JOURNAL OF RESEARCH of the National Bureau of Standards
Vol. 84, No. 4, July–August 1979

Enthalpies of Solution of KBr, KI, KIO_3, and KIO_4 in H_2O

M. E. Efimov, G. N. Klevaichuk, V. A. Medvedev

Institute of High Temperatures, Academy of Sciences, Moscow, USSR

and

Marthada V. Kilday

Center for Thermodynamics and Molecular Science, National Bureau of Standards, Washington, DC 20234

March 7, 1979

Enthalpy of solution measurements of four potassium salts in H_2O were made in either an adiabatic or an isoperibol calorimeter or both. The following summarizes the measured and recommended values:

Salt	$\Delta H°(\infty, 298.15\ K)$, $kJ \cdot mol^{-1}$		
	Isoperibol	Adiabatic	Recommended
KBr	19.851 ± 0.027	19.709 ± 0.045	19.78 ± 0.08
KI	20.145 ± 0.024	—	20.15 ± 0.20
KIO_3	27.628 ± 0.059	—	27.65 ± 0.10
KIO_4	—	63.49 ± 0.20	63.50 ± 0.30

The value for KIO_4 has been corrected for the hydrolysis of the periodate ion. The $\Delta C_p = -(82.5 \pm 4.3) J \cdot mol^{-1} \cdot K^{-1}$ for the unhydrolysed reaction. For the reaction of KBr in H_2O, ΔC_p was measured as $-(166.6 \pm 7.2)\ J \cdot mol^{-1} \cdot K^{-1}$ in the temperature range 298 K to 319 K.

Measurements with the isoperibol calorimeter are also reported for the endothermic reaction of tris(hydroxymethyl)aminomethane, SRM 724a, in aqueous NaOH ($0.05\ mol \cdot L^{-1}$).

Comparisons of measurements by different calorimeters on the same samples reveal unidentified calorimetric errors for endothermic reactions which are greater than the imprecision of the measurements.

Key Words: Endothermic solution reactions, enthalpy of solution, KBr, KI, KIO_3, KIO_4, tris(hydroxymethyl)aminomethane, solution calorimetry, thermochemistry.

1. Introduction

Parker [1][1] has summarized enthalpy of solution data through 1963 for KBr, KI, and KIO_3. Since then other measurements [2–6] have been made, but differences still exist in the measured values beyond the assigned uncertainties which are undesirably large. This work was undertaken in an attempt to resolve or explain some of these differences since accurate enthalpy of solution data are needed for calculating the enthalpy and entropy of formation of the anions.

Only one other measurement of the enthalpy of solution of KIO_4 has been reported previously [7] and more information about this material was needed. However, the solution of KIO_4 in water proceeded slowly and measurements with an isoperibol calorimeter proved unsatisfactory. Therefore, the adiabatic solution calorimeter was used for the measurements reported here.

Measurements of the enthalpy of solution of the same sample of KBr were made with the isoperibol (at Moscow) and the adiabatic (at Washington) calorimeters. Both of these calorimeters are capable of calorimetric imprecision of less than $0.01\ kJ \cdot mol^{-1}$ for this reaction, and yet the mean values for the enthalpy of solution differed by more than $0.14\ kJ \cdot mol^{-1}$ when using the same sample of KBr. This large and unexplained discrepancy has necessitated the assignment of overall uncertainties to the recommended values which are larger than normal, and may be an indication of presently unknown systematic errors.

The enthalpy of solution measurements made by E., K., and M. at the Institute of High Temperatures (USSR) with KBr, KI, KIO_3 and SRM 724a are described in section 2;

---

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

those made by M.V.K. at the National Bureau of Standards (USA) with KBr and KIO_4 are described in section 3. The 1975 Atomic Weights [8] were used in calculating the following molecular masses for this work; KBr, 119.0023; KI, 166.0028; KIO_3, 214.0010; KIO_4, 230.0004; and H_2O, 18.0152. Energy conversions are made using 4.184 joules = 1 thermochemical calorie.

2. Measurements with the Isoperibol Calorimeter (USSR)

The potassium salts used in the calorimetric measurements were treated as follows: commercial "chemically pure" samples of KBr and KIO_3 were thrice recrystallized from double-distilled water. A similar sample of KI was not recrystallized. The salts were ground in an agate mortar, dried in vacuum (approximate pressure: 0.1 Pa or 10^{-3} mm Hg) at 373 K to constant mass, and stored with a desiccant. These materials were all prepared by E., K., and M. in Moscow, were assumed to be pure, and were not analyzed.

An LKB 8700 Precision Calorimetry System[2] was used for the enthalpy of solution measurements at Moscow. The mean temperature of each experiment was 298 K, the water ($\sim$100 g) in the reaction vessel was weighed to the nearest mg, and the mass of the calorimetric samples of the salts in glass ampoules (filled in air) was estimated to be uncertain by 50 μg. The energy of breaking the ampoules and comparisons of measurements with standard materials were determined previously [9].

The energy equivalent in each experiment was determined as the mean of two electrical calibrations, one before and one after the chemical reaction. During the endothermic solution reactions the vessel temperature decreased over approxi-

---

[2] Commercial materials are identified in this paper in order to specify the experimental procedure adequately. Such identification does not imply recommendation nor endorsement by the National Bureau of Standards (U.S.A.).

Table 1. Data for measurements of the enthalpy of solution of KBr(c) in $H_2O(\ell)$ with the isoperibol calorimeter (USSR)

KBr	Conc. (m)	ε	$\Delta R/R_{av}$	$-Q$	$-Q$ amp	$\Delta H_m(T)$		T	Q_T	ϕ_L°	$\Delta H^\circ(\infty, 298.15\ K)$
x10^5	x10^5	x10^1	x10^7	x10^3	x10^3	x10^3	x10^0	x10^2	x10^0	x10^0	x10^0
g	mol/kg	J/temp. unit	temp. unit	J	J	J/g	J/mol	K	J/mol	J/mol	J/mol
Series I:											
120030	10064	111822	180923	202312	26	168529	20055	29843	45	280	19820
100035	8356	111246	151829	168904	30	168814	20089	29840	41	278	19852
90038	7598	111223	136917	152283	32	169097	20123	29838	37	275	19885
70064	5894	111397	106348	118469	35	169036	20116	29850	58	266	19908
50060	4211	111575	75816	84591	38	168903	20100	29832	28	247	19881
40010	3350	111612	60571	67605	40	168868	20096	29831	27	233	19890
30013	2515	111906	45205	50587	42	168414	20042	29829	24	216	19850
25016	2105	111426	37782	42099	43	168117	20006	29823	13	203	19816
20019	1683	111318	30221	33642	44	167830	19972	29827	20	187	19805
14979	1260	111396	22640	25221	44	168078	20002	29826	19	164	19857
9992	838	110684	15160	16780	45	167472	19930	29823	14	146	19798
										Mean	19851
										sdm	11
										Uncertainty (95%)	25
Series II:											
54073	4551	[a]112003	81363	91129	38	168459	20047	29846	51	249	19849
49758	4189	112013	74951	83955	39	168648	20070	29828	21	245	19846
53544	4508	112090	80580	90322	38	168616	20066	29830	24	249	19841
										Mean	19845
										sdm	2
										Uncertainty (95%)	10

[a] Calculated from one electrical calibration following the solution reaction.

ately the same range as the temperature increase for the lectrical calibrations. Correction to the temperature change, T, for the heat exchange with the environment was calcuated by the Dickinson method. The thermistor of the alorimeter was calibrated by comparison with a quartz thermometer which was standardized at the fixed triple point of water (accuracy > 0.005 K). The measured enthalpy of solution for each experiment was corrected to 298.15 K using ΔC_p values calculated from the heat capacities of the crystal salts [10] and of their solutions [1].

able 2. Data for measurements of the enthalpy of solution of KI(c) in $H_2O(\ell)$ with the isoperibol calorimeter (USSR)

KI	Conc. (m)	ε	$\Delta R/R_{av}$	$-Q$	$-Q$ amp	$\Delta H_m(T)$		T	Q_T	ϕ°_L	$\Delta H^\circ(\infty, 298.15\ K)$
$x10^5$	$x10^5$	$x10^1$	$x10^7$	$x10^3$	$x10^3$	$x10^3$	$x10^0$	$x10^2$	$x10^0$	$x10^0$	$x10^0$
g	mol/kg	J/temp. unit	temp. unit	J	J	J/g	J/mol	K	J/mol	J/mol	J/mol
120060	7160	112869	130502	147296	29	122661	20362	29838	37	247	20152
99991	6082	112451	108798	122345	32	122324	20306	29836	34	242	20098
90029	5475	112496	98381	110675	33	122896	20401	29835	33	239	20195
70035	4189	112405	76401	85878	36	122571	20347	29833	30	231	20146
50040	2991	112345	54454	61176	40	122175	20281	29842	45	215	20111
39983	2399	112178	43765	49095	41	122685	20366	29829	23	206	20183
30011	1803	111902	32892	36807	42	122502	20336	29828	22	187	20171
24970	1503	113219	27034	30607	43	122402	20319	29727	20	177	20162
20009	1197	112307	21826	24512	44	122282	20299	29827	20	161	20158
15013	901	111929	16392	18348	45	121913	20238	29825	17	145	20110
10012	602	111564	10970	12238	46	121781	20216	29825	17	126	20107
										Mean	20145
										sdm	10
										Uncertainty (95%)	22

Table 3. Data for measurements of the enthalpy of solution of $KIO_3(c)$ in $H_2O(\ell)$ with the isoperibol calorimeter (USSR)

KIO_3	Conc. (m)	ε	$\Delta R/R_{av}$	$-Q$	$-Q$ amp	$\Delta H_m(T)$		T	Q_T	ϕ°_L	$\Delta H^\circ(\infty, 298.15\ K)$
$x10^5$	$x10^5$	$x10^1$	$x10^7$	$x10^3$	$x10^3$	$x10^3$	$x10^0$	$x10^2$	$x10^0$	$x10^0$	$x10^0$
g	mol/kg	J/temp. unit	temp. unit	J	J	J/g	J/mol	K	J/mol	J/mol	J/mol
20022	5574	112578	136744	153944	32	128237	27443	29866	96	-123	27662
00014	4627	112917	114134	128877	35	128824	27568	29838	44	- 71	27684
90028	4205	111902	103334	115633	36	128402	27478	29838	44	- 33	27555
70015	3280	111328	81361	90578	38	129316	27674	29832	33	- 3	27710
50002	2336	111624	57807	64527	41	128967	27599	29832	34	39	27594
40026	1872	111509	46457	51804	42	129322	27675	29831	32	53	27654
29494	1366	112201	34523	38735	43	131186	28074	29827	24	68	28030*
25009	1165	112286	28820	32361	44	129224	27654	29828	26	73	27607
19978	924	112934	22974	25945	45	129644	27745	29826	22	78	27689
14997	696	112266	17287	19407	45	129105	27629	29826	22	81	27570
10006	469	111442	11628	12958	46	129037	27615	29825	21	83	27553
										Mean	27628
										sdm	19
										Uncertainty (95%)	43

mitted from mean

In tables 1, 2, and 3 are the data for 11 enthalpy of solution measurements each of KBr, KI, and KIO_3 in water made early in 1975. The respective concentration ranges are 8 to 101, 6 to 72, and 4 to 56 $mmol \cdot kg^{-1}$; the experiments are listed in order of descending concentration.

Three additional measurements of the KBr reaction (listed as Series II) were made in September 1977 to check the effects of long term storage of the sample in a closed container over a desiccant. The KBr sample in the first experiment of Series II was used without further treatment. For the second experiment, the sample was again ground in an agate mortar and heated in air at 373 K for 25 h. The sample in the third experiment was reground but not heated. The values obtained in Series II agree well with each other, but are lower than the value obtained in Series I at the same concentration by approximately the combined uncertainties for the two series. This problem will be discussed later in greater detail.

The sample mass and the concentration of the final solution are given in the first two columns of the tables. ϵ is the mean of the electrical energy equivalents for the initial and final systems expressed as joules (temperature unit)$^{-1}$; $\Delta R/R_{av}$ is the ratio of the increment in the thermistor resistance to the average resistance (this value is proportional to ΔT) and is expressed in temperature units; Q is the measured heat of the solution reaction and $Q = \epsilon(\Delta R/R_{av})$; Q_{amp} is the energy for breaking the ampoules plus a vaporization correction for the air space in each ampoule; and $\Delta H_m(T)$ is the enthalpy of solution at the concentration, m, and at the mean temperature of reaction, T. Q_T is the correction to $T = 298.15$ K, ϕ_L° is the correction to infinite dilution [1], and ΔH° (∞, 298.15 K) is the enthalpy of solution at infinite dilution at the standard temperature of reaction. For each group of experiments the mean and th uncertainty at the 95 percent confidence interval are given The values in the last column were treated by dispersa analysis, i.e., a value was omitted from the mean if i differed from the mean by more than permitted in the norma r-distribution [11]; the value in table 3 marked * was thu omitted from the mean.

In table 4 are the data for six measurements of th enthalpy of solution of the endothermic reaction of NB Standard Reference Material No. 724a, tris(hydroxymethyl)aminomethane, in aqueous NaOH (0.050 $mol \cdot L^{-1}$) These values will later be compared with previously published measurements with the adiabatic calorimeter. For th correction to the standard temperature, Q_T, in table 4, ΔC $= 1.025 \pm 0.025$ $J \cdot g^{-1} \cdot K^{-1}$ [12]. The correction to th standard NaOH concentration, 0.050 $mol \cdot L^{-1}$, is $-87.$ $(0.05\text{-}m) + 43.2\ (0.05\text{-}m)^2$ [12]. The concentration of th NaOH stock solution used for the calorimetric solutions wa measured before the first experiment, and after the third an sixth experiments; the six experiments were completed withi a period of three days. An overall uncertainty of 0.13 $J \cdot g^{-}$ in the mean value is the sum of the following uncertainties sample mass, 0.014 $J \cdot g^{-1}$; correction to standard temperature, 0.004 $J \cdot g^{-1}$; correction to standard concentration, 0.0 $J \cdot g^{-1}$; and experimental uncertainty (95%), 0.072 $J \cdot g^{-1}$.

3. Measurements with the Adiabatic Calorimeter (USA)

The platinum-lined, adiabatic solution calorimeter use by M.V.K. for measuring the enthalpy of solution of KBr an KIO_4 in H_2O was described in detail previously [13]. Th KBr was from the same sample described in section 2 o

Table 4. Data for measurements of the enthalpy of solution of tris(hydroxymethyl)aminomethane, SRM 724a, in aqueous NaOH (0.05 $mol \cdot L^{-1}$) with the isoperibol calorimeter (USSR).

SRM 724a Mass	Conc. (m)	ε	ΔR/R$_{av}$	-Q	-Q amp	ΔH$_m$(T)	T	Q$_T$	Corr. to 0.050 mol/L NaOH	ΔH(298.15 K, 0.050 mol/L)	
x10^6	x10^4	x10^1	x10^8	x10^4	x10^4	x10^3	x10^2	x10^3	x10^3	x10^3	
g	mol/L	J/temp. unit	temp. unit	J	J	J/g	K	J/g	J/g	J/g	kJ/mol
505222	494	112255	640193	718649	295	142186	29831	164	53	141969	17198
509775	493	112299	645362	724735	293	142110	29832	174	61	141875	17186
503170	492	112263	637789	716001	295	142239	29831	164	70	142005	17202
501369	490	112301	635122	713248	296	142201	29831	164	88	141949	17195
513528	487	112286	650938	730912	292	142275	29832	174	114	141987	17200
501019	485	112199	634918	712372	296	142126	29831	164	132	141830	17181
									Mean	141936	17194
									sdm	28	3
									Uncertainty (95%)	72	9

which measurements were made with the isoperibol calorimeter. Three portions of this material were vacuum dried for 26 h at 375 K; in each portion the loss in mass was less than 0.01 percent. Therefore no corrections to the calorimetric results were made for volatile matter. The KIO_4 was a commercial sample of chemically pure grade obtained from a Hungarian firm; it was not further purified, but was dried in vacuum at about 373 K by the coauthors (USSR). (Some preliminary experiments with a commercial sample obtained in the U.S. without any further treatment gave very erratic results—this may have been caused by non-uniformly distributed H_2O.)

Attempts to determine the purity of the KBr and KIO_4 samples from freezing temperature measurements were unsuccessful. The KBr apparently sublimed before melting, and the KIO_4 underwent decomposition and loss of mass before melting.

The calorimetric samples of both KBr and KIO_4 were transferred in the laboratory atmosphere to the platinum sample holder (see [13]). The sample holder has interchangeable cylinders of different capacities; the 3.0-cm^3 cylinder was used in the KBr work, and the 0.7-cm^3 cylinder, in the KIO_4 work. The calorimeter contained approximately 300 mL of H_2O weighed to the nearest mg.

Each experiment consisted of electrical calibrations of the initial and final systems, and precisely measured electrical energy was added during the endothermic solution reactions to prevent a decrease in the calorimeter temperature. Details of the measurement procedures and calculations were given previously [12, 13]. The measurements reported here were completed between December 1976 and May 1977. In ugust 1975 the quartz oscillator thermometer was last alibrated by comparison with a calibrated platinum resistnce thermometer. Previous observations of this quartz thermometer system indicated that the frequency change of he quartz oscillator with temperature was linear between 95 and 350 K. During a previous period of 19 months the slope of the frequency-temperature line changed by less than .01 per cent and the intercept, by ± 0.01 K; these changes re within the measurement uncertainties. (In the experimenal measurements, the absolute temperature is needed only o the nearest 0.01 K for the temperature of reaction; and the lope for ΔT over a relatively small temperature range must emain constant only during the course of the experiment ince each system is calibrated electrically.) The NBS alibrations of the electrical energy measurement standards ere as follows: 0.1-Ω, 10-Ω, and 10-kΩ standard resistors n January 1973 and December 1977, and the saturated tandard cell in March 1973 and January 1978. Records of requent calibrations of these standards over a period of more han a decade provide confidence in the values used to better han 0.005 percent.

The data for measurements of enthalpies of solution of the Br in H_2O (7 experiments) are given in table 5, and of KIO_4

Table 5. Data for measurements of enthalpy of solution of KBr(c) in $H_2O(\ell)$ with the adiabatic solution calorimeter (USA).

Expt. No.	KBr x10^5	Conc.(m) x10^5	ε x 10^2 Initial	ε x 10^2 Final	ΔT x10^6	EIt x10^3	$-q_{vap}$ x10^3	$-Q_{react}$ x10^3	ΔH(T) x10^3	ΔH(T) x10^0	T x10^3	Q_T x10^0	corr. to ∞ dil. x10^0	ΔH°(∞,Δ298.15 K) x10^0
	g	mol/kg	J/K		K	J	J	J	J/g	J/mol	K	J/mol	J/mol	J/mol
1249	151871	4220	173288	173030	362041	881999	88	255004	167908	19982	298280	22	- 245	19759
1250	149711	4160	173418	173158	375941	880966	153	229352	153197	18231	308546	1732	- 245	19718
1251	151432	4209	173584	173383	391011	889088	252	210496	139004	16542	318686	3421	- 245	19718
1252	150124	4172	173368	173173	373823	889038	119	241194	160663	19119	303475	887	- 245	19761
1253	150356	4178	173218	172995	371364	894845	88	251902	167536	19937	298000	- 25	- 245	19667
1254	252195	7008	173324	173037	267641	887941	75	424364	168268	20024	297945	- 34	- 272	19718
1256	54045	1504	173182	173038	461172	888227	20*	89872	166291	19789	298239	15	- 179	19625
													Mean	19709
													sdm	18
													Uncertainty(95%)	42

---

*The sample holder volume in the last experiment is 0.7 cm^3, and 3.0 cm^3 in all others.

in H_2O (20 experiments), in table 6. In these tables the Expt. No. is a serial number of experiments with the adiabatic solution calorimeter. The electrical energy equivalents, ϵ, of the initial (ϵ_i) and final (ϵ_f) systems are given. The net temperature change, ΔT, is the result of the endothermic solution reaction and the addition of precisely measured electrical energy, EIt. A correction, q_{vap}, is made for the heat absorbed during the vaporization of water into the air space in the sample holder when it is exposed to the calorimetric solution. $q_{vap} = \Delta H_{vap}\left(V - \frac{s}{d}\right)(1 - RH)$ where ΔH_{vap} is the enthalpy of vaporization of water per unit volume [14], V is the volume of the sample holder, s is the mass of sample, d is the density of the sample, and RH is the relative humidity of the atmosphere where the sample holder was filled (in this work $RH = 0.35 \pm 0.10$). The endothermic heat of the solution reaction is

$$Q_{\text{react}} = \frac{\epsilon_i + \epsilon_f}{2}(\Delta T) - (EIt) - q_{vap}$$

The enthalpy of solution at the mean temperature of reaction T, is $\Delta H(T) = -Q_{\text{react}}/s$. Buoyancy factors of 1.00029 fo KBr and 1.00018 for KIO_4 were used to obtain the mass o sample; the densities were 2.75 g·cm^{-3} for KBr [15], an 3.66 g·cm^{-3} for KIO_4 which was the mean of two measurements (3.648 and 3.662 g·cm^{-3}) on this sample by displacement of CCl_4 as previously described [16a].

The reaction of KBr in H_2O was rapid at the moderat stirring rate of 550 rpm and the reaction period for a experiments in table 5 was about 15 min. The arrangement i chronological according to experiment number. The data fo T and $\Delta H(T)$ in the first five experiments at a concentratio of 42 mmol·kg^{-1} are plotted in figure 1. A least squares fit a linear equation to these data (temperature range 298 K t

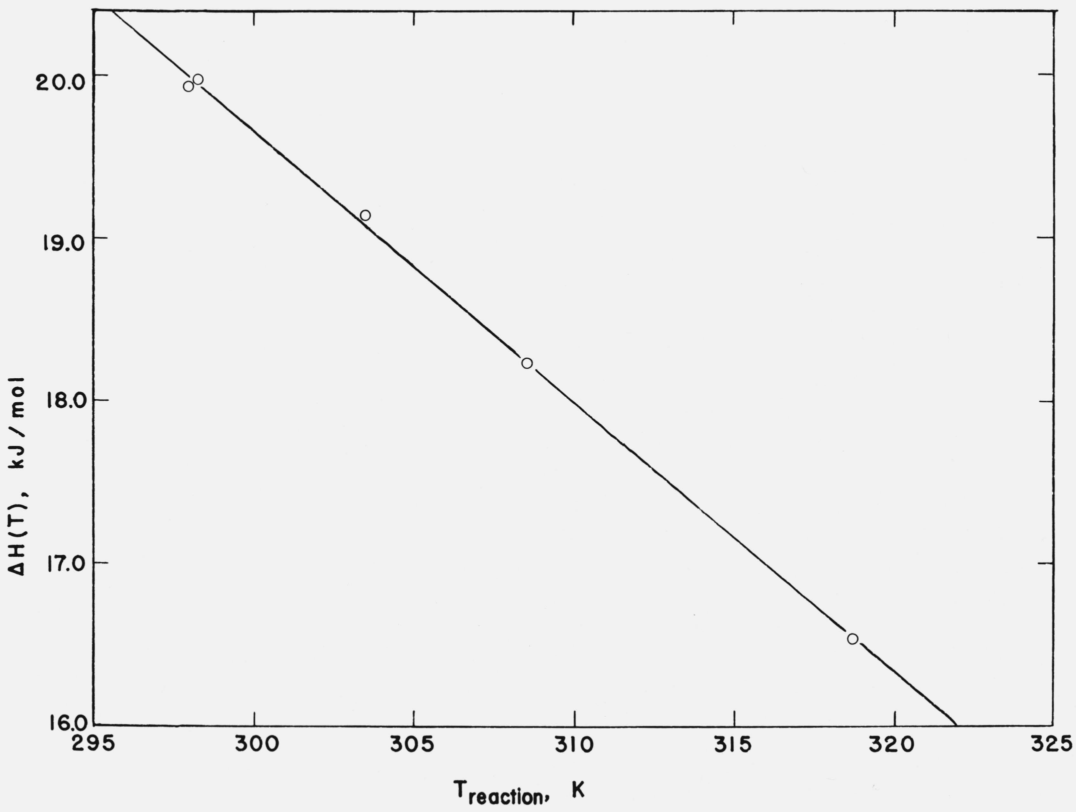

FIGURE 1. *Plot of the enthalpy of solution of KBr(cr) in H_2O at a concentration of 42 mmol·kg^{-1} as a function of the mean temperature of reaction.*

The line shown is the result of a least squares fit of a linear equation to the data; the slope or $\Delta C_p = -(166.6 \pm 7.2)$ J·mol^{-1}·K^{-1}.

Table 6. Data for measurements of enthalpy of solution of $KIO_4(c)$ in $H_2O(\ell)$ with the adiabatic solution calorimeter (USA).

Expt. No.	Reaction Period	KIO_4	Conc. (m)	$\varepsilon \times 10^2$		ΔT	EIt	$-q_{vap}$	$-Q_{react}$	Cal. unc.	$\Delta H(T)$		T	Q_H	$\Delta H(T)_{corr.}$
		$x10^5$	$x10^5$	Initial	Final	$x10^6$	$x10^3$	$x10^3$	$x10^3$	$x10^2$	$x10^3$	$x10^0$	$x10^3$	$x10^0$	$x10^0$
	min.	g	mol/kg	J/K		K	J	J	J	%	J/g	J/mol	K	J/mol	J/mol
1246	178	82714	1182	173197	173157	318005	882587	19	222755	14	271077	62348	298273	1105	63453
1245	218	85118	1224	173161	173108	376419	882981	18	231252	19	271684	62487	298443	1095	63582
1284	43	89687	1290	173370	173298	376125	894781	24	242804	6	270724	62267	303340	819	63086
1296	73	88981	1280	173312	173219	365507	874242	24	240920	8	270755	62274	303367	817	63091
1295	48	89769	1291	173416	173372	368176	880914	27	242492	5	270129	62130	306047	699	62829
1241	123	87131	1253	173400	173367	372211	881455	31	236072	10	270939	62316	308464	---	---
1244	58	86949	1250	173420	173330	374464	883342	36	234079	6	269214	61919	311190	522	62441
1293	23	50232	722	173438	173432	430024	880822	48	134962	6	268677	61796	313165	---	---
1247	33	23830	343	173465	173416	471669	882464	54	64345	12	270016	62104	313498	---	---
1292	53	89502	1287	173581	173463	371240	884798	41	240574	5	268792	61822	314038	446	62268
1242	93	87750	1262	173414	173340	363712	868036	42	237401	8	270542	62225	314136	---	---
1282	38	87771	1262	173524	173495	375862	887655	45	235454	4	268259	61700	315579	409	62109
1287	23	87598	1260	173495	173452	376191	887637	45	235000	3	268271	61702	316418	391	62093
1243	53	83036	1194	173510	173398	379450	881129	49	222099	6	268448	61743	316585	387	62130
1281	38	90276	1298	173480	173423	377623	896365	49	241323	5	267317	61483	317733	364	61847
1239	53	88064	1266	173554	173479	372397	881641	52	235419	5	267327	61485	318605	348	61833
1240	53	87531	1258	173532	173576	376843	887898	52	233820	6	267128	61440	318622	347	61787
1238	83	87188	1254	173576	173500	374264	882490	52	232948	7	267179	61451	318630	347	61798
1283	33	88294	1270	173746	173656	371929	881014	63	234907	5	266050	61192	322760	278	61471
1291	18	89565	1288	174083	174002	368830	875508	103	233484	3	260687	59958	334314	155	60113

319 K) gave the slope or $\Delta C_p = -(166.6 \pm 7.2)$ $J \cdot mol^{-1} \cdot K^{-1}$ where the uncertainty is at the 95 percent confidence level. This value was used in calculating Q_T, the corrections to $T = 298.15$ K given in table 5. It is in excellent agreement with -167 $J \cdot mol^{-1} \cdot K^{-1}$ calculated from the heat capacity of the pure crystal [17] and the apparent molal heat capacity at the mean concentration [1]. The corrections to infinite dilution in table 5 were obtained from Parker's Table XVA [1].

The last two experiments in table 5 at other concentrations confirm Parker's ϕ_L values within the uncertainties.

The reaction of KIO_4 in H_2O was slow and required about 3 hours at 298 K. Therefore, experiments were done at higher temperatures in order to reduce the time and the experimental uncertainty. Because of the relatively high density of KIO_4 a high stirring rate, 700 rpm, and the smallest sample cylinder, 0.7 cm^3 in volume, were used. The experiments in table 6 are arranged according to ascending temperature of reaction, T. The experiment number indicates the chronological order of the experiments. In general the duration of the reaction period decreases with increasing temperature, however, it is also dependent on the sample mass and the manner in which the sample holder opens. The estimated calorimetric uncertainty for the individual experiments given in table 6 was calculated as a percentage of the temperature change of the solution reaction, $\Delta T_{\text{react}} = Q_{\text{react}}\left(\frac{\epsilon_i + \epsilon_f}{2}\right)$, according to the following equation:

$$\text{Cal. unc.} = \frac{2(sds)(\Delta t)}{\Delta T_{\text{react}}} \times 100$$

where *sds* is the standard deviation of the slope of the rating period following the reaction, and Δt is the time interval from the mid-time of this rating period back to the time of initiating the reaction. This calculation has been described in detail [16b] and is a useful indicator for sources of error beyond the measurement error.

In table 6, Q_H is a correction for the heat of hydrolysis of the periodate ion (to be discussed in section 4), and $\Delta H(T)_{corr}$ is the enthalpy of solution of the unhydrolysed reaction.

Figure 2 is a plot the data from table 6 for $\Delta H(T)$ and $\Delta H(T)_{\text{corr}}$ as a function of T. The concentration was about 12 $mmol \cdot kg^{-1}$ in all except two experiments which were not plotted nor included in averages. The circled points represent the enthalpies of solution under the experimental conditions, $\Delta H(T)$. The radius of the circle is equal to the estimated calorimetric uncertainty of the individual experiment. An apparent change of slope occurred at about 317 K. The two points marked "A" at 308 K and 314 K (Expt. Nos. 1241 and 1242) deviate from the line by more than their individual experimental uncertainties; this suggests sample inhomogeneity. These two experiments were not included in the calculations. Linear equations were fitted to the data for th 10 points below 317 K and the 6 points above 317 K by th method of least squares with the following result (i $kJ \cdot mol^{-1}$):

$$\begin{array}{llll} \Delta H(T) & = 62.447 - & 0.0401\,(T - 298.15\ \text{K}), & \\ \pm 0.047 & \ \ \pm 0.026 & \pm 0.0021 & \\ & & 298\ \text{K} \leq T < 317\ \text{K} & (1 \end{array}$$

$$\begin{array}{llll} \Delta H(T) & = 61.710 - & 0.0938\,(T - 316\ \text{K}), & \\ \pm 0.07 & \ \ \pm 0.041 & \pm 0.0050 & \\ & & 316\ \text{K} \leq T < 335\ \text{K} & (\end{array}$$

(The uncertainties are the standard deviations.) The fit of th data for all 16 experiments to a quadratic equation resulte in 62.399 ± 0.034, −0.0151 ± 0.0042, and −0.00144 0.00012 for the constants of the first, second, and thir terms, respectively; the standard deviation of the fit wa 0.057 $kJ \cdot mol^{-1}$. This partially hydrolysed reaction may b expressed by the following equation:

$$KIO_4(cr) + (4400 + 2x)H_2O(l)$$
$$= [K^+ + (1 - x)IO_4^- + xH_4IO_6^- + 4400\ H_2O]_{(sln)} \quad ($$

The points shown as "x" in figure 2 represent the values $\Delta H(T)_{\text{corr}}$ given in table 6 which are the measured enthalpie of solution corrected for the hydrolysis of the periodate io (to be discussed in section 4). Obviously the hydrolysis wa the cause of the apparent change of slope observed in th experimental results.

4. Discussion and Summary

Parker summarized and evaluated the published dat through 1963 for the enthalpies of solution in H_2O of KBr KI, and KIO_3. Her selected values are given in table 7 wit the individual values on which her selection was based, a well as the results of measurements since 1965. The uncertainties assigned to the various values were estimated b Parker and ourselves based on the experimental procedures the number of measurements, the experimental imprecision the magnitude of the corrections to the standard temperature etc. The uncertainties given for this work include th experimental uncertainty at the 95 percent confidence level 10 $J \cdot mol^{-1}$ for uncertainty in the sample mass, an 10 $J \cdot mol^{-1}$ for uncertainty in the ϕ_L° values for KBr and K the latter uncertainty was estimated to be 40 $J \cdot mol^{-1}$ fo KIO_3. For KIO_4, an additional uncertainty of 80 $J \cdot mol^{-1}$ wa added because of the unknown sample purity and homogeneity.

The experimental results for the solution of crystallin KIO_4 in H_2O given in section 3 include a partial hydrolysi reaction for which a correction must be made in order t obtain only the periodate as the anion product. Crouthamel

Hayes, and Martin [33] have reported $\Delta H = 10.9$ kcal (or 45.6 kJ) from 0 °C to 70 °C for the reaction

$$H_4IO_6^- = 2H_2O + IO_4^- \qquad (4)$$

From their work, Parker [34] derived the following equation

$$\log K_H = \frac{2382}{T} - 9.591$$

from which the ionization constant for the hydrolysis reaction, K_H, can be calculated at various temperatures. When the degree of ionization, $\alpha = \frac{K_H}{K_H + 1}$, calculated for the experiments given in table 6 was multiplied by 45600 J·mol^{-1} we obtained the corrections, Q_H, which were added to $\Delta H(T)$. The fit of 15 temperature and corrected enthalpy values, $\Delta H(T)_{\mathrm{corr}}$, to a linear equation by the method of least squares gave the following equation:

$$\underset{\pm 0.059}{\Delta H(T)_{\mathrm{corr}},\ \mathrm{kJ \cdot mol^{-1}}} = \underset{\pm 0.031}{63.528} - \underset{\pm 0.0020}{0.0825}\ (T - 298.15\ \mathrm{K}) \qquad (5)$$

where the uncertainties are the standard deviations. (Expt. No. 1291 was not included here because of its large residual deviation.) Thus, $\Delta C_p = -(82.5 \pm 4.3)$ J·mol^{-1}·K^{-1} for the

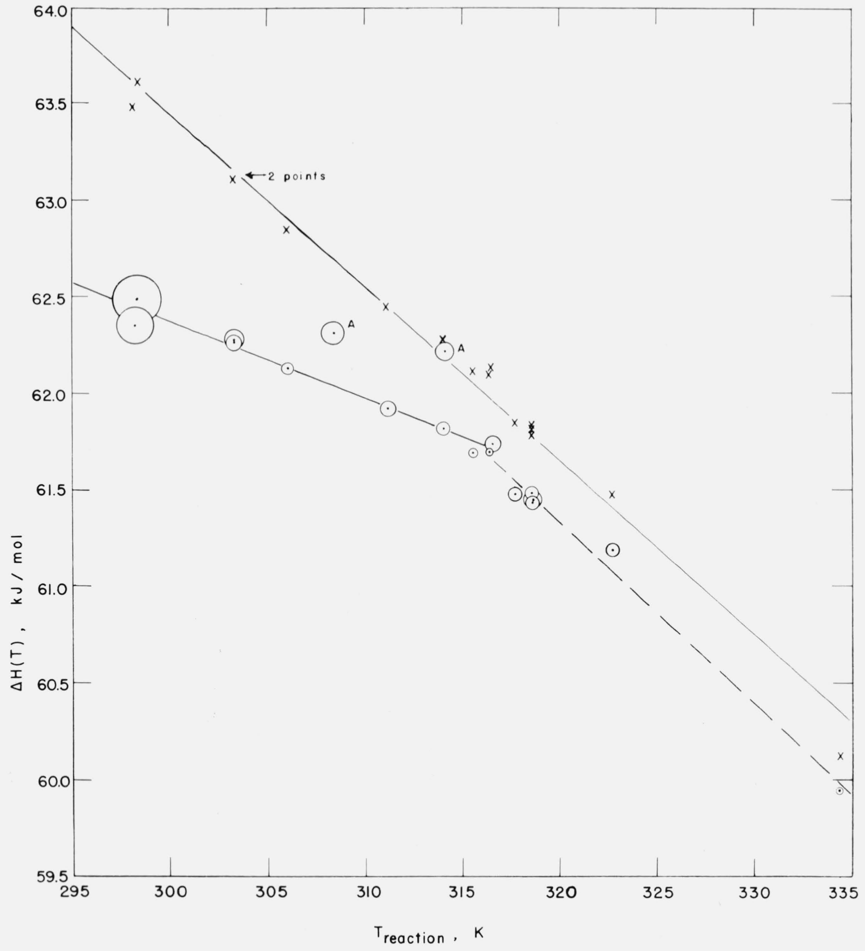

FIGURE 2. *Plot of the enthalpy of solution of $KIO_4(cr)$ in H_2O as a function of the mean temperature of reaction.*

The points surrounded by a circle represent the measured values, ΔH(T), from table 6; the radius of the circle is equal to the estimated calorimetric uncertainty for the experiment. The points marked "A" were omitted from the calculations because of their large displacement from the group which may indicate sample inhomogeneity. The values corrected for the partial hydrolysis of the periodate ion, $\Delta H(T)_{\mathrm{corr}}$, are shown as X's.

Table 7. Comparison of this work with other published values, and recommended values for enthalpies of solution of KBr, KI, KIO_3, and KIO_4

Authors, Year, and Reference	T	No. of Meas.	Concentration	ΔH°(∞, T)
	K		mol/kg	kJ/mol
<u>KBr</u>				
Thomsen, 1883 [18]	292.8	2	0.28	19.95 ± 0.40
Brönsted, 1906 [19]	293.2	8	0.08	19.90 ± 0.20
Walden, 1907 [20]	289.8	2	0.28	19.78 ± 0.20
Wüst and Lange, 1925 [21]	298.15	31	5.25-0.37	19.99 ± 0.20
Popov, Bundel, and Choller, 1930 [22]	273.	7	0.19	19.60 ± 0.25
Chipman, Johnson and Maass, 1929 [23]	289.0-300.2	30	0.43-0.09	19.89 ± 0.40
Fedorov and Sil'chenko, 1937 [24]	296.6	3	0.56-0.14	20.46 ± 0.50
Lange and Martin, 1937 [25]	---	1	0.13	20.01 ± 0.20
Popov, Skuratov, and Strel'tsova, 1940 [26]	273.6	---	0.12	19.00 ± 0.40
Hietala, 1960, [27]	298.15	3	0.28	19.828 ± 0.085
Parker's "Best" value, 1965 [1]	298.15	---	---	19.874 ± 0.084
Krestov and Abrosimov, 1967 [2]	298.15	4	0.042-0.009	19.790
Tsvetkov and Rabinovich, 1969 [3]	298.15	1	0.111	19.80 ± 0.20
Joly, Thourey, and Pérachon, 1973 [5]	298.15	---	0.0174	19.581 ± 0.088
Olofsson, 1977 [6]	298.15	7	0.07-0.05	19.813 ± 0.044
This work (USSR)	298.15	11	0.1-0.008	19.851 ± 0.027
This work (USA)	298.15	7	0.042-0.015	19.709 ± 0.044
Recommended Value	298.15	---	---	19.78 ± 0.08
<u>KI</u>				
Thomsen, 1883 [18]	292.	2	0.28	20.21 ± 0.40
Wüst and Lange, 1925 [21]	298.15	24	7.95-0.29	20.49 ± 0.25
Lange and Martin, 1937 [25]	298.15	1	0.11	20.39 ± 0.25
Popov, Shuratov, and Strel'tsova, 1940 [26]	293.6	1	0.09	20.04 ± 0.40
Bobtelsky and Lairsch, 1950 [28]	297.6	1	0.30	21.00 ± 0.80
Kapustinskii and Drakin, 1952 [29]	298.15	1	0.0008	20.21 ± 0.30
Parker's "Best" value, 1965 [1]	298.15	---	---	20.33 ± 0.13
Tsvetkov and Rabinovich, 1969 [2]	298.15	1	0.111	20.18 ± 0.25
Joly, Thourney and Pérachon, 1973 [5]	298.15	---	0.0184	20.58 ± 0.21
This work (USSR)	298.15	11	0.006-0.07	20.145 ± 0.024
Recommended Value	298.15	---	---	20.15 ± 0.20
<u>KIO_3</u>				
Berthelot, 1878 [30]	285.2	1	0.12	23.43 ± 0.85
Thomsen, 1883 [18]	292.2	3	0.13-0.10	27.78 ± 0.40
von Stackelberg, 1898 [31]	289.2	4	0.22-0.11	27.66 ± 0.40
Spencer and Hepler, 1960 [32]	298.15	5	0.01-0.006	27.74 ± 0.20
Parker's "Best" value, 1965 [1]	298.15	---	---	27.74 ± 0.21
Masal'skaya, et al, 1971 [4]	298.15	8	---	27.30 ± 0.20
This work (USSR)	298.15	10	0.005-0.06	27.628 ± 0.059
Recommended Value	298.15	---	---	27.65 ± 0.10
<u>KIO_4</u>				
Shidlovskii and Voskresenskii, 1965 [7]	298.15	4	0.015	64.6 ± 0.8
This work (USA)	298.15	16	0.012	63.49 ± 0.20
Recommended Value	298.15	---	---	63.50 ± 0.30

unhydrolysed reaction. Parker [34] estimated 0.04 kJ·mol^{-1} for the correction to infinite dilution and we obtain for the unhydrolysed reaction

$$\mathrm{KIO_4}(cr) = \mathrm{K^+ + IO_4^-}$$
$$\Delta H^\circ(298.15\,\mathrm{K}) = (63.49 \pm 0.11)\,\mathrm{kJ \cdot mol^{-1}} \qquad (6)$$

From their solubility data, Crouthamel et al. [33] calculated 63.2 kJ·mol^{-1} which is in good agreement with eq (6).

Unfortunately, little information is available regarding experimental procedures or sample purity for most of the values given in table 7. We do know that "This work (USA)" is the only work done with an adiabatic solution calorimeter; all others used isoperibol calorimeters. Without knowing the experimental procedures for the other values listed in table 7, it is impossible to relate them to the undesirably large difference in the KBr results from the two calorimeters in this work. The experimental imprecision for the calorimeters in this work is certainly smaller than for any of the others, however, the accuracy is uncertain by at least the difference in the two KBr values.

The degree of purity of the samples used probably contributes to the spread of the results in table 7, but not to the difference in KBr results in this work which were made with the same sample. Since this sample was recrystallized three times and vacuum dried to constant mass, it is probably of high purity. The recommended value for KBr is the mean of the two values obtained in this work, and the uncertainty is large enough to include both values from this work as well as a majority of the other measurements at the standard temperature.

A larger uncertainty was assigned to the recommended value for KI than for KBr because of the unknown purity; the sample in this work was not recrystallized. This recommended value and its uncertainty are now within the assigned uncertainties of most of the other measurements at the standard temperature.

The $\mathrm{KIO_3}$ sample in this work was recrystallized and vacuum dried, and is assumed to be of high purity. The uncertainty of the recommended value is primarily due to the calorimetric uncertainty.

The $\mathrm{KIO_4}$ sample was not purified nor analysed and there was evidence of sample inhomogeneity in some of the experimental results. Therefore, the uncertainty on the recommended value is large enough to include the other measurement of the enthalpy of reaction, 63.6 kJ·mol^{-1} [7], plus the correction for hydrolysis of the periodate ion.

The measurements reported here were made by two calorimeters of different types using different measurement procedures. Both calorimeters are capable of high precision and reproducibility in the measurements. The results obtained for the enthalpy of solution in water from the same sample of KBr are an indication of the accuracy of the measurements. The difference of 142 J·mol^{-1} between the mean enthalpies of solution obtained with the two calorimeters is a more realistic uncertainty in the accuracy of the measurements than the estimated experimental uncertainty of less than 50 J·mol^{-1}.

The reason for the discrepancy in the KBr results is unknown. The possibility of a systematic error was considered since the procedures used with the two calorimeters are significantly different. In the adiabatic calorimeter the adiabatic shield follows closely the temperature of the reaction vessel so that there is essentially no heat exchange between the vessel and the shield. In the isoperibol calorimeter the constant temperature of the jacket is below the calorimeter temperature for endothermic reactions, and above for exothermic reactions [35]. Both calorimeters are calibrated before and after the reaction with the addition of electrical energy which results in an increase in the calorimeter temperature (as in exothermic reactions). However, the procedures differ for endothermic reactions. In the isoperibol calorimeter, the vessel temperature is allowed to decrease in the same temperature range as the increase for the electrical calibrations. In the adiabatic calorimeter, precisely measured electrical energy is added during the endothermic reaction to maintain an increase in the calorimeter temperature (as with exothermic reactions) and to insure operation of the shield temperature control which operates by the addition of electrical energy.

The measurements of an exothermic reaction by the two calorimeters were in excellent agreement. The possibility of errors resulting from a reversal of the direction of the calorimeter temperature change in endothermic reactions led to the measurements in the isoperibol calorimeter (USSR) of another endothermic reaction, tris(hydroxymethyl) aminomethane or SRM 724a[3] in aqueous NaOH (0.050 mol·L^{-1}), reported in section 2. In addition, seven measurements of the enthalpy of solution of the same sample of KBr used in this work were made by Olofsson in Sweden [6] using another isoperibol calorimeter (LKB 8721) which was similar to that used for the USSR work. The results of her measurements are as follows:

Expt. No.	mmol KBr	$\Delta H(\infty, 298.15\ \mathrm{K})$, kJ·mol^{-1}
892	6.4124	19.807
893	5.3143	19.842
894	6.2843	19.835
895	7.5081	19.857
902	6.8160	19.760
903	6.4580	19.738
904	6.7984	19.851
		Mean = 19.813
		Sdm = 0.018

---

[3] Standard Reference Material 724a for solution calorimetry is available through the Office of Standard Reference Materials at the National Bureau of Standards, Washington, DC 20234.

In each experiment the calorimetric solution was 102.6 mL of distilled water at 297.6 K. The first three measurements used the KBr sample as received; the last four used the same KBr sample which was finely ground in an agate mortar and dried at 413 K for 2 h; there appears to be no significant difference in the results. The procedure at this laboratory is to maintain the jacket temperature above the temperature of the calorimeter for both endothermic and exothermic reactions.

The results of these and some previous enthalpy of solution measurements of exothermic and endothermic reactions where the same samples were used, are summarized in table 8. It is evident that there is good agreement in the values obtained by all three calorimeters for the enthalpy of solution of the exothermic reaction of SRM 724a in aqueous HCl. For the endothermic reaction in aqueous NaOH, the agreement is also good between the two isoperibol calorimeters, but the value from the adiabatic calorimeter is a little low although still within experimental uncertainties; the Swedish value is between those of USSR and USA. For the KBr reaction the difference in the values for the two isoperibol calorimeters is more than twice the sum of the standard deviations of the means; the two values reported in this work differ by nearly five times that amount, and again the adiabatic calorimeter has the lowest value with the Swedish value in the middle.

It is difficult to explain this disagreement. The reaction is rapid and complete within 15 min. It was shown in section 2 that grinding and heating the sample did not affect the enthalpy of solution significantly. However, the disagreement between earlier (Series I) and later (Series II) measurements at the same concentration were puzzling. Comparison of the mean values and the imprecisions for the KBr reaction does not give a full picture of the problems involved.

Figure 3 is a plot of ΔH° (∞, 298.15 K) as a function of the final concentration for the reaction of the KBr in H_2O. The 7 triangles represent the USA measurements; the 7 squares, the Swedish measurements; and the 14 circles, the USSR measurements. In Series I (open circles) the data points form a surprising curve which indicates an apparent concentration dependence. Similar plots of the data for KI and KIO_3 did not show any concentration dependence. The following is the result of a least squares fit of a quadratic equation to the data plotted in figure 3 for Series I (table 1):

$$\begin{array}{lllll} \Delta H(\infty, 298.15\ \mathrm{K}),\ \mathrm{kJ \cdot mol^{-1}} & & & & \\ \pm 0.22 & = 19.765\ + & 4.60(m) & - & 40.5(m)^2 \\ & \ \ \pm 0.020 & \pm 0.99 & & \pm 9.2 \end{array}$$

where m is the final concentration in mol·kg^{-1} and the uncertainties are the standard errors. The chronological order of these experiments was random over a period of about two months.

The scatter of the USA values in figure 3 is greater than can be attributed to the estimated calorimetric uncertainty which is equal to the radius of the circle circumscribed by a triangle. The scatter of the Swedish values is also abnormally large. It should be noted that in table 8 the standard deviations of the mean for the KBr reactions are 2 to 5 times larger than those for the endothermic reaction of SRM 724a in the three different calorimeters. This is possible evidence of occluded moisture in the samples which was not removed by vacuum drying at 373 K.

The curvature in the Series I values shown in figure 3 would appear to be the result of inadequate ϕ_L corrections. The Series I data have a maximum between 0.04 and 0.07 mol·kg^{-1}. In Parker's table XVA [1] there is a maximum for

Table 8. Values reported for some measurements of the enthalpies of solution of exothermic and endothermic reactions where the same samples were used in different calorimeters.

Reaction	ΔH(298.15 K),[a] kJ·mol^{-1}		
	Isoperibol		Adiabatic
	LKB-8721 (Sweden)	LKB-8700 (USSR)	(USA)
[b]SRM 724a in aqueous HCl	-29.76 ± 0.01 [36]	-29.77 ± 0.01 -29.75 ± 0.01 [9]	-29.77 ± 0.02 [12]
[b]SRM 724a in aqueous NaOH	17.189 ± 0.004 [37]	17.194 ± 0.003 [This work]	17.177 ± 0.007 [12]
KBr in H_2O	19.813 ± 0.018 [6]	19.851 ± 0.011 [This work]	19.709 ± 0.018 [This work]

[a] The uncertainties are the standard deviations of the mean. Only the KBr values are corrected to infinite dilution. The concentration of SRM 724a is 5 g·L^{-1} in HCl (aq, 0.100 mol·L^{-1}) or in NaOH (aq, 0.0500 mol·L^{-1}).

[b] SRM 724a is a standard reference material for solution calorimetry, tris(hydroxymethyl)aminomethane, available at the National Bureau of Standards (U.S.) Washington, DC 20234.

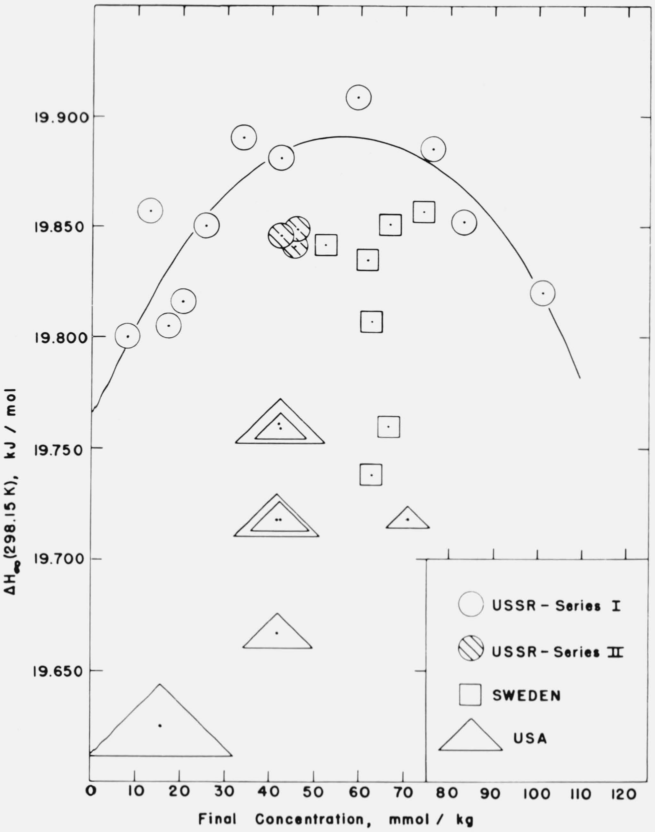

FIGURE 3. *Plot of the results of measurements of the enthalpy of solution of the same sample of KBr(cr) in H_2O by 3 calorimeters as a function of concentration.*

Isoperibol calorimeters of the same type were used in Sweden and USSR; an adiabatic calorimeter was used in USA. The radius of a circle circumscribed by a triangle is equal to the estimated calorimetric uncertainty for an experiment. The radius of a circle or a circle circumscribed by a square is equal to the standard deviation of the mean for the group of measurements with the respective calorimeter.

KBr in the range of 0.09 to 0.14 mol·kg^{-1}; her dilution data for KI and KCl show maxima at 0.06 to 0.08 and 0.15 to 0.20 mol·kg^{-1}, respectively. Since we would expect the maximum for KBr to be between those for KI and KCl, it appears that the Series I maximum is in error. The fact that the value near the maximum was not reproduced in Series II also suggests a systematic error rather than an error in the dilution corrections.

The curvature in the Series I points, apparently with concentration, and the discrepancy between values measured with the three different calorimeters are probably the result of several variables or errors. Certainly the unusually high imprecision of the measurements in Sweden, in the USA, and in the USSR at the lower concentrations, can be attributed to sample inhomogeneity. Some possible sources of error are changes due to aging the sample, variations in particle size (hence different probability of occluded impurities), cold spots due to inadequate stirring, and calorimetric errors such as that discussed above or others.

The data give little evidence that aging the sample is a source of error. The chronology of the various sets of measurements and the mean values for "enthalpy of solution at infinite dilution" corresponding to the concentration range, 30 to 80 mmol·kg^{-1} are as follows:

Place	Date	"$\Delta H(\infty$, 298.15 K)", kJ·mol^{-1}
USSR	Early 1975	19.891 (Series I)
USA	January 1977	19.724
Sweden	June 1977	19.813
USSR	September 1977	19.845 (Series II)

Certainly sample aging is not the major cause of the discrepancy between values although for an unknown reason the USSR Series II value is significantly lower than the corresponding value in Series I.

The KBr sample was crushed in a mortar but it was not sieved. Therefore some variation in particle size might be expected. Conceivably, vibration could cause some separation with the coarser particles above the finer particles. For the USA measurements which are arranged chronologically in table 5, the first four experiments gave the highest values and the fifth, next to the lowest value. The lowest value was obtained with a small sample which was the last in the bottle and was observed to be quite finely divided. This result would be expected if surface energies were significant although it is contrary to our previous experience with adenine where somewhat larger values for the enthalpy of solution were obtained with more finely divided materials [16b].

The stirring rate is not necessarily a measure of the effectiveness of stirring in different calorimeters since the size and shape of the vessel and stirrer propeller are important factors. However, in Olofsson's measurements the highest stirring rate was used. In isoperibol calorimeters it is essential that the stirring be sufficient to prevent the formation of "cold spots" which invalidate the assumptions made in calculating corrections for heat transfer between the reaction vessel and the constant-temperature jacket. This may be a cause for the disagreement between the two isoperibol calorimeters. However, in the adiabatic calorimeter, cold spots—especially at the bottom of the vessel, are of little importance, because the only possible heat transfer occurs at the top of the vessel where the effects of thermal gradients have been dissipated in the solution and in the heavy silver coating on the outer surface of the vessel.

In summary, the abnormally large experimental imprecision obtained in each series of the measurements of the enthalpy of solution of KBr in water can probably be attributed to sample inhomogeneity. The relatively large discrepancy in the values obtained by the different calorimeters must at present remain an unexplained uncertainty in the calorimetry. However, it is important to recognize the existence of these potential errors in order to avoid overestimating the accuracy of measurements. The measurements in this work have been made with concern for high accuracy as well as high precision and yet the uncertainties in the recommended values for the enthalpies of solution of KBr, KI, KIO_3, and KIO_4 have not been significantly reduced.

The authors (USSR) are grateful to G. M. Poltoratskii for sending the tables with the results of his work on KIO_3. All of the authors express their appreciation to G. Olofsson for permitting the use of her KBr results for our comparison, and for her valuable suggestions in this work.

5. References

[1] Parker, V. B., Thermal Properties of Uni-univalent Electrolytes Nat. Stand, Ref. Data Ser., Nat. Bur. Stand. (U.S.) 2, 66 pages (April 1965).

[2] Krestov, G. A., and Abrosimov, V. K., Izv. Vyssh, Ucheb. Zaved. SSR, Khim. i Khim. Tekhnol. No. 9, 1005 (1967).

[3] Tsvetkov, V. G., Rabinovich, I. B., Zhur. Fiz. Khim. **43,** 1213 (1969).

[4] Masal'skaya, L. P., Akhimov, E. I., Mishchenko, K. P., Poltoratskii, G. M., Zhur. Obshchei Khim. **41,** 2585 (1971).

[5] Joly, R.-D., Thourey, J., and Pérachon, G., C. R. Acad. Sc. Paris, Series C, **277,** 1179 (1973).

[6] Olofsson, G., Thermochemistry, Chemical Center, Lund, Sweden, private communications of unpublished data, October 1977 and August and November 1978.

[7] Shidlovskii, A. A., Voskresenskii, A. A., Zhur. Fiz. Khim. **39,** No. 6, 1523 (1965).

[8] Commission on Atomic Weights, Pure and Appl. Chem., **47,** 75–95 (1976).

[9] Medvedev, V. A., and Efimov, M. E., Zhur. Fiz. Khim., **49,** No. 5, 1324 (1975); a new value for SRM 724a is 245.64 ± 0.18 $\text{kJ}\cdot\text{g}^{-1}$, which is the mean of 17 experiments since 1972 where the uncertainty is twice the standard deviation of the mean.

[10] Kelley, K. K., and King, E. G., U.S. Bur. Mines Bull. 592, Washington, DC (1961).

[11] Nalimov, V. V., Prim. Mat. Stat. Anal. Veshchestra, Moskva, Ezd-vo Fiz. Mat. Lit., p. 168 (1960).

[12] Prosen, E. J., and Kilday, M. V., J. Res. Nat. Bur. Stand. (U.S.) **77A** (Phys. and Chem.) No. 5, 581–597 (1973).

[13] Prosen, E. J., and Kilday, M. V., J. Res. Nat. Bur. Stand. (U.S.) **77A** (Phys. and Chem.) No. 2, 179–203 (1973).

[14] Osborne, N. S., Stimson, H. F., and Fiock, E. F., J. Res. Nat. Bur. Stand. (U.S.) **5,** 411 (1930).

[15] Weast, R. C., editor, CRC Handbook of Chemistry and Physics, 58th Edition, CRC Press, Inc., Cleveland, OH 44128 (1977–78).

[16] Kilday, M. V., J. Res. Nat. Bur. Stand. (U.S.) **83,** (a) No. 6, (Nov.–Dec. 1978). (b) No. 4, 347–370 (July–August 1978).

[17] Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., Selected values of chemical thermodynamic properties, NBS Circular 500 (U.S. Government Printing Office, Washington, DC, 1952).

[18] Thomsen, J., Thermochemische Untersuchungen, J. Barth Verlag, Leipzig (1882–1886).

[19] Brönsted, J. N., Z. physik. Chem., **56,** 645–685 (1906).

[20] Walden, P. T., Z. physik. Chem., **58,** 479–511 (1907).

[21] Wüst, J., and Lange, E., Z. physik. Chem. **116,** 161–214 (1925).

[22] Popov, M. M., Bundel, A., and Choller, V., Z. physik. Chem. **A147,** 320–318 (1930).

[23] Chipman, H. R., Johnson, F. M. G., and Maass, O., Proc. Trans. Nova Scotian Inst. Sci., **17,** pt. 3, 149–167 (1929).

[24] Fedorov, A. S., and Sil'chenko, G. F., Ukrain, Khim. Zhur. **12,** 53–60 (1937).

[25] Lange, E., and Martin, W., Z. physik. Chem., **A180,** 233–245 (1937).

[26] Popov, M. M., Skuratov, S. M., and Strel'tsova, M. M., Zhur. Obshchei Khim., **10,** 2023–2027 (1940).

[27] Hietala, J., Ann. Acad. Sci. Fennicae Ser. AVI No. **63,** 57 (1960).

[28] Bobtelsky, M., and Lairsch, R. D., J. Chem. Soc., **1950,** 3612–3615.

[29] Kapustinskii, A. F., and Drakin, S. I., Zhur. Fiz. Khim. **26,** 581–585 (1952).

[30] Berthelot, M., Ann. chim. et phys. [5] **13,** 20–29 (1878).

[31] von Stackelberg, E., Z. physik. Chem. **26,** 533–563 (1898).

[32] Spencer, J. G., Jr., and Hepler, L. G., J. Phys. Chem. **64,** 499–500 (1960).

[33] Crouthamel, C. E., Hayes, A. M., and Martin, D. S., J. Am. Chem. Soc. **73,** 82–87 (1951).

[34] Parker, V. B., private communication (February 1979).

[35] Montgomery, R. L., Melaugh, R. A., Lau, C. C., Meier, G. H., Chan, H. H., and Rossini, F. D., J. Chem. Thermodynamics **9,** 915–936 (1977).

[36] Sunner, S., and Wadsö, I., Science Tools, **13,** 1 (1966).

[37] Hill, J. O., Öjelund, G., and Wadsö, I., J. Chem. Thermodynamics, **1,** 111 (1969).