A THERMODYNAMIC INVESTIGATION OF SOME ALKALI-METAL POLYHALIDE COMPOUNDS

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ABSTRACT

An isoperibol solution reaction calorimeter has been constructed. The precision and accuracy of the calorimeter were checked by measuring the enthalpy of reaction of tris(hydroxymethyl)aminomethane, THAM, in:

(a) excess 0.1 mol dm^{-3} aqueous hydrochloric acid

(b) excess 0.05 mol dm^{-3} aqueous sodium hydroxide

The mean of 8 runs were:

(a) ΔH_{298} $(1296 < n < 1780)$ = -29.87 ± 0.05 kJ mol^{-1}.
Literature: $\Delta H_{298} = -29.790 \pm 0.031$ kJ mol^{-1}, n=1345.

(b) ΔH_{298} $(1241 < n < 1550)$ = $+17.18 \pm 0.05$ kJ mol^{-1}.
Literature: $\Delta H_{298} = +17.177 \pm 0.023$ kJ mol^{-1}.

(n is the mole ratio of water to THAM.)

From measurement of the enthalpy of hydrolysis the standard enthalpy of formation of rubidium tetrafluoroiodate has been derived: $\Delta H_f^o(RbIF_4,c)_{298} = -1121.51 \pm 6.33$ kJ mol^{-1}. Heat capacity measurements for $RbIF_4$ over the range 273-303 K are also reported.

The standard enthalpies of formation of some alkali-metal polyhalides have been derived from calorimetric measurements, in the isoperibol mode, of the enthalpy of reaction of the crystalline polyhalides with:

(i) excess aqueous silver nitrate
(ii) excess aqueous sulphur dioxide

The following standard enthalpies of formation at 298.15 K are reported:

(i) ΔH_f^o ($CsICl_2$,c) = -512.01 ± 4.14 kJ mol^{-1};

ΔH_f^o ($RbICl_2$,c) = -492.31 ± 4.12 kJ mol^{-1};

ΔH_f^o ($CsIBr_2$,c) = -446.32 ± 4.08 kJ mol^{-1};

ΔH_f^o ($RbIBr_2$,c) = -429.11 ± 4.22 kJ mol^{-1};

ΔH_f^o (CsI_3,c) = -359.79 ± 5.77 kJ mol^{-1};

ΔH_f^o ($CsICl_4$,c) = -571.91 ± 6.90 kJ mol^{-1} and

ΔH_f^o ($RbICl_4$,c) =-554.36 ± 6.99 kJ mol^{-1}.

(ii) ΔH_f^o ($CsICl_2$,c) = -530.35 ± 0.67 kJ mol^{-1};

ΔH_f^o ($RbICl_2$,c) = -461.36 ± 1.40 kJ mol^{-1} and

ΔH_f^o (CsI_3,c) = -381.96 ± 1.05 kJ mol^{-1}.

The standard enthalpy of formation in (i) for CsI_3 is in good agreement with literature values derived from e.m.f. studies and from dissociation pressure measurements.

The standard enthalpy of formation of $AgIO_3$(c) and the enthalpy change for the process

$$SO_2(aq) + I^-(aq) \rightleftharpoons SO_2.I^-(aq)$$

were also derived from calorimetric measurements to supplement the ancillary data required to calculate the standard enthalpies of formation listed above.

'Thermochemical radii' of the ions ICl_2^-, IBr_2^-, ICl_4^- and I_3^- have been calculated by the Kapustinskii-Yatsimirskii procedure in order to estimate lattice energies of the salts listed in (i) and ΔH_f^o (IX_n^-,g) (where X_n = Cl_2,Br_2,Cl_4 and I_2). Additional lattice energies, standard enthalpies of formation and enthalpies of decomposition of other alkali-metal and alkaline-earth salts containing these ions are reported.

'Thermochemical radii' of the ions Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}, ClO_3^-, BrO_3^- and IO_3^- have been calculated to investigate the relationship between the 'thermochemical radius' and the geometric size of an ion of given symmetry. Lattice energies of alkali-metal and alkaline-earth salts containing these ions have been estimated and compared with literature values.

CONTENTS

SECTION I INTRODUCTION

SECTION II RESULTS AND DISCUSSION

SECTION III EXPERIMENTAL

APPENDIX I

APPENDIX II

APPENDIX III

LIST OF FIGURES

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DEDICATION

To Lesley

SECTION I

INTRODUCTION

I-A HISTORY AND INTRODUCTION

The ability of halide ions to associate with either halogen or interhalogen molecules and thus form polyhalide ionic compounds has been recognised for over 150 years. In 1814 Gay-Lussac assumed that polyiodides formed when iodine dissolves in aqueous potassium iodide solution[1]. This assumption was confirmed in 1819 by the preparation of the solid strychnine triiodide, $C_{21}H_{22}O_2N_2.HI_3$, which was the first known crystalline polyhalide compound[2]. Johnson[3] also reported the preparation of a triiodide salt,KI_3,by the evaporation of a concentrated iodine -potassium iodide solution. However, Abbeg and Hamburger[4], and later Bancroft et al.[5] showed that Johnson's compound was simply a mixture of potassium iodide and iodine.

The first complete study of the preparation of alkali-metal polyhalides was reported in 1892 by Wells and co-workers[6-8]. These investigators prepared the polyhalide compounds contained in Table I-A-1, by dissolving the appropriate metal halide in water followed by the addition of the necessary halogen or halogens.

A large number of publications concerning polyhalide compounds have been reported in the literature and were especially numerous during the first three decades of this century. Much of this older work has been thoroughly reviewed in Gmelin's treatise[9]. Several reviews concerning interhalogen compounds and polyhalide complex ions have been published[10-13]. The recent reviews by Popov[10,11] are both extensive and authoritative, covering the literature to late 1970. Popov[10] has defined a polyhalide complex ion as an aggregate of three or more halogen atoms carrying either a positive or negative charge. Polyhalide ions can therefore be represented by the following general formula:

$$X_mY_nZ_p^{\pm}$$

where X,Y and Z represent the constituent halogen atoms. The sum m+n+p is usually an odd number: 3,5,7 or 9. Table I-A-2 lists polyhalide anions, stated by Popov to be 'identified more or less convincingly as anions of electrovalent salts'. This table does not include compounds whose identification seems doubtful.

Polyhalide anionic salts are most easily formed with large monovalent cations such as alkali-metal or tetra-alkylammonium ions. However, several polyhalide salts containing polyvalent cations, e.g. alkaline-earth metal ions, have been prepared[14,15]. Tetrachloroiodate salts containing the metals Be,Mn,Co,Ni and Zn as cations have also been reported in the literature[16].

TABLE I-A-1

ALKALI-METAL POLYHALIDES PREPARED BY WELLS[6-8]

CsI_3	RbI_3	$KI_3.H_2O$
$CsBrI_2$		
$CsIBr_2$	$RbIBr_2$	$KIBr_2.H_2O$
$CsIBrCl$	$RbIBrCl$	
$CsICl_2$	$RbICl_2$	$KICl_2.H_2O$
$CsBr_3$	$RbBr_3$	
$CsClBr_2$	$RbClBr_2$	
$CsCl_2Br$	$RbCl_2Br$	
$CsICl_4$	$RbICl_4$	$KICl_4.H_2O$
		$NaICl_4.2H_2O$
		$LiICl_4.4H_2O$

TABLE I-A-2

POLYHALIDE COMPLEX ANIONS IN CRYSTALLINE SALTS[10]

Trihalides	Pentahalides	Heptahalides	Polyiodides
I_3^-	I_5^-	I_7^-	I_4^-
I_2Br^-	I_4Cl^-	IF_6^-	I_9^-
I_2Cl^-	I_4Br^-	I_6Br^-	
IBr_2^-	$I_2Br_3^-$	Br_6Cl^-	
ICl_2^-	$I_2Br_2Cl^-$	$Cl_2F_4I^{-*}$	
$IBrCl^-$	$I_2BrCl_2^-$		
$IBrF^-$	$I_2Br_3^-$		
Br_3^-	$I_2Cl_3^-$		
Br_2Cl^-	$IBrCl_3^-$		
$BrCl_2^-$	ICl_4^-		
Cl_3^-	ICl_3F^-		
	IF_4^-		
	BrF_4^-		
	ClF_4^-		

*see reference 73

I-B GENERAL METHODS OF PREPARATION OF POLYHALIDE COMPOUNDS

The experimental procedures for the preparation of a polyhalide compound can involve one or more of the following :

(a) reaction of a crystalline halide with a gaseous or liquid halogen or interhalogen;

(b) reaction of a halide with a halogen or interhalogen dissolved in water or in a non-aqueous solvent;

(c) displacement of a less electronegative halogen in a polyhalide by a more electronegative halogen.

These general methods of preparation have been reviewed by Chattaway and Hoyle,[17] Cremer and Duncan[18,19] and more recently by Popov and Buckles[20] and by Schmeisser[21]. The gas-solid reactions in most cases are slow and often do not yield pure products.

Phase studies of binary systems alkali-halide— halogen or interhalogen and of ternary systems alkali-halide—H_2O—halogen or interhalogen have been studied, by numerous investigators, to identify and characterise the polyhalide compound formed by a particular preparative procedure. In a number of cases the experimental results clearly establish the existence of different polyhalides. However, some claims have been made for compounds whose existence has not been confirmed by other methods.

Popov[10] has reviewed most of the phase studies concerned with polyhalide compounds, the earlier reports being largely involved with the investigation of systems containing polyhalide salts of X_n^- anions (I_3^-,Br_3^- etc.).

These investigations confirm, for example, the existence of $KI_3.H_2O$ in the system $KI—H_2O—I_2$ but give no evidence for anhydrous KI_3[22]. Similar studies of the $CsI—I_2—H_2O$ system have shown that only the anhydrous polyhalides CsI_3 and CsI_4 are formed[23]. Contrary to some literature reports it should be noted that anhydrous $KICl_2$ can be prepared and is stable at room temperature[24].

Recently, studies have been made of ternary systems containing mixed trihalide salts. The systems $CsCl—ICl—H_2O$,[25] $RbCl—ICl—H_2O$,[26,27] $RbBr—IBr—H_2O$[28] and $CsBr—I_2—H_2O$[29] were found to contain only one polyhalide salt, i.e. anhydrous $CsICl_2$, $RbICl_2$,$RbIBr_2$ and CsI_2Br respectively being formed as new phases.

Similar studies of the systems $MCl—ICl_3—HCl—H_2O$, where M=K,Rb and Cs, have been reported by Stepin and co-workers[30-34]. $KICl_4.H_2O$, $RbICl_4$ and $CsICl_4$ were identified as the individual polyhalide compounds present.

The interaction of the components in the binary systems $CsCl—ICl$,[25] $RbCl—ICl$[25] and $RbBr—IBr$[28] have been studied by a differential thermal analysis method. The formation of $CsICl_2$,$RbICl_2$ and $RbIBr_2$ respectively were observed.

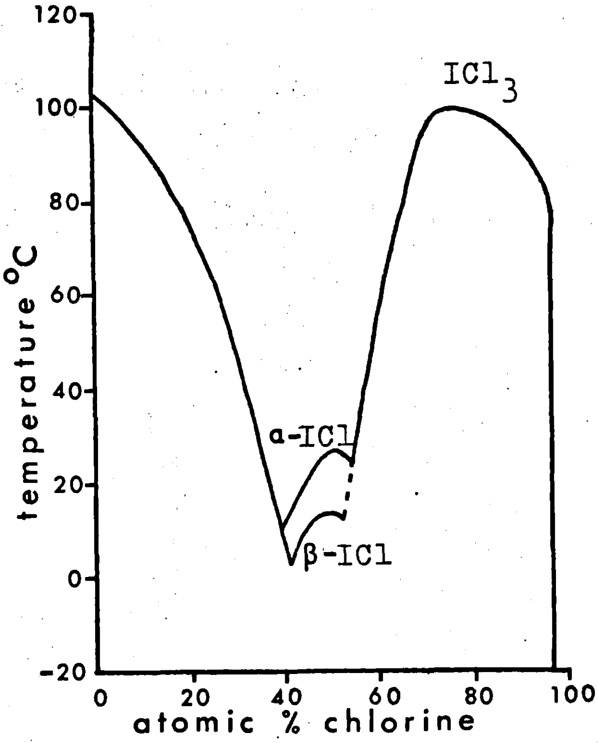
I-C NEUTRAL INTERHALOGENS

Iodine monochloride, ICl

Iodine monochloride was first prepared, in an impure form, by passing chlorine over crystalline iodine and collecting a portion of distillate between 100° and 102°[35]. Stortenbecker obtained ICl of fairly high purity by repeated re-crystallisation of the distillate in its own mother liquor[36]. Cornog and Karges have described a more convenient preparation which involves the addition of iodine to liquid chlorine followed by re-crystallisation, giving a completely pure product.[37]

ICl is a reddish-brown liquid at room temperature and can exist in two solid modifications: α-ICl, ruby-red needles, m.p. 27.53°, and β-ICl which are brownish-red plates, m.p. 13.9°. The latter form readily converts into the α-form on standing. Phase relations between the two forms, and ICl_3, in the iodine-chlorine system are shown in the following diagram[38].

FIGURE I-C-1 PHASE RELATIONS IN THE SYSTEM IODINE-CHLORINE



The boiling point of ICl at atmospheric pressure cannot be determined exactly since ICl is largely dissociated into I_2 and Cl_2 at this temperature (*ca*. 100°).

Calder and Giauque[39] have reported several thermodynamic properties of ICl, derived from a heat capacity study over the temperature range 17 to 332 K. These authors have also measured the total vapour pressure and partial pressures of ICl and Cl_2 over liquid ICl and these data were employed to calculate the partial pressure of ICl over the solid and liquid phases from 250 to 330 K. The standard enthalpy change for the following process was also reported by Calder and Giauque:

$$I_2(g) + Cl_2(g) = 2ICl(g) \quad \Delta H^o_{298} = -27.41 \pm 0.4 \text{ kJ mol}^{-1}$$

Other thermodynamic properties of ICl, together with the $\Delta H^o_{f_{298}}$ and $\Delta G^o_{f_{298}}$ values for ICl in CCl_4 solution, are collected in the National Bureau of Standards Technical Note 270-3[42].

Iodine trichloride, ICl_3

Iodine trichloride was first prepared by passing chlorine over crystalline iodine but this method results in poor yields and impure products[35]. Schmeisser[21] has reviewed the various preparative procedures for ICl_3 and recommends the method of Thomas and Dupuis, which involves the addition of finely powdered iodine to an excess of liquid chlorine at *ca*. -78°. After allowing the precipitated ICl_3 to stand at this temperature for several hours the excess chlorine is removed by evaporation to give a quantitative yield of ICl_3. ICl_3 was obtained as either a loose orange powder or as long orange-yellow needles[40].

Lamoreaux and Giauque[41] have reported the heat capacity of ICl_3 over the temperature range 15-320 K together with other thermodynamic parameters in a continuation of the thermodynamic study of the iodine -chlorine system which previously concerned ICl[39]. Measurement of the Cl/I atomic composition ratio in the gas over solid ICl_3 and the liquid which is in equilibrium with it on the ICl side of the melting curve was made. This ratio was also determined at the ICl_3:ICl eutectic temperature, 296.21 K, and enabled calculation of the partial pressures of ICl and Cl_2 over this solid-liquid equilibrium system. These data, combined with the previous studies of ICl,were employed to calculate the enthalpy of formation of ICl_3 from either ICl and Cl_2 or from $\frac{1}{2}I_2$ and $\frac{3}{2}Cl_2$.

The following table contains some of the thermodynamic constants derived from this study. Other data reported for ICl_3 are collected in the National Bureau of Standards Technical Note 270-3[42].

TABLE I-C-1

Property	
$\Delta H^o_{f_{298}} ICl_3(c)$	-89.29^a
$\Delta G^o_{f_{298}} ICl_3(c)$	-22.65^a
$S^o_{298} ICl_3(c)$	-169.03^b

a kJ mol^{-1}, b JK^{-1} mol^{-1}

Earlier measurements of the I_2—Cl_2 system, which include C/I atomic composition ratios, were made by Stortenbecker[36] and by Nies and Yost[43].

Bromine chloride, BrCl

Bromine chloride was first observed by Balard who noticed that the intensity of the colour of chlorine and bromine diminished on mixing the two elements in the gaseous phase[44]. However, it was not until a century later that spectroscopic evidence had established the existence of BrCl beyond doubt. Such studies of bromine-chlorine mixtures, either in the gaseous state or in CCl_4 solution, indicated the presence of a new absorption band at ca. 370nm, which was assigned to the compound[45]. Similar observations led to the conclusion that the system

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$

has an equilibrium constant of ca. 5 at 20° and that the equilibrium mixture contains approximately 80% BrCl at this temperature[46].

Until very recently BrCl had not been isolated as a pure compound. Schmeisser and Tytko have successfully prepared pure bromine chloride from elemental bromine and chlorine[47]. The preparation was carried out in difluorodichloromethane with bromine being quantitatively chlorinated by a large excess of chlorine at -79° under U.V. irradiation. Removal of BrCl from the equilibrium mixture was achieved by precipitation on cooling to between -110° and -120°. Excess chlorine and solvent were removed under high vacuum at the same temperature to yield an orange powder.

This powder was then sublimed at -79°, whereupon orange-coloured crystals (m.p. -56.5°) formed which were reported to be completely stable at -79°.

These authors reported that BrCl was stable at room temperature in acetonitrile because of the formation of an adduct between BrCl and this solvent. The ionic equilibrium

$$2BrCl_{solv} \rightleftharpoons Br^{+}_{solv} + BrCl_2^{-}$$

was shown by a U.V. spectroscopic study to exist in these solutions. The following equilibrium has been studied by a number of different methods:

$$Br_2(g) + Cl_2(g) \rightleftharpoons 2BrCl(g) \qquad (1)$$

(a) U.V. spectra studies in various solvents[48]
(b) e.m.f. measurements in HCl solutions[49]
(c) equilibria in complex systems involving metal halides[50] and nitrogen oxides or oxyhalides[51]

These methods gave values for the equilibrium constant of process (1) varying from 0.11 to 0.34. However, no direct measurement of the equilibrium was made until Mattraw et al. derived an equilibrium constant from a mass-spectographic analysis of process (1), a value of 0.15 being obtained[52]. From this datum, together with thermodynamic data for BrCl(g), standard state values for $Br_2(l)$, $Br_2(g)$ and $Cl_2(g)$, the thermodynamic constants contained in the following table were reported. These values have been revised with more recent ancillary data and are collected in the National Bureau of Standards Technical Note 270-3[42].

TABLE I-C-2

STANDARD STATE THERMODYNAMIC
PROPERTIES OF BrCl(g) at 298 K

$\frac{1}{2}Cl_2(g) + \frac{1}{2}Br_2(l) = BrCl(g)$

Property	Mattraw et al.	N.B.S. Tech. Note 270-3
ΔH_f^o	14.77	14.64[a]
ΔG_f^o	-0.78	-0.96[a]
S^o	239.85	239.99[b]
C_p^o	34.99	34.98[b]

[a] kJ mol^{-1}, [b] JK^{-1} mol^{-1}

The degree of dissociation and standard thermodynamic constants of BrCl, in CCl_4 solution, have been reported by Popov and Mannion[53]. The data from this study are reported in the National Bureau of Standards Technical Note 270-3[42].

Iodine monobromide, IBr

Iodine monobromide can be prepared by the direct combination of iodine with bromine. Gutmann[54] has described the preparation of a pure sample of IBr which was purified, by repeated partial crystallisation, to an almost constant conductance of 7 x 10^{-6} ohm^{-1} cm^{-1}, measured at 55°.

IBr exists as black-brown crystals (m.p.40°, b.p. 119°) at room temperature. The degree of dissociation of IBr, at 298 K, in the gaseous phase, was reported to be ca. 8.9%[55].

The thermodynamic properties of IBr have been the subject of several studies.[55–60] However, no recent thermochemical studies appear to have been made. The data from the above studies are reported in the National Bureau of Standards Technical Note 270-3.[42] The standard free energy and enthalpy of formation of IBr in CCl_4 solutions are also reported.[42]

Iodine monofluoride, IF

Iodine monofluoride cannot be isolated as a pure compound at room temperature since rapid disproportion-ation into iodine and iodine pentafluoride occurs above -14°.

$$5IF \longrightarrow 2I_2 + IF_5$$

A value of $\Delta G^{o}_{298} = -178.7$ kJ mol^{-1}[64] can be calculated for this disproportionation from the free energies of formation of IF_5 and IF.[61] The value of ΔG^{o} becomes positive at temperatures above 800 K (+23.8 kJ mol^{-1} at 800 K) hence IF should be the stable and abundant species under these conditions.

Iodine monofluoride was first observed by Durie in the emission spectrum of the bright yellow-green flame produced by the combustion of either methyl iodide[62] or iodine[63] in fluorine. A dissociation energy of 276.9 kJ mol^{-1} was calculated from this spectrum.[63] The enthalpy of formation at 0 K of gaseous IF can therefore be obtained from the dissociation energies of I_2, F_2 and IF. Upon correction of this value to 298 K, together with data for the crystalline, rather than the gaseous state of iodine, the value ΔH^{o}_{f} IF(g)$_{298}$ $= -94.6 \pm 3.8$ kJ mol^{-1} was obtained.[64] Other thermodynamic properties are compiled by Stein.[64]

Schmeisser and Scharf[65] have prepared iodine monofluoride by passing a mixture of nitrogen-diluted fluorine through a solution of iodine in CCl_3F at -78°. The same workers have also prepared IF from IF_3 and iodine in the presence of MeCN or pyridine at -40°[66] and by the thermal decomposition of IF_3 between -28° and 12°.

$CsIF_2$ could not be prepared by reacting equimolar amounts of CsF and IF in acetonitrile at -40°, the product being Cs_3IF_6. The reaction of IF with CsCl under identical conditions gave $CsIF_4$ and $CsICl_2$.[67]

However, the salt Et_4NIF_2 was prepared in acetonitrile solution by the following method:[68]

$$Et_4NICl_2 + 2AgF \longrightarrow Et_4NIF_2 + 2AgCl\downarrow$$

The corresponding silver, potassium and caesium salts could not be prepared by this method.

Iodine trifluoride, IF_3

Schmeisser and Scharf have prepared iodine trifluoride by passing a stream of fluorine, diluted with nitrogen, through a solution of iodine in CCl_3F at -78°.[65] The trifluoride was obtained as a yellow solid upon evaporation of the solvent under vacuum at -78°. Differential thermal analysis showed that IF_3 decomposes, at -28°, into IF and IF_5.[66]

Two fluoroiodate (III) anions are known. Tetrafluoroiodate salts, MIF_4 (M=K,Rb and Cs), can be prepared by the reaction of IF_5 with an alkali-metal fluoride in acetonitrile solution at -50°.[69] Schmeisser et al. have reported the synthesis of Cs_3IF_6 by reacting IF_3 with CsF (1:3 molar ratio) in MeCN at -78°.[66] The bright yellow compound decomposes at approximately 104°.

The reaction of IF_3 with CsCl in MeCN appears to be complex and leads to the formation of a mixture of polyhalide salts[69].

$$6IF_3 + 6CsCl \longrightarrow 3CsIF_4 + CsIF_6 + CsICl_2 + CsICl_4$$

Christe and Naumann have reported the Raman and infra-red spectra of $CsIF_4$ (prepared from IF_3) and of Cs_3IF_6[70]. The Raman spectrum of $CsIF_4$ was found to be very different from that previously reported and strongly resembled those of XeF_4, BrF_4^- and ClF_4^- being consistent with a square-planar structure of D_{4h} symmetry. Distinct differences in the spectra of $CsIF_4$ and Cs_3IF_6 suggested that a formulation of $CsIF_4.2CsF$ for Cs_3IF_6 was unlikely.[71]

The complete exchange of fluorine atoms for the trifluoroacetate group has been observed in the reaction of $CsIF_4$ and Cs_3IF_6 with excess trifluoroaceticanhydride in MeCN. Identical products were obtained by the direct reaction of IF_3 with a stoichiometric amount of CsF and an excess of $(CF_3CO)_2O$.[72]

$$CsIF_4 + 4(CF_3CO)_2O \longrightarrow CsI(OCOCF_3)_4 + 4CF_3COF \qquad (2)$$

$$IF_3 + CsF + 4(CF_3CO)_2O \longrightarrow CsI(OCOCF_3)_4 + 4CF_3COF$$

$$Cs_3IF_6 + 6(CF_3CO)_2O \longrightarrow Cs_3I(OCOCF_3)_6 + 6CF_3COF \qquad (3)$$

$$IF_3 + 3CsF + 6(CF_3CO)_2O \longrightarrow Cs_3I(OCOCF_3)_6 + 6CF_3COF$$

The above reactions are similar to the reaction of R_4NIF_6 with $(CF_3CO)_2O$ reported by Klamm and Meinert.[73]

$$R_4NIF_6 + 2(CF_3CO)_2O \longrightarrow R_4NIF_4(OCOCF_3)_2 + 2CF_3COF$$

Conductimetric titrations between $(CF_3CO)_2O$ and $CsIF_4$ or Cs_3IF_6 in MeCN were described to support the stoichiometry given in equations (2) and (3).

The reaction of IF_3 with $(CF_3CO)_2O$ in MeCN as solvent was shown by a conductimetric titration to consist of the following steps:[74]

$$2IF_3CH_3CN \rightleftharpoons [IF_2(CH_3CN)_2]^+[IF_4]^-$$

$$[IF_2(CH_3CN)_2]^+ + 2(CF_3CO)_2O \longrightarrow [I(OCOCF_3)_2(CH_3CN)_2]^+ + 2CF_3COF$$

$$IF_4^- + 4(CF_3CO)_2O \longrightarrow [I(OCOCF_3)_4]^- + 4CF_3COF$$

The literature contains no thermodynamic data for iodine trifluoride. However, the average bond energy has been estimated to be 272 kJ mol^{-1} from the bond energies of the other halogen fluorides[64]. The enthalpy of formation of gaseous IF_3 from the elements at 298 K has also been estimated[64].

Iodine pentafluoride, IF_5

Iodine pentafluoride was first prepared in measurable quantities by Moissan[75,76], from the reaction between elemental iodine and fluorine at room temperature. Prideaux[77] confirmed Moissan's preparation which was improved by Ruff et al.[78,79] Iodine pentafluoride can also be prepared by the fluorination of I_2, HI, I_2O_5 and metal iodides with various fluorinating agents[78-84].

IF_5 is a colourless liquid at room temperature, m.p. 9.43° and b.p. 100.5°[64]. Conductance studies indicate a degree of self-ionization in the liquid state and a specific conductance of 5.4×10^{-6} ohm^{-1} cm^{-1} was reported by Rogers et al.[85]

$$2IF_5 \rightleftharpoons IF_4^+ + IF_6^-$$

The standard enthalpy of formation of $IF_5(l)$ has been reported in three studies. Woolf derived a value of $\Delta H_f^o\ IF_5(l)$, at 20°, from calorimetric measurement of the enthalpy of reaction of the compound with aqueous potassium hydroxide[86]. Woolf[87] has corrected this result with the appropriate heat capacity data to 25° and revised ancillary data to give $\Delta H^o_{f298} IF_5(l) = -884.92 \pm 2.09$ kJ mol^{-1}. Jenkinson has measured the enthalpy of reaction of IF_5 with excess aqueous NaOH and derived $\Delta H^o_{f298} IF_5(l) = -884.71 \pm 1.13$ kJ mol^{-1}.[88] The enthalpy of formation of IF_5 has also been determined by fluorine bomb calorimetry[89]. Iodine was burned in an atmosphere of fluorine, under varying pressures to give a mixture of IF_5 and IF_7. The quantity of IF_7 was almost negligible under mild fluorinating conditions and was determined by chemical analysis. A value of $\Delta H^o_{f298} IF_5(l) = -881.99 \pm 1.34$ kJ mol^{-1} was reported from this study.

The heat capacity, enthalpy of fusion and vaporisation together with the standard entropy of gaseous IF_5 have been reported by Osbourne et al.[90] Other properties are listed by Stein[64].

Hexafluoroiodate salts, MIF_6 (M=K,Rb and Cs) have been prepared by the reaction of either the metal fluoride[91] or the iodide[92] with an excess of boiling IF_5. Tetra-alkylammonium hexafluoroiodates were prepared, by Klamm and Meinert, from $AgIF_6$[93].

$$IF_5 + AgF \xrightarrow[-40^o]{CH_3CN} AgIF_6$$

$$AgIF_6 + R_4NCl \xrightarrow[-40^o]{CH_3CN} AgCl\downarrow + R_4NIF_6 \quad (R=Me \text{ and } Et)$$

Klamm and Meinert have also studied the chemical properties of the hexafluoroiodate ion in the form of its tetraethylammonium salt. This salt was soluble in acetonitrile but in moist acetonitrile was hydrolysed, according to the following equation:[73]

$$Et_4NIF_6 + H_2O \longrightarrow Et_4NIOF_4 + 2HF$$

The tetrafluoro-oxyiodate was not isolated. Infra-red spectra of the reaction products showed bands that were characteristic of the $IO_2F_2^-$ anion as well as a band at 880-890cm^{-1} which was assigned to the IOF_4^- anion. Hexafluoroiodate salts were also reported to react with HCl, SO_2Cl and $SO_2Cl_2^-$ to give ICl_4^- ions.

Colorimetric and conductimetric titrations of Et_4NIF_6 with Et_4NCl in dilute acetonitrile solution indicated a 1:2 reaction which the authors[73] suggested as evidence for a new ternary polyhalide ion $IF_4Cl_2^-$.

$$IF_6^- + 2Cl^- \longrightarrow IF_4Cl_2^- + 2F^-$$

Iodine pentafluoride does not react with chlorine -containing interhalogens (ICl, ICl_3, BrCl) at room temperature[94]. However, upon addition of pyridine to a solution of IF_5 and chlorine halide in trifluoro-trichloroethane, yellow adducts are precipitated.

$$XCl + 2Py + IF_5 \longrightarrow XPy_2ClIF_5$$

where X = I, ICl_2, Br or Cl

The complex appears to be ionic with the structure $XPy_2^+ICIF_5^-$. Iodine pentafluoride reacts under similar conditions with tetra-alkylammonium chlorides in a 1:1 molar ratio. Klamm and Meinert[94] suggested that the first stage of the reaction involves a previously unknown, unstable interhalogen, IF_4Cl and was represented by the following equation:

$$R_4NCl \quad + \quad IF_5 \longrightarrow R_4NF \quad + \quad IF_4Cl$$

The tetra-alkylammonium fluoride then reacts with IF_5 to give the corresponding hexafluoroiodate salt:

$$R_4NF \quad + \quad IF_5 \longrightarrow R_4NIF_6$$

while the IF_4Cl was thought to react with the tetra-alkylammonium chloride to give a tetrafluorodichloroiodate (V) salt.

$$R_4NCl \quad + \quad IF_4Cl \longrightarrow R_4NIF_4Cl_2$$

The standard enthalpy of formation of the following alkali-metal hexafluoroiodate salts were derived from measurement of the enthalpy of aqueous alkaline hydrolysis[95].

$\Delta H^o_{f_{298}} KIF_6(c) = -1492 \pm 2.5$, $\Delta H^o_{f_{298}} RbIF_6(c) = -1473 \pm 2.0$,

and $\Delta H^o_{f_{298}} CsIF_6(c) = -1466 \pm 2.0$ kJ mol^{-1}

A study of the I_2—IF_5 system in Freon 11, between -80° and -30°, has indicated an addition product $I_2.3IF_3$ although no conclusive evidence for this stoichiometry was given[96]. The addition of pyridine or an alkali-metal fluoride to the above solution results in the following reactions:

$$I_2.3IF_5 + 2Py \longrightarrow IPy_2^+IF_6^-$$

$$I_2.3IF_5 + 5MF \longrightarrow 5MIF_4 \qquad (M=K \text{ and } Cs)$$

A 1:1 stoichiometry for the addition compound, therefore cannot be excluded.

The addition of iodine to a solution of IF_5 in trifluorotrichloroethane, at temperatures above -30°, was reported to produce $I^+IF_6^-$[97]. $IPy_2^+IF_6^-$, dipyridine iodine (I) hexafluoroiodate (V) precipitated on the addition of pyridine. This compound was stable, m.p. 166°, and could be re-crystallised from acetonitrile. Conductance data and the infra-red spectrum indicated the ionic structure rather than $IF_3.Py$. The compound was also prepared by the following reactions:

$$IPy_2F + IF_5 \xrightarrow{\text{Freon 11}} IPy_2IF_6$$

$$KIF_6 + IPy_2NO_3 \xrightarrow{\text{MeCN}} IPy_2IF_6 + KNO_3$$

Meinert et al.[98] have reported an addition compound from the reaction of XeF_2 with IF_5. $XeF_2.2IF_5$ was prepared by dissolving XeF_2 in IF_5 and concentrating the solution at 5°. These authors also claimed that XeF_4 reacted with liquid IF_5 to give IF_7.

Nikolaev et al. however, have reported that XeF_4 was readily soluble in IF_5 at room temperature. On removal of excess IF_5 a solid compound, stable to 92°, and shown by analysis to be $XeF_4.IF_5$ was obtained. No evidence for iodine heptafluoride in solutions of XeF_4 in IF_5 was found[99,100].

Iodine Heptafluoride, IF_7

During the preparation of IF_5 Ruff and Keim[101] noticed the presence of a very volatile impurity which was suspected to be a higher fluoride. No evidence was found for the reaction between fluorine and iodine pentafluoride at 25° but the heptafluoride was obtained in good yield at 250° to 270°. Schumb and Lynch[102] have described an apparatus for preparing IF_7 from the elements and for purification of the compound by fractional sublimation. The reaction of IF_7 with either water or with glass results in IOF_5 being present as an impurity in many samples of IF_7. Since iodine is difficult to dry Bartlett and Levchuk have recommended the use of PdI_2 as a starting material[103].

Iodine heptafluoride is a colourless gas which condenses to a white solid at 0°. The solid sublimes at 4.77° and melts under its own vapour pressure forming a colourless liquid at 6.45°[64].

Bernstein and Katz have reported equilibrium pressure measurements of the dissociation of IF_7 over the temperature range 450° to 550°[104].

$$IF_7(g) \longrightarrow IF_5(g) + F_2(g)$$

From these measurements the enthalpy of formation of both IF_5 and IF_7 can be calculated. The updated value derived from this work is given by Cox:[105] $\Delta H^o_{f_{298}} IF_7(g) = -953.88 \pm 7.78$ kJ mol^{-1}. A value of $\Delta H^o_{f_{298}} IF_7(g) = -951.44 \pm 4.77$ kJ mol^{-1} has been derived from a fluorine bomb calorimetric study[89].

Other thermodynamic properties are compiled by Stein[64]. No complexes of alkali-metal fluorides with iodine heptafluoride are known and attempts at their preparation have proved unsuccessful[102].

I-D INFRA-RED AND RAMAN SPECTRA OF POLYHALIDE ANIONS

The vibrational spectra of polyhalide anions in the solid state and in solution have been extensively studied by many investigators[106-120]. Recently Gabes[117-119] has reported a very complete vibrational study of several trihalide ions (I_3^-, IBr_2^-, ICl_2^-, Br_3^- and $BrCl_2^-$). Much of the earlier work concerning these ions was incomplete and is discussed by Gabes.

Pentahalide anions have not been as extensively studied as trihalide ions. The Raman and infra-red spectra of the tetrachloroiodate ion are reported in the literature[106,114-116]. Yagi and Popov[120] have reported the infra-red spectra of organic salts containing the mixed pentahalide anions $I_2Cl_3^-$ and I_2ClBr^-.

I-E THERMODYNAMIC PROPERTIES OF ANIONIC POLYHALIDE COMPOUNDS

The majority of the thermodynamic data reported in the literature for anionic polyhalide compounds can be conveniently separated into two main sections:

(1) Stability constant data for polyhalide anions in (a) aqueous and (b) non-aqueous solution

(2) Data for crystalline anionic polyhalide compounds

Thermodynamic data for crystalline anionic polyhalide compounds are very sparse and will be discussed in section II-A (p.46).

The following table contains data reported, by the National Bureau of Standards,[42] for several trihalide ions.

(1) Stability constants of polyhalide anions

A large number of publications concerning stability constants of polyhalide ions are reported in the literature. Recently studies of this type have been largely carried out in non-aqueous solvents rather than in water.

(a) In aqueous solution

Much of the pre-1930 work on this subject has been reviewed by Gmelin[9]. However,many of the earlier studies did not take into account the role of ionic strength in solution equilibria or hydrolysis of the polyhalide species. Most of these equilibria have been re-investigated.

Because of its relative stability in aqueous solution the triiodide ion has been thoroughly investigated[122-129].

TABLE I-E-1

STANDARD STATE THERMODYNAMIC PROPERTIES OF AQUEOUS TRIHALIDE ANIONS[a]

Ions	$-\Delta H^{o}_{f_{298}}$ kJ mol^{-1}	$-\Delta G^{o}_{f_{298}}$ kJ mol^{-1}	S^{o}/J K^{-1} mol^{-1}
Cl_3^-		c	
Br_3^-	130.42 131.13 ±0.54[b]	107.07 107.03[b]	215.48 212.76[b]
Br_5^-	142.26	103.76	316.73
Br_2Cl^-	170.29	128.45	188.70
I_3^-	51.46	51.46	239.32
ICl_2^-		161.08	
I_2Cl^-		132.63	
IBr_2^-		123.01	
I_2Br^-	128.03	110.04	197.48

[a] all std. state m=1 aq except b

[b] Ref.[121]

[c] A value of ΔG^{o}_{f} = '-20.' k cal mol^{-1} is reported in Ref.[42]

Thermodynamic constants reported for this ion, by several authors, are collected in Table I-E-2.

TABLE I-E-2

THERMODYNAMIC CONSTANTS FOR THE REACTION [10]

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

Temp	K_f	Temp	K_f	Temp	K_f
15	935	0	1420	15	949
20	824	10	1071	20	842
25	723	20	825	25	751
30	626	30	645	30	666
35	547	40	510	35	593
$\Delta H = -19.92 \pm 1.67$ kJ mol^{-1}		$\Delta H = -18.16$ kJ mol^{-1}		$\Delta H = -17.01$ kJ mol^{-1}	
		$\Delta S = -6.15$ JK^{-1} mol^{-1}		$\Delta S = -2.05$ JK^{-1} mol^{-1}	

Awtrey and Connick[128] have also reported an enthalpy of formation for the triiodide ion, determined from a spectrophotometric study, of -21.34 ± 1.67 kJ mol^{-1}. Recently Mironov and Lastovkina have reported stability constants and other thermodynamic constants for the following reaction in 0.1M perchloric acid at an ionic strength of 3.0.

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$

These data are contained in Table **I-E-5.**

Measurements of the stability constant of the tribromide ion in aqueous solution are less numerous than for the I_3^- ion reflecting the much higher reactivity of bromine. In most cases stability constant data gives evidence for the existence of the Br_5^- ion especially in concentrated aqueous solutions of bromine.

Scaife and Tyrrell have derived equilibrium constants for the following processes (1) and (2) from experiments which involved equilibrating bromine between two aqueous solutions, one of which contained potassium bromide.[130]

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad (1)$$

$$Br_3^- + 2Br^- \rightleftharpoons Br_5^- \qquad (2)$$

Equilibrium constants for reactions (1) and (2) were determined at 5°, 25° and 30°, the values reported being 19.85, 16.85 and 15.28 for (1) and 1.94, 1.45 and 1.30 $l\ mol^{-1}$ for (2).

Mussini and Fàita[131] have reported equilibrium constants and standard state thermodynamic values for the following process from an e.m.f. study of the bromine/bromide ion system in aqueous solution at various temperatures:

$$Br_2(aq) + Br^-(aq) = Br_3^-(aq)$$

The following values were reported: $\Delta G^o = -7.150 \pm 0.025$ kJ mol^{-1}, $\Delta H^o = -9.523 \pm 0.071$ kJ mol^{-1} and $\Delta S^o = -7.95 \pm 0.38$ J deg^{-1} mol^{-1}.

Popov[10] has described other studies concerning the Br_3^- and Br_5^- ion[132-134]. Mironov and Lastovkina have reported thermodynamic constants for the Br_3^- ion, derived from stability constant data, and these results are contained in Table I-E-5.

Because of its extreme instability in aqueous solution the trichloride ion has not been the subject of many investigations in this solvent. Sherrilland Izard[135] have investigated the solubility of chlorine in aqueous chloride solutions and determined a stability constant of ca. 0.2 l mol^{-1}. Zimmerman and Strong[136] have studied the absorption spectrum of chlorine dissolved in aqueous hydrochloric acid of varying concentration which were maintained at a constant ionic strength of 1.0 by the addition of perchloric acid. A stability constant of 0.191 ± 0.016 l mol^{-1} was derived from this study together with an estimation of the enthalpy of formation of approximately 8 kJ mol^{-1}.

Cerquetti et al.[137] have derived the equilibrium constant, K_1, for the following process, over the temperature range 25-80° by measurement of the e.m.f. of the cell illustrated below.

$$Cl_2(gas) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq) \qquad (3)$$

$$H_2, 1\ atm \,|\, HCl, 1M \,|\, Cl_2, p\ atm$$

Measurement of chlorine solubility in parallel to the e.m.f. measurements allowed the determination of the equilibrium constant, K_2, of process (4) to be made and thus the thermodynamic functions for all the species in the $Cl_2/Cl^-/Cl_3$ system to be calculated, Table I-E-3.

$$Cl_2(aq) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq) \qquad (4)$$

TABLE I-E-3

Reaction	K_1[a]	K_2[a]	ΔH^o kJ mol^{-1}	ΔG^o kJ mol^{-1}	ΔS^o J K^{-1} mol^{-1}
$Cl_2(gas) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq)$	0.0119		−31.33	+11.00	−141.4
$Cl_2(aq) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq)$		0.215	−10.04	+3.81	−46.4

[a] Units for K_1 and K_2 are not reported in reference 137

Recently Shimonis[138] has determined the stability constant, K, of the trichloride ion from a potentiometric study of the following process in aqueous hydrochloric acid (1-5M):

$$Cl_2(aq) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq)$$

The value of K and the stability of the Cl_3^- ion were both found to decrease with increasing hydrochloric acid concentration.

No mention of the existence of the pentachloride ion appears to be present in the literature.

Stability constants of mixed trihalide ions have been determined in aqueous solution by a number of investigators. The results of these studies are contained in Tables I-E-4,5 and 6. Table I-E-6 contains the recent results of Mironenko et al. which are interesting since the stability of these polyhalide ions were measured in the presence of alkali-metal cations (K^+,Rb^+ and Cs^+). The stability of the complex ions was observed to decrease in the following sequence:

$$I_2Br^- \longrightarrow I_2Cl^- \longrightarrow Br_2Cl^-$$

The effect of the alkali-metal background was found to depend directly on the above order of stability being at a maximum for the least stable ion (Br_2Cl^-). The greatest stability of each complex ion was exhibited in the presence of the K^+ ion and the least in the presence of the Cs^+ion. These authors postulated that this effect was due to the large hydrated K^+ ion having less polarising action on the polyhalide anion than the smaller less solvated Rb^+ and Cs^+ ions.

No stability constant data for the tetrachloroiodate ion or for other pentahalide ions appear to have been reported in the literature.

TABLE I-E-4

STABILITY CONSTANTS OF MIXED TRIHALIDE IONS IN AQUEOUS SOLUTION AT 25°[10]

Ion	Dissociation Products	K_f l mol^{-1}	Method	Reference
I_2Cl^-	$I_2 + Cl^-$	1.66	a	139
		1.59	b	122
		5.7[d]	a	140
I_2Br^-	$I_2 + Br^-$	12.2	b	122
		13.0[d]	a	140
IBr_2^-	$IBr + Br^-$	370	c	141
$IBrCl^-$	$IBr + Cl^-$	435	c	141
ICl_2^-	$ICl + Cl^-$	166	c	141
Br_2Cl^-	$Br_2 + Cl^-$	1.47	a	142

[a] Spectrophotometry, [b] Solubility, [c] Distribution, [d] at 22°

TABLE I-E-5

THERMODYNAMIC CONSTANTS FOR THE REACTION
$X_2(aq) + Y^-(aq) \rightleftharpoons X_2Y^-(aq)$ at 25°
IN 0.1M ACID AND IONIC STRENGTH OF 3.0 [11,143-145]

Ions	Method	$K_f(M^{-1})$	$-\Delta G^\circ$ kJ mol^{-1}	$-\Delta H^\circ$ kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}
$ClBr_2^-$	a	1.4±0.3	0.84±0.4	9.2±0.8	-29.3±4.2
ClI_2-	b	2.0±0.1	1.67±0.4	-7.1±0.4	29.3±4.2
Br_3^-	c	11.3±1.4	-6.02±0.79	-6.95±0.59	3.10±6.69
Br_3^-	a	11.1±0.3	-5.98±0.29	-6.86±0.59	2.97±2.93
Br_3^-	d	12.7±0.3	-6.28±0.38	-6.82±0.63	1.84±3.35
BrI_2^-	b	13.3±0.6	6.3±0.08	7.5±1.3	-4.2±3.3
BrI_2^-	a	13.3±0.6	6.3±0.08	9.2±0.4	-9.2±1.7
I_3^-	b	385±20	14.6±0.08	13.0±2.1	5.9±8.4
I_3^-	a	385±20	14.6±0.008	13.8±0.8	2.9±3.8

a Calorimetric, b Temperature coefficient, c Extraction, d Spectroscopic.

TABLE I-E-6

THERMODYNAMIC CONSTANTS OF SOME TRIHALIDE IONS AT IONIC STRENGTH 0.63-0.70 IN THE PRESENCE OF CATIONS K^+, Rb^+ and Cs^+ [146]

Complex Ion	Cation	$-\Delta G$ kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
Br_2Cl^-	K^+	0.50	6.7	-20.9
	Rb^+	-0.4	4.6	-14.2
	Cs^+	-0.8	5.0	-18.8
I_2Cl^-	K^+	1.3	-3.3	15.5
	Rb^+	0.8	-2.5	10.9
	Cs^+	0.8	-1.3	7.1
I_2Br^-	K^+	6.7	5.4	4.2
	Rb^+	6.3	1.30	16.7
	Cs^+	6.7	2.9	12.6

(b) In non-aqueous solution

Much of the literature concerning stability constants of polyhalide ions in non-aqueous solution has been thoroughly reviewed by Popov[10,11].

A general characteristic property of polyhalide ions in such solvents is the dramatic increase in the magnitude of the stability constant compared with the value obtained in aqueous solution. Stability constant data for the ions Cl_3^-, Br_3^- and I_3^- in several non-aqueous solvents are contained in the following table to illustrate this observation[147].

TABLE I-E-7

STABILITY CONSTANTS* OF Cl_3^-, Br_3^- and I_3^- IN APROTIC SOLVENTS

Ion	Solvent		
	CH_3NO_2	$(CH_3)_2CO$	CH_3CN
I_3^-	$10^{6.7}$	$10^{8.3}$	$10^{6.6}$
Br_3^-	$10^{7.0}$	$10^{9.0}$	10^{7}
Cl_3^-	10^{13}	10^{12}	10^{10}

*Units for these stability constants are not reported in reference 147

The formation of alkali and alkaline-earth polyiodides in DMSO[148] and alkaline-earth polyiodides in DMF[149] have been recently studied by Gorenbein et al. Enthalpies of formation of these polyhalide complexes in the above solvents were derived from a titration-calorimetry study of the following reaction:

$$xI_2(\text{non aq}) + MI_x(\text{non aq}) \longrightarrow M(I_3)_x(\text{non aq})$$

where M=Li,Na,K,Rb,Cs,Ca,Sr and Ba

The results derived from these experiments were compared with previous studies, reported by Gorenbein et al., of these complexes in acetonitrile and acetone[150,151].

SECTION II

RESULTS AND DISCUSSION

II-A THERMOCHEMISTRY OF ALKALI-METAL POLYHALIDES

Introduction

The standard enthalpies of formation reported in this section were derived from experimentally determined enthalpies of reaction and appropriate ancillary data. All values are quoted at 298.15 K. The dilution factor,n, refers to the mole ratio of water to reactant. Heats of mixing and ampoule-breaking have been considered to be negligible. The error limits assigned to the experimental and derived results and ancillary data are discussed in Appendix III.

No standard enthalpy of formation data for the polyhalide compounds prepared in sections III-A-(1) to III-A-(7) are reported in the literature. However, the standard enthalpies of formation of several crystalline polyiodides are reported[152-154]. Babkov and Stepin[152] have derived values for ΔH_f^o CsI_3(c) and ΔH_f^o RbI_3(c) from dissociation pressure measurements. Topol[153-154] has reported e.m.f. measurements, over the temperature range ca. 25-110°, of solid-state cells containing MI_3 (where $M=Cs^+,Rb^+,NH_4^+$ and R_4N^+) of the following type:

$$Ag|AgI|C,\ MI_x - MI_{x+2y}$$

C=carbon

$$Ag|AgI|C,I_2(c)$$

to obtain thermodynamic data for the reaction

$$MI_x(c) \quad + \quad yI_2(c) \quad = \quad MI_{x+2y}(c)$$

The standard entropies, free energies and enthalpies of formation of these polyhalides were calculated from the e.m.f. data. From the free energies and the vapour pressure of crystalline iodine, dissociation pressure expressions for the polyhalides were calculated over the experimental temperature range. The thermodynamic data reported by Topol for the ammonium, rubidium and caesium polyiodide systems are contained in the following tables.

VALUES OF ΔG^o, ΔH^o and ΔS^o at 25° FOR THE REACTION[153]

$$MI_x(c) + yI_2(c) = MI_{x+2y}(c)$$

MI_x-MI_{x+2y}	$-\Delta G^o$/kJ mol^{-1}	$-\Delta H^o$/kJ mol^{-1}	$-\Delta S^o$/J K^{-1}
RbI-RbI_3	10.0±0.4 (9.2)	13.0 (9.6)	9.6 (1.3)
NH_4I-NH_4I_3	7.5±0.4 (7.5)	8.8 (4.6)	4.6 (-9.6)
CsI-CsI_3	14.6±0.4 (14.2)	15.5 (10.9)	3.8 (-11.3)
CsI_3-CsI_4	2.64±0.13 (2.30)	3.35 (3.8)	2.5 (5.0)

VALUES OF ΔG^o_f, ΔH^o_f and S^o at 25° FOR POLYIODIDES[153]

Polyiodide	$-\Delta G^o_f$/kJ mol^{-1}	$-\Delta H^o_f$/kJ mol^{-1}	S^o/J K^{-1} mol^{-1}
RbI_3	335.6	341.4	224.3
NH_4I_3	120.1	210.0	230
CsI_3	348.1	352.3	243
CsI_4	350.6	356.1	297

The values in parentheses were calculated by Foote et al.[155-157] from solubility data for these polyiodides in benzene and toluene.

Morss[158] has recently reported the standard enthalpy of formation of crystalline caesium tribromide. A value of ΔH_f^o $CsBr_3(c) = -433.8 \pm 2.0$ kJ mol^{-1} was derived from the reaction of $CsBr_3$ with excess 0.01 mol dm^{-3} KI solution. The following calorimetric reaction was studied in an isoperibol calorimeter:

$$CsBr_3(c) + 3I^-(aq) = Cs^+(aq) + 3Br^-(aq) + I_3^-(aq)$$

This type of reaction could not be carried out with $(C_2H_5)_4NCl_3$ for three reasons:

(i) The compound was impure,

(ii) Dissolution of the compound was accompanied by violent evolution of Cl_2,

(iii) The very soluble but impure compound $(C_2H_5)_4NI$ was formed.

Morss also comments that the type of reaction given above was limited to trihalide ions of the type X_3^- which dissociate in aqueous solution to yield homonuclear molecules X_2. Ions of the type X_2Y^-, e.g. Cl_2Br^-, ICl_2^-, which yield heteronuclear interhalogen molecules XY may not have an unambiguous set of reaction products if the molecule XY were not completely reduced.

The dissociation pressures of $CsBr_3$ and $(C_2H_5)_4NCl_3$ were also reported, a value of ΔH_f^o $CsBr_3(c) = -431.8$ kJ mol^{-1} being derived from these measurements.

$$CsBr_3(c) = CsBr(c) + Br_2(g)$$

An enthalpy of decomposition, $\Delta H = 70.4$ kJ mol^{-1}, was derived for the decomposition of $(C_2H_5)_4NCl_3(c)$:

$$(C_2H_5)_4NCl_3(c) = (C_2H_5)_4NCl(c) + Cl_2(g)$$

Experimental Results

(1) Rubidium tetrafluoroiodate, $RbIF_4$

Enthalpy of hydrolysis data for $RbIF_4$ are recorded in Table II-A-1. The calorimetric reaction was fast, but not violent, being complete within two minutes. The measured enthalpy of reaction, ΔH_R, refers to the process summarised in equation (1); ΔH_R being expressed per mole of $RbIF_4$.

(2) The enthalpy of reaction data for the reactions of the polyhalides prepared in sections III-A-(2) to III-A-(8) with excess aqueous silver nitrate, saturated with $AgIO_3$, are recorded in Tables II-A-2 to II-A-8. The calorimetric reactions were moderately fast, being complete within five minutes. The measured enthalpies of reaction, ΔH_R, refer to the processes summarised in equations (2)-(8) and are expressed per mole of polyhalide.

The enthalpy of reaction data for the reactions of $CsI_3(c)$, $CsICl_2(c)$ and $RbICl_2(c)$ with excess aqueous sulphur dioxide solution are recorded in Tables II-A-10 to II-A-12. The calorimetric reactions were fast, being complete within two minutes. The experimentally observed enthalpy changes, ΔH_R include the enthalpy of reaction between aqueous I^- and Cl^- ions and SO_2 to form $SO_2.X^-$ species. The correction of ΔH_R values for $SO_2.X^-$ formation is discussed on page 72 .

TABLE II-A-1

Enthalpy data for the reaction

$$5RbIF_4(c) + (m+9)H_2O(l) \longrightarrow (5RbF + 3HIO_3 + 15HF) \; mH_2O + I_2(c) \text{———} (1)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
1.5833	2024	41.71
1.5370	2085	41.17
1.5109	2121	40.25
1.4753	2172	41.80
1.4454	2217	42.05
1.3861	2312	42.13
1.3814	2319	39.45
1.2362	2592	41.50

Mean ΔH_R = $\underline{-41.26 \pm 0.79 \text{ kJ mol}^{-1}}$; hence from (1)

$$5\,\Delta H_f^o\,RbIF_4(c) = 5\,\Delta H_f^o\,RbF(2{,}000\,H_2O) + 3\,\Delta H_f^o\,HIO_3\,(4{,}000\,H_2O) + 15\,\Delta H_f^o\,(750\,H_2O) - 9\,\Delta H_f^o\,H_2O\,(l) - 5\,\Delta H_R$$

Using ancillary data contained in table II-A-15

$$\underline{\Delta H_f^o\,RbIF_4(c) = -1121{\cdot}51 \pm 6{\cdot}33 \text{ kJ mol}^{-1}}$$

TABLE II-A-2

Enthalpy data for the reaction

$$3CsICl_2(c) + \left[(p+9)AgNO_3\right]mH_2O + (q+3)H_2O(l) \longrightarrow 6AgCl(c) + 2AgI(c) + AgIO_3(c) + (pAgNO_3 + 6HNO_3 + 3CsNO_3)(m+q)H_2O \text{ ——— } (2)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.35154	5226	127.67
0.35530	5171	126.39
0.36560	5025	127.19
0.35620	5158	127.37
0.36158	5081	127.51
0.34116	5385	128.37
0.30102	6104	127.95
0.35708	5145	127.19
0.36437	5042	128.11
0.34618	5307	127.36

Mean ΔH_R = $\underline{-127.51 \pm 0.40 \text{ kJ mol}^{-1}}$; hence from (2)

$$3\Delta H_f^o \, CsICl_2(c) = 6\Delta H_f^o \, AgCl(c) + 2\Delta H_f^o \, AgI(c) + \Delta H_f^o \, AgIO_3(c) + 3\Delta H_f^o \, CsNO_3(aq) + 6\Delta H_f^o \, HNO_3(2,000 \, H_2O) - 9\Delta H_f^o \, AgNO_3(2,000 \, H_2O) - 3\Delta H_f^o \, H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o \, CsICl_2(c) = -512.01 \pm 4.14 \text{ kJ mol}^{-1}}$$

TABLE II-A-3

Enthalpy data for the reaction

$3RbICl_2(c) + [(p+9)AgNO_3]mH_2O + (q+3)H_2O(l) \longrightarrow$
$6AgCl(c) + 2AgI(c) + AgIO_3(c) + (pAgNO_3 + 6HNO_3 +$
$3RbNO_3)(m+q)H_2O$ —————— (3)

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.27506	5721	140.39
0.23255	6767	140.60
0.33361	4717	140.21
0.30763	5115	140.27
0.29039	5419	139.50
0.35133	4479	140.23
0.39548	3979	139.59
0.36198	4347	141.10
0.32949	4776	140.42

Mean ΔH_R = $\underline{-140.26 \pm 0.37\ \text{kJ mol}^{-1}}$; hence from (3)

$$3\Delta H_f^o\ RbICl_2(c) = 6\Delta H_f^o\ AgCl(c) + 2\Delta H_f^o\ AgI(c) + \Delta H_f^o\ AgIO_3(c) + 3\Delta H_f^o\ RbNO_3(aq) + 6\Delta H_f^o\ HNO_3(2{,}000\ H_2O) - \Delta 9\ H_f^o\ AgNO_3(2{,}000\ H_2O) - 3\Delta H_f^o\ H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\ RbICl_2(c) = -492.31 \pm 4.12\ \text{kJ mol}^{-1}}$$

TABLE II-A-4

Enthalpy data for the reaction

$$3CsIBr_2(c) + \left[(p+9)AgNO_3\right]mH_2O + (q+3)H_2O(l) \longrightarrow$$
$$6AgBr(c) + 2AgI(c) + AgIO_3(c) + (pAgNO_3 + 6HNO_3 +$$
$$3CsNO_3)(m+q)H_2O \text{———————} (4)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.31460	7410	139.69
0.29318	7951	140.30
0.32880	7090	139.96
0.29866	7805	140.06
0.34481	6761	139.00
0.31829	7324	139.69
0.22705	10261	140.55
0.33177	7027	139.66
0.31316	7444	139.32
0.30744	7583	139.74

Mean ΔH_R = $\underline{-139.80 \pm 0.32 \text{ kJ mol}^{-1}}$; hence from (4)

$$3\Delta H_f^o\ CsIBr_2(c) = 6\Delta H_f^o\ AgBr(c) + 2\Delta H_f^o\ AgI(c) +$$
$$\Delta H_f^o\ AgIO_3(c) + 3\Delta H_f^o\ CsNO_3(aq) + 6\Delta H_f^o\ HNO_3(3{,}000\ H_2O)$$
$$- 9\Delta H_f^o\ AgNO_3(2{,}000\ H_2O) - 3\Delta H_f^o\ H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\ CsIBr_2(c) = -446.32 \pm 4.08 \text{ kJ mol}^{-1}}$$

TABLE II-A-5

Enthalpy data for the reaction

$$3RbIBr_2(c) + [(p+9)AgNO_3]mH_2O + (q+3)H_2O(l) \longrightarrow 6AgBr(c) + 2AgI(c) + AgIO_3(c) + (pAgNO_3 + 6HNO_3 + 3CsNO_3)(m+q)H_2O \text{———} (5)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.29340	7026	149.37
0.28082	7363	150.31
0.26698	7745	151.10
0.30994	6671	150.68
0.32852	6294	149.34
0.35326	5853	150.62
0.34001	6081	150.45
0.33173	6233	149.13
0.32096	6442	149.61
0.31522	6559	149.94

Mean ΔH_R = $\underline{-150.06 \pm 0.48 \text{ kJ mol}^{-1}}$; hence from (5)

$$3\Delta H_f^o\ RbIBr_2(c) = 6\Delta H_f^o\ AgBr(c) + 2\Delta H_f^o\ AgI(c) + \Delta H_f^o\ AgIO_3(c) + 3\Delta H_f^o\ RbNO_3(aq) + 6\Delta H_f^o\ HNO_3(3{,}000\ H_2O) - 9\Delta H_f^o\ AgNO_3(2{,}000\ H_2O) - 3\Delta H_f^o\ H_2O(l) - 3\Delta H_R$$

Using the ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\ RbIBr_2(c) = -429.11 \pm 4.22 \text{ kJ mol}^{-1}}$$

TABLE II-A-6

Enthalpy data for the reaction

$$3CsI_3(c) + \left[(p+9)AgNO_3\right]mH_2O + (q+3)H_2O(l) \longrightarrow$$
$$8AgI(c) + AgIO_3(c) + (pAgNO_3 + CsNO_3 + 6HNO_3)(m+q)H_2O \quad (6)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.41261	6916	149.12
0.27584	10344	148.56
0.39708	7186	147.80
0.37840	7541	148.67
0.37012	7709	149.85
0.34583	8250	151.59

Mean ΔH_R = $\underline{-149.27 \pm 1.39 \text{ kJ mol}^{-1}}$; hence from (6)

$$3\Delta H_f^o\, CsI_3(c) = 8\Delta H_f^o\, AgI(c) + \Delta H_f^o\, AgIO_3(c) + 6\Delta H_f^o\, HNO_3(3{,}000\ H_2O) + 3\Delta H_f^o\, CsNO_3(aq) - 9\Delta H_f^o\, AgNO_3(2{,}000\ H_2O) - 3\Delta H_f^o\, H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\, CsI_3(c) = -359.79 \pm 5.77 \text{ kJ mol}^{-1}}$$

TABLE II-A-7

Enthalpy data for the reaction

$$3CsICl_4(c) + \left[(p+15)AgNO_3\right]mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3CsNO_3 + 12HNO_3)(m+q)H_2O \text{———} (7)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.15790	13971	281.96
0.14867	15008	283.44
0.17809	12528	280.21
0.15869	14060	283.12
0.13872	16084	282.87
0.16945	13167	282.49
0.16658	13394	281.20
0.12664	17618	281.90
0.13492	16537	281.99
0.16213	13762	283.44

Mean ΔH_R = $\underline{-282.26 \pm 0.74 \text{ kJ mol}^{-1}}$; hence from (7)

$$3\Delta H_f^o \, CsICl_4(c) = 12\Delta H_f^o \, AgCl(c) + \Delta H_f^o \, AgI(c) + 2\Delta H_f^o \, AgIO_3(c) + 3\Delta H_f^o \, CsNO_3(aq) + 12\Delta H_f^o \, HNO_3(4{,}000 \; H_2) - 15\Delta H_f^o \, AgNO_3(2{,}000 \; H_2O) - 6\Delta H_f^o \, H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$\underline{\Delta H_f^o \, CsICl_4(c) = -571.91 \pm 6.90 \text{ kJ mol}^{-1}}$

TABLE II-A-8

Enthalpy data for the reaction

$$3RbICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3RbNO_3 + 12HNO_3)(m+q)H_2O \qquad (8)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.14260	13799	293.20
0.12134	16216	293.53
0.14780	13313	292.67
0.14478	13591	292.09
0.13469	14609	293.46
0.13890	14166	293.69
0.11999	16399	292.00
0.15696	12536	292.34
0.14009	14046	292.75

Mean ΔH_R = $\underline{-292.86 \pm 0.49 \text{ kJ mol}^{-1}}$; hence from (8)

$$3\Delta H_f^o\ RbICl_4(c) = 12\Delta H_f^o\ AgCl(c) + \Delta H_f^o\ AgI(c) + 2\Delta H_f^o\ AgIO_3(c) + 3\Delta H_f^o\ RbNO_3(aq) + 12\Delta H_f^o\ HNO_3(4{,}000\ H_2O) - 15\Delta H_f^o\ AgNO_3(2{,}000\ H_2O) - 6\Delta H_f^o\ H_2O(l) - 3\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\ RbICl_4(c) = -554.36 \pm 6.69 \text{ kJ mol}^{-1}}$$

TABLE II-A-9

Enthalpy of reaction of $CsIBr_2$ with aqueous $AgNO_3$ (mole ratio 1:2)

Enthalpy data for the reaction

$$5CsIBr_2(c) + [10\ AgNO_3]mH_2O + (q+3)H_2O(l) \longrightarrow$$
$$10AgBr(c) + [HIO_3 + 5HNO_3 + 5CsNO_3]\ (m+q)H_2O + 2I_2(c) \qquad (9)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.55057	4234	91.89
0.48643	4793	92.25
0.60548	3850	90.90
0.51202	4553	92.69
0.50088	4654	92.43

Mean ΔH_R = $\underline{-92.03 \pm 0.80\ \text{kJ mol}^{-1}}$; hence from (9)

$$5\Delta H_f^o\ CsIBr_2(c) = 10\Delta H_f^o\ AgBr(c) + \Delta H_f^o\ \underline{HIO_3(23{,}000\ H_2O)}$$
$$+ 5\Delta H_f^o\ HNO_3(4{,}000\ H_2O) + 5\Delta H_f^o\ CsNO_3(aq) - 3\Delta H_f^o\ H_2O(l)$$
$$- 10\Delta H_f^o\ AgNO_3(2{,}000\ H_2O) - 5\Delta H_R$$

Using ancillary data contained in table II-A-14

$$\underline{\Delta H_f^o\ CsIBr_2(c) = -450.15 \pm 6.41\ \text{kJ mol}^{-1}}$$

TABLE II-A-10

Enthalpy data for the reaction

$$CsI_3(c) + (p+1)SO_2.mH_2O + (q+2)H_2O(l) \xrightarrow{\Delta H_{R'}} (CsI + 2HI + H_2SO_4 + pSO_2)(m+q)H_2O \qquad (10)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.62265	4583	46.81
0.84640	3371	47.10
0.59006	4836	46.39
0.24931	11445	47.78
0.62732	4549	46.08

Mean $\Delta H_R = -46.83 \pm 0.82$ kJ mol^{-1}

$\underline{\Delta H_{R'} = -42.33 \pm 0.82 \text{ kJ mol}^{-1}}$; hence from (10)

$$\Delta H_f^o\ CsI_3(c) = \Delta H_f^o\ CsI(aq) + 2\Delta H_f^o\ HI(5{,}000\ H_2O) + \Delta H_f^o\ H_2SO_4(5{,}000\ H_2O) - \Delta H_f^o\ SO_2(400\ H_2O) - 2\Delta H_f^o\ H_2O(l) - \Delta H_{R'}$$

Using ancillary data contained in table II-A-16

$\underline{\Delta H_f^o\ CsI_3(c) = -381.96 \pm 1.05 \text{ kJ mol}^{-1}}$

TABLE II-A-11

Enthalpy data for the reaction

$$CsICl_2(c) + (p+1)SO_2.mH_2O + (q+2)H_2O(l) \xrightarrow{\Delta H_R}$$

$$(CsCl + HCl + HI + H_2SO_4 + pSO_2)(m+q)H_2O \text{———————} (11)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.22299	8240	116.65
0.26961	6814	116.36
0.31279	5873	116.01
0.30069	6110	116.54
0.31409	5849	116.07
0.29988	6126	116.64
0.32766	5607	116.34
0.32982	5570	116.42
0.30399	6044	116.71

Mean ΔH_R = -116.42 ± 0.19 kJ mol^{-1}

$\Delta H_{R'}$ = $\underline{-114.92 \pm 0.19 \text{ kJ mol}^{-1}}$; hence from (11)

$$\Delta H_f^o \, CsICl_2(c) = \Delta H_f^o \, CsCl(aq) + \Delta H_f^o \, HCl(7{,}000 \, H_2O)$$
$$\Delta H_f^o \, HI(7{,}000 \, H_2O) + \Delta H_f^o \, H_2SO_4(6{,}000 \, H_2O) - \Delta H_f^o \, SO_2$$
$$(400 \, H_2O) - 2 \, \Delta H_f^o \, H_2O(l) - \Delta H_{R'}$$

Using ancillary data contained in table II-A-16

$$\underline{\Delta H_f^o \, CsICl_2(c) = -530.35 \pm 0.67 \text{ kJ mol}^{-1}}$$

TABLE II-A-12

Enthalpy data for the reaction

$$RbICl_2(c) + (p+1)SO_2.mH_2O + (q+2)H_2O(l) \xrightarrow{\Delta H_R}$$

$$(RbCl + HCl + HI + H_2SO_4 + pSO_2)(m+q)H_2O \text{——————} (12)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.28050	5610	128.06
0.28137	5593	129.01
0.25458	6182	128.26

Mean ΔH_R = -128.44 ± 1.24 kJ mol^{-1}

$\Delta H_{R'}$ = -126.94 ± 1.24 kJ mol^{-1}; hence from (12)

ΔH_f^o $RbICl_2(c)$ = ΔH_f^o RbCl(aq) + ΔH_f^o HCl(6,000 H_2O)
+ ΔH_f^o HI(6,000 H_2O) + ΔH_f^o H_2SO_4(6,000 H_2O) − ΔH_f^o SO_2
(400 H_2O) − $2H_2O(l)$ − $\Delta H_{R'}$

Using ancillary data contained in table II-A-16

ΔH_f^o $RbICl_2(c)$ = -461.36 ± 1.40 kJ mol^{-1}

TABLE II-A-13

Enthalpy data for the reaction

$$AgNO_3(c) + (p+1)KIO_3.mH_2O \xrightarrow{\Delta H_R} AgIO_3(c) + [pKNO_3 + (p-1)KIO_3]mH_2O \qquad (13)$$

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.29572	3191	29.605
0.31843	2964	29.436
0.31317	3013	29.363
0.31662	2981	29.403
0.31385	3007	29.532
0.29916	3155	29.581
0.30057	3140	29.638
0.31152	3029	29.620
0.31413	3004	29.535
0.30500	3094	29.683

Mean ΔH_R = $\underline{-29.540 \pm 0.077 \text{ kJ mol}^{-1}}$; hence from (13)

$$\Delta H_f^o\ AgIO_3(c) = \Delta H_f^o\ KIO_3(3{,}000\ H_2O) + \Delta H_f^o\ AgNO_3(c) - \Delta H_f^o\ KNO_3(3{,}000\ H_2O) + \Delta H_R$$

Using ancillary data contained in table II-A-17

$$\underline{\Delta H_f^o\ AgIO_3(c) = -168.86 \pm 0.72 \text{ kJ mol}^{-1}}$$

TABLE II A-14

Compound	$-\Delta H^{o}_{f_{298}}$ /kJ mol^{-1}	Reference
AgI(c)	61.84 ± 0.1	159
AgBr(c)	100.37 ± 0.1	159
AgCl(c)	127.07 ± 0.1	159
$AgIO_3$(c)	168.86 ± 0.72	This work
$AgNO_3$ (2,000 H_2O)	101.73 ± 0.1	159
$CsNO_3$(aq)	465.01 ± 0.84	160,161
$RbNO_3$(aq)	458.06 ± 0.84	160,161
HNO_3 (2,000 H_2O)	206.94 ± 0.46	161
HNO_3 (3,000 H_2O)	206.97 ± 0.46	161
HNO_3 (4,000 H_2O)	207.00 ± 0.46	161
H_2O(l)	285.83 ± 0.04	162
HIO_3 (23,000 H_2O)	221.94 ± 0.4	88,163
I_2(aq)	22.59 ± 0.42	105

TABLE II A-15

Compound	$-\Delta H^{o}_{f_{298}}$ /kJ mol^{-1}	Reference
RbF (2,000 H_2O)	575.51 ± 0.4	164
HIO_3 (4,000 H_2O)	221.76 ± 0.4	88
HF (750 H_2O)	322.90 ± 0.29	105
H_2O(l)	285.83 ± 0.04	162

TABLE II A-16

Compound	$-\Delta H^{o}_{f_{298}}$/kJ mol^{-1}	Reference
CsCl(aq)	424.90 ± 0.38	105,160
RbCl(aq)	417.95 ± 0.38	105,160
CsI(aq)	314.72 ± 0.39	105,160
HCl (6,000 H_2O)	166.90 ± 0.004	105
HCl (7,000 H_2O)	166.91 ± 0.004	105
HI (5,000 H_2O)	56.73 ± 0.02	105
HI (6,000 H_2O)	56.75 ± 0.02	105
HI (7,000 H_2O)	56.76 ± 0.02	105
H_2SO_4 (5,000 H_2O)	897.01 ± 0.5	42
H_2SO_4 (6,000 H_2O)	897.60 ± 0.5	42
SO_2(400 H_2O)	329.24 ± 0.1	42
H_2O(l)	285.83 ± 0.04	162

TABLE II A-17

Compound	$-\Delta H^{o}_{f_{298}}$/kJ mol^{-1}	Reference
KNO_3 (3,000 H_2O)	457.69 ± 0.5	164
$AgNO_3$(c)	124.39 ± 0.1	159
KIO_3 (3,000 H_2O)	472.62 ± 0.5	163,164

Discussion

The following sections describe the literature which supports the calorimetric reaction stoichiometries given in equations (2)-(8). Section III-C-2 (page143) contains experimental evidence to support the stoichiometry of equation (1).

Cremer and Duncan[165] have thoroughly studied the properties of several alkali-metal polyhalides in aqueous solution. In particular $KICl_2$, $KIBr_2$ and $KICl_4$ were found to be only partially hydrolysed and detailed experiments were performed to identify and explain the formation of the hydrolysis products from these compounds. These authors established the presence of a reversible equilibrium between the polyhalide ion and its hydrolysis products, for example:

$$5IBr_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Br^- + 6H^+ \qquad (14)$$

Similar equilibria were reported for dichloriodate and tetrachloroiodate compounds:

$$5ICl_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Cl^- + 6H^+ \qquad (15)$$

$$5ICl_4^- + 9H_2O \rightleftharpoons I_2 + 3IO_3^- + 20Cl^- + 18H^+ \qquad (16)$$

Qualitative tests gave evidence for the hydrolysis products indicated in equations (14)-(16) together with undissociated polyhalide ions and the metal cation.

Cremer and Duncan investigated the action of aqueous silver nitrate with an aqueous solution of $KIBr_2$ to support the above equations. The following observations were made when $AgNO_3$ (0.1M) was slowly run into a large excess of aqueous $KIBr_2$:

(i) Silver was precipitated quantitatively as AgBr,

(ii) Elemental iodine was precipitated simultaneously and attained a maximum concentration when 2 moles of $AgNO_3$ per mole of $KIBr_2$ had been added,

(iii) The iodine finally reacted with an excess of $AgNO_3$, the reaction being complete when 3 moles of $AgNO_3$ had been added per mole of $KIBr_2$,

(iv) The resulting solution contained 1 mole of KNO_3 and 2 moles of HNO_3,

(v) The precipitate formed after the reaction had gone to completion was a mixture of AgBr, AgI and $AgIO_3$.

The overall reaction was therefore represented by the following equation:

$$3KIBr_2 + 9AgNO_3 + 3H_2O = 6AgBr + 2AgI + AgIO_3 + 3KNO_3 + 6HNO_3 \qquad (17)$$

The reaction was suggested to take place in consecutive stages starting from the initial equilibrium of the dibromoiodate salt in aqueous solution:

$$5IBr_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Br^- + 6H^+$$

Addition of $AgNO_3$ first precipitated AgBr; AgI was not precipitated since there were no I^- ions present and $AgIO_3$ was not precipitated because of its large solubility compared to AgBr (K_s AgBr:K_s $AgIO_3$ = 7.7 x 10^{-13}:0.92 x 10^{-8}). The removal of Br^- ions from the solution caused the equilibrium to be displaced to the right and I_2 was precipitated with the AgBr.
Two moles of $AgNO_3$ per mole of $KIBr_2$ were required to precipitate all the Br^- ions. The iodine then reacted with $AgNO_3$ according to the following equation:

$$3I_2 + 6Ag^+ + 3H_2O = 5AgI + 6H^+ + AgIO_3 \qquad (18)$$

0.8 moles of $AgNO_3$ were required to react with the iodine per mole of $KIBr_2$. Summation of these equations produced the equation representing the complete reaction.

These workers found that $AgNO_3$ reacted in a similar manner with $KICl_2$ and established that the reaction followed a similar mechanism; the overall reaction being quantitatively represented by the following equation:

$$3KICl_4 + 15AgNO_3 + 6H_2O = 12AgCl + AgI + 2AgIO_3 + 3KNO_3 + 12HNO_3 \quad (19)$$

The reaction stages described above were observed during the calorimetric experiments with the compounds contained in Tables II-A-2 to II-A-8. A mixture of silver halide particles and precipitated iodine was observed as each polyhalide reacted with the calorimetric fluid. The coloration due to iodine was discharged as the reactions proceeded to completion.

Results of the experiments contained in Table III-C-1 (page144) confirm that the overall reaction stoichiometry of $AgNO_3$ with the polyhalides are represented by equations (2)-(8).

Further evidence that only AgBr is quantitatively precipitated up to a 1:2 molar ratio was obtained by performing calorimetric reactions at a 1:2 molar ratio of $CsIBr_2$:$AgNO_3$. The results of these experiments are contained in Table II-A-9 and good agreement was found between the standard enthalpy of formation of $CsIBr_2$(c) derived from these measurements, -450.15 ± 6.41 kJ mol^{-1} and the result contained in Table II-A-4, -446.32 ± 4.08 kJ mol^{-1}. A correction for the enthalpy of solution of the dissolved iodine was made[105].

Wagman and Kilday[166] have reported enthalpies of precipitation of AgBr, AgI and AgCl from studies of the following reactions:

$$AgNO_3(c) + KX(\infty H_2O) \longrightarrow AgX(c) + KNO_3(\infty H_2O)$$

$$AgNO_3(c) \longrightarrow AgNO_3(\infty H_2O)$$

$$\therefore AgNO_3(\infty H_2O) + KX(\infty) \longrightarrow AgX(c) + KNO_3(\infty H_2O)$$

These authors comment that the excellent agreement of values derived from these results with literature values indicates that silver halides formed in the calorimetric experiments were in their thermodynamic standard states. The effects of such factors as particle size or degree of crystallinity for these halides must therefore be smaller than can be detected by their present calorimetric techniques. This supports the assumption in the present work that the final states of the silver halides produced in the calorimetric reactions are in their thermodynamic standard states.

Thermometric titrations of aqueous $AgNO_3$ against aqueous $CsIBr_2$ were carried out to investigate the reaction sequence described by Cremer and Duncan. The results of these experiments are contained in Table III-D-3 (page 148) with a titration curve for $CsIBr_2/AgNO_3$ shown in Figure III-D-3 (page 152). Three distinct 'breaks' in the curve were observed at mole ratios ($CsIBr_2:AgNO_3$) of 2.00, 2.47 and 2.67:1 with the end-point of the reaction at a mole ratio of 3.00:1. The titration was reproducible, the error being <u>ca</u>. ± 0.05 mole. The portion of the curve up to the 2.00:1 mole point was assigned to the precipitation of AgBr. From a mole ratio of 2.00:1 to 2.67:1 iodine reacts with silver nitrate, according to equation (18), to give AgI and iodate ions. Finally the last 0.33 moles were assigned to the precipitation of $AgIO_3$. The enthalpy change from the 2.67:1 mole ratio point to the end-point of the reaction was measured (experiment 3 Table III-D-3) and was found to be in good agreement with the enthalpy of reaction, measured in a separate experiment of $AgNO_3$ against KIO_3 (experiment 2 Table III-D-3). Both results were corrected for the enthalpy of solution of silver iodate[167].

A single titration of $AgNO_3$ against aqueous $CsICl_4$ was performed and this titration curve is shown in Figure III-D-4, (page 153). Two distinct 'breaks' in the curve were observed at mole ratios ($CsICl_4:AgNO_3$) of ca. 4.00:1 and 4.33:1 with the end-point of the reaction at a mole ratio of 5.0:1.

These points on the curve can be assigned as follows: Equation (16) represents the equilibrium for a tetrachloroiodate salt in aqueous solution, i.e.

$$5ICl_4^- + 9H_2O \rightleftharpoons 3IO_3^- + 20Cl^- + 18H^+ + I_2$$

AgCl was precipitated up to a mole ratio of 4.00:1. Iodine then reacted with $AgNO_3$ from a mole ratio of 4.00:1 to 4.33:1 to give AgI and iodate ions. Finally, silver iodate was precipitated from a mole ratio of 4.33:1 to the end-point of the titration.

The approximate nature of these titrations compared to the more precise ampoule-solution-reaction calorimetry experiments reported in this work must be stated. Extrapolation of complex titration curves is difficult and for this reason enthalpies of reaction for the complete titrations were not calculated.

Cremer and Duncan[165] have reported that $KIBr_2$ is quantitatively reduced by SO_2 in dilute aqueous solution; the reaction being represented by the following equation:

$$KIBr_2 + SO_2 + 2H_2O = KI + 2HBr + H_2SO_4 \qquad (20)$$

However, these authors did not consider that the formation of $SO_2.X^-$ species (page 72) may influence the stoichiometry given in equation (20).

Aqueous sulphur dioxide solution has often been referred to as a solution of 'sulphurous acid', H_2SO_3. H_2SO_3 is present in very small quantities if at all in such solutions and the equilibria in aqueous SO_2 solutions is reported to be best represented as follows:[168]

$$SO_2 + xH_2O \; = \; SO_2.xH_2O$$

$$SO_2 + xH_2O \; = \; H_2SO_3 \qquad K<<<1$$

$$SO_2.xH_2O \; = \; HSO_3^-(aq) + H_3O^+(aq) + (x-2)\,H_2O$$

The first acid dissociation constant for 'sulphurous acid' is defined as:

$$K_1 = \frac{[HSO_3^-]\,[H^+]}{[\text{Total dissolved } SO_2]-[HSO_3^-]-[SO_3^{2-}]} = 1.3 \times 10^{-2}$$

Solutions of SO_2 are often used as reducing agents:

$$SO_4^{2-} \; + \; 4H^+ \; + \; 2e^- \; = \; 2H_2O \; + \; SO_2 \qquad E^o{=}0.17\text{ V}$$

The mechanism of reduction of a polyhalide by aqueous SO_2 would appear to be as follows; the polyhalide hydrolysis products reacting according to equations (22) and (23).

$$5IBr_2^- + 3H_2O \rightleftharpoons 2I_2 + 10Br^- + IO_3^- + 6H^+ \qquad (21)$$

$$2I_2 + 4H_2O + 2SO_2 \longrightarrow 4I^- + 8H^+ + 2SO_4^{2-} \qquad (22)$$

$$IO_3^- + 3H_2O + 3SO_2 \longrightarrow I^- + 6H^+ + 3SO_4^{2-} \qquad (23)$$

Combining equations (21), (22) and (23) and expressing the reaction per mole of IBr_2^- we have:

$$IBr_2^- + 2H_2O + SO_2 \longrightarrow 2Br^- + I^- + SO_4^{2-} + 4H^+$$

A clear, pale yellow-green solution was obtained during a calorimetric reaction when a polyhalide was reduced by aqueous sulphur dioxide solution. This colour was almost certainly due to the formation of 1:1 charge-transfer complexes, $SO_2.X^-$ (where X=Cl,Br and I) which absorb strongly in the U.V./visible region of the spectrum. A number of spectroscopic studies have been made of this weak complex-formation, both in water and in non-aqueous solution. Witekowa et al.[169] and Jander and Turk[170] have used ultraviolet spectra to obtain evidence of, and equilibrium data for, the aqueous $SO_2.I^-$ complex. Witekowa et al.[171,172] have further presented qualitative evidence for the corresponding bromide and chloride complexes. Lichtin has also obtained qualitative[173] and quantitative[174] evidence for all three aqueous $SO_2.X^-$ complexes.

Stability constants of $SO_2.X^-$ species in DMSO, MeCN and water have been very recently reported by Salama and Wasif[175]. These data are collected in the following table.

TABLE II-A-18

STABILITY CONSTANTS at 25° OF $SO_2.X^-$ SPECIES IN VARIOUS SOLVENTS/$l\ mol^{-1}$

X	Cl	Br	I
DMSO	26	21	12
MeCN	376	160	38
H_2O	-	0.22	0.36

$SO_2.Cl^-$ could not be detected in water but $SO_2.Br^-$ and $SO_2.I^-$ were sufficiently stable for stability constant data to be determined. Woodhouse and Norris[176] have also reported an ultraviolet spectrophotometric study of $SO_2.X^-$ complexes in acetonitrile.

The enthalpy change for process (24) was derived from calorimetric data obtained for process (25).

$$SO_2(aq) + I^-(aq) \rightleftharpoons SO_2.I^-(aq) \quad \Delta H_{complex} \qquad (24)$$

$$KI(c) + SO_2(aq) \overset{\Delta H_1}{\rightleftharpoons} K^+(aq) + SO_2.I^-(aq) \qquad (25)$$

Two determinations of ΔH_1 were made with a mass of KI calculated to duplicate the $I^-(aq)$ concentration in the reactions of $CsI_3(c)$ with $SO_2(aq)$, page 59; the SO_2 solution was prepared as described in section III-F-3. Results for ΔH_1 were +19.37 and +19.08 kJ mol^{-1}. The enthalpy of solution of KI(c) is well known:[164]

$$KI(c) \longrightarrow K^+(aq) + I^-(aq) \qquad \Delta H_{sol} = +20.72 \text{ kJ mol}^{-1}.$$

$$\text{Hence } \Delta H_{complex} = \Delta H_1 - \Delta H_{soln} = 19.23 - 20.72 = -1.50 \text{ kJ mol}^{-1}$$

This value was used to correct the mean enthalpy of reaction datum for $CsI_3(c)$ contained in Table II-A-10. Similar corrections were applied to the mean ΔH_R data obtained for $CsICl_2$ and $RbICl_2$ contained in Tables II-A-11 and 12. No correction for $SO_2.Cl^-$ species was made.

Shamir and Wasif[175] have reported stability constants of $SO_2.I^-$ at 20° and 40°. From these results $\Delta H_{complex}$ = 4.12 kJ mol^{-1} was calculated[177].

The disagreement between the standard enthalpies of formation derived from the calorimetric experiments of crystalline $CsICl_2$, $RbICl_2$ and CsI_3 with (1) aqueous silver nitrate and (2) aqueous sulphur dioxide can be seen from data collated in the following table:

Compound MIX(c)	$-\Delta H_f^o$ MIX(c)/kJ mol^{-1} (1)	(2)
$CsICl_2$	512.01 ± 4.14	530.35 ± 0.67
$RbICl_2$	492.31 ± 4.12	461.36 ± 1.40
CsI_3	359.79 ± 5.77	381.96 ± 1.05

However, the standard enthalpy of formation datum for CsI_3 reported in column (1) of the above table can be compared with the literature values reported for this compound[152,153]. These data are summarized in Table II-A-19.

TABLE II-A-19

STANDARD ENTHALPY OF FORMATION DATA FOR CsI_3(c)

$-\Delta H_f^o$ (CsI_3,c)/kJ mol^{-1}	Reference
359.79 ± 5.77	This work
357.69	152
363.63	153

The literature data were revised with more recent values of ΔH_f^o CsI_3(c)[105,160,196] and ΔH_f^o I_2(g)[105] . The good agreement between the above data gives additional support to the calorimetric reaction stoichiometry summarised in equation (6), page 55, and also indicates that the reactions of CsI_3, $CsICl_2$ and $RbICl_2$ with aqueous SO_2 are probably more complex than summarised by equations (10) - (12). These reactions require further investigation.

Experimental evidence should be obtained for the final states given in these equations since there is a possibility of side reactions occuring which would affect the overall reaction stoichiometry. Vogel[200] states that the following expermental conditions must be observed for the accurate iodimetric determination of an aqueous solution of sulphur dioxide:

(a) the solutions should be very dilute;

(b) the solution of sulphur dioxide must be added slowly with constant stirring to the iodine solution, and not conversely; and

(c) exposure of the aqueous sulphur dioxide solution to the air should be minimised.

The expermental calorimetric conditions for reactions (10) - (12) did not fulfil the second condition since iodine produced by hydrolysis of the polyhalides reacted with excess aqueous sulphur dioxide.

(3) There is a discrepancy of ca. 4 kJ mol^{-1} between the literature values reported for ΔH_f^o $AgIO_3(c)$ Table II-A-20.

Shidlovskii and Voskresenskii[178] derived their value from the measurement of the enthalpy of reaction for the following process:

$$AgNO_3(c) + HIO_3(c) + aq = HNO_3(aq) + AgIO_3(c)$$

These authors only state that 'analytical reagent' reactants were used and do not mention the purity of either reagent. The value for ΔH_f^o $HIO_3(c)$ used by these authors in calculating their standard enthalpy of formation was taken from Circular 500[164].

Skinner, who reports a value for ΔH_f^o $HIO_3(c)$ of -231.84 kJ mol^{-1}, comments that iodic acid dehydrates on heating and is difficult to prepare in a pure and completely dry state[163].

This value, together with more recent ancillary data (Table II-A-17), was used to revise the ΔH_f^o $AgIO_3(c)$ value reported by Shidlovskii and Voskresenskii.

Stern et al.[179] derived their value for the standard enthalpy of formation of $AgIO_3$ from the measurement of the enthalpy of reaction for the following process:

$$AgNO_3(aq) + KIO_3(aq) \xrightarrow{\Delta H_R} AgIO_3(c) + KNO_3(aq)$$

Ampoules containing aqueous $AgNO_3$ were broken into a large excess of aqueous KIO_3. The value of ΔH_R was corrected for heats of dilution but no allowance was made for dissolution of a small amount of silver iodate (ca. 1%).

Stern's value was also re-calculated by using the ancillary data contained in Table II-A-17 and by applying a correction for the enthalpy of solution of the dissolved $AgIO_3$[167].

The revised values are contained in Table II-A-20. There is excellent agreement between the revised value calculated from Stern's original data and the value reported in the present work. However, the revised value of Shidlovskii and Voskresenskii lies outside these values and may place doubt on the purity of the sample of HIO_3 used in their experiments.

Bousquet,et al.[180]have obtained standard enthalpies of formation of a number of alkaline-earth iodates and periodates using Stern's method.

TABLE II-A-20

STANDARD ENTHALPY OF FORMATION DATA FOR $AgIO_3(c)$

Authors	$-\Delta H^o_{f_{298}}$ $AgIO_3(c)/kJ\ mol^{-1}$
(1) Shidlovskii and Voskresenskii	169.9 ± 0.4
(2) Stern et al.	174.1
(1) Revised	163.7
(2) Revised	168.9
This work	168.86 ± 0.72

LATTICE ENERGY CALCULATIONS AND THE STABILITY OF ALKALI-METAL POLYHALIDES

Lattice energies of the polyhalide salts prepared in section III-A have been calculated using the Kapustinskii equation (Appendix II):

$$U_o = \frac{242.8}{(r_c+r_a)}\left[1-\frac{0.0345}{(r_c+r_a)}\right] \text{ kJ mol}^{-1} \qquad (1)$$

where r_c and r_a are expressed in nanometers.

The 'thermochemical radius' of the complex cation was found by the method of Yatsimirskii (Appendix II). Consider two salts M_1X and M_2X (where $X=ICl_2$, IBr_2, I_3^- etc.) then:

$$M_1X(c) \longrightarrow M_1^+(g) + X^-(g) \qquad U_1 + 2RT \qquad (2)$$

and

$$M_2X(c) \longrightarrow M_2^+(g) + X^-(g) \qquad U_2 + 2RT \qquad (3)$$

subtracting (2) from (3) gives

$$U_1-U_2 = \Delta H_f^o\, M_1^+(g) - \Delta H_f^o\, M_2^+(g) - \Delta H_f^o\, M_1X(c) + \Delta H_f^o\, M_2X(c) \qquad (4)$$

From equation (1)

$$U_1-U_2 = C\left[\frac{1}{r_{M_1^+}+r_{X^-}}\left(1-\frac{0.0345}{r_{M_1^+}+r_{X^-}}\right)-\frac{1}{r_{M_2^+}+r_{X^-}}\left(1-\frac{0.0345}{r_{M_2^+}+r_{X^-}}\right)\right] \qquad (5)$$

Equation (5) reduces to

$$r^4 + 2r^3(m_1+m_2) + r^2\left[m_1^2 + m_2^2 + 4m_1m_2 + C(m_1-m_2)\right]$$
$$+ r\left[2m_1^2\, m_2 + 2m_1m_2^2 + C(m_1^2 - m_2^2) - 0.069\, C(m_1-m_2)\right]$$
$$+\left[m_1^2m_2^2 + C(m_1^2m_2 - m_2^2m_1) + 0.0345\, C(m_2^2 - m_1^2)\right] = 0 \qquad (6)$$

where: m_1 and m_2 = $r_{M_1^+}$ and $r_{M_2^+}$ and $r = r_{X^-}$, the 'thermochemical radius' of the complex cation

and $C = \dfrac{242.8}{U_1-U_2}$

Thus by calculating U_1-U_2 from equation (4) the 'thermochemical radius' of the complex anion was found by solving equation (6). A computer programme was written to calculate the coefficients of r^n in equation (6) which was then solved by an iterative method (Appendix II).

The 'thermochemical radii' of the polyhalide ions ICl_2^-, IBr_2^-, I_3^- and ICl_4^- were calculated by this procedure. These radii are collected in Table II-B-1 together with the standard enthalpy of formation data for the caesium and rubidium polyhalides from which they are derived. The relevant ancillary data for these calculations were obtained from Johnson[181] and are contained in Table II-B-2.

TABLE II-B-2

Ionic	Radius/pm	ΔH_f^o $M^+(g)$/kJ mol^{-1}
Rb^+	147	491.20
Cs^+	168	459.82

TABLE II-B-1

THERMOCHEMICAL RADII OF POLYHALIDE IONS

Compound	$-\Delta H_f^o(MIX,c)/kJ\ mol^{-1}$	Thermochemical radius/pm
$CsICl_2$	512.01	466
$RbICl_2$	492.31	
$CsIBr_2$	446.32	404
$RbIBr_2$	429.11	
$CsICl_4$	571.91	412
$RbICl_4$	554.36	
CsI_3	357.69	551
RbI_3	335.47	

The lattice energies of the polyhalide salts contained in Table II-B-1 were then calculated by substitution of the respective 'thermochemical radius' into equation (1). It is difficult to assign error limits to these values. A difference of ± 10 pm in the 'thermochemical radius' generates an uncertainty of approximately ± 6-7 kJ mol^{-1} in the lattice energy values.

The standard enthalpy of formation of the gaseous X^- anion can now be calculated:

$$MX(c) \longrightarrow M^+(g) + X^-(g) \qquad U_o + 2RT \qquad (7)$$

$$\therefore \Delta H_f^o\,(X^-,g) = U_o + 2RT - \Delta H_f^o\,M^+(g) + \Delta H_f^o\,MX(c) \qquad (8)$$

The results of these calculations are collected in Table II-B-3. From the knowledge of the 'thermochemical radius' of the particular X^- anion and of $\Delta H_f^o\,(X^-,g)$ the lattice energy and enthalpy of formation of any salt containing that anion can be calculated from equations (1) and (8). Tables II-B-4 - II-B-6 contain the results of these calculations. All the relevant ancillary data, except for $\Delta H_f^o\,(NH_4{}^+,g)$,[182] were taken from Johnson[181].

The enthalpy of formation data indicate that all of these polyhalides, except the lithium and sodium salts, should be thermally stable with respect to their elements at room temperature. However, polyhalides do not decompose to their elements but to the corresponding metal halide, containing the most electronegative halogen, plus the interhalogen or halogen,[183] e.g.

$$MICl_2(c) \longrightarrow MCl(c) + ICl(g) \qquad (9)$$

$$MIBr_2(c) \longrightarrow MBr(c) + IBr(g) \qquad (10)$$

TABLE II-B-3

ENTHALPY OF FORMATION DATA FOR GASEOUS POLYHALIDE IONS

Calculated from	$-\Delta H_f^o(IX^-,g)$/kJ mol^{-1} ($X = Cl_2$, Br_2 and Cl_4)
$CsICl_2$	604.87
$RbICl_2$	604.55
$CsIBr_2$	502.35
$RbIBr_2$	502.18
$CsICl_4$	632.77
$RbICl_4$	632.60
CsI_3	491.55
RbI_3	490.71

TABLE II-B-4

LATTICE ENERGY AND ENTHALPY OF FORMATION DATA FOR DICHLOROIODATE SALTS

Salt	Ionic Radius M^{n+}/pm	$\Delta H_f^o(M^{n+},g)$ kJ mol^{-1}	U_o/kJ mol^{-1}	$-\Delta H_f^o$ ($M^{n+}(ICl_2^-)_n$,c) kJ mol^{-1}
$LiICl_2$	60	687.4	431	353
$NaICl_2$	100	610.5	403	402
$KICl_2$	133	514.6	382	477
$RbICl_2$	147	491.2	374	492
$CsICl_2$	168	459.8	362	512
NH_4ICl_2	144	619	376	367
$Mg(ICl_2)_2$	68	2348.5	1276	144
$Ca(ICl_2)_2$	99	1923.8	1210	503
$Sr(ICl_2)_2$	116	1789.5	1177	604
$Ba(ICl_2)_2$	134	1657.7	1144	703

TABLE II-B-5

LATTICE ENERGY AND ENTHALPY OF FORMATION DATA FOR DIBROMOIODATE AND TETRACHLOROIODATE SALTS

Compound	U_o/kJ mol^{-1}		$-\Delta H_f^o(M^{n+}(IX^-)_n,c)$ /kJ mol^{-1}	
	X=Br_2	X=Cl_4	X=Br_2	X=Cl_4
LiIX	484	477	304	427
NaIX	449	442	346	469
KIX	423	417	416	540
RbIX	413	408	429	554
CsIX	399	394	446	572
NH_4IX	415	410	303	429
$Mg(IX)_2$	1430	1408	94	332
$Ca(IX)_2$	1349	1329	437	678
$Sr(IX)_2$	1308	1289	531	772
$Ba(IX)_2$	1267	1250	621	865

TABLE II-B-6

LATTICE ENERGY AND ENTHALPY OF FORMATION DATA FOR TRIIODATE SALTS

Compound	U_o/kJ mol^{-1}	$-\Delta H_f^o(M^{n+}(I_3)_n, c)$/kJ mol^{-1}
LiI_3	377	184
NaI_3	355	239
KI_3	339	318
RbI_3	332	336
CsI_3	323	357
NH_4I_3	334	209
$Mg(I_3)_2$	1118	-248
$Ca(I_3)_2$	1067	127
$Sr(I_3)_2$	1041	236
$Ba(I_3)_2$	1015	342

TABLE II-B-7

CALCULATED ENTHALPIES OF DECOMPOSITION FOR DICHLOROIODATE, DIBROMOIODATE AND TRIIODATE SALTS

Compound	$-\Delta H^{o}_{D}$/kJ mol^{-1}		
	X = Br_2	X = Cl_2	X = I_2
LiIX	-5.5	-38.5	-24.7
NaIX	26.8	8.5	13.4
KIX	64.6	58.6	52.8
RbIX	80.5	78.9	70.0
CsIX	92.2	96.5	82.6
NH_4IX	73.4	69.1	69.3
$Mg(IX)_2$	342.0	462.8	545.5
$Ca(IX)_2$	156.3	256.9	345.3
$Sr(IX)_2$	103.3	189.4	268.5
$Ba(IX)_2$	52.3	122.0	198.1

TABLE II-B-8

CALCULATED ENTHALPIES OF DECOMPOSITION FOR TETRACHLOROIODATE SALTS

$MICl_4(c)$	ΔH_D^o/kJ mol^{-1}
Li	74
Na	67
K	63
Rb	62
Cs	60
NH_4	62
Mg	188
Ca	175
Sr	168
Ba	162

$$MI_3(c) \longrightarrow MI(c) + I_2(g) \qquad (11)$$

$$MICl_4(c) \longrightarrow MICl_2(c) + Cl_2(g) \qquad (12)$$

Enthalpies of decomposition, ΔH_D^o , for processes (9)-(12) were calculated from the enthalpy of formation data, with ancillary data for the standard enthalpy of formation of MX(c), ICl(g), IBr(g) and $I_2(g)$ taken from standard sources[164,105]. The results of these calculations are contained in Tables II-B-7 and II-B-8.

If ΔS^o values were available for processes (9)-(12) then the standard free energy change and hence the equilibrium constants for the decomposition reactions could be calculated. ΔS^o and ΔG^o values for the following decomposition processes were calculated from the data reported by Babkov and Stepin[152].

$$MI_3(c) \longrightarrow MI(c) + I_2(g) \qquad (M=Cs \text{ and } Rb)$$

These values (kJ mol^{-1}) together with $T\Delta S^o$ (T=298 K) are contained in Table II-B-9.

TABLE II-B-9

Compound	ΔS^o	ΔH_D^o	$T\Delta S^o$	ΔG^o	$K \times 10^3$
$CsI_3(c)$	0.188	71.97	56.02	15.94	1.61
$RbI_3(c)$	0.194	69.31	57.81	12.69	5.96

The positive value of ΔG^o and the small value of the equilibrium constant, K, for each reaction confirm that $CsI_3(c)$ and $RbI_3(c)$ are thermally stable at room temperature. Entropy data are not available for the other polyhalides contained in Tables II-B-7 and II-B-8. However, if ΔS^o values are assumed to be approximately equal for all these polyhalides, then ΔG^o values may be estimated. If $T\Delta S^o$ is taken as +60 kJ mol^{-1} then positive ΔG^o values are found for all the caesium, rubidium and ammonium salts which confirms the observed thermal stability of these compounds. The potassium salts appear to have small negative ΔG^o values but are reported to be stable although much less so than either the rubidium or caesium salts. Sodium and lithium dichloroiodates and dibromoiodates are not reported in the literature; the large negative ΔG^o values found for these compounds are in agreement with this fact. The ΔG^o values for the alkali-metal tetrachloroiodates are probably negative,which indicates that these compounds decompose, at room temperature with loss of chlorine, to the respective dichloroiodate salt. The alkaline-earth polyhalide salts contained in Tables II-B-7 and II-B-8, have substantial positive ΔH^o_D values which suggests large positive ΔG^o values and hence thermal stability. Alkali-metal tetrachloroiodate salts have been prepared by Celis and Moles[15,16]. Fialkov[184] and Stepin et al.[185] found no interaction between alkali and alkaline-earth metal iodides and iodine. Calcium,strontium and barium iodides were found by other workers to be insoluble in liquid iodine[186]. However, Topol[153] has prepared CsI_3, RbI_3 and NH_4I_3 by allowing stoichiometric amounts of the metal iodide to react with iodine at 65°, in an evacuated sealed vessel for one week. Korenman,[187] Stylin[188] and Gorenbein et al.[189,190] have prepared alkali and alkaline-earth triiodides in aqueous solution.

Ephraim[191] has measured the dissociation pressures of a number of caesium, rubidium, potassium and ammonium trihalides. The temperatures at which the dissociation pressures reached one atmosphere, for the caesium and rubidium polyhalides, were employed as an indication of the relative stabilities of these compounds. These results are contained in Table II-B-10.

TABLE II-B-10

THERMAL DISSOCIATION OF POLYHALIDE SALTS

Anion	Rb	Cs
	Temperature	
I_3^-	192	250
Br_3^-	105.5	147.5
IBr_2^-	186.5	242.5
ICl_2^-	151	209
$ClBr_2^-$	81	124
Cl_2Br^-	93	138
I_2Br^-	-	201.5

Cremer and Duncan[192] have reported a completely different method for determining the relative stabilities of polyhalide salts. The crystalline polyhalide was equilibrated with carbon tetrachloride, only the halogen or interhalogen passing into solution, equilibria of the following type being established:

$$KICl_2(c) \rightleftharpoons KCl(c) \quad + \quad ICl\ (CCl_4\ \text{solution})$$

The concentration of the halogen or interhalogen was determined titrimetrically and gave an indication of the stability of the polyhalide. Carbon tetrachloride was chosen for its inertness to the dissolved halogen or interhalogen and because of the lack of solvates between this solvent and the polyhalide under investigation. Benzene was employed by Abbeg and Hamburger[4] for work of this type with polyiodides but does not fulfill the second condition[192]. The results from Cremer and Duncan's study are contained in Table II-B-11.

TABLE II-B-11

EQUILIBRIUM CONCENTRATIONS OF HALOGEN OR INTERHALOGEN IN CARBON TETRACHLORIDE OVER VARIOUS TRIHALIDES at 25° [192]

Cation	I_3^-	IBr_2^-	$IBrCl^-$	ICl_2^-
K		0.0473	0.61	0.029
Rb	0.0059	0.0010	0.0108	0.00035
Cs	0.00075	0.00014	0.00035	0.00006
NH_4	0.0120	0.00842	0.122	0.0057

Values of 0.0438 and 0.0155 were determined for $CsBr_3$ and CsI_2Br.

The orders of relative stability reported by Ephraim and by Cremer and Duncan can be compared with the relative stability order indicated by the standard enthalpy of formation data reported in section II-A-2 of this work.

Ephraim I_3^- Br_3^- IBr_2^- ICl_2^- $ClBr_2^-$ Cl_2Br^- I_2Br^-

Cremer and Duncan ICl_2^- $IBrCl^-$ IBr_2^- I_3^- I_2Br^- Br_3^-

This work ICl_4^- ICl_2^- IBr_2^- I_3^-

less stable ⟶

The dissociation pressures of $KICl_2$[192,193], $KIBr_2$[192], $CsIBr_2$[29], CsI_3[152] and $CsBr_3$[158] have been re-determined by several investigators since the first older study of these polyhalides by Ephraim[191]. Table II-B-12 contains enthalpies of decomposition derived from a least squares analysis of this data; ΔH_D referring to the following decomposition processes:

$$\mathrm{MIX(c)} \overset{\Delta H_D}{\rightleftharpoons} \mathrm{MX(c)} + \mathrm{IX(g)}$$

where(M=K, Rb and Cs and X=I_2, Cl_2, Br_2 and IBr)

Several comments have been made concerning the methods of preparation of the polyhalides used by Ephraim for dissociation pressure measurements. Cremer and Duncan[192] have suggested that Ephraim's sample of $KIBr_2$, obtained by crystallisation from aqueous solution, was in fact the monohydrate $KIBr_2.H_2O$. These authors also state that halogen or interhalogen were continually absorbed in Ephraim's apparatus, by traps of sulphuric acid and phosphorus, in an attempt to prevent halogen or interhalogen from reaching the mercury manometer. Thus a true equilibrium between the polyhalide and its dissociation products may not have been achieved.

The preparative methods for potassium dichloroiodate described by Ephraim[191] were repeated by Cornog and Bauer[193] who obtained a compound which had identical properties with their sample of $KICl_2.H_2O$, suggesting that Ephraim had prepared $KICl_2.H_2O$ and not $KICl_2$.

Cornog and Bauer have reported dissociation pressures of both anhydrous $KICl_2$ and the monohydrate $KICl_2.H_2O$[193]. Their data, Table II-B-13, shows that the dissociation pressure of the hydrate was due almost entirely to the partial pressure of water and that the partial pressure of ICl from the hydrate was almost the same as the dissociation pressure of anhydrous $KICl_2$. These authors suggest that Cremer and Duncan had prepared $KICl_2.H_2O$ as indicated by the data in Table II-B-13.

Standard enthalpies of formation were calculated from the enthalpy of decomposition data recorded in Table II-B-12 and were compared with the values reported in this work. The ancillary data used for these calculations is contained in Table II-B-14; errors for ΔH_D are two standard deviations.

The agreement between the standard enthalpy of formation data derived from the dissociation pressure measurements of Ephraim and the values derived from calorimetric measurements is not good. This fact together with the comments concerning the methods of preparation used by Ephraim suggests that many of his measurements may be unreliable. However, the value for CsI_2Br is in good agreement with the value derived from the dissociation measurements of Plyushchev et al.[29].

The value of ΔH_f^o $KICl_2(c)$ derived from the data of Cornog and Bauer, who were careful to prepare the anhydrous salt, is in good agreement with the value reported in this work.

TABLE II-B-12

ENTHALPIES OF DECOMPOSITION FOR ALKALI-METAL POLYHALIDES

Compound	ΔH_D/kJ mol^{-1}	$-\Delta H_f^o$ MIX(c)/kJ mol^{-1}	
		From ΔH_D	This work
$KICl_2$	35.81±1.53[191]	454.15±1.55	
$KICl_2$	40.21±3.06[192]	458.55±3.07	477
	51.51±1.53[193]	469.85±1.55	
$RbICl_2$	54.38±2.11[191]	471.77±2.16	492.31±4.12
$CsICl_2$	53.61±1.72[191]	478.57±1.78	512.01±4.14
$KIBr_2$	46.53±5.36[191]	397.93±5.36	416
	26.81±2.30[192]	378.21±2.31	
$RbIBr_2$	49.21±1.72[191]	397.68±1.74	429.11±4.22
$CsIBr_2$	58.30±3.26[191]	423.21±3.29	446.32±4.08
CsI_2Br	51.12±1.91[191]	394.38±1.95	
	53.61±0.19[25]	396.87±0.46	
CsI_3	65.44±5.45[191]	351.17±5.47	
	71.96[152]	357.69	359.79±5.77
	77.90[153]	363.63	336
RbI_3	40.21±8.90[191]	306.23±8.90	
	69.45[152]	335.47	336
	75.39[153]	341.41	

TABLE II-B-13

THE DISSOCIATION PRESSURE OF $KICl_2.H_2O$

Temp	P_{ICl}/mm	P_{H_2O}/mm	$P=P_{ICl}+P_{H_2O}$ mm	P^a mm
25	0.1	9.9	10.0	9.2
30	0.2	15.0	15.2	14.2
35	0.4	20.6	21.0	20.6
40	0.7	29.6	30.3	29.5

[a] Interpolated dissociation pressure, from results of Cremer and Duncan ref.192.

TABLE II-B-14

Ancillary Data

Compound	$-\Delta H_f^o$/kJ mol^{-1}	Reference
CsCl(c)	442.47±0.42	105,160,194
RbCl(c)	434.90±0.40	105,160,194
KCl(c)	435.85±0.10	164
CsBr(c)	405.68±0.40	105,160,194
RbBr(c)	389.24±0.10	164
KBr(c)	392.17±0.10	164
IBr(g)	-40.769±0.205	105
ICl(g)	-17.508±0.213	105
I_2(g)	-62.421±0.013	105
CsI(c)	348.15±0.40	105,160,194
RbI(c)	328.44±0.10	164

The 'thermochemical radii' of the ions contained in Table II-B-15 and Table 3 Appendix II were calculated to investigate the relationship between the circumscribed sphere of an ion and its 'thermochemical radius'. Kapustinskii and Yatsimirskii[195] have previously investigated this problem. The former has defined the 'thermochemical radius' of a non-spherical complex-ion as being 'the radius of the hypothetical spherical ion that can replace the given ion iso-energetically in the crystal lattice'. Table II-B-16 contains the ratio of the 'thermochemical radius', r_t, to the 'radius of the circumscribed sphere', r_c, the latter being calculated by Kapustinskii and Yatsimirskii from interionic distances and van der Waals radii data. Enthalpy of formation data for the halide, nitrate and sulphate salts were taken from a standard reference[164]. Data for the chlorate, bromate and iodate calculations are collected in Table 3 Appendix II (page180) other ancillary data were taken from Johnson[181].

The 'thermochemical radii' calculated for bromate and iodate ions, from the various data sources contained in Table 3 Appendix II, can be seen to cover a large range. This range of values reflect the disagreement between various workers for several enthalpy of formation values of these salts. The r_t values contained in Table II-B-15 were selected from the values listed in Appendix II.

There is fair agreement between the r_t/r_c values reported by Kapustinskii and the values calculated in this work. It would appear that there is a simple relationship between r_t and r_c for a complex ion; this ratio being approximately constant for an ion of given symmetry, i.e. ca. 0.80 for a tetrahedral ion and ca. 0.68 for a triangular ion.

TABLE II-B-15

THERMOCHEMICAL RADII/pm

Pair of salts	Cl^-	Br^-	I^-	NO_3^-	SO_4^{2-}	ClO_3^-
Cs/K	193	213	242	210	264	221
Cs/Na	185	204	230	193	258	208
Na/K	178	197	221	181	256	198
Mean radius	185	205	231	195	259	209
Crystal radius	181	195	216			

Pair of salts	BrO_3^-	IO_3^-	Pair of salts
Li/Cs	209	191	Cs/K
Li/K	195	188	Li/Na
Na/Cs	189	178	Li/K
Mean radius	198	186	Mean radius

TABLE II-B-16

RATIO OF 'THERMOCHEMICAl RADIUS' r_t TO THE RADIUS OF THE CIRCUMSCRIBED SPHERE r_c

Ion	r_t/pm	r_c/pm	r_t/r_c	
				This work
NO_3^-	189	279	0.67	0.70
CO_3^{2-}	185	279	0.66	
ClO_4^-	236	290	0.81	
MnO_4^-	240	310	0.79	
BF_4^-	228	286	0.80	
SO_4^{2-}	230	294	0.78	0.88
CrO_4^{2-}	240	316	0.76	
MoO_4^{2-}	254	326	0.78	
ClO_3^-	200	203	0.98	1.03
BrO_3^-	191	238	0.80	0.83
IO_3^-	182	240	0.76	0.78

The 'thermochemical radii' of ClO_3^-, BrO_3^- and IO_3^- are in the reverse order to that which may be predicted from geometric data. The reason for this reverse order is not clear and was not explained by Kapustinskii. The 'thermochemical radius' of the halide ions contained in Table II-B-15 are larger, ca. 2% Cl^-, 5% Br^-, 7% I^-, than the corresponding crystallographic radii of these ions.

Lattice energies for alkali-metal and alkaline-earth salts containing the ions listed in Table II-B-15 were calculated by the Kapustinskii equation (page 77 equation (1)). The results of these calculations are contained in Tables II-B-17 to II-B-21 and are compared with the literature values[196,197].

TABLE II-B-17

LATTICE ENERGY DATA FOR ALKALI-METAL HALIDES/kJ mol^{-1}

	I	II	III	IV	V	VI	This work
LiF				1021	1038	1025	
LiCl		816	834	841	858	862	860
LiBr				808	791	803	797
LiI				753	732	745	735
NaF	908			908	921	912	
NaCl	774			774	778	778	756
NaBr	736			745	736	736	706
NaI	695			699	686	695	657
KF	808	803	795	808	812	816	
KCl	703	690	690	707	707	711	686
KBr	674	665	665	682	674	674	645
KI	636	623	628	644	632	640	603
RbF	770			774	774	778	
RbCl	674	665	665	678	686	686	660
RbBr	649			657	649	661	622
RbI	611			623	611	623	584
CsF	736	736	707	724	732	749	
CsCl	644	632	636	649		653	625
CsBr	623			631		631	591
CsI	590			598		603	560

TABLE II-B-18

LATTICE ENERGY DATA FOR METAL NITRATES/kJ mol^{-1}

	(I)	(II)	(III)	(IV)	This work
Li			808	833	823
Na	757		724	745	727
K	686		657	682	662
Rb	661	615		653	638
Cs	632	602		620	605
NH_4		598		661	643
Mg					2406
Ca	2222			2213	2187
Sr	2096			2105	2082
Ba	2008			1987	1981

TABLE II-B-19

LATTICE ENERGY DATA OF ALKALI-METAL AND ALKALINE-EARTH SULPHATES/kJ mol^{-1}

	I	(IIa)	(IIb)	a	This work
Li		2782	2782		2036
Na	2029	2598	2590		1834
K	1862	2452	2448		1695
Rb	1795	2379	2414		1641
Cs	1728	2347	2347		1568
Mg				2870	2657
Ca	2653			2598	2451
Sr	2602			2473	2352
Ba	2423			2418	2254

a see Ref **197**.

TABLE II-B-20

LATTICE ENERGY DATA FOR METAL CHLORATES/kJ mol^{-1}

	(I)	(II)	This work
Na	736	770	698
K	669	711	638
Rb	640	690	616
Cs	619		585
NH_4			
Ca	2155		2100
Sr	2033		2003
Ba	1954		1910

TABLE II-B-21

LATTICE ENERGY DATA FOR METAL BROMATES AND IODATES/kJ mol^{-1}

Li	815	849
Na	720	747
K	657	679
Rb	633	654
Cs	601	619
NH_4	638	659
Mg	2283	2478
Ca	2065	2136
Sr	1966	2031
Ba	2168	2246

SECTION III

EXPERIMENTAL

III-A PREPARATIONS AND ANALYSES

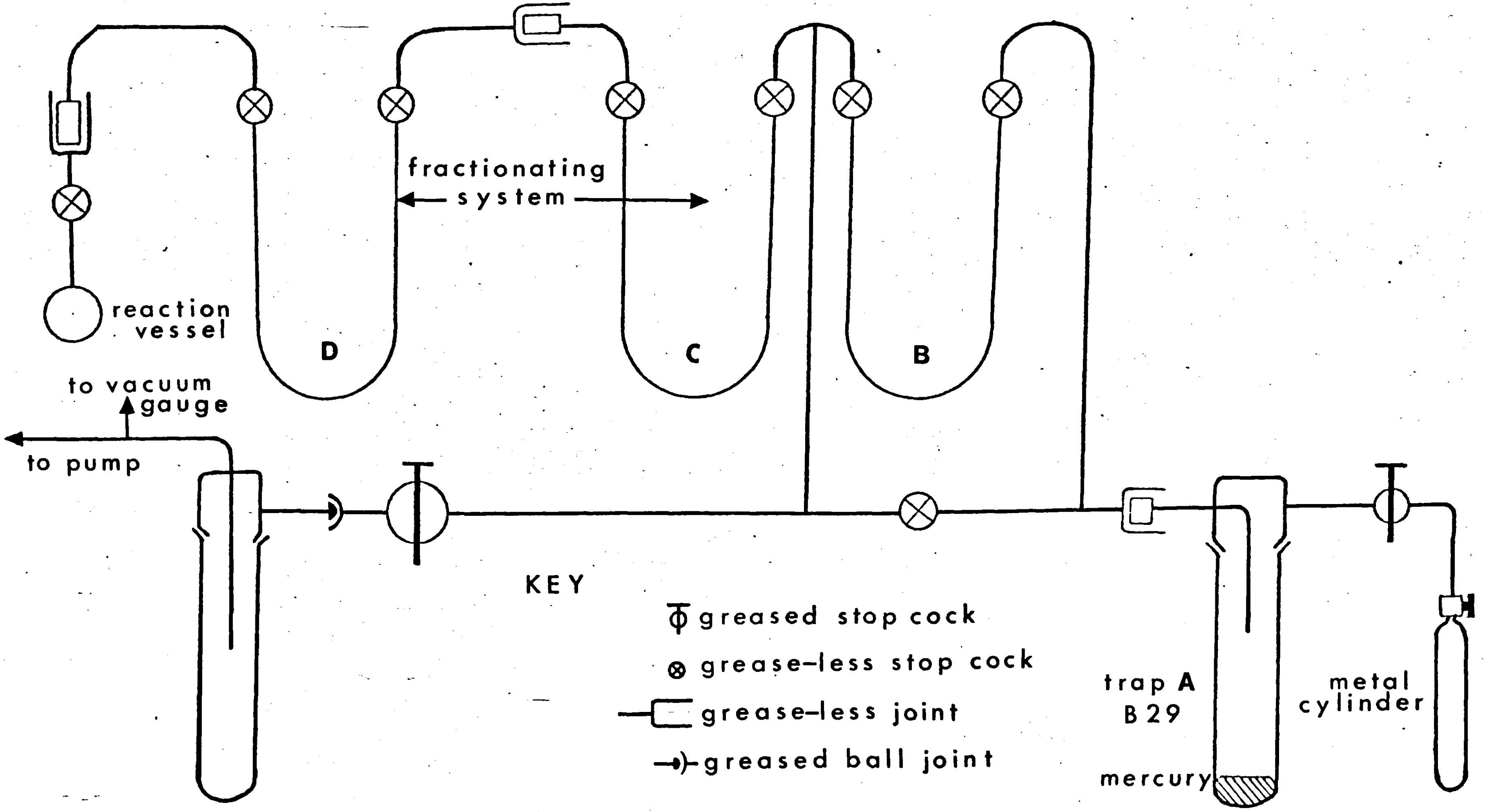
(1) Rubidium Tetrafluoroiodate, $RbIF_4$

The preparation of alkali-metal tetrafluoroiodates by various methods is well established[69,92,198]. Rubidium tetrafluoroiodate was prepared, by the method of Hargreaves and Peacock[92], from rubidium iodide and an excess of iodine pentafluoride. The iodine pentafluoride (Matheson and Co. Ltd.), supplied in metal cylinders, was contaminated with iodine and HF. It was purified by shaking with mercury (to remove I_2) followed by distillation in a grease-free vacuum line. Mercury reacts slowly with IF_5 at room temperature but rapidly with iodine. The vacuum line used is shown in Figure III-A-1.

Initial purification of the IF_5 was carried out in a B29 test-tube connected, via a greaseless socket (J.Young Scientific Glassware Ltd.), to the grease-free section of the vacuum line. Due to the high reactivity of the IF_5, Kel-F grease (3M Co.) was used for all the greased joints. Approximately 20cm^3 of iodine pentafluoride were distilled from the metal cylinder, via a greased stopcock into trap A, which was maintained at -80°, (solid CO_2 and acetone). Hydrogen fluoride was removed by this procedure. Iodine was removed by carefully shaking the liquid IF_5 with approximately 5cm^3 of triply-distilled mercury contained in trap A. The almost colourless IF_5 was again fractionated, at -80°, into trap B and was stored at -186°.

After purification the IF_5 was always handled in the grease-free section of the vacuum line. This part of the line was capable of maintaining a pressure of 10^{-4} torr. The vacuum taps were of the 'Uniform' type, (Glass Precision Engineering Co. Ltd.). These taps have teflon plungers giving a glass-to-teflon seal. The greaseless cones and sockets contained a teflon 'O ring' backed by a ring of viton. Therefore, only glass and teflon came into contact with the IF_5 once it had been initially purified.

FIGURE III-A-1 VACUUM LINE SYSTEM FOR HANDLING IODINE PENTAFLUORIDE



Rubidium iodide (B.D.H. Ltd.) was finely powdered and dried at 120° for 24 h before use. RbI (5g,24mmol) was transferred into a Pyrex reaction vessel together with a small teflon-coated magnetic follower. The transfer was carried out in a dry-box, and the reaction vessel weighed before and after the transfer to ascertain the weight of RbI in the vessel. Iodine pentafluoride (ca. 30cm^3,0.5mol), which had been fractionated at -80° into trap C, was distilled into the reaction vessel which was maintained at -186°. Iodine was immediately liberated when the IF_5 made contact with the iodide. The mixture was stirred for 20 min at 20°. Excess IF_5 was removed under vacuum into trap D, leaving a red-brown solid, due to contamination with iodine. The iodine was removed by prolonged pumping (ca. 48 h) at room temperature. Residues were pure white powders. The weight of the reaction vessel and product was found to be identical to the theoretical weight based on RbI.

$$5RbI + 4IF_5 \longrightarrow 5RbIF_4 + 2I_2$$

The product was handled under dry-box conditions.

Analysis: $RbIF_4$: Found, F,26.4%; Calc.,26.35%

Several attempts were made to prepare $CsIF_4$ using the same method. The observed weight change and fluorine analysis indicated that $CsIF_4$ contaminated with $CsIF_6$ was produced. A sample of sufficient purity for calorimetric measurements was not prepared. The reaction of CsF with IF_3 can be employed to give a pure sample of $CsIF_4$[70].

The preparation of the polyhalides in sections III-A-2 - III-A-8 was first described by Wells and Wheeler [6-8]. Schmeissmer [21] has recently reviewed the preparation of some of the compounds prepared by these authors.

(2) Caesium dichloroiodate, $CsICl_2$

A solution of CsCl (16.8g,0.1mol, B.D.H. AnalaR, in 170cm^3 H_2O) was prepared in a two-necked 500cm^3 flask. Powdered iodine (12.7g,0.05mol,B.D.H. AnalaR) was added and the mixture warmed to 80^o with constant stirring. Chlorine (Matheson Co. Ltd.) was introduced into the hot solution, through a side tube, until all the I_2 was just dissolved. An excess of Cl_2 was avoided to prevent the formation of $CsICl_4$.
Golden yellow crystals formed on cooling the solution with an ice-bath. The crystals were re-crystallised from hot hydrochloric acid ($HCl:H_2O = 1:1$) and dried on a sintered glass funnel and then in a desiccator over P_2O_5.

$$CsCl + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}I_2 = CsICl_2$$

(3) Caesium dibromoiodate, $CsIBr_2$

A solution of CsBr (10.6g,0.05mol, B.D.H. in 100cm^3 H_2O)was prepared and powdered iodine (6.4g, 0.025 mol, B.D.H. AnalaR) was added. The mixture was warmed to 60^o with constant stirring. Bromine (4g, 0.025mol, B.D.H.) was run into the mixture to give a deep red solution which was stirred for 15 min. Glistening orange-red crystals appeared on cooling the solution to 0^o. The crystals were dried on a sintered glass funnel and then in a desiccator over P_2O_5.

$$CsBr + \tfrac{1}{2}I_2 + \tfrac{1}{2}Br_2 = CsIBr_2$$

(4) Caesium tetrachloroiodate, $CsICl_4$

A solution of CsCl (10.0g,0.06mol, B.D.H. AnalaR in 150cm^3 H_2O) was prepared in a 250cm^3 two-necked flask. Concentrated hydrochloric acid (50cm^3) and powdered iodine (7.5g,0.03mol, B.D.H. AnalaR) were added and the mixture heated to 75° after fitting the flask with a reflux-condenser.

Chlorine gas was passed into the solution until all the iodine had dissolved and a constant weight obtained. On cooling to 0° orange-yellow crystals formed which were quickly dried on a sintered glass funnel, re-crystallised from hot hydrochloric acid ($HCl:H_2O$ = 1:1, saturated with Cl_2) and dried over P_2O_5. The desiccator was filled with dry chlorine to minimise decomposition of the sample. $CsICl_4$ slowly decomposes at room temperature, to $CsICl_2$[183,199].

$$CsICl_4 \longrightarrow CsICl_2 + Cl_2$$

(5) Rubidium dichloroiodate, $RbICl_2$

Rubidium polyhalides are very soluble in water, therefore concentrated solutions are required for successful preparation of these compounds.

A saturated solution of RbCl (15g,0.125mol, B.D.H.) was prepared in a 100cm^3 two-necked flask. Powdered iodine (16g,0.075mol, B.D.H. AnalaR) was added and the mixture heated to 70° with constant stirring. Chlorine was passed into the solution until all the iodine was just dissolved. An excess of Cl_2 was avoided to prevent the formation of $RbICl_4$. On cooling to 0° orange-yellow crystals formed, which were dried on a sintered glass funnel and in a desiccator over P_2O_5.

Re-crystallisation was not attempted because of the high solubility of $RbICl_2$.

$$RbCl + \tfrac{1}{2}Cl_2 + \tfrac{1}{2}I_2 = RbICl_2$$

(6) Rubidium dibromoiodate, $RbIBr_2$

A saturated solution of RbBr (20.0g,0.12mol, Koch-Light Laboratories Ltd.) was prepared in a $100cm^3$ flask. Powdered iodine (15.34g,0.06mol, B.D.H. AnalaR) was added and the mixture warmed to 70^o with constant stirring. Bromine (9.66g,0.06mol, B.D.H.) was slowly added and the deep orange-red solution stirred for 15 min. Glistening orange-red crystals formed on cooling the solution to 0^o. The crystals were dried on a sintered glass funnel and then over P_2O_5 in a desiccator.

$$RbBr + \tfrac{1}{2}I_2 + \tfrac{1}{2}Br_2 = RbIBr_2$$

(7) Rubidium tetrachloroiodate, $RbICl_4$

RbCl (20g,0.165mol, B.D.H.) was dissolved in $100cm^3$ of 1:1 $HCl:H_2O$ contained in a $250cm^3$ two-necked flask. Powdered iodine (20.9g,0.083mol, B.D.H. AnalaR) was added and the flask fitted with a reflux condenser. The mixture was heated to 65^o with constant stirring while chlorine was bubbled into the solution until all the iodine had dissolved and a constant weight obtained. On cooling to 0^o orange-yellow crystals formed. The crystals were dried quickly on a sintered glass funnel and then over P_2O_5 in a chlorine-filled desiccator.
$RbICl_4$ slowly decomposes at room temperature.

$$RbICl_4 \longrightarrow RbICl_2 + Cl_2$$

(8)Caesium triiodide, CsI_3

Caesium triiodide was prepared by the method of Babkov and Stepin[152]. A solution of CsI (9.6g,0.037 mol, B.D.H.) was prepared with 80cm^3 of distilled water. 30cm^3 of a saturated alcoholic solution of iodine was added to the ice-cold caesium iodide solution with constant stirring. The dark violet crystals were dried on a sintered glass funnel and over P_2O_5 in a desiccator.

ANALYTICAL PROCEDURES

(1) Alkali-metal analysis

Duplicate samples of polyhalide (containing ca. 0.1g of Cs or Rb) were hydrolysed in a flask fitted with a reflux condenser. The liberated iodine was removed by vigorous boiling for 90 min.
The alkali-metal present was estimated gravimetrically as the tetraphenylborate[200].

(2) Total halide analysis

Polyhalides are reduced by aqueous sulphur dioxide[165] solution[18] or aqueous sodium sulphite[17] to the mono-halides which can then be estimated by either a volumetric or by a gravimetric procedure. A weighed sample of polyhalide (ca. 0.2g) was reduced with saturated aqueous sulphur dioxide (100cm^3). The solution was boiled to remove dissolved sulphur dioxide and the halides estimated by Volhard's method[200].

(3) Iodine analysis

Iodide can be estimated in the presence of chloride or bromide ions as PdI_2 [200]. A weighed sample of polyhalide (containing not more than 0.1g of iodide) was reduced with aqueous sulphur dioxide solution. Excess SO_2 was removed by boiling the solution which was then cooled to 70°. An aqueous solution of palladous chloride (0.25g in 100cm^3 containing 1% HCl) was slowly added with constant stirring. After allowing the precipitated PdI_2 to settle for 24 h it was collected on a sintered glass crucible and dried at 100°.
The percentage bromine or chlorine in each polyhalide was calculated using the total halide result and the percentage iodine determined as above.

(4) Iodine analysis of CsI_3

A sample of CsI_3 (ca. 0.3g) was reduced with aqueous sulphur dioxide solution. The excess SO_2 was removed by vigorous boiling. Iodine from the sample was then estimated by Volhard's method[200].

(5) Fluorine analysis of $RbIF_4$

$RbIF_4$ is hydrolysed completely and rapidly in aqueous solution (section III-C). Fluorine analysis was carried out using a Specific Ion Meter (Orion model 401) coupled to a combination fluoride ion selective electrode, (Orion model 96-09). In solutions with $pH \lesssim 5$ hydrogen ion complexes with fluoride ion, forming HF or HF_2^-, which cannot be detected by the electrode. Sodium acetate was used to buffer the pH to above 5 as described in the instructions supplied with the electrode. A 15% solution of sodium acetate was prepared by dissolving sodium acetate (B.D.H. AnalaR) in distilled water. All standard solutions and the unknown solution were diluted 10:1 with the buffer solution.

AnalaR sodium fluoride (B.D.H. min 99%) was used to prepare the standard solutions. Two standards were selected in the concentration range of the unknown. The first was ten times the concentration of the second. For example, if the unknown was calculated to have a fluoride ion concentration of 5×10^{-3}M then standards of 10^{-3}M and 10^{-2}M were prepared. All solutions were stirred throughout the determinations. A weighed sample of $RbIF_4$ was hydrolysed in a stoppered plastic bottle. The hydrolysate was diluted 10:1 with acetate buffer. Standard filling solution (Orion 90-00-01) was added to the combination fluoride electrode which was connected to the meter. The electrode was first inserted into the more concentrated standard.

By adjustment of the calibration control on the meter a reading of 100, at the mid-point of the logarithmic scale, was obtained. The electrode was removed, carefully blotted with absorbent tissues and placed into the second standard. A reading of 10 was then obtained by altering the second calibration control on the meter. This action does not affect the mid-scale calibration. The electrode was removed, blotted and placed in the unknown sample. A direct reading of fluoride ion concentration could be made from the scale. The percentage of fluorine in the sample was calculated knowing the original weight of the sample hydrolysed. A background of iodate and iodine was found to have no effect on the response of the electrode. Standard solutions were made up therefore as described above. Analytical results for the compounds prepared in this section are contained in Table III-A-1.

TABLE III-A-1

Compound	Cs		Rb		I		Cl		Br	
	%		%		%		%		%	
	F	C	F	C	F	C	F	C	F	C
$CsICl_2$	40.33 40.30	40.19			38.38	38.37	21.39	21.44		
$CsIBr_2$	31.82 31.80	31.67			30.55	30.24			37.62	38.09
$CsICl_4$	33.58 33.79	33.09			31.62	31.60	34.96	35.31		
$RbICl_2$			30.21 30.19	30.17	44.46	44.80	25.30	25.03		
$RbIBr_2$					34.02	34.09			42.76	42.94
$RbICl_4$					35.80	35.83	40.06	40.04		
CsI_3					74.06	74.12				

III-B CALORIMETRY

Three solution reaction calorimeters were used in the course of this work.

(1) Enthalpies of reaction for the alkali-metal polyhalides contained in Tables II-A-2 - II-A-12 were determined by a calorimeter designed and constructed in this laboratory by the author.

(2) The enthalpy of hydrolysis of $RbIF_4$ was determined by an older calorimeter designed and constructed in this laboratory which is described elsewhere[205].

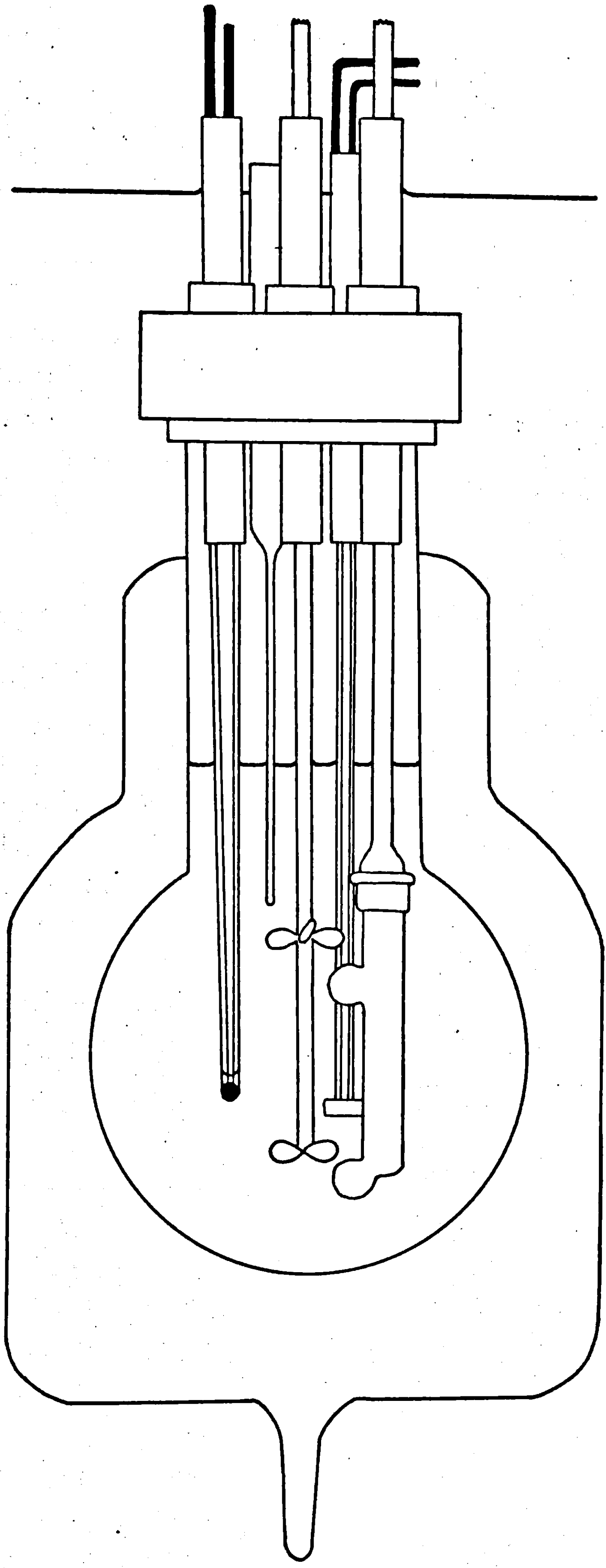
(3) An L.K.B. 8700-1 Precision Calorimetry System was employed to measure the enthalpy of reaction of $AgNO_3$ with aqueous KIO_3 solution.

(1) This calorimeter was operated in a partial differential isoper<u>ibol</u> mode. The calorimeter vessels were of the glass Dewar type, details being shown in Figures III-B-1 and in Figures III-B-2(a), (b) and (c). Each vessel consists of a thin-walled borosilicate glass Dewar vessel. A threaded aluminium flange, bonded to the neck of each vessel, locates an aluminium lid which screws onto the flange. Glass tube inserts, e.g. thermistor tube; were carried by individual aluminium ferrules which screw into the calorimeter lids.
The internal vessel, capacity $100cm^3$, has very thin (*ca.* 1mm) walls. Individual components of the calorimeter were constructed as follows:

Stirrer assembly

The stirrer assemblies were of precision-bore glass tube (5mm external diameter) and rod (3mm diameter) the latter forming the stirrer shaft. The precision-bore tube was firmly cemented, with epoxy resin, into

FIGURE III-B-1 CALORIMETER VESSEL



the central ferrule of the calorimeter lid.
A double-bladed glass propeller on one end of the rod and a PTFE paddle fixed to the stirrer shaft ca. 1cm below the surface of the liquid ensured efficient stirring of the calorimetric fluid. A servo-controlled motor, (Electrocraft type E-150MGH) was coupled to the stirrer shaft and the variable speed controller was set to 700 r.p.m.

Ampoule and ampoule-holder assembly

Calorimetric ampoules,8cm long,Figure III-B-2(d), were glassblown from B5 sockets. The ampoules had two fracture bulbs, and reaction was initiated by breaking the bulbs against the stirrer paddles. The B5 cone of the ampoule holder shaft (3mm precision glass rod) fitted into the B5 socket at the neck of the ampoule.

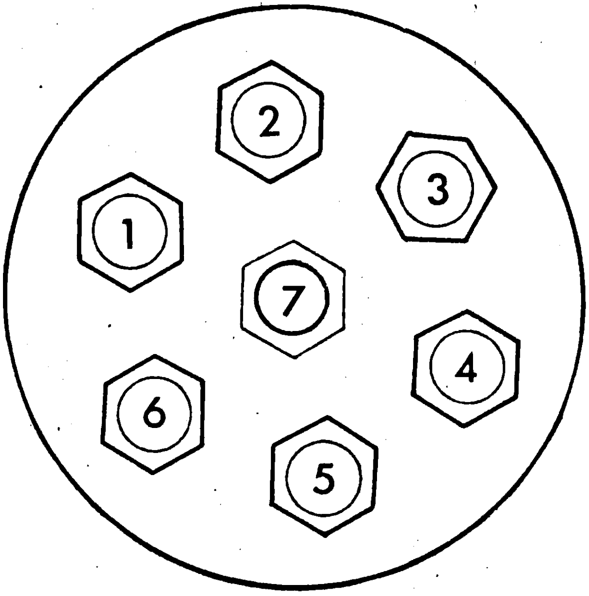
Thermistor tube

Assembly of the thermistor tube was carried out in three stages Figure III-B-2(c). The thermistor (YSI 100KΩ part No. 44011) was first sealed, with epoxy resin, into a tapered, thin-walled glass tube containing a drop of silicone oil for good heat transfer. Two screened co-axial leads were carefully soldered to the protruding thermistor leads. This assembly was sealed with silicone rubber (Hopkin and Williams Ltd., cold cure silastomer 9161) into a length of glass tube. Only the tapered glass tube was in contact with the calorimetric fluid.

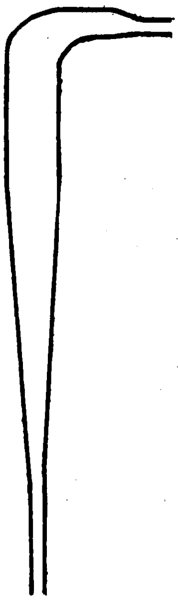
Calorimetric calibration heaters

The calorimetric heaters (Tronac Inc., Provo, Utah type R24) were of nominal 100Ω resistance PTFE encapsulated resistors of low thermal capacity with double leads. The exact resistance was measured at 25.0°, by

FIGURES III-B-2(a) CALORIMETER LID AND 2(b) TITRANT DELIVERY TUBE

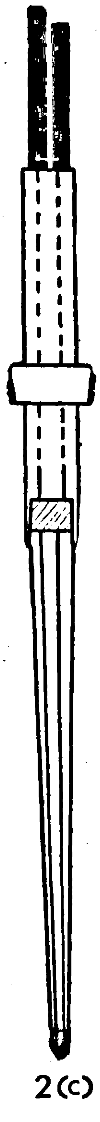


1 Thermistor tube; 2 Unused; 3 Calibration heater; 4 Ampoule holder; 5 Cooling tube; 6 Titrant delivery-tube; 7 Stirrer-shaft guide.

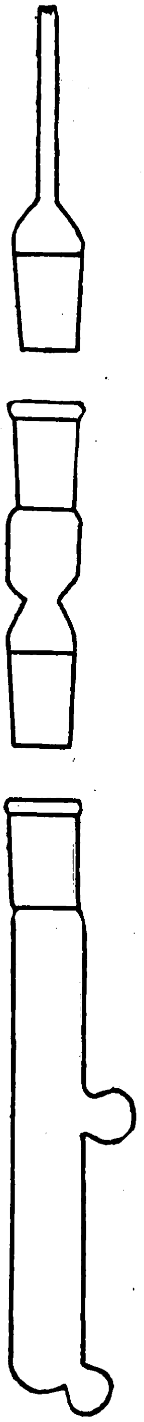


2(b)

FIGURES III-B-2(c) THERMISTOR TUBE AND 2(d) AMPOULE ASSEMBLY



2(c)



2(d)

a precision potentiometer (Stabaumatic, type 5545 Tinsley & Co.). Each heater was sealed by its leads into a short length of glass tube with silicone rubber.

Cooling tube

A thin glass capilliary tube (sealed at one end) dipping into the calorimetric fluid was used to cool the calorimeter. Liquid nitrogen was employed as a coolant.

The above components were cemented into the ferrules with epoxy resin. Two calorimeter vessels were constructed. The second vessel did not have an ampoule holder assembly but was otherwise identical to the first vessel.

Thermostatic bath

The calorimeters were immersed in a well stirred water bath maintained at $25.0 \pm 0.005^{\circ}$.
Expanded polystyrene sheets and a 'lid' of polyolefin spheres (Gallenkamp Ltd.) were used to insulate the bath. The complete calorimeter system was operated in a room which was maintained at $25 \pm 2^{\circ}$. A proportional controller (Tronac model 1040) was used to control the temperature of the water bath.

Temperature measuring circuits

Temperature changes were detected by thermistors connected to an a.c. differential thermistor bridge (Carwyn Instruments type 401B). Details of this instrument are given in Appendix I. The block diagram for the temperature measuring circuits is contained in Figure III-B-3(a).

FIGURE III-B-3(a) TEMPERATURE MEASURING CIRCUIT BLOCK DIAGRAM

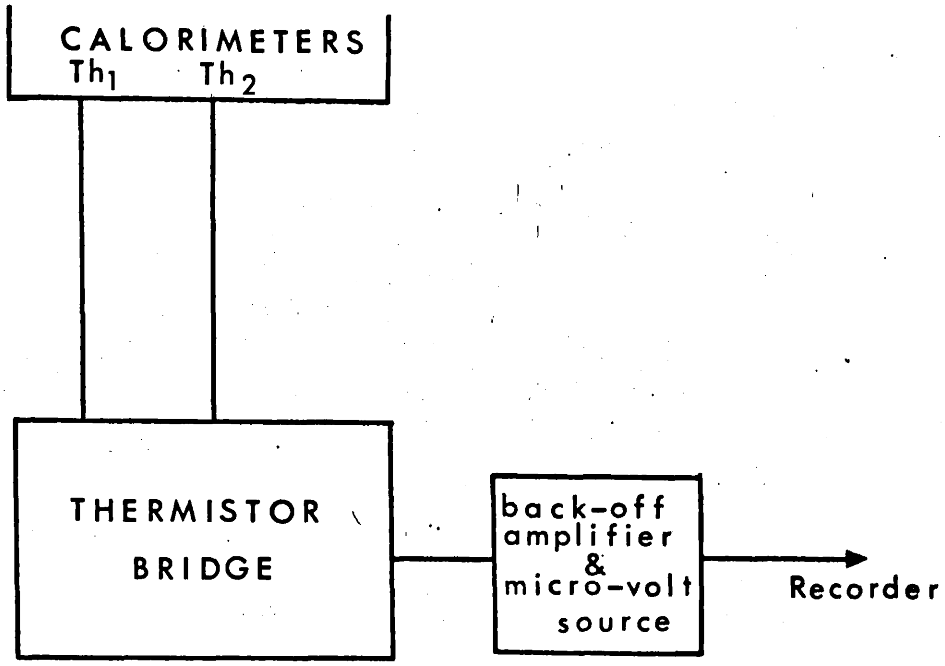
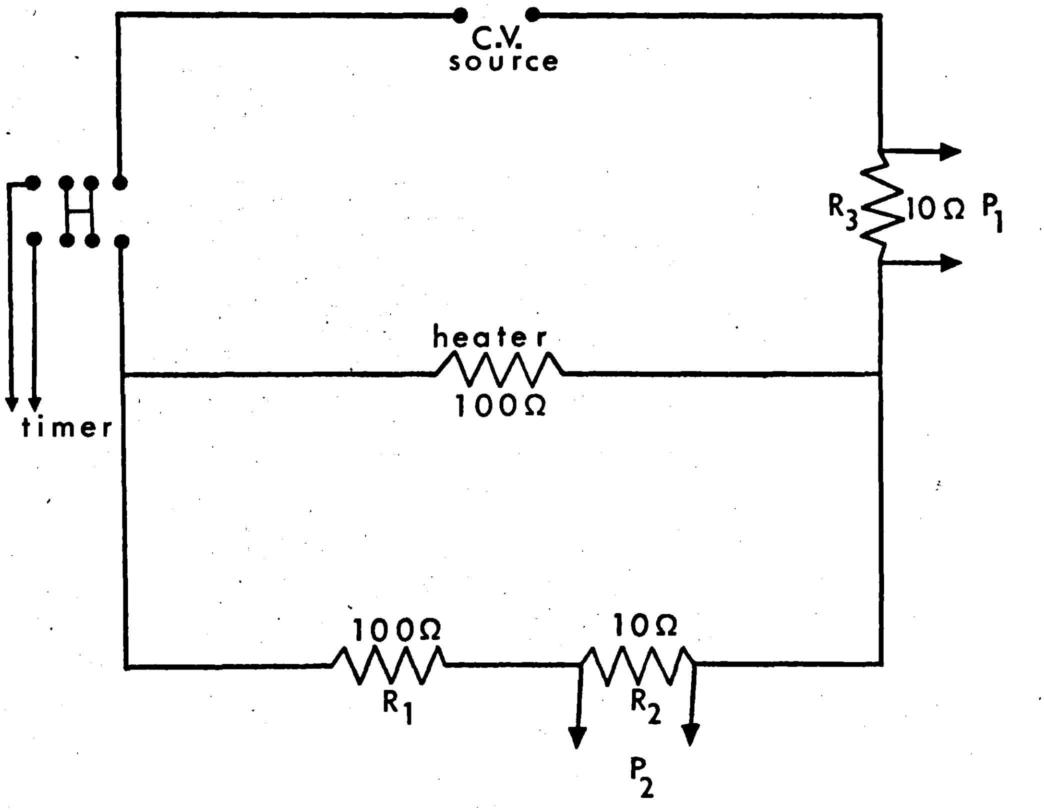


FIGURE III-B-3(b) CALORIMETER HEATER CIRCUIT



Three thermistor inputs are provided by the bridge (inputs A, B and C). The bridge may be switched to read the temperature of any individual thermistor against a helipot dial. In this case the bridge functions as a null-indicator and is operating in the 'single channel mode'. Alternatively the temperature difference between any thermistor pair, e.g. A/B, B/C or A/C etc. can be monitored. Here the bridge was operating in the 'differential mode' and the output voltage was one volt for temperature differences of 0.001° to 1.0° depending on the position of the range switch.

A coarse and fine 'back-off' control was provided which allows differences in individual thermistor resistances to be taken up. The out-of-balance potential caused by a difference in thermistor temperature can be reduced by these controls. However, the back-off controls were found to cover too small a range and to be too imprecise for the calorimeter described in this work. An additional circuit was constructed to overcome this problem and is described in Appendix I. The sensitivity of the chart recorder was adjusted so that 1cm of chart paper $=0.04\text{V} \hat{=} 0.0004^{\circ}$. The thermistor bridge was operated on the range $1^{\circ} \hat{=} 1$ volt.

Calibration Heater and Heater Control Circuit

Heaters of measured power (*ca.* 0.3 watt) were used for the calibration experiment. The heaters were connected into the circuit shown in Figure III-B-3(b) which provides current from a 6 volt constant voltage supply (Ether type AA 100). Precision wire-wound resistors (Alma type JG2Z10R and JG2Z100R) were employed in the construction of the circuit. An oil-filled 10Ω standard resistor (Croydon Precision Instruments Co., type R.S.I. ± 0.005%) provided a potential to measure the total current flow in the circuit.

The resistances in the potential divider were measured by a precision potentiometer (Stabaumatic type 5545, Tinsley and Co.).

During a calorimetric calibration potentials P_1 and P_2 were measured by a potentiometer (Tinsley & Co. type 3387B) which is part of the calorimeter electronics. A timer was simultaneously actuated when the heater was switched to the constant voltage source. The time of heating was measured to ± 0.01 seconds.

The heater circuit was modified after the calorimeter was used to obtain the results contained in Tables III-B-1, III-B-2 and III-A-2. A digital voltmeter (SM210, S.E. LABS(EMI) Ltd,) was used to measure directly the potential across the heater. The second pair of leads provided by the heater was used, with the digital voltmeter connected into the circuit as shown in Figure III-B-4.

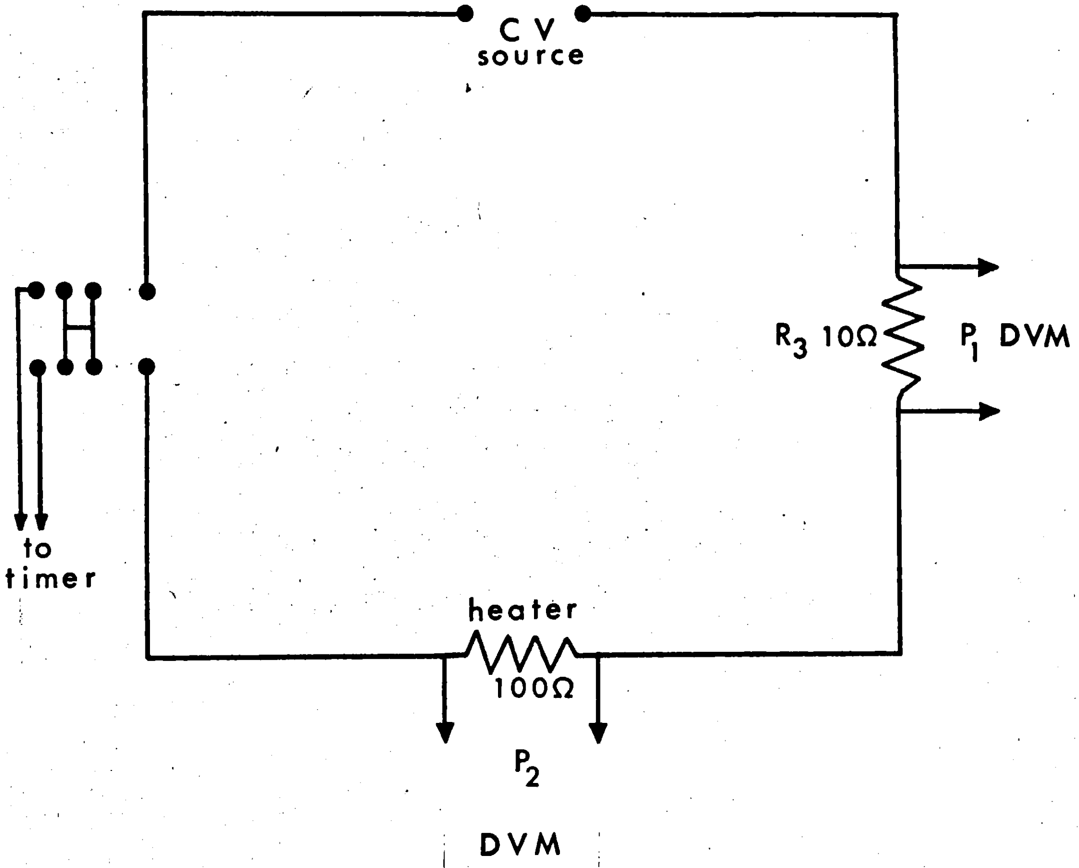
Operation of the calorimeter

A typical calorimetric run for tris(hydroxymethyl) aminomethane (THAM) is described below to explain the operation of the calorimeter. This procedure can be separated into three main parts:

(1) Ampoule-loading and initial setting up

An empty ampoule was weighed together with the greased ampoule adaptor and inserted into a small B5 test-tube (Figure III-B-2(d)). The ampoule was filled with powdered, dried THAM. A small glass funnel was employed to ensure that all the solid rested below the top bulb of the ampoule (any solid above this bulb is not washed out of the ampoule by the calorimetric fluid). The ampoule adaptor was inserted into the ampoule and the now stoppered ampoule was re-weighed with the test-tube. This method prevents weighing errors caused by loss of grease from one ground glass joint to another. For hygroscopic samples the procedure of ampoule filling can be carried out in a dry-box.

FIGURE III-B-4 DIGITAL VOLTMETER CALORIMETER HEATER CIRCUIT



The mass of THAM was corrected to vacuo (Appendix I). A loop of platinum wire, wound around the glass hooks on the ampoule neck and ampoule-holder shaft, was used to secure the ampoule on the ampoule-holder. The precision rod was located in its guide in the calorimeter lid and the ampoule bulbs positioned under their respective stirrer paddles. Movement of the assembly was prevented by clamping the rod. 100cm^3 of 0.10M hydrochloric acid (B.D.H. A.V.S.), warmed to 25°, were carefully transferred by pipette into the calorimeter Dewar and the calorimeter lid screwed onto the neck of the vessel. The reference vessel was filled with 100cm^3 of distilled water. The vessels were then immersed in the thermostat bath (to the level indicated in Figure III-B-1) and their respective stirrer motors connected and switched on. Using the thermistor bridge in the single-channel mode, the temperature of each vessel was checked against the helipot dial. The reading on the helipot for each thermistor, at 25.0°, was determined in a separate experiment.

The temperature of each calorimeter vessel was adjusted, to 25.00 ± 0.05°, as indicated by the reading on the helipot dial by using its heater or cooling tube. The vessels were then left to equilibrate for 1.5 h.

(2) Reaction experiment

10cm of chart paper was checked, using the millivolt source, to correspond to 0.0400 volts. With the thermistor bridge switched to A/B the bridge was unbalanced, by means of the coarse back-off control to 0.3 volt. The chart recorder pen was positioned to the middle of the chart recorder paper, by adjustment of the millivolt source and this reading recorded.

A fore-period of at least 20 min was recorded. The ampoule was carefully unclamped and the ampoule bulbs fractured by turning the bulbs into the stirrer paddles. The ampoule was then carefully adjusted to its former position. A blank 'run' showed that any effect caused by ampoule breaking was negligible As the temperature rise in the calorimeter took place the recorder pen was brought back onto scale by adjustment of the millivolt source. An after-period of at least 25 min was then recorded. With the thermistor bridge switched to position A, the calorimeter was cooled (using liquid N_2 in the cooling tube) to 25.0°. The calorimeters were left to equilibrate for 1.5 h.

(3) Calibration experiment

The thermistor bridge was set to A/B and the milli-volt source to the initial value used in the reaction experiment. A fore-period of 20 min was recorded. The calibration heater was then switched on and a pen displacement identical to the reaction period recorded. An after -period of 25 min was recorded and the heating time noted. After cooling the calorimeter to 25° the two potentials P_1 and P_2, (Figure III-B-3(b)), were measured. The power, P and the total resistance of heater plus leads R_h were calculated from these two potentials. If P_1 and P_2 are in volts and R_1 and R_2 are in Ω then we have:

$$P = AP_2(P_1/R_3 - P_2/R_2) \text{ watts}$$

and

$$R_h = AP_2/(P_1/R_3 - P_2/R_2) \text{ ohms}$$

where $$A = \frac{R_1 + R_2}{R_2}$$

For the digital voltmeter heater circuit (Figure III-B-4) the identical expressions for P and R_h are:

$$P = P_2 . P_1/R_3 \quad \text{watts}$$

$$\underline{R(\text{meas.})} = \frac{P_2}{P_1/R_3}\ \Omega$$

Theory of thermistor-bridge operation

Basically the bridge was a unit-ratio bridge where one element was slightly unbalanced (Figure III-B-12). With a bridge drive voltage E, the out-of-balance voltage is given by the expression:

$$e = \tfrac{1}{2} \frac{\Delta R}{(2R - \Delta R)} . E \qquad (1)$$

If ΔR is very much less than R then (1) reduces to:

$$e = E(\Delta R/4R)$$

The out-of-balance voltage is therefore directly proportional to ΔR and hence the thermistor temperature. However, $\Delta R/R$ is 1.33% for a 0.3^o change on the 1.0^o range. Thus the bridge output voltage is not directly proportional to thermistor temperature. However, non-linearity errors were compensated by the electrical calibration experiment being arranged to exactly duplicate the reaction heat output. Non-linearity errors cancelled when the ratio of the voltage changes was calculated.

The corrected temperature changes for the reaction and calibration experiments were calculated from the out--of-balance potential displayed by the thermistor bridge. The reaction of THAM with either excess HCl or NaOH was fast, being complete in under two minutes.
Moderately fast reactions (complete in ca. 5 min) were observed for the polyhalide compounds (Figure III-B-5). The values of V_1 and V_2 were obtained by the linear extrapolation of the reaction fore- and after-periods to the time of ampoule breaking. The value of V_2 should be found by extrapolation of the after-period to the time corresponding to 0.63 of the voltage change ($t_{0.63}$). However, using a chart recorder the position of $t_{0.63}$ cannot be found and must be estimated. The difference between the V_2 value at $t_{0.63}$ and at the time of ampoule breaking for a THAM reaction was negligible.
For a moderately fast reaction the difference was slightly larger but was found to be almost equal to the uncertainty in the estimation of $t_{0.63}$.

Extrapolation of the calibration voltage-time traces was carried out by Dickinson's equal area method[201,202]. This procedure may be simplified due to the linear nature of the voltage-time profile during heating. V_3 and V_4 were obtained from the extrapolated fore-and after-periods at the time corresponding to half the voltage change. Extrapolation of a typical calibration voltage-time profile is shown in Figure III-B-6.

Justification for regarding the fore-and after-periods as linear is contained in Appendix I.
The calorimetric enthalpy change was calculated using the following formula:

FIGURE III-B-5 TYPICAL $CsIBr_2/AgNO_3$ REACTION TRACE

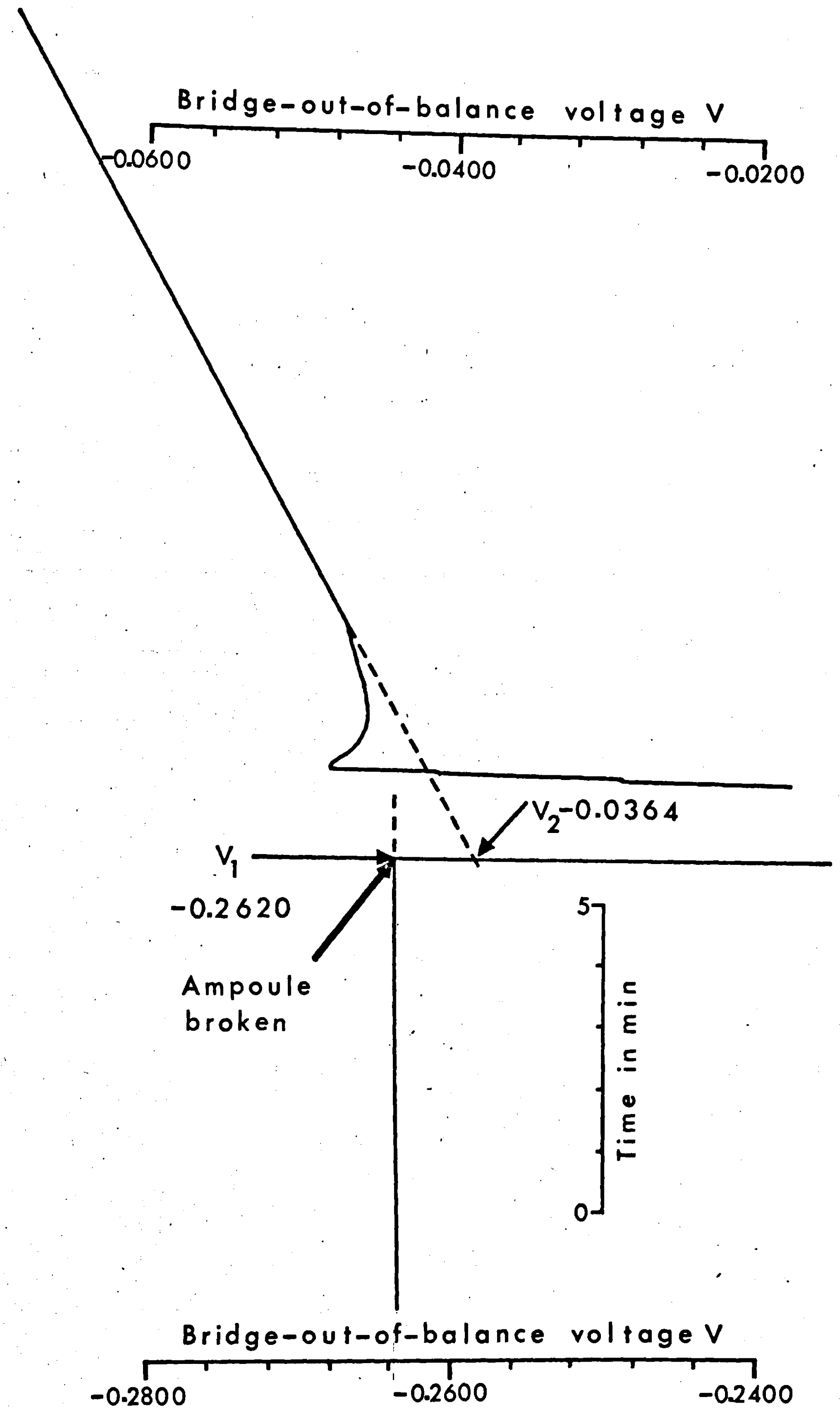
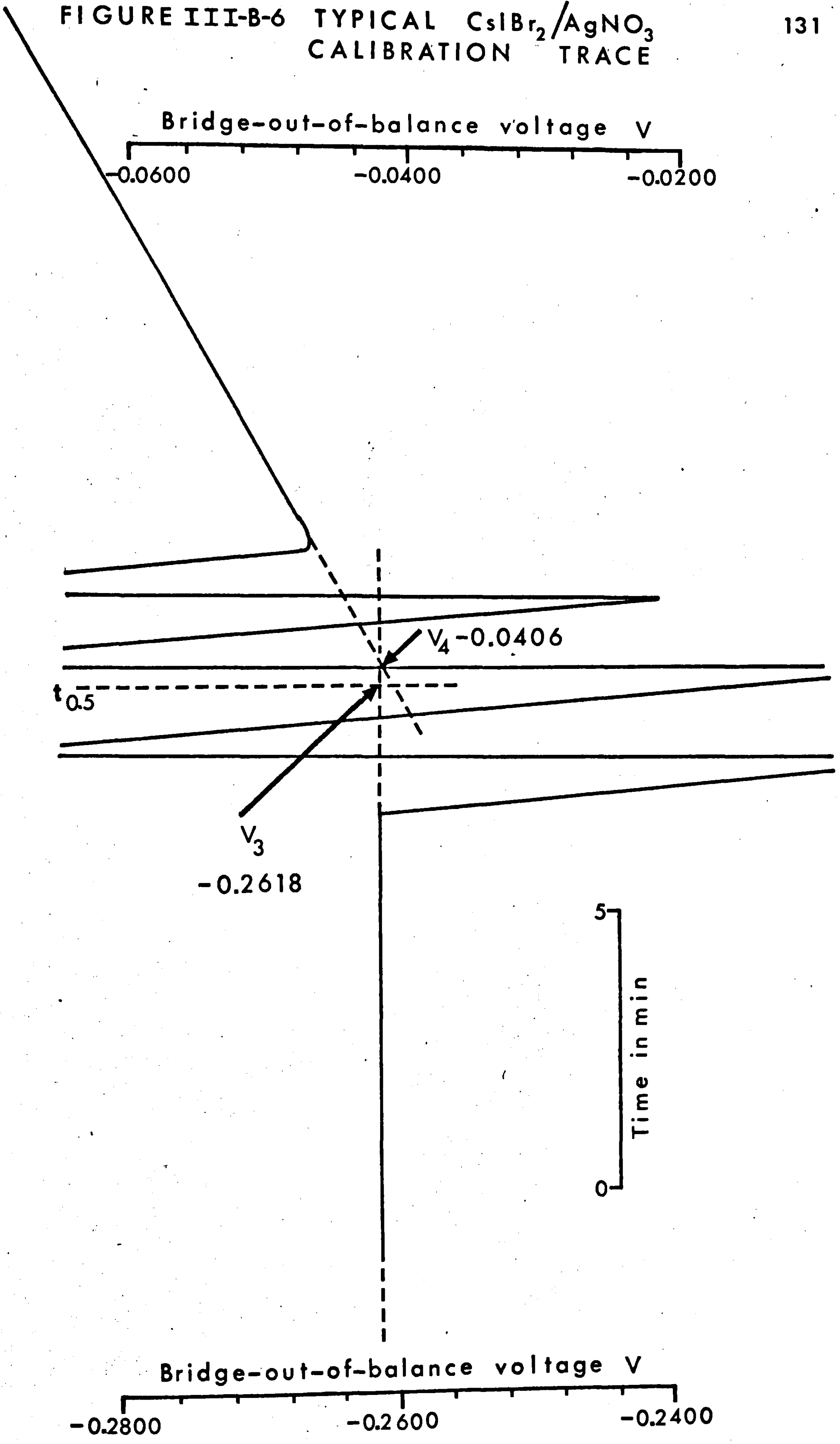


FIGURE III-B-6 TYPICAL $CsIBr_2/AgNO_3$ CALIBRATION TRACE



$$-\Delta H_R = \frac{f.P.M.t}{m} \cdot \frac{\Delta T_r}{\Delta T_c} \quad \text{kJ mol}^{-1}$$

where

f = a factor to correct for heat dissipated in the heater leads

P = power of the heater

M = molecular weight of compound

m = mass of compound contained in the ampoule

t = time of heating (sec.)

and ΔT_r is the out-of-balance voltage for the reaction period, and ΔT_c for the calibration experiment.

$$f = \frac{R(\text{meas.})}{R_h}$$

where

R(meas.) is the resistance of the heater element and R_h the resistance of the heater leads calculated from P_1 and P_2 obtained during the calibration experiment.

Tris(hydroxymethyl)aminomethane (THAM B.D.H. Aristar) grade, min. 99.9%) was employed as the standard reference material to determine the accuracy of the calorimeter. The enthalpy of reaction of THAM in excess aqueous hydro-chloric acid (0.100M, B.D.H. A.V.S.) and in excess aqueous sodium hydroxide solution 0.050M were measured. Calorimetric sodium hydroxide solution was prepared from 1M stock solution (B.D.H. A.V.S.). The concentration was checked by titration against potassium hydrogen phthalate using phenolpthalein as indicator. The enthalpy of reaction of THAM in aqueous NaOH is dependant on the NaOH concentration[203,204]. The results obtained for eight consecutive runs are contained in Tables III-B- 1 and 2. Uncertainties in ΔH_R are

TABLE III-B-1

ENTHALPY OF REACTION OF THAM WITH EXCESS 0.1M HCl

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.51919	1296	29.85
0.45355	1484	29.85
0.42905	1568	29.81
0.39068	1723	29.93
0.42063	1600	29.95
0.46171	1458	29.83
0.43110	1561	29.80
0.37804	1780	29.90

ΔH_R (mean) = −29.87 ± 0.05 kJ mol^{-1} (lit.,[204] ΔH_{298} −29.790 ± 0.031 kJ mol^{-1}, n = 1345).

TABLE III-B-2

ENTHALPY OF REACTION OF THAM WITH EXCESS 0.05M NaOH

w/g	dilution,n	$-\Delta H_R$/kJ mol^{-1}
0.53886	1249	17.11
0.54207	1241	17.24
0.43408	1550	17.13
0.45913	1465	17.12
0.44748	1504	17.15
0.45655	1474	17.14
0.49068	1371	17.27
0.51338	1311	17.24

ΔH_R (mean) = 17.18 ± 0.05 kJ mol^{-1} (lit.,[204] ΔH_{298} 17.177 ± 0.023 kJ mol^{-1}).

expressed at the 95% confidence level assessed by the 'students t' distribution. The weight of THAM was corrected to vacuo, using M.W. THAM = 121.37, density 1.35g cm^{-3}.

(2) This calorimeter was an all glass Dewar type which has been used in this Department for several years. It is fully described elsewhere[205]. Detailed accounts of operating procedures are available[205].

The calorimeter was operated in duplicate in the isoperibol mode. The experimental precision and accuracy has been checked by measuring the enthalpy of neutralization of THAM in excess 0.1 mol dm^{-3} aqueous hydrochloric acid[205]. The mean of 10 runs was ΔH_{298} $(1200<n<1364) = -29.79 \pm 0.08$ kJ mol^{-1}. Prosen and Kilday[204] report $\Delta H_{298} = -29.790 \pm 0.03$ kJ mol^{-1}.

Temperature changes were monitored by a F53 thermistor (Standard Telephone and Cable Ltd.) connected as one arm of a conventional Wheatstone bridge. The out-of-balance bridge signal was displayed directly on a 1mV pen-recorder (Bryans Ltd. model 2700). Displacement of the pen from the middle of the chart was linear with respect to changes in thermistor resistance[206]. The sensitivity of the recorder was adjusted to give 1Ω = 1cm of chart paper. The calibration heaters and heater control circuit were identical to those described in section III-B-(1). Calorimetric ampoules were glass-blown from thin-walled B7 sockets and have two fragile fracture bulbs. $RbIF_4$ was carefully loaded into the ampoules under dry-box conditions. To avoid errors due to loss of grease an arrangement identical to that shown in Figure III-B-2(d) was used. The heat due to ampoule breaking was shown to be negligible from a blank calorimetric run.

The ratio of the temperature changes for the reaction and calibration periods was calculated from the resistance-time records. Hydrolysis of $RbIF_4$ was rapid being complete in ca. one min. A typical reaction profile is shown in Figure III-B-7. Extrapolation of the calorimetric resistance-time records was carried out as described in section III-B-(1). Wellum[207] has shown that the expression:

$$\frac{\Delta T_r}{\Delta T_c} = \frac{\ln(R_1/R_2)}{\ln(R_3/R_4)}$$

is correct to within 0.1% if the initial and final resistances during reaction and calibration are within $40\,\Omega$. A resistance-time record for a calibration experiment is shown in Figure III-B-10.
Similar calibration traces were obtained for this calorimeter.

The enthalpy change for the reaction was calculated from the expression:

$$-\Delta H_R = \frac{f.P.t.M}{1000.W} \cdot \frac{\Delta T_r}{\Delta T_c} \text{ kJ mol}^{-1}$$

(3) The enthalpy of reaction of crystalline $AgNO_3$ with aqueous KIO_3 solution, saturated with $AgIO_3$, was determined using a L.K.B. 8700-1 Calorimetry System. Details of the construction and operating procedures are given in the instruction manual. The basic principle of this calorimeter is identical to that described in section III-B-(2), but certain experimental details differ. A block diagram of the calorimeter is shown in Figure III-B-8.

FIGURE III-B-7 TYPICAL $RbIF_4$ HYDROLYSIS REACTION TRACE

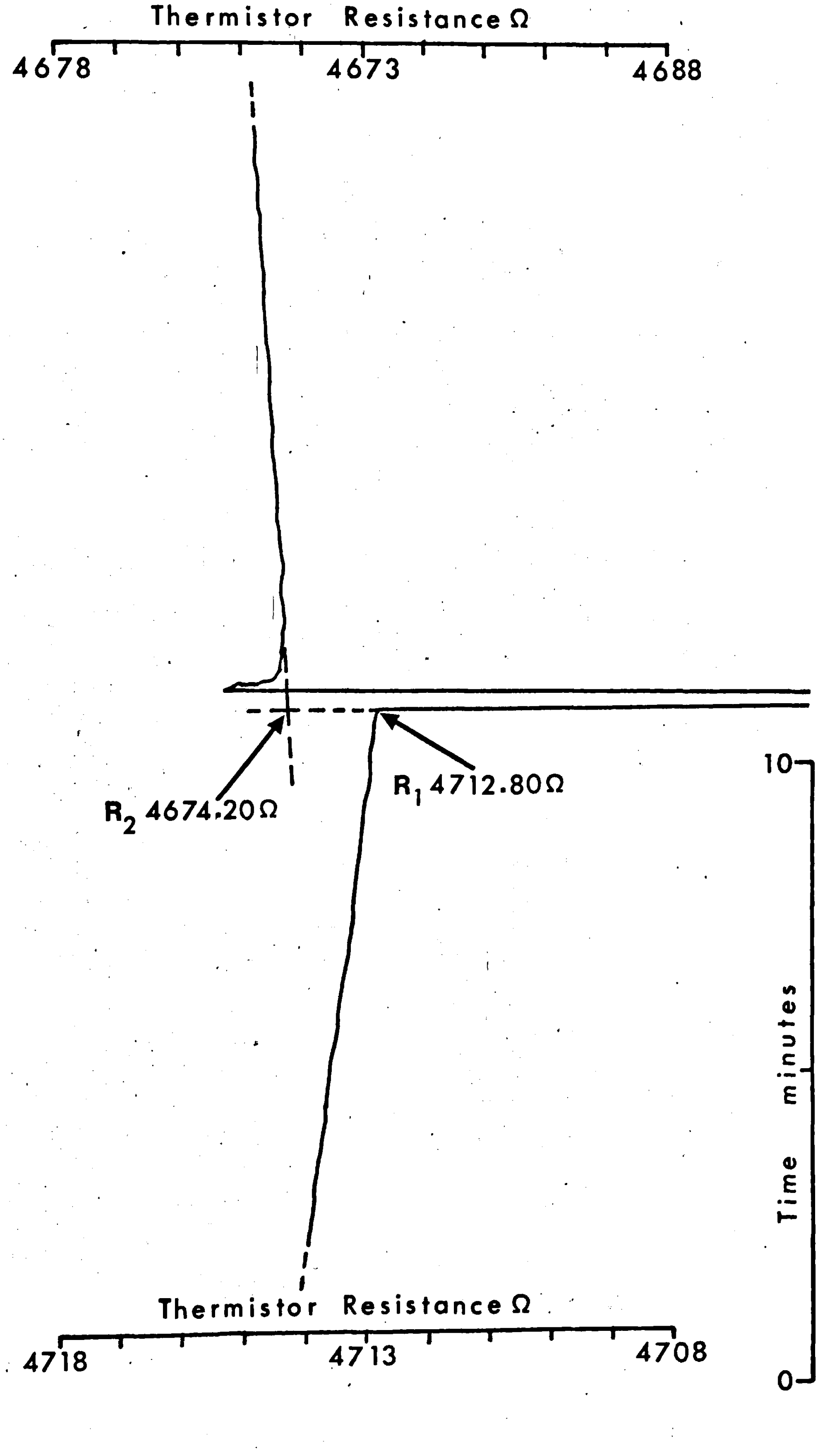
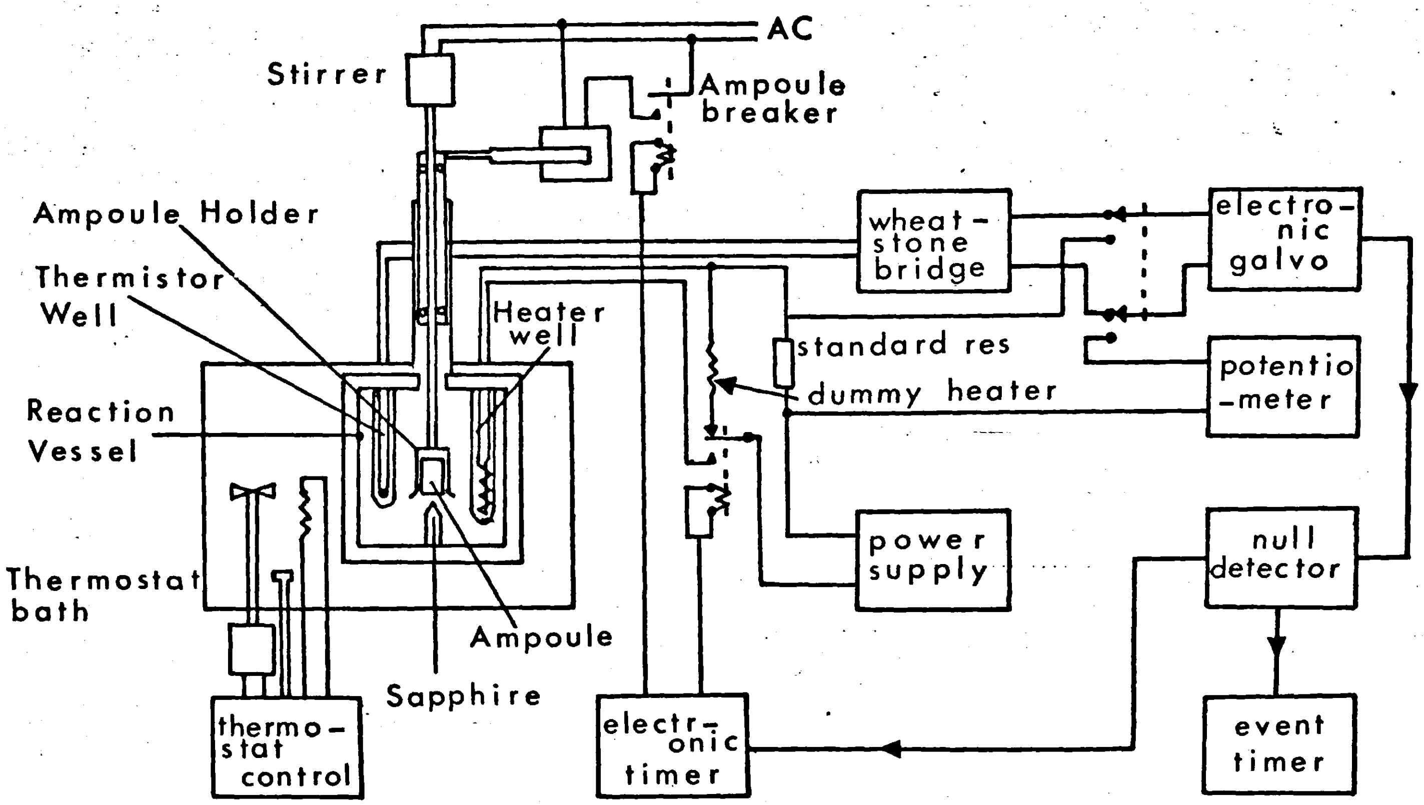


FIGURE III-B-8 LKB 8700 CALORIMETRY SYSTEM BLOCK DIAGRAM



The calorimeter vessel was a thin-walled Pyrex cylinder of 100cm^3 capacity. A thermistor and calibration heater are contained in glass oil-filled wells supported from the lid of the vessel. The stirrer consists of a stainless-steel spindle attatched to a gold ampoule holder. Ampoule breaking was achieved by lowering the stirrer/ampoule assembly vertically onto a sapphire tipped glass rod located in the base of the vessel.

The power dissipated in the heater could be selected from values of 20,50,200, and 500mW, the corresponding I^2 values being (0.4,1,2,4 and 10) x 10^{-3} A^2 respectively. The value selected, 500mW gave a heating period of ca. 110 sec.

A chart recorder (Bryans Ltd., model 2700) was used to monitor the out-of-balance potential from the Wheatstone bridge in which the thermistor was connected. The sensitivities of the null-potentiometer and chart recorder were adjusted to give 0.1Ω≡1cm of chart paper.

The reaction was initially fast, but slowed after ca. one min and was complete only after ca. 20 min (Figure III-B-9). The value of R_2 was found by extrapolating the after-period back to the time corresponding to 0.63 of the resistance change. However, as described in section III-B-(1) the exact position of $t_{0.63}$ must be estimated. This estimation probably gives an uncertainty of ca. ± 0.005Ω in the value of R_2 which is within experimental limits. Extrapolation of the calibration fore- and after-periods was carried out as described in section III-B-(1). Figure III-B-10 illustrates a typical calibration resistance-time profile.

The resistance of the heater was found by use of the circuit shown in Figure III-B-11. The current was adjusted so that the potential drop across the standard 50Ω resistor was 1.0000 volts.

FIGURE III-B-9 TYPICAL $AgNO_3/KIO_3$ REACTION TRACE

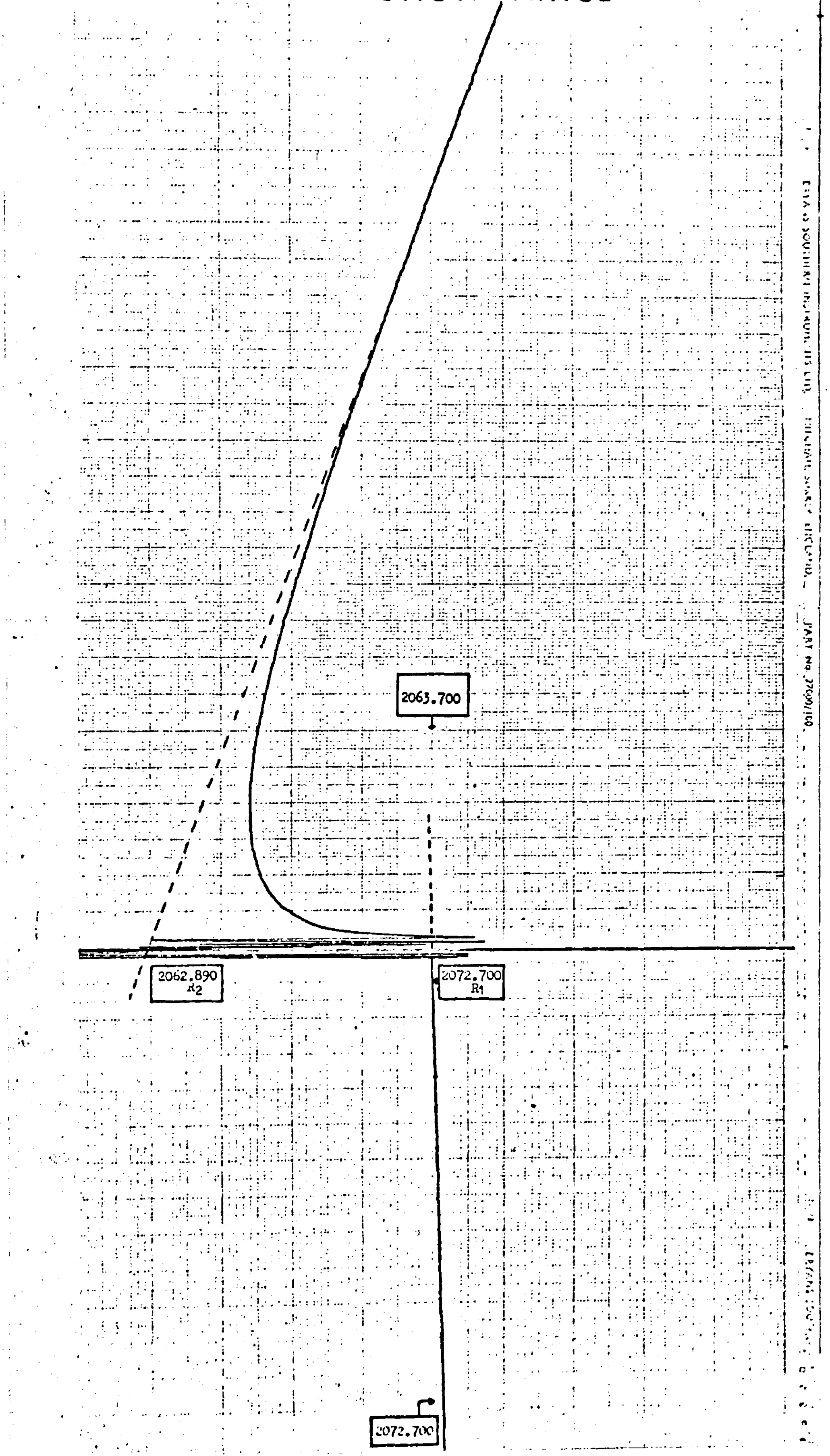


FIGURE III-B-10 TYPICAL $AgNO_3/KIO_3$ CALIBRATION TRACE

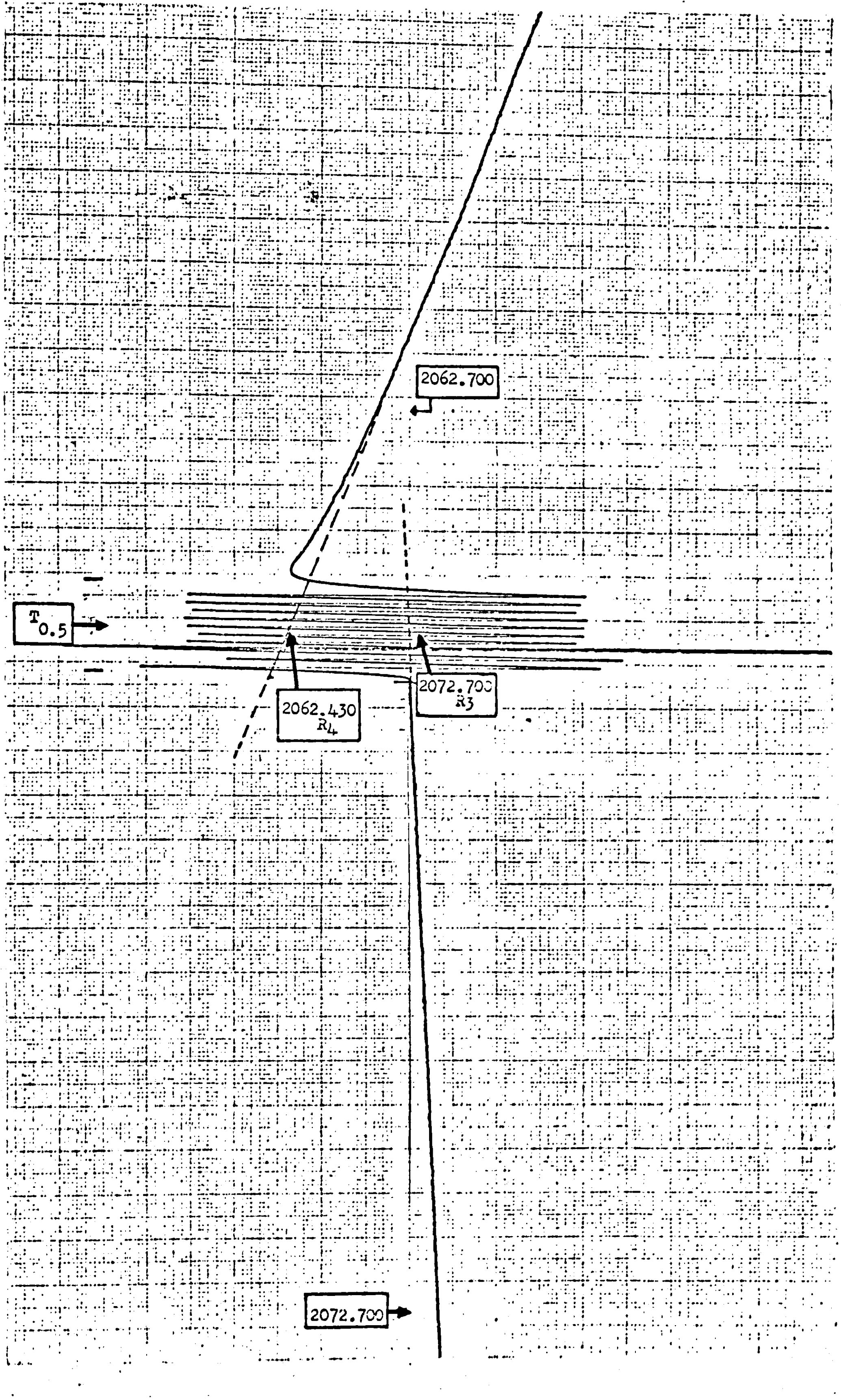


FIGURE III-B-11 LKB 8700 HEATER CIRCUIT

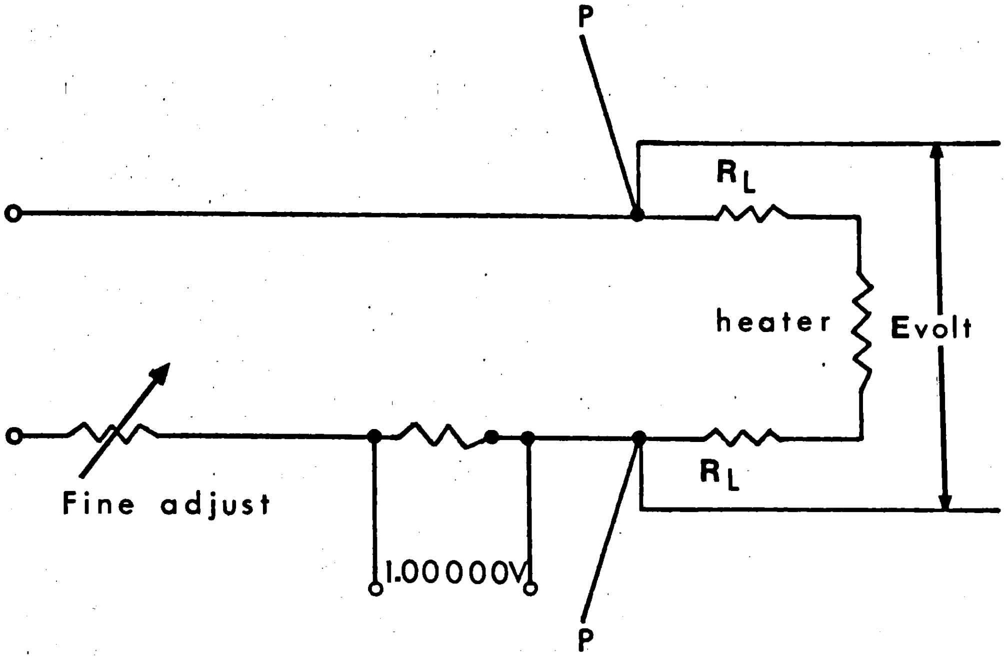
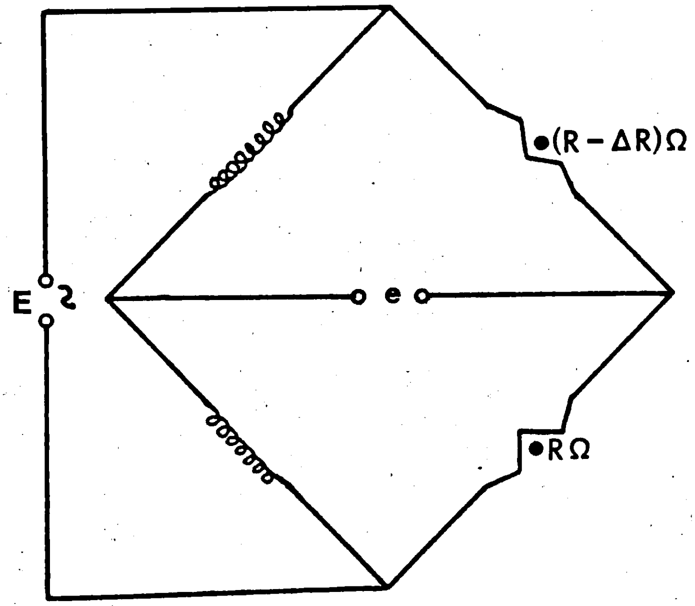


FIGURE III-B-12 SIMPLIFIED UNIT RATIO BRIDGE CIRCUIT



The potential drop across the heater was then measured and its resistance calculated.

The equation used to determine the enthalpy change during the reaction is:

$$-\Delta H_R = \frac{P.t.M}{1000.W} \cdot \frac{(\Delta R/R_m)\text{reaction}}{(\Delta R/R_m)\text{calibration}} \quad \text{kJ mol}^{-1}$$

where

P = power of heater $R_h.I^2$

R_h= corrected resistance of heater (corrected for the resistance of the leads)

I = calibration current

w = weight of compound

M = molecular weight of compound

t = heating time (sec.)

ΔR = resistance change = $R_{\text{initial}} - R_{\text{final}}$

and R_m = mean resistance = $R_{\text{initial}} - \Delta R/2$

The performance of the calorimeter was checked by the exothermic neutralization of THAM in excess 0.1 mol dm^{-3} aqueous HCl. A value of ΔH_{298} = -29.732 kJ mol^{-1} was obtained (literature ΔH_{298}= -29.790 ± 0.03 kJ mol^{-1}).

This calorimeter was also employed to measure the enthalpy change for the following process:

$$SO_2(aq) + I^-(aq) \rightleftharpoons SO_2I^-(aq)$$

These results are discussed in section II-A-(2) page 72.

III-C DETERMINATION OF CALORIMETRIC REACTION STOICHIOMETRY

(1) For polyhalides prepared in sections III-A-2 - III-A-8

(a) A weighed sample of polyhalide (ca. 0.3g) was reacted with a known excess of 0.10M aqueous silver nitrate solution (ca. 25cm^3) contained in a stoppered conical flask. The precipitated silver halides were filtered off and the residual silver nitrate estimated by Volhard's method[200]. The amount of $AgNO_3$ that had reacted with the polyhalide, and hence the mole ratio $AgNO_3$:polyhalide, was calculated. Results for these polyhalides are contained in Table III-C-1.

(b) A weighed sample of each caesium polyhalide was reacted, at 25°, with excess $AgNO_3$ (100cm^3, 0.25M saturated at 25° with $AgIO_3$). The precipitated silver salts were collected on a weighed sintered-glass crucible (No.4), washed free of excess $AgNO_3$ with ice-cold saturated $AgIO_3$ solution and dried at 120°. Results are contained in Table III-C-1.

(2) For $RbIF_4$

(a) Aqueous hydrolysis of $RbIF_4$ was rapid (ca. 2 min) resulting in the separation of elemental iodine. Qualitative tests were carried out on the hydrolysate and gave indication for the presence of the following:

(i) Fluoride ions ($CaCl_2$ test)
(ii) Iodate ions (5% thiocyanate and starch paper)

Iodide ions were found to be absent (aqueous $AgNO_3$ followed by concentrated ammonia).

(b) Quantitative determinations of iodate and iodine in the aqueous hydrolysate were made as follows:

(i) Two samples of $RbIF_4$ (ca. 0.2g,0.7mmol) were hydrolysed in water ($25cm^3$) contained in a stoppered conical flask. The liberated iodine was removed by vigorous boiling for 30 min. The remaining iodate was analysed by the addition of KI solution (10% 10 cm^3) followed by titration of the liberated iodine against 0.1M sodium thiosulphate. Fresh starch solution was used as indicator. The following results were calculated from the titrations: $RbIF_4 : IO_3^- = 1.67, 1.65:1$.

(ii) After similar hydrolysis, iodine was separated by repeated extractions with carbon tetrachloride. The iodine present was determined by titration against standard sodium thiosulphate (0.10M). Titration of the aqueous portion was carried out as in (i).

Found: $RbIF_4 : IO_3^- = 1.67:1$ and $RbIF_4 : I_2 = 5.02:1$.

The overall stoichiometry for the aqueous hydrolysis of $RbIF_4$ is quantitatively represented by the following equation:

$$5RbIF_4 + 9H_2O \longrightarrow 5RbF + 15HF + 3HIO_3 + I_2$$

TABLE III-C-1

Compound	w/g	mass of precipitate g		Mole Ratio $AgNO_3$:polyhalide
		Found	Calc.	
CsI_3	0.22659	0.27991	0.28035	2.99
$CsICl_2$	0.36106	0.58014	0.58669	2.99
$CsIBr_2$	0.30644	0.45538	0.45738	2.95
$CsICl_4$	0.16444	0.34102	0.34396	4.94
$RbICl_2$				2.96
$RbIBr_2$				2.97
$RbICl_4$				4.96

III-D TITRATION CALORIMETRY

The calorimeter described in section III-B-(1) was adapted to perform as a titration calorimeter. The following modifications were made:

(1) Titrant delivery tube

A tapered glass tube, *ca*. 8cm in length, Figure III-B-2(b), with a right angle bend 1cm from one end and formed into a capillary at the other, was cemented with epoxy resin, into an unused ferrule which was screwed into the calorimeter lid. The tube dipped approximately 1cm below the surface of the calorimetric fluid.

(2) Constant delivery rate syringe

A 10cm^3 precision syringe ('Re-Pette' Jencons Ltd.) was actuated by an electric syringe drive (Razel Scientific Instruments, U.S.A., type A-99). The syringe was connected, via a hypodermic needle, to a length of polyethylene tubing (*ca*. 12 metres long and 1mm diameter). The other end of the tube was fitted onto the titrant delivery tube. The tubing was coiled around a piece of brass tube (5cm in diameter) which was immersed in the constant temperature bath and acted as a reservoir of *ca*. 13cm^3 capacity. The titrant was therefore, delivered at the same temperature as the calorimetric fluid. The motor speed could be set by a dial (reading 00 to 99) and a setting of 52 was used throughout the titration experiments. In a performance test of the syringe the weight of water delivered with time, and the reproducibility in delivery of a fixed mass of water was measured. The water was collected, at 25°, in a 10cm^3 volumetric flask positioned beneath the titrant delivery tube.

The results are contained in Table III-D-1.

The accuracy of the calorimeter was checked by the determination of the heat of neutralization of aqueous HCl with aqueous NaOH. Results are collected for six consecutive experiments in Table III-D-2. A typical titration is described as follows to explain the operation of this calorimeter.

The syringe and titrant reservoir were filled with aqueous hydrochloric acid (1.00M B.D.H.), care being taken to exclude air bubbles. By adjustment of the syringe plunger a small air bubble, volume ca. 0.1cm^3 was produced at the tip of the titrant delivery tube. Any 'back lash' between the syringe plunger shaft and drive ram was taken up by switching on the motor until the bubble at the tip started to reduce in size. The bubble prevents premature mixing of the titrant and titrand solutions.

100cm^3 of carbonate-free aqueous NaOH (0.03M), warmed to 25^o, was carefully transferred by pipette into the calorimeter vessel, and the lid of the calorimeter screwed onto the neck of the Dewar. The reference Dewar was similarily filled with 100cm^3 of distilled water. The temperature of each vessel was adjusted as described in section III-B-(1) and the calorimeters left to equilibrate for 30 min.

Using the millivolt source 10cm of chart paper was checked to correspond to 0.2000 volts. The millivolt source was then switched off and remained inoperative while recording a titration trace which was contained within one chart width. A chart speed of 3cm min^{-1} was used.

With the thermistor bridge switched to A/B the bridge was unbalanced, by use of the coarse back-off control, to 0.3 volts. The chart recorder pen was positioned on the left hand side of the chart paper by adjustment of the pen zero control.

TABLE III-D-1

CALIBRATION DATA FOR CONSTANT DELIVERY RATE SYRINGE

Mass H_2O w/g	Time/sec. T	w/g/T x 10^3
2.0158	350.68	5.748
2.0178	350.30	5.760
2.0279	350.24	5.790
2.0264	350.00	5.789
2.0137	350.38	5.747
2.0165	350.32	5.756
0.5790	100.24	5.776
1.1568	200.18	5.779
1.7330	300.32	5.770
2.3036	400.32	5.754
2.8569	500.24	5.711

TABLE III-D-2

ENTHALPY OF NEUTRALIZATION OF $HCl(0.3M)$ WITH $NaOH(0.006M)$

$-\Delta H_R/kJ\ mol^{-1}$
55.99
55.42
55.65
55.29
56.15
55.91

ΔH_R mean = -55.74 ± 0.36 kJ mol^{-1} (literature[208] 55.80 ± 0.06 kJ mol^{-1}

TABLE III-D-3

Experiment No.	Titrand	$-\Delta H_R/kJ\ mol^{-1}$
1	KBr, 0.015M	84.71
2	KIO_3,0.0028M	51.17*
3	$CsIBr_2(aq)$	51.90
4	$CsIBr_2(aq)$	
5	$CsIBr_2(aq)$	
6	$CsICl_4(aq)$	

* per mole of $AgIO_3$

A base line of 5 min duration was recorded. The syringe drive was switched on to deliver titrant which was stopped ca. 100 sec after the end-point was observed on the chart paper.

The calorimeter vessel was cooled back to the original base-line and allowed to equilibrate for 30 min. A base-line of 5 min was recorded and the calibration heater switched on to give a chart displacement identical to the reaction period. Typical reaction and calibration voltage-time plots are shown in Figures III-D-1 and 3, together with the method of extrapolation. The extrapolated ordinate height BB' was proportional to the heat evolved during the titration reaction. Similarily, for the calibration experiment, the ordinate height at the mid-point of the voltage-time plot was a measure of the heat evolved during the calibration. The number of moles titrant reacted in the titration was calculated from the distance on the abscissa of the chart. The enthalpy change for the titration reaction was calculated using the following expression:

$$-\Delta H_R = \frac{f.P.t.N.\ BB'_{reaction}}{1000.\ BB'_{calibration}} \quad \text{kJ mol}^{-1}$$

where f,P and t are as described in section III-B-(1) and where N was the number of moles of titrant reacted during the titration.

The calorimeter was employed to investigate the mechanism of the reaction between aqueous $CsIBr_2$ and silver nitrate solution. The results are fully discussed for these experiments in section II-A-2. Further ancillary titrations, to help clarify the $CsIBr_2/AgNO_3$ results were also studied. The titrations involved in this investigation are contained in Table III-D-3.

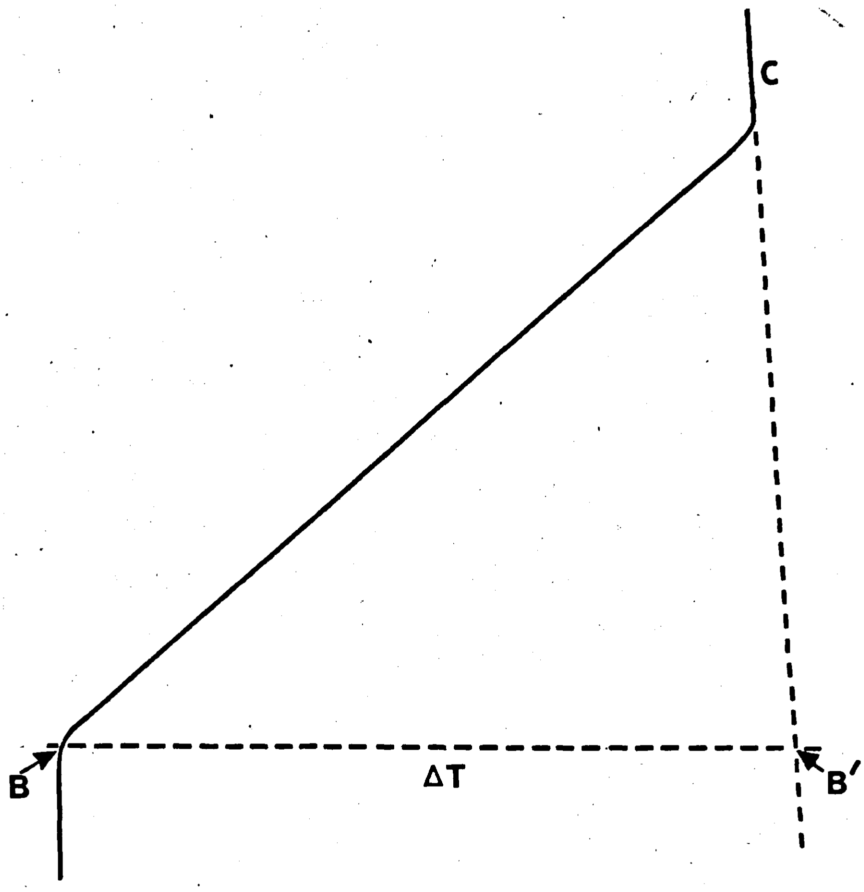


FIGURE III-D-1 THERMOMETRIC TITRATION HCl/NaOH REACTION

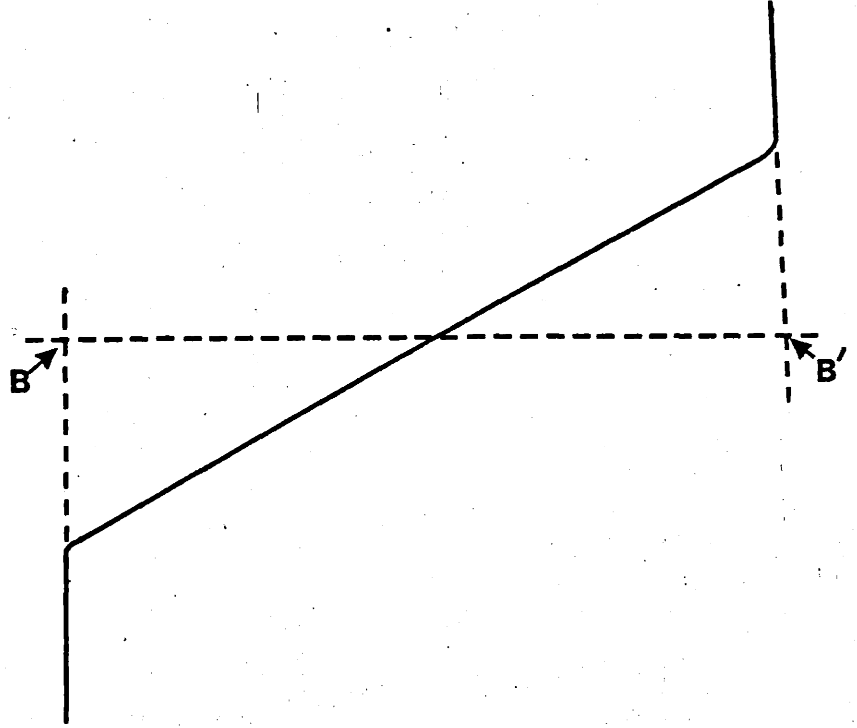


FIGURE III-D-2 THERMOMETRIC TITRATION HCl/NaOH CALIBRATION

In each case the titrant was aqueous $AgNO_3$ solution (1.0M B.D.H. A.V.S.). Enthalpies of reaction when calculated are also listed.

A single titration of aqueous $CsICl_4$ against $AgNO_3$ was also performed. Titration curves for $CsIBr_2$ and $CsICl_4$ are illustrated in Figure III-D-3 and Figure III-D-4. For experiment No.3 only the latter part of the titration curve was recorded at higher sensitivity, to enable a ΔH_R value to be deduced. Samples of polyhalide were weighed directly into the calorimetric vessel to yield an aqueous solution upon addition of $100cm^3$ of distilled water.

FIGURE III-D-3 THERMOMETRIC TITRATION $CsIBr_2/AgNO_3$

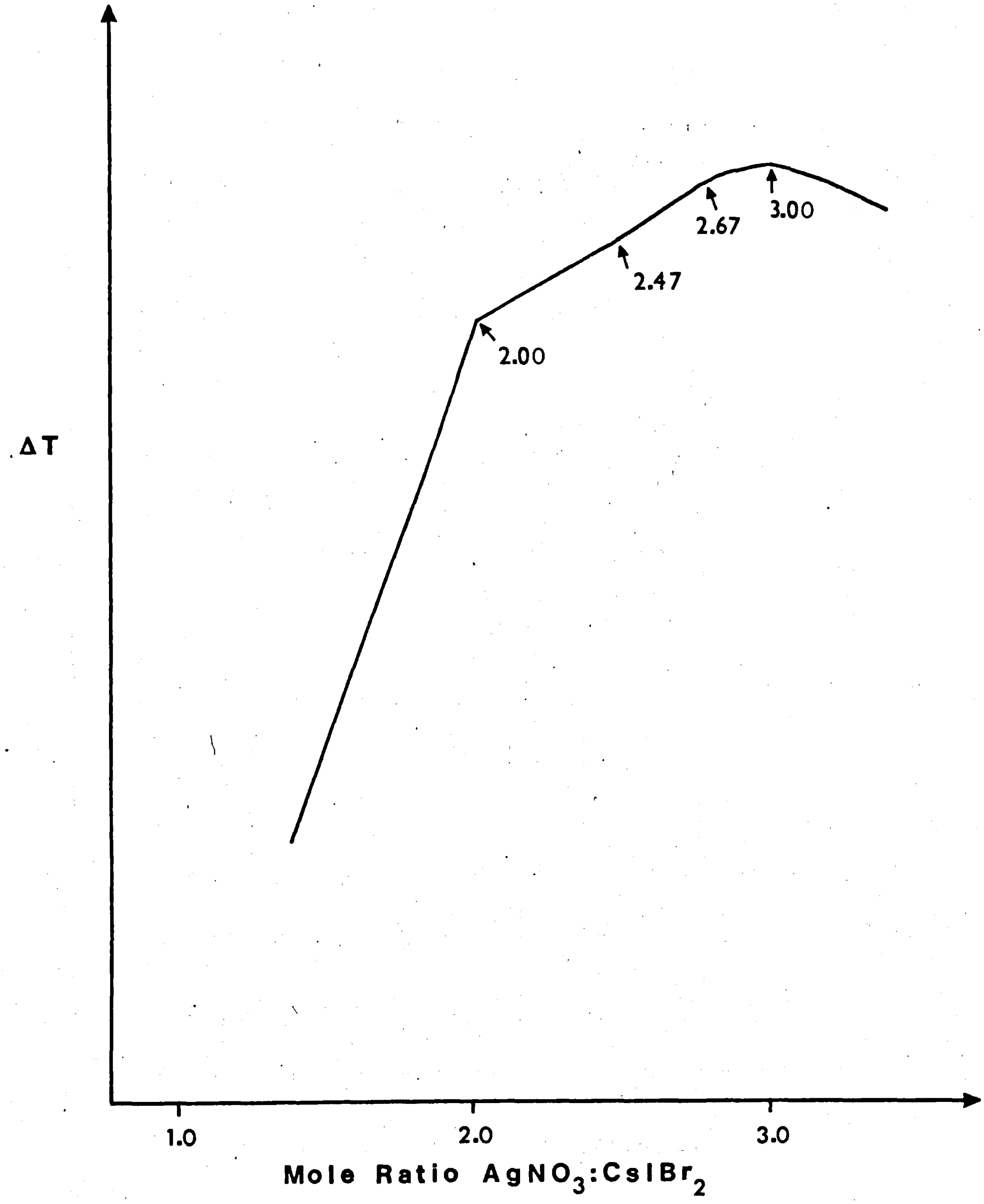
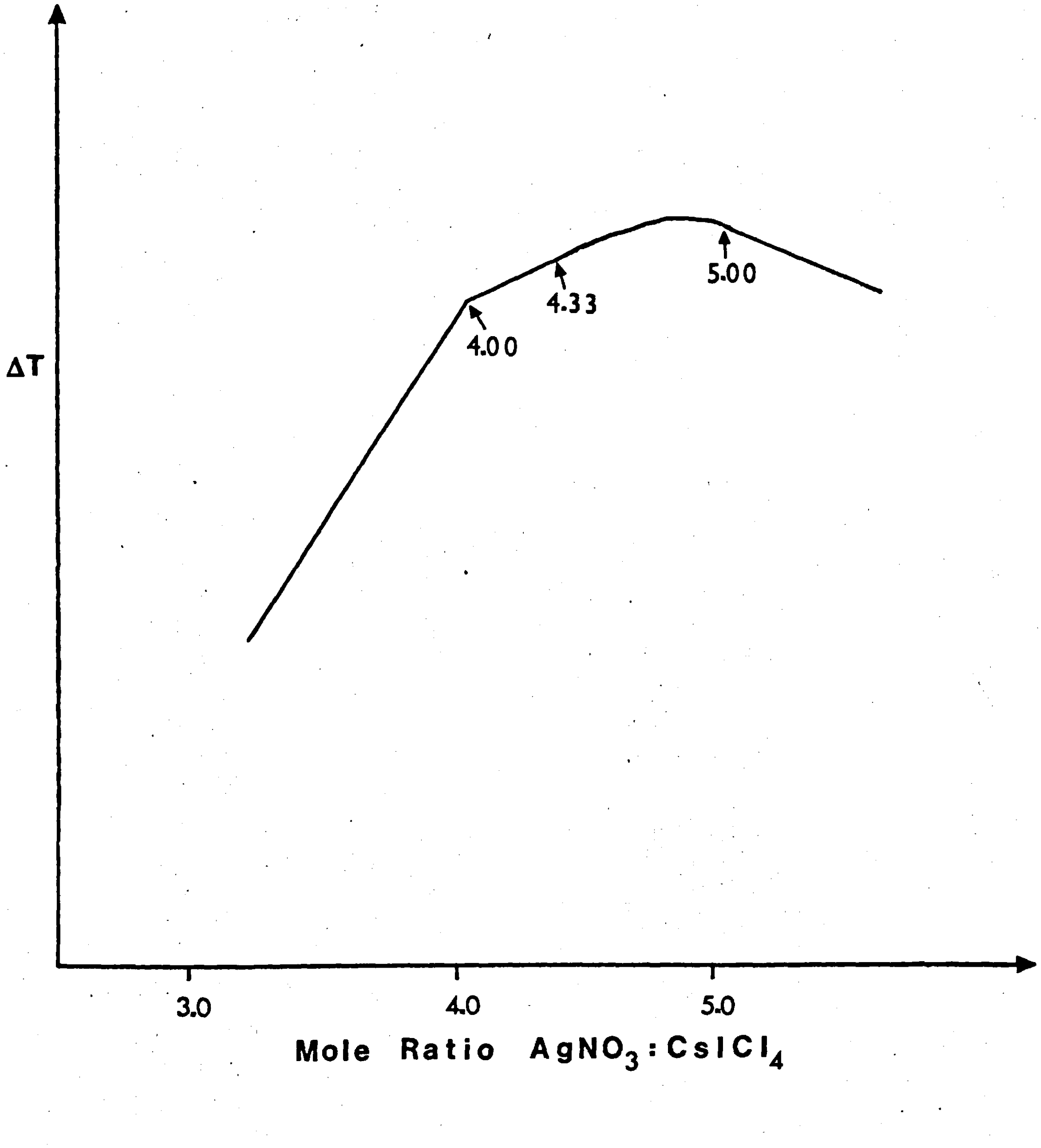


FIGURE III-D-4 THERMOMETRIC TITRATION $CsICl_4/AgNO_3$



III-E DIFFERENTIAL SCANNING CALORIMETRY AND HEAT CAPACITY MEASUREMENTS

A Perkin-Elmer differential scanning calorimeter (Model DSC-1B) coupled to a Leeds & Northrup Speedomax-W recorder was used in these experiments. Operation and calibration of the instrument was performed according to the instruction manual supplied with the calorimeter. Samples of $RbIF_4$ were weighed (Cahn electrobalance) into aluminium pans which were then hermetically sealed. The transfer of sample and sealing of the pans was carried out under dry-box conditions.

A sample of $RbIF_4$ was scanned over the range -100 to +180°. A single exotherm at ca. 165° was observed which appeared to correspond to the decomposition of the sample.

Heat capacity measurements

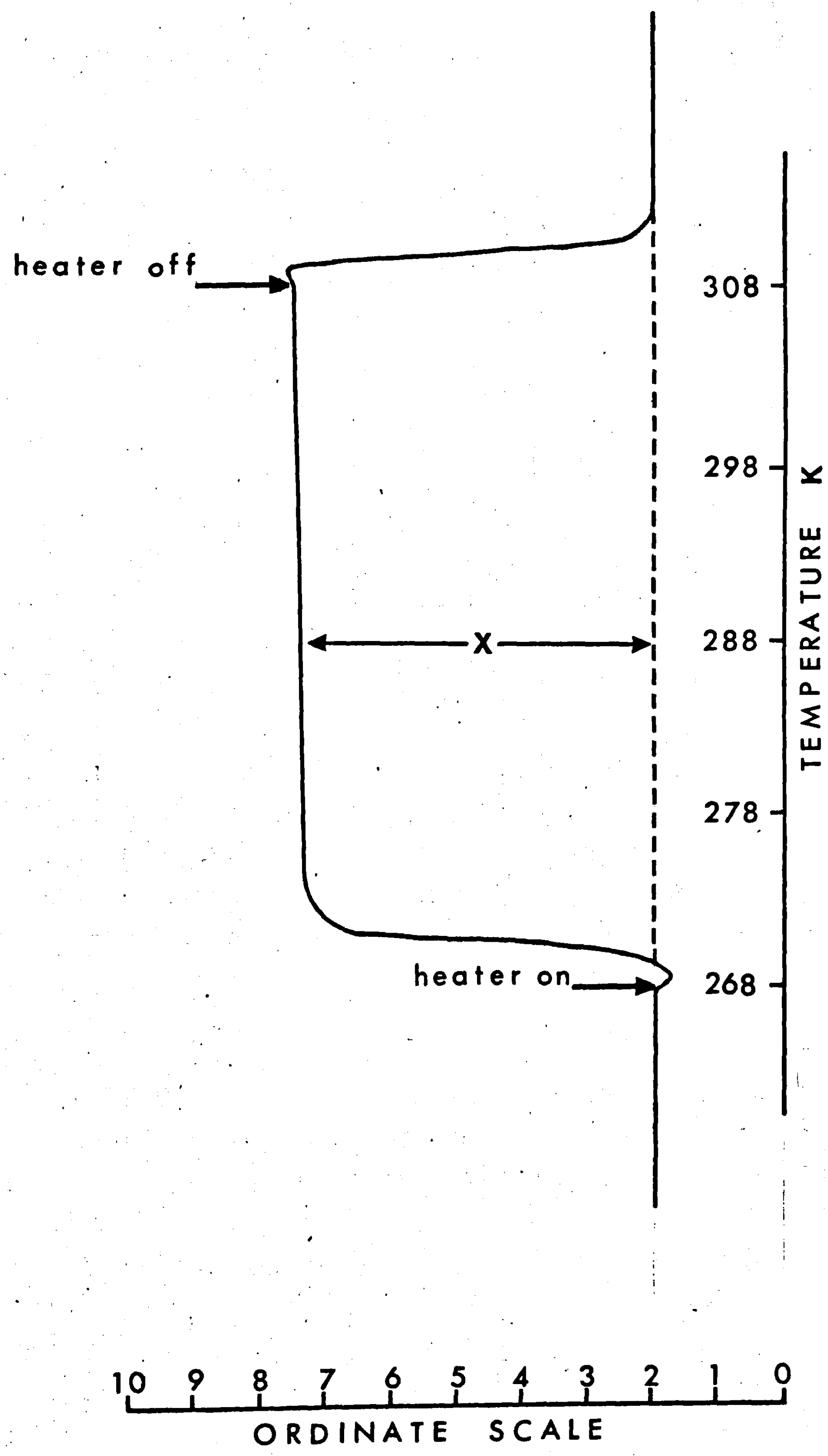
When a sample is subjected to a linear temperature increase, the rate of heat flow into the sample is proportional to its instantaneous specific heat.

$$\frac{\delta H}{\delta t} = m.c.\frac{\delta T}{\delta t}$$

where $\delta H/\delta t$ is the rate of heat flow (Joules sec^{-1}), m is the sample weight (g), c the instantaneous specific heat ($J\ K^{-1}\ g^{-1}$) and $\delta T/\delta t$ the programmed heating rate ($K\ sec^{-1}$).

The rate of heat flow into the sample is proportional to the ordinate deflection on the chart paper, from the interpolated isothermal base-line (Figure III-E-1).

FIGURE III-E-1. HEAT CAPACITY TRACE



III-F PREPARATION OF CALORIMETRIC SOLUTIONS AND REAGENTS

(1) Silver nitrate solutions for reactions (2) to (8)

Calorimetric silver nitrate solutions were prepared by dissolving $AgNO_3$(B.D.H. AnalaR) in saturated silver iodate solution at 25°. The excess $AgIO_3$ was removed by filtration to give a solution of $AgNO_3$ saturated with $AgIO_3$. Silver iodate is slightly soluble in water (ca. 0.05g dm^{-3})[209]. By presaturating the calorimetric fluid with $AgIO_3$ all the silver iodate produced in these reactions can be considered to be in its standard state.

Silver nitrate solutions, prepared as above, of the following concentrations were used for these reactions:

$CsICl_2$,0.036M, $RbICl_2$,0.045M, $CsIBr_2$,0.025M,
$RbIBr_2$,0.03M, CsI_3,0.03M, $CsICl_4$,0.025M,
and $RbICl_4$,0.025 M.

(2) KIO_3 solution for reaction (13)

Calorimetric solutions of KIO_3 (0.02M) were prepared by dissolving dried (ca. 24h at 120°) finely powdered KIO_3(B.D.H. AnalaR) in saturated silver iodate solution as described in (1). $AgIO_3$ produced in this reaction was therefore precipitated in its standard state. AnalaR $AgNO_3$ (B.D.H.) was finely powdered and dried before use (ca. 24h at 100°).

All solutions containing silver salts were stored at 25° in the dark.

(3) Aqueous sulphur dioxide solutions for reactions (10) to (12)

The preparation of sulphate free SO_2 solution has been described by Johnson and Sunner[210].

$$\text{Hence } \frac{\delta H}{\delta t} = Q.x$$

where Q is the ordinate calibration factor and x is the ordinate deflection. To obtain specific heat values Q and $\delta T/\delta t$ must be known. However, if a substance of known specific heat (e.g. sapphire) is used to calibrate the instrument we have at any temperature, T K

$$Q.x_1 = m_1.c.\frac{\delta T}{\delta t} \qquad (1)$$

and

$$Q.x_s = m_s.C_s.\frac{\delta T}{\delta t} \qquad (2)$$

where x_1 and x_s are the ordinate deflections of the sample and the standard respectively, m_s is the mass and C_s the specific heat of the sapphire standard. Combining (1) and (2) we have:

$$c = \frac{C_s.m_s x_1}{m_1.x_s}$$

The temperature calibration of the instrument was checked using n-octacosane (m.p. 61.2° supplied by the N.P.L.) and n-tridecane (m.p. -5.5°). The instrument was operated according to the instructions supplied with the sapphire standard, and a scan speed of 4K $\min^{-1}$ was used. Results are contained in Table III-E-1.

A least squares regression programme was used to fit the data to an equation of the form $C_p = AT + B$. The overall accuracy of the measurements was estimated to be ± 2%.

TABLE III-E-1

HEAT CAPACITY OF RUBIDIUM TETRAFLUOROIODATE

T(K)	273	278	283	288	293	298	303
$C_p/JK^{-1}\ mol^{-1}$	120.2	124.0	127.7	135.0	138.8	144.5	148.3

$C_p = 0.975T - 146.6$

Saturated sulphur dioxide solution, at 25°, was prepared by passing the gas (B.D.H. Ltd.) into $500cm^3$ of freshly-boiled distilled water. This solution was then diluted ten times with distilled water (boiled as above). Nitrogen was kept above the surface of the solution which was stored in a dark cupboard. The concentration of the solution was estimated by reacting aliquots, ($25cm^3$), with standard iodine solution (B.D.H. 0.05M A.V.S.) and titrating the excess iodine with 0.10M standard thiosulphate solution (B.D.H. A.V.S.) using freshly-prepared starch as an indicator.

The dilute solutions (0.15M) were quickly transferred by pipette to the calorimeter vessel and the air space above the calorimetric fluid was flushed with dry nitrogen.

III-G RAMAN SPECTRA

Solid-state Raman spectra of the alkali-metal polyhalides prepared in sections III-A-(2) - (8) were obtained using a Coderg PHO Spectrometer. A Coherent Radiation Model 52 krypton gas laser (6471 Å) was used for excitation. The solid samples were powdered and loaded into capillary tubes which were subsequently sealed. The Raman spectra obtained were in complete agreement with the literature spectra[106-120].

Suggestions for future work

Of the experimental methods described in this thesis for the thermochemical investigation of crystalline polyhalides only the calorimetric reaction of these compounds with aqueous silver nitrate seems capable of extension to polyhalides in general. Although the e.m.f. method reported by Topol[153,154] was suitable for polyiodides the replacement of interhalogens for iodine in the solid-state cells would probably produce experimental problems if reactions of the following type were to be investigated by this method:

$$MX(c) + IX(c) = MIX_2(c) \quad (X=Cl \text{ and } Br)$$

One problem could be dissociation of the interhalogen IX into I_2 and X_2 if e.m.f. measurements were made over a similar temperature range (25°- 110°) to that employed for the polyhalide e.m.f. measurements. ICl is largely dissociated into I_2 and Cl_2 at 100° while IBr is reported to be approximately 9% dissociated in the gaseous state at 298 K (section I-C).

The dissociation pressure method has already been discussed in section II-B. Heat capacity corrections could be applied to these results if heat capacity data were available for these polyhalide compounds. Such data could be obtained from D.S.C. experiments similar to those reported in this work for $RbIF_4$.

The reaction of other polyhalides (Table I-A-2, page 14) with aqueous silver nitrate could be investigated. For example trihalide ions of the type X_2Y dissociate in aqueous solution to give X_2 and Y^-. The reactions of the ions I_2Br^- and I_2Cl^- should therefore be similar to the reactions of the ions IBr_2^- and ICl_2^- that are described in this work. The following reactions are hence likely:

$$3CsI_2Br + 9AgNO_3 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 3AgBr + 6HNO_3 + 3CsNO_3$$

$$3CsI_2Cl + 9AgNO_3 + 3H_2O \longrightarrow 5AgI + AgIO_3 + 3AgCl + 6HNO_3 + 3CsNO_3$$

Other calorimetric reactions could be investigated. The hydrolysis of a polyhalide in aqueous alkali is complete, the polyhalide behaving effectively as halogen or interhalogen plus halide, giving a mixture of halide and halate ions:

$$3ICl_2^- + 6OH^- \rightleftharpoons 6Cl^- + 2I^- + IO_3^- + 3H_2O$$

However, most of the observed enthalpy of reaction would be due to the enthalpy of neutralisation of the acids produced on hydrolysis of the polyhalide. This could make the reaction unsuitable.

Skinner and Howard[163,211] have reported measurements of the heats of reaction at 25° of aqueous hydrazine with the following: Aqueous solutions of HCl,HBr,HI, liquid bromine, crystalline iodine and crystalline iodic acid. All these reactions were reported to take place rapidly and quantitatively at room temperature. Reactions of the following type were studied:

$$[HX,nH_2O] + m_1[N_2H_4,300H_2O] \longrightarrow [N_2H_5X,(m_1-1)N_2H_4,(n+300m_1)H_2O]$$

$$Br_2(liq.) + m_2[N_2H_4,300H_2O] \longrightarrow \tfrac{1}{2}N_2(g) + [2N_2H_5Br,(m_2-2.5)N_2H_4,300m_2H_2O]$$

$$HIO_3(c) + (n+\tfrac{3}{2})[N_2H_4,2HCl,mH_2O] \longrightarrow \tfrac{3}{2}N_2(g) + [3H_2O(liq) + HI,3HCl,\tfrac{3}{2}mH_2O] + n[N_2H_4,2HCl,mH_2O]$$

This investigation suggests that aqueous hydrazine could be a suitable calorimetric reagent for the reduction of polyhalides, the hydrazine reacting with the hydrolysis products of the polyhalide:

$$5ICl_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Cl^- + 6H^+$$

Crystalline salts containing the polyhalogen cations ICl_2^+, BrF_2^+ and IF_4^+ have been prepared. These compounds are reviewed by Popov[10]. The compounds $AlICl_6$ and $SbICl_8$ are the best characterised and were prepared by the reaction of aluminium chloride or antimony chloride with iodine trichloride in a sealed tube. The ionic structures $ICl_2^+SbCl_6^-$ and $ICl_2^+AlCl_4^-$ were confirmed by X-ray crystallography[13]. It would be instructive to devise suitable calorimetric reactions for these compounds.

APPENDIX I

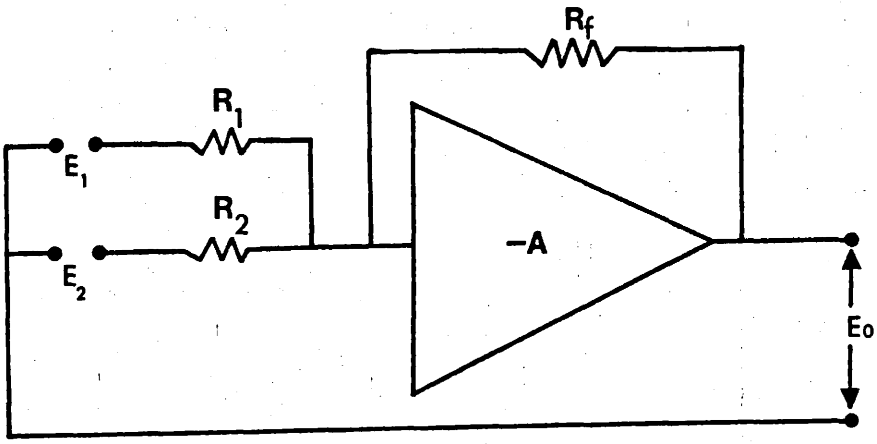
Specification of Differential Thermistor Bridge

Bridge drive voltage: 5KHz, square-wave 2.0 volts p-p.
Discrimination: Better than 2×10^{-5} °C.
Bridge noise: Less than 10^{-5} °C r.m.s.
Power dissipation: 10 microwatts per thermistor.
Stability: Typically $<10^{-4}$ °C for 24 hours in a thermostatted room.
Sensitivity: Variable by a four position decade switch from 1°C/volt to 0.001°C/volt.

Thermistor Bridge back-off circuit

The circuit consists of a summing operational amplifier which is connected between the thermistor bridge and the chart recorder. One input of the amplifier is connected to the bridge output socket and the other input to a variable millivolt source (Time Electronics Ltd., type 404S). The millivolt source is adjustable from 0.000 volts to 0.999 volts in 0.1 mV steps and the polarity of the output voltage can be reversed by a switch. Positioning of the chart recorder pen could therefore be achieved by adjustment of the millivolt source voltage; the operational amplifier 'feeding' a voltage equal to the algebraic sum of the voltages on its inputs to the chart recorder.

Figure 1



The theory of operation of an operational amplifier is as follows:

Consider that only currents are flowing in resistors R_1 and R_2 (Figure 1) and ignore the effect of the amplifier. This is valid as long as the forward amplification of the amplifier is high and if a virtual short exists across the amplifier terminals.

(These conditions are fulfilled by a modern operational amplifier). Then by Ohm's Law: current in the input resistors R_1 and R_2 are

$$\frac{E_1}{R_1} \text{ and } \frac{E_2}{R_2} \text{ respectively}$$

Similarily the current in the feed-back resistor R_f due to the output voltage, Eo, is $\frac{Eo}{R_f}$

Kirchoff's first law states that the sum of these currents flowing into a common amplifier input junction must be equal to zero. Hence, setting the sum of the currents equal to zero we have:

$$\frac{E_1}{R_1} + \frac{E_2}{R_2} + \frac{Eo}{R_f} = 0$$

Solving this expression for the output voltage, Eo, gives

$$Eo = -\left[\frac{R_f}{R_1}E_1 \quad \frac{R_f}{R_2}E_2\right]$$

But $R_1 = R_2 = R_f = 1K\Omega$

Hence: $\underline{Eo = -(E_1 + E_2)}$

Justification of Linear Extrapolation of Voltage-Time Fore- and After-Periods

$$\frac{dT}{dt} = K(T-T_j) + w \quad \text{Newton's Law of Cooling}$$

where

T = Temperature (K)

t = Time (minutes)

T_j = Temperature of calorimeter jacket

K and w are constants

$$\therefore \quad \frac{1}{K} \ln \left| \left[K(T-T_j) + w \right] \right| = t+c \text{ by integration}$$

where c is an integration constant

$$\therefore \quad T = {}^{1}/_{K} e^{K(t+c)} - {}^{w}/_{K} + T_j$$

But $$T = \frac{B}{\ln {}^{R}/_{A}} \quad \text{Thermistor relationship}$$

where A and B are thermistor constants

R = Thermistor resistance

$$\therefore \quad 1 = \ln \frac{R}{A} \left| \frac{e^{K(t+c)}}{BK} + \frac{T_j}{B} - \frac{w}{BK} \right|$$

Differentiating,

$$\frac{dR}{dt} = \pm \frac{R}{B} (\ln {}^{R}/_{A})^2 . e^{K(t+c)}$$

Because of the modulus in $\ln| \, |$, the sign of ${}^{dR}/_{dt}$ must be determined separately.

Differentiating again

$$\frac{d^2R}{dt^2} = \frac{R}{B^2}\left[(\ln {}^{R}/_{A})^4 + 2(\ln {}^{R}/_{A})^3\right] e^{2K(t+c)}$$

$$\frac{-KR}{B}\ (\ln {}^{R}/_{A})^2 . e^{K(t+c)}$$

For a straight fore- and after-period,

$$\frac{dR}{dt} = \text{constant}$$

and $$\frac{d^2R}{dt^2} = 0$$

Typical values of various constants and thermistor constants are:

$B = 4.011 \times 10^3$ K	$R = 100{,}000\Omega$
$A = 0.142\Omega$	$R_j = 99865\Omega$
$K = -0.01\ \text{min}^{-1}$	$w = 0.03K\ \text{min}^{-1}$

For the after-period

$$c = \frac{1}{K}\ \ln\left\|\left[K\left(\frac{B}{\ln {R_o}/_{A}} - \frac{B}{\ln {R_j}/_{A}}\right) + w\right]\right\|$$

where R_o = Resistance of thermistor at the start of the after-period

R_j = Thermistor resistance corresponding to jacket temperature

$\therefore\ c \mathrel{\hat{=}} +571$ min for the after-period

$$\therefore \frac{dR}{dt} = 14.97\Omega \, \text{min}^{-1} \text{ (at } t = 0)$$

and

$$\frac{d^2R}{dt^2} = 0.1523\Omega \, \text{min}^{-2} \text{ (at } t=0)$$

Therefore for extrapolation from $t = 0$ min to $t \simeq -5$ min for the after-period, the resistance would change from 14.97 min^{-1} to 15.27 min^{-1} giving a maximum error in the resistance of $\pm$ 0.6 , and an error in the bridge output voltage of $\simeq$0.0002 volts. Since voltages can only be determined to $\pm$ 0.0002 volts, the possible error will be insignificant. Similar results (with smaller d^2R/dt^2 value) can be obtained for the fore-period.

In conclusion, it can be stated that the extrapolation of fore- and after-periods as straight lines is justified provided:

(i) The lines are drawn using as short a section of the fore- and after-periods as possible, ignoring the 'overshoot' which occurs at the start of the after-period.

(ii) The extrapolation periods are not more than five minutes

(iii) The calorimeter design should be such as to minimise the values for dR/dt (i.e. K and w both very small).

Correcting Weights to Vacuo[200]

For experiments where very accurate weighings are necessary a correction should be made for the effect of the buoyancy of the air. This correction involves reducing the weighings to vacuo.

The weight of an object in vacuo=weight of the object in air + weight of air displaced by the object - weight of air displaced by the balance weight.

$$W_v = W_a + d_a \left(\frac{W_v}{d_b} - \frac{W_a}{d_w} \right)$$

where W_v = weight in vacuo, W_a = apparent weight in air, d_a = density of air, d_w = density of weights and d_b = density of body.

The density of air is normally about 0.0012g cm^{-3}. Since the difference in W_v and W_a does not normally exceed 1-2 parts per thousand.

$$W_v = W_a + d_a \left(\frac{W_a}{d_b} - \frac{W_a}{d_w} \right)$$

The density of stainless-steel balance weights is 8.0g cm^{-3}.

$$W_v = W_a + W_a \left[0.0012 \left(\frac{1}{d_b} - \frac{1}{8.0} \right) \right]$$

$$= W_a + \frac{k(W_a)}{1000}$$

where $k = 1.20 \left(\frac{1}{d_b} - \frac{1}{8.0} \right)$

The density of THAM is given as 1.35g cm^{-3}.[204]

APPENDIX II

Lattice energies have been reviewed comprehensively by Waddington[212] and other authors[197,213-215].

The lattice energy of an ionic crystal, U_0, at 0 K may be defined as the internal energy change that takes place when one mole of the compound, at one atmosphere pressure, is converted into its constituent gaseous ions at infinite separation:

$$MX_n(\text{cryst.}) \longrightarrow M^{n+}(g) + nX^-(g) \quad \Delta H = U_0 \tag{1}$$

At temperatures above 0 K a further small quantity, (n+1)RT must be added for the energy required to expand (n+1) moles of gas to an infinitely small pressure.

The lattice energy at 298 K, U_{298} can be related to other thermodynamic quantities by the Born-Haber cycle as illustrated below:

$$\begin{tikzcd}
MX_n(c) \arrow[r, "U_{298}(MX_n) + (n+1)\,RT"] & M^{n+}(g) & + & nX^-(g) \\
& M(g) \arrow[u, "\sum_1^n I_n + \frac{5}{2}nRT"'] & & nX(g) \arrow[u, "-nE_a - \frac{5}{2}nRT"'] \\
& M(s.s.) \arrow[u, "\Delta H_f^\circ(M,g)"'] \arrow[uul, "\Delta H_f^\circ(MX_n,c)"] & & nX(s.s.) \arrow[u, "n\Delta H_f^\circ(X,g)"']
\end{tikzcd}$$

The use of the Born-Haber cycle in the calculation of lattice energies is restricted to those compounds for which appropriate ionisation potentials and electron affinity data are available.

For ionic compounds with exactly known structural parameters lattice energies can be obtained from extended classical calculations. These calculations involve the summing of attractive and repulsive interactions between ions in the crystal lattice and have been discussed by Waddington[212].

Kapustinskii[214,216] has developed a semi-empirical expression for the determination of lattice energies where precise structural data is lacking.
He demonstrated that if the Madelung constants (the sum of the coulombic interaction terms characteristic of a crystal structure) for a number of crystals were divided by ν, the number of ions in one molecule, then values of A/ν were almost constant (Table 1).

TABLE 1

Structure	Madelung Constant, A	$\frac{A}{\nu}$	Average co-ordination number
Caesium chloride	1.763	0.88	8.0
Sodium chloride	1.748	0.87	6.0
Fluorite	2.519	0.84	5.33
Wurtzite	1.641	0.82	4.0
Rutile	2.408	0.80	4.0
Anastase	2.400	0.80	4.0
Cuprite	2.221	0.74	2.67

The equilibrium internuclear distance, r_o, in an ionic compound increases slightly with co-ordination number; thus the variations of A/vr_o are even less than A/v. Kapustinskii's postulate is that there exists for any compound, whatever its crystal structure, an equivalent 'iso-energetic' structure of the sodium chloride type, the energy of which can be expressed by using the Madelung constant and ionic radii appropriate to the sixfold co-ordination of NaCl type crystals.

The Kapustinskii expressions are derived either from the classical Born-Landé or Born-Mayer equations which are respectively:

$$U_o = \frac{N_A A e^2}{4\pi \varepsilon_o} \frac{v}{2} \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{1}{n} \right) \text{———} (7)$$

$$U_o = \frac{N_A A e^2}{4\pi \varepsilon_o} \frac{v}{2} \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{p}{(r_c + r_a)} \right) \text{———} (8)$$

where N_A is the Avogadro number, A the Madelung constant, Z_c and Z_a the cationic and anionic charges, e the electronic charge, r_c and r_a the cation and anion radii expressed in nanometres. v is the number of ions in the formula of the crystal.

If the constant value of 0.0345 nm is assumed for p in equation (7) the following Kapustinskii Born-Mayer equation is obtained where the numerical constants have been collected and evaluated:

$$U_o = 121.4\, v \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{p}{(r_c + r_a)} \right) \text{———} (9)$$

Lattice energies calculated by equation (9) are generally lower than the Born-Haber cycle values because this equation does not take into account the attractive London type forces present in the crystal lattice.

The contribution of the various components of lattice energy to the total lattice energy for a number of crystals is shown in Table 2.

TABLE 2

COMPONENTS OF LATTICE ENERGY /kJ mol^{-1}

Compound	U_o	U_C	U_B	U_L	U_Z
NaCl	766	863	114	25	8
CsI	580	619	90	54	3
AgI	795	808	138	128	3
CuBr	870	925	114	64	4

where U_C is the coulombic energy, U_B the Born term, U_L the London energy term and U_Z the zero point energy term.

A difficulty when using the Kapustinskii equation is to assign a value to the ionic radius if a complex cation or anion is present. Yatsimirskii[217] has proposed a method to overcome this difficulty.

Consider the reaction:

$$MX(c) \longrightarrow M^+(g) + X^-(g)$$

The enthalpy of reaction is given by $U_o + 2RT$

$$U_o + 2RT = \Delta H_f^o\, M^+(g) + \Delta H_f^o\, X^-(g) - \Delta H_f^o\, MX(c)$$

If two salts, M_1X and M_2X, have a common anion then

$$U_1 + 2RT = \Delta H_f^o\, {M_1}^+(g) + \Delta H_f^o\, X^-(g) - \Delta H_f^o\, M_1X(c) \qquad (10)$$

$$U_2 + 2RT = \Delta H_f^o\, {M_2}^+(g) + \Delta H_f^o\, X^-(g) - \Delta H_f^o\, M_2X(c) \qquad (11)$$

(10) - (11), $U_1 - U_2 = \Delta H_f^o \; M_1{}^+(g) - \Delta H_f^o \; M_2{}^+(g)$
$- \Delta H_f^o \; M_1X(c) + \Delta H_f^o \; M_2X(c)$ (12)

From the Kapustinskii equation:

$$U_1 - U_2 = C \left[\frac{1}{r_{M_1^+} + r_{X^-}} \left(1 - \frac{0.0345}{r_{M_1^+} + r_{X^-}} \right) - \frac{1}{r_{M_2^+} + r_{X^-}} \left(1 - \frac{0.0345}{r_{M_2^+} + r_{X^-}} \right) \right] \quad (13)$$

Thus, if the enthalpies of formation of the gaseous ions and crystalline salts and the ionic radii of $M_1{}^+$ and $M_2{}^+$ are known then equations (12) and (13) may be equated and the quantity r_{X^-} calculated.
Radii obtained from these calculations are known as 'thermochemical radii'. These radii can then be inserted into equation (8), from which the lattice energy of any salt containing that anion may be calculated, provided the ionic radius of the cation is known.
Substitution of the lattice energy into equation (10) or (11) will give the standard enthalpy of formation of the gaseous anion X^-, i.e. $\Delta H_f^o(X^-,g)$.

Therefore, although it is necessary to make several assumptions, the Kapustinskii equation provides a useful method to obtain approximate lattice energies, especially when the experimental data necessary for more precise calculation is lacking.

A computer programme, written in Fortran IV, was employed to calculate the 'thermochemical radii' contained in Table 3 of this Appendix.
Six input data are required and were represented in the programme as follows:

M1 and M2 = cationic crystal radii

H1 = $\Delta H_f^o(M_1{}^+,g)$

H2 = $\Delta H_f^o(M_2{}^+,g)$

X1 = $\Delta H_f^o(M_1X,c)$

X2 = $\Delta H_f^o(M_2X,c)$

Coefficients of equation (6) page 78 were represented in the programme by A,B,C and D, hence:

$$r^4 + 2Ar^3 + Br^2 + Cr + D = 0$$

was solved by the Newton-Raphson iterative method.
An identical programme was written for use with a Hewlett Packard HP-65 programmable calculator.
The 'thermochemical radii' of the polyhalide ions contained in Table III-B-1 were calculated with this programme.
The quartic equation was solved by a standard iterative programme supplied with the calculator (programme STD 14A)
The computer and calculator programmes are listed on the following pages.

```
              PROGRAM KAP (INPUT,OUTPUT)
              REAL M1,M2
              DO 200 J = 1,14
              READ 1, M1, M2, H1, H2, X1, X2
        1     FORMAT (4F8.3,2F9.2)
              U = (M1-M2) + (X2-X1)
              E = 242.8/U
              A = M1+M2
              B = M1**2 + M2**2 + 4*(M1*M2) + E*(M1-M2)
              C = 2*M2*M1**2 + 2*M1*M2**2 + E*(M1**2-M2**2) -0.069*E*(M1-M2)
              D = M1**2*M2**2 + E*(M1**2*M2-M2**2*M1) + 0.0345*E*(M2**2-M1**2)
              PRINT 6
        6     FORMAT (1H1,48H     M1       M2      H1      H2      X1      X2)
              PRINT 3, M1, M2, H1, H2, X1, X2
        3     FORMAT (6(F8.3,2X))
              PRINT 7
        7     FORMAT (1X,//,42H      A           B           C          D)
              PRINT 4, A, B, C, D
        4     FORMAT (4(F13.5,2X))
              R = 0.5
              DO 5 I=1,50
              Y1 =R**4 + 2*A*R**3 + B*R**2 + C*R + D
              Y2 = 4*R**3 + 6*A*R**2 + 2*B*R + C
              PRINT 9, Y1, R
        9     FORMAT (1X,F16.10,5X,F7.5)
              H = R -(ABS(Y1/Y2))
              IF (R-H.LT. 0.00001) GO TO 10
              R = H
        5     CONTINUE
        10    PRINT 8,H
        8     FORMAT (1X,//,25H THERMOCHEMICAL RADIUS IS, F8.5)
              PRINT 11, Y1
        11    FORMAT (1X,//,18H VALUE Y1(ROOT) IS, F16.10)
              PRINT 12, I
        12    FORMAT (1X,//,36H NUMBER OF APPROXIMATIONS TO ROOT IS, I2)
        200   CONTINUE
              END
```

HP-65 CALCULATOR PROGRAMME

Key Entry	Code Shown	Comments	Key Entry	Code Shown	Comments
LBL	23	DATA INPUT USING	STO2	33 02	$M1^2$ in STO2
A	11	STACK	RCL3	34 03	
f	31	STORES	f-1	32	
REG	43	CLEARED	$\sqrt{x}$	09	
STO1	33 01	X STO1	STO7	33 07	$M2^2$ in STO7
gR↓	35 08		RCL4	34 04	
STO2	33 02	H STO2	RCL3	34 03	
gR↓	35 08		X	71	
STO3	33 03	M2 STO3	4	04	
gR↓	35 08		X	71	
STO4	33 04	M1 STO4	STO8	33 08	4(M1.M2)inSTO8
RTN	24		RCL4	34 04	
LBL	23		RCL3	34 03	
B	12	242.8 STO5	-	51	
STO5	33 05		RCL1	34 01	
RTN	24		X	71	
LBL	23		STO9	33 09	E(M1-M2) STO9
C	13	0.0345 STO6	RCL2	34 02	
STO6	33 06		RCL7	34 07	
RTN	24	END OF INPUT	+	61	COEF B calc'ed
LBL	23	Calculation of	RCL8	34 08	
D	14	COEF of QUARTIC	+	61	&stored inSTO5
RCL2	34 02	EQUATION	RCL9	34 09	
RCL1	34 01		+	61	
+	61		STO5	33 05	
RCL5	34 05		RTN	24	END of CARD 1
÷	81		LBL	23	Calc of COEF C
g	35		A	11	
1/x	04		RCL2	34 02	
STO1	33 01	E calc'ed STO1	RCL3	34 03	
RCL4	34 04		X	71	
f -1	32		2	02	
$\sqrt{x}$	09		X	71	

Key Entry	Code Shown	Comments	Key Entry	Code Shown	Comments
ST08	33 08	2 $M1^2$ M2 ST08	RTN	24	END of CARD 2
RCL7	34 07		LBL	23	CARD 3 Calc of
RCL4	34 04		A	11	COEF D
X	71		RCL2	34 02	
2	02		RCL7	34 07	
X	71		X	71	
RCL8	34 08		ST05	33 05	$M1^2$.$M2^2$ in ST05
+	61	2M1$M2^2$+2M2$M1^2$ ST08	RCL2	34 02	
ST08	33 08		RCL3	34 03	
RCL2	34 02		X	71	
RCL7	34 07		ST08	33 08	M2.$M1^2$ in ST08
-	51		ST07	33 07	
RCL1	34 01		RCL4	34 04	
X	71		X	71	
RCL8	34 08		ST09	33 09	$M2^2$.M1 in ST09
+	61	2M1$M2^2$+2M2$M1^2$	RCL8	34 08	
ST08	33 08	+E($M1^2$-$M2^2$) ST08	RCL9	34 09	
RCL4	34 04		-	51	
RCL3	34 03		RCL1	34 01	
-	51		X	71	E($M1^2$M2-$M2^2$M1)
RCL1	34 01		RCL5	34 05	
X	71		+	61	
RCL6	34 06		ST08	33 08	$M1^2M2^2$ +E($M1^2M2^2$ -$M2^2$M1)inST08
X	71		RCL7	34 07	
2	02		RCL2	34 02	
X	71		-	51	
ST09	33 09	0.069.E(M1-M2)	RCL1	34 01	
RCL8	34 08	in ST09	X	71	
RCL9	34 09		RCL6	34 06	
-	51		X	71	
ST09	33 09	COEF C in ST09	RCL8	34 08	
RCL4	34 04		+	61	
RCL3	34 03	COEF A calc'ed	ST08	33 08	COEF D calc'ed
+	61		RTN	24	&stored in 8 END of CARD 3

Step	Instructions	Keys	Display
1	Enter card 1		
2	Input M_1 0.147	↑	
3	Input M_2 0.168	↑	
4	Input H 31.38	↑	
5	Input X -19.70	A	
6	Input 242.8	B	242.8
7	Input 0.0345	C	0.0345
8	Calculation of coeff. B	D	-0.28792
9	Record value of B		
10	Enter card 2		
11	Calculation of coeff. A and C	A	0.31500
12	Record value of A		
13	Coeff. C recalled from ST09	RCL9	-0.09183
14	Record value of C		
15	Enter card 3		
16	Calculation of coeff. D	A	-0.00543
17	Record value of D		

A=0.31500, B=-0.28792, C=-0.09183, D=-0.00543.

$H=\Delta H_f^o\ M_1{}^+(g) - \Delta H_f^o\ M_2{}^+(g)$

$X=\Delta H_f^o\ M_2X(c) - \Delta H_f^o\ M_1X(c)$

Solve $r^4 + 2Ar^3 + Br^2 + Cr + D = 0$ by programme STD 14A Enter f(r) as below with not more than 32 steps, i.e.

.63+X.28792-X.09183-X.00543-

TABLE 3

THERMOCHEMICAL RADII OF ClO_3^-, BrO_3^-, and IO_3^-/pm

Pair of salts M_1/M_2	$-\Delta H_f^o$ $M_1X(c)$ kJ mol^{-1}	$-\Delta H_f^o$ $M_2X(c)$ kJ mol^{-1}	r_t/pm
$X = BrO_3^-$			
Li/Na	320.08[221]	350.62	338
Li/Na	320.08	321.33	237
Li/K	320.08	391.20[164]	195
Li/Cs	320.08	346.44	209
Na/K	350.62[219]	332.21	103
Na/K	321.33[220]	332.21	147
Na/Cs	350.62	346.44[224]	152
Na/Cs	321.33	346.44	189
K/Cs	332.21[164]	346.44	268
$X = IO_3^-$			
Cs/Na	526.35[223]	489.95	210
Cs/K	526.35	508.36[164]	292
Cs/K	526.35	499.82[163]	191
Na/K	489.95[222]	508.36	163
Na/K	489.95	499.82	146
Li/Na	513.46[219]	489.95	188
Li/K	513.46	508.36	178
Li/K	513.46	499.82	170
$X = ClO_3^-$			
Cs/Na	395.81[218]	358.69[164]	208
Cs/K	395.81	391.20[164]	221
Na/K	358.69[164]	391.20	198

APPENDIX III

Errors

The precision of experimentally determined enthalpies of reaction are usually quoted as twice the standard deviation of the mean, $\bar{s}$:

$$\bar{s} = \left[\frac{\Sigma(x-\bar{x})^2}{n(n-1)}\right]^{\frac{1}{2}}$$

where $\bar{x}$ is the arithmetic mean of n results. Results are expressed in the form $\bar{x} \pm 2\bar{s}$, assuming a normal distribution at the 95% confidence interval. However, for $n \leqslant 20$ the error is more correctly assessed by the 'students t' distribution. Results throughout this work are therefore reported as $\bar{x} \pm t\bar{s}$ where t is the 'students t' value for (n-1) degrees of freedom at the 95% confidence interval[225].

For a series of values

$$\Delta H = \Delta H_1 + \Delta H_2 \ldots \Delta H_n$$

where ΔH_i has an uncertainty interval of $\pm x_i$ then the error for ΔH was taken as:

$$\pm \left[\sum_{i=1}^{n} (x_i)^2\right]^{\frac{1}{2}}$$

Certain ancillary data contained in Tables II-A-14, 15 and 16 were taken from NBS publications[42,159,164]. However, some of the data sources for these values are unlisted. Thus, the procedure followed in assigning an uncertainty interval is identical to that used in 'CATCH' tables[105]; i.e. the uncertainty interval is assumed to be ten times the last figure given.

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THERMOCHEMISTRY OF FLUORINE COMPOUNDS

IV. RUBIDIUM TETRAFLUOROIODATE

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ABSTRACT

From measurement of the heat of hydrolysis, at 25 °C, the enthalpy of formation of rubidium tetrafluoroiodate is derived: $\Delta H_f^\circ[\text{RbIF}_4, \text{cryst.}]_{298} = -1121.51 \pm 6.33$ kJ mol^{-1}. Heat capacity measurements for $RbIF_4$ over the range 273–303 K are also reported.

INTRODUCTION

The preparation of alkali-metal tetrafluoroiodates by various methods is well established[1–3]. Vibrational spectra of $CsIF_4$ reported by Christe[4] indicate that the IF_4^- anion has a square-planar structure of D_{4h} symmetry and not C_{2v} symmetry as first reported[5]. No thermodynamic data are available for these salts.

EXPERIMENTAL

Preparations

$RbIF_4$ was prepared, by the method of Hargreaves and Peacock[1], from RbI (5 g, 23.5 mmol, B.D.H.) and an excess of IF_5 (30 cm^3, 0.51 mol, Matheson Co. Ltd.). IF_5 was purified by shaking with mercury followed by trap-to-trap distillation using a grease-free vacuum line. The reaction mixture was stirred for 20 min at 20 °C. Excess IF_5 and iodine were removed by prolonged pumping at room temperature. Residues were pure white powders, which were subsequently manipulated under dry-box conditions. The change in weight of the pyrex reaction vessel was found to be identical with the theoretical increase (based on RbI).

Several attempts were made to prepare $CsIF_4$ using the same method. In each case the experimental weight change and fluorine analysis indicated that $CsIF_4$:$CsIF_6$ mixtures were produced.

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Analysis and determination of hydrolysis stoichiometry

Aqueous hydrolysis was rapid (about 2 min) but not violent, resulting in the separation of elemental iodine. Qualitative tests on the aqueous hydrolysate gave the following indications: fluoride ions (calcium chloride test), iodate ions (5% aqueous thiocyanate and starch paper), and the absence of iodide ions (aqueous silver nitrate followed by aqueous ammonia).

Quantitative determination of fluoride ion after hydrolysis (Orion selective ion fluoride electrode) gave the following result: found 26.4%; calc. for $RbIF_4$, 26.35%.

Quantitative determinations of iodate and iodine in the aqueous hydrolysate were made as follows:

(a) Two samples of $RbIF_4$ (ca. 0.2 g, 0.7 mmol) were hydrolysed in water (25 cm^3) and the liberated iodine removed by vigorous boiling for 30 min. The residual iodate was analysed titrimetrically (addition of iodide followed by titration of liberated iodine against 0.1M thiosulphate) giving the results $RbIF_4:IO_3 = 1.67$, 1.65:1.

(b) After a similar hydrolysis, iodine was separated by repeated extractions with carbon tetrachloride and the iodine content of the combined extracts determined titrimetrically (0.1 M thiosulphate). The aqueous portion was titrated for iodate as in (a). Found: $RbIF_4:IO_3 = 1.67:1$ and $RbIF_4:I_2 = 5.02:1$.

The overall stoichiometry is hence quantitatively represented by the following equation:

$$5RbIF_4+9H_2O \rightarrow 5RbF+15HF+3HIO_3+I_2.$$

Calorimeter and calorimetric procedure

The calorimeter used has been fully described elsewhere[6]. 200 cm^3 of distilled water were used as the calorimetric fluid. The calorimetric reaction was fast, but not violent, being complete within 2 min. The measured heat of reaction, ΔH_R, refers to the process summarised in eqn (1).

$$5RbIF_4(\text{cryst})+(n+9)H_2O(\text{liq}) \rightarrow [(5RbF+3HIO_3+15HF)nH_2O(\text{liq})] + I_2(\text{cryst}) \qquad (1)$$

DSC and heat capacity measurements

The heat capacity of $RbIF_4$ was measured using a Perkin-Elmer differential scanning calorimeter (Model DSC 1), with encapsulation in sealed aluminium pans, at a scan speed of 4 K min^{-1}. Sapphire was used as calibrant, and temperature measurement was checked using n-octacosane (m.p. 61.2 °C) supplied as a standard from the National Physical Laboratory, Teddington, and n-tridecane (m.p. −5.5 °C). $RbIF_4$ was also scanned in the direct mode over the range −100 to +180 °C. A single exotherm (165 °C) was observed which appeared to correspond with decomposition of the sample.

RESULTS

Experimental calorimetric results are in Table 1. The standard heat of formation of $RbIF_4$ was calculated by substitution of appropriate ancillary data (Table 2) into eqn (2).

$$5\Delta H_f^\circ[RbIF_4, \text{cryst.}]_{298} = 5\Delta H_f^\circ[RbF, 2000\ H_2O] + 3\Delta H_f^\circ[HIO_3, 4000\ H_2O] + 15\Delta H_f^\circ[HF, 750\ H_2O] - 9\Delta H_f^\circ[H_2O, \text{liq}] - 5\,\Delta H_R \qquad (2)$$

Heats of mixing and heat of solution of iodine were disregarded; weights were not corrected to vacuo. Uncertainty intervals in ΔH_R are expressed as twice the standard deviation of the mean.

TABLE 1

EXPERIMENTAL DATA FOR HYDROLYSIS OF RUBIDIUM TETRAFLUOROIODATE
Mean $\Delta H_R = -41.25 \pm 0.22$ kJ mol^{-1}; hence ΔH_f° [$RbIF_4$ (cryst.)]$_{298}$ = -1121.51 ± 6.33 kJ mol^{-1}.

w (*g*)	$-\Delta H_R$ (*kJ mol*$^{-1}$)
1.5833	41.71
1.5370	41.17
1.5109	40.25
1.4753	41.80
1.4454	42.05
1.3861	42.13
1.3814	39.45
1.2362	41.50

TABLE 2

ANCILLARY HEAT OF FORMATION DATA

Compound	ΔH_f° (*kJ mol*$^{-1}$)
H_2O (liq.)[7]	-285.829 ± 0.04
RbF (2,000 H_2O)[8]	-575.513 ± 0.4
HIO_3 (4,000 H_2O)[9]	-221.785 ± 0.4
HF (750 H_2O)[10]	-322.90 ± 0.29

TABLE 3

HEAT CAPACITY OF RUBIDIUM TETRAFLUOROIODATE

T (K)	273	278	283	288	293	298	303
C_p (JK^{-1} mol^{-1})	120.2	124.0	127.7	135.0	138.8	144.5	148.3

Heat capacity data are collected in Table 3, and are represented, following a least-squares procedure, by the following equation:

$$C_p = 0.975T - 146.6$$

The overall accuracy is estimated to be ±2%.

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