Heats of Formation of Tin and Titanium Iodides

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Heats of formation, $\Delta H_f^\ominus$ (298 K), for TiI_4 (335.9), SnI_2 (143.9), SnI_4 (215.3), and CuI (68.2 kJ mol^{-1}) have been determined from heats of solution in 0.1 mol dm^{-3} $FeCl_3$ and 3 mol dm^{-3} HCl. The value for SnI_2 has been confirmed from heats of solution of SnI_2 and iodine in ethyl acetate.

ENTHALPIES of formation of the lower titanium iodides were required in order to estimate the stabilities of complex titanium iodides. Since only estimated values are available,[1] we have made direct calorimetric measurements of the heats of solution in iron(III) chloride–hydrochloric acid mixtures after checking that the reactions are quantitative. Acidic solutions of $FeCl_3$ have been used previously as calorimetric media for alloys [2] and extensively as oxidants in mineral processing and dissolution.[3] Quantitative analytical assessment was not provided in the previous work.[4,5] The calorimetric method has been tested with the chemically related tin

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[1] D. R. Stull and H. Prophet, J.A.N.A.F. Thermochemical Tables, 2nd edn., N.S.R.D.S.-N.B.5, 37, 1971, U.S. Govt. Printing Offices, Washington, D.C.

[2] W. Biltz and C. Haase, *Z. anorg. Chem.*, 1923, **129**, 141.

[3] J. E. Dutrizac and R. J. C. MacDonald, *Minerals Sci. and Eng.*, 1974, **6**, 59.

[4] S. W. Gorbatscheff and I. A. Kassatkina, *Z. anorg. Chem.*, 1930, **191**, 104.

[5] K. F. Shimizu and E. A. Kelly, *J. Amer. Pharm. Assoc.*, 1942, **31**, 103.

iodides; a heat of formation for tin(II) iodide has been reported.[6]

EXPERIMENTAL

Materials.—Tin(IV) and titanium(IV) iodides were prepared by heating iodine with excess of metal at 200—250 °C and separated by sublimation *in vacuo*. Tin(IV) iodide was further purified by recrystallisation from pure chloroform. Tin(II) and titanium(III) iodides were prepared from stoicheiometric amounts of the elements, the former by heating at 450 °C for 5 d, the latter by heating initially at 300 °C and then in a temperature gradient (550—750 °C) for 5 d. Titanium(II) iodide was derived from the tri-iodide by disproportionation *in vacuo* at 400 °C and by reducing the tetraiodide with aluminium at 350 °C for 5 d. Other iodides were prepared by standard methods. Analytical purity was checked as described below and powdered materials were identified by their *X*-ray patterns.

Table 1

Comparison of iron(III) chloride oxidation with silver iodide precipitation

	[HCl]/mol dm^{-3}	Weight of salt/mg	Weight determined by: I_2 extraction	Weight determined by: Fe^{2+} formation	Weight determined by: AgI precipitation
KI	2.5	360.3	359.5	360.6	
	2.5	313.2	313.0	314.2	
	6	333.2	333.6		
	6	375.2	374.5		
		402.8			403.1
		413.3			413.6
CdI_2	3	389.4	383.9		
	3	321.4	317.4		
	4.5	324.2	323.5	324.7	
	6	462.6	460.7		
	6	397.5	398.1		
		582.5			581.2
		399.1			399.2
AsI_3	3	132.6	132.2		
	3	213.2	212.7		
	4.5	191.5	190.4		
	4.5	152.0	151.8	152.0	
		317.1			316.9
		251.1			250.6

Analytical Method.—Not more than 5 mmol of iodide ion in the form of solid iodide was placed in an extraction flask made from a standard B24 stoppered Erlenmeyer flask (250 cm^3) fitted with a burette tap at the basal level and inclined upwards at 30° to the base. (For lower iodides which contain oxidisable metal the above quantity must be correspondingly reduced.) Iron(III) chloride solution (50 cm^3, 0.1 mol dm^{-3}) in hydrochloric acid was added and the mixture stirred magnetically until all the solid had dissolved. Benzene–carbon tetrachloride (3 : 2 or 1 : 1, 25 cm^3) was then added and the aqueous phase was extracted by moderate stirring. The organic phase was separated *via* the side arm into water (50 cm^3) contained in another stoppered conical flask. (A few drops of dilute detergent were required to detach solvent from the water–air interface and to facilitate displacement of water in the side tube.) Three further extracts were combined with the initial extract and the iodine content was titrated with standard thiosulphate solution after adding some potassium iodide to speed up the back extraction. The iron(II) ion produced was titrated *in situ* with standard dichromate after diluting the acid to 1.5 mol dm^{-3} HCl. Potassium, cadmium, and arsenic iodides were used as trial substances, and the method was compared with the standard gravimetric technique (Table 1). Some results with tin and titanium iodides, and also with some insoluble iodides, are collected in Table 2. Details of distribution ratios after each extraction are given in Table 3.

Table 2

Iron(III) chloride oxidation of hydrolysable and insoluble iodides

	[HCl]/mol dm^{-3}	Weight of salt/mg	Weight determined by: I_2 extraction	Weight determined by: Fe^{2+} production
SnI_2	3	361.4	360.8	361.0
SnI_4	3	254.6	253.5	256.0
	3	251.9	251.3	
TiI_2	3	194.5	194.7	194.0
TiI_3	3	99.2	98.8	
		148.7	148.4	
TiI_4	3	246.2	247.0	
CuI	3	197.6	197.6	
	3	308.1	307.9	
HgI_2	10	159.5	160.7	
		220.6	220.0	
PbI_2 [a]	3	441.3	443.1	
TlI	6	284.9	296.4	286.1
AgI [b]	10	200.0	199.4	
$CuTiI_4$ [c]	3	206.3	206.1	205.8

[a] 100 ml of oxidant used to keep $PbCl_2$ in solution. [b] Mercury(II) chloride (1.35 g) was added to dissolve AgI and extracted over a 20-h period. [c] An independent copper analysis by electrodeposition gave 10.2% (calc. 10.25%).

Table 3

Iodine extraction and distribution

Partition	Cumulative titres as % of total [a]: CdI_2 (1)	AsI_3 (2)	(3)	(4)	(5)	Distribution ratio [mean of (1)—(3)] [b]
1	88.6	86.7	88.9	84.6	90.3	14.7
2	98.2	97.7	98.4	97.4	98.8	10.5
3	99.6	99.6	99.7	99.5	99.8	8.6
4	100.0	100.0	100.0	100.0	100.0	

[a] Conditions: for (1)—(3), 0.1 mol dm^{-3} $FeCl_3$, 4.5 mol dm^{-3}, C_6H_6–CCl_4 (3 : 2); for (4), 0.1 mol dm^{-3} $FeCl_3$, 3 mol dm^{-3} HCl, CCl_4; for (5) 0.1 mol dm^{-3} $FeCl_3$, 3 mol dm^{-3} HCl, C_6H_6–CCl_4 (1 : 1). [b] The distribution ratio is defined as the amount of iodine extracted into the organic phase divided by the residual iodine in an equal volume of aqueous phase.

Calorimetric Method.—Heats of solution were measured in a Dewar-vessel isoperibol calorimeter with a thermistor as the temperature sensor. The external temperature was held at 24.5 ± 0.001 °C. The amplified output of a Leeds and Northrup (type 9828) null detector in an unbalanced Wheatstone network was used to follow heating curves continuously. The calorimeter behaviour was validated by checking the heat of solution of tris(hydroxymethyl)methylamine in 0.1 mol dm^{-3} HCl. A mean value of 29.74(7) kJ mol^{-1} was obtained. Each run was calibrated electrically using a constant voltage source capable of being read to 10 μV (Fenlow 701 digital voltmeter). Solid and liquid samples were contained in a glass tube, the threaded ends of which were closed with poly(tetrafluoroethylene) (ptfe) or

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[6] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and F. Jaffe, ' Selected Values of Chemical Thermodynamic Properties, N.B.S. Circular 500, 1592, U.S. Govt. Printing Offices, Washington, D.C.; D. D. Wagman, W. H. Evans, V. B. Parker, T. Halow, S. M. Bailey, and R. H. Schumm, N.B.S. Tech. Note 270–3, 1968.

Polythene foils held in ptfe screw tops. Both foils were pierced by a sharpened glass plunger to release the contents. The heat of breaking was deducted from the heats of reaction. Approximately 250 cm^3 of solvent were used. Because the solids under investigation were unstable to hydrolysis, especially when being ground, all handling and loading of samples was in a glove-box which was continuously purged with dry nitrogen.

Initial experiments were made with organic extractant present. The density of the extractant was adjusted to be just greater than that of the solution of $FeCl_3$ in order for it to be dispersed on stirring. However, irregular heating curves led to this method being abandoned in favour of a single-phase system since the solubility of iodine in all the solutions was sufficient to ensure complete solution of liberated iodine. [A solubility of 195 mg of iodine in 100 g of solution was determined in 2.86 mol dm^{-3} HCl at 24.5 °C. Addition of 0.1 mol dm^{-3} $FeCl_3$ left the solubility unaltered (194 mg) within experimental error. The solubility of iodine in water at 25 °C is 33.6 mg in 100 g.]

The dissolution of tin iodides produced erratic heating curves and considerable scatter in the results. This was overcome by dispersing the iodides in an inert material. Potassium chloride was used as a diluant with SnI_2. Ground silica had to be used with the tin(IV) salt because its small heat of solution would have been obscured by the large endothermicity of dissolution of KCl. Results in acid solutions stronger than 9 mol dm^{-3} were less precise because of initial precipitation of iodine which only dissolved slowly.

DISCUSSION

The heats of formation of SnI_4 and TiI_4 could be determined by 'hot-zone' calorimetry[7] from the elements, but this method is not suitable for lower iodides which only form over a period of days by equilibration of the metal and the highest iodide. A rapid quantitative reaction on the preformed iodide is required and this is possible with acid oxidants. Iron(III) ion was used in preference to oxidants such as Ce^{4+}, $[MnO_4]^-$, $[Cr_2O_7]^{2-}$, and $[IO_3]^-$, which can in theory oxidise iodide beyond the zero oxidation state although in practice kinetic factors may inhibit further oxidation. Such effects were observed when dichromate was used as an oxidant. The reaction stoicheiometry with oxo-anions also involves larger contributions from auxiliary heats which increase the overall error.

The following equations are involved in determining the heat of formation of an iodide by the iron(III) chloride method. Equation (2) is used to determine the difference

$$MI_n(s) + (n + m)FeCl_3 \longrightarrow MCl_{n+m} + \frac{n}{2}I_2 + (n + m)\,FeCl_2 \quad (1)$$

$$KI(s) + FeCl_3 \longrightarrow KCl + 0.5I_2 + FeCl_2 \quad (2)$$

$$K[I_3](aq) + FeCl_3 \longrightarrow KCl + 1.5I_2 + FeCl_2 \quad (3)$$

$$KI(aq) + FeCl_3 \longrightarrow KCl + 0.5I_2 + FeCl_2 \quad (4)$$

in the heats of formation of iron(II) and iron(III) chlorides in solution without the necessity of handling hygroscopic iron chlorides. The difference between reactions (3) and (4) gives a heat of solution of iodine and overcomes experimental difficulties caused by slow dissolution of elemental iodine. It follows that the heat of formation of a lower iodide involves the heats of reactions (1)—(4), the heats of solution of the chlorides produced, and a knowledge of the heats of formation of KI(s), KCl(s), KI(aq), KI_3(aq), and MCl_{n+m}. If the lower iodide is determined in terms of the highest corresponding iodide the heats of formation of the chlorides can be eliminated, *e.g.* from equations (5) and (6) we obtain (7). In practice

$$TiI_3(s) + 4FeCl_3 \longrightarrow TiCl_4 + 4FeCl_2 + \tfrac{3}{2}I_2;\ \Delta H_5 \quad (5)$$

$$TiI_4(s) + 4FeCl_3 \longrightarrow TiCl_4 + 4FeCl_2 + 2I_2;\ \Delta H_6 \quad (6)$$

$$\Delta H_f(TiI_3) = \Delta H_f(TiI_4) - \Delta H_{soln}(\tfrac{1}{2}I_2) + \Delta H_5 - \Delta H_6 \quad (7)$$

TABLE 4

Heats of solution in 0.1 mol dm^{-3} $FeCl_3$ and 3 mol dm^{-3} HCl

Salt	Weight/g	Heat released/J	Molar heat/ kJ mol^{-1}
$TiCl_4$(l)	0.4325	466.83	−204.77
	0.6299	674.2	−203.1
	0.6447	690.0	−202.92
		Mean	−203.6 ± 0.7
TiI_3	0.1831	105.30	−319.5
	0.3032	174.70	−320.08
	0.3203	184.53	−320.0
	0.6121	350.7	−318.3
	0.6930	400.3	−320.9
		Mean	−319.8 ± 0.7
KI(s)	0.2953	−22.35	12.57
	0.4674	−34.54	12.27
	0.5452	−40.69	12.39
		Mean	12.41 ± 0.11
KI(aq) [a] (86.6 mg of KI per g of soln.)	5.2995 (1)	101.37	−36.99
	5.3087 (4)	103.27	
	5.3073 (2)	100.96	−35.99
	5.3137 (5)	98.42	
	5.2986 (3)	99.08	−35.85
$K[I_3]$(aq) (33.64 mg of I_2 per g of KI soln.)	5.4322	98.30	−32.56
	5.4313	95.31	−31.19
$SnCl_2$	0.1248	65.01	−98.76
	0.2227	117.21	−99.83
	0.3019	158.86	−99.75
	0.3283	172.83	−99.81
	0.4980	263.69	−100.39
		Mean	−99.7 ± 0.2
SnI_2 [b]	Mean (5 values)		−76.6 ± 3.6
SnI_2–KCl (1.095 : 1)	0.6231	6.07	−72.22
	0.6337	6.12	−72.81
	0.7544	6.38	−73.67
		Mean	−72.9 ± 0.3
SnI_4 [b]	Mean (3 values)		5.94 ± 0.7
SnI_4–SiO_2 (0.975 : 1)	0.8354	−4.79	6.19
	1.1645	−5.145	6.65
		Mean	6.42 ± 0.2
KCl	0.6223	−143.49	17.19
	0.6320	−149.20	17.60
	0.9272	−217.48	17.49
		Mean	17.43 ± 0.2

[a] (1)—(3) are successive additions to an iron(III) chloride solution; (4) and (5) are successive additions to a fresh solution.
[b] Irregular dissolution rate.

when the heats of reactions (2)—(4) are available, only the heat of reaction (1) and the heat of solution of the

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[7] W. H. Evans, in 'Experimental Thermochemistry, ed. H. A. Skinner, Interscience, New York, ch. 13, vol. 2, 1962.

TABLE 5

Heats of solution in 0.1 mol dm^{-3} $FeCl_3$ and 9 (*a*) and 22 (*b*) mol dm^{-3} HCl

Salt	Weight/g	Heat released/J	Molar heat/kJ mol^{-1} (*a*)	(*b*)
$TiCl_4$(l)	0.4672	308.15	−125.2	−121.8
	1.0068	666.5	−125.4	
TiI_3	0.3967	228.8	−247.2	
KI(s)	0.6755	9.74	−2.39	−3.85
KI(aq)	5.3566	428.8	−132.0	*
$K[I_3]$(aq)	5.4841	378.2	−88.5	*
KCl	0.8591	23.0	−2.00	−0.76

* Iodine dissolves too slowly for heat measurement.

TABLE 6

Heats of solution in ethyl acetate

Compound	Weight/g	Total weight in final soln./g	Heat released/J	Molar heat of soln./kJ mol^{-1}
I_2	0.7059	0.7059	−35.72	12.98
	0.7849	1.4908	−41.24	13.33
	0.7812	7.2720	−39.51	12.84
			Mean	13.05 ± 0.2
SnI_2 [a]	0.3058	0.3058	334.7	−407.1
	0.2329	0.6519	39.14	−62.6
	0.2418	0.8937	37.13	−57.2
	0.4325	1.3262	59.42	−51.2
SnI_4 [b]	0.7449	0.7449	−0.83	0.70
	0.9214	1.6663	−4.62	3.14
	0.7551	2.4214	−3.77	7.59

[a] Successive additions to the final solution of I_2 in ethyl acetate. [b] Added after SnI_2 addition.

TABLE 7

Heats of solution of copper halides in 0.1 mol dm^{-3} $FeCl_3$ and 3 mol dm^{-3} HCl

Salt	Weight/g	Heat released/J	Molar heat of soln./kJ mol^{-1}
CuI	0.3066	−46.54	29.14
	0.3324	−51.37	29.67
$CuCl_2$	0.2959	58.66	−26.65
	0.5579	107.64	−25.94
CuCl	0.7587	61.56	−7.98
	0.8527	69.23	−8.00

The following auxiliary heats of formation were used:[1,6] KI(100 H_2O), −307.40; $K[I_3]$(100 H_2O), −303.76; $SnCl_2$(s), −325.10; CuCl, −134.72; $CuCl_2$, −220.08; KI(s), −327.65; KCl(s), −436.68; TiI_4(s), −376.14; and $TiCl_4$(l), −804.16 kJ mol^{-1}.

TABLE 8

Heats of formation estimated from electronegativities

Salt	Mean χ_M	Heat of formation/kJ mol^{-1} Expt.	Calc.
TiI_3	1.58	−338.4	−337
TiI_4	1.70	−376.1 [9]	−363
SnI_2	1.80	−143.9	−149
SnI_4	1.94 (5)	−215.3, −214.3	−206

metal chloride in the reaction medium need be measured to obtain the heat of formation of another iodide. Errors in the heats of formation for tin iodides of ±2.3 kJ mol^{-1} and for TiI_3 of ±3.3 kJ mol^{-1} were estimated from the experimental mean deviations, but these do not take into account any errors in the quoted auxiliary heats (Table 7).

The value obtained for SnI_2 (−143.9 kJ mol^{-1}) agrees with the reported value [6] (−144.0 kJ mol^{-1}), but ref. 8 shows that Berthelot's value was an estimate from those of surrounding iodides and not an experimental value. Similarly there is no experimental value for SnI_4 with which to compare the iron(III) chloride determination, and hence we made an independent check by oxidising SnI_2 with iodine in ethyl acetate in which all the components are readily soluble. The heat of solution of iodine in ethyl acetate was independent of iodine content, whereas the heats of solution of tin iodides in acetate solutions of iodine were concentration dependent. These heats were extrapolated to infinite dilution from plots of the logarithm of solution heats against concentration. (The initial heat of solution of SnI_2 yielded an impossibly high value for the heat of formation of SnI_4 and we attribute this exceptional value to heats of complexing of SnI_4 with oxygen-donor solvent impurities. Impurity levels between 0.01 and 0.1%, for example of the hydrolytic products ethanol and acetic acid, could easily account for the extra heat. The same solvent was used in successive measurements.) The heat of formation found for SnI_4 (214.3 kJ mol^{-1}) compares favourably with that determined by the iron(III) chloride method (215.3 kJ mol^{-1}).

The heat of formation of TiI_2 could not be measured because of its slow dissolution in acidic $FeCl_3$, whereas titanium-(III) and -(IV) iodides dissolved in less than 10 min in 3 mol dm^{-3} acid solution and a heat of formation of the tri-iodide (−338.4 kJ mol^{-1}) was derived in terms of the well established value for the tetraiodide.[9] However, when a value for the tetraiodide was derived in terms of the tetrachloride from equation (6) an extremely low value (−272.5 kJ mol^{-1}) instead of the accepted value (−376.1 kJ mol^{-1}) was obtained. This difference was far outside calorimetric and analytical error and we need to postulate that the titanium species formed when titanium iodides dissolve differ from those when titanium chlorides dissolve in the same acid solution.

There is consistency when TiI_4 is compared with TiI_3 or when $TiCl_4$ is compared with $TiCl_3$ (*i.e.* $\Delta H_f[TiCl_4 - TiCl_3]$ determined from heats of solution in 0.1 mol dm^{-3} $FeCl_3$ and 3 mol dm^{-3} HCl is −84.5 kJ mol^{-1} compared with a literature value of −82.8 kJ mol^{-1}) but not when TiI_4 is compared with $TiCl_4$ or $TiCl_3$. It is known from studies on Raman spectra [10,11] that the $[TiCl_6]^{2-}$ ion, which might be expected in the above solution, is in fact only formed in 'fuming', presumably saturated, HCl. Oxo-species containing Ti–O–Ti or Ti–OH–Ti [10] and $[TiCl_4O_2]^{4-}$ or $[TiCl_5O]^{3-}$ (ref. 11) have been postulated without much evidence. The salt $Cs_2[TiCl_4O]\cdot H_2O$,[12]

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[8] M. Berthelot, *Ann. Chim. Phys.*, 1878, **15**, 185.

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[10] D. M. Adams and D. C. Newton, *J. Chem. Soc.* (*A*), 1968, 2262.

[11] J. E. D. Davies and D. A. Long, *J. Chem. Soc.* (*A*), 1968, 2560.

[12] I. Morozov and G. M. Toptygina, *Russ. J. Inorg. Chem.*, 1960, **5**, 1218.

presumably $Cs_2[TiCl_4(OH)_2]$, can be isolated from solutions of HCl below *ca.* 30% by weight. The isolation of this salt implies the presence of other anionic species $[TiCl_{6-n}(OH)_n]^{2-}$ in solution. It is known that the displacement of chloride by hydroxide is much slower than the reverse process. Hence we expect that $TiCl_4$ in 3 mol dm^{-3} HCl rapidly attains a high Cl : O ratio in the dissolved species because the chloride ligand is only slowly displaced and this would not be observed on the time scale of our calorimetry. The titanium iodides would behave differently because iodide is displaced leaving the titanium susceptible to both chloride and water. The high $H_2O : Cl^-$ ratio in solution would then produce lower Cl : O ratios than those from titanium chlorides.

The thermal effect of replacing Cl^- by $[OH]^-$ can be roughly evaluated by equating heats of formation of hydroxo-species with those of the corresponding fluoro-species and numerical evidence for this will be presented elsewhere. An upper limit to the increased stability when a single chloride ligand is replaced is given by $\frac{1}{4}[\Delta H_f(TiF_4) - \Delta H_f(TiCl_4)] = -210$ kJ mol^{-1}, which means that the species formed when titanium iodides dissolve in 3 mol dm^{-3} HCl solutions of $FeCl_3$ contain, on average, half a hydroxide group more than in the species formed from titanium chlorides. An example would be the replacement of a quarter of the species $[TiCl_4(OH)_2]^{2-}$ in the titanium chloride solution by $[TiCl_2(OH)_4]^{2-}$ in the titanium iodide solution. Increasing acidity of the iron(III) chloride reagent would be expected to reduce and finally remove the discrepancy, and indeed in 9 mol dm^{-3} HCl the difference is roughly halved. Unfortunately we were unable to obtain a heat of solution of iodine in 22 mol dm^{-3} HCl because iodine dissolved too slowly in this medium. Neither were we able to obtain such heats from the temperature variation of solubility. The usual relation between solubility and temperature was not obeyed because the solubility was controlled by opposing processes. Polyhalide formation was in competition with salting-out effects. Both effects increase with increasing acid concentration and at some stage between 9 and 22 mol dm^{-3} the solubility of iodine reaches a maximum. This effect has been observed previously in neutral solutions of metal halides but at lower concentrations.[13,14] Polyhalide formation is also illustrated by the distribution ratios which decrease as the HCl : I_2 ratio increases, and for this reason changing to an extractant in which iodine was more soluble did not reduce the total number of extractions needed (see Table 3).

$$I_2 + Cl^- \rightleftharpoons [I_2Cl]^- \qquad (8)$$

The consistency of the heat of formation of TiI_3 determined in 3 and 9 mol dm^{-3} HCl in comparison with TiI_4, as well as the literature-consistent value for $TiCl_3$ in comparison with $TiCl_4$, gives credence to the new value for the tri-iodide. An independent check was obtained by reversing Pauling's electronegativity derivation [15] in which the heat of formation of halides MX_n is given by $96.5n(x_M - x)^2$ kJ mol^{-1} where x_M is the electronegativity of the metal and x that of the halogen. The heats of formation in a halide series can be plotted as a function of x and the gradients between successive pairs of halides MX_n–MY_n, given by $96.5n[(x_M - x_X)^2 - (x_M - x_Y)^2]/(x_X - x_Y)$, simplifies to $193n[\frac{1}{2}(x_X + x_Y) - x_M] = S$. The heat of formation of an iodide can then be extrapolated from the bromide using the gradient between MBr_n and MI_n, *i.e.* $\Delta H_f(MI_n) = \Delta H_f(MBr_n) - S(x_{Br} - x_I)$. Using Allred and Rochow electronegativity values for halogens [16] and mean electronegativities of the metal in each oxidation state derived from chlorides and bromides, gives the values in Table 8. (Fluoride values are excluded because they produce different electronegativities for the metals as could be expected from structural dissimilarities between fluorides and other halides.)

It should be possible to generalize the above methods and make them applicable to a variety of simple and complex iodides. For water-soluble iodides which ionise there is no analytical advantage, apart from halogen specificity, over the usual oxidimetric or argentimetric methods. Similarly heats of solution could be determined in neutral solutions. However, the iron(III) chloride method can be applied both to water-insoluble iodides, as well as to the larger class of more or less covalent iodides, which often tend to hydrolyse slowly. For example, the heat of formation of copper(I) iodide was determined in terms of that of the chloride (−68.2 kJ mol^{-1}) in excellent agreement with the accepted value (−67.8 kJ mol^{-1}). [In relation to $CuCl_2$ the value was more divergent (−72.0 kJ mol^{-1}), reflecting uncertainty in the heat of formation of $CuCl_2$. A revised value of −216.3 kJ mol^{-1} is suggested for the latter.]

A change to adiabatic calorimetry would be necessary for slower rates of solution, *e.g.* TiI_2, and to higher acidities to ensure well defined hydrolysates.

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[15] L. Pauling, 'Nature of the Chemical Bond,' 3rd edn., Cornell University Press, 1966, p. 92.

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