THERMOCHEMISTRY OF SOME ALKYLAMMONIUM HALIDES AND POLYHALIDE COMPLEX COMPOUNDS.

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ABSTRACT.

The standard enthalpies of formation of the alkylammonium polyhalides $\left[R_nNH_{4-n}\right]ICl_4(c)$ (R= CH_3, C_2H_5 ; $1 \leqslant n \leqslant 4$) have been calculated from measured enthalpies of reaction with aqueous silver nitrate; standard enthalpies of formation of $CH_3NH_3ICl_4$ and $(C_2H_5)_3NHICl_4$ have been determined by an extrapolation procedure. These calculated enthalpies of formation have been used to determine the thermochemical radii of $\left[R_nNH_{4-n}{}^{+}\right]$, (R = CH_3, C_2H_5 ; $1 \leqslant n \leqslant 4$) and also to obtain the lattice energies of the alkylammonium polyhalide compounds. Standard enthalpies of formation of the gaseous cations have been derived as

$\Delta H_f^{\ominus} MeNH_3{}^{+}(g)$ = 624 kJ mol^{-1}

$\Delta H_f^{\ominus} Me_2NH_2{}^{+}(g)$ = 604 kJ mol^{-1}

$\Delta H_f^{\ominus} Me_3NH^{+}(g)$ = 589 kJ mol^{-1}

$\Delta H_f^{\ominus} Me_4N^{+}(g)$ = 580 kJ mol^{-1}

$\Delta H_f^{\ominus} EtNH_3{}^{+}(g)$ = 607 kJ mol^{-1}

$\Delta H_f^{\ominus} Et_2NH_2{}^{+}(g)$ = 570 kJ mol^{-1}

$\Delta H_f^{\ominus} Et_3NH^{+}(g)$ = 517 kJ mol^{-1}

$\Delta H_f^{\ominus} Et_4N^{+}(g)$ = 462 kJ mol^{-1}

The standard enthalpies of formation of ethyl-substituted ammonium halides $(C_2H_5)_nNH_{4-n}X(c)$ (X=Cl, Br, I ; $1 \leqslant n \leqslant 3$) have been obtained from measured enthalpies of reaction with aqueous sodium hydroxide. Results for $(C_2H_5)_2NH_2Cl$ and $(C_2H_5)_3NHCl$ are in good agreement with values already reported in the literature.

These standard enthalpies of formation were linearly related to the number of ethyl groups, n. Standard enthalpies of formation of tetraethylammonium halides (Cl, Br, I) have been obtained by extrapolation. The lattice energies of these salts have been calculated using the thermochemical radius procedure.

From the calculated thermochemical radii of the cations and the lattice energies the standard enthalpies of formation of methyl-and ethyl-substituted ammonium dichloroiodate, dibromoiodate and tri iodate have been estimated.

The standard enthalpies of formation of alkylammonium polyhalides have been used to estimate the standard enthalpies of dissociation of various polyhalides; these results have been used to discuss the thermodynamic stabilities of the polyhalide compounds.

The proton affinities of methyl and ethyl substituted amines have been calculated and are in good agreement with reported values derived from different experimental methods.

The standard enthalpies of formation of some I(III) species have been calculated from measured enthalpies of hydrolysis. Values obtained are:

$\Delta H_f^\ominus ICl_3(c) = -89.89 \pm 1.85$ kJ mol^{-1}

$\Delta H_f^\ominus (CH_3COO)_3I(c) = -1047.80 \pm 4.50$ kJ mol^{-1}

$\Delta H_f^\ominus ICl_2AlCl_4(c) = -827.56 \pm 6.20$ kJ mol^{-1}

The thermal titrations of hydrolysed ICl_3 and $(CH_3COO)_3I$ against aqueous silver nitrate have been performed and used as a basis for a discussion of reaction mechanisms of these compounds.

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DEDICATION

TO MY FAMILY

FARINAZ AND BEHRAD

CHAPTER 1

INTRODUCTION

INTRODUCTION

1-A

Polyhalide complex anions and cations have been known for many years and have been the subject of a number of reviews. The tendency of halide ions to co-ordinate with either halogens or interhalogens to form complex anions is well-known. Shortly after the discovery of iodine, Pelletier and Caventou (1) reported the preparation of an addition compound of strychnine and iodine which they called "hydroidüre iodure". This was undoubtedly strychnine tri-iodide, $C_{21} H_{22} O_2 N_2 . HI_3$. It also became apparent that the solubility of iodine in water or in ethanol was increased very considerably by the addition of potassium iodide. The reason for the increased solubility of iodine was debated for sometime, and many investigators were unwilling to accept the formation of the tri-iodide ion in solution as an adequate explanation. The question appears to have been settled by Johnson (2) who claimed to have isolated large blue crystals by evaporation of concentrated iodine-potassium iodide solutions and, on the basis of his analysis, identified the compound as potassium tri-iodide. Ironically, however, the right conclusion about the existence of the tri-iodide ion in solution was based on wrong results since Abbey and Hamburger, who thoroughly investigated the potassium tri-iodide-iodine system, found no evidence for the existence of unsolvated potassium tri-iodide (3) and Bancroft et al (4) showed that Johnson's compound was simply a mixture of potassium iodide and iodine.

Some polyhalogen complexes are too unstable to be isolated in the form of crystalline salts but exist in aqueous and nonaqueous solutions. The composition of such complexes can only be obtained from the study of their solution properties. The growing popularity of nonaqueous solvents as media for inorganic reaction likewise extended the scope of research on polyhalide complexes since many of them are only stable in inert solvents.

Polyhalide ions have been defined as addition products of a halide ion acting as a Lewis base with a halogen or interhalogen species acting as a Lewis acid, the resulting product being an anion. Later, however, it became evident that positively charged halogen aggregates can also exist; and for this to include these a polyhalide complex ion can be defined as an aggregate consisting of three or more atoms carrying either a positive or negative charge with a generalized formula:

$$Xm\ Yn\ Zp\pm$$

where X, Y and Z represent either an identical, two different or, in the case of the anions, three different halogen atoms. The sum m + n + p is usually an odd number that can be 3,5,7 or 9. Table 1-A-1 lists polyhalide ions identified more or less convincingly as anions or cations of electrovalent salts.

Table 1-A-1

Polyhalide complex ions in crystalline salts.

X_3^-	X_5^-	X_7^-	X_9^-	Xn^-	Xn^+
I_3^-	I_5^-	I_7^-	I_9^-	I_4^-	ClF_2^+
I_2Br^-	I_4Cl^-	I_6Br^-			I_2Cl^+
I_2Cl^-	I_4Br^-	IF_6^-			IF_4^+
IBr_2^-	$I_2Br_3^-$	Br_6Cl^-			IF_2^+
ICl_2^-	$I_2Br_2Cl^-$				ICl_2^+
$IBrCl^-$	$I_2BrCl_2^-$				$BrICl^+$
$IBrF^-$	$I_2Br_3^-$				BrF_2^+
Br_3^-	$IBrCl_3^-$				
Br_2Cl^-	ICl_4^-				
$BrCl_2^-$	ICl_3F^-				
Cl_3^-	IF_4^-				
	BrF_4^-				
	ClF_4^-				

1-B GENERAL METHODS OF PREPARATION OF POLYHALIDE COMPLEXES

Such complexes have been prepared by various methods. In general, the preparation of anionic polyhalides complexes simply involves the addition of halogen or halogens to a desired halide under experimental conditions dictated by nature of the reactants and the products. The experimental procedure may involve

(a) Reaction of a solid halide with gaseous or liquid halogen or interhalogen.

(b) Reaction of gaseous halide and halogen dissolved in water or in a nonaqueous solvent.

(c) Reaction of gaseous halogen with halide dissolved in an appropriate solvent.

(d) Displacement of less electronegative halogen in polyhalide with more electronegative one.

Chattaway and Hoyle(5), Cremer and Duncan (6) and more recently, Popov and Buckles (7) and Schmeisser(8) have employed these methods to prepare polyhalides.

The gas-solid reactions in most cases are rather difficult and slow and often do not yield pure products. A large majority of polyhalide salts (excluding those containing fluorine) can be prepared either in methanol or ethanol solutions. In the case of rather unstable polyhalides a solvent more inert to halogenation has to be selected, such as acetic acid, carbon tetrachloride or dichloromethane. Polyfluorides are often prepared by direct reaction of a liquid halogen fluoride with a halide salt. It is relatively simple to prepare polyhalide salts of high stability such as the tri-iodides, dichloroiodates and dibromoiodates but the difficulties increase rapidly with decreasing thermal and/or chemical stability of the polyhalide ions. For example, the trichloride ion is quite unstable either in crystalline salts or in solution and readily dissociates to chlorine and chloride ions. Consequently few salts of Cl_3^- have been reported in the literature.

In the formation of polyhalide complexes, the final product is usually determined by the composition of the reacting mixture, rather than by the nature of the halide ion and the interhalogen or halogen molecules. Thus, potassium dichloroiodate (I) can be obtained by the reaction of potassium iodide with chlorine, potassium chloride with iodine monochloride, or potassium tetrachloroiodate (III) with potassium iodide.

In replacement reactions, for example, reaction of bromine with di-iodobromate or tri-iodide ion I_3, formation of IBr_2^- invariably occurs with no further reaction towards the formation of a tri-bromide.

Cremer and Duncan (6) observed that while it was possible to add a halogen molecule to a polyhalide ion e.g. $ICl_2^- + Cl_2 \rightarrow ICl_4^-$, their attempts to add an interhalogen molecule to a polyhalide ion were unsuccessful. In other words, the reactions $ICl_2^- + IBr$ would not lead to the formation of the corresponding pentahalide ion. However, recent evidence indicates that a variety of pentahalide ions may be formed by the addition of interhalogen molecules to the tri halide ions.

$$(CH_3)_4NICl_2 + IBr \longrightarrow (CH_3)_4NI_2Cl_2Br$$

Alkali metal ions with large radii such as rubidium and caesium readily form anhydrous tri-iodides. The tendency to form hydrates, on the other hand, is much less pronounced than with the lighter alkali metals. Briggs and Hubard,(9) studied the temperature - composition diagram of the $CsI - I_2 - H_2O$ system and observed only the formation of anhydrous caesium tri-iodide and tetraiodide. Magnetic susceptibility measurements led to the conclusion that the latter compound is a double salt .

Apparently unsuccessful attempts have been made to prepare polyhalides of silver; the existence of silver tri-iodide has been postulated (10), but subsequent work did not confirm this.

A large variety of polyhalide salts and of polyiodides in particular, can be prepared with bulky organic cations. Tetra-alkylammonium salts have been used extensively in such preparations (5) together with other similar cations, such as trialkylsulphonium, tetraphenylarsonium, etc.

Foote and Fleisher (11) reported the preparation of the tetramethylammonium salt of I_3^-, I_5^-, I_9^-, I_{10}^- and I_{11}^- by suspending tetramethylammonium iodide and iodine in toluene and determining the composition of solid phase from the original charge and from the iodine concentration in the solution at equilibrium.

(a) Mixed Tri halide anions.

Salts of trihalide ions containing every possible combination of the three halogens, chlorine, bromine and iodine have been prepared. Once again the cations are either heavy alkali metals or large organic cations. The formation of such salts is restricted to cations with a unipositive charge. In contrast to tri-iodide it is possible to prepare stable anhydrous potassium dichloriodate (1).

Mixed trihalide ions do not exhibit any isomerism. This is understandable in view of the fact that their stabilities are dependent on obtaining the most stable configuration which invariably places the heavier halogen at the centre of the linear or nearly linear trihalide ion.

(b) Mixed pentahalide anions.

Most of the mixed pentahalide salts which have been reported are characterized by greater stability than their trihalide analogues. Exceptions do occur but as a generality the statement seems to be valid. In particular, this increased stability is observed in the case of tetrachloroiodate (III) salts which can be readily obtained as solid or in solution either by the addition of chlorine to the dichloroiodate (I) ion or by addition of iodine trichloride to a chloride. The nature of the cation seems to be of secondary importance. Anhydrous salts of sodium, potassium, rubidium and caesium can be easily obtained (12, 13) although the salts of the first two elements can also be obtained as hydrates. It is also possible to prepare tetrachloroiodates of the alkali earth salts and of divalent transition metals such as cobalt, nickel and manganese (14, 15).

Tetramethylammonium chloro tri-iodoiodate (III), $(CH_3)_4NClI_4$, and the corresponding tetramethylammonium salts were prepared by Chattaway and Hoyle (5), These salts seem to be less stable than the tetrachloroiodate but they have not been thoroughly investigated.

Numerous organic salts of pentahalide anions have recently been reported (16). They can be fairly easily prepared by dissolving an appropriate dichloroiodate salt in 1,2 - dichloroethane, adding a slight excess of iodine monochloride and precipitating the resulting pentahalide salts. It is possible to prepare a large variety of mixed pentahalide salts (17) containing chlorine, bromine and iodine (See Table 1-B-1).

Table 1-B-1 salts of mixed pentahalide anions

$(CH_3)_4NICl_2 \cdot IBr$

$(CH_3)_4NICl_2 \cdot ICl$

$Py \cdot HICl_2 , ICl$

$Py \cdot HICl_2 \cdot IBr$

$Py \cdot HIBr_2 \cdot IBr$

$(CH_3)_4NIBr_2 \cdot IBr$

$(CH_3)_4NIBr_2 \cdot ICl$

$(C_4H_9)_4NIBr_2 \cdot ICl$

1-C THE NATURE OF BONDING AND THE STRUCTURE OF POLYHALOGEN COMPLEXES

The formation of the trihalide ions was originally explained by an electrostatic ion-dipole attraction between a halide ion and a polarizable halogen molecule (18). This interpretation, however, cannot account satisfactorily for the centrosymmetric trihalide ions, such as ICl_2^- or in some instances I_3^-.

A covalent type of bonding was proposed by Kimball (19) in which the increase in valency of the central atom is achieved by promotion of s- and p- electrons to d-orbitals On this basis formation of localized bonds, therefore, is a result of a sp^3d - or sp^3d^2- hybridization; this view gained general acceptance but a different scheme of bonding has been proposed by Pimentel (20), who pointed out that the formation of I_3^- ion can be due to the delocalization of the 5p-electron of the iodine atoms. This idea was further explored by Hach and Rundle (21), and by Rundle (22) who have shown that the resonance form of the tri-iodide ion,

$$I\text{-}I \text{----} I^- \qquad I^- \text{-----} I\text{-}I$$

does not require iodine to violate the octet rule or use d-orbitals in the bonding. The above authors, however, restricted their proposal for the nature of bonding in polyhalides to the polyiodides and state that in mixed polyhalide ions the usual explanation involving the use of iodine d-orbitals of central atom is undoubtedly correct.

Subsequent studies of the nuclear quadrupole coupling constants for chlorine and iodine atoms in $CsICl_2$, $RbICl_2$, $KICl_2$, $KICl_2 \cdot H_2O$, $CsICl_4$, $RbICl_4$, $KICl_4$ and $NaICl_4 \cdot H_2O$, however, led Cornwell and Yamasaki$^{(23,24)}$ to a different conclusion. The coupling constants they have obtained are in agreement with the resonance hybrid structure proposed for these ions. They found, for example, that the I-Cl bond in ICl_2^- and ICl_4^- have a rather large proportion of ionic character, corresponding to about half an electron on the chlorine atom, and this would be consistent with the structure in which the iodine valence orbitals used in polyhalides are made up mainly from 5s-and 5p- orbitals. If the above description of the bonding is correct, then each I-Cl bond would be essentially "half bond" and the frequency for I-Cl stretching in the ICl_2^- ion should occur at the lower value than the corresponding vibration in ICl. Far infrared and Raman spectra of Br_3^-, ICl_2^-, $BrCl_2^-$ and ICl_4^- ions were determined in nitrobenzene solution by Person et.al, $^{(25)}$ and it was found that indeed the vibrational frequencies were drastically decreased. For example, while the I-Cl stretching mode in gaseous iodine monochloride is at 382 cm^{-1} $^{(26)}$, the asymmetric stretch of ICl_2^- (ν_3) is invariably located in the 220-225 cm^{-1} region. From these data the authors calculated the halogen-halogen stretching force constant in polyhalide ions and the interaction force constant between bond stretching co-ordinate at 180° and at 90° to each other. The values they obtained are again consistent with the description of the bonding using only p-orbitals.

Crystal structures of the polyhalide ions have been intensively studied sometimes with conflicting conclusions. Early work on the trihalide ion by Mooney(27) indicated that in ammonium tri-iodide the I_3^- group forms essentially a linear ion which, however, is not centrosymmetrical, the two I-I distances being 2.82 Å and 3.10 Å . The structures observed for tri-iodide ion are interesting in that symmetrical as well as asymmetrical **tri**-iodide ions have been found to exist in the solid tri-iodide. A recent example of the first category is that tri-iodide ion in tetraphenylammonium tri-iodide; the tri-iodide in $N(C_2H_5)_4I_7$ may be added to this group because this heptaiodide is essentially a network of cations, centrosymmetrical tri-iodide ions, and iodine molecules.

The most detailed investigations of the asymmetrical tri-iodide ion is that in CsI_3, where a difference in the two bond lengths of 0.20Å , and a bond angle of 176°, are observed; these deviations from a centrasymmetric ion are certainly significant. The average of the two bond lengths does not differ much from the bond length found in the centrosymmetric ions and is 0.26Å longer than the I-I distance in an isolated iodine molecule.

Other trihalide centrosymmetric $Cl-I-Cl^-$ ions are found in $N(CH_3)_4ICl_2$ and $PICl_6$ in which the bond lengths are not significantly larger than the sum of the covalent radii of I and Cl, 2.35 and 2.32Å respectively, or atomic distance in the ICl molecule. Neither is the I-Br bond length in Br-I-Cl, 2.50 Å, significantly larger than the sum of the covalent radii of iodine and bromine in tribromide ion 2.53Å ; however, the Br-Br distance seems to be appreciably larger than the bond lengths in the bromine molecule; the difference, 0.25Å, is probably insignificant, even though the structure of $[N(CH_3)_3H^+]_2Br^-.Br_3$ has not yet been refined to the greatest possible accuracy.

Recent reinvestigation of interatomic distances in the dichloroiodate ion, however, gives values which differ considerably from those found by the earlier investigator. Romming (28) found that in piperazinium di-dichloroiodate (I), $C_4H_{10}N_2 \cdot 2HICl_2$, the ICl_2^- ion is linear but not symmetrical, with the two I-Cl distances being 2.69 and 2.47 Å respectively, likewise, Visser and Vos report that in the tetramethylammonium dichloroiodate (I), $(CH_3)_4NICl_2$, while the ion is both linear and symmetrical, the I-Cl distances is 2.55Å (29). In both cases the interatomic distances are much longer than those reported by Mooney (30) and are longer than the sum of the covalent radii.

The structures of pentahalide ions and of higher aggregates do not show the same regularity. In fact, while only three pentahalide ions have been examined in any detail, it seems that there are two different classes. In potassium tetrachloroiodate(III) , which is characterized by high stability and the ease with which it forms crystalline salts, the five halogen atoms form a planar structure in which the central iodine has four coplanar bonds with the chlorine atoms. The I-Cl distance is 2.34 Å e.g. the same as in the ICl_2^- ion. According to Mooney, this structure represents an octahedral hybridization around the iodine atom with two vacant positions on the co-ordination sphere rather than a square-planar configuration. Similarly, a recent refinement of the crystal structure of $KICl_4 \cdot H_2O$ (31) has shown that the I-Cl bonds are considerably longer than those reported by Mooney. The bond lengths are not equal and range from 2.42Å to 2.60Å .

An analogous structure is claimed for potassium tetrafluorobromate $KBrF_4$(III). Although originally it was postulated by Siegel (32) that this pentahalide ion has a tetragonal structure with F-F distances of 2.81 and 3.03Å and Br-F distances of 1.81Å , Sly and March (33), after re-examination of Siegel's data, concluded that they are more indicative of the square-planar configuration strongly resembling the ICl_4^- ion.

An entirely different structure was found, however, for the pentaiodide ion I_5^- in tetramethylammonium pentaiodide (34), $(CH_3)_4NI_5$. The salt exists in the shape of monoclinic crystals with a = 13.34Å , b = 13.09Å , c = 8.90Å and B =105°50'. Pentaiodide ions form nearly square iodine nets within which V-shape pentaiodide ions can be distinguished. The ions are planar to within 0.12Å , and the apex angle is 94°0'. The structure can be roughly described as consisting of an iodine to which two iodine molecules are attached. The distance between the I^- ion at the apex and the nearest neighbour is 3.14 Å while the I-I distances in the two molecules are 2.93Å . These distances are short enough to indicate a rather strong interaction and justify the consideration of I_5^- species as a chemical entity. In a subsequent redetermination of structure Brockena et al (35) modified the I-I distance to 3.17 and 2.81 Å , respectively, but confirmed the overall structure.

1-D STABILITY OF POLYHALIDE COMPLEX SALTS

All polyhalides decompose to some extent into a halogen or interhalogen compound and a lower halide. In many cases the dissociation pressure is already appreciable at room temperature. It is found that the dissociation always takes place in such a way that the halogen or interhalogen molecules formed contain the heaviest halogen atoms. For example,

$CsICl_2$ dissociates into CsCl+ICl and not to $CsI+Cl_2$; similarly, in solution the ICl_2^- ion dissociates into Cl^-+ICl.

The stability of solid polyhalides depends on numerous factors such as the size and the symmetry of the cation and size, symmetry and chemical reactivity of the polyhalide ion. Almost all polyhalides dissociate spontaneously to solid halide containing the most electronegative element and gaseous halogen or interhalogen. Relative values of vapour pressures at a given temperature or the temperature at which vapour pressure of the gaseous product reaches a given value are good indication of the relative thermal stabilities of the polyhalide. The dissociation pressures of caesium and rubidium polyhalides have been determined by Ephraim (36), who measured the temperature at which the dissociation pressures of the polyhalide reaches one atmosphere (see Table 1-D-1).

It is evident that the caesium salts are considerably more stable than rubidium salts. The data also illustrates the influence of symmetry on the stability of the polyhalide ions. For example, with respect to dissociation, salts of centrosymmetric dibromoiodates are much more stable than those of the asymmetric I_2Br^- ion.

A different and perhaps somewhat more accurate method

Table 1-D-1.

Thermal dissociation of polyhalides salts (Temperature at pressure of 1 Atm).

ANION	Rb	Cs
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

of determining the relative stabilities of polyhalide salts has been derived by Cremer and Duncan(37). These authors suspended polyhalide salts in carbon tetrachloride solution. After equilibrium was established, they determined the concentration of the halogen in the carbon tetrachloride. The concentration of the free halogen in solution gave an indication of instability of the corresponding polyhalide. See Table 1-D-2 and 1-D-3.

It is tempting to explain the dependence of the stability of a crystalline polyhalide on the nature of its cation from the fact that the lattice energy of the monohalide formed in the dissociation reaction will be large for small, highly charged and asymmetrical cations. It is impossible to prove however, that this will be the dominating factor. The standard free enthalpy of dissociation also depends on the lattice energy of the polyhalide, and on the difference in entropy between the solid polyhalide and the monohalide. Even if the influence of the entropy is neglected, the difference between lattice energies of different polyhalide can not be expected to be negligible, especially when their crystals are not isomorphous.

a) IN AQUEOUS SOLUTION.

The behaviour and the stability of polyhalideions in aqueous solutions have been the subject of many investigations. In spite of this large volume of work, only a few polyhalide

Table 1-D-2.

Concentration of halogens (eq/l) in equilibrated polyhalide salts - CCl_4 system.

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	0.0122	0.057

Table 1-D-3.

Influence of cations on stability of polyhalides.

Cations	Conc.of Halogen in CCl_4	Cation	Conc.of Halogen in CCl_4
NH_4IBr_2	0.00842	$(CH_3)_3NHIBr_2$	0.00249
$CH_3NH_3IBr_2$	0.00134	$(CH_3)_4NIBr_2$	0.00004
$(CH_3)_2NH_2IBr_2$	0.00004	$(C_2H_5)_3CH_3BIBr_2$	0.00002

ions have been thoroughly studied, such that properties can be considered as established beyond reasonable doubt. Unfortunately, many early investigators neglected to take into account the hydrolysis reaction. Physicochemical methods have been used extensively in the studies of polyhalide ions in solutions. Spectrophotometry, electrical conductance, potentiometry and stability measurements have been heavily relied on to provide information on the nature and the structure of both anionic and cationic polyhalides.

The existence in aqueous solutions of all possible trihalide ions consisting of the varying combination of chlorine, bromine and iodine has been amply proven by a variety of techniques. Even the highly unstable tri-chloride ion exists in concentrated chloride solutions saturated with chlorine. Some of the thermodynamic properties of aqueous trihalide are shown in table 1-D-4. (Reported by The National Bureau of Standards Technical Note 210-3).

Because of its relative stability in aqueous solution the tri-iodide ion has been thoroughly investigated (39-46). Thermodynamic constants reported for this ion, are collected in Table 1-D-5.

Awtrey and Connick (40) have also reported an enthalpy of formation for tri-iodide ion, determined from a spectroscopic study, of -21.34 ± 1.67 kJ mol $^{-1}$. Recently Mironov and Lastovkima

Table 1-D-4.

Standard state thermodynamic properties of aqueous trihalide anions (a)

Ion	$-\Delta H^\ominus_f$ 298 kJ mol^{-1}	$-\Delta H^\ominus_f$ 298 kJ mol^{-1}	$S^\ominus$ 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 (38)

c: A value of $\Delta G^o f = -20$ kcal mol^{-1} is reported in Ref.(39).

Table 1-D-5.

Thermodynamic constants for reaction

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
$\Delta H=-19.92$		$\Delta H=-18.16$		$\Delta H=-17.01$	
$\pm$ 1.67		kJ mol^{-1}		kJ mol^{-1}	
kJ mol^{-1}		$\Delta S=-6.15$ J K^{-1} mol^{-1}		$\Delta S=-2.05$ J K^{-1} mol^{-1}	

have reported stability constants and other thermodynamic constants for the following reaction in 0.1 M perchloric acid at an ionic strength of 3.0.

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

These data are contained in Table 1-D-6.

Measurements of the stability constant of the tribromide ion, Br_3^-, in aqueous solutions are less numerous than for the I_3^- ion, reflecting the much higher reactivity of bromine. There is some evidence for the formation of Br_5^- ion in concentrated aqueous solution of bromine. Scaife and Tyrell (45) equilibrated bromine vapour between two aqueous solutions one of which contained potassium bromide. Since at equilibrium the activity of bromine in two solutions should be equal, the analysis of the aqueous solution gives a measure of the free bromine concentration in the KBr - Br_2 solution. From these data the formation constant of the tribromide ion can be easily deduced. The data, however, could be only explained on postulating two simultaneous equilibria

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

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

Equilibrium constants for the two reactions were determined at three temperatures. The values obtained were 19.85, 16.85 and 15.28 $l\ mol^{-1}$ for reactions (1) at $5,^{o}$ 25^{o} and 30^{o}, respectively, and 1.94, 1.45 and 1.30 for reaction (2) at the same respective temperatures. The results agree quite well with the older measurements by Jones and Baeckstrom(46) who used the same experimental technique and obtained K_f values of 16 and 2.5 respectively for the two equilibria at 25°.

Because of its extreme instability, the tri-chloride ion has not been investigated in aqueous solution to any significant extend. The solubility of chlorine in aqueous chloride solution was investigated by Sherrll and Izard (47) in 1931. They determined the formation constant to be ≈ 0.2. Zimmerman and Strong (48) studied the absorption spectrum of chlorine dissolved in aqueous solution containing varying concentration of hydrochloric acid. The solutions were maintained at a constant ionic strength of 1.00 by the addition of perchloric acid. The formation constant was calculated to be 0.191 ± 0.016. They estimated the enthalpy of formation to be about 8.0 kJ mol $^{-1}$.

Cerquetti et al (49), have determined equilbrium constants, K, for the following process, over the temperature range 25-80°C by measurement of the e.m.f of the cell illustrated below.

$$Cl_{2\,(g)} + Cl^- \,(aq) \rightleftharpoons Cl_3^- \,(aq) \qquad (3)$$

$$H_2, 1\ \text{atm} \,\Big|\, \text{HCl, IM} \,\Big|\, Cl_2, \text{P atm.}$$

Measurement of chlorine solubility in parallel to the e.m.f. measurements allowed the determination of the

Table 1-D-6.

Thermodynamic constants for the reaction

X_2 (aq) + y^- (aq) $\longrightarrow$ X_2H^- (aq) at 25C° in 0.1M acid

and ionic strength of 3.0 .

Ions	Methods	$K_f(M^{-1})$	$-\Delta G^\ominus$ kJ mol^{-1}	$-\Delta H^\ominus$ kJ mol^{-1}	$\Delta S^\ominus$ 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	-6.29±0.38	-6.82±0.63	1.87±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

equilibrium constant, K_2, for process (4) to be made and thus thermodynamic functions for all the species in the $Cl_2/Cl^-/Cl_3$ system to be calculated, (Table 1-D-7).

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

Rcently Shimonis (50) has determined the stability constant, K, of tri-chloride 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 pentachloride ions appears to be present in the literature, neither stability constant data for the tetrachloroiodate nor for other pentahalide ions seems to have been reported.

b) POLYHALIDE IONS IN NONAQUEOUS SOLVENTS

The stability and behaviour of polyhalide complex ions in solution are drastically influenced by the nature of the solvent. In fact, aqueous solutions are far from ideal media for the study of polyhalides due to hydrolysis. While hydrolysis can be more or less suppressed by the addition of an acid in fairly high concentration, this not only increases the ionic strength but also introduces another reactive species in to the system.

Table 1-D-7.

REACTION	$K_1{}^a$	$K_2{}^a$	$\Delta H^\ominus$ kJ mol^{-1}	$\Delta G^\ominus$ kJ mol^{-1}	$\Delta S^\ominus$ J $K^{-1} mol^{-1}$
$Cl_2(g) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq)$	0.0119		-31.33	+11.00	-141.40
$Cl_2(aq) + Cl^-(aq) \rightleftharpoons Cl_3^-(aq)$		0.215	-10.04	+3.81	-46.40

a; unit for K_1 , K_2 are not reported in ref. (49).

Certain reactive nonaqueous media polyhalides may undergo solvolysis. Many organic solvents can readily be halogenated by polyhalogen compounds. On the other hand, it is usually possible to select a solvent sufficiently inert which would not complicate a particular study by undergoing a side reaction with the solute.

A characteristic feature of polyhalide solutions in most nonaqueous solvents is a dramatic increase in the stability constant of the polyhalide ions. This simply means that polyhalide ions are more stable in nonaqueous solvents.

The formation of tri-chloride, tri-bromide and tri-iodide ions were determined polarographically in nitromethane, acetone and acetonitrile by Nelson and Iwamoto (51). These values are listed in Table 1-D-8.

It is seen that in all these cases the values of the formation constants are very large compared to those in water. It is interesting to note that the order of stabilities of polyhalide ions in all of these solvents is the reverse of that in water. The trichloride ion is the most stable and the tri-iodide is the least stable. The value for the stability constant of I_3^- in acetonitrile compares favourably with the K_f of 10^7 value reported by

Skelly (52) on the basis of electrical conductance measurements. The influence of solvent upon dissociation of the tri-bromide ion has been studied spectrophotometrically by Dubois and Herzog (53) in water-methanol mixtures (Table 1-D-9).

Popov has estimated the enthalpy of the reaction $Br^- + Br_2 \longrightarrow Br_3^-$ in methanol using the data in table 1-D-9 and suggested it to be 24.20 ± 3.10 kJ mol^{-1}. Somewhat different results were obtained by other investigators in water-acetic acid mixtures (54), using both sodium bromide and hydrobromic acid as sources of the bromide ions. The formation constant increased with increasing concentration of acetic acid just as in the case of water-methanol mixtures, but the increase continued only up to about 95 volume % of the acid K_f= 103 l/mol ^{1} and then the K_f value dropped sharply to K_f= 51 l/mol ^{1}.

The stability of the tetrachloroiodate (III) ions in solution likewise depends on the nature of the solvent. It dissociates to ICl_2^- and Cl_2 in acetonitrile and 1,2 dichloroethane solutions, the respective dissociation constants being 1.43×10^{-4} and 1.85×10^{-4} (55). In trichloroacetic acid it dissociates completely to iodine monochloride, chlorine and the chloride ion.

Electrical conductance studies on tetra-alkylammonium polyhalides have been carried out in acetonitile (56) and in

Table 1-D-8.

Stability constants of trihalide ions in aprotic solvents.

Ions	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^{19}

Table 1-D-9.

Formation constants of Br_3^- ion in methanol and water methanol.

Solvent (% wt)	Temp. °(C)	K_f 1/mol
CH_3OH	-15	355 ± 24
CH_3OH	+ 5	260 ± 9
CH_3OH	+18	204 ± 13
CH_3OH	+28	177 ± 8
7% H_2O	18	190 ± 11
20% H_2O	18	165 ± 14
28.4% H_2O	18	148 ± 11
H_2O	16.5	17.4

1,2 - dichloroethane (57). Analysis of data showed that in the former case the salts behaved as strong electrolytes and were essentially completely dissociated. In the latter case simple tetra-alkylammonium halides showed the characteristic behaviour of weakly dissociated electrolytes with $K_d = 10^{-2}$. The solubility of polyhalide salts in acetonitrile was likewise larger by two orders of magnitude than the solubility of the halides.

1-E POLYHALOGEN COMPLEX CATIONS.

Compounds containing positive polyhalide ions are relatively rare, (Table 1-E-1).

The BrF_2^+ ion was discovered by Emeleus et. al. when studying the electrolysis of BrF_3 (58). This provided strong evidence for the existence of BrF_2^+ ions by experiments in which the ion was titrated conductometrically with BrF_4^- ions. The reaction that takes place during the titration is of the following type.

$$BrF_2^+ SbF_6^- + Ag^+ BrF_4^- \longrightarrow AgSbF_6 + 2BrF_3$$

$BrF_2^+ SbF_6^-$ can be prepared from BrF_3 and SbF_5. In a similar fashion $IF_4^+ SbF_6^-$ can be prepared from IF_5 and SbF_5. Gutmann and Emeleus (63) treated suspensions of finely divided niobium and tantalium in bromine with bromine trifluoride. After refluxing the mixture for a few minutes,

Table 1-E-1.

Polyhalide complex cations.

BrF_2^+
IF_4^+
ICl_2^+
ClF_2^+
$BrICl^+$
IF_2^+
I_2Cl^+

the liquid was removed by pumping, and $BrF_2^+TaF_6^-$ and $BrF_2^+NbF_6^-$ compounds were obtained.

Vonk and Wiebenga (62) prepared $ICl_2^+SbCl_6^-$ and $ICl_2^+AlCl_4^-$ by reaction of $SbCl_5$ and $AlCl_3$ respectively with ICl_3 in an appropriate solvent at 100°C in a sealed tube. Christe and Pavlath prepared Cl_2F^+ compounds. (59) This compound can be made by halide ion transfer from a interhalogen like Cl_3F to a Lewis acid such as SbF_5 or AsF_5. Shamir and Lustig (60) prepared $BrICl^+SbCl_6^-$ by reaction of antimony pentachloride with iodine monochloride followed by addition of chlorine into the reactor vessel at -196°. They also prepared $ICl_2^+SbF_5Cl^-$ using antimony pentafluoride and iodine in the presence of excess chlorine followed by heating at 100°C for about 24 hr. Attempts were made to make ICl_4^+ but the product at the end of the reaction was the ICl_2^+ compound.

Salts of I(III) have been prepared by Fichter and Stern (61). They prepared iodine (III) tri-chloroacetate, $(CCl_3COO)_3I$, by reacting trichloroacetic acid with iodine and acetic anhydride in the presence of fuming nitric acid.

The structure of positive polyhalide compounds has been investigated by X-ray diffraction studies on two compounds containing positive polyhalide ions, namely $ISbCl_8$ and

$IAlCl_6$. They both contain the ICl_2^+ ions and the dimensions determined for this ion in the two compounds are essentially the same.

Unlike the ICl_2^- ion, the ICl_2^+ ion is not linear but bent. It appears from the atomic distances that each ICl_2^+ ion interacts rather strongly with the two Cl atoms of the anions, the latter lying in the plane of the ICl_2^+ ions, thus giving a distorted square planar arrangment about the I atom. The I-Cl distances in ICl_2^+ ion are within the limit of error 2.29Å equal to the sum of the covalent radii of iodine and chlorine 2.33Å , the other two I-Cl distances in the square are very much larger than the sum of the covalent radii 2.89Å , but far smaller than the sum of the van der waals radii 3.95Å .

The ICl_2^+ ion has a V-shape with iodine at the apex and a bond angle of 92° - 95°. The I- I distances are 2.29 and 2.33Å in $SbICl_8$ and 2.26 and 2.29Å in $AlICl_6$. The iodine atoms are also weakly co-ordinated to two chlorine atoms of the $SbCl_6^-$ and $AlCl_4^-$ groups, which raises the possibility of resonance forms.

$$ICl_2^+\ SbCl_6^- \longleftrightarrow ICl_4^-\ SbCl_4^+$$

$$ICl_2^+\ AlCl_6^- \longleftrightarrow ICl_4^-\ AlCl_2^+$$

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CHAPTER 2

RESULTS AND DISCUSSION

2A RESULTS

Experimental values for enthalpies of reaction of tetrachloroiodate salts with aqueous silver nitrate are summarised in Tables 2-A-1 to 2-A-10 together with calculated values of the standard enthalpies of formation.

Enthalpies of aqueous alkaline hydrolysis of the compounds $(C_2H_5)_nNH_{4-n}X$ (1 n 3 ; X = Cl, Br, I) are listed in Tables 2-A-11 to 2-A-19, together with the calculated standard enthalpies of formation.

Appropriate ancillary data are given in Tables 2-A-20 and 2-A-21.

Table 2-A-1.

Enthalpy data for the reaction:

$$3KICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c)$$
$$+ AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3KNO_3 + 12HNO_3)\ (m+q)H_2O \quad (1)$$

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.1492	11450	307.40
0.1335	12796	300.00
0.1386	12326	302.50
0.1405	12159	302.20
0.1493	11442	292.35
0.1338	12768	295.12

Mean $\Delta H_R^\ominus$ = -299.90 ± 5.70 kJ mol^{-1}

$$3\Delta H_f^\ominus KICl_4(c) = 12\Delta H_f^\ominus AgCl(c) + \Delta H_f^\ominus AgI(c) + 2\Delta H_f^\ominus AgIO_3(c) + 3\Delta H_f^\ominus KNO_3$$
$$(3000H_2O) + 12\Delta H_f^\ominus HNO_3(4000H_2O) - 15\Delta H_f^\ominus AgNO_3\ (2000H_2O) - 6\Delta H_f^\ominus H_2O(l)$$
$$- 3\Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20

$\Delta H_f^\ominus KICl_4(c) = -\ 545.00 \pm 6.10$ kJ mol^{-1}

Table 2-A-2

Enthalpy data for the reaction:

$$3KICl_4 \cdot H_2O\ (c) + (p+15)\ AgNO_3\ mH_2O + (q+3)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2\,AgIO_3(c) + (pAgNO_3 + 3KNO_3 + 12HNO_3)\ (m+q)H_2O \quad (2)$$

W/g	dilution, n	$-\Delta H^{\ominus}_R$ kJ mol^{-1}
0.1397	12944	282.30
0.1415	12779	283.00
0.1407	12852	288.00
0.1259	14363	287.45
0.1781	10153	271.43
0.1551	11659	282.08
0.1283	14094	295.50

Mean$\Delta H^{\ominus}_R$ = $\underline{-\ 284.30 \pm 6.80 \text{ kJ mol}^{-1}}$

$$3\Delta H^{\ominus}_f\ KICl_4 \cdot H_2O(c) = 12\Delta H^{\ominus}_f AgCl(c) + \Delta H^{\ominus}_f AgI(c) + 2\Delta H^{\ominus}_f AgIO_3(c) + 3\Delta H^{\ominus}_f KNO_3\ (3000H_2O) + 12\Delta H^{\ominus}_f\ HNO_3\ (4000H_2O) - 15\Delta H^{\ominus}_f\ AgNO_3\ (2000H_2O) - 3\Delta H^{\ominus}_f\ H_2O(l) - 3\Delta H^{\ominus}_R$$

using ancillary data contained in table 2-A-20

$\underline{\Delta H^{\ominus}_f KICl_4\ H_2O(c) = -846.60 \pm 7.10 \text{ kJ mol}^{-1}}$

Table 2-A-3

Enthalpy data for the reaction:

$$3(CH_3)_4\ NICl_2(c) + (p+9)\ AgNO_3\ mH_2O + (q+3)H_2O\ (l) \longrightarrow 6AgCl(c)$$
$$+\ 2AgI\ (c) + AgIO_3(c) + (3(CH_3)_4NNO_3 + 6HNO_3 + pAgNO_3)\ (m+q)H_2O \qquad (3)$$

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.2022	7460	127.71
0.1260	11972	129.00
0.1221	12354	123.34
0.1063	14191	123.46
0.1166	12937	125.47
0.1063	14191	131.43
0.1078	13993	126.30
0.1104	13664	127.09

Mean $\Delta H_R^\ominus = \underline{-\ 126.73 \pm 2.70\ \ kJ\ mol^{-1}}$

$$3\Delta H_f^\ominus\ (CH_3)_4NICl_2(c) = 6\Delta H_f^\ominus\ AgCl(c) + 2\Delta H_f^\ominus AgI(c) + \Delta H_f^\ominus AgIO_3(c)$$
$$+\ 3\Delta H_f^\ominus\ (CH_3)_4NNO_3(aq) + 6\Delta H_f^\ominus\ HNO_3\ (4000H_2O) - 3\Delta H_f^\ominus\ H_2O(l)$$
$$-9\Delta H_f^\ominus\ AgNO_3\ (2000H_2O)\ -3\Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21

$\underline{\Delta H_f^\ominus\ (CH_3)_4NICl_2(c) = -\ 357.40 \pm 3.00\ \ kJ\ mol^{-1}}$

Table 2-A-4

Enthalpy data for the reaction:

$$3\ (CH_3)_4NICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl + AgI + 2AgIO_3(c) + (pAgNO_3 + 3(CH_3)_4NNO_3 + 12HNO_3)\ (m+q)H_2O \qquad (4)$$

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.1393	13654	274.02
0.1258	15119	269.23
0.1356	14026	272.64
0.1257	15131	271.31
0.1393	13654	264.36
0.1260	15095	280.33

Mean $\Delta H_R^\ominus$ = $\underline{-\ 272.00 \pm 6.10\ \text{kJ mol}^{-1}}$

$$3\Delta H_f^\ominus\ (CH_3)_4NICl_4(c) = 12\Delta H_f^\ominus\ AgCl(c) + \Delta H_f^\ominus\ AgI(c) + 2\Delta H_f^\ominus\ AgIO_3(c) + 3\Delta H_f^\ominus\ (CH_3)_4NNO_3\ (aq) + 12\Delta H_f^\ominus\ HNO_3\ (4000H_2O) - 15\Delta H_f^\ominus\ AgNO_3\ (2000H_2O) - 6\Delta H_f^\ominus\ H_2O(l) - 3\Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21

$\underline{\Delta H_f^\ominus\ (CH_3)_4NICl_4(c) = -\ 426.50 \pm 6.20\ \text{kJ mol}^{-1}}$

Table 2-A-5

Enthalpy data for the reaction:

$3(CH_3)_3NHICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c)$
$+ AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3(CH_3)_3NHNO_3 + 12HNO_3)\ (m+q)H_2O$ (5

W/g	dilution, n	$-\Delta H_R^{\ominus}$ kJ mol^{-1}
0.1288	14169	280.00
0.1076	16960	278.60
0.1723	10592	280.55
0.1350	13518	279.41
0.1494	12215	281.55
0.1686	10824	279.40
0.1402	13017	278.67

Mean $\Delta H_R^{\ominus} = -\ 279.74 \pm 1.00$ kJ mol^{-1}

$$3\Delta H_f^{\ominus}(CH_3)_3NHICl_4(c) = 12\Delta H_f^{\ominus}\ AgCl(c) + \Delta H_f^{\ominus}AgI(c) + 2\Delta H_f^{\ominus}AgIO_3(c)$$
$$+ 3\Delta H_f^{\ominus}(CH_3)_3NHNO_3(aq) + 12\Delta H_f^{\ominus}HNO_3\ (4000H_2O) - 15\Delta H_f^{\ominus}AgNO_3\ (2000H_2O)$$
$$- 6\Delta H_f^{\ominus}H_2O(l) - 3\Delta H_R^{\ominus}$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H_f^{\ominus}(CH_3)_3NHICl_4(c) = -\ 429.45 \pm 1.64$ kJ mol^{-1}

Table 2-A-6.

Enthalpy data for the reaction:

$$3(CH_3)_2NH_2ICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + (3(CH_3)_2NH_2NO_3 + 12HNO_3)\ (m+q)H_2O \qquad (6)$$

W/g	dilution, n	$-\Delta H^{\ominus}_R$ kJ mol^{-1}
0.0600	29117	290.26
0.0945	18487	292.50
0.1029	16978	293.45
0.0830	21048	291.40
0.0978	17863	292.27

Mean$\Delta H^{\ominus}_R$ = -292.00 ± 1.70 kJ mol^{-1}

$$3\Delta H^{\ominus}_f(CH_3)_2NH_2ICl_4(c) = 12\Delta H^{\ominus}_f\ AgCl(c) + \Delta H^{\ominus}_f AgI(c) + 2\Delta H^{\ominus}_f AgIO_3(c) + 3\Delta H^{\ominus}_f(CH_3)_2NH_2NO_3(aq) + 12\Delta H^{\ominus}_f HNO_3\ (4000H_2O) - 15\Delta H^{\ominus}_f AgNO_3(2000H_2O) - 6\Delta H^{\ominus}_f H_2O(l) - 3\Delta H^{\ominus}_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H^{\ominus}_f(CH_3)_2NH_2ICl_4(c) = -424.80 \pm 2.00$ kJ mol^{-1}

Table 2-A-7.

Enthalpy data for the reaction:

$$3NH_4ICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c)$$
$$+ AgI(c) + 2AgIO_3(c) + (3NH_4NO_3 + pAgNO_3 + 12HNO_3)\ (m+q)H_2O \qquad (7)$$

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.1558	10213	311.13
0.1258	12648	311.40
0.1492	10665	308.23
0.1532	10386	317.48
0.1326	12000	317.48
0.1624	9798	314.13
0.1621	9816	308.16

Mean $\Delta H_R^\ominus$ = $\underline{-\ 311.82 \pm 3.20 \text{ kJ mol}^{-1}}$

$$3\Delta H_f^\ominus NH_4ICl_4(c) = 12\Delta H_f^\ominus AgCl(c) + \Delta H_f^\ominus AgI(c) + 2\Delta H_f^\ominus AgIO_3(c)$$
$$+ 3\Delta H_f^\ominus NH_4NO_3(aq) + 12\Delta H_f^\ominus HNO_3\ (4000H_2O) - 15\Delta H_f^\ominus AgNO_3\ (2000H_2O)$$
$$- 6\Delta H_f^\ominus H_2O(l) - 3\Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\underline{\Delta H_f^\ominus NH_4ICl_4(c) = -417.20 \pm 3.60 \text{ kJ mol}^{-1}}$

Table 2-A-8.

Enthalpy data for the reaction:

$$3C_2H_5NH_3ICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c)$$
$$+ AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3C_2H_5NH_3NO_3 + 12HNO_3)\ (m+q)\ H_2O\ (8$$

W/g	dilution,n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.1139	15334	300.00
0.1511	11559	301.30
0.1068	16508	296.00
0.1115	15664	307.05
0.1452	12029	299.24
0.1245	14029	297.60
0.2528	6909	295.31

Mean $\Delta H_R^\ominus$ = $\underline{-299.50 \pm 3.80\ \text{kJ mol}^{-1}}$

$$3\Delta H_f^\ominus C_2H_5NH_3ICl_4(c) = 12\Delta H_f^\ominus AgCl(c) + \Delta H_f^\ominus AgI(c) + 2\Delta H_f^\ominus AgIO_3(c)$$
$$+ 3\Delta H_f^\ominus C_2H_5NH_3NO_3(aq) + 12\Delta H_f^\ominus NHO_3\ (4000H_2O) - 15\Delta H_f^\ominus AgNO_3\ (2000H_2O)$$
$$- 6\Delta H_f^\ominus H_2O(l) - 3\Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\underline{\Delta H_f^\ominus C_2H_5NH_3ICl_4(c) = -453.30 \pm 4.50\ \text{kJ mol}^{-1}}$

Table 2-A-9.

Enthalpy data for the reaction:

$$(C_2H_5)_2NH_2ICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \rightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3(C_2H_5)_2NH_2NO_3 + 12HNO_3)\ (m+q)H_2O \qquad (9)$$

W/g	dilution, n	$-\Delta H^\ominus_R$ kJ mol^{-1}
0.0882	21564	299.26
0.1848	10292	296.75
0.0997	19077	306.60
0.1066	17842	305.35
0.0966	19689	303.13
0.1272	14953	301.14
0.1340	14194	302.44

Mean$\Delta H^\ominus_R$ = $\underline{-302.00 \pm 3.30 \text{ kJ mol}^{-1}}$

$$3\Delta H^\ominus_f(C_2H_5)_2NH_2ICl_4(c) = 12\Delta H^\ominus_f AgCl(c) + \Delta H^\ominus_f AgI(c) + 2\Delta H^\ominus_f AgIO_3(c) + 3\Delta H^\ominus_f(C_2H_5)_2NH_2NO_3(aq) + 12\Delta H^\ominus_f HNO_3\ (4000H_2O) - 15\Delta H^\ominus_f AgNO_3\ (2000H_2O) - 6\Delta H^\ominus_f H_2O(l) - 3\Delta H^\ominus_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\underline{\Delta H^\ominus_f\ (C_2H_5)_2NH_2ICl_4(c) = -483.30 \pm 4.10 \text{ kJ mol}^{-1}}$

Table 2-A-10.

Enthalpy data for the reaction:

$$3(C_2H_5)_4NICl_4(c) + (p+15)AgNO_3\ mH_2O + (q+6)H_2O(l) \longrightarrow 12AgCl(c) + AgI(c) + 2AgIO_3(c) + (pAgNO_3 + 3(C_2H_5)_4NNO_3 + 12HNO_3)\ (m+q)H_2O \qquad (10)$$

W/g	dilution, n	$-\Delta H^\ominus_R$ kJ mol^{-1}
0.0767	28850	270.00
0.0761	29077	275.60
0.1067	20738	279.63
0.0959	23074	273.84
0.0930	23793	272.92
0.0823	26887	275.15
0.0747	29622	269.12

Mean $\Delta H^\ominus_R = -\ 273.75 \pm 3.50$ kJ mol^{-1}

$$3\Delta H^\ominus_f(C_2H_5)_4NICl_4(c) = 12\Delta H^\ominus_f AgCl(c) + \Delta H^\ominus_f AgI(c) + 2\Delta H^\ominus_f AgIO_3(c) + 3\Delta H^\ominus_f(C_2H_5)_4NNO_3(aq) + 12\Delta H^\ominus_f HNO_3\ (4000H_2O) - 15\Delta H^\ominus_f AgNO_3\ (2000H_2O) - 6\Delta H^\ominus_f H_2O(l) - 3\Delta H^\ominus_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H^\ominus_f(C_2H_5)_4NICl_4(c) = -\ 574.60 \pm 4.10$ kJ mol^{-1}

Table 2-A-11.

Enthalpy data for the reaction:

$$C_2H_5NH_3Cl(c) + OH^-(aq) \longrightarrow C_2H_5NH_2(aq) + H_2O(l) + Cl^-(aq) \qquad (11)$$

W/g	dilution, n	$+\Delta H_R^\ominus$ kJ mol^{-1}
0.31797	1423	9.74
0.26560	1704	9.77
0.38662	1170	9.65
0.45140	1002	9.65
0.27306	1657	9.63
0.28950	1563	9.61
0.37949	1193	9.64

Mean $\Delta H_R^\ominus = \underline{+9.67 \pm 0.06 \text{ kJ mol}^{-1}}$

$\Delta H_f^\ominus C_2H_5NH_3Cl(c) = \Delta H_f^\ominus C_2H_5NH_2(aq) + \Delta H_f^\ominus H_2O(l) + \Delta H_f^\ominus Cl^-(aq)$
$-\Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\underline{\Delta H_f^\ominus C_2H_5NH_3Cl(c) = -333.90 \pm 0.50 \text{ kJ mol}^{-1}}$

Table 2-A-12.

Enthalpy data for the reaction:

$$(C_2H_5)_2NH_2Cl(c) + OH^-(aq) \longrightarrow (C_2H_5)_2NH(aq) + H_2O(l) + Cl^-(aq) \qquad (12)$$

W/g	dilution, n	$-\Delta H^\ominus_R$ kJ mol^{-1}
0.29367	2068	1.79
0.30793	1973	1.81
0.26387	2302	1.77
0.24441	2485	1.76
0.27672	2195	1.87
0.27766	2188	1.82
0.36516	1663	1.80

Mean$\Delta H^\ominus_R$ = -1.80 ± 0.04 kJ mol^{-1}

$$\Delta H^\ominus_f(C_2H_5)_2NH_2Cl(c) = \Delta H^\ominus_f(C_2H_5)_2NH(aq) + \Delta H^\ominus_f H_2O(l) + \Delta H^\ominus_f Cl^-(aq) - \Delta H^\ominus_f OH^-(aq) - \Delta H^\ominus_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H^\ominus_f(C_2H_5)_2NH_2Cl(c) = -355.40 \pm 0.70$ kJ mol^{-1}

Table 2-A-13.

Enthalpy data for the reaction:

$$(C_2H_5)_3NHCl(c) + OH^-(aq) \longrightarrow (C_2H_5)_3N(aq) + H_2O(l) + Cl^-(aq) \qquad (13)$$

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.17228	4434	9.10
0.22262	3432	8.80
0.22604	3380	8.10
0.22688	3367	8.53
0.23714	3222	8.63
0.20578	3713	8.62
0.42168	1812	8.58

Mean $\Delta H_R^\ominus = \underline{-8.62 \pm 0.29 \text{ kJ mol}^{-1}}$

$$\Delta H_f^\ominus(C_2H_5)_3NHCl(c) = \Delta H_f^\ominus(C_2H_5)_3N(aq) + \Delta H_f^\ominus H_2O(l) + \Delta H_f^\ominus Cl^-(aq) - \Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$$\underline{\Delta H_f^\ominus (C_2H_5)_3NHCl(c) = -387.50 \pm 0.60 \text{ kJ mol}^{-1}}$$

Table 2-A-14.

Enthalpy data for the reaction:

$$C_2H_5NH_3Br(c) + OH^-(aq) \longrightarrow C_2H_5NH_2(aq) + Br^-(aq) + H_2O(l) \qquad (14)$$

W/g	dilution, n	$+\Delta H_R^\ominus$ kJ mol^{-1}
0.50984	1370	16.20
0.28359	2464	16.24
0.32530	2148	16.20
0.44482	1571	16.40
0.35794	1952	16.80
0.38632	1823	16.22
0.44698	1563	15.91

Mean $\Delta H_R^\ominus = \underline{+ 16.28 \pm 0.26 \text{ kJ mol}^{-1}}$

$$\Delta H_f^\ominus C_2H_5NH_3Br(c) = \Delta H_f^\ominus C_2H_5NH_2(aq) + \Delta H_f^\ominus Br^-(aq) + \Delta H_f^\ominus H_2O(l) - \Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\underline{\Delta H_f^\ominus C_2H_5NH_3Br(c) = -294.80 \pm 0.60 \text{ kJ mol}^{-1}}$

Table 2-A-15.

Enthalpy data for the reaction:

$$(C_2H_5)_2NH_2Br(c) + OH^-(aq) \longrightarrow (C_2H_5)_2NH(aq) + Br^-(aq) + H_2O(l) \qquad (15)$$

W/g	dilution, n	$+\Delta H_R^\ominus$ kJ mol^{-1}
0.19701	4336	4.88
0.21414	3989	5.03
0.27536	3102	4.88
0.24480	3489	4.96
0.26836	3183	4.93
0.30833	2770	4.98
0.32499	2628	4.78

Mean $\Delta H_R^\ominus = +4.92 \pm 0.08$ kJ mol^{-1}

$$\Delta H_f^\ominus(C_2H_5)_2NH_2Br(c) = \Delta H_f^\ominus(C_2H_5)_2NH(aq) + \Delta H_f^\ominus Br^-(aq) + \Delta H_f^\ominus H_2O(l) - \Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H_f^\ominus(C_2H_5)_2NH_2Br(c) = -316.50 \pm 0.70$ kJ mol^{-1}

Table 2-A-16.

Enthalpy data for the reaction:

$$(C_2H_5)_3NHBr(c) + OH^-(aq) \longrightarrow (C_2H_5)_3N(aq) + Br^-(aq) + H_2O(1) \quad (16)$$

W/g	dilution, n	$-\Delta H^\ominus_R$ kJ mol^{-1}
0.21778	4636	0.86
0.21110	4782	0.91
0.38289	2637	0.87
0.25876	3902	0.87
0.22996	4390	0.80
0.32756	3082	0.98

Mean $\Delta H^\ominus_R$ = -0.88 ± 0.05 kJ mol^{-1}

$$\Delta H^\ominus_f(C_2H_5)_3NHBr(c) = \Delta H^\ominus_f(C_2H_5)_3N(aq) + \Delta H^\ominus_f Br^-(aq) + \Delta H^\ominus_f H_2O(1) - \Delta H^\ominus_f OH^-(aq) - \Delta H^\ominus_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H^\ominus_f(C_2H_5)_3NHBr(c) = -350.50 \pm 0.10$ kJ mol^{-1}

Table 2-A-17.

Enthalpy data for the reaction:

$$C_2H_5NH_3I(c) + OH^-(aq) \longrightarrow C_2H_5NH_2(aq) + I^-(aq) + H_2O(l) \qquad (17)$$

W/g	dilution, n	$+\Delta H^\ominus_R$ kJ mol^{-1}
0.41013	2340	20.40
0.38673	2481	20.33
0.27848	3446	20.27
0.42505	2258	20.20
0.35815	2679	19.00
0.26707	3593	20.26

Mean $\Delta H^\ominus_R$ = $+20.10 \pm 0.57$ kJ mol^{-1}

$$\Delta H^\ominus_f C_2H_5NH_3I(c) = \Delta H^\ominus_f C_2H_5NH_2(aq) + \Delta H^\ominus_f I^-(aq) + \Delta H^\ominus_f H_2O(l) - \Delta H^\ominus_f OH^-(aq) - \Delta H^\ominus_R$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H^\ominus_f C_2H_5NH_3I(c) = -234.10 \pm 0.80$ kJ mol^{-1}

Table 2-A-18.

Enthalpy data for the reaction:

$$(C_2H_5)_2NH_2I(c) + OH^-(aq) \longrightarrow (C_2H_5)_2NH(aq) + I^-(aq) + H_2O(l) \qquad (18)$$

W/g	dilution, n	$+\Delta H_R^\ominus$ kJ mol^{-1}
0.12810	8704	17.41
0.20109	5545	17.48
0.19662	5671	16.11
0.18811	5927	13.35
0.15119	7375	15.94
0.12534	8896	13.50
0.21140	5274	17.57

Mean $\Delta H_R^\ominus$ = $\underline{+15.90 \pm 1.70 \text{ kJ mol}^{-1}}$

$$\Delta H_f^\ominus(C_2H_5)_2NH_2I(c) = \Delta H_f^\ominus(C_2H_5)_2NH(aq) + \Delta H_f^\ominus I^-(aq) + \Delta H_f^\ominus H_2O(l) - \Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$$\underline{\Delta H_f^\ominus(C_2H_5)_2NH_2I(c) = -263.00 \pm 1.80 \quad \text{kJ mol}^{-1}}$$

Table 2-A-19.

Enthalpy data for the reaction:

$$(C_2H_5)_3NHI(c) + OH^-(aq) \longrightarrow (C_2H_5)_3N(aq) + I^-(aq) + H_2O(l) \qquad (19)$$

W/g	dilution, n	$+\Delta H_R^\ominus$ kJ mol^{-1}
0.17279	7352	1.95
0.16270	7808	1.90
0.20624	6160	1.63
0.15358	8272	2.20
0.14182	8958	2.05
0.12419	10229	2.20

Mean $\Delta H_R^\ominus$ = $+1.99 \pm 0.23$ kJ mol^{-1}

$$\Delta H_f^\ominus(C_2H_5)_3NHI(c) = \Delta H_f^\ominus(C_2H_5)_3N(aq) + \Delta H_f^\ominus I^-(aq) + \Delta H_f^\ominus H_2O(l)$$
$$- \Delta H_f^\ominus OH^-(aq) - \Delta H_R^\ominus$$

using ancillary data contained in tables 2-A-20 and 2-A-21:

$\Delta H_f^\ominus(C_2H_5)_3NHI(c) = -289.00 \pm 0.50$ kJ mol^{-1}

Table 2-A-20

Ancillary data

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}	Ref.
$AgCl(c)$	127.07 ± 0.10	1
$AgI(c)$	61.84 ± 0.10	1
$AgIO_3(c)$	166.20 ± 0.70	2
$KNO_3(3000\ H_2O)$	457.67 ± 0.50	3
$HNO_3(4000\ H_2O)$	207.00 ± 0.46	3
$AgNO_3(2000\ H_2O)$	101.73 ± 0.10	1
$AlCl_3$ (aq)	1033.45 ± 4.00	1
H_2O (l)	285.83 ± 0.04	4
CH_3COOH (3000 H_2O)	487.00 ± 1.00	1
Cl^- (aq)	167.08 ± 0.004	5
Br^- (aq)	121.50 ± 0.004	5
I^- (aq)	56.90 ± 0.01	5
OH^- (aq)	230.02 ± 0.00	5
IO_3^- (aq)	221.33 ± 4.00	5
I_2 (aq)	22.59 ± 0.40	5

Table 2-A-21

Ancillary data

CATION	$-\Delta H_f^\ominus$ kJ mol^{-1}	Ref.
NH_4^+ (aq)	132.51	6(i)
$CH_3NH_3^+$(aq)	124.93	" "
$(CH_3)_2NH_2^+$ (aq)	120.25	" "
$(CH_3)_3NH^+$ (aq)	112.92	" "
$(CH_3)_4N^+$ (aq)	103.34	20
$C_2H_5NH_3^+$ (aq)	156.06	6(i)
$(C_2H_5)_2NH_2^+$ (aq)	188.70	" "
$(C_2H_5)_3NH^+$ (aq)	216.73	" "
$(C_2H_5)_4N^+$ (aq)	248.00	this work.*

AMINE	$-\Delta H_f^\ominus$ kJ mol^{-1}	Ref.
$C_2H_5NH_2$ (aq)	101.25	6(i)
$(C_2H_5)_2NH$ (aq)	134.30	" "
$(C_2H_5)_3N$ (aq)	174.05	" "

(i): Reference 6 has not given the uncertainty for the reported values.

* : Extrapolation procedures (page 82).

The enthalpies of formation of the aqueous cations listed above are based on $\Delta H_f^\ominus H^+(aq) = 0$.

2-B DISCUSSION

The stoichiometries of the reactions in the calorimetric work (equation 1-10) have been thoroughly studied by Cremer and Duncan (7) and Peake (8) who investigated 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. Cremer and Duncan suggested the presence of a reversible equilibrium between the polyhalide ion and its hydrolysis products, for example:

$$5IBr_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Br^- + 6H^+ \quad (20)$$

Similar equilibria were reported for dichloroiodate and tetrachloroiodate compounds:

$$5ICl_2^- + 3H_2O \rightleftharpoons 2I_2 + IO_3^- + 10Cl^- + 6H^+ \quad (21)$$

$$5ICl_4^- + 9H_2O \rightleftharpoons I_2 + 3IO_3^- + 20Cl^- + 18H^+ \quad (22)$$

Quantitative tests gave evidence for the hydrolysis products indicated in equations(20-22) together with undissociated polyhalide ions and the metal cation.

Cremer and Duncan also studied the action of aqueous silver nitrate upon aqueous $KIBr_2$. The following observations were made when $AgNO_3$ (0.1 mol dm^{-3}) 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 completed 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:

$$3KIBr_2(c) + 9AgNO_3(aq) + 3H_2O(l) \longrightarrow 6AgBr(c) + 2AgI(c) + AgIO_3(c) + 3KNO_3(aq) + 6HNO_3(aq) \qquad (23)$$

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 ($K_s AgBr : K_s AgIO_3 = 7.7 \times 10^{-13} : 0.92 \times 10^{-8}$). The removal of Br^- ions from the solution caused the equilibrium to be displaced to the right and I_2 was precipitated with 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:

$$3I_2 + 6Ag^+ + 3H_2O \longrightarrow 5AgI + 6H^+ + 6AgIO_3 \qquad (24)$$

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 also found that $AgNO_3$ reacted in a similar manner with $KICl_4$, and suggested that the reaction followed a similar mechanism. The overall reaction can be represented by the following equation:

$$3KICl_4(c) + 15AgNO_3(aq) + 6H_2O(l) \longrightarrow 12AgCl(c)$$
$$+ AgI(c) + 2AgIO_3(c) + 3KNO_3(aq) + 12HNO_3(aq) \qquad (25)$$

The reaction sequences were observed during the calorimetric reaction experiment with the compounds in Table 2-A-1 to 2-A-10. A mixture of silver halide particles and precipitated iodine was observed when each polyhalide reacted with the calorimetric fluid. The coloration due to iodine was discharged as the reaction proceeded to completion.

Evidence that only AgBr precipitated when $CsIBr_2(c)$ reacted with aqueous $AgNO_3$ with a mole ratio of 1:2 was obtained by Peake (8). Wagman and Kilday (9) have reported enthalpies of precipitation of AgBr, AgI and AgCl from studies of the following reaction:

$$AgNO_3(c) + KX(\infty H_2O) \longrightarrow AgX(c) + KNO_3(\infty H_2O)$$
$$AgNO_3(c) \xrightarrow{\infty H_2O} AgNO_3(\infty H_2O)$$
$$\therefore \quad AgNO_3(\infty H_2O) + KX(\infty H_2O) \longrightarrow AgX(c) + KNO_3(\infty H_2O)$$

These authors suggested that the excellent agreement of values derived from these results with literature values indicate that silver halides formed in the calorimetric experiments were in their thermodynamic standard states. This supports the assumption in the present work that the final states of the silver halides produced in the calorimetric reaction are also in their standard states.

Thermometric titration of aqueous $AgNO_3$ against aqueous $CsIBr_2$ was carried out by Peake (8) to investigate the reaction sequence described by Cremer and Duncan. He observed three distinct breaks corresponding to the precipitation of AgBr, AgI and $AgIO_3$ and the mole ratio of $CsIBr_2/AgNO_3$ was determined.

2-B-1 : $KICl_4(c)$, $KICl_4,H_2O(c)$

The enthalpies of formation of these compounds were determined from the enthalpies of the reaction with excess 0.025 mol dm^{-3} silver nitrate (Tables 2-A-1 and 2-A-2). A prediction of the enthalpy of formation of anhydrous $KICl_4(c)$ was made, based on the lattice energy of this compound and the thermochemical radius of ICl_4^-, together with the enthalpy of formation of gaseous $ICl_4^{-(10)}$; (see page 91 equation (35)). The value obtained from this procedure (-538 kJ mol^{-1}) is in excellent agreement with that obtained experimentally (-545 kJ mol^{-1}).

Reggiani et al (11), have measured the enthalpies of formation of $CuCl_2.2MCl$, $CuCl_2.2MCl,2H_2O$ (M=K, Rb,NH_4) and found that the differences between the enthalpies of formation of anhydrous and hydrated forms of the above salts is ca. 301 kJ mol^{-1} for the addition of each water molecule. On this basis it was estimated that the differences between the enthalpy of formation of anhydrous $KICl_4$(c) and $KICl_4.H_2O$(c) would be 301 kJ mol^{-1}, in good agreement with the observed value of 310 kJ mol^{-1}.

The observed stability of the hydrate, compared with the anhydrous crystal,presumably results from the differences in crystal structure (12); this is discussed in detail by Page (13), but it is clear from the vibrational spectra that the environment of the ICl_4^- ion differs in the two compounds. A simple three-band Raman spectrum of $KICl_4$ with bands at 286 (ν_1,A_{1g}), 260(ν_4,B_{2g}) and 128(ν_2,B_{1g}) cm^{-1} may be readily interpreted in terms of D_{4h} (square planar) point group symmetry, whereas the more complex pattern from the distorted ICl_4^- ion in $KICl_4$, H_2O (together with some coincident IR bands) illustrates the effect of the lower site symmetry. The splittings in the Raman spectrum follow closely those in $SCl_3^+ICl_4^-$ (Form I) (14) in which the ICl_4^- ion has been shown to have a similar distortion (15).

2-B-2 : $Et_n NH_{4-n} X(c)$, X = Cl, Br, I; $1 \leqslant n \leqslant 4$

The enthalpies of formation of mono-,di-and triethylammonium halides have been calculated from the enthalpies of reaction of these compounds with excess sodium hydroxide (0.1 mol dm^{-3}) at 298K. The reaction is similar to that performed by Wilson et al (16).

$$Et_nNH_{4-n}X(c) + O\bar{H}\ (aq) \longrightarrow Et_nNH_{3-n}(aq)$$
$$+ X^-(aq) + H_2O(1) \qquad (26)$$

Results of these measurements are contained in tables 2-A-11 to 2-A-19.

In some previous work by Wilson (16), the enthalpies of formation of mono-,di- and trimethylammonium halides were plotted against the number of methyl groups,n, and a linear decrease with the addition of each methyl group was observed. Thus it was suggested that calculation of the enthalpies of formation of the tetramethylammonium halides could be made by extrapolation. A similar procedure can also be used to calculate the lattice energies of the tetramethylammonium halide salts.

The enthalpies of formation of mono-, di- and triethylammonium halides were plotted against the number of ethyl groups,n. It was observed that with the addition of each ethyl group there was a linear increase in the enthalpy of formation. Hence, the enthalpies of formation of tetraethylammonium halides were calculated by extrapolation (Fig 2-B-I). These results are contained in table 2-B-1.

Of these salts, only$\Delta H_f^\ominus$ $(C_2H_5)_2NH_2Cl(c)$ and $\Delta H_f^\ominus(C_2H_5)_3NHCl(c)$ have been previously reported. Mortimer et al (17 obtained $\Delta H_f^\theta(C_2H_5)_2NH_2Cl(c)$ = - 358.15 ± 0.8 kJ mol^{-1} compared with the value from this work of -355.40 ± 0.70 kJ mol^{-1}. A previous value for $\Delta H_f^\theta(C_2H_5)_3NHCl(c)$ of -385.76 kJ mol^{-1} (18) compared well with the value obtained in this work, -387.50 ± 0.60 kJ mol^{-1}. The uncertainty in the former value has not been reported in reference 18 .

2-B-3: $R_nNH_{4-n}\ ICl_4(c)$, $R=CH_3, C_2H_5$; $1 \leqslant n \leqslant 4$

The enthalpies of formation of methyl- and ethylammonium tetrachloroiodate salts have been calculated from the enthalpies of the reaction of these compounds with excess silver nitrate (0.025 mol dm^{-3}). The calorimetric reaction is as follows:

$$R_nNH_{4-n}\ ICl_4(c) + (p+15)AgNO_3mH_2O + (q+6)H_2O \longrightarrow$$
$$12AgCl(c) + AgI(c) + 2AgIO_3(c) + pAgNO_3 + 3R_nNH_{4-n}NO_3$$
$$+ 12\ HNO_3\ (m+q)H_2O \qquad (27)$$

Experimental values are summarized in tables 2-A-1 to 2-A-10. Of these compounds only $CH_3NH_3ICl_4(c)$ and $(C_2H_5)_3NHICl_4(c)$ were not sufficiently pure for calorimetry, therefore the enthalpies of formation were calculated by extrapolation procedures. Fig 2-B-II, 2-B-III and table 2-B-2. As is shown in Fig. 2-B-II there is hardly any change in the enthalpies of formation with the addition of each methyl group from NH_4ICl_4 to Me_4NICl_4. In the case of ethylammonium tetrachloroiodate (Fig. 2-B-III), with the addition of each ethyl group there is a linear increase in the enthalpy of formation from NH_4ICl_4 to Et_4NICl_4.

The enthalpy of formation of $(C_2H_5)_4N^+(aq)$ was determined by plotting the enthalpies of formation of $NH_4^+(aq)$, $C_2H_5NH_3^+(aq)$, $(C_2H_5)_2NH_2^+(aq)$ and $(C_2H_5)_3NH^+(aq)$ against the number of ethyl groups. A linear increase was observed with the addition of each ethyl group and the enthalpy of formation of aqueous $(C_2H_5)_4N^+$ was calculated by extrapolation Fig. 2-B-IV. This value was used to calculate the enthalpy of formation of $(C_2H_5)_4NNO_3(aq)$ for the reaction (10) page 63 .(See table 2-A-21).

Fig. (2-B-1) Enthalpies of formation of ethylammonium halide against the number of ethyl groups in the cation.

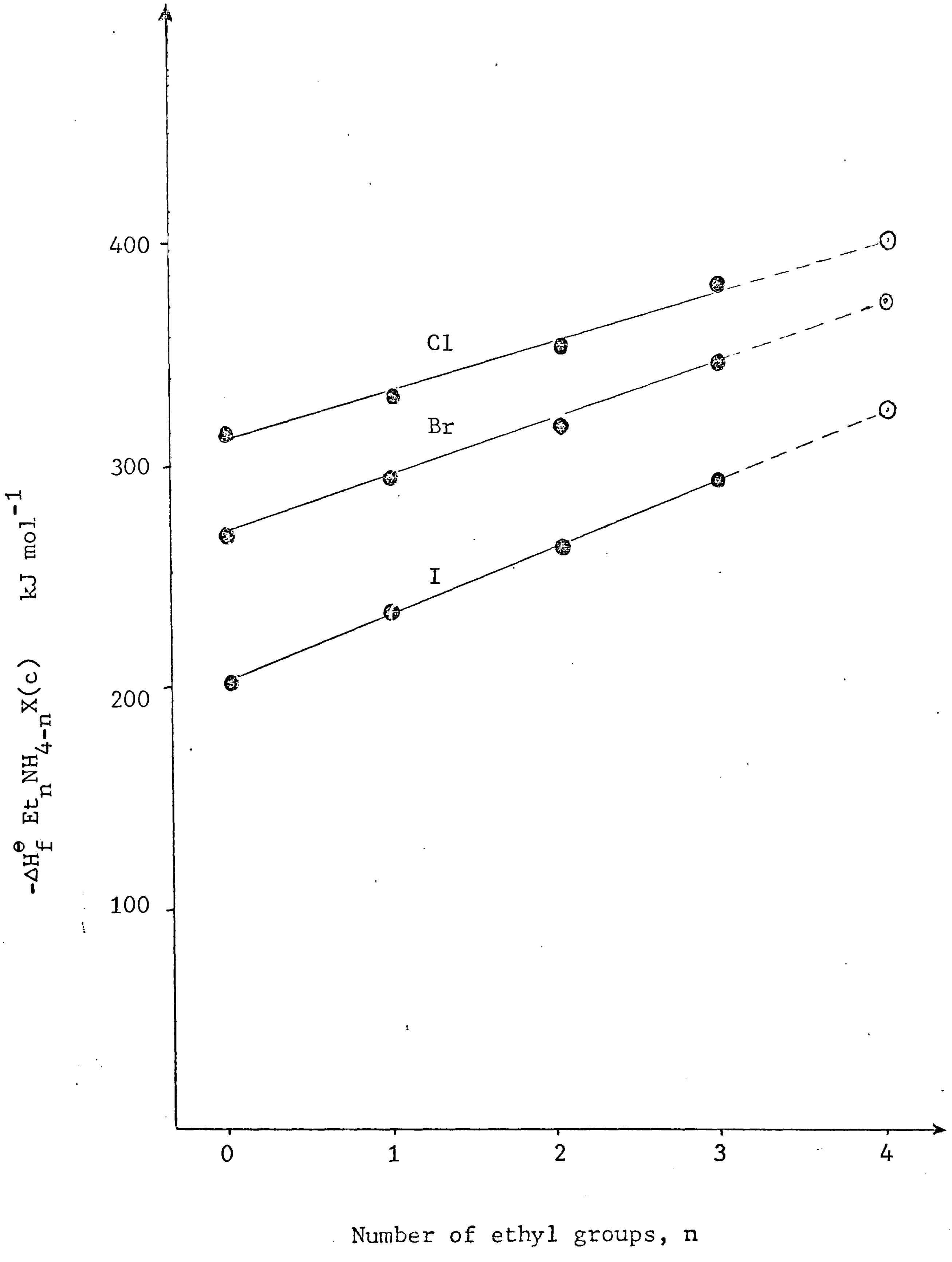


Fig. (2-B-II) Enthalpies of formation of methylammonium tetrachloroiodate against the number of methyl groups in the cation.

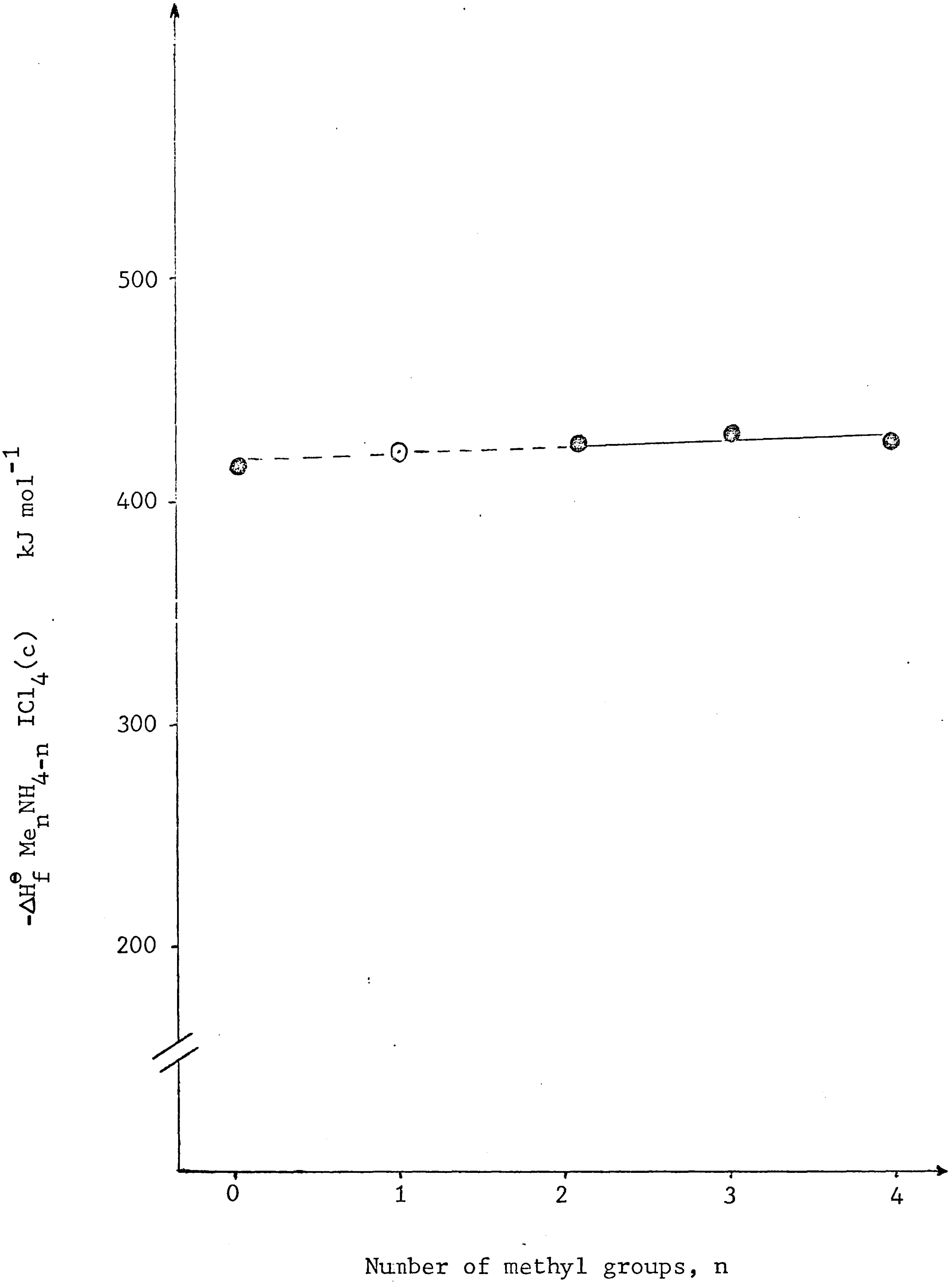


Fig. (2-B-III) Enthalpies of formation of ethylammonium tetrachloroiodate against the number of ethyl groups in the cation.

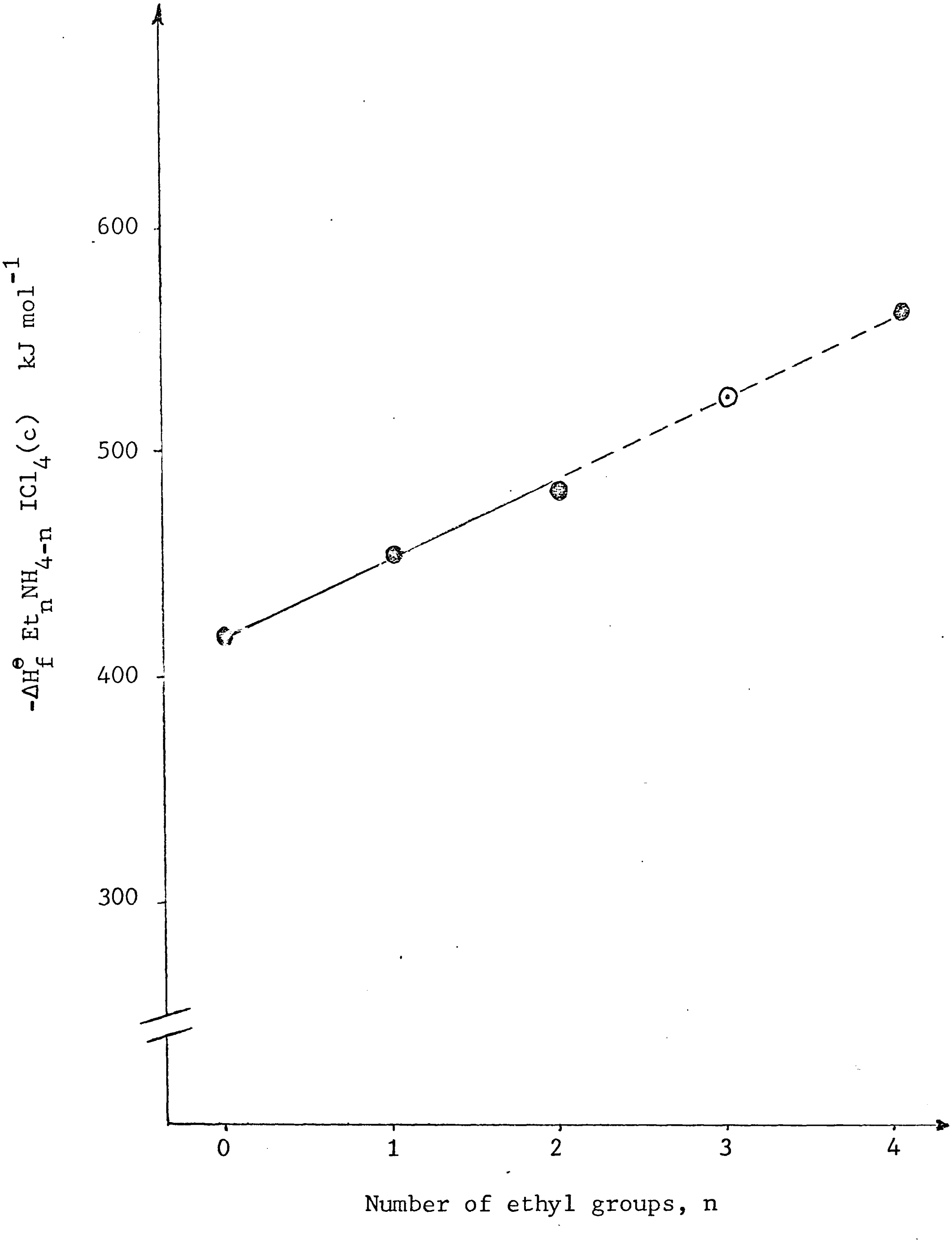


Fig. (2-B-IV) enthalpies of formation of aqueous ethylammonium ions against the number of ethyl groups in the cation.

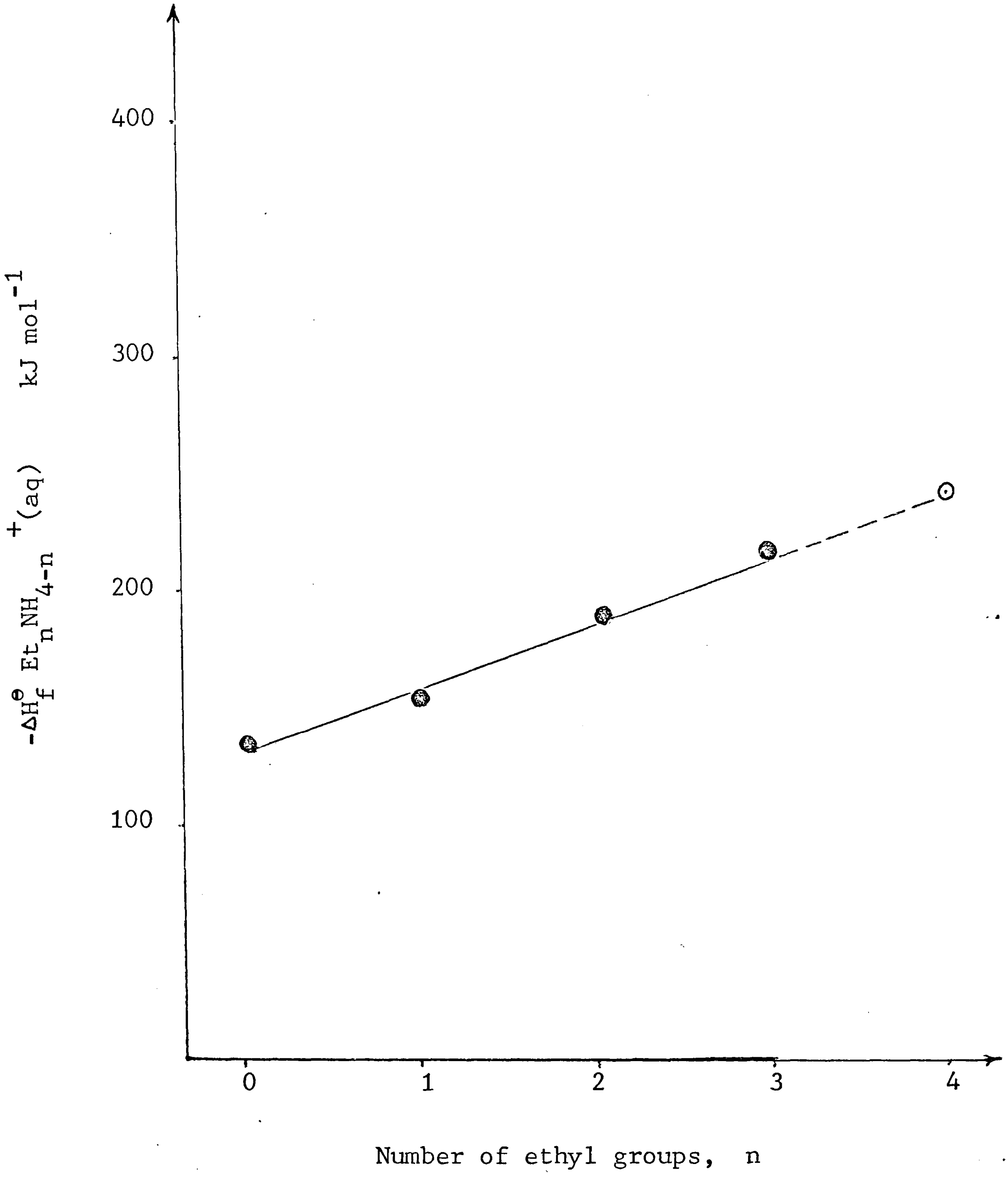


Table 2-B-1.

The enthalpies of formation of ethylammonium halides.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}
$C_2H_5NH_3Cl(c)$	333.90
$C_2H_5NH_3Br(c)$	295.00
$C_2H_5NH_3I(c)$	234.08
$(C_2H_5)_2NH_2Cl(c)$	355.40
$(C_2H_5)_2NH_2Br(c)$	316.50
$(C_2H_5)_2NH_2I(c)$	263.10
$(C_2H_5)_3NHCl(c)$	387.50
$(C_2H_5)_3NHBr(c)$	350.50
$(C_2H_5)_3NHI(c)$	298.00
$(C_2H_5)_4NCl(c)$	414.00 *
$(C_2H_5)_4NBr(c)$	377.00 *
$(C_2H_5)_4NI(c)$	317.00 *

* extrapolation.

Table 2-B-2.

The enthalpies of formation of methyl and ethylammonium tetrachloroiodates.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}
$CH_3NH_3ICl_4(c)$	425.00 *
$(CH_3)_2NH_2ICl_4(c)$	424.80
$(CH_3)_3NHICl_4(c)$	429.45
$(CH_3)_4NICl_4(c)$	426.50
$C_2H_5NH_3ICl_4(c)$	453.30
$(C_2H_5)_2NH_2ICl_4(c)$	483.30
$(C_2H_5)_3NHICl_4(c)$	526.00 *
$(C_2H_5)_4NICl_4(c)$	574.60

* extrapolated value.

2-C : LATTICE ENERGY AND THE ENTHALPY OF FORMATION OF THE GASEOUS CATIONS.

Lattice energies, U_o, of methyl-and ethylammonium halides (Cl, Br, I) have been calculated using the Kapustinskii equation (Appendix I).

$$U_o = \frac{242.8}{(r_c+r_a)} \left[1 - \frac{0.0345}{(r_c+r_a)} \right] \text{kJ mol}^{-1} \qquad (28)$$

where r_c and r_a are the "thermochemical radii" of cation and anion respectively (nanometers). Kapustinskii 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'.

Thermochemical radii of $MeNH_3^+$, $Me_2NH_2^+$, Me_3NH^+, Me_4N^+, $EtNH_3^+$, $Et_2NH_2^+$, Et_3NH^+ and Et_4N^+ cations have been calculated using the Yatsirmirskii method (Appendix I). Consider two salts MX_1 and MX_2 ($M=R_nNH_{4-n}^+$), then:

$$MX_1(c) \longrightarrow M^+(g) + X_1^-(g) \qquad U_1 + 2RT \qquad (29)$$

$$MX_2(c) \longrightarrow M^+(g) + X_2^-(g) \qquad U_2 + 2RT \qquad (30)$$

subtracting (30) from (29) gives:

$$U_1 - U_2 = H_f^{\ominus}X_1^{-}(g) - H_f^{\ominus}X_2^{-}(g) - H_f^{\ominus}MX_1(c) + H_f^{\ominus}MX_2(c) \qquad (3$$

from equation (28)

$$U_1 - U_2 = C\ \frac{1}{r_M^{+} + r_{X_1}^{-}}\left(1 - \frac{0.0345}{r_M^{+} + r_{X_2}^{-}}\right) - \frac{1}{r_M^{+} + r_{X_2}^{-}}\left(1 - \frac{0.0345}{r_M^{+} + r_{X_2}^{-}}\right) \qquad (32)$$

Equation (32) can be expanded to a quartic

$$r^4 + 2r^3(m_1 + m_2) + r^2\left[m_1^2 + m_2^2 + 4m_1m_2 + C(m_1 - m_2)\right]$$
$$+ r\left[2m_1^2m_2 + 2m_1m_2^2 + C(m_1^2 - m_2^2) - 0.069\ C(m_1 - m_2)\right]$$
$$+\left[m_1^2m_2^2 + C(m_1^2m_2 - m_2^2m_1) + 0.0345\ C(m_2^2 - m_1^2)\right] = 0 \qquad (33)$$

$m_1 = r_{X_1}^{-}$, $m_2 = r_{X_2}^{-}$ and $r = r_M^{+}$ and ;

$$C = \frac{242.8}{U_1 - U_2}$$

$U_1 - U_2$ can be calculated from equation (31). Hence the thermochemical radii of the complex cations were found by solving equation (33).

A Hewlett Packard HP-65 programmable calculator was used to solve the above equation (Appendix I). Calculated radii are collected in table 2-C-1.

The lattice energies of the salts contained in table 2-B-1 and 2-B-2 were calculated by substitution of the appropriate thermochemical radius into equation (28). It is difficult to judge the limit of error for these values. A difference of $\pm$ 0.010 nm in the thermochemical radius generates an uncertainty of approximately 6-7 kJ mol^{-1} in the calculated lattice energies. These lattice energies are summarized in tables 2-C-2 and 2-C-3.

Standard enthalpies of formation of the gaseous, $M^+(g)$, cations can now be calculated from the following equation:

$$MX(c) \longrightarrow M^+(g) + X^-(g) \qquad U_o + 2RT \qquad (34)$$

$$\therefore \quad \Delta H_f^\ominus M^+(g) = \Delta H_f^\ominus MX(c) - \Delta H_f^\ominus X^-(g) + U_o + 2RT \qquad (35)$$

The results of these calculations are collected in table 2-C-5 . From the enthalpies of formation of $(CH_3)_nNH_{4-n}$ $ICl_4(c)$, (Table 2-B-2), thermochemical radii of cations have been calculated (Table 2-C-1). These values have been used to calculate the lattice energies of methyl-substituted ammonium halides (Cl,Br,I). Table 2-C-4 contains these values, which are in excellent agreement with the values reported by Wilson (16). The enthalpies of formation of the gaseous methyl-substituted ammonium cations were determined from these lattice energies and compared with values obtained by Wilson (Table 2-C-5).

Lattice energies of methyl- and ethyl- substituted ammonium dichloroiodate, dibromoiodate and tri-iodate can now be calculated from equation (28) using the thermochemical radii of the constituent cation and anion (8) in the compound. Hence, the enthalpies of formation of these compounds have been predicted from equation (8),(tables 2-C-6, 2-C-7 and 2-C-8); all relevant ancillary data were taken from table 2-C-9. With regard to $\Delta H_f^\ominus(CH_3)_4NICl_2(c)$, the estimated enthalpy of formation is in reasonable agreement with the experimental value:

$$\underset{\text{estimated}}{\Delta H_f^\ominus(CH_3)_4NICl_2(c)} - \underset{\text{experimental}}{\Delta H_f^\ominus(CH_3)_4NICl_2(c)} = 12\ \text{kJ mol}^{-1} \qquad (36)$$

This once again gives confidence in the estimation procedure based on lattice energy and thermochemical radii calculation.

The lattice energy of tetraethylammonium halide (Cl, Br, I) or polyhalide salts can be estimated by the extrapolation procedure (16). For example, if the lattice energies of the mono-,di- and tri-ethylammonium tetrachloroiodate are plotted against the number of ethyl groups,because of the linear relationship of these lattice energies with n, it is possible to calculate the lattice energies of the ethyl-substituted ammonium tetrachloroiodate salts simply by extrapolation. Fig. 2-C-1 shows a single example of this kind of plot. As it is seen, there is a small increase in U_o value from NH_4ICl_4 to $C_2H_5NH_3ICl_4$ and then a linear decrease from $C_2H_5NH_3ICl_4$ to $(C_2H_5)_4NICl_4$.

Fig (2-C-1) Lattice energies of ethylammonium tetrachloroiodate against the number of ethyl groups in the cation

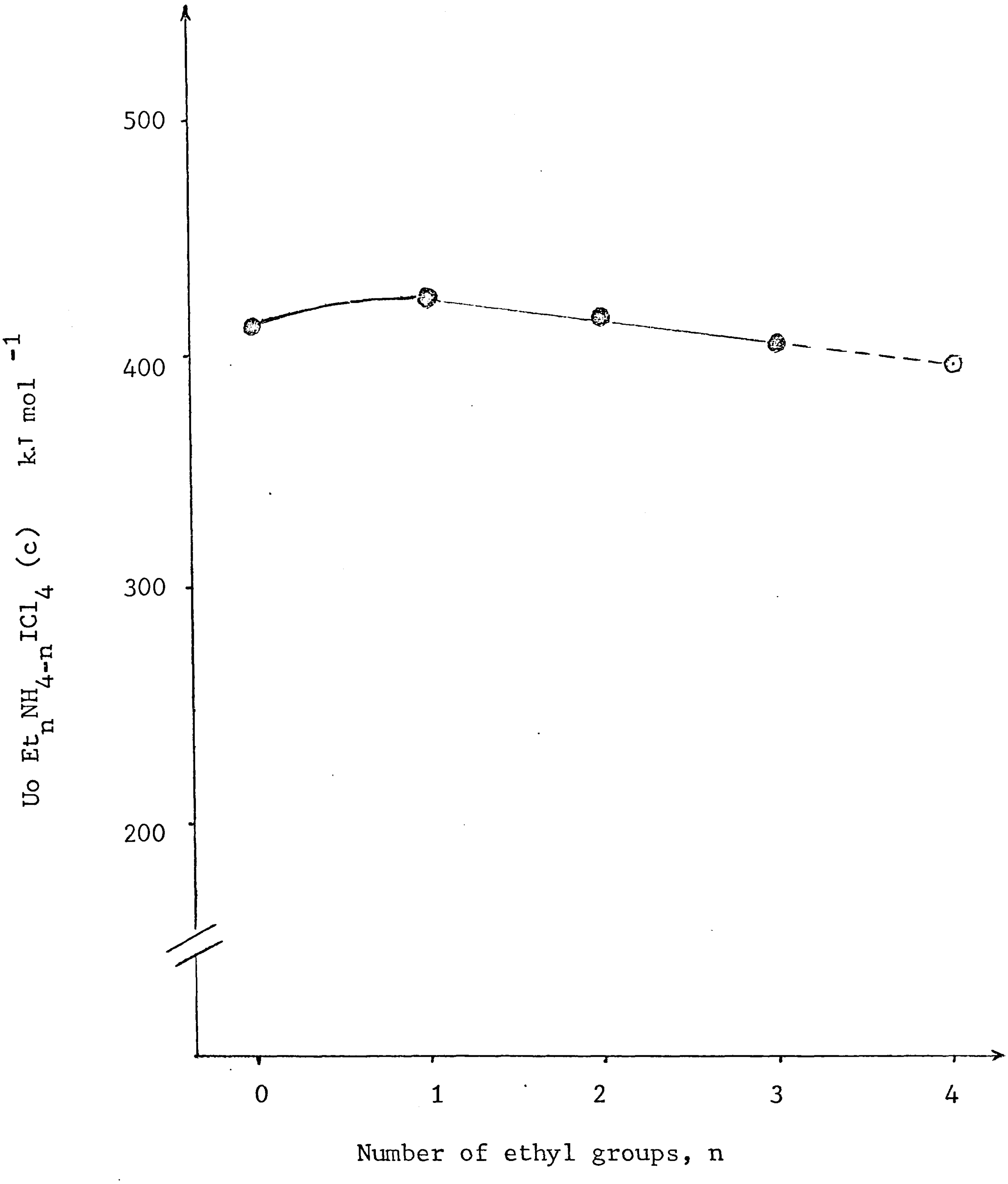


Table 2-C-1

Thermochemical radii of methyl and ethyl substituted cations.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}	Thermochemical radius (n m)
$CH_3NH_3ICl_4$ (c)	425.00	0.140
$(CH_3)_2NH_2ICl_4$ (c)	424.50	0.170
$(CH_3)_3NHICl_4$ (c)	429.45	0.190
$(CH_3)_4NICl_4$ (c)	426.43	0.210
$C_2H_5NH_3ICl_4$ (c)	453.32	0.125
$(C_2H_5)_2NH_2ICl_4$ (c)	483.26	0.135
$(C_2H_5)_3NHICl_4$ (c)	526.00	0.150
$(C_2H_5)_4NICl_4$ (c)	574.63	0.160

Table 2-C-2

Lattice energy and enthalpy of formation of ethylammonium halides.

Compound	Uo kJ mol^{-1}	$-\Delta H_f^\ominus$ MX(c) kJ mol^{-1}
$C_2H_5NH_3Cl$ (c)	704	333.90
$(C_2H_5)_2NH_2Cl$ (c)	684	355.40
$(C_2H_5)_3NHCl$ (c)	660	387.50
$(C_2H_5)_4NCl$ (c)	641	414.00
$C_2H_5NH_3Br$ (c)	677	294.80
$(C_2H_5)_2NH_2Br$ (c)	659	316.50
$(C_2H_5)_3NHBr$ (c)	633	350.50
$(C_2H_5)_4NBr$ (c)	612	377.00
$C_2H_5NH_3I$ (c)	640	234.10
$(C_2H_5)_2NH_2I$ (c)	624	263.00
$(C_2H_5)_3NHI$ (c)	601	289.00
$(C_2H_5)_4NI$ (c)	583	317.00

Table 2-C-3.

Lattice energy and the enthalpy of formation of methyl-and ethylammonium substituted tetrachloroiodate salts.

Compound	Uo/kJ mol^{-1}	$-\Delta H_f^\theta$ MX (c) kJ mol^{-1}
$CH_3NH_3ICl_4$ (c)	412	425.00
$(CH_3)_2NH_2ICl_4$ (c)	392	424.80
$(CH_3)_3NHICl_4$ (c)	380	429.45
$(CH_3)_4NICl_4$ (c)	369	426.50
$C_2H_5NH_3ICl_4$ (c)	423	453.30
$(C_2H_5)_2NH_2ICl_4$ (c)	416	483.30
$(C_2H_5)_3NHICl_4$ (c)	406	526.00
$(C_2H_5)_4NICl_4$ (c)	399	574.60

Table 2-C-4

Lattice energies of methylammonium halides.

COMPOUND	U_o kJ mol^{-1} This work	U_o kJ mol^{-1} Ref.16
$CH_3NH_3Cl(c)$	675	656
$CH_3NH_3Br(c)$	650	629
$CH_3NH_3I(c)$	616	608
$(CH_3)_2NH_2Cl(c)$	624	627
$(CH_3)_2NH_2Br(c)$	602	605
$(CH_3)_2NH_2I(c)$	573	587
$(CH_3)_3NHCl(c)$	594	596
$(CH_3)_3NHBr(c)$	574	579
$(CH_3)_3NHI(c)$	547	565
$(CH_3)_4NCl(c)$	566	566
$(CH_3)_4NBr(c)$	548	553
$(CH_3)_4NI(c)$	524	544

Table 2-C-5.

Calculated enthalpies of formation of gaseous cations.

Cation	$\Delta H_f^\ominus M^+(g)$/ kJ mol^{-1} This work.	$\Delta H_f^\ominus M^+(g)$/kJ mol^{-1} Ref. 16
$CH_3NH_3^+(g)$	624	604
$(CH_3)_2NH_2^+(g)$	604	582
$(CH_3)_3NH^+(g)$	589	559
$(CH_3)_4N^+(g)$	580	536
$C_2H_5NH_3^+(g)$	607	-
$(C_2H_5)_2NH_2^+(g)$	570	-
$(C_2H_5)_3NH^+(g)$	517	-
$(C_2H_5)_4N^+(g)$	462	-

The enthalpies of formation of the gaseous anions e.g. $Cl^-(g)$, $Br^-(g)$ and $I^-(g)$ have been taken from the reference 5 .

Table 2-C-6

Estimated values for the enthalpy of formation and lattice energy of methyl-and ethyl substituted ammonium dichloroiodate salts.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}	U_o kJ mol^{-1}
$CH_3NH_3ICl_2(c)$	363	378
$(CH_3)_2NH_2ICl_2(c)$	365	361
$(CH_3)_3NHICl_2(c)$	371	350
$(CH_3)_4NICl_2(c)$	370	341
$C_2H_5NH_3ICl_2(c)$	389	387
$(C_2H_5)_2NH_2ICl_2(c)$	420	381
$(C_2H_5)_3NHICl_2(c)$	464	372
$(C_2H_5)_4NICl_2(c)$	513	366

Table 2-C-7

Estimated enthalpy of formation and lattice energy of methyl- and ethyl-substituted ammonium dibromoiodate salts.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}	U_o kJ mol^{-1}
$CH_3NH_3IBr_2(c)$	301	418
$(CH_3)_2NH_2IBr_2(c)$	301	398
$(CH_3)_3NHIBr_2(c)$	302	384
$(CH_3)_4NIBr_2(c)$	300	373
$C_2H_5NH_3IBr_2(c)$	333	433
$(C_2H_5)_2NH_2IBr_2(c)$	359	422
$(C_2H_5)_3NHIBr_2(c)$	401	411
$(C_2H_5)_4NIBr_2(c)$	449	404

Table 2-C-8

Estimated enthalpy of formation and lattice energy of methyl- and ethyl ammonium tri-iodate salts.

COMPOUND	$-\Delta H_f^\ominus$ kJ mol^{-1}	U_o kJ mol^{-1}
$CH_3NH_3I_3(c)$	187	334
$(CH_3)_2NH_2I_3(c)$	211	320
$(CH_3)_3NHI_3(c)$	218	312
$(CH_3)_4NI_3(c)$	220	305
$C_2H_5NH_3I_3(c)$	232	344
$(C_2H_5)_2NH_2I_3(c)$	261	336
$(C_2H_5)_3NHI_3(c)$	307	329
$(C_2H_5)_4NI_3(c)$	359	325

Table 2-C- 9

Ancillary data

Anion	radii n m	Reference	$-\Delta H^{\ominus}_{f}$ $X^{-}(g)$ kJ mol^{-1}	Reference
Cl^{-}	0.181	18	246.02	5
Br^{-}	0.195	18	233.89	5
I^{-}	0.216	18	196.60	5
ICl^{-}_{4}	0.412 (a)	8	632.70	8
ICl^{-}_{2}	0.466 (a)	8	604.70	8
IBr^{-}_{2}	0.404 (a)	8	502.30	8
I^{-}_{3}	0.551 (a)	8	490.60	8

a: Thermochemical radius.

The enthalpy of formation data indicate that all methyl- and ethylammonium polyhalides should be thermally stable with respect to their elements at room temperature. However, polyhalides do not generally decompose to their elements, but to the corresponding metal halides (in this case methyl and ethylammonium halide) containing the most electronegative halogen, plus interhalogen or halogen (23), e.g.

$$MICl_2(c) \longrightarrow MCl(c) + ICl\ (g) \qquad (37)$$

$$MIBr_2(c) \longrightarrow MBr(c) + IBr\ (g) \qquad (38)$$

$$MI_3(c) \longrightarrow MI(c) + I_2\ (g) \qquad (39)$$

$$MICl_4(c) \longrightarrow MICl_2(c) + Cl_2\ (g) \qquad (40)$$

Enthalpies of decomposition, $\Delta H^{\ominus}_D$, for processes (37)-(40) were calculated from the enthalpy of formation data, with ancillary data for the standard enthalpy of formation of ICl (g), IBr (g) and I_2 (g) taken from standard sources (5), together with enthalpies of formation of methyl and ethylammonium halides taken from reference (16) and this work respectively. Table 2-C-11 contains these results.

If $\Delta S^{\ominus}$ values were known for processes (37)-(40), then the standard free energy change and hence the equilibrium constants for the decomposition reaction could be calculated. If, for example, the dissociation process:

$$KICl_4(c) \longrightarrow KICl_2(c) + Cl_2\ (g)$$

for which the relevant enthalpy value, $\Delta H^{\ominus}_D$, has been calculated from the relationship $\Delta H^{\ominus}_D \simeq \Delta U(KICl_4 - KICl_2)$ is 26 kJ mol^{-1}, (44) then $\Delta H_D^\ominus = +61$ kJ mol^{-1}. Assuming that entropy contributions from $KICl_4$ and $KICl_2$ will largely cancel, and that the $T\Delta S^\ominus$ term for Cl_2 is + 67 kJ mol^{-1} at ambient temperature $^{(10)}$, then the free energy of dissociation, $\Delta G_D^\ominus = -6$ kJ mol^{-1}, and the equilibrium constant, $K_P = 11$. The observed stability is not unreasonable, since activation barriers to ionic mobility in the solid state are doubtless high. Thermal stability will be strongly temperature-dependent, not only due to the loss of chlorine, but also since the $KICl_2 \longrightarrow KCl+ICl$ dissociation will become significant.

The equilibrium constants for the dissociation processes of methyl- and ethylammonium tetrachloroiodates have been calculated. Assuming that $T\Delta S^\ominus$ for all these dissociation processes is + 67 kJ mol^{-1}, $\Delta G_D^\ominus$ can be calculated from the $\Delta H_D^\ominus$ data and hence the equilibrium constant can be estimated. Table 2-C-12 containes these values. The enthalpies of decomposition of methyl and ethylammonium dibromoiodate and tri iodate have also been calculated. The enthalpies of decomposition for these polyhalides are listed in table 2-C-11.

Hydration enthalpies.

The enthalpies of solvation of methyl- and ethyl-substituted ammonium halides (Cl, Br, I) have been estimated using the following equation:

$$\Delta H^\ominus \text{ solvation} = \Delta H_f^\ominus M^+(aq) + \Delta H_f^\ominus X^-(aq) - \Delta H_f^\ominus M^+(g) - \Delta H_f^\ominus X^-(g) \qquad (41)$$

where $M = (R_nNH_{4-n})$; $1 \leqslant n \leqslant 4$ and X = Cl, Br, I

Table 2-C-11

Calculated enthalpies of decomposition for tetrachloroiodate, dibromoiodate, dichloroiodate and tri-iodate salts.

	$\Delta H_D^{\ominus}$/kJ mol^{-1}			
COMPOUND	X=ICl_4	X=IBr_2	X=ICl_2	X=I_3
CH_3NH_3 X	62.00	82.87	82.21	48.72
$(CH_3)_2NH_2$ X	59.80	84.47	91.41	71.72
$(CH_3)_3NH$ X	58.45	89.07	105.21	77.42
$(CH_3)_4N$ X	69.50	89.27	111.51	73.82
$C_2H_5NH_3$ X	64.30	78.77	72.61	60.34
$(C_2H_5)_2NH_2$ X	63.30	83.27	82.11	60.32
$(C_2H_5)_3NH$ X	62.00	91.27	94.01	71.42
$(C_2H_5)_4N$ X	61.60	112.77	116.51	104.42

Table 2-C-12

Calculated dissociation constant of methyl and ethyl ammonium tetrachloroiodate salts.

COMPOUND	$\Delta H_D^\ominus$ kJ mol^{-1}	$T\Delta S^\ominus$ kJ mol^{-1}	$\Delta G_D^\ominus$ kJ mol^{-1}	K
$CH_3NH_3ICl_4$	62.00	67.00	-5.00	7.40
$(CH_3)_2NH_2ICl_4$	59.80	67.00	-7.20	17.80
$(CH_3)_3NHICl_4$	58.45	67.00	-8.55	30.57
$(CH_3)_4NICl_4$	56.00	67.00	-11.00	81.45
$C_2H_5NH_3ICl_4$	64.30	67.00	-2.70	2.94
$(C_2H_5)_2NH_2ICl_4$	63.30	67.00	-3.70	4.40
$(C_2H_5)_3NHICl_4$	62.00	67.00	-5.00	7.40
$(C_2H_5)_4NICl_4$	61.60	67.00	-5.40	8.00

These solvation enthalpies have been used to obtain the single ion hydration enthalpies of methyl-and ethyl-substituted ammonium cations. Table 2-C-13 contains these values.

The single ion hydration enthalpies can also be estimated using the Born equation (41), in which the change in Gibbs' free energy on transferring a gaseous ion is calculated from the following expression:

$$\Delta G^{\ominus} = \frac{-N_A Z^2 e^2}{8\pi \varepsilon_o r} \left(1 - \frac{1}{D}\right)$$

where N_A is the Avogadro number, Z is the charge of the ion, e is the electronic charge, ε_o is the permittivity of free space, r is the radius of the ion and D is the bulk dielectric constant of the medium. The entropy change is given by differentiation with respect to temperature:

$$\Delta S^{\ominus} = \frac{N_A Z^2 e^2}{8\pi \varepsilon_o D r} \left(\frac{\partial \ln D}{\partial T}\right)$$

Therefore the corresponding enthalpy of transfer of the ion from the gas phase to the medium of dielectric constant D may be calculated. In practice, cation values obtained from this method agree more closely with those obtained from experiment if the cation radius r, (from crystal measurements) is replaced by an effective radius r_{eff}, equalling r + 0.85 (A^o) (42).

The hydration enthalpies of alkali metal (43) and tetramethyl- and tetraethyl ammonium cations have been plotted (Fig. 2-C-2) against the reciprocal r_{eff}, (for tetramethyl-and tetraethyl-ammonium cations the values used were , $r_c + 0.85$ A^o where r_c

is the radius of the circumscribing sphere of the cations) and a straight line obtained. In additional calculations, the radii of the circumscribing spheres of the propyl and butylammonium cations have been computed (6.08 and 7.38 A^{o} respectively) and approximate enthalpies of hydration of these cations have been predicted by appropriate extrapolation as 100 and 80 kJ mol^{-1} respectively, Figure 2-C-2. Since the charge density is inversely proportional to the square of the radius of the circumscribing sphere, a significant weaking of the electrostatic interaction between the cation and the surrounding water molecules would be expected as the radius increases.

Table 2-C-13.

Single ion hydration enthalpies

Cation	Radius Å (P)	$-\Delta H^{\ominus}$hyd./kJmol^{-1} From equation(41)	$-\Delta H^{\ominus}$hyd./kJmol^{-1} From Born equation
Li^+	0.60	-	481
Na^+	0.95	-	389
K^+	1.33	-	320
NH_4^+	1.48	-	300
Rb^+	1.48	-	300
Cs^+	1.69	-	276
$CH_3NH_3^+$	-	291	-
$(CH_3)_2NH_2^+$	-	266	-
$(CH_3)_3NH^+$	-	244	-
$(CH_3)_4N^+$	(3.35)*	225	167
$C_2H_5NH_3^+$	-	305	-
$(C_2H_5)_2NH_2^+$	-	301	-
$(C_2H_5)_3NH^+$	-	278	-
$(C_2H_5)_4N^+$	(4.77)*	252	125

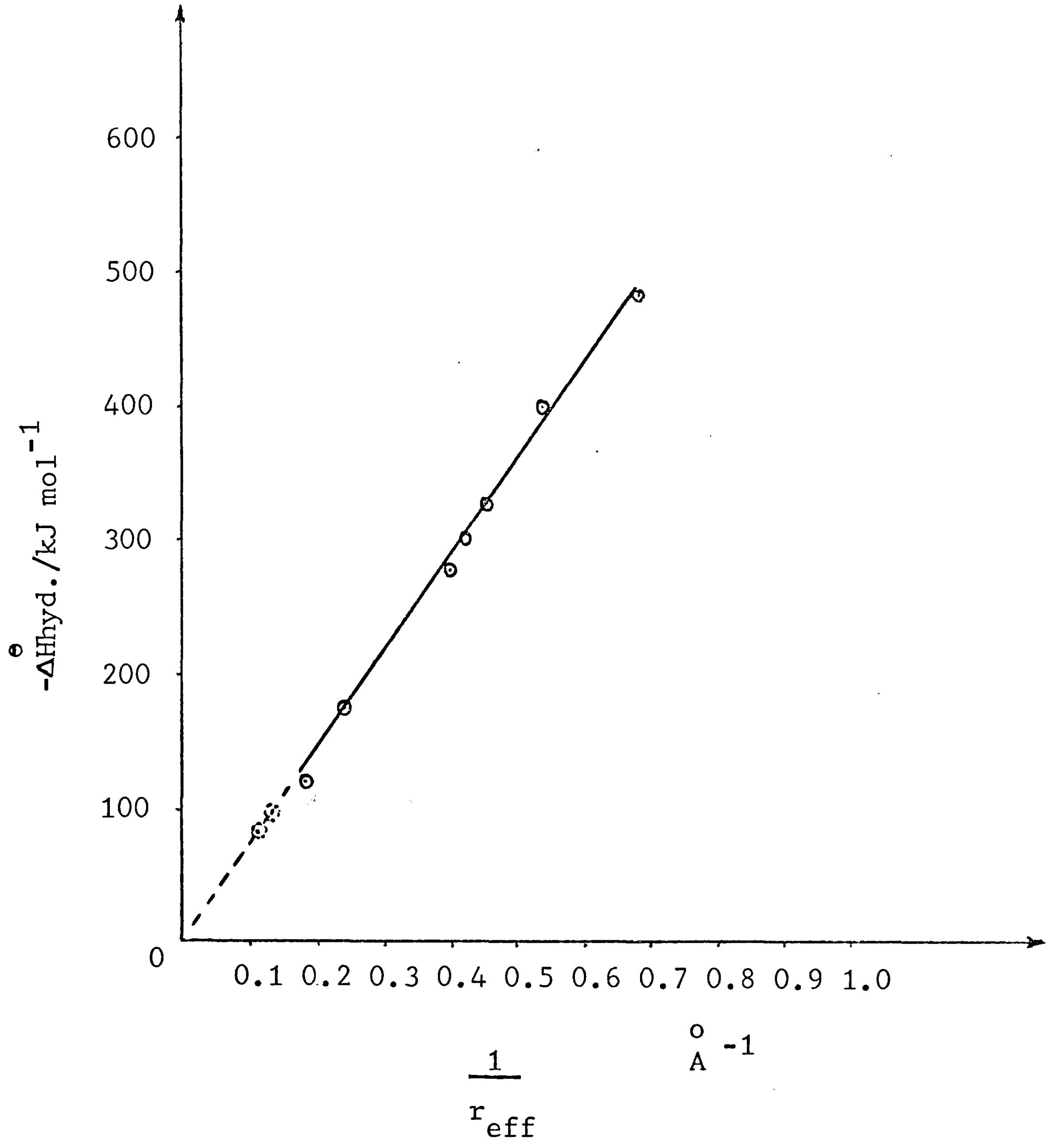
(P) = Pauling radius.

* = radius of the circumscribing spheres calculated in this work.

The hydration enthalpies of the anions e.g. Cl^-, Br^- and I^- have been taken from the reference 45 .

Fig 2-C-2

Plot of the enthalpies of hydration against $\frac{1}{r_{eff}}$:



2-D Proton Affinity

Proton-transfer reactions are among the most important classes of chemical reactions and have been studied extensively in solution over a long period of time.

Studies of such processes in the gas-phase are much less common. High pressure (<u>ca</u> 1 10^{-5} torr)[19] mass spectrometer sources were first used to study proton-transfer reactions in the gas phase. By assuming that exothermic proton transfers occurred rapidly in the gas phase, these studies were used, qualitatively and semiquantitively, to determine relative gas-phase basicities and proton affinities of various molecules. The gas-phase basicity (GB) is defined as the negative of the free energy change for the protonation reaction (1), while the proton affinity (PA) is the negative of the enthalpy change for reaction (1).

$$A(g) + H^+(g) \longrightarrow AH^+(g) \qquad (1) \qquad \begin{aligned} -\Delta G^o(g) &= GB(A) \\ -\Delta H^o(g) &= PA(A) \end{aligned}$$

$$AH^+(g) + B(g) \longrightarrow A(g) + BH^+(g) \qquad (2) \qquad \begin{aligned} \Delta G^o(g) &= GB(B)-GB(A) \\ \Delta H^o(g) &= PA(B)-PA(A) \end{aligned}$$

Thus, the magnitude of the proton-transfer reaction (2) gives the relative gas-phase basicities of A and B.

Munson (21) determined the relative basicities of ammonia and the methylamines in the gas phase by high-pressure mass spectrometer techniques. Later Beauchamp and Butrill (22) and Brauman and Blair (23) established relative basicities for some organic bases in the gas phase. The above authors observed that the order of gas-phase basicities of the methylamines was

$[NH_3] < MeNH_2 < Me_2NH < Me_3N$. This order differs from that observed in aqueous solution : $[NH_3] < Me_3N < MeNH_2 < Me_2NH$.

Ion-molecule reactions in the gas phase were first studied under equilibrium conditions in a high-pressure mass spectrometer by Kebarle and Godbole (24). Equilibrium constants for proton-transfer reactions were first measured by Bowers, Webb and Aue (25) using an ion cyclotron resonance drift cell at high pressures (10^{-4} - 10^{-3} torr).

Techniques for measurement of Proton Affinities

There are several techniques for measurement of proton affinities. Measurements of equilibrium constants for proton-transfer reaction (2) give free energies equal to the difference in the gas-phase basicities of the molecules A and B. These free energies differ from enthalpies for proton transfer by a $T\Delta S^{o}$ term. In a few cases these entropy terms have been determined by measuring equilibrium constants over a wide range of temperature using a variable-temperature high-pressure mass spectrometer (26) and variable-temperature ion cyclotron resonance drift and trapped ion cells (these techniques will be discussed later). In such measurements the entropy terms for proton-transfer reaction have been very small except in cases where intermolecular hydrogen bands are formed.

A- Absolute Proton Affinities

Since the measurement of proton-transfer equilibrium constants can give relative gas phase bacisities and proton affinities, only a few experimentally determined absolute proton affinities are required in order to set up a scale of absolute proton affinity values. Where absolute proton affinities have been measured for several compounds related by a series of proton-transfer equilibrium measurements, the absolute and relative proton affinity data may be compared to give a valuable check on the consistency of these independent measurements. Absolute proton affinities have been most often measured by appearance potential measurements to give enthalpies of formation of positive ions derived from proton-or electron - impact induced molecular fragmentation on radical ionisation. Ceyer et al (27) have measured the absolute proton affinity of NH_3 (851.86 ± 5.40)kJ mol^{-1} using the molecular beam-photoionisation technique (28). This value is in good agreement with the value previously reported by Wolf et. al. (29) of 846.40 kJ mol^{-1}. On the basis of such measurements for the enthalpy of formation of t-butyl cation and ammonium ion, Aue et al (30), have assigned the proton affinity scale, such that the proton affinity of isobutene is 823.80 kJ mol^{-1} and that of ammonia is 857.70 kJ mol^{-1} These absolute proton affinity assignments are somewhat arbitrary and agree only within error limits of several kJ mol^{-1}. Absolute proton affinities from appearance potential measurements may suffer from errors in enthalpies of formation of the molecules and radicals involved. In addition the enthalpies of formation must be corrected from OK to 298K by estimation of heat capacity changes. As a result, the absolute assignment of proton affinity scale is still in doubt and errors up to several kJ mol^{-1} are possible.

B- Ion cyclotron Resonance spectrometry

Ion cyclotron resonance spectorscopy is based on the dynamics of charged particles in magnetic and electric fields(31). For example, a swarm of ions of a given mass produced by electron impact, will have a distribution of velocities but a sharp cyclotron frequency, which depends only on mass, electric charge and magnetic field. If ions are generated between a pair of parallel plates in a magnetic field and an alternating electric field is applied normal to the magnetic field at a known frequency, the ions absorb energy from alternating the electric field and are accelerated to larger velocities and orbital radii. An absorption of energy is reflected as a change in the power required from the source of energy. The absorption of energy by a swarm of ions can thus be detected if an oscillator which is extremely sensitive to changes in load is used as the source of energy.

There are several methods for measuring relative proton affinities using the ion cyclotron resonance spectroscopy.

(a) Drift-Cell Ion Cyclotron Resonance Spectrometry

In this method, a signal results when the cyclotron frequency of an ion equals the frequency of the marginal oscillator detector. At this point the ions of a particular mass and charge are in resonance, and they absorb power from the marginal oscillato in a fixed magnetic field. The power absorbed is proportional to the number of ions and is thus a measure of ion intensity. The relative intensities of ions in an ICR cell can be measured in two ways. The first involves operating the marginal oscillator at constant frequency and varying the magnetic field. The cyclotron frequency of an ion is directly proportional to the magnetic field. As the magnetic field is varied, ions of different masses come into resonance. In the second method, the instrument is operated at a constant magnetic field and the frequency of the marginal oscillator is varied until it matches the cyclotron frequency of an ion.

(b) Trapped-Ion-cell Ion cyclotron Resonance spectrometry

In trapped-ion-cell spectrometry, the ions do not drift out of the cell within a few milliseconds as in the drift cell. Instead, they are trapped within the cell for periods in excess of 1000 msec. Such long ion trapping times permit hundreds of collisions to occur and result in proton-transfer equilibrium at lower pressures (ca (1-4)X10^{-6} torr) than in the drift cell. At higher pressures, however, ion loss from the trapped ion becomes a major problem, so that the total number of ion-molecule collisions attainable is comparable to that in the drift cell. Absolute pressure measurement in the trapped ion cell must be accomplished indirectly using an ion gauge calibrated against a capacitance manometer at higher pressures. An example of an experimental equilibrium constant determination by this technique for the azetidine – pyrrolidine give good agreement with the value obtained from drift-cell measurements.

(c) High-pressure mass spectrometry

This technique has more recently been applied to proton-transfer equilibria by Kebarle's group (32) and its application to proton-transfer reactions has been reviewed recently by Kebarle (33). The method involves generation and reaction of ions in a field-free high-pressure region and diffusion of the ions through a small slit into a low-pressure region where they are accelerated and mass analysed. A potential problem with this technique is that the need to sample the thermal reaction mixture for mass spectral analysis could lead to artifacts such as collisional decomposition of proton-bound dimers. Such problems can be largely avoided, however, and the high-pressure mass spectrometric technique has the advantage of a large sensitivity range, which makes possible the measurement of larger equilibrium constants than by ion cyclotron resonance techniques.

(d) Flowing afterglow techniques

The flowing afterglow technique involves a fast helium flow system at 0.5 torr in a reaction tube. Ions are generated by electron impact from gases introduced into the helium flow upstream from the filament. The ions generated can react with other neutral molecules introduced through nozzles downstream. Further downstream the ions can be sampled through an orifice which leads to a quadrupole mass filter. In this method the rate constant is measured and from the rate constants of the forward and reverse reactions of an equilibrium. The equilibrium constant may be obtained, or the equilibrium constant may be measured directly at sufficiently high pressures of reactant gases. Such measurements have been the source of relative proton affinities for molecules of low basicity such as N_2, H_2, CO, CO_2, CH_4 and C_2H_6 (34).

(e) Variable-Temperature Equilibrium Measurements

The temperature dependence of proton-transfer equilibrium constants has been measured by Yamdogni and Kebarle (26) using variable temperature high-pressure mass spectrometry. From such measurements, the entropy change for proton-transfer between organic amines are found to be generally very small. In the case of α,ω - diaminoalkanes, however, the entropy changes are large because of the entropy loss on forming cyclic intramolecularly hydrogen bonded structures for the ammonium ions. Entropy terms for many ionic clustering reactions have also been determined by high-pressure mass spectrometry (35). Variable temperature ion cyclotron resonance drift- and trapped-ion - cell.instruments have been recently developed by Wren (36) for the measurement of rate and equilibrium constants.

The above methods are complex and involve high energy processes and expensive equipment; therefore it would be practically important if an alternative method could be used which might serve as a check. The most useful application of proton affinity is to determine the enthalpy of formation of the gaseous ions and the basicity of a molecule in the gas phase.

The proton affinity can be expressed by the following thermodynamic cycle for the methyl-and ethyl-substituted ammonium halide salts;

$R = CH_3 \ , \ C_2H_5$

$$\begin{tikzcd}
R_n\,NH_{3-n}(g) + H^+(g) + X^-(g) \arrow[rr, "PA(R_nNH_{3-n})"] & & \left[R_nNH_{4-n}\right]^+(g) + X^-(g \\
\\
\text{ELEMENTS} \arrow[uu, "{\Delta H_f^\ominus\left[R_nNH_{3-n}\right](g) \quad \Delta H_f^\ominus\left[H^+\right](g) \quad \Delta H_f^\ominus\left[X^-\right](g)}"] \arrow[rr, "\Delta H_f^\ominus R_nNH_{4-n}X(c)"] & & R_nNH_{4-n}X(c) \arrow[uu, "U"']
\end{tikzcd}$$

From the cycle;

$$PA\left(R_nNH_{3-n}\right) = \Delta H_f^\ominus\left[R_nNH_{3-n}\right](g) + \Delta H_f^\ominus\left[H^+\right](g) + \Delta H_f^\ominus\left[X^-\right](g) - \Delta H_f^\ominus\left[R_nNH_{4-n}\right]X(c) - U \qquad (42)$$

For methyl and ethylammonium salts the enthalpies of formation of the amine in the gas phase are known (6) and the enthalpy of formation of the $\left[H^+\right](g)$ and $\left[X^-\right](g)$ species have been reported in the literature (5). The enthalpy of formation of methyl-and ethyl-substituted ammonium halides (Cl, Br, I) salts have been investigated by Wilson (16) in addition to this work and the lattice energies of these compounds have been calculated. The lattice energies of the ethyl-substituted ammonium halides were calculated using the Kapustinskii/Yatsimirskii approach via thermochemical radii of the related cations (page 89). By inserting these values in equation (42) the proton affinities of the relevant amine have been calculated. Table 2-D-1 contains these values compared with values already reported (30). In this table, values obtained by the current thermochemical method are in excellent agreement with the values reported by other investigators (37,38). The errors in this procedure can be due to the errors involved in the enthalpies of formation of the participants in equation (36) used for calculating the proton affinity of a particular amine. For example, in the case of di-ethylamine the error can be due to the uncertainty in the value of the $\Delta H_f^\ominus C_2H_5NH_2X(c)$ (X=Cl, Br, I) , $\Delta H_f^\ominus X^-(g)$ (Cl^-, Br^-, I^-) and $\Delta H_f^\ominus$ H^+ (g). The errors due to the lattice energy calculation have been described in page (91).

Table 2-D-1.

Proton affinities of methyl and ethyl amines.

Amine	(PA)/kJ mol^{-1} this work	Ref. (38)
NH_3	865	858
CH_3NH_2	893	896
$(CH_3)_2NH$	920	922
$(CH_3)_3N$	930	938
$C_2H_5NH_2$	890	908
$(C_2H_5)_2NH$	900	942
$(C_2H_5)_3N$	930	967

Table (2-D-2)

Ancillary data

COMPOUND	$-\Delta H_f^\ominus$/kJ mol^{-1} Ref.(6)
CH_3NH_2 (g)	22.97
$(CH_3)_2NH$ (g)	18.45
$(CH_3)_3N$ (g)	24.31
$C_2H_5NH_2$ (g)	47.15
$(C_2H_5)_2NH$ (g)	71.42
$(C_2H_5)_3N$ (g)	95.81

ion	$-\Delta H_f^\ominus$/kJ mol^{-1} (Ref 5)
H^+ (g)	-1536.20
Cl^- (g)	246.02

2-E Iodine (III) Compounds.

Little information concerning iodine (III) compounds is available. Apart from iodine trichloride, ICl_3, thermochemical data for iodine (III) compounds are non-existent. In this section, measurements of standard enthalpies of formation for ICl_3 (c) and two other iodine (III) species, ICl_2AlCl_4 and $I(CH_3COO)_3$ have been made, via the enthalpies of aqueous hydrolysis.

2-E (a) ICl_3 (c)

The standard enthalpy of formation of ICl_3 has been measured previously by Lamoreaux and ~~Giauque~~ (39) from heat capacity measurements over the temperature range 15-320 K as -89.29 ± 0.60 kJ mol^{-1}. This value has been used as a check on the validity of the hydrolysis reaction employed in the present work:

$$5ICl_3(c) + 9H_2O(l) \longrightarrow I_2(aq) + 3IO_3^-(aq) + 18H^+(aq) + 15Cl^-(aq) \qquad (43)$$

An ampoule containing powdered ICl_3 was broken into $100cm^3$ of water as in previous experiments. Experimental enthalpies of hydrolysis are listed in table 2-E-a. The enthalpy of formation of $ICl_3(c) = -89.89 \pm 1.85$ kJ mol^{-1} calculated on the basis of equation (43) is in excellent agreement with the value reported by Giauque et al (39). The good agreement between these two independent values can be regarded as supporting evidence for equation (43).

The reaction of ICl_3 with silver nitrate was also investigated. The following equation for this reaction is proposed:

$$3ICl_3(c) + 12AgNO_3(aq) + 6H_2O(l) \longrightarrow 9AgCl(c) + AgI(c) + 2AgIO_3(c) + 12HNO_3(aq) \qquad (44)$$

Confirmation of the stoichiometry of reaction (44) was sought by titration of the nitric acid produced in the reaction. The acid was first neutralized with a known excess of sodium hydroxide (0.1 mol dm^{-3}) and then the excess sodium hydroxide was back titrated with hydrochloric acid (0.1 mol dm^{-3}) (table 2-E-b). The results confirmed the production of 12 moles of nitric acid. This is consistent with equation (44).

In a further experiment, a thermal titration of $ICl_3(c)$ against $AgNO_3(aq)$ was employed to investigate the mechanism of reaction (44). The experimental procedure is described in Chapter 3, page 170 . A known weight of $ICl_3(c)$ was dissolved in 100 cm^3 of water in the calorimetric vessel and $AgNO_3$ (1.0 mol dm^{-3}) was introduced at a constant flow rate via a 10 cm^3 syringe connected by polythene tubing to the reaction vessel, temperature change being monitored on a chart recorder. Three distinct breaks in the curve were observed, due to the successive precipitation of AgCl, AgI and $AgIO_3$. The overall mole ratio of $AgNO_3/ICl_3$, corresponding to equation (44), may be calculated from the titration curve (Fig. 2-E-1). The first break is assigned to the precipitation of AgCl up to the mole ratio of 3.00:1. Iodine then reacted with silver nitrate from a mole ratio of 3.00:1 to 3.33:1 to give AgI and iodate ions. Finally, silver iodate was precipitated from a mole ratio of 3.33:1 to the end point of the titration. To calibrate the reaction, the heater was switched on to give a chart displacement appropriate to the reaction displacement (Fig. 2-E-2) and the enthalpies of formation of AgCl(c) and $AgIO_3$(c) were calculated from the reaction and calibration curves. Calculation of the enthalpy of formation of $AgIO_3$(c) is not very accurate, since the heat evolved from the final step is relatively small. It was not possible to monitor the heat produced from the reaction of silver with iodide ions because of the small amount of iodide ions present. The results of these measurements are compared with the literature values, in Table 2-E-2, and show good agreement, thus lending support to the above interpretation.

2-E (b) Iodine-tri acetate $(CH_3COO)_3I$ (III)

The standard enthalpy of formation of iodine tri-acetate has been calculated from measured enthalpies of aqueous hydrolysis. The calorimetric reaction proposed (by analogy with ICl_3) is as follows:

$$5(CH_3COO)_3I(c) + 9H_2O(l) \longrightarrow I_2(c) + 3IO_3^-(aq) + 15CH_3COO^-(aq$$
$$+ 18H^+(aq) \qquad (45)$$

Attempts to check the validity of this equation have been made using the following experiments:

(1) A known weight of $(CH_3COO)_3I$ was dissolved in water and the total acid titrated using aqueous sodium hydroxide (0.1 mol dm^{-3}). The hydrolysate is expected to consist of a strong acid (HIO_3) and a weak acid (CH_3COOH) in the relative proportions 1:5. A polentiometric titration of this mixture shows <u>one</u> end point, corresponding to the total acid content, This is discussed further in appendix IV. A similar, synthetic, mixture of HIO_3 and CH_3COOH showed identical behaviour, corresponding to the total acid content. The total acid determined thus is consistent with the equation (45), (Table 2-E-3).

(2) As a further check of equation (45) the iodine produced was extracted with carbon tetrachloride and a known excess of sodium thiosulphate (0.1 mol dm^{-3}) added. Back titration of the thiosulpate with standard iodine solution (0.1 mol dm^{-3}) yielded a value for iodine in good agreement with that predicted by equation (45), (table 2-E-3).

Enthalpies of aqueous hydrolysis were measured by breaking ampoules containing approximately 0.2g of iodine triacetate into 100 cm^3 of distilled water and the standard enthalpy of formation calculated as -1047.80 ± 4.5 kJ mol^{-1} on the basis of equation (45). Table 2-E-4 contains the results of these measurements.

Table 2-E-1(b)

W/g ICl_3(c)	moles HNO_3 (Expected)	moles HNO_3 (Found)
0.0879	1.50×10^{-3}	1.50×10^{-3}
		1.45×10^{-3}

Table 2-E-1(a)

Enthalpy data for the reaction:

$$5ICl_3(c) + 9H_2O(l) \longrightarrow I_2(aq) + 3IO_3^-(aq) + 15Cl^-(aq) + 18H^+(aq)$$

W/g	dilution, n	$-\Delta H^\ominus_R$ / kJ mol^{-1}
0.1023	8140	31.00
0.2054	4054	29.40
0.2830	2942	29.20
0.2885	2886	29.00

Mean $\Delta H^\ominus_R$ = $-\ 29.65 \pm 1.70$ kJ mol^{-1}

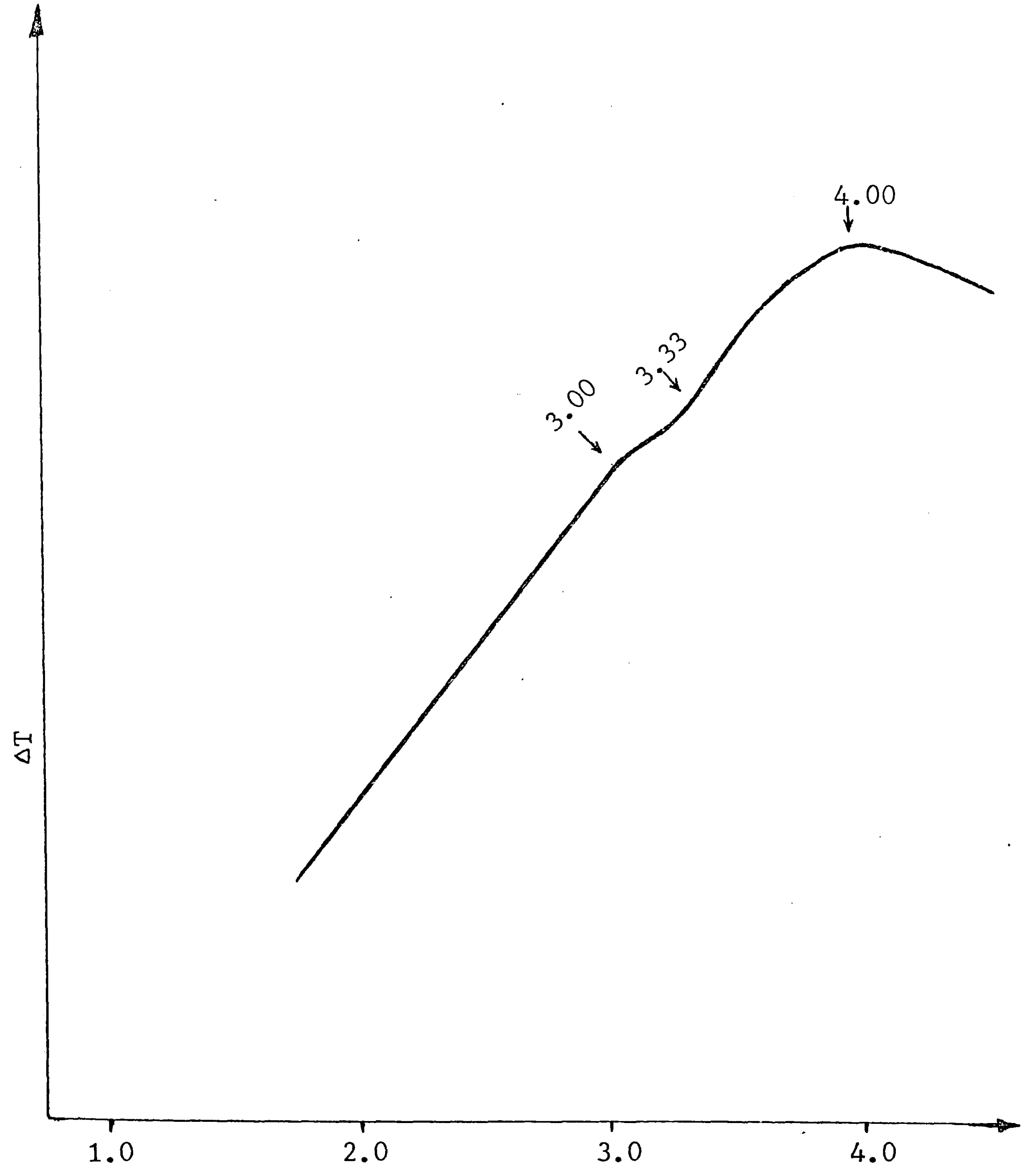
$$5\Delta H^\ominus_f ICl_3(c) = 3\Delta H^\ominus_f IO_3^-(aq) + 15\Delta H^\ominus_f Cl^-(aq) + \Delta H^\ominus_f I_2(aq) + 18\Delta H^\ominus_f H^+(aq)$$

$$- 9\Delta H^\ominus_f H_2O(l) - 5\Delta H^\ominus_R$$

using ancillary data contained in table 2-A-20:

$\Delta H^\ominus_f ICl_3(c) = -89.89 \pm 1.85$ kJ mol^{-1}

Fig. (2-E-1) THERMOMETRIC TITRATION $ICl_3/AgNO_3$



Mole ratio $AgNO_3$: ICl_3

Fig. (2-6-2) THERMOMETRIC TITRATION OF AQUEOUS ICl_3 WITH AQUEOUS $AgNO_3$

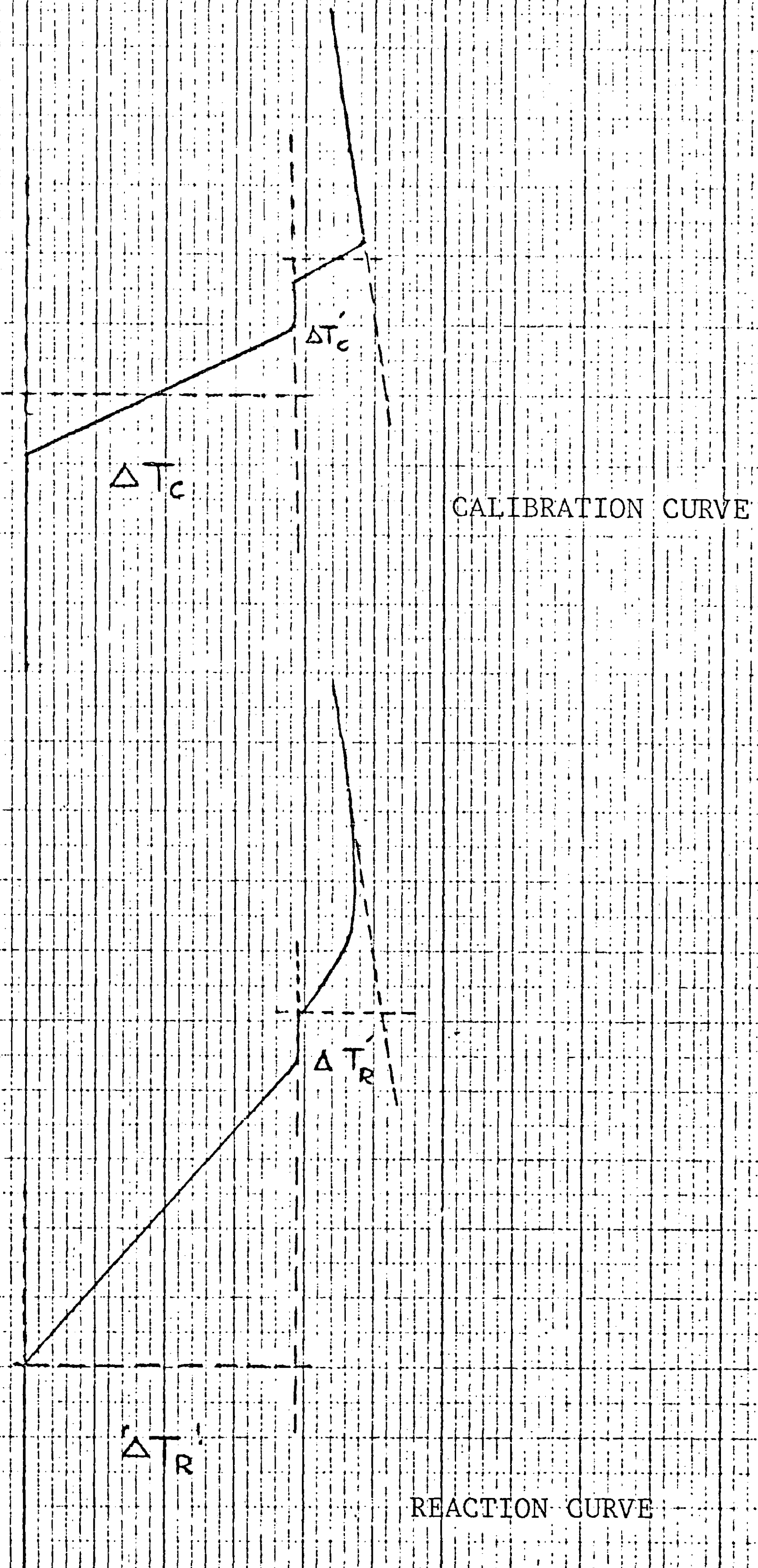


Table 2-E-2

Precipitates	$-\Delta H_f^\ominus$ / kJ mol^{-1} this work	$-\Delta H_f^\ominus$ / kJ mol^{-1} lit.values
AgCl(c)	129.83	127.07 (a)
$AgIO_3$(c)	143.00	166.20 (b)

(a): Ref.(1)   (b): Ref. (2)

Table 2-E-3

	moles
total acid (expected)	0.1567
total acid (Found)	0.1575
Iodine (expected)	3.0×10^{-4}
Iodine (Found)	3.0×10^{-4}

Table 2-E-4

Enthalpy data of the reaction:

$5(CH_3COO)_3I(c) + 9H_2O(l) \longrightarrow I_2(c) + 3IO_3^-(aq) + 15CH_3COO^-(aq) + 18H^+(aq)$

W/g	dilution, n	$-\Delta H^\ominus_R$ / kJ mol^{-1}
0.0623	27073	27.95
0.1890	8924	28.61
0.3153	5349	29.08
0.1557	10833	28.67
0.2200	7666	29.14
0.1841	9161	29.35
0.1846	9137	27.00

Mean $\Delta H^\ominus_R$ = -28.54 ± 0.86 kJ mol^{-1}

$$5\Delta H^\ominus_f(CH_3COO)_3I(c) = \Delta H^\ominus_f I_2(c) + 3\Delta H^\ominus_f IO_3^-(aq) + 15\Delta H^\ominus_f CH_3COO^-(3000H_2O) + 18\Delta H^\ominus_f\ H^+(aq) - 9\Delta H^\ominus_f H_2O(l) - 5\Delta H^\ominus_R$$

using ancillary data table 2-A-20:

$\Delta H^\ominus_f\ (CH_3COO)_3I(c) = -\ 1047.80 \pm 4.50$ kJ mol^{-1}

2-E(c) Dichloroiodonium tetrachloroaluminate, ICl_2AlCl_4

The standard enthalpy of formation of ICl_2AlCl_4 has been calculated from measured enthalpies of aqueous hydrolysis. The calorimetric reaction proposed (by analogy with ICl_3 and $(CH_3COO)_3I$) is as follows:

$$5ICl_2AlCl_4(c) + 9H_2O(l) \xrightarrow{HCl(aq)} 5AlCl_4^-(aq) + I_2(aq) + 3IO_3^-(aq) + 10Cl^-(aq) + 18H^+(aq) \qquad (46)$$

Under the acid condition of the above hydrolysis it was assumed that no hydrolysis of the $AlCl_4^-$ ion occurred and that the species remains essentially intact. Wood (40) et. al. have measured the enthalpy of formation of $NaAlCl_4$ from the enthalpy of solution of this compound with aqueous HCl (0.1 mol dm^{-3}) at 298K. These authors suggest simple dissociation for dissolution of the species in aqueous HCl;

$$NaAlCl_4(c) \xrightarrow{HCl(aq)} AlCl_4^-(aq) + Na^+(aq)$$

A Raman spectrum of the aqueous solution showed no evidence for species other than $AlCl_4^-$.

The enthalpy of formation of $AlCl_4^-(aq)$ has been calculated previously (40) on the basis of the following reaction:

$$AlCl_3(c) + HCl(aq) \longrightarrow AlCl_4^-(aq) + H^+(aq)$$

using the values for $AlCl_3(c)$ and HCl(aq) given in table 2-A-20. The standard enthalpy of formation of ICl_2AlCl_4 was calculated as -827.56 ± 6.2 kJ mol^{-1} based on the values of the measured enthalpies of hydrolysis (table 2-E-4) and ancillary data in table 2-A-20.

Table 2-E-4.

Enthalpy data for the reaction:

$$5ICl_2AlCl_4(c) + 9H_2O \xrightarrow{HCl} 5AlCl_4^-(aq) + I_2(aq)$$
$$+ 3IO_3^-(aq) + IOCl^-(aq) + 18H^+(aq)$$

W/g	dilution, n	$-\Delta H_R^\ominus$/kJ mol^{-1}
0.0935	21761	320.00
0.0995	20448	321.56
0.0639	31841	323.11
0.1086	18735	316.00
0.1048	19414	321.50
0.0889	22887	323.35
0.1187	17141	320.78

$\text{Mean}\Delta H_R^\ominus = \underline{-320.90 \pm 2.6 \quad \text{kJ mol}^{-1}}$

$$5\Delta H_f^\ominus ICl_2AlCl_4(c) = 5\Delta H_f^\ominus AlCl_4^-(aq) + \Delta H_f^\ominus I_2(aq) + 3\Delta H_f^\ominus IO_3^-(aq)$$
$$+ 10\Delta H_f^\ominus Cl^-(aq) + 18\Delta H_f^\ominus H^+(aq) - 9\Delta H_f^\ominus H_2O(l) - 5\Delta H_R^\ominus$$

using ancillary data contain in table 2-A-20.

$\underline{\Delta H_f^\ominus ICl_2AlCl_4(c) = -827.56 \pm 6.2 \quad \text{kJ mol}^{-1}}$

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CHAPTER 3

EXPERIMENTAL

3-A PREPARATION AND ANALYSIS.

Most of the compounds prepared in this work were highly moisture sensitive, therefore filtration was carried out under closed suction and the removal of the samples took place in a dry box. In the case of polyhalides the crystals were dried in a desiccator filled with chlorine gas to minimise the decomposition.

(a) Tetrachloroiodate salts.

(1) Potassium tetrachloroiodate monohydrate, $KICl_4.H_2O$

Potassium iodate (15.0g, 0.07 mol, B.D.H.) was added in small quantities to concentrated hydrochloric acid ($50cm^3$) with continuous stirring. Vigorous reaction occurred with the liberation of chlorine to produce yellow crystals of $KICl_4.H_2O$ which were filtered off under suction. Prolonged pumping was avoided as loss of water from the hydrate resulted. The crystals were dried in a desiccator over $CaCl_2$ for 1 hour (Found: Cl, 46.18%; I, 40.80%, Calc. for $KICl_4.H_2O$: Cl, 46.06%; I, 40.96%).

(2) Anhydrous potassium tetrachloroiodate, $KICl_4$

$KIBr_2$ (10.0g, 0.03 mol) was mixed with an excess of sulphuryl chloride. Yellow crystals of the anhydrous $KICl_4$ were filtered in a closed suction and dried in a desiccator filled with chlorine gas (Found: Cl, 42.98%; I, 38.56%, Calc. for $KICl_4$: Cl, 43.00 %; I, 38.94%).

(3) Tetramethylammonium dichloroiodate (I) $(CH_3)_4NICl_2$

Tetramethylammonium chloride (21.9g, 0.20 mol, B.D.H.) was added to glacial acetic acid (400 cm^3). Iodine chloride (32.5g, 0.20 mol, B.D.H) was reacted with this mixture with continuous stirring. Yellow crystals of $(CH_3)_4NICl_2$ were filtered and washed several times with carbon tetrachloride. The product was recrystallized from isopropyl alcohol containing a small quantity of iodine monochloride $^{(I)}$. The crystals were dried in a desiccator filled with chlorine gas to minimise decomposition of the sample. (Found: Cl, 26.78%;I, 46.22%, Calc. for $(CH_3)_4NICl_2$: Cl, 26.10%;I, 46.69%).

(4) Tetramethylammonium tetrachloroiodate(III), $(CH_3)_4NICl_4$

This compound was prepared by suspending some of the $(CH_3)_4NICl_2$ (prepared above) in glacial acetic acid containing a small amount of ICl, followed by chlorination for about three hours. Yellow crystals of $(CH_3)_4NICl_4$ were filtered off and dried in a desiccator over $CaCl_2$. (Found: Cl, 41.10%;I, 36.92%, Calc. for $(CH_3)_4NICl_4$: Cl, 41.37%;I, 37.00%).

(5) Trimethylammonium tetrachloroiodate, $(CH_3)_3NHICl_4$

Iodine monochloride (I), (10.46 g , 0.064 mol, B.D.H.) was added to concentrated hydrochloric acid(200 cm^3) in a 500 cm^3 two-necked flask. Trimethylammonium chloride (16.5 g, 0.064 mol, B.D.H. was added with continuous stirring. Chlorine gas was introduced in the reaction vessel for about three hours. Canary-yellow crystals of $(CH_3)_3NHICl_4$ were formed on cooling. The crystals were filtered off and dried in a desiccator over $CaCl_2$.

(Found: Cl, 42.60%;I, 38.48%, Calc. for$(CH_3)_3NHICl_4$: Cl, 43.00%; I, 38.60%).

(6) Dimethylammonium tetrachloroiodate, $(CH_3)_2NH_2ICl_4$

Iodine monochloride (10.0 g, 0.06 mol, B.D.H.) was dissolved in concentrated hydrochloric acid (100 cm^3) in a 250 cm^3 two-necked flask. Dimethylammonium chloride (5.0 g, 0.06 mol, B.D.H.) was added with continuous stirring. Chlorine gas was introduced into the mixture for about two hours. Orange-yellow crystals formed on cooling. The crystals were filtered off under closed suction and dried in a desiccator over $CaCl_2$. (Found: Cl, 45.10 %; I, 40.06%, Calc. for $(CH_3)_2NH_2ICl_4$: Cl, 45.05%; I, 40.31%).

(7) Monomethylammonium tetrachloroiodate, $CH_3NH_3ICl_4$

All attempts to prepare this compound resulted in product being contaminated with the starting materials.

(8) Ammonium tetrachloroiodate, NH_4ICl_4

Iodine monochloride (30.37 g. , 0.19 mol, B.D.H.) was dissolved in concentrated hydrochloric acid (75 cm^3) in a 250 cm^3 two-necked flask with continuous stirring. Ammonium chloride (10.0 g. , 0.19 mol, B.D.H.) was reacted and followed by passage of chlorine gas for about three hours.Orange-yellow crystals were formed and recrystallised from concentrated hydrochloric acid containing a small quantity of ICl. On cooling, sharp needle-like crystals precipitated. These were filtered off under suction and dried in an atmosphere of Cl_2 over $CaCL_2$.

(Found: Cl, 49.66%;I, 43.60%, Calc. for NH_4ICl_4:Cl, 49.45%; I, 44.26%).

(9) Monoethylammonium tetrachloroiodate, $C_2H_5NH_3ICl_4$

Monoethylammonium chloride (10.0 g, 0.123 mol, B.D.H.) was dissolved in di-chloromethane (75 cm^3) in a two-necked flask. Iodine monochloride (20.0 g, 0.123 mol, B.D.H.) was added with continuous stirring. Chlorine gas was introduced in to the mixture for about two hours. Orange-yellow crystals were formed on cooling The crystals were filtered off under suction and dried in a desiccator filled with Cl_2 over $CaCl_2$. (Found: Cl, 44.96%;I,39,30% Calc. for $C_2H_5NH_3ICl_4$: Cl, 45.06%;I, 40.32%).

(10) Di-ethylammonium tetrachloroiodate, $(C_2H_5)_2NH_2ICl_4$

Iodine monochloride (30.0 g, 0.185 mol, B.D.H.) was dissolved in concentrated hydrochloric acid (75 cm^3) in a two-necked flask. Di-ethylammonium chloride (20.0 g, 0.185 mol, B.D.H.) was added with continuous stirring. Chlorine gas was introduced in to the reaction vessel for about three hours. Pale orange-yellow crystals were formed on cooling. The crystals were filtered off under suction and dried in a desiccator filled with chlorine gas over $CaCl_2$. (very hygroscopic).(Found: Cl, 42.00%;I, 36.90%, Calc. for $(C_2H_5)_2NH_2ICl_4$: Cl, 41.50%;I, 37.00%).

(11) Tri-ethylammonium tetrachloroiodate, $(C_2H_5)_3NHICl_4$

All attempts to prepare this compound resulted in product being contaminated with the starting materials.

(12) Tetra-ethylammonium tetrachloroiodate, $(C_2H_5)_4NICl_4$

Tetra-ethylammonium chloride (10.0g , 0.06 mol, B.D.H.) was dissolved in glacial acetic acid (200 cm^3) in a 500 cm^3 two-necked flask. Iodine monochloride (9.8g , 0.06 mol, B.D.H.) was added with continuous stirring. Yellow crystals were formed on cooling and were filtered off under suction. The compound was dried in an atmosphere of chlorine gas over $CaCl_2$. (Found: Cl, 35.20; I, 31.50%. Calc. for $(C_2H_5)_4NICl_4$: Cl, 35.56; I, 31.83%).

(b) Substituted ethylammonium halides $(C_2H_5)_nNH^+_{4-n}X^-$ $(1 \leqslant n \leqslant 4$, X=Cl, Br, I).

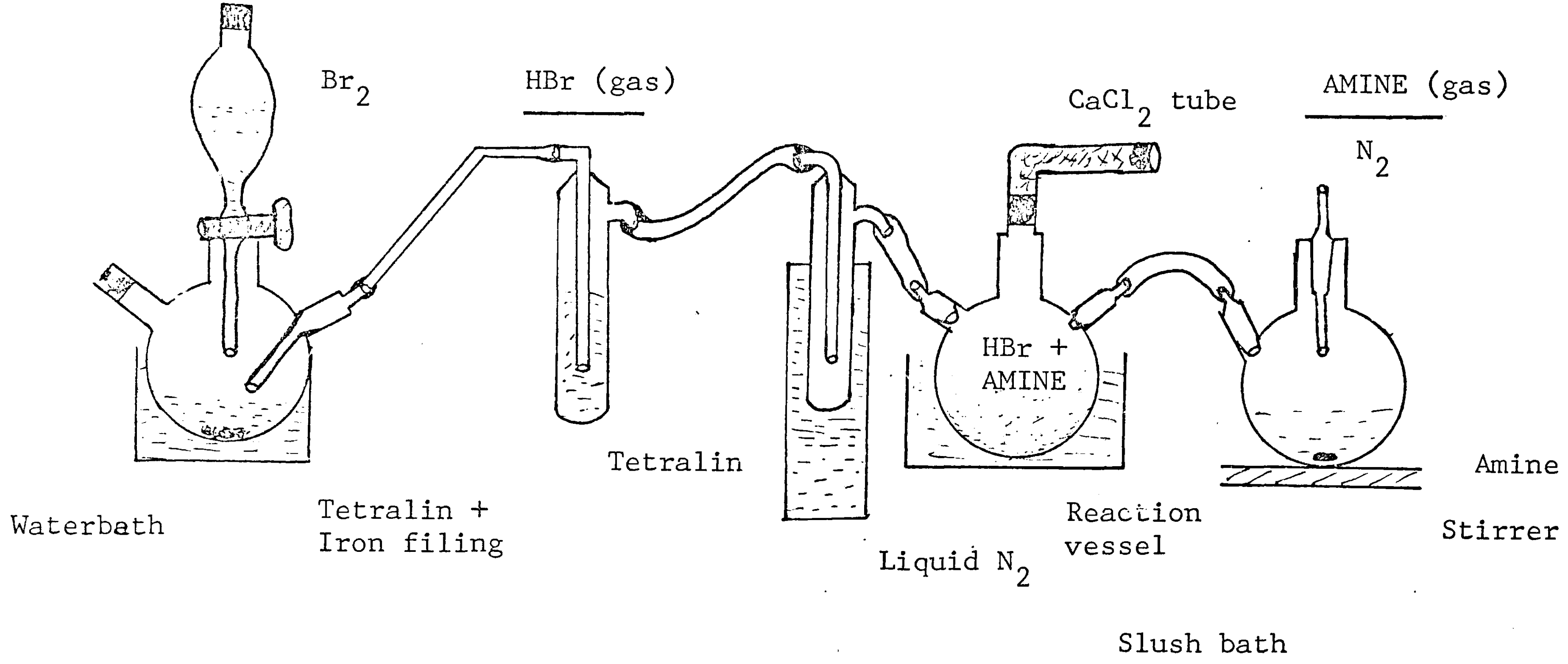
(A) Mono, di and Tri-ethylammonium chloride, $C_2H_5NH_3Cl$, $(C_2H_5)_2NH_2Cl$, $(C_2H_5)_3NHCl$.

These salts were obtained commercially and the purity was monitored by halide analysis. For calorimetric work a purity of at least 99% was necessary.

(1) Mono-ethylammonium Bromide, $C_2H_5NH_3Br$

This compound was prepared by reacting hydrobromic acid gas with mono-ethylamine gas in a reaction vessel placed in a slush bath of acetone and dry ice Fig. (3-A-1). Hydrobromic acid was prepared by reacting bromine with tetralin (tetrahydronaphtalene) containing pure iron filings.(2) Since initial cooling was necessary, the reaction vessel was placed in a water bath. As soon as the reaction became sluggish,the vessel was heated to 30 to 40 ^oC. Hydrobromic gas was passed through a trap filled with tetralin in order to

FIG. 3-A-1



APPARATUS FOR PREPARING SOME ETHYLAMMONIUM BROMIDE AND IODIDE.

eliminate small quantities of Br_2. A second trap was employed and cooled to -60°C to remove the last trace of moisture. HBr produced in this method was reacted with mono-ethylamine in the reaction vessel. Nitrogen gas was used as the carrier. White crystals were formed on cooling at -70°C and filtered under suction and dried in a vacuum desiccator over $CaCl_2$. (Found: Br, 63.54 %, Calc. for $C_2H_5NH_3Br$: Br, 63.46%).

(2) Di-ethylammonium bromide, $(C_2H_5)_2NH_2Br$

Di-ethylamine (10.0 g, 0.065 mol, B.D.H.) was dissolved in di-chloromethane (75 cm^3) in a two-necked flask. Hydrobromic acid (2 gas was introduced in to the reaction vessel for about two hours. White crystals were formed on cooling. The compound was recrystallised from a small amount of ethanol and filtered off under suction and dried in a stream of N_2 gas and stored in a desiccator over $CaCl_2$. (Found: Br, 51.96%, Calc. for $(C_2H_5)_2NH_2Br$: Br, 51.92%).

(3) Tri-ethylammonium bromide, $(C_2H_5)_3NHBr$

This compound was prepared using the same method of preparing mono and di-ethylammonium bromide. (Found: Br, 43.88%, Calc. for $(C_2H_5)_3NHBr$: Br, 43.93%).

(4) Mono-ethylammonium iodide, $C_2H_5NH_3I$

Mono-ethylammonium iodide was prepared by reacting hydrogen iodide, HI with mono-ethylamine.

Hydrogen iodide was prepared by dissolving iodine in tetralin (tetrahydronaphtalene) and slowly adding this mixture to the boiling tetralin (3). Hydrogen iodide produced was passed through a trap containing tetralin to absorb any trace of iodine. A second trap was employed and cooled to -60°C to remove any moisture. Hydrogen iodide then dissolved in carbon tetrachloride ($75\ \mathrm{cm}^3$). An excess of HI was provided in carbon tetrachloride and mono-ethylamine slowly was added to this mixture. White crystals were formed on cooling. The compound was filtered off under suction and dried by a stream of N_2 gas. To remove the last trace of possible contamination, the crystals were placed in glass tube and pumped down at 50°C in a water bath. Crystals were highly hygroscopic. (Found: I, 73.30%. Calc. for $C_2H_5NH_3I$: I, 73.39%).

IMPORTANT: Hydrogen iodide and iodide salts were highly light sensitive, therefore every precaution was taken in handling these compounds.

(5) Di-ethylammonium iodide, $(C_2H_5)_2NH_2I$

This compound was prepared the same way that mono-ethylammonium iodide was made. (Found: I, 62.70%. Calc. $(C_2H_5)_2NH_2I$: I, 63.16%).

(6) Tri-ethylammonium iodide, $(C_2H_5)_3NHI$

This compound was prepared the same way the mono-ethylammonium iodide was made. (Found: I, 56.00%. Calc. for $(C_2H_5)_3NHI$: I, 55.44%).

(C) Iodine (III) compounds.

(1) Iodine tri-chloride.

Iodine tri-chloride was prepared by reacting liquid chlorine with powdered iodine. Chlorine gas was liquified on a cold finger cooled to -79°C. Powdered iodine (B.D.H.) was then reacted with liquid chlorine in a flask placed in a Dry ice-acetone bath. The reaction vessel was allowed to remain in the cooling bath for a few hours and the excess Cl_2 was then left to evaporate at room temperature to give a quantitative yield of ICl_3(4). ICl_3 is either a loose orange powder or long orange-yellow needles. (Found: Cl, 44.68; I, 54.20%, Calc. for ICl_3: Cl,45.59; I, 54.40%).

(2) Iodine tri-acetate, $(CH_3COO)_3I$

Powdered iodine (7.05 g, 0.05 mol, B.D.H.) was added to glacial acetic acid (10.0 g, 0.16 mol M&B) in the presence of acetic anhydride (12-15 cm^3). On addition of the fuming nitric acid (5-7 cm^3) a yellow solution developed. Iodine tri-acetate precipitated on cooling. The compound was filtered off under suction and dried. Iodine tri-acetate was highly light sensitive, therefore it was stored in a brown bottle.(Found: I, 41.99%, Calc. for $(CH_3COO)_3I$: I, 41.76%).

(3) Dichloroiodonium aluminium tetrachloride, ICl_2AlCl_4

$IAlCl_6$ was prepared by heating equivalent amounts of ICl_3 and $AlCl_3$ in chloroform or carbon tetrachloride as a solvent to about 100°C in a sealed tube. After cooling a crust of red $IAlCl_6$ crystals was formed (5). The crystals were filtered off under suction in a dry box and washed several times with a small quantity of solvent and dried. (Found: Cl, 34.86; I, 57.78%, Calc. for $IAlCl_6$: Cl, 34.60; I, 58.00%).

(C) Analytical procedures.

(1) Total halide analysis.

A known weight of polyhalide (ca 0.2g) was reduced with a saturated solution of sulphur dioxide (75 cm^3); a yellow solution indicates the presence of the SO_2X^- complex. The solution was then boiled to remove dissolved sulphur dioxide. Mono-halides produced were estimated by potentiometric titration. For this determination, a buffer solution of glacial acetic acid (5.7 cm^3) and sodium acetate (6.2g) in 1000 cm^3 of distilled water was prepared (pH=4). 150 cm^3 of this buffer was mixed with the mono-halide solution. A combined glass silver chloride electrode (EA 246) connected to a pH-meter (E512, METROHN, HERISAY) was employed for the titration. Silver nitrate (0.1 mol dm^3) was used to titrate the halides. A titration curve (1st derviative) $\delta pH/\delta V$ was plotted and the end point calculated and hence the percentage of the halides computed.

(2) Halides analysis.

A known sample of the ammonium halide salt (ca 0.2g) was dissolved in distilled water (ca 30 cm^3). 150 cm^3 of the buffer solution (above) was added. The halide was titrated against silver nitrate (0.1 mol dm^3) using a combined silver chloride electrode (above). The amount of the halide was estimated from the titration curve and therefore the percentage of the halide computed.

3-B CALORIMETRY.

Two solutions calorimeters employed in this work. (1) Enthalpies of reaction of polyhalide compounds contained in table 2-A-1 to 2-A-10, 2-D-1, 2-E(a). (b) and 2-E(c) were determined by the calorimeter designed and constructed in this laboratory. (2) An L.K.B. 8700-1precision calorimeter was used to measure the enthalpies of reaction of ethyl-substituted ammonium halides contained in table 2-A-11 to 2-A-19.

(1) This calorimeter was operated in a partial diffential isoperibol mode. Vessels consist of thin-walled borsilicate glass Dewars each with a threaded aluminium lid which screws onto the flange. Glass tube inserts e.g. thermistor tubes, were fixed by individual aluminium ferrules which screw into the calorimeter lid. The internal vessel, capacity 100 cm^3, has very thin (ca 1mm) walls. Individual components of the calorimeter were constructed as follows and Figure 3-B-1 and 3-B-2(a), (b), (c) shows the calorimeter and some of its components.

Thermistor tube.

Assembly of the thermistor tube is as follows: the thermistor (YSI 100K 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 a low vapour pressure resin, into a length of glass tube. Only the tapered glass tube was in contact with the calorimeter fluid.

Fig. (3-B-1) CALORIMETER VESSEL

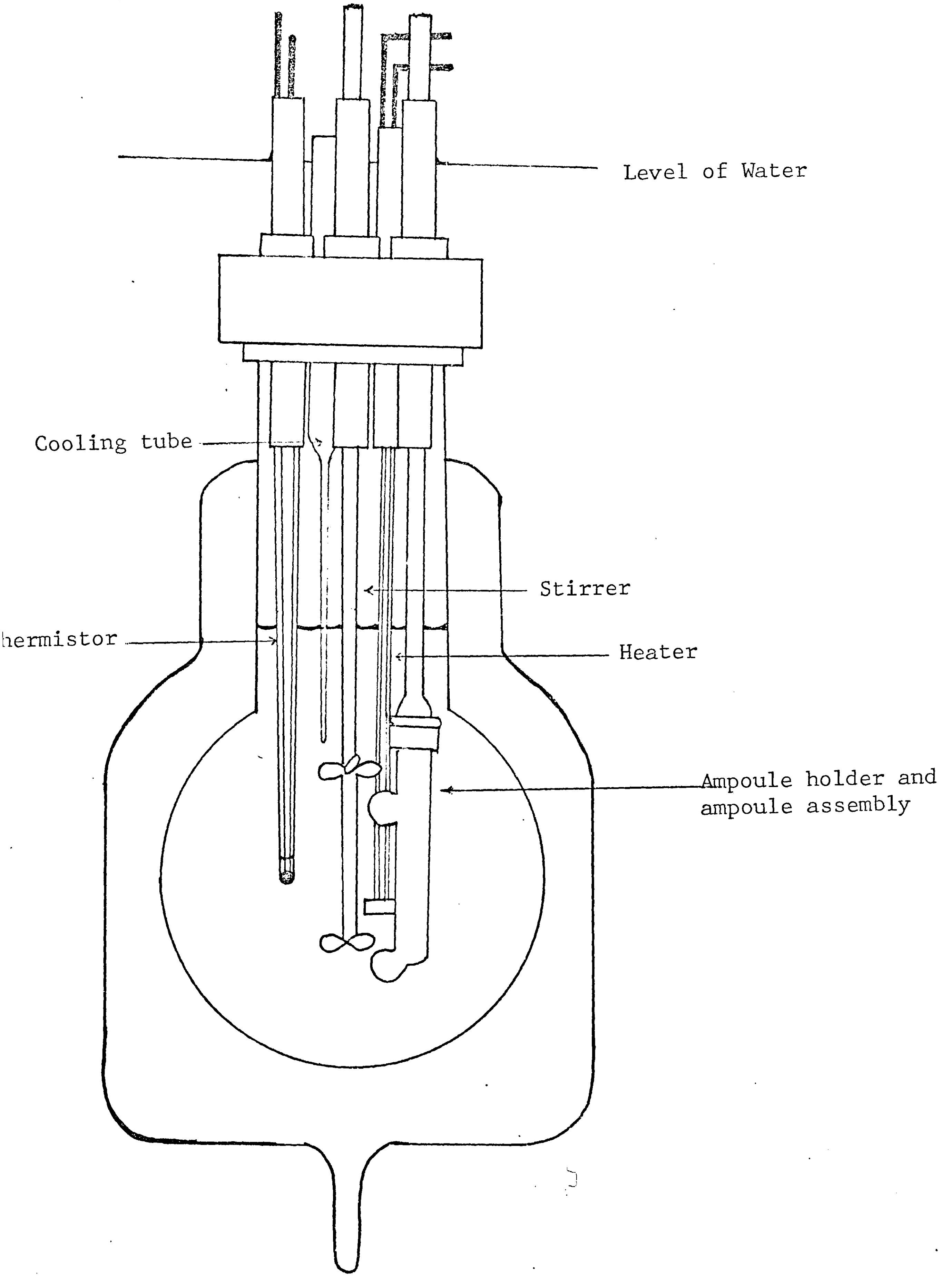
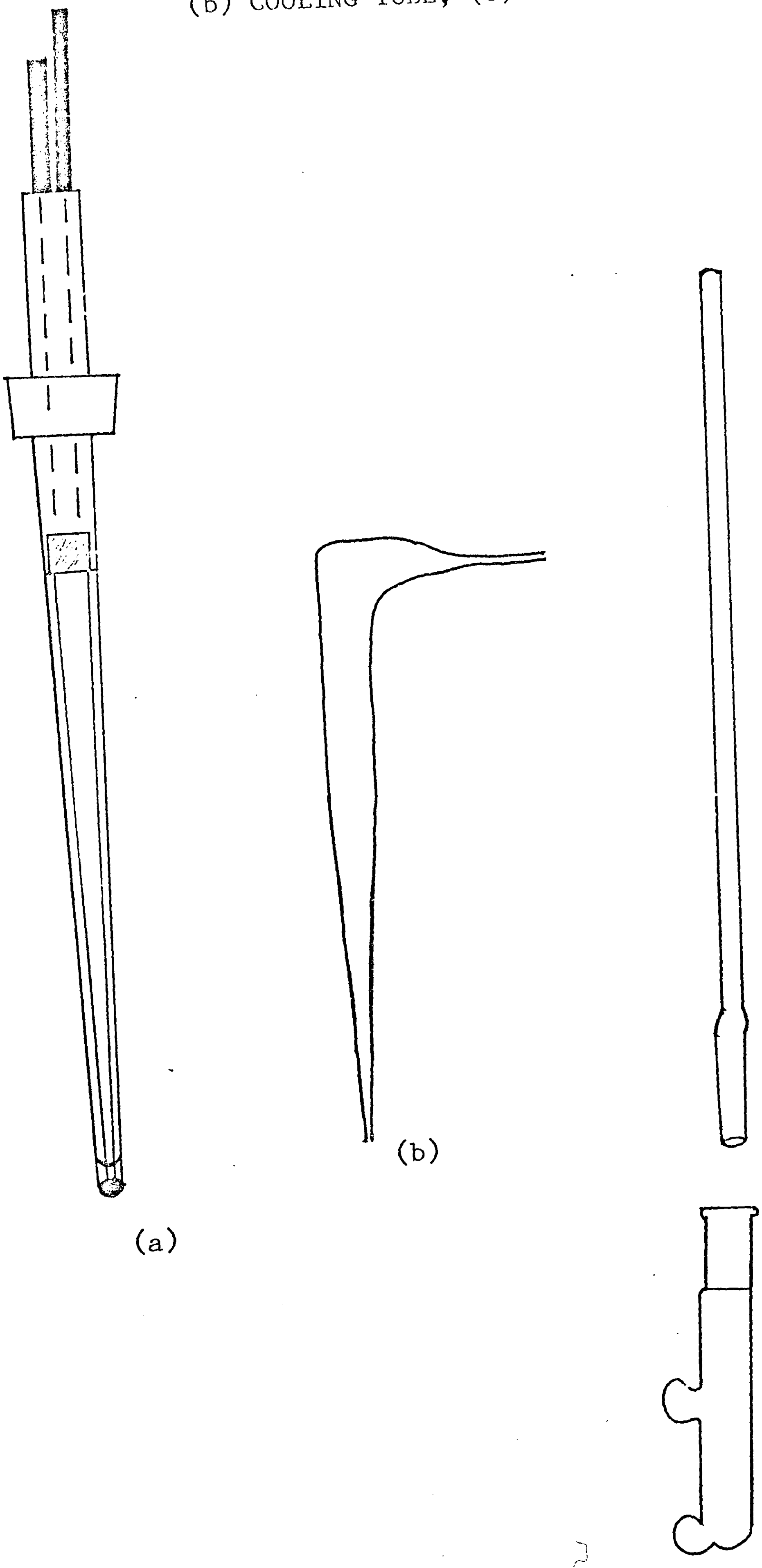


Fig. (3-B-2) : (a) THERMISTOR TUBE

(b) COOLING TUBE, (c) AMPOULE ASSEMBLY



(a)

(b)

(c)

Calorimeter calibration heater.

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°C, by 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. .

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 the central ferrules of the calorimeter lid. A double-bladed glass propeller on one end of the rod and a PTFE paddle fixed to the stirrer shaft <u>ca</u>.1 cm below the surface of the liquid ensured efficient stirring of the calorimetric fluid. The stirrer shaft was coupled to the stirrer motor (Motomatic, motor generator, Model E550.000) and the variable speed controller was set to 250 r.p.m.

Ampoule and ampoule-holder assembly.

Calorimetric ampoules, 8cm long,Figure 3-B-2(c) were glass-blown 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.

Cooling tube.

A thin glass capillary 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 any 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 ± 0.005 °C.

Expanded polystyrene sheets were used to insulate the bath. The complete calorimeter system was operated in a room which was maintained at 25 ± 2°. A proportional controller (Tronac model 1040) was used to control the temperature of the water bath.

Temperature measuring circuits.

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

Three thermistor inputs are provided by the bridge (inputs A,B and C). The bridge may be switched to read the 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 a

Fig. 3-B-3. , TEMPERATURE MEASURING CIRCUIT BLOCK DIAGRAM

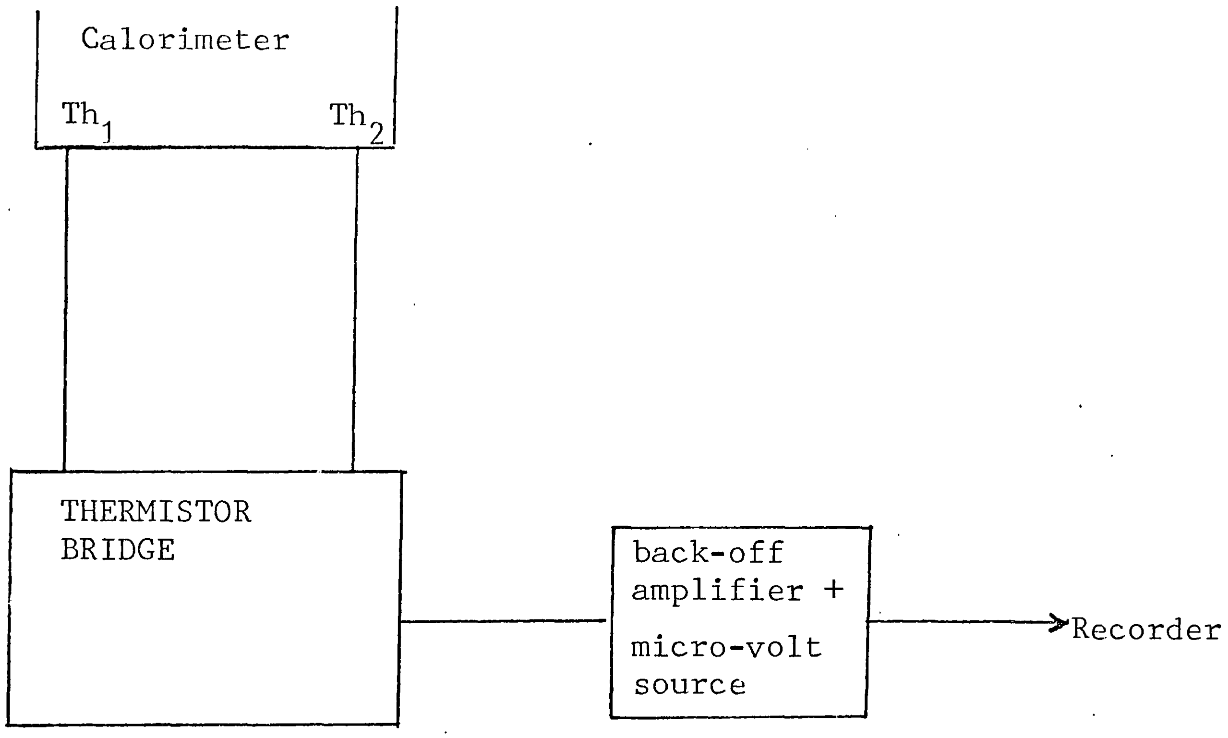
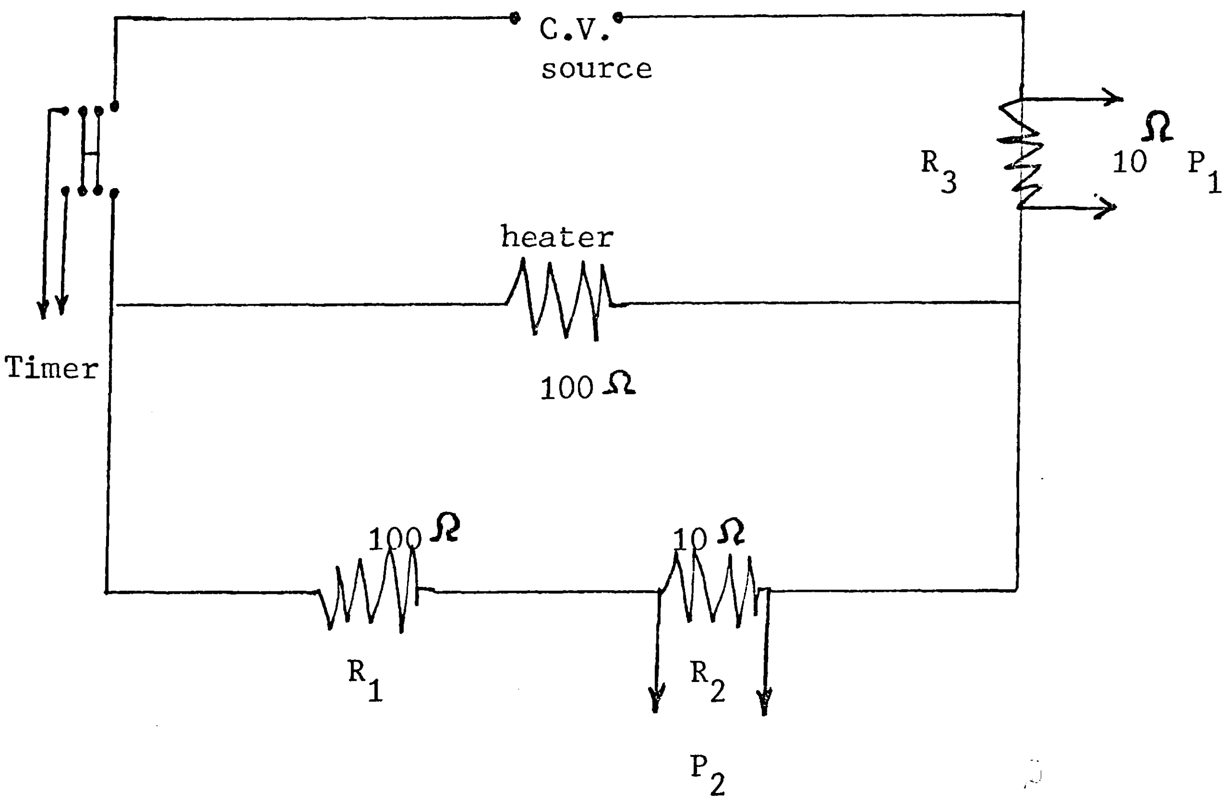


Fig. 3-B-4 , CALORIMETER HEATER CIRCUIT



temperature difference 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 difference 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 II . The sensitivity of the chart recorder was adjusted so that 1cm of chart paper = 0.04V $\triangleq$ 0.0004°. The thermistor bridge was operated on the range 1° $\approx$ 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 in to the circuit shown in Fig. 3-B-4 , 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 10 Ω 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 determined by a potentiometer (Tinsley and 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 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 Fig. 3-B-5.

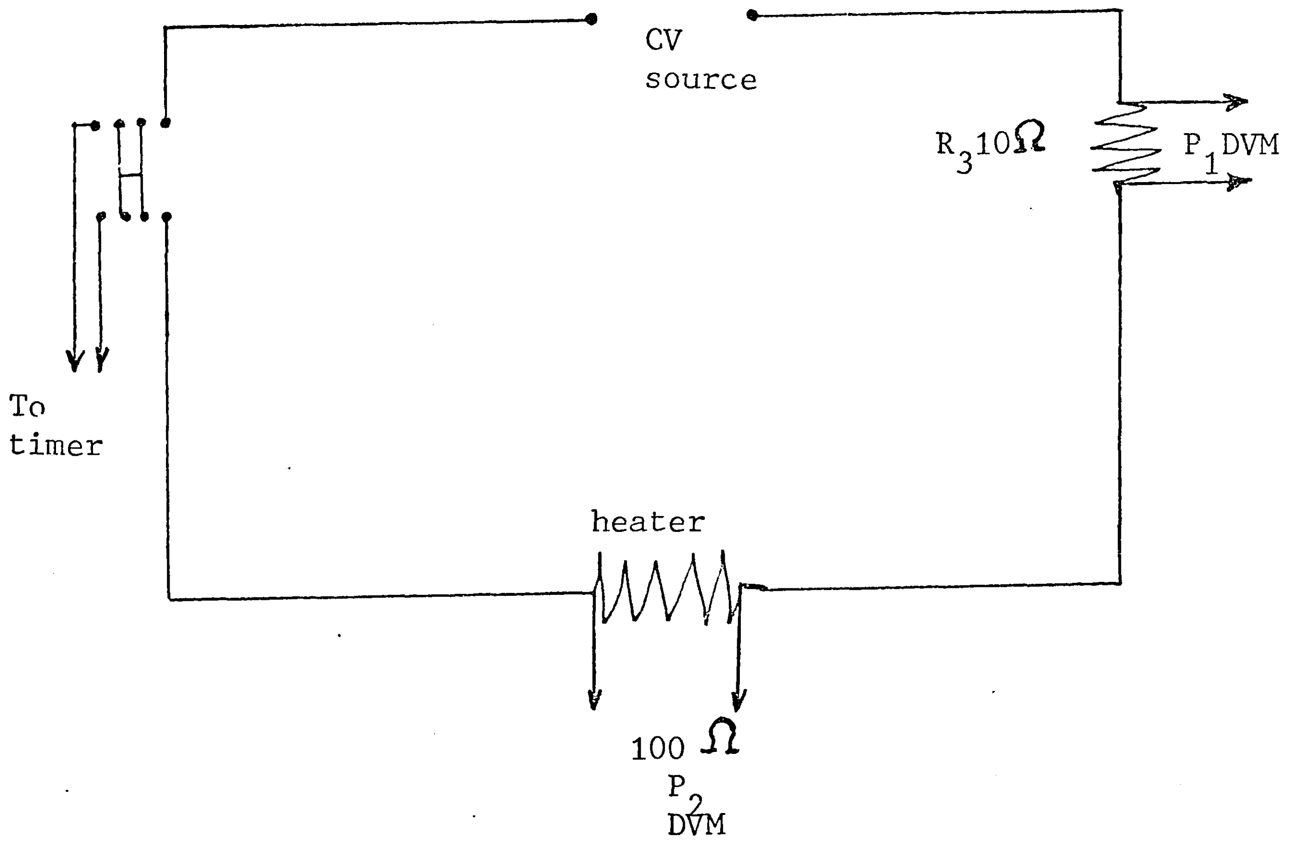
Operation of the calorimeter.

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 mai parts:

(1) Ampoule-loading and initial setting up.

An empty ampoule was weighed together with the ampoule adapter. The ampoule was filled with powdered, dried THAM (ca0.40g). 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 calorimeter fluid). The ampoule adapter was inserted into the ampoule and the stoppere ampoule was re-weighed. For hygroscopic samples the procedure of ampoule filling can be carried out in a dry-box. 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

Fig. 3-B-5. DIGITAL VOLTMETER CALORIMETER HEATER CIRCUIT



by clamping the rod. 100 cm^3 of 0.10 mol dm^{-3} hydrochloric acid (B.D.H. A.V.S.), warmed to 25°C, 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 100 cm^3 of distilled water. The vessels were then immersed in the thermostatic bath (to the level indicated in Figure 3-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.

10 cm 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 15 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 20 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 millivolt source to the initial value used in the reaction experiment. A fore-period of 15 min was recorded. The calibration heater was then switched on and a pen displacement identical to the reaction period recorded. An after-period of 20 min. was recorded and the heating time noted. During the heating the potential difference across the heater and across the standard resistor was measured by the digital voltmeter 1 volt and 10 volt respectively. Thus the power, P, was calculated from the following expression

$$P = \frac{V_1 V_2}{10}$$

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 excess HCl was fast, being complete in under two minutes. Moderately fast reactions (completed in ca 5-7 min.) were observed for the polyhalide compounds (Fig. 3-B-6). The values of V_1 and V_2 were obtained by the linear extrapolation of the reaction fore-and

Fig. 3-B-6. TYPICAL $KICl_4/AgNO_3$ REACTION TRACE

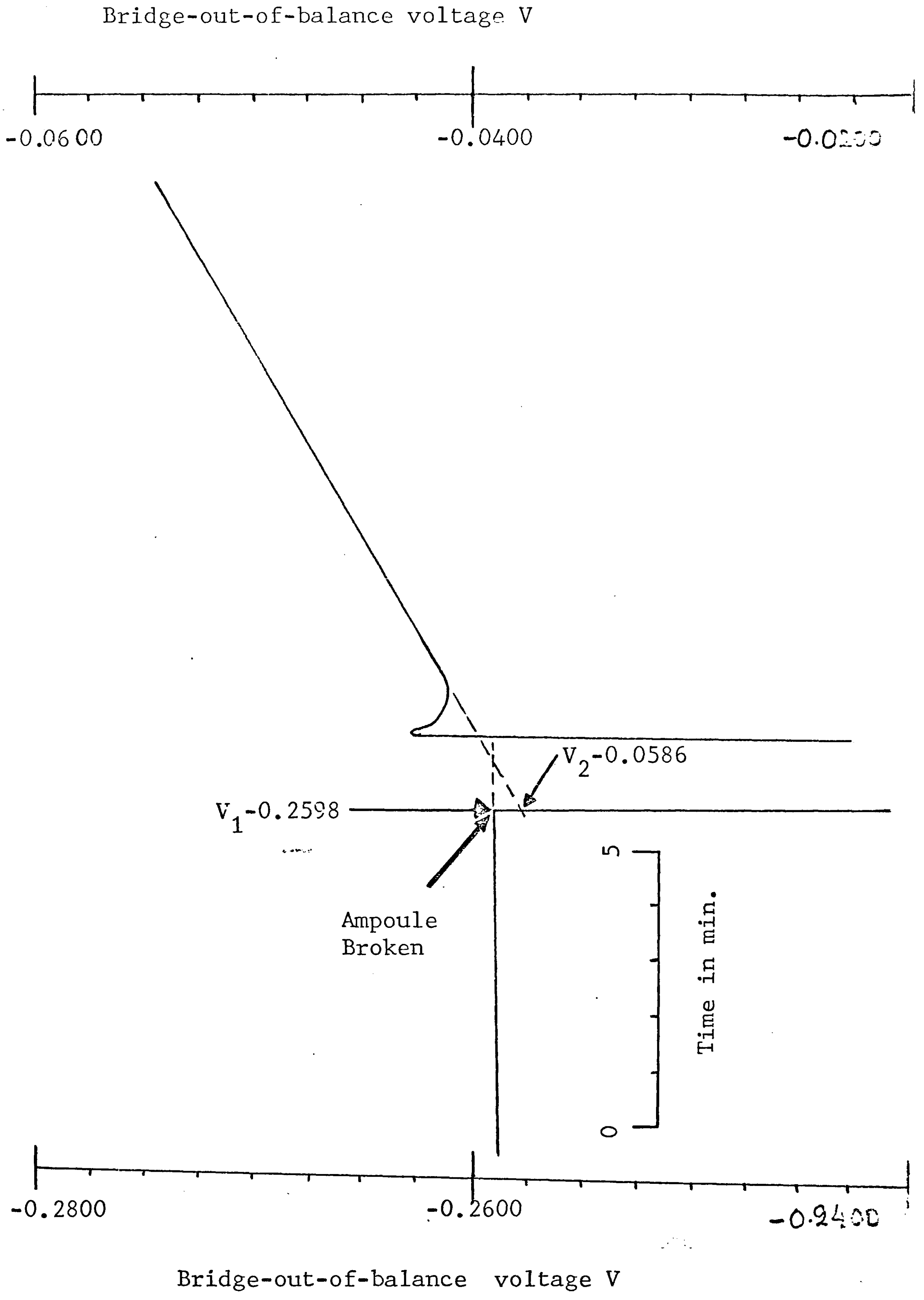
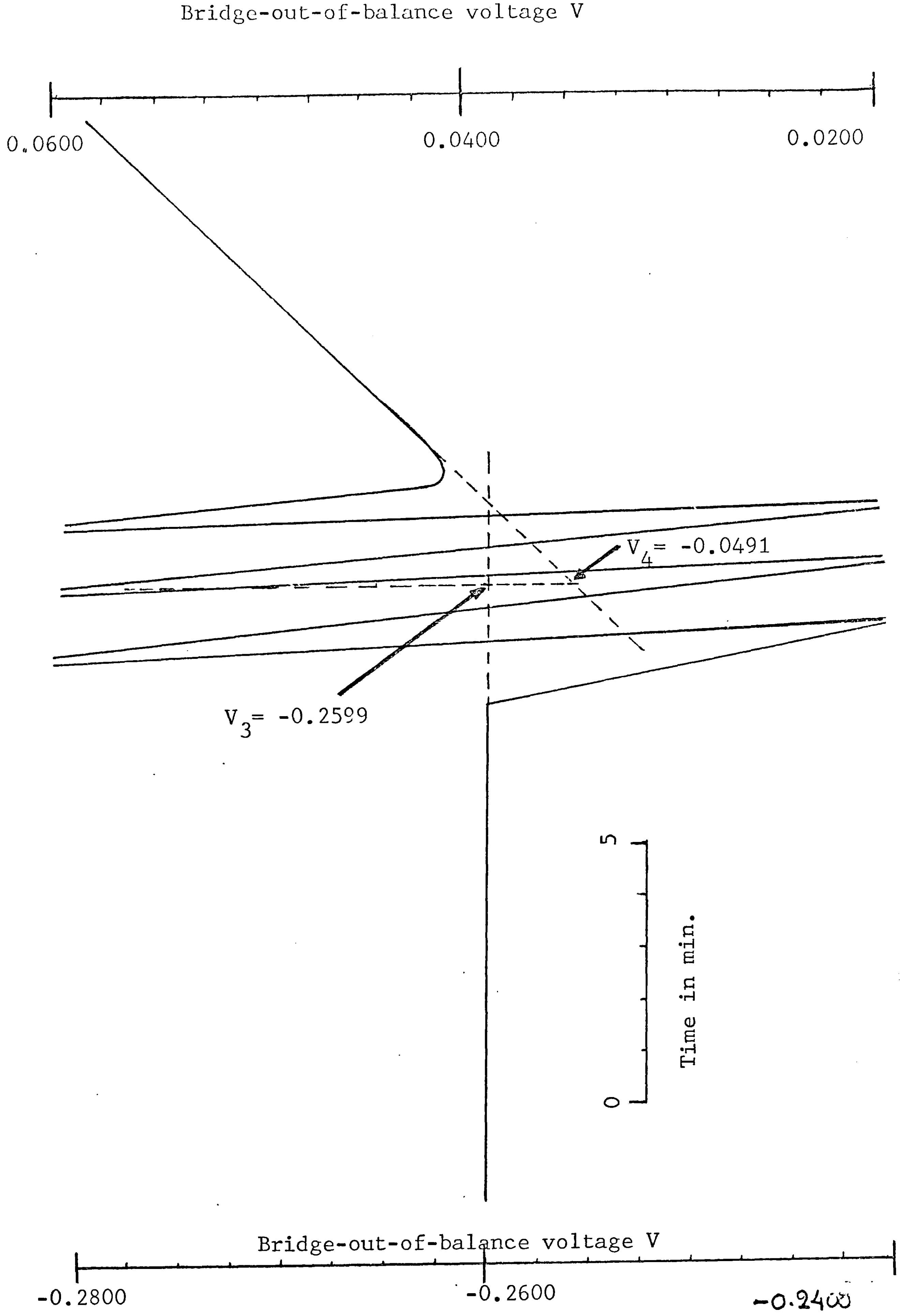


Fig. 3-B-7. TYPICAL $KICl_4/AgNO_3$ CALIBRATION TRACE.



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 of 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.

Extrapolation of the calibration voltage-time traces was carried out by Dickinson's equal area method (6),(7). 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 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 3-B-7. The calorimetric enthalpy change was calculated using the following formula:

$$-\Delta H_R = P \times \frac{\Delta T_R}{\Delta T_C} \times \frac{M}{W} \times \frac{t}{1000} \qquad \text{kJ mol}^{-1}$$

where

P = Power of the heater

M = Molecular weight of compound

W = 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.

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 results are contained in table 3-B-1. Uncertainties in ΔH_R^θ are expressed at

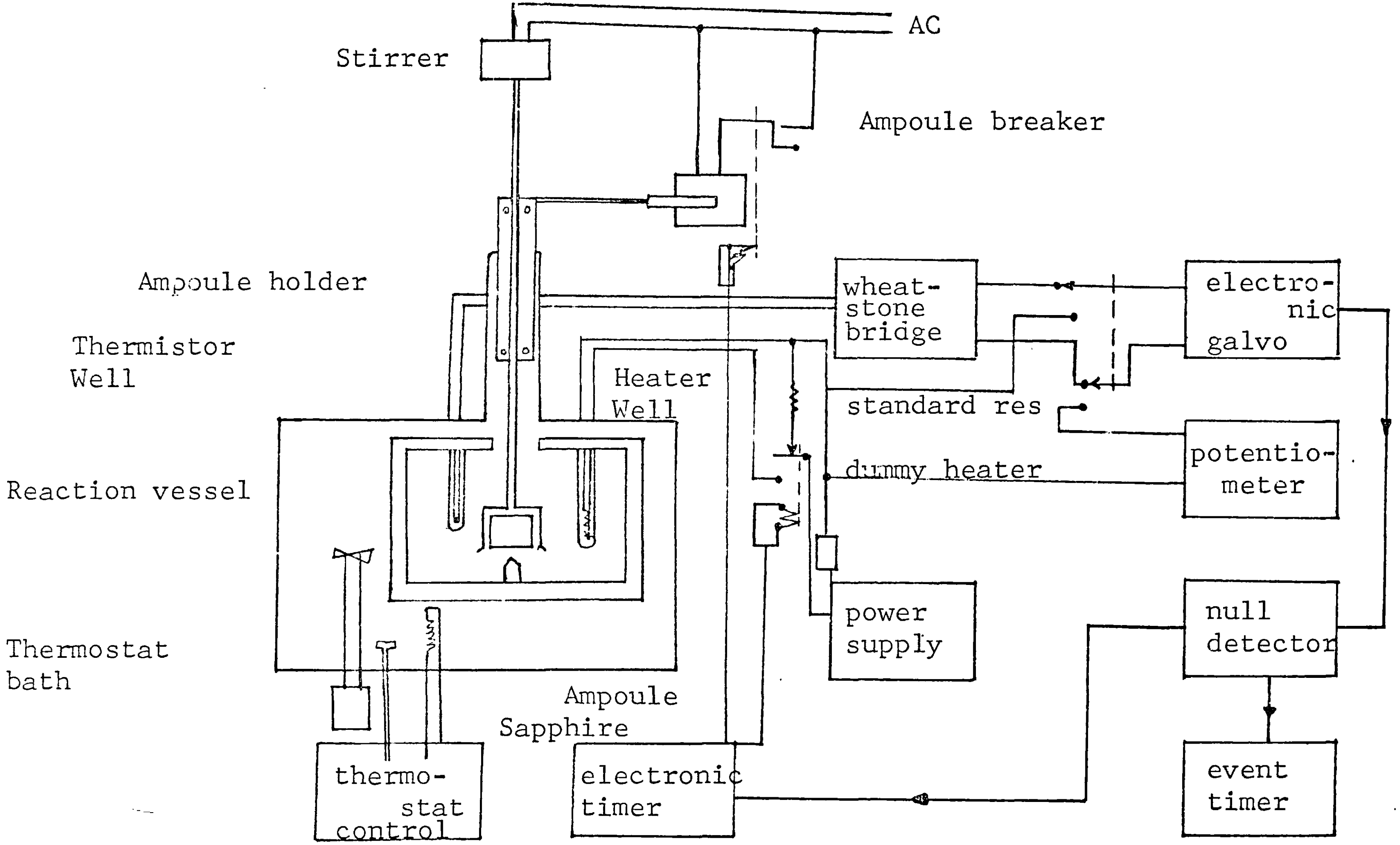
TABLE 3-B-1.

Enthalpy of reaction of THAM with excess 0.1M HCl.

W/g	dilution, n	$-\Delta H_R^\ominus$ kJ mol^{-1}
0.4970	1353	29.96
0.4120	1632	29.77
0.3800	1769	29.65
0.3285	2047	29.79
0.3064	2194	29.84
0.4403	1527	29.88
0.3387	1985	29.94
0.3770	1783	29.84

Mean $-\Delta H_R^\ominus$ = $\underline{29.82 \pm 0.09 \text{ kJ mol}^{-1}}$ (lit.(8), $-\Delta H_R$ = 29.790 ± 0.031 kJ mol^{-1}, n=1345

FIGURE 3-B-8 LKB 8700 CALORIMETRY SYSTEM
BLOCK DIAGRAM



the 95% confidence level assessed by the 'student ' distribution

(2) The enthalpies of the reaction of ethyl substituted ammonium halide salts (Cl, Br, I) with sodium hydroxide (0.1 mol dm^{-3},) were determined using the L.K.B. 8700-1 calorimeter . Figure 3-B-8 sho a diagram of the calorimeter.

The calorimeter vessel was a thin-walled Pyrex cyclinder of 100 cm^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 attachec to a gold ampoule holder. Ampoule breaking was achieved by lowering the stirrer/ampoule assembly vertically onto a aapphire 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 500 mw, the corresponding I^2 values being (0.4, 1,2, 4 and 10) x 10^{-3} A^2 respectively. The value selected, 500 mw, 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 overall reactions were fast and completed after 2-3 min (Fig. 3-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. Extrapolation of the calibration fore-and after- periods was carried out as described in section 3-B-(1). Figure 3-B-10 illustrates a typical calibration resistance-time profile. The equation used to determine the enthalpy change during the reaction is:

$$-\Delta H^{\ominus}_{R} = \frac{P.t.M}{1000.W} \cdot \frac{(R/_{Rm})\ \text{reaction}}{(R/_{Rm})\ \text{calibration}}\ \text{kJ mol}^{-1}$$

where

P = Power of heater

W = Weight of compound

M = molecular weight of compound

t = heater time (sec.)

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

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

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 $\Delta H^{\ominus}_{298}$ = -29.700 kJ mol^{-1} was obtained (lit. $\Delta H^{\ominus}_{298}$ = - 29.790 ± 0.03 kJ mol).

Fig. 3-B-9. TYPICAL $C_2H_5NH_3Cl$/NaOH REACTION TRACE.

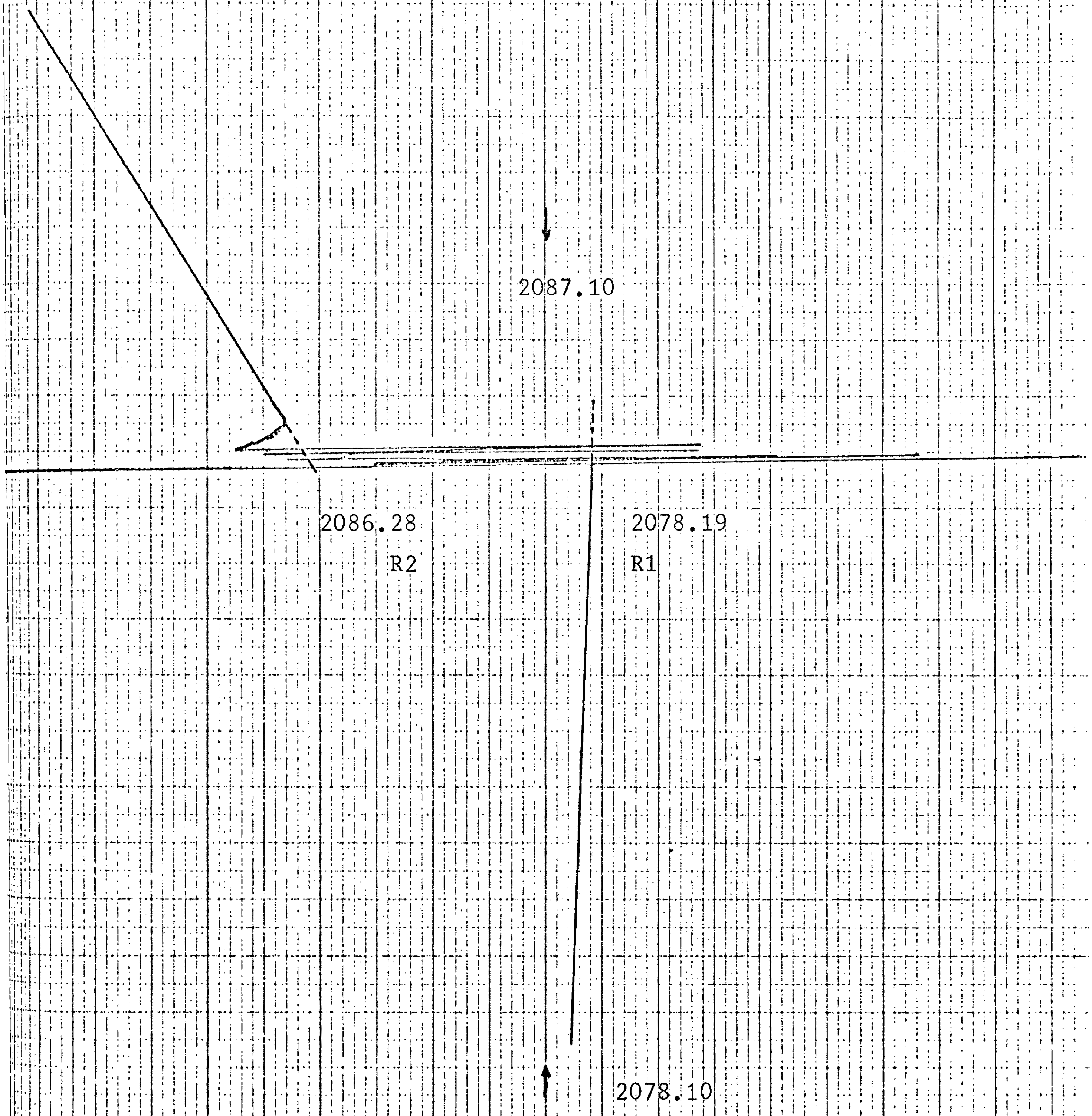
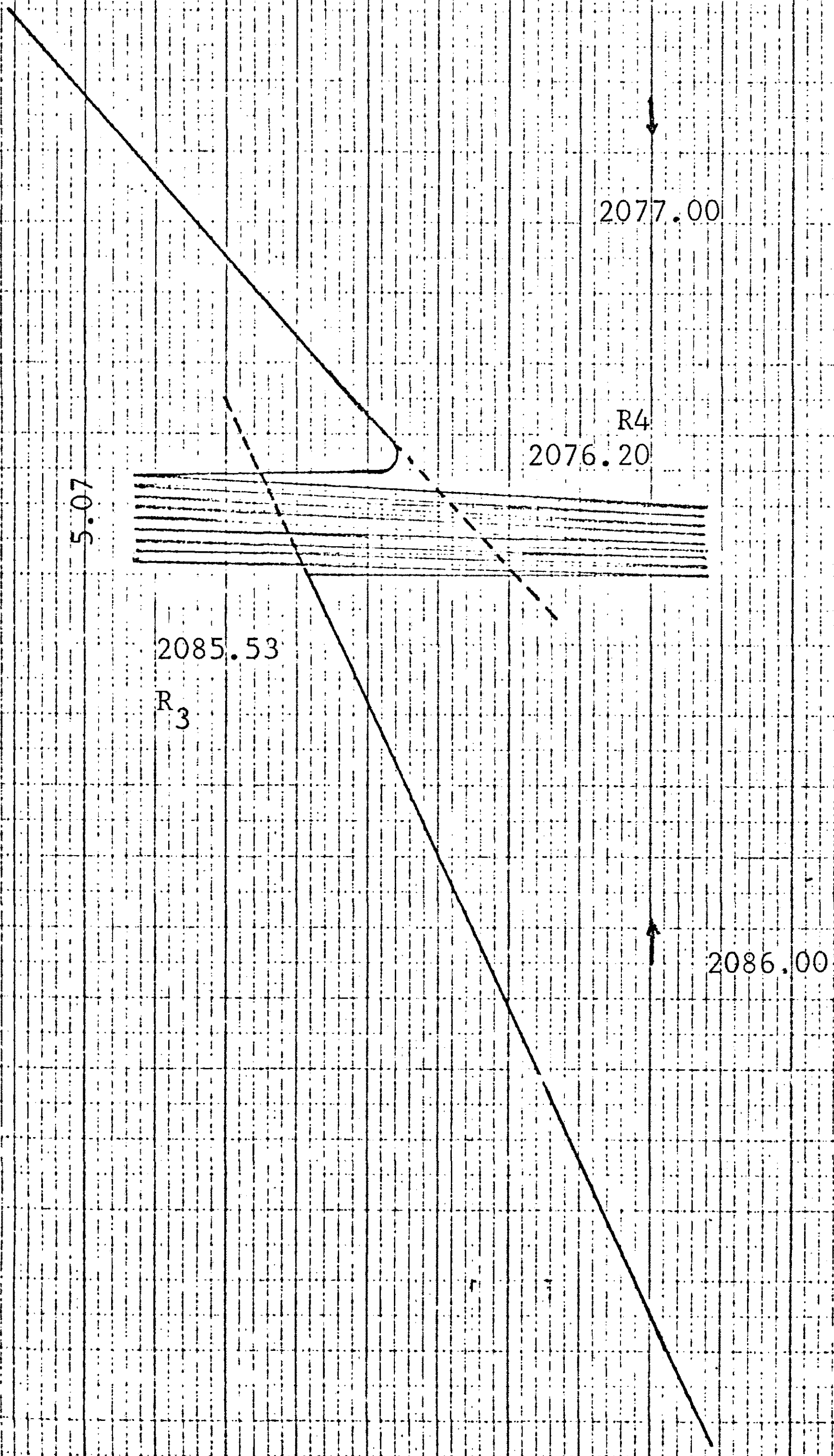


Fig. 3-B-10. TYPICAL $C_2H_5NH_3Cl/NaOH$ CALIBRATION TRACE



3-C TITRATION CALORIMETRY

The calorimeter described in section 3-B-(1) was employed to perform as a titration calorimeter. The following alterations were made:

(1) Titration delivery tube.

A tapered glass tube, ca. 8cm in length, Fig. 3-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 calorimeter fluid.

(2) Constant delivery rate syringe.

A 10cm^3 precision syringe ('Re-Pette' Jencons Ltd.) was actuated by an electric syringe drive (Harvard Apparatus, Model 975). 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 calorimeter fluid. The motor speed could be set by a dial (reading 1 to 30) and a setting of 15 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^o, in a 10cm^3 volumetric flask positioned beneath the titrant delivery tube. The results are contained in table 3-C-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 in table 3-C-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.

100 cm^3 of aqueous NaOH (0.0075M),warmed to 25°, 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 similarly filled with 100cm^3 of distilled water. The temperature of each vessel was adjusted as described in section 3-B-(1) and 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 1cm 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. 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 3-C-1 and 2, together with the method of extrapolation. The extrapolated ordinate height AA' was proportional to the heat evolved during the titration reaction. Similarly, 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 (Table 3-C-2):

$$-\Delta H^{\ominus}_{R} = \frac{\text{P. t. N. AA' reaction}}{\text{1000. AA' Calibration}}$$

where P and t are described in section 3-B-(1) and N is the number of moles of titrant reacted during the titration.

The calorimeter was employed to investigate the mechanism of the reaction of aqueous ICl_3 and aqueous $(CH_3COO)_3I$ with silver nitrate. The results are fully discussed for these experiments in section 2-E.

Fig. 3-C-1. THERMOMETRIC TITRATION HCl/NaOH REACTION

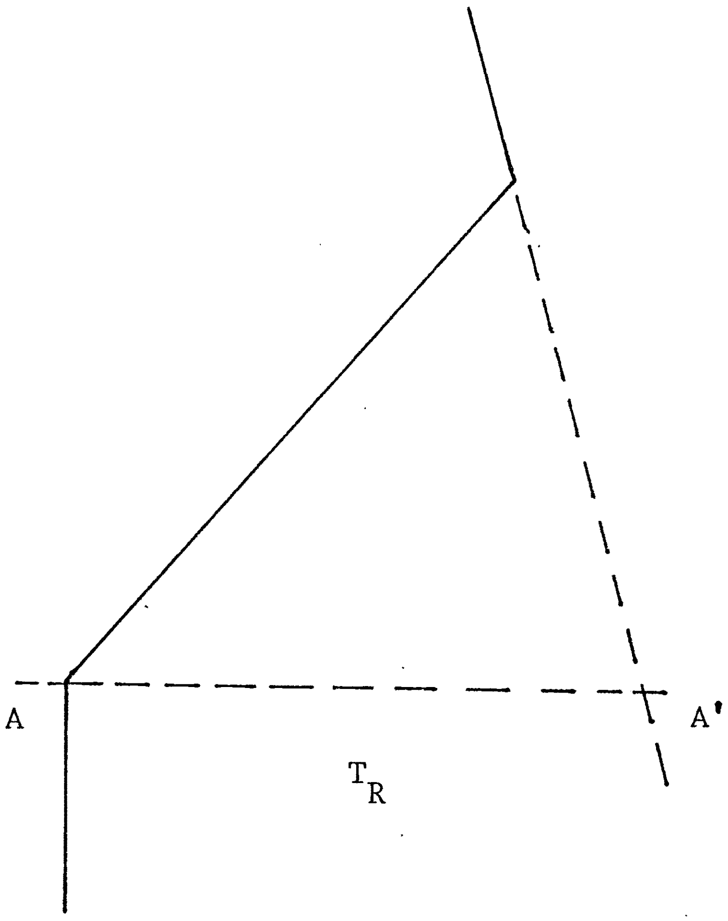


Fig. 3-C-2. THERMOMETRIC TITRATION HCl/NaOH CALIBRATION

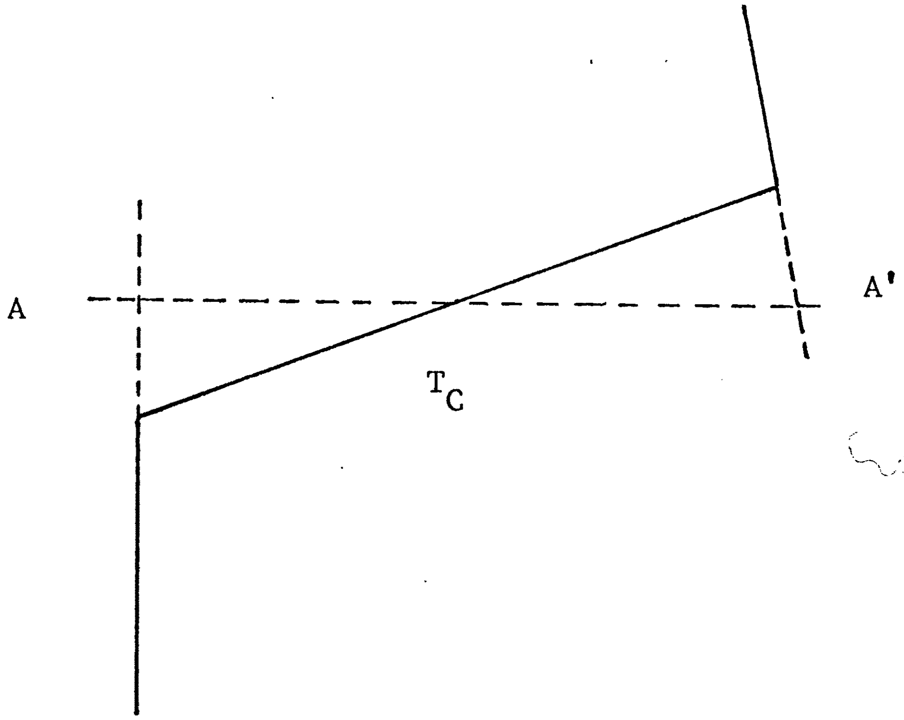


Table 3-C-1.

Calibration data for constant delivery rate syringe.

Mass H_2O W/g	Time/sec. T	W/g/T X10^{-3}
0.5790	304.2	1.903
0.4417	232.2	1.902
0.5412	285.0	1.900
0.7999	420.0	1.904
1.0385	545.0	1.905
0.6664	350.0	1.904
0.8373	440.0	1.903
0.7220	380.0	1.900
0.5237	275.5	1.901
0.5706	300.0	1.902

Table 3-C-2

Enthalpy of neutralization of HCl (1.0M) with NaOH (0.0075M).

$-\Delta H^{\theta}_{R}$ kJ mol^{-1}
54.00
56.32
53.40
56.74
55.94
55.20
55.50

ΔH^{θ}_{R} mean = -55.30 ± 1.18 kJ mol^{-1} (lit.(9) -55.80 ± 0.06)

3-D PREPARATION OF CALORIMETRIC SOLUTIONS.

(a) Silver nitrate solutions for reactions (1) to (10)

Calorimetric silver nitrate solutions were prepared by dissolving $AgNO_3$ (B.D.H. Analar R)in saturated silver iodate solution at 25°C. The excess silver iodate was removed by filtration to give a solution of $AgNO_3$ saturated with $AgIO_3$ at 25°. Silver iodat is slightly soluble in water (ca. 0.05g dm^3)$^{(10)}$. 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 above, had the concentration of 0.025 mol dm^3 for all the polyhalides except for NH_4ICl_4 0.1 mol dm^3.

(b) Sodium hydroxide solutions for reactions (11) to (19).

Sodium hydroxide used for these reactions was a stock solution of 0.1 mol dm^3. 100 cm^3 of this solution was pipetted for the calorimetric reaction.

3-E DETERMINATION OF CALORIMETRIC REACTION STOICHIOMETRY.

(a) For the reaction of polyhalides with silver nitrate.

(1) A weighed sample of polyhalide (ca. 0.3g) was reacted with a known excess of 0.1 mol dm^{3} aqueous silver nitrate solution (ca. 25 cm^{3}) contained in a stoppered conical flask. The precipitated silver halides were filtered off and the residual silver nitrate estimated by Volhard's method (11). The amount of $AgNO_3$ that had reacted with polyhalide, and hence the mole ratio $AgNO_3$:Polyhalide, was calculated.

(2) A weighed sample of polyhalide was reacted, at 25°C, with excess $AgNO_3$ saturated with $AgIO_3$. The precipitated silver salts we 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°C. The mole ratio $AgNO_3$:Polyhalide was determined.

3-F RAMAN SPECTRA.

Solid-state Raman spectra of the polyhalide compounds prepared in this work were obtained using a Coderg PHO Raman spectrometer. A coherent Radiation Model 52 krypton gas laser (647.1 nm) was used for excitation. The solid sample of polyhalide was powdered and loaded into capillary tubes which were sealed. For ICl_4^- compounds three bands were observed at 286 (ν_1,A_{1g}), 260(ν_4,B_{2g}) and 128 (ν_2,B_{1g}) cm^{-1} characteristic of this ion. In the case of ICl_2^+ ion three bands were observed at 365 (ν_1,a_1), 345 (ν_3,b_1) and 140 (ν_2,a_1) cm^{-1}.

Suggestions for further work.

Alkylammonium polyhalides with larger cations, e.g. propyl and butyl, can be readily prepared by reacting the appropriate alkylammonium halide with either chlorine gas or interhalogen compounds in a suitable solvent. For example, tetrabutylammonium tetrachloroiodate, $(C_4H_9)_4ICl_4$, is prepared by reacting tetrabutylammonium iodide with chlorine gas using chloroform as a solvent. The calorimetric reaction of these compounds with aqueous silver nitrate may be employed and the enthalpies of formation of these compounds calculated. This depends on the availability of the ancillary data for the reaction and also on the solubility of the alkylammonium salts in water. Enthalpy of formation data could then be used to calculate the thermochemical radii of the related cations and hence the lattice energies of the parent salts. Consequently, the enthalpies of formation of the gaseous cations may be determined using the method carried out in the present work (section 2-C). Such data allows us to estimate some thermodynamic properties of the cations in the gas phase and also to discuss the stabilities of the polyhalide compounds.

The enthalpies of formation of mono-, di- and tri-propyl and butylammonium halides (Cl, Br, I) can be investigated if the solubilities of the related amines in the aqueous solution are known. These enthalpies of formation can then be plotted against the number of propyl and butyl groups in order to investigate functional relationships. If there is a linear relationship between the enthalpies of formation of the mono-, di- and tri-propyl and butylammonium halides with the number of the propyl and butyl groups, the enthalpies of formation of the tetra-propyl and butylammonium halide (Cl, Br, I) could be determined by extrapolation procedures. These enthalpies of formation data can lead to more data relevant to the thermodynamic properties of the alkylammonium halide salts and therefore alkylammonium cations in particular.

Polyhalide complex cationic compounds, e.g. those containing IF_4^+, BrF_2^+, ICl_2^+ and I_2Cl^+ ions are preparable (see page 44). ICl_2SbCl_6 may, for example, be prepared by reacting $SbCl_5$ with ICl_3 in the presence of a suitable solvent. The enthalpy of formation of this compound can be determined using the appropriate calorimetric reaction. From the calorimetric work other thermodynamic properties on ICl_2^+ species could be obtained. These data may then be compared with the data already known for ICl_2^- species.

Compounds containing I (III) e.g. $I(CCl_3COO)_3$, $I(CHCl_2COO)_3$ and $I(CH_2ClCOO)_3$ are easy to prepare (12) and hydrolysis reaction of these compounds can be investigated. It would be interesting to see if there is any relationship between the enthalpies of formation of these compound with the substitution of hydrogen with chlorine in the acetyl group.

APPENDIX I

Waddington (13) and other authors (14,15-17) have reviewed lattice energies extensively. The lattice energy of an ionic crystal, U_o, is defined as the internal energy change when one mole of the compound, at one atmosphere pressure and at absolute zero temperature, is converted in to its constituent gaseous ions at infinite separation:

$$MX_n(c) \longrightarrow M^{n+}(g) + nX^-(g) \qquad \Delta H=U_o \qquad (1)$$

At temperature 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 298K, U_{298}, can be related to other thermodynamic quantities by the Born-Haber cycle as shown below:

$$\begin{tikzcd}
MX_n(c) \arrow[r, dash, "U_{298}(MX_n) + (n+1)RT"] & M^+(g) & + & nX^-(g) \\
& M(g) \arrow[u, "\sum_1^n I_n + 5/_2 nRT"'] & & nX(g) \arrow[u, "-nE_a - 5/_2 nRT"'] \\
& M(s.s.) \arrow[u, "\Delta H_f^o(M,g)"'] \arrow[uul, "\Delta H_f^o(MX_n,c)"] & & nX(s.s.) \arrow[u, "n\Delta H_f^o(X,g)"']
\end{tikzcd}$$

$\Delta H_f^\theta(MX_n,c)$, $\Delta H_f^\theta(M,g)$ and $H_f^\theta(X,g)$ are the enthalpies of formation of crystalline MX_n, gaseous M and X. $\sum_1^n In$ is the sum of the first, n ionisation potentials of M, and Ea is the electron affinity of the radical X. These values are corrected to 298K by the addition of $^5/_2$ nRT terms. No interaction is considered between the ions $M^{n+}(g)$ and

$X^-(g)$ as they are in the hypothetical ideal gas state.

From the cycle:

$$U_{298}(MXn) = \Delta H_f^\ominus(M,g) + n\Delta H_f^\ominus(X,g) + \sum_1^n In - nEa - \Delta H_f^\ominus(MX_n,c) - (n+1)RT \qquad (2)$$

consider $M(s.s.) \longrightarrow M^{n+}(g) + ne^-(g)$ $\qquad \Delta H_f^\ominus(M^{n+},g)$

and $nX(s.s.) + ne^- \longrightarrow nX^-(g)$ $\qquad n\Delta H_f^\ominus(X^-,g)$

Equation (2) becomes

$$U_{298}(MX_n) = \Delta H_f^\ominus(M^+,g) + n\Delta H_f^\ominus(X^-,g) - \Delta H_f^\ominus(MX_n,c) - (n+1)RT \qquad (\text{:}$$

The lattice energy at 298K can be related to lattice energy at absolute zero by:

$$U_{298} = U_o + \int_0^{298} Cp^o(M^+) + nCp^o(X^-) - Cp^o(MXn) \; . \; dT - (n-1)R\text{1} \qquad (4)$$

where the specific heats $Cp^o(M^+)$ and $Cp^o(X^-)$ are $^5/_2R$ for an ideal monotomic gas, then equation (4) becomes:

$$U_{298} = U_o + {}^3/_2(n-1)RT - \int_0^{298} Cp^\ominus(MXn). \quad dT \qquad (5)$$

If the specific heat temperature function of the compound MXn is known from 0-298K the integration can be performed.

Lattice energies can be obtained from extended classical calculations, if structural parameters for ionic compounds are known. These calculations involve the summing of attractive and repulsive interactions between ions in the crystal lattice.$^{(13)}$

Kapustinskii (17,18) has suggested a semi-empirical equation for the calculated of lattice energies where precise structural date is lacking. He showed that if the Madelung constants (the sum of the coulombic interaction terms characteristic of a crystal structure) for a number of crystals was divided by ν, the number of ions in one molecule, then values of A/ν were almost constant (table 1).

The Kapustinskii equation can be derived either from the classical Born-Landé or Born-Mayer equations which are respectively

$$U_o = \frac{N_A A e^2}{4\pi\varepsilon_o} \quad \frac{\nu}{2} \quad \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{1}{n}\right) \qquad (6)$$

$$U_o + \frac{N_A A e^2}{4\pi\varepsilon_o} \quad \frac{\nu}{2} \quad \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{}{(r_c + r_a)}\right) \qquad (7)$$

Where N 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, is the number of ions in the formula of the crystal.

If we assume a constant value of 0.0345 nm for ρ in equation (7) the following Kapustinskii Born-Mayer equation is obtained where the numerical constants have been calculated and evaluated:

$$U_o = 121.4 \ \nu \ \frac{Z_c Z_a}{(r_c + r_a)} \left(1 - \frac{\rho}{(r_c + r_a)}\right) \qquad (8)$$

Lattice energies calculated by equation (8) 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.

TABLE 1

Structure	Madelung constant, A	A/ν	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

If a complex cation or anion is present, to assign a value to the ionic ratius raises a difficulty when using the Kapustinskii equation. Yatsiminskii (19) 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

$$U_o + 2RT = \Delta H_f^{\ominus} M^{+}(g) + \Delta H_f^{\ominus} X^{-}(g) - \Delta H_f^{\ominus} MX(c)$$

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

$$U_1 + 2RT = \Delta H_f^{\ominus} M_1^{+}(g) + \Delta H_f^{\ominus} X^{-}(g) - \Delta H_f^{\ominus} M_1X(c) \qquad (9)$$

$$U_2 + 2RT = \Delta H_f^{\ominus} M_2^{+}(g) + \Delta H_f^{\ominus} X^{-}(g) - \Delta H_f^{\ominus} M_2X(c) \qquad (10)$$

(9) - (10),

$$U_1 - U_2 = \Delta H_f^{\ominus} M_1^{+}(g) - \Delta H_f^{\ominus} M_2^{+}(g) - \Delta H_f^{\ominus} M_1X(c) + \Delta H_f^{\ominus} M_2X(c) \qquad (11)$$

From the Kapustinskii equation:

$$U_1 - U_2 = C \left[\frac{1}{r_{M_1^+} + r_{X^-}} \left(1 - \frac{0.0345}{r_{M_1^+} + r_{X^-}} \right) - \frac{1}{r_{M_2^+} + r_{X^-}} \left(1 - \frac{0.0345}{r_{M_2^+} + r_{X^-}} \right) \right] \qquad (12)$$

Therefore, if the enthalpies of the gaseous ions and crystalline salts, and ionic radii of M_1^+ and M_2^+ are known the equations (11) and (12) may be used and the value of r_{X^-} calculated.

Radii obtained from these equations are known as 'thermochemical radii'. These radii can be inserted in equation (7), 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 (9) or (10) will give the standard enthalpy of formation of the gaseous anion X^-. 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 Hewlett Packard HP-65 programmable calculator was used to calculat the thermochemical radii. The programme supplied with the calculator (Math 1-08 A) is listed on the following pages.

Math (1 - 08 A)

Fourth Degree Polynomial Equation.

This programm can be used in conjunction with Math 1 - 07 A, Cubic Equation and Math 1 - 06 A, Quadratic Equation, to find the roots (real and/or imaginary) of a fourth degree polynomial equation of the form:

$$X^4 + a_3X^3 + a_2X^2 + a_1X + ao = o$$

where ai (i = 0, 1, 2, 3) are real.

LINE	INSTRUCTIONS	DATA	KEYS		DISPLAY
1	Enter program *Math 1–08A*				
2		a_3	R/S		
3		a_2	R/S		
4		a_1	R/S		
5		a_0	R/S		b_0
6	If $b_0 \neq 0$, go to 17				
7	$b_0 = 0$ hence $y_1 = 0$				
8	Enter program *Math 1–06A*				
9			D	A	D_1
10	If $D_1 < 0$, $y_0 = 0$, go to 13				
11	$D_1 > 0$, y_2 v_3 are real		B		y_2
12	Record y_2, y_3		R/S		y_3
13	y_0 = Max. of real roots	y_0	STO	4	
14	Enter program *Math 1–08A*				
15	Compute A ± C, B ± D		B		
16	Go to 32				
17	Enter program *Math 1–07A*				
18			A		y_1
19	Record y_1		R/S		
20	Enter program *Math 1–06A*				
21			A		D_2
22	If $D_2 < 0$, $y_0 = y_1$, go to 25				
23	$D_2 > 0$, y_2, y_3 are real		B		y_2

24	Record y_2, y_3		R/S		y_3
25	y_0 = Max. of real roots	y_0	STO	4	
26	Enter program *Math 1–03A*				
27		a_3	R/S		
28		a_2	R/S		
29		a_1	R/S		
30		a_0	R/S		
31	Compute A ± C, B ± D		B		
32	Enter program *Math 1–06A*				
33			A		D_3
34	If $D_3 < 0$, go to 38				
35	$D_3 > 0$, roots are real		B		root
36			R/S		root
37	Go to 40				
38	$D_3 < 0$, roots are u ± iv		C		u
39			R/S		v
40	Solve the 2nd quadratic		E	A	D_4
41	If $D_4 < 0$, go to 44				
42	$D_4 > 0$, roots are real		B		root
43			R/S		root
	(All roots are found)				
44	$D_4 < 0$, roots are s ± it		C		s
45			R/S		t

QUADRATIC EQUATION

CODE	KEYS
23	LBL
11	A
33 03	STO 3
35 08	g R↓
33 02	STO 2
35 08	g R↓
41	↑
61	+
33 01	STO 1
34 02	RCL 2
35 07	g x⇄y
81	÷
42	CHS
41	↑
32	f^{-1}
09	$\sqrt{x}$
34 03	RCL 3
41	↑
61	+
34 01	RCL 1
81	÷
51	–
24	RTN
23	LBL
12	B
31	f
09	$\sqrt{x}$
33 01	STO 1
61	+
35 07	g x⇄y
34 01	RCL 1
51	–
35 07	g x⇄y
84	R/S
35 07	g x⇄y

CODE	KEYS
24	RTN
23	LBL
13	C
42	CHS
31	f
09	$\sqrt{x}$
35 07	g x⇄y
84	R/S
35 07	g x⇄y
24	RTN
23	LBL
14	D
01	1
34 01	RCL 1
34 02	RCL 2
24	RTN
23	LBL
15	E
01	1
34 07	RCL 7
34	RCL
09	9
24	RTN
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP

CODE	KEYS
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP
35 01	g NOP

R_1	Used	R_4		R_7	
R_2	b	R_5		R_8	
R_3	c	R_6		R_9	

CUBIC EQUATION

CODE	KEYS
23	LBL
11	A
00	0
33 04	STO 4
34 03	RCL 3
35	g
06	ABS
34 03	RCL 3
81	÷
33 06	STO 6
34 03	RCL 3
35	g
06	ABS
34 01	RCL 1
35	g
06	ABS
61	+
43	EEX
42	CHS
02	2
23	LBL
01	1
01	1
00	0
71	x
35 22	g x≤y
22	GTO
01	1
33 07	STO 7
23	LBL
02	2
34 07	RCL 7
01	1
00	0
81	÷
33 07	STO 7
34 06	RCL 6
42	CHS
33 06	STO 6
23	LBL
03	3
34 07	RCL 7
34 06	RCL 6
71	x
34 04	RCL 4
61	+
33 05	STO 5
34 04	RCL 4
35 23	g x=y
22	GTO
04	4
34 05	RCL 5
34 01	RCL 1
61	+
34 05	RCL 5
71	x
34 02	RCL 2
61	+
34 05	RCL 5
71	x
34 03	RCL 3
61	+
33 08	STO 8
35	g
06	ABS
43	EEX
42	CHS
04	4
35 24	g x>y
22	GTO
04	4
34 05	RCL 5
33 04	STO 4
34 08	RCL 8
34 06	RCL 6
71	x
00	0
35 24	g x>y
22	GTO
03	3
22	GTO
02	2
23	LBL
04	4
34 05	RCL 5
84	R/S
34 01	RCL 1
61	+
33 08	STO 8
34 05	RCL 5
71	x
34 02	RCL 2
61	+
33 03	STO 3
01	1
34 08	RCL 8
34 03	RCL 3
84	R/S
35 01	g NOP
35 01	g NOP

R_1	Used	R_4	Used	R_7	Used
R_2	Used	R_5	Used	R_8	Used
R_3	Used	R_6	Used	R_9	Used

FOURTH DEGREE POLYNOMIAL EQUATION

CODE	KEYS
33 08	STO 8
84	R/S
33 07	STO 7
84	R/S
33 06	STO 6
84	R/S
33 05	STO 5
23	LBL
11	A
34 07	RCL 7
42	CHS
33 01	STO 1
34 08	RCL 8
34 06	RCL 6
71	x
34 05	RCL 5
04	4
71	x
51	−
33 02	STO 2
34 07	RCL 7
04	4
71	x
34 08	RCL 8
32	f^{-1}
09	$\sqrt{x}$
51	−
34 05	RCL 5
71	x
34 06	RCL 6
32	f^{-1}
09	$\sqrt{x}$
51	−
33 03	STO 3
84	R/S
23	LBL
12	B
02	2
33	STO
81	÷
08	8
34 04	RCL 4
02	2
81	÷
33 04	STO 4
32	f^{-1}
09	$\sqrt{x}$
34 05	RCL 5
51	−
31	f
09	$\sqrt{x}$
33 05	STO 5
00	0
35 23	g x=y
22	GTO
01	1
34 08	RCL 8
34 04	RCL 4
71	x
34 06	RCL 6
02	2
81	÷
51	−
34 05	RCL 5
81	÷
33 06	STO 6
22	GTO
02	2
23	LBL
01	1
34 08	RCL 8
32	f^{-1}
09	$\sqrt{x}$
34 07	RCL 7
51	−
34 04	RCL 4
02	2
71	x
61	+
31	f
09	$\sqrt{x}$
33 06	STO 6
23	LBL
02	2
34 08	RCL 8
61	+
33 07	STO 7
34 04	RCL 4
34 05	RCL 5
61	+
33	STO
09	9
01	1
34 08	RCL 8
34 06	RCL 6
51	−
34 04	RCL 4
34 05	RCL 5
51	−
24	RTN

R_1	b_2	R_4	Y_0, B	R_7	a_2, A + C
R_2	b_1	R_5	a_0, D	R_8	a_3, A
R_3	b_0	R_6	a_1, C	R_9	B + D

APPENDIX II

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 Electronic 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 record 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 voltage on its inputs to the chart recorder.

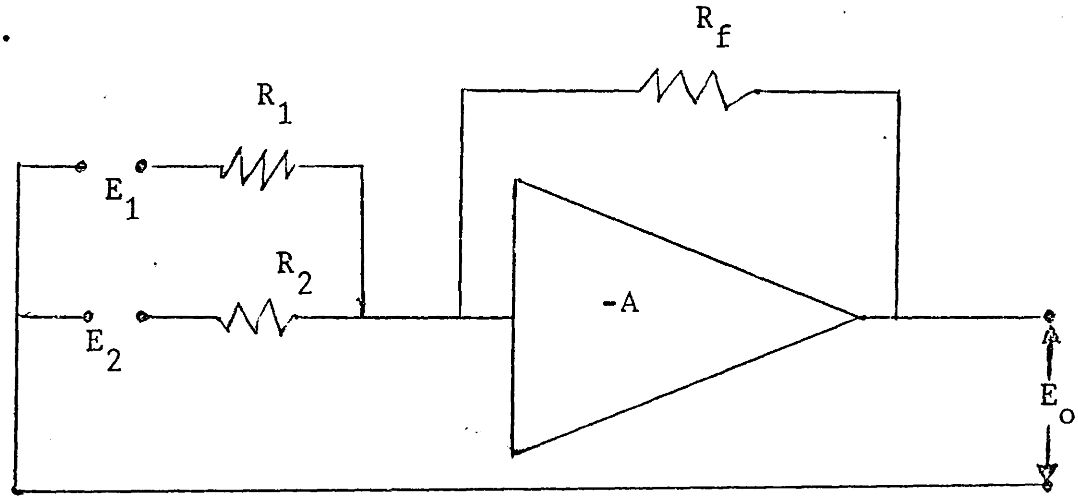


Figure 1.

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: currents in the input resistors R_1 and R_2 are

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

similarly the current in the feed-back resistor R_f due to the output voltage, E_o is $\frac{E_o}{R_f}$. 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:

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

solving this expression for the output voltage, E_o, gives

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

But $R_1 = R_2 + R_f = 1K\Omega$ hence: $E_o = - (E_i + E_2)$

Specification of Differential Thermistor Bridge.

Bridge drive voltage: 5KHZ, square-wave 2.0 volts P-P.

Discrimination: Better than 2X 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.

APPENDIX III

ERRORS.

The uncertainties of the heat of reaction of any compound undertaken in this work has been quoted as twice the standard deviation of the mean, $\bar{s}$:

$$\bar{s} = \left[\frac{\sum (X-\bar{X})^2}{n(n-1)} \right]^{1/2}$$

where $\bar{X}$ is the arithmetic mean of n results.

All 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 'student t' distribution Therefore all results in this work are reported as $\bar{X} \pm t\bar{s}$ where t is the 'student t' value for the (n-1)degree of freedom at the 95% confidence interval.(20)

For the uncertainty of the enthalpy of formation where:

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

and ΔH_i has an uncertainty interval of $\pm X_i$, then the error for ΔH was taken as:

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

APPENDIX IV

Titration Curves for Strong and Weak Acid Mixture.

The derivation of a theoretical titration curve for a mixture of a strong and weak acid is usually fairly simple, provided the weak acid has a dissociation constant smaller than 1×10^{-4}. The PH of the solution at any point short of the first equivalence point is found from the formal concentration of the strong acid. Neutralization of the strong acid is complete at the first equivalence point; for purposes of PH calculation, the solution is then treated as that of a simple weak acid. The remainder of the titration curve is therefore characteristic of the weak acid.

Curves with two inflection points are obtained for mixtures of this type. Where the weak acid has a dissociation constant smaller than approximately 10^{-5}, the PH change at the first equivalence point is well-marked. However, if the weak acid has a dissociation constant greater than 10^{-5}, only a single inflection point is observed, corresponding to the <u>total</u> acid content of the solution.

Titration of the mixture of iodic acid and acetic acid ($K_a = 1.80 \times 10^{-5}$) with aqueous sodium hydroxide 0.1 mol dm^{-3} falls into this latter category and only one end point for the <u>total</u> acid was observed.

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