n_j = mole fraction component j
n_j = weight fraction component j
P = pressure, lb./sq. ft. abs., or p.s.i.a.
Re = Reynolds number
r_i = interfacial resistance, sec./ft.
s = speed of rotation, r.p.m.
T = thermodynamic temperature, ° R.
u = hydrodynamic velocity, ft./sec.
Z = compressibility factor of gas phase
Δ = difference in
η = absolute viscosity, lb. sec./sq. ft.
θ = time, sec.
Σ = summation operator
σ = specific weight of phase, lb./cu. ft.
σ_k = concentration of component k, lb./cu. ft.
∂ = partial differential operator

Subscripts

av = average
d = diffusion
e = experimental
i = conditions at interface
j, 1 = stagnant component, methane
k, 7 = diffusing component, *n*-heptane
n = index
s = smooth
t = conditions at exit of transfer section (terminal)

Superscripts

0 = pure state
* = average

LITERATURE CITED

(1) Amdur, I., Irvine, J.W., Jr., Mason, E.A., Ross, J., *J. Chem. Phys.* **20**, 436 (1952).
(2) Am. Petrol. Proj. 44, Petrol. Res. Lab., Carnegie Inst. Technol., "Selected Values of Properties of Hydrocarbons and Related Compounds."
(3) Berry, V.J., Jr., Koeller, R.C., "Diffusion in Compressed Binary Gaseous Systems," A.I.Ch.E. Joint Symposium on Nonequilibrium Fluid Mechanics, Kansas City, 1959.
(4) Bridgeman, O.C., *J. Am. Chem. Soc.* **49**, 1174 (1927).
(5) Carmichael, L.T., Reamer, H.H., Sage, B.H., Lacey, W.N., *Ind. Eng. Chem.* **47**, 2205 (1955).
(6) Carmichael, L.T., Sage, B.H., *A.I.Ch.E.J.* **2**, 273 (1956).
(7) Carmichael, L.T., Sage, B.H., Lacey, W.N., *Ibid.*, **1**, 385 (1955).
(8) Fick, Adolf, *Ann. Phys.* **94**, 59 (1855).
(9) O'Hern, H.A., Jr., Martin, Joseph, J., *Ind. Eng. Chem.* **47**, 2081 (1955).
(10) Opfell, J.B., Sage, B.H., *Ibid.*, **47**, 918 (1955).
(11) Reamer, H.H., Opfell, J.B., Sage, B.H., *Ibid.*, **48**, 275 (1956).
(12) Reamer, H.H., Richter, G.N., DeWitt, W.M., Sage, B.H., *Trans. Am. Soc. Mech. Engrs.* **80**, 1004 (1958).
(13) Reamer, H.H., Sage, B.H., *Rev. Sci. Instr.* **24**, 362 (1953).
(14) *Ibid.*, **29**, 709 (1958).
(15) Robb, W.L., Drickamer, H.G., *J. Chem. Phys.* **19**, 1504 (1951).
(16) Sage, B.H., Lacey, W.N., *Trans. Am. Inst. Mining Met. Engrs.* **136**, 136 (1940).
(17) Schlinger, W.G., Reamer, H.H., Sage, B.H., Lacey, W.N., API Biennial Vol., 70-106 (1952-53).
(18) Scott, E.J., Tung, L.H., Drickamer, H.G., *J. Chem. Phys.*, **19**, 1075 (1951).
(19) Timmerhaus, K.D., Drickamer, H.G., *Ibid.*, **20**, 981 (1952).
(20) Walker, R.E., DeHaas, N., Westenberg, A.A., *Ibid.*, **32**, 1314 (1960).

RECEIVED for review April 30, 1962. Accepted September 17, 1962.

Heats of Formation of the Sparingly Soluble Iodates of Silver (I), Thallium (I), Lead (II), and Barium (II)

J. H. STERN, R. PARKER, L. S. PEAK, and W. V. VOLLAND
Department of Chemistry, Long Beach State College, Long Beach 4, Calif.

Heats of formation of sparingly soluble iodates were determined by combining measured heats of precipitation with auxiliary data necessary to correct the calorimetric results to standard states. The following values are reported for the standard heats of formation, ΔH^0_{f298} in kcal./mole: silver iodate (c), −41.6; thallium iodate (c), −65.7; lead iodate (c), −120.8 and barium iodate (c), −249.5.

THIS INVESTIGATION is part of a study in this laboratory (*5*, *6*) of thermodynamic properties of various oxidation states of iodine and its compounds. No heats of formation of these iodates are listed by the National Bureau of Standards (*3*). Latimer (*2*) gives only the heats of formation of $AgIO_3$ and $TlIO_3$.

Heats of precipitation in dilute aqueous solutions were measured for systems of the following type:

$$M^{x+}(aq) + xIO_3^-(aq) \rightarrow M(IO_3)_x \text{ (finely divided)};$$

where $M^{x+} = Ag^+, Tl^+, Pb^{2+}$, and Ba^{2+}.

These heats were combined with appropriate corrections to standard states and supporting thermodynamic data to yield heats of formation. The stoichiometry of the reactions is well established since the solubility of these iodates is very low (*2*, *4*).

Table I. Heat of Reaction of Metallic Ion with Iodate Ion in Aqueous Solution

Metal Nitrate, Moles/Liter	KIO_3, Moles/Liter	ΔT_{corr}	Total Energy Change, Cal.	$-\Delta H$, Kcal./Mole
		Silver (I) Ion		
0.3871	0.1828	0.0834	13.5	12.0
0.3871	0.1828	0.0829	13.5	11.6
0.3871	0.1828	0.0864	14.0	12.0
0.3871	0.1824	0.0842	13.9	12.0
			Av.	11.9 ± 0.2
		Thallium (I) Ion		
0.3454	0.1824	0.1165	40.0	11.8
0.3454	0.1824	0.1305	33.4	11.9
0.3454	0.1824	0.0875	22.5	12.0
0.3452	0.0572	0.1168	40.0	11.8
0.3452	0.0344	0.0756	20.1	12.0
0.3452	0.0344	0.1030	26.6	11.6
			Av.	11.9 ± 0.2
		Lead (II) Ion		
0.2478	0.1892	0.0630	10.3	10.4
0.2478	0.1819	0.0580	9.45	10.0
0.2478	0.1819	0.0625	10.1	10.6
0.2478	0.1819	0.0623	9.98	10.6
0.2794	0.1827	0.0505	9.92	10.4
0.2794	0.1827	0.0483	10.2	10.6
0.2794	0.1370	0.0268	5.43	10.1
0.2794	0.1370	0.0561	11.8	10.4
0.2794	0.0914	0.0478	10.1	10.6
0.2794	0.0914	0.0497	10.6	10.3
0.2794	0.0685	0.0415	9.12	10.4
			Av.	10.4 ± 0.2
		Barium (II) Ion		
0.3106	0.2240	0.0920	25.7	12.3
0.2879	0.1732	0.1450	40.0	12.1
0.2879	0.1881	0.1060	28.0	12.0
0.2879	0.1881	0.1225	32.4	12.1
			Av.	12.1 ± 0.1

EXPERIMENTAL

Materials. $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, KIO_3, (A.R., Mallinckrodt) and recrystallized $TlNO_3$ (C.P., Fairmount) were dried at 100° C. Their solutions were prepared with triply distilled water.

Calorimeter and Heat Measurements. The calorimeter has been described elsewhere (*5*). The reactions were carried out at 25° C. in a large excess (200 to 250 ml.) of aqueous potassium iodate. The cation solutions were weighed into thin glass ampules (4 to 8 ml.) which were then submerged in the reaction solution. After crushing the ampule, the reaction proceeded very rapidly with thermal equilibrium attained in less than 60 seconds. Heat of dilution corrections were measured similarly. No heat effects were observed when dry precipitates were immersed in aqueous iodate solutions.

Completeness of reaction was checked by treating decantates from silver and thallium iodates with sodium chloride solutions and those of lead and barium iodates with sodium sulfate solutions. No reaction was observed in any case.

Observed temperature changes ($\pm 3 \times 10^{-4}$ degrees) were corrected for heat exchange, and electrical energy calibrations were made before and after each run. The average of these energy equivalents was used in all calculations.

RESULTS AND INTERPRETATION

Heats of Reaction. All heats of reaction are given in Tables I. Precision indices associated with all average heats are standard deviations and concentrations are in moles per liter.

Table II. Heats of Dilution of $M(NO_3)_x$

Nitrate	Moles/Liter Initial	Moles/Liter Final	No. of Runs	ΔH_D, Kcal./Mole
$AgNO_3$	0.393	0.012	2	0.2 ± 0.04
$TlNO_3$	0.345	0.010	3	0.4 ± 0.06
$Pb(NO_3)_2$	0.248	0.0039	1	1.13
	0.248	0.0052	1	1.30
	0.248	0.0043	1	1.14
	0.244	0.0099	1	1.12
			Av. ΔH_D for $Pb(NO_3)_2$ =	1.2 ± 0.1
			$Ba(NO_3)_2$ from N.B.S. Tables (*3*) =	−0.9

Heats of Dilution. The appropriate heat of dilution corrections of the reaction solutions were determined to correct the calorimetric reaction results (Table I) to standard states. No thermal effect was observed from variation of potassium iodate concentrations during the reaction runs (thallium and lead). Table II lists all summarized and average values of heats of dilution for the cation nitrate solutions.

Heats of Formation. All pertinent heats of formation with the exception of that recently determined for iodate ion (*6*) (−54.8 kcal./mole) were obtained from the National Bureau of Standards tables (*3*). These were combined with the average heats of reaction and dilution (Tables I and II) to yield heats of formation of the sparingly soluble iodates. Table III shows these experimental heats together with values given by Latimer (*2*).

Table III. Heats of Formation of Sparingly Soluble Iodates at 25° C.

Iodate	ΔH_f^0 Kcal./Mole This work	ΔH_f^0 Kcal./Mole Latimer
$AgIO_3$	−41.6	−41.7
$TlIO_3$	−65.7	−65.7
$Pb(IO_3)_2$	−120.8	
$Ba(IO_3)_2$	−249.5	

The heats of formation of $AgIO_3$ and $TlIO_3$ are in excellent agreement with those given by Latimer for crystalline iodates. The very small difference in the case of $AgIO_3$ may be due to the exothermic effect of forming macrocrystalline surfaces from the finely divided particles which were produced under experimental conditions (*1*). The assigned over-all uncertainty of ±0.5 kcal./mole is attributed primarily to this effect and to the estimated errors in the values taken from the literature. The errors resulting from the experiments are considerably lower since the measured heats are small when compared to the final values.

LITERATURE CITED

(1) Giauque, W.F., *J. Am. Chem. Soc.* **71**, 3192 (1949).
(2) Latimer, W.M., "Oxidation Potentials," 2nd ed., Prentice-Hall, Englewood Cliffs, N. J., 1952.
(3) Nat. Bur. Std. (U. S.) **Circ. 500**, 1952 Reprinted July 1961.
(4) Seidell, A., "Solubility of Inorganic and Metal Organic Compounds," **Vol. I**, 3rd ed., Van Nostrand, New York, 1940.
(5) Stern, J.H., Passchier, A.A., J. CHEM. ENG. DATA **7**, 73 (1962).
(6) Stern, J.H., Passchier, A.A., *J. Phys. Chem.* **66**, 752 (1962).

RECEIVED for review June 26, 1962. Accepted September 5, 1962. Work supported by grants from the Research Corporation and the National Science Foundation.