for

TABLE 7. Data used in the calculation of the entropy of the aqueous silver ion from the enthalpies of the five silver halide precipitation reactions

All values are at 298.15 K

Reaction	I	II	III	IV	V
	KCl(c) in AgNO ₃ (aq)	AgNO ₃ (c) in KCl(aq)	KBr(c) in AgNO ₃ (aq)	AgNO ₃ (c) in KBr(aq)	AgNO ₃ (c) in KI(aq)
ΔH_r , kJ · mol ⁻¹	-48.588	-43.540	-65.168	-62.553	-88.773
q (demix), kJ · mol ⁻¹	+0.010	—	+0.008	—	—
ϕ_L (solvent), kJ · mol ⁻¹	-0.238	+0.335	-0.238	+0.280	+0.209
$-\phi_L(\text{KNO}_3)$, kJ · mol ⁻¹	+0.356	+0.163	+0.356	+0.163	+0.167
ΔH° , kJ · mol ⁻¹	-48.460	-43.042	-65.042	-62.110	-88.397
$\Delta H^\circ(\infty)$ (solute), kJ · mol ⁻¹	17.218	22.727	19.772	22.727	22.727
ΔH° pptn, kJ · mol ⁻¹	-65.678	-65.769	-84.814	-84.837	-111.124
ΔG° , kJ · mol ⁻¹	-55.652	-55.652	-70.206	-70.206	-91.827
ΔS° pptn, J · mol ⁻¹ · K ⁻¹	-33.63	-33.93	-49.00	-49.07	-64.72
S° [AgX(c)], J · mol ⁻¹ · K ⁻¹	96.36	96.36	107.11	107.11	115.48
S° [X ⁻ (aq)], J · mol ⁻¹ · K ⁻¹	56.73	56.73	82.84	82.84	106.70
S° [Ag ⁺ (aq)], J · mol ⁻¹ · K ⁻¹	73.26	73.56	73.27	73.34	73.50

TABLE 8. Selection of ΔG° of the precipitation reaction

All values are at 298.15 K.

Author	log K_s	Reference
AgCl:		
Goodwin (1894).....	-9.865	[28]
Jonte and Martin (1952).....	-9.752	[29]
Gledhill and Malan (1954).....	-9.748	[13]
Bardin and Bystritskii (1971).....	-9.765	[30]
Anderson, Butler, and Woolley (1971).....	-9.75	[31]
Electrochemical (Ag/AgCl, Cl ⁻ and Ag/Ag ⁺).....	-9.752	
Broadbank, et al. (1968).....	-9.755	[32]
Selected.....	-9.750	
$\Delta G^\circ = -55.651 \pm 0.012$ kJ · mol ⁻¹ $= -13.301 \pm 0.003$ kcal · mol ⁻¹		
AgBr:		
Thiel (1900).....	-12.18	[33]
Gledhill and Malan (1954).....	-12.204	[13]
Hill (1908).....	-12.270	[34]
Goodwin (1894).....	-12.43	[28]
Do.....	-12.38	
Berne and Leden (1953).....	-12.34	[35]
Electrochemical.....	-12.309	
Selected.....	-12.300	
$\Delta G^\circ = -70.206 \pm 0.100$ kJ · mol ⁻¹ $= -16.780 \pm 0.025$ kcal · mol ⁻¹		
AgI:		
Thiel (1900).....	-15.958	[33]
Goodwin (1894).....	-16.11	[28]
Do.....	-16.01	
Hill (1908).....	-15.978	[34]
Electrochemical.....	-16.088	
Selected.....	-16.088	
$\Delta G^\circ = -91.827 \pm 0.100$ kJ · mol ⁻¹ $= -21.947 \pm 0.025$ kcal · mol ⁻¹		

the Ag/Ag⁺(aq) and the Ag/AgX(c), X⁻(aq) electrodes [1, 4]. These values are listed as "Electrochemical." The activity coefficients were taken as unity in all cases. The standard Gibbs energy of precipitation at 298.15 K is then

$$\Delta G^\circ = RT \ln K_s = 5.7079 \log K_s, \text{ kJ} \cdot \text{mol}^{-1}$$

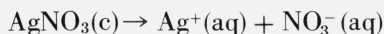
$$= 1.36422 \log K_s, \text{ kcal} \cdot \text{mol}^{-1}.$$

8. Entropy of the Aqueous Silver Ion

The calculation of the entropy of precipitation of the silver halides is summarized in table 7. ΔS° pptn = $(\Delta H^\circ$ pptn - $\Delta G^\circ)/T$. The entropies of the silver halide salts were calculated by graphical reintegration of the corresponding heat capacity data [36, 37]; the

entropies of the aqueous halide ions are the recommended CODATA values [38].

We have also calculated a value for the entropy of the silver ion from the data on $\text{AgNO}_3(\text{aq})$, using the CODATA preliminary value for the nitrate ion [39]. The solubility, 15.01 molal at 298.15 K, was taken from the measurements of Skarulis and Ricci [40]; the activity coefficient at saturation was calculated to be 0.082 [41, 42]. Combining these data with our selected best value of the enthalpy of solution we obtain



$$\Delta G^\circ = -1.029 \pm 0.040 \text{ kJ} \cdot \text{mol}^{-1}$$

$$= -0.246 \pm 0.010 \text{ kcal} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(\infty) = 22.730 \pm 0.42 \text{ kJ} \cdot \text{mol}^{-1}$$

$$= 5.433 \pm 0.010 \text{ kcal} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ = 79.69 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$= 19.05 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

The entropy of $\text{AgNO}_3(\text{c})$, $140.92 \pm 0.63 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ($33.68 \pm 0.15 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), was measured by Smith, Brown, and Pitzer [22], and the CODATA value for $\text{NO}_3^-(\text{aq}) = 146.94 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ($35.12 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$). Hence, we obtain for the $\text{Ag}^+(\text{aq})$ from AgNO_3

$$S^\circ(298.15 \text{ K}) = 73.67 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

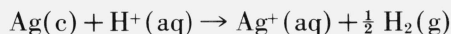
$$= 17.61 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

in excellent agreement with the values obtained from the halides.

We can also obtain a value for the entropy of $\text{Ag}^+(\text{aq})$ from our recalculation and reextrapolation of the data of Owen and Brinkley [4] for the silver electrode. We have fitted the values of E° in volts to a quadratic function of the temperature, obtaining the equation (T in K):

$$E^\circ = -0.79910 + 9.930 \times 10^{-4}(T - 298.15) + 4.05 \times 10^{-7}(T - 298.15)^2$$

Thus, for the reaction



$$\Delta S^\circ(298.15 \text{ K}) = 95.81 \pm 0.13 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$S^\circ[\text{Ag}^+(\text{aq})] (298.15 \text{ K}) = 73.08 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

$$= 17.47 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

The entropies of $\text{Ag}(\text{c})$ and $\text{H}_2(\text{g})$ are taken from [43] and [38] respectively.

Table 9 summarizes the values obtained in this paper for the entropy of $\text{Ag}^+(\text{aq})$ with estimated overall

uncertainties. We have assigned a smaller weight to the value obtained from the EMF measurements because of the uncertainty in the temperature coefficient, and to the value from AgI because of the relatively large uncertainty in the entropy of $\text{AgI}(\text{c})$ [37]. As a final mean value we have selected

$$S^\circ[\text{Ag}^+(\text{aq})] (298.15 \text{ K}) = 73.42 \pm 0.20 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ = 17.55 \pm 0.05 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

This value is in almost exact agreement with the value, $17.54 \pm 0.15 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, obtained by Pitzer and Smith [44], based on the solution data on $\text{Ag}_2\text{O}(\text{c})$ and on earlier measurements of the precipitation of AgCl . We believe the excellent concordance obtained in the various determinations listed in table 9 indicates that the silver halides encountered in the various calorimetric experiments are in the same thermodynamic states as those in the solubility measurements and in the electrochemical measurements. The effects of such factors as particle size or degree of crystallinity for these halides under ordinary conditions must be smaller than can be detected by our present calorimetric techniques.

TABLE 9. Selection of entropy of $\text{Ag}^+(\text{aq})$

Source	$S^\circ(298.15 \text{ K})$	
	$\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
EMF.....	73.08 ± 0.40	17.47 ± 0.10
AgCl	73.41 ± 0.20	17.55 ± 0.05
AgBr	73.31 ± 0.35	17.52 ± 0.09
AgI	73.50 ± 0.80	17.57 ± 0.20
AgNO_3	73.67 ± 0.15	17.61 ± 0.04
Weighted mean.....	73.42 ± 0.20	17.55 ± 0.05

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