THERMODYNAMIC PROPERTIES OF PERCHLORATES

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by

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To my parents and Jenny

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Abstract

The standard heats of formation of alkyl ammonium perchlorates, $R_nNH_{4-n}ClO_4$ (R = Me, n = 1 - 4; R = Et, n = 1 - 4; R = Pr, n = 1 and 3), have been determined by solution reaction calorimetry. Using these and corresponding data for the alkyl ammonium halides and nitrates, a set of self-consistent 'thermochemical' radii for the alkyl ammonium ions were obtained. The Kapustinskii equation was used to estimate lattice energies of the alkyl ammonium perchlorates and these data were included in a thermochemical cycle to derive the proton affinities of the parent alkyl amines.

The polymorphic phase transitions of these alkyl ammonium perchlorates have been investigated via Differential Scanning Calorimetry over the temperature range -90° to $250^{\circ}C$. The transition temperatures and enthalpies have been recorded. The enthalpy of the II - I phase transition of ammonium perchlorate has been reported for the first time by a direct method. These data allow the effect of increasing the size of the alkyl group and the transition temperatures to be correlated.

The triarylmethyl perchlorates, $(p\text{-}X\text{-}C_6H_4)_3CClO_4$ (where X = H, Me and MeO), have been synthesised and their standard heats of formation determined by solution reaction calorimetry. An improved synthesis of tri(p-nitrophenyl)methyl chloride has also been reported.

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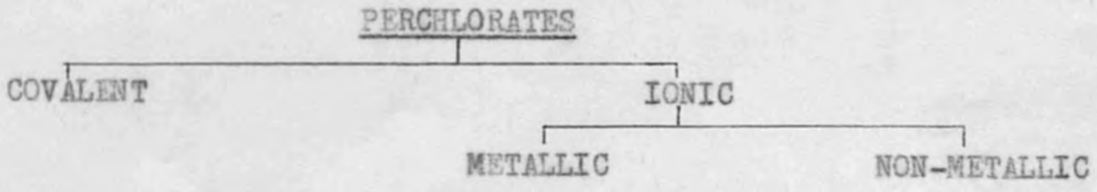
SECTION 1

1a Introduction

The rapidly expanding literature on perchlorates over the past few years indicates the considerable interest in this field (Dorofeenko et al, 1965 and references therein). This interest stems from the fact that perchlorates are a ready source of oxygen and thus have considerable potential in modern explosive and propellant technology.

Perchlorates, in general, can be subdivided into ionic and covalent types. The ionic category can be further divided into metallic and non-metallic. Examples of compounds which fall into these categories are given in the chart below.



e.g.	e.g.	e.g.
CH_3OClO_3	$LiClO_4$	$NH_4^+ ClO_4^-$
$C_2H_5OClO_3$	$KClO_4$	$R_4N^+ClO_4^-$
$C_6H_5COOClO_3$	$Mg(ClO_4)_2$	$NO_2^+ ClO_4^-$
		$N_2H_5^+ ClO_4^-$
		$Ph_3C^+ ClO_4^-$

The chemistry and thermodynamic data for ionic and covalent perchlorates have been reviewed by Burton and Praill in 1955, Schumacher in 1960 and Dorofeenko et al in 1965.

The simple covalent esters, such as methyl and ethyl perchlorates are colourless oils which are powerful shock-sensitive explosives (Hare and Boye, 1841). Very few of these covalent esters have been investigated owing to their instability. These covalent esters are characterised by possessing a Cl-O-C unit.

Ammonium perchlorate is the most important member of the non-metallic category and in the last few years there have been three reviews on this compound (Hall and Pearson, 1967; Jacobs and Whitehead, 1969; Keenan and Siegmund, 1969). Pearson in 1968 has also reviewed the thermal decomposition and thermodynamic data of many non-metallic perchlorates.

The non-metallic perchlorates are safer to handle than covalent perchlorates; however, they are still powerful explosives. Compounds which contain the combustible material and the oxidant in the same molecule, are in general much more violent in their explosive action than mixtures comprising separate fuels and oxidants. Methyl-substituted ammonium perchlorates, for example, have been patented as explosives (Lungsgaard and Herbst, 1921). They are reported to be stable compounds, which, with the exception of dimethyl ammonium perchlorate are non-hydroscopic. These compounds are, however, much more sensitive to shock than ammonium perchlorate. Stammler et al, 1966, report safety tests carried out on these compounds, in comparison to RDX (hexamethylene tetranitramine) and ammonium perchlorate. The results are recorded in table 1.1 as the height from which a 2 Kg. weight causes 50% detonations, under standard conditions.

Table 1.1

Sensitivity Tests on Amine Perchlorates

Compound	Height (cm)
RDX	33
NH_4ClO_4	100
$MeNH_3ClO_4$	20
$Me_2NH_2ClO_4$	22
Me_3NHClO_4	25
Me_4NClO_4	35
$(CH_2NH_3)_2(ClO_4)_2\ \frac{1}{2}H_2O$	35

Mixtures of ethylenediamine diperchlorate with picric acid have also been patented as explosives (Vogl, 1946).

These alkyl-substituted ammonium perchlorates can be prepared by the reaction of the appropriate amine with perchloric acid

$$R_nNH_{3-n} + HClO_4 = R_nNH_{4-n}ClO_4$$

or metathesis between an alkyl ammonium halide and silver perchlorate.

$$R_nNH_{4-n}Cl + AgClO_4 = R_nNH_{4-n}ClO_4 + AgCl$$

The solubilities of some of these amine perchlorates in water have been reported (Hofmann et al, 1910 b) and their explosion temperatures are in the range 250° - 300°C (Datta and Chatterjee, 1919).

Thermodynamic data for these alkyl-substituted ammonium perchlorates, do not appear to have been reported in the literature. The standard heats of formation of the related alkyl- substituted ammonium nitrates and chlorides have, however, been reported by Wagman et al, 1968. The standard heats of formation of methyl- and ethyl- substituted ammonium nitrates were initially measured by Cottrell and Gill, 1951, by bomb calorimetry and have been updated by Wagman. The source of Wagman's data is not clear as the compilation does not include references. Aston and Ziemer, 1946, studied the heat of reaction of aqueous methylamine with hydrochloric acid in order to obtain the standard heat of formation of methyl ammonium chloride.

The majority of the present work is concerned with the thermodynamic properties of non-metallic perchlorates, mainly alkylammonium perchlorates but including some triarylmethyl perchlorates. The synthetic precursor for the triarylmethyl perchlorates was the corresponding triarylmethanol. Two synthetic routes are available for the preparation of triarylmethanols.

1) A direct route via a Grignard procedure, which should be suitable for triarylmethanols containing the following substituents in the benzene ring, Me, Et, Cl, Br and MeO. The reaction is summarised by

$$\mathrm{ArMgBr + ArCOOMe} \xrightarrow[\text{2. } \mathrm{H^+/H_2O}]{\text{1. } \mathrm{Et_2O}} \mathrm{Ar_3COH}$$

where Ar = p-substituted phenyl

2) The second route involves the preparation of the triarylmethane, which is subsequently oxidised to the triarylmethanol. Tri(p-nitrophenyl)methanol was prepared in this manner. Tri(p-nitrophenyl)methane is first prepared by nitrating triphenylmethane (Montagne, 1905).

$$\mathrm{Ph_3CH} \xrightarrow[-65^{\circ}\mathrm{C}]{\mathrm{HNO_3}} \mathrm{(p\text{-}NO_2C_6H_4)_3CH}$$

The tri(p-nitrophenyl)methane can then be oxidised to tri(p-nitrophenyl)methanol by chromium(III) trioxide in glacial acetic acid

$$\mathrm{(p\text{-}NO_2Ph)_3CH} \xrightarrow[\mathrm{ACOH}]{\mathrm{CrO_3}} \mathrm{(p\text{-}NO_2Ph)_3COH}$$

Triarylmethyl perchlorates can be prepared from the triarylmethanols by reacting the latter with perchloric acid

$$Ph_3COH + HClO_4 = Ph_3CClO_4 + H_2O$$

or by the reaction of triarylmethyl chlorides with silver perchlorate in a polar non-aqueous solvent.

$$Ph_3CCl + AgClO_4 = Ph_3CClO_4 + AgCl$$

The triarylmethyl perchlorates were among the first carbonium salts to be prepared (Gomberg, 1907; Gomberg and Cone, 1909). They are coloured crystalline salts which have high melting points (Pfeiffer, 1927). Their structure has been investigated by electrical conductivity in non-aqueous solvents (Hofman et al, 1910 a; Lifschitz and Girbes, 1928; Ziegler and Wollschitt, 1930; Longworth and Mason, 1966) and by absorption spectroscopy (Hantzsch, 1921; Anderson, 1930).

Although the amine and triaryl carbonium perchlorates have been known since the beginning of the century, very little thermodynamic data are available. However, much of the ancillary data have been recorded so that the standard heats of formation of alkyl-substituted ammonium perchlorates and triarylmethyl perchlorates can be measured readily. The standard heats of formation of aqueous alkyl-substituted ammonium ions and aqueous perchlorate ions have been reported by Wagman et al, 1968. With these data the standard heats of formation of the alkyl-substituted ammonium salts can be obtained by a direct heat of solution experiment. The standard heats of formation of triphenylmethane ($C_{19}H_{16}$) and triphenylmethanol ($C_{19}H_{16}O$) have been obtained by bomb calorimetry

$$\Delta H_f^\circ (C_{19}H_{16}, c) = 40.9 \pm 0.4 \text{ Kcal.mole}^{-1} \text{ (Coops et al, 1964)}$$

$$\Delta H_f^\circ (C_{19}H_{16}O, c) = 0.8 \pm 0.6 \text{ Kcal.mole}^{-1} \text{ (Parks et al, 1964)}$$

In view of the lack of thermodynamic data for organic perchlorates, the main aim of this work has been the determination of standard heats of formation of amine and triarylmethyl perchlorates. The standard heats of formation were determined by solution-reaction calorimetry and these results are presented in Section 4. These data permit tentative evaluation of these ionic perchlorates as potential explosives in terms of their thermodynamic stability and enthalpies of decomposition.

1b Lattice Energy

The lattice energy of a compound, U_o, at 0°K, is defined as the internal energy change observed when one mole of the solid, at one atmosphere pressure, is converted into defined infinitely dilute ideal gaseous ions. At 0°K these ions are stationary. According to this definition energy must be supplied to dissociate the crystal lattice and so the overall process is endothermic.

The Born-Haber cycle can be used to relate the lattice energy at 298°K, U_{298}, to other thermodynamic quantities. Such a cycle, for the compound MX_n, is shown in Fig. 1.1.

Fig. 1.1

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

In this cycle, $\Delta H_f^{\circ}(MX_n, c)$, $\Delta H_f^{\circ}(M, g)$ and $\Delta H_f^{\circ}(X, g)$ represent the standard heats of formation of crystalline MX_n, gaseous M and gaseous X from their elements in their standard states. In this cycle M and X represent general cations and anions. $\sum_1^n In$ is the sum of the first n ionisation potentials and $E_a(X)$ is the electron affinity of X. These values are corrected to 298°K by the $^5/_2nRT$ terms. The ions M^{n+} (g) and X^- (g) are in a hypothetical infinitely dilute ideal gas state and so there is no need to consider any interaction between them.

The lattice energy can be related to the other terms in the Born-Haber cycle by the equation

$$U_{298}(MX_n) = \Delta H_f^{\circ}(m,g) + \sum_{1}^{n} In + \Delta H_f^{\circ}(X,g) - nE_a - \Delta H_f^{\circ}(MX_n,c) - (n+1)RT$$

Since $M\ (s.s.) \longrightarrow M^{n+}\ (g) + ne\ (g)$ .... $\Delta H_f^{\circ}\ (M^{n+},g)$

and $X\ (s.s) + e \longrightarrow X^-\ (g)$ .... $\Delta H_f^{\circ}\ (X^-,g)$

the above equation can be condensed to

$$U_{298}\ (MX_n) = \Delta H_f^{\circ}(m^+,g) + n\,\Delta H_f^{\circ}(X^-,g) - \Delta H_f^{\circ}(MX_n,c) - (n+1)RT$$

The lattice energy at 298°K is related to the lattice energy at 0°K by the equation

$$U_{298} = U_o + {}^3/_2\ R.\ 298(n+1) - \int_o^{298} C^{\circ}p\ (MX_n)\ dT$$

This calculation can be performed if the specific heat-temperature function from 0° - 298°K is known for MX_n.

Lattice energies can also be obtained from classical extended calculations.by summing the interionic attractive and repulsive interactions. Waddington, 1959, discusses the equations used for such calculations. These calculations are, however, limited to those compounds whose crystal structures have been determined.

The use of the Born-Haber cycle is also limited to those compounds for which the appropriate ionisation potential and electron affinity data are available. For those compounds for which these data are lacking, e.g. alkyl-substituted ammonium salts, estimation procedures for lattice energy must be used. The most useful of these is the semi-empirical Kapustinskii equation (Kapustinskii, 1933 and 1956). Kapustinskii has shown that, if the Madelung constants (terms characteristic of the crystal structure) for a number of structures were divided by the number of ions per molecule ($^M/_v$, the values obtained were almost constant. (Table 1.2).

Table 1.2

Structure	Madelung Const., M	$^M/_v$	Average Coordination Number
Caesium chloride	1.763	0.88	8.0
Sodium chloride	1.748	0.87	6.0
Fluorite	2.519	0.84	5.33
Wurtzite	1.641	0.82	4.0
Rutile	2.408	0.80	4.0
Anastase	2.400	0.80	4.0
Cuprite	2.221	0.74	2.67

The values of M/v vary in approximately the same order as the values of the average coordination number around the ions. The equilibrium internuclear distance (r_o) in an ionic compound generally increases slightly with coordination number and so values of $M/v\ r_o$ will be almost constant. Kapustinskii assumes $M/v\ r_o$ is constant so that, for a given salt

$$\frac{M_1}{r_1} = \frac{M_2}{r_2}$$

where subscript 1 refers to the salt's real Madelung constant and internuclear separation and subscript 2 refers to theoretical Madelung constant and internuclear separation. Thus, Kapustinskii considers all salts to theoretically crystallise in a sodium chloride lattice and their lattice energies are given by

$$U_K = \frac{M_1 N_o v Z_+ Z_- e^2}{r_1} \left[1 - \frac{0.345}{r_1} \right]$$

where N_o is the Avogadro number, Z_+ and Z_- are the cationic and anionic charges, e is the electronic charge and M_1 and r_1 are the Madelung and internuclear separation terms for the compound in a sodium chloride lattice. Kapustinskii further assumes that the anion and cation 'touch', so that the internuclear separation term can be replaced by the sum of the anionic and cationic radii.

$$r_1 = r_c + r_a$$

Thus for a univalent-univalent system, Kapustinskii's equation becomes

$$U_K = \frac{574.4}{(r_c+r_a)} \left[1 - \frac{0.345}{r_c+r_a} \right]$$

where r_c and r_a are the Goldschmidt cationic and anionic radii for coordination number 6.

Lattice energies obtained from the Born-Haber cycle, extended calculation and Kapustinskii equation are compared in table 1.3.

Table 1.3

Comparison of Lattice Energies for Alkali Metal Halides (Kcal.mole^{-1})

Salt	Born-Haber	Extended Calculations(a)	Kapustinskii Eqn.(b)
NaCl	183.8	183.5	179.9
NaBr	175.9	175.5	175.5
NaI	164.5	164.3	161.0
KCl	166.8	167.9	162.7
KBr	160.7	161.3	161.3
KI	151.0	152.4	146.8
RbCl	162.0	162.0	158.2
RbBr	155.2	156.1	149.7
RbI	146.5	148.6	141.0

(a) Kapustinskii, 1943

(b) Huggins, 1938.

A comparison of the values of lattice energies obtained from the Kapustinskii equation with the other values in table 1.3 shows that the estimated values are in general too low. Yatsimirskii, 1961, has therefore modified Kapustinskii's equation to

$$U_y = \frac{287.2\ v\ Z_+\ Z_-}{r_c + r_a}\left[1 - \frac{0.345}{r_c + r_a}\right] + 2.5\ v\ Z_+\ Z_-$$

The correction term adds 5 Kcal.mole^{-1} to the original lattice energies for a uni- univalent salt. The problem arises, when considering a complex cation or anion, of defining and then assigning an ionic radius. Yatsirirskii, 1947, proposed the following method.

Consider two salts with a common anion. Their lattice enthalpies are given by

$$M_1X\ (c) = M_1^+\ (g) + X^-\ (g) \qquad \ldots.\ \Delta H_1$$

$$M_2X\ (c) = M_2^+\ (g) + X^-\ (g) \qquad \ldots.\ \Delta H_2$$

and

$$\Delta H_1 - \Delta H_2 = U_1 - U_2 = \Delta H_f^{\circ}(M_1^+, g) - \Delta H_f^{\circ}(M_2^+, g) - \Delta H_f^{\circ}(M, X, c) + \Delta H_f^{\circ}\ (M_2X, c)$$

From the Kapustinskii equation

$$U_1 - U_2 = A\left[\frac{1}{(r_{M_1^+} + r_{X^-})}\left[1 - \frac{0.345}{(r_{M_1^+} + r_{X^-})}\right] - \frac{1}{(r_{M_2^+} + r_{X^-})} \times \left[1 - \frac{0.345}{(r_{M_2^+} + r_{X^-})}\right]\right]$$

The last two equations can be equated and rearranged into a form to obtain the anionic radii. Radii obtained in this way are termed 'thermochemical' radii. Thus, if the standard heats of formation of the gaseous cations and the crystalline salts, and the Goldschmidt radii of M_1^+ and M_2^+ are known, then the 'thermochemical' radii of the anion can be calculated. These radii can then be inserted into the Kapustinskii/Yatsimirskii equation to obtain the lattice energy for another salt or series of salts containing this anion.

This method can be used in a similar manner to obtain the radius of a complex cation, by considering two salts with a common cation. This method has been used in Section 5 to obtain the 'thermochemical' radii of the methyl- and ethyl- substituted ammonium ions. The above equations can also be used to obtain the standard heat of formation of a complex gaseous ion, e.g. $\Delta H_f^\circ(ClO_4^-, g)$, assuming all the ionic radii are known. Lattice energies calculated via the Kapustinskii/Yatsimirskii equation, for the alkyl substituted ammonium salts, are presented in Section 5.

The lattice enthalpies of ammonium halides have been used to obtain the proton affinity of gaseous ammonia (Grimm, 1927). Consider ammonium chloride as an example

$$NH_4Cl\ (c) \;=\; NH_4^+\ (g) + Cl^-\ (g) \qquad \ldots\ \Delta H_L^\circ$$

$$NH_4^+\ (g) \;=\; NH_3\ (g) + H^+\ (g) \qquad \ldots\ P$$

where P is the proton affinity.

Thus $$\Delta H_L{}^{\circ} = \Delta H_f{}^{\circ}(NH_4{}^+,g) + \Delta H_f{}^{\circ}(Cl^-,g) - \Delta H_f{}^{\circ}(NH_4Cl,c)$$

and $$P = \Delta H_f{}^{\circ}(NH_3,g) + \Delta H_f{}^{\circ}(H^+,g) - \Delta H_f{}^{\circ}(NH_4{}^+,g)$$

adding and rearranging,

$$P = \Delta H_f{}^{\circ}(NH_3,g) + \Delta H_f{}^{\circ}(H^+,g) + \Delta H_f{}^{\circ}(Cl^-,g) - \Delta H_L{}^{\circ} - \Delta H_f{}^{\circ}(NH_4Cl,c)$$

Waddington, 1959, suggests that this method could be extended to obtain the proton affinities of alkyl substituted amines, provided that their lattice enthalpies were known. The data determined and correlated in the present work make such determinations possible and they are considered further in Section 5.

1c Polymorphism in Alkyl Ammonium Salts

The polymorphic phase changes which occur in ammonium halides have been summarised by Stammler, 1967, and are reported in table 1.4 (Phase IV denotes the lowest temperature forms). The phase III to phase II transition is thought to be due to the onset of orientational disorder ('order-disorder') of the ammonium cations. This concept was introduced by Frenkel in 1935 and is supported by Levy and Peterson, 1953, on the basis of neutron diffraction experiments. The latter authors also propose that the phase II to phase I transition are due to the onset of rotation of the $NH_4{}^+$ ion.

Table 4.1

Transition Temperatures and Crystal Structures (in parentheses) of Ammonium Halides

$$\mathrm{NH_4Cl} \qquad \text{Phase III (CsCl)} \xrightleftharpoons{-30.5^\circ\mathrm{C}} \text{Phase II (CsCl)} \xrightleftharpoons{184.3^\circ\mathrm{C}} \text{Phase I (NaCl)}$$

$$\mathrm{NH_4Br} \quad \text{Phase IV (CsCl?)} \xrightleftharpoons{-165^\circ\mathrm{C}} \text{Phase III } (\mathrm{PH_4I}) \xrightleftharpoons{-38.1^\circ\mathrm{C}} \text{Phase II (CsCl)} \xrightleftharpoons{137.8^\circ\mathrm{C}} \text{Phase I (NaCl)}$$

$$\mathrm{NH_4I} \qquad \text{Phase III } (\mathrm{PH_4I}) \xrightleftharpoons{-41.6^\circ\mathrm{C}} \text{Phase II (CsCl)} \xrightleftharpoons{-17.6^\circ\mathrm{C}} \text{Phase I (NaCl)}$$

Mueller and Joebstl, 1965, have linearly related the transition temperatures of monovalent inorganic azides to the cationic radii of Tl^+, Rb^+ and Cs^+. They report that as the cationic radius increases, the transition temperature decreases. The transitions in these compounds have been interpreted as being of the 'order-disorder' type with respect to the orientation of the azide ions.

The transition temperatures for phase III to phase II in the ammonium halides also decrease with increasing anionic radius. However, this decrease is not linear (Stammler, 1965). Stammler also reports several other trends from the data in table 4.1.

a) The phase II to phase I transition temperatures are more sensitive to changes in anionic radius than those of phase III to phase II.

b) The phase II to phase I transition temperatures drop more steeply from NH_4Br to NH_4I than from NH_4Cl to NH_4Br. This trend is reversed when considering the phase III to phase II transitions.

c) The difference in the phase II to phase I and the phase III to phase II transition temperatures falls from 215°C for NH_4Cl to 24°C for NH_4I.

Stammler explains these trends in terms of the changes in the crystal cell parameters for the different phases.

Polymorphism among alkyl- substituted ammonium salts was first reported by Hendricks, 1930 and Southard et al, 1932, for n-amyl ammonium chloride. The specific heat vs. temperature graph for this compound shows the existence of two phase changes (at 222° and 246°K). Rapid quenching of the sample prior to determining the specific heat values resulted in a greater magnitude for the 222°K (-51°C) peak. Storage of the sample at low temperatures caused an increase in magnitude of the 246°K (-27°C) peak. These phenomena were interpreted as the co-existence of the two phases, i.e. hybrid crystals. A similar observation has been reported for alkali nitrates (Kennedy et al, 1953).

Specific heat studies have revealed transitions at 220° and 264°K for methyl ammonium chloride (Aston and Ziemer, 1946) and 210° and 242°K for n-pentyl ammonium chloride (Southard et al, 1932).

Tsau and Gilson, 1968, have reported the phase transformations of alkyl ammonium chlorides and bromides from C_1 to C_{16} using Differential Scanning Calorimetry. These authors confirm the above transitions for methyl and n-pentyl ammonium chlorides. Two transitions were observed for the chlorides of the C_1 and C_3 to C_8 amines and for all bromides except those of the C_2 and C_5 to C_9 amines. The chlorides of C_9 and C_{11} to C_{16} amines and C_7 and C_9 ammonium bromides showed three thermal transitions. No transitions were reported for ethyl ammonium chloride and the bromides of the C_5 and C_8 amines both had a single transition. Tsau and Gilson's results are summarised in Fig. 1.2 and Fig. 1.3 where high and low transition temperatures are plotted vs. carbon number. The broken lines provide continuity in regions where no transition temperatures are reported. Several features can be noted from these graphs.

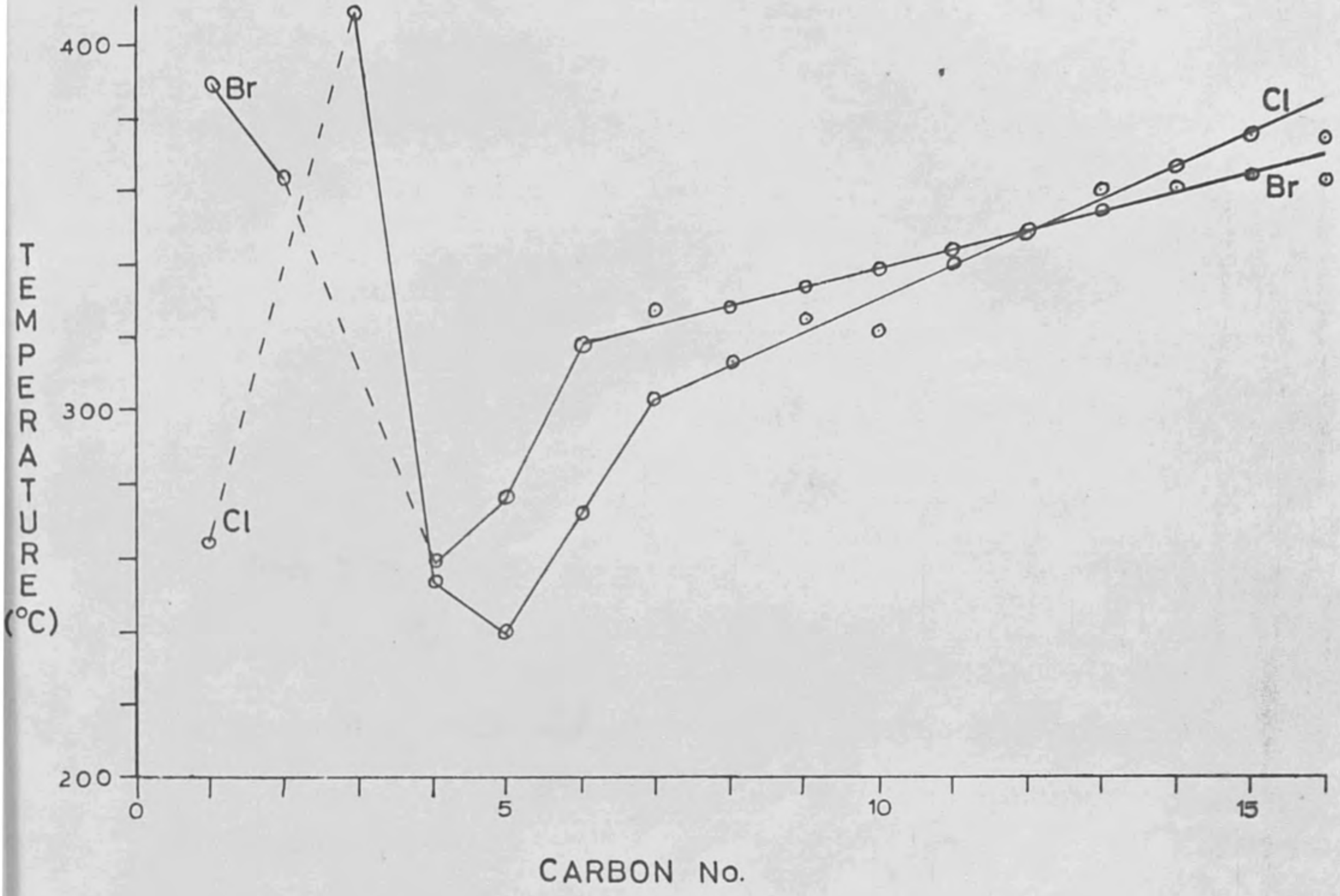
1) High temperature phase transitions increase almost linearly for C_7 - C_{15} alkylamine chlorides (C_{10} is an exception) and for the C_6 - C_{15} alkylamine bromides.

2) There is a sharp increase in the high temperature transitions from C_5 to C_7 amine chlorides and C_4 - C_6 amine bromides.

3) The low-temperature transitions above C_9 alter in a 'zig-zag' pattern which is almost identical for the bromides and chlorides.

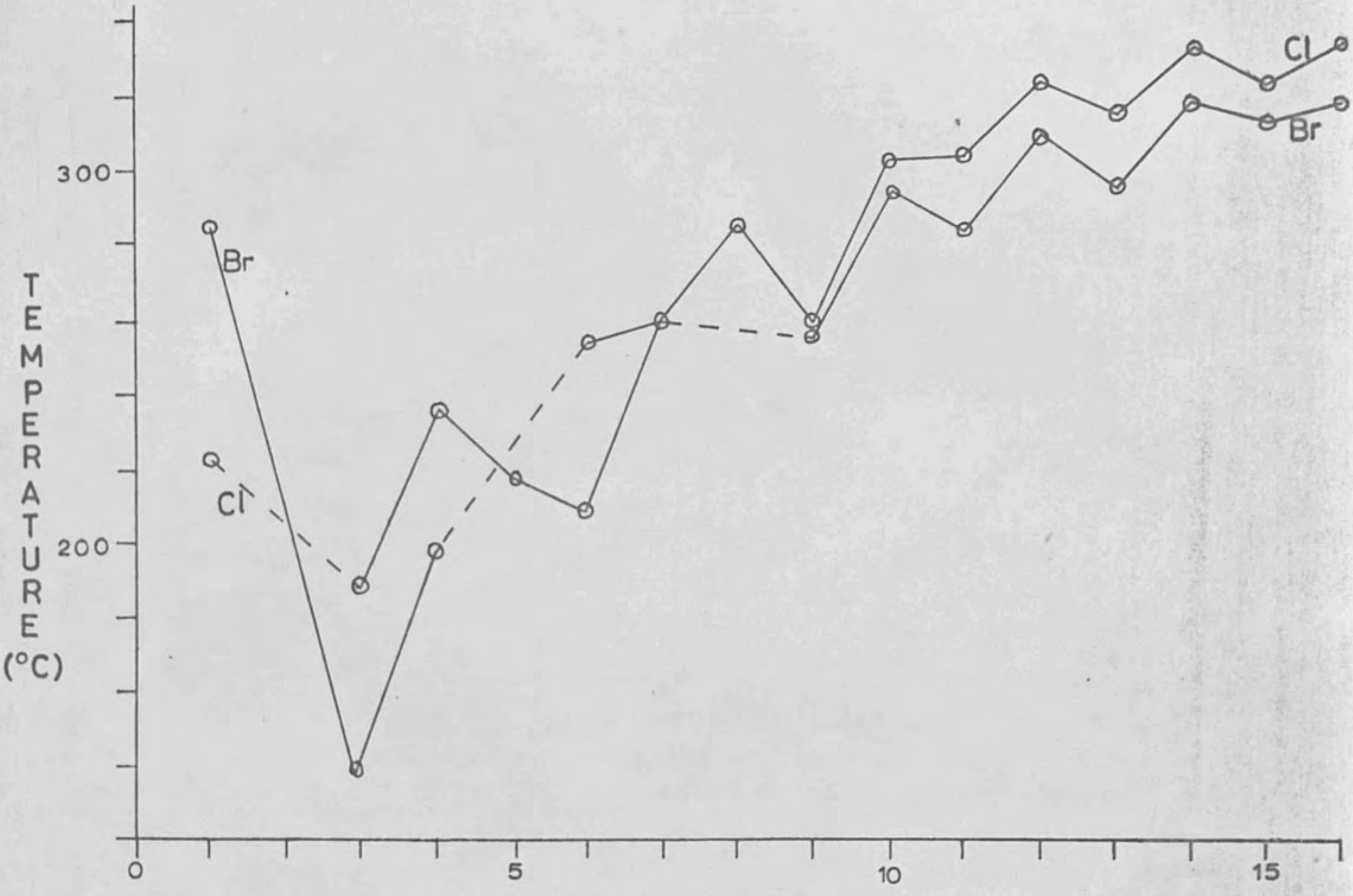
Tsau and Gilson attempt to generalise these phase transitions by assuming that the low-temperature phases are monoclinic and the high temperature phases are tetragonal. This generalisation does not seem to be justified (they account for three phases) since the majority of compounds have four polymorphic phases. Their work is, however, still in progress and they hope to obtain the

Fig. 1·2



High Temperature Transitions of Alkyl Ammonium Halides

Fig. 1·3



Low Temperature Transitions of Alkyl Ammonium Halides

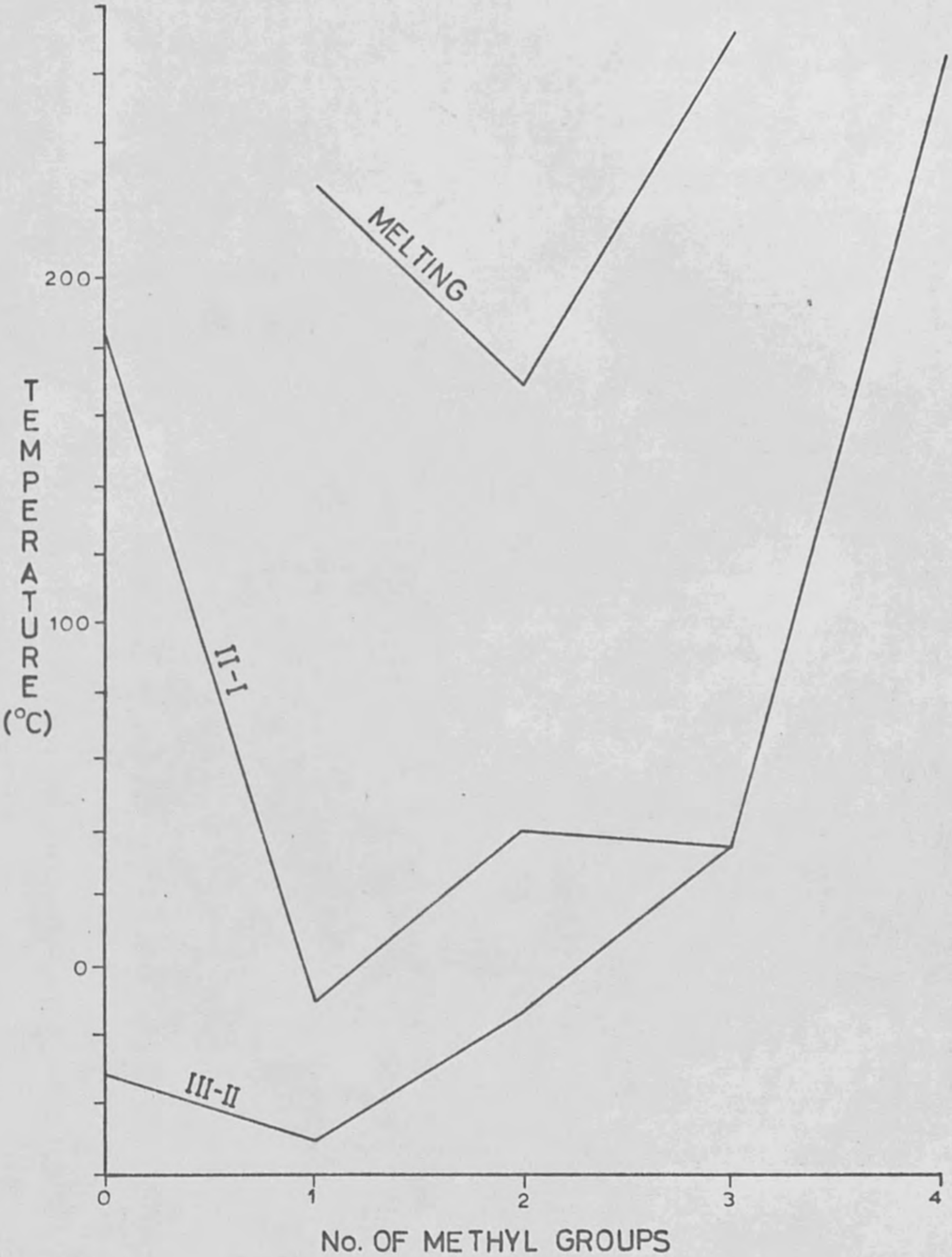
X-ray diffraction patterns of these compounds in order to elucidate the nature of the polymorphic phases. Insufficient data were recorded to enable any conclusions to be drawn from the enthalpies of transition or fusion.

Stammler, 1967, reports the transitions of a series of methyl-substituted ammonium chlorides, $Me_nNH_{4-n}Cl$, where n = 1-4. Stammlers results are presented graphically in Fig. 1.4, where transition temperatures are plotted against the number of methyl groups. The following features can be noted from this graph.

1) A melting point minimum for dimethyl ammonium chloride.
2) A transition temperature minimum for phase III to phase II and phase II to phase I at monomethyl ammonium chloride.
3) Only one transition temperature for tri- and tetramethyl ammonium chlorides.

Stammler's transition temperatures for methyl ammonium chloride are in agreement with those mentioned earlier (Aston and Ziemer, 1946; Tsau and Gilson, 1968) and his X-ray diffraction pattern confirms that phase I is tetragonal (Hendricks, 1928). Stammler, however, suggests cell parameters different from those reported by Hendricks. Stammler's results include several reflections which were not reported by Hendricks.

Fig. 1·4



Transition Temperatures of

Methyl Substituted Ammonium Chlorides

The X-ray diffraction pattern at -13°C indicates the formation of a second phase within the tetragonal lattice, and as the temperature is lowered the diffraction pattern changes, showing that the tetragonal symmetry is destroyed. Below -50°C the diffraction pattern changes again and this phase change is reported as an 'order-disorder' transition.

The two phase transitions for dimethyl ammonium chloride are confirmed by X-ray diffraction studies; however, Stammler only interprets the diffraction pattern for phase I (hexagonal).

Fig. 1.4 indicates that there are only two polymorphic phases for trimethyl ammonium chloride between -150° and 275°C (melting point, with decomposition). X-ray diffraction studies confirm this. Stammler reports that phase I is tetragonal and that phase II is probably orthorhombic.

The room temperature modification (tetragonal) of tetramethyl ammonium chloride is in agreement with that reported by Wyckoff, 1963. The structure of this phase is related to phosphonium iodide in that the tetrahedral cations occupy the PH_4^+ positions which form a body-centred lattice. The chloride ions fit into the interstial 'holes' in this lattice. The high temperature modification of tetramethyl ammonium chloride was not reported by Stammler due to instrumental difficulties.

Stammler et al, 1966, also report the thermal transitions of methyl-substituted ammonium perchlorates. These are compared and discussed with the data obtained in the present work in Section 5.

1d Decomposition of Ammonium and Amine Salts

I. Ammonium Perchlorate

The thermal decomposition of ammonium perchlorate has been extensively documented in the past few years (Hall and Pearson, 1967; Jacobs and Whitehead, 1969; Keenan and Siegmund, 1969). An outline of the present state of knowledge of ammonium perchlorate decomposition is presented below.

Ammonium perchlorate is stable at room temperature but decomposes at measureable rates at temperatures above 150°C. The decomposition processes can be divided into three regions, low and high temperature decomposition and combustion.

a) Low temperature decomposition

The low temperature decomposition occurs below 300°C at atmospheric pressure. It is an autocatalytic reaction which ceases when 28-30% of the sample has decomposed. The residue is quite stable at these temperatures, unless it is rejuvenated by sublimation or recrystallisation (Bircumshaw and Newman, 1955 a and 1955 b).

The first detailed analyses of the decomposition products were published in a series of papers by Dode (Dode, 1934, 1938 a and 1938 b). He found, however, that the stoichiometry of the decomposition could not be presented adequately by any single equation. Thus the equation proposed by Dode is a generalisation of the overall product distribution.

$$4\ NH_4ClO_4 = 2Cl_2 + 2N_2O + 3O_2 + 8H_2O$$

Hall and Pearson, 1967, report that an experimental enthalpy of the low temperature (below $300^{\circ}C$) decomposition of ammonium perchlorate is -40.9 ± 1.3 $Kcal.mole^{-1}$ and they conclude that the decomposition occurs by two possible reactions for which the standard heats of formation at $298^{\circ}K$ are calculated.

$$4NH_4ClO_4 = 2Cl_2 + 2N_2O + 3O_2 + 8H_2O$$

$$\Delta H = -35.4 \ Kcal.mole^{-1}$$

and

$$2NH_4ClO_4 = Cl_2 + N_2 + 2O_2 + 4H_2O$$

$$\Delta H = -45.2 \ Kcal.mole^{-1}.$$

b) <u>High temperature decomposition</u>

At temperatures above $350^{\circ}C$, where the high temperature decomposition occurs, the decomposition goes to completion. Dode (1934, 1938 a and 1938 b) proposed the equation.

$$2NH_4ClO_4 = Cl_2 + 2NO + O_2 + 4H_2O$$

for the decomposition above 350°C, to account for the major decomposition products. The results of Bircumshaw and Newman, 1955 a and 1955 b confirm the above equation.

c) Combustion

At temperatures above 440° to 450°C ammonium perchlorate explodes or deflagrates. Escales, 1910, proposed the equation

$$4NH_4ClO_4 = 4HCl + 2N_2 + 5O_2 + 6H_2O$$

for ammonium perchlorate explosion in a closed bomb.

Mechanism of decomposition

There are three possible routes by which ammonium perchlorate could decompose:

i) Proton transfer

$$NH_4ClO_4 = NH_3 + HClO_4$$

This could also be a reversible process controlling the sublimation.

ii) Electron transfer between anion and cation

$$NH_4^{+}ClO_4^{-} = NH_4^{\cdot} + ClO_4^{\cdot}$$

iii) Decomposition of the anion. This appears to be the process by which lithium and potassium perchlorates decompose to give chlorides as products.

Bircumshaw and Newman conclude that, since the proton transfer step is the basis of the ammonium perchlorate sublimation, it is umlikely to be the first step in the low temperature decomposition They propose that the high temperature decomposition is via perchlorate ion decomposition, since the decomposition occurs in a comparable temperature range to that of lithium and potassium perchlorates. They account for the low temperature decomposition by electron transfer between the amion and an interstitial ammonium cation, with the subsequent dissociation of the ammonium radical

$$ClO_4^- + NH_4^+ = ClO_4^{\cdot} + NH_4^{\cdot}$$

$$NH_4^{\cdot} = NH_3 + H^{\cdot}$$

followed by electron transfer

$$ClO_4^{\cdot} + ClO_4^- \longrightarrow ClO_4^- + ClO_4^{\cdot}$$

or chain termination

$$H^{\cdot} + ClO_4^{\cdot} = HClO_4$$

A hydrogen atom can also react with perchloric acid, thus

$$H^{\cdot} + HClO_4 = H_2O + ClO_3$$

The ClO_3 radicals act as electron traps and hence enhance the decomposition. The electron transfer process

$$ClO_4^{\cdot} + ClO_4^- \longrightarrow ClO_4^- + ClO_4^{\cdot}$$

will eventually produce a ClO_4 radical on the surface which can then decompose. The point on the surface where the ClO_4 radical has been formed and decomposed has lost an electron and must therefore have a resultant positive charge. This excess positive charge can be removed either by an electron from the crystal interior or the migration of a NH_4^+ ion from a nearby lattice site. This NH_4^+ ion can then take part in an electron transfer reaction in the neighbourhood of the decomposition site. Continuation of the process gives rise to a decomposition centre. The decomposition process disorganises the crystal lattice and allows the sublimation process to increase because of increased surface area. Both the decomposition and the sublimation processes compete for perchlorate ions on the surface. The low temperature decomposition is thought to cease at 30% because the sublimation process is proceeding more rapidly than the decomposition process.

Microcinematography (Rayevskiy and Manelis, 1963) and catalysed decomposition studies (Solymosi and Krix, 1962; Galweyn and Jacobs, 1959 and 1960; Verneker and Maycock, 1967) support the electron transfer mechanism.

Jacobs and Russell-Jones, 1967 and 1968 report that the energies of activation of the low temperature decomposition, the high temperature decomposition and the sublimation process were the same. This suggested a common rate-determining step for all processes and a unified mechanism for the decomposition, represented by

$$\begin{tikzcd}
NH_4^+ClO_4^- \text{ (c)} \arrow[r, shift left] & NH_3 \text{ (a)} \arrow[l, shift left] \arrow[d, shift left] & + & HClO_4 \text{ (a)} \arrow[d, shift left] \arrow[r] & \text{products} \\
\text{sublimate} & NH_3 \text{ (g)} \arrow[l] \arrow[u, shift left] & + & HClO_4 \text{ (g)} \arrow[u, shift left] \arrow[r] & \text{products}
\end{tikzcd}$$

((a) represents an absorbed species)

In contradiction to the results of Bircumshaw and Newman, Jacobs and Russell-Jones propose that the fundamental step is proton transfer. This results in absorbed ammonia and perchloric acid on the surface of the crystal. It is thought that the low temperature decomposition reaction is initiated on the crystal surface, although it may be completed in the gas phase. Since the reaction is catalysed by perchloric acid and retarded by ammonia, it was proposed by Davis et al, 1967, that the low temperature decomposition proceeds via a bi-molecular reaction between absorbed perchloric acid molecules.

$$2HClO_4 \text{ (a)} = H_2O \text{ (g)} + ClO_3^{\cdot} \text{ (g)} + ClO_4^{\cdot} \text{ (g)}$$

The unstable chlorine oxide radicals rapidly decompose to yield oxygen radicals and ClO radicals which oxidise the ammonia. Further details of the oxidation are a matter of conjecture.

If the oxidation of ammonia proceeds with less than 100% efficiency, then there will be an accumulation of ammonia on the crystal surface. The presence of ammonia retards the decomposition and this may be the reason for the failure of the low temperature decomposition mechanism after 30% decomposition. Raising the temperature causes the desorption of the ammonia and hence the decomposition reaction can proceed. Decomposition may occur in the gas phase if the desorbed species do not diffuse rapidly from the crystal. If rapid diffusion does take place, then the sublimation process can occur.

II. Ammonium Nitrate

The thermal decomposition of ammonium nitrate has been the subject of several investigations (Brent, 1952; Wood and Wise, 1954; Feick and Hainer, 1954; Cawthon and Taylor, 1954 a).

Ammonium nitrate decomposes between its melting point (170°C) and 300°C to give mainly nitrous oxide, water and small amounts of nitrogen. In the temperature range 300° - 350°C, the decomposition becomes explosive and the product composition changes to favour N_2, NO and NO_2.

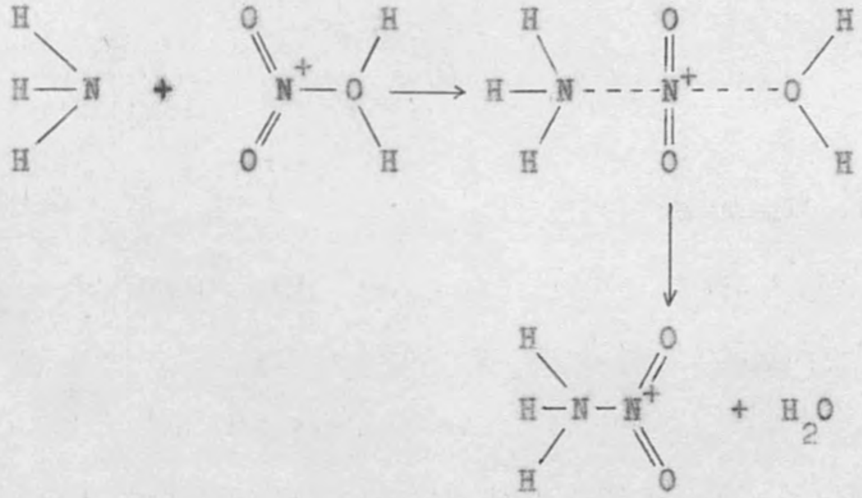
Cawthon and Taylor, 1954 a, summarise their studies by proposing the following mechanism. The initial reaction, which takes place in the ammonium nitrate melt, is proton transfer

$$NH_4^+NO_3^- = NH_3 + HNO_3$$

Two moles of nitric acid then react to give a hydrated nitronium ion and a nitrate ion

$$2HNO_3 = H_2NO_3^+ + NO_3^-$$

The reaction up to this stage is similar to that proposed by Jacobs and Russell-Jones, 1967 and 1968, for ammonium perchlorate. The hydrated nitronium ions react with the ammonia, thus



This reaction is assumed to be the rate controlling step. The nitramide then rapidly decomposes to give the observed products.

$$NH_3NO_2^+ + NO_3^- = N_2O + H_2O + HNO_3$$

The overall decomposition of ammonium nitrate is summarised by the equation

$$NH_4NO_3 = N_2O + 2H_2O$$

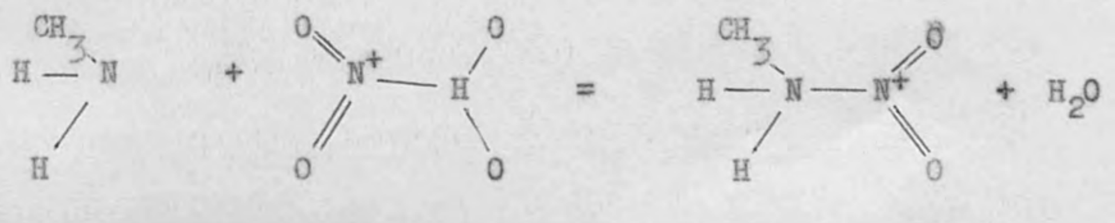
III. Amine Nitrates

Two reports have appeared on the kinetics and decomposition of amine nitrate compounds. Robertson, 1948, studied the thermal decomposition of ethylenediamine dinitrate and ammonium nitrate, along with pentaerythritol tetranitrate and nitroglycerin. He reports that ethylenediamine dinitrate decomposes autocatalytically in the temperature range 230° - 350°C. Ethylenediamine dinitrate is also interesting in that if forms a eutectic mixture with ammonium nitrate at 100°C (Campbell and Campbell, 1947).

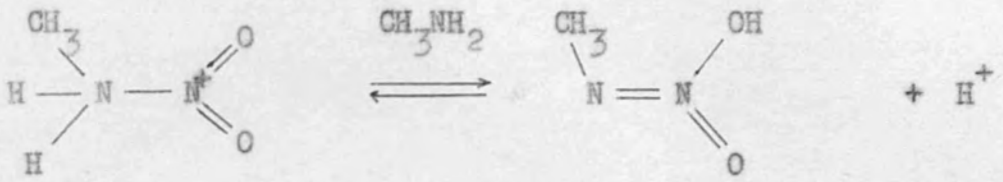
Cawthon and Taylor, 1954 b, set out to formulate a general mechanism which could be used to interpret the decomposition of primary aliphatic amine nitrates. Their work involved a study of the decomposition products of methyl ammonium nitrate, isobutyl ammonium nitrate, tertiary butyl ammonium nitrate, trifluoroethyl ammonium nitrate and dimethyl ammonium nitrate. Their decomposition reactions, which are initially similar to ammonium nitrate decomposition reactions, are outlined below for methyl ammonium nitrate.

$$CH_3NH_3^+NO_3^- = CH_3NH_2 + HNO_3$$

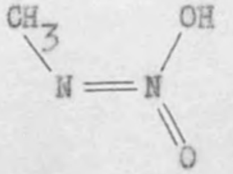
$$2HNO_3 = H_2NO_3^+ + NO_3^-$$



At this stage there are two possible paths by which the nitramine can rapidly decompose. The first is the normal aliphatic nitramine decomposition to give nitrous oxide



This reaction is the rate determining step



$$+ \quad CH_3NH_3^+ = CH_3^+ + N_2O + CH_3NH_3OH$$

$$CH_3NH_3OH = CH_3NH_2 + H_2O$$

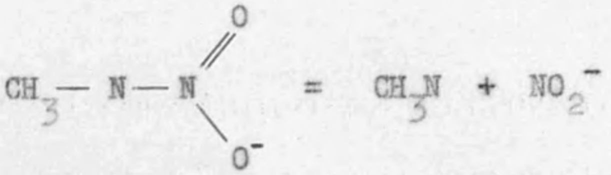
$$CH_3^+ + NO_3^- = CH_3ONO_2$$

The net reaction according to this route is given by

$$2CH_3NH_3NO_3 = CH_3ONO_2 + CH_3NH_2 + N_2O + 2H_2O$$

In the general case, if the carbonium ion has a hydrogen atom on its alpha-carbon atom, then an olefin will be observed in the decomposition products.

This decomposition scheme does not account for the observed products since more nitrogen than nitrous oxide is formed. The other decomposition path, however, accounts for this.



$$CH_3-N-N{=}O(O^-) = CH_3N + NO_2^-$$

$$CH_3N \longrightarrow CH_2NH \longrightarrow \text{non-volatile products}$$

$$NO_2^- \quad \underset{RNH_2}{\overset{RNH_3^+}{\rightleftarrows}} \quad H_2NO_2^+$$

$$CH_3NH_2 + H_2NO_2^+ = CH_3\overset{+}{N}H_2-N=O + H_2O$$

$$CH_3\overset{+}{N}H_2-N=O = CH_3^+ + N_2 + H_2O$$

IV. Amine Perchlorates

Guillory and King, 1969, have recently studied the thermal decomposition of methyl- substituted ammonium perchlorates using mass spectrometry. They propose that these amine perchlorates decompose principally via proton transfer

$$Me_n\,NH_{4-n}\,ClO_4 = Me_n\,NH_{3-n} + HClO_4 \qquad (n = 1-3)$$

Mack and Wilmot, 1967, also propose that proton transfer is the first step in the decomposition of hydroxylamine and hydrazine perchlorates. The thermal decomposition of hydroxylamine and hydrazine perchlorates has been studied in some detail and it is outlined briefly below.

a) Hydroxylamine perchlorate

The thermal decomposition of this compound was studied by Grelecki and Cruice, 1966, in the range 120° - 150°. They showed that the decomposition approximated to

$$14\ NH_3OHClO_4 = 7\ N_2O + 2Cl_2 + 10\ HClO_4 + 23\ H_2O$$

Mack and Wilmot, 1967, support Grelecki and Cruice's proposition that the initial step in the decomposition was via proton transfer.

b) Hydrazine monoperchlorate

The thermal decomposition of this compound has been studied by Hermoni and Salmon, 1964, and Grelecki and Cruice, 1966, in the region 140° - 230°C. These workers propose that the decomposition mechanism begins with proton transfer

$$N_2H_5ClO_4 = N_2H_4 + HClO_4$$

followed by the decomposition of the perchloric acid into radicals

$$HClO_4 = HO^{\cdot} + ClO_3^{\cdot}$$

These radicals then react with undecomposed hydrazine monoperchlorate

$$HO^{\cdot} + N_2H_5ClO_4 = H_2O + NH_4ClO_4 + \tfrac{1}{2}N_2$$

$$ClO_3^{\cdot} + 7\ N_2H_5ClO_4 = 3\ H_2O + 6\ NH_4ClO_4 + 3\tfrac{1}{2}\ N_2 + NH_4Cl + HClO_4$$

These reactions can be summarised by the overall equation

$$8\ N_2H_5ClO_4 = 7\ NH_4ClO_4 + NH_4Cl + 4\ N_2 + 4\ H_2O$$

c) Hydrazine diperchlorate

The thermal decomposition was studied by Grelecki and Cruice, 1966, in the range 100° - 150°C. The decomposition products were analysed by mass spectrometry. The authors proposed the equation

$$12\ N_2H_6\ (ClO_4)_2 = 4\ NH_4ClO_4 + 12\ HClO_4 + 22\ H_2O + 10\ N_2 + 5\ O_2 + 4\ Cl_2$$

to account for the decomposition products. During the early stages of decomposition, only perchloric acid was detected, and so the initial decomposition step was thought to be

$$N_2H_6(ClO_4)_2 = N_2H_5ClO_4 + HClO_4$$

As in the case of hydrazine monoperchlorate, the perchloric acid can decompose into radicals, which can then react with the remaining hydrazine diperchlorate or the formed hydrazine monoperchlorate.

The thermal decompositions outlined above for the non-metallic perchlorates and nitrates assist considerably in formulating decomposition paths for assessing the propellant potential of the alkyl ammonium perchlorates and nitrates (Section 5).

SECTION 2

Preparation of Materials and Analysis

The majority of chemicals used in this work, unless stated, were supplied by B.D.H. Chemicals Ltd. They were purified before use by distillation or recrystallisation. Tetrabutyl and tetrapropyl ammonium bromides were supplied by Eastman Kodak Ltd. The term perchloric acid in this work refers to 72% AnalaR perchloric acid, by weight, in water.

The purity of the amine perchlorate samples was found by chlorine analysis. This was effected by fusing the perchlorate compound for five minutes in a nickel crucible with anhydrous sodium carbonate. A piece of platinum wire was used as a catalyst (Schumacher, 1960). This technique reduces the perchlorate to chloride, which was determined using a standard argentimetric technique. This analytical procedure is accurate to ± 0.5%. The presence of small quantities of impurity, which are chemically similar to the compound under study, will not significantly alter the heat of solution. The figure in parentheses after the percentage purity indicates the number of determinations.

Elemental analysis was carried out by A. Bernhardt, Elbach uber Engelskirchen, West - Germany.

The author acknowledges the receipt of specimen samples of amine perchlorates and nitrates from Prof. H. Beachell and Dr. G. Pearson.

Methyl Ammonium Perchlorate

Perchloric acid was neutralised with aqueous methylamine solution (25-30%) at 0°C, using bromothymol blue as an indicator. A solid product was obtained by removing the water on a rotary evaporator. The product was twice recrystallised from ethanol and dried at 70°C and 0.2mm.Hg over P_2O_5. The purity found by chloride determination was 98.6%(3).

Analysis:	C	H	N	Cl
Calculated for CH_6NClO_4	9.13%	4.60%	10.65%	26.96%
Found	9.32%	4.69%	10.77%	26.58%

Dimethyl Ammonium Perchlorate

Dimethylamine gas (Matheson Co. Inc.) was slowly passed into perchloric acid at 0°C using bromothymol blue as an indicator. The product was obtained by evaporating the solution to dryness and recrystallising twice from ethanol. The sample was dried over P_2O_5 at 60°C and 0.2mm.Hg. The purity found by chloride determination was 98.5%(2).

Analysis:	C	H	N	Cl
Calculated for $C_2H_8NClO_4$	16.51%	5.54%	9.63%	24.36%
Found	16.64%	5.52%	9.52%	23.99%

Isopropanol/ether (1:3) and benzonitrile were found, in the course of further preparations, to be better recrystallising solvents.

Trimethyl Ammonium Perchlorate

Perchloric acid was neutralised with aqueous trimethylamine solution (25% w/v) at 0°C using bromothymol blue as an indicator.

The solid product, after evaporating off the water, was twice recrystallised from isopropanol. The compound was dried at 80°C and 0.2mm.Hg over P_2O_5. The purity found by chloride determination was 99.0%(2).

Analysis:	C	H	N	Cl
Calculated for $C_3H_{10}ClO_4$	22.59%	6.32%	8.78%	22.22%
Found	22.69%	6.47%	8.95%	22.00%

Tetramethyl Ammonium Perchlorate

Tetramethyl ammonium hydroxide solution (25% in water) was neutralised with perchloric acid at 0°C using bromothymol blue as an indicator. A colourless solid was precipitated, which was filtered off and twice recrystallised from water. The product was dried over anhydrous calcium sulphate at ambient temperature and 0.5mm.Hg. The purity found by chloride determination was 99.8%(3).

Analysis:	C	H	N	Cl
Calculated for $C_4H_{12}NClO_4$	27.67%	6.97%	8.07%	20.42%
Found	27.78%	7.06%	7.87%	20.32%

Ethyl Ammonium Perchlorate

Ethylamine solution (70% in water) was added dropwise to perchloric acid at 0°C untill the resulting solution was neutral to bromothymol blue. The solid product, obtained by evaporating off the water, was twice recrystallised from ethanol, and dried over P_2O_5 at 70°C and 0.1mm.Hg. The purity was found to be 100.2%(2) by chloride determination.

Diethyl Ammonium Perchlorate

Perchloric acid was slowly neutralised by diethylamine at 0°C using bromothymol blue as an indicator. On evaporation to dryness a semi-solid product was obtained, which was recrystallised from ethanol. A further recrystallisation gave a compound which was 101·4%(2) pure, by chloride determination, after drying at 70°C and 0·2mm.Hg over P_2O_5.

Analysis:	C	H	N	Cl
Calculated for $C_4H_{12}NClO_4$	27·67%	6·97%	8·07%	20·42%
Found	27·86%	7·08%	8·10%	20·70%

Triethyl Ammonium Perchlorate

Perchloric acid was neutralised, using bromothymol blue as an indicator, with triethylamine at 0°C and the solution evaporated to dryness. The crude residue thus obtained was recrystallised twice from ethanol and the crystalline product was dried over P_2O_5 at 70°C and 0·2mm.Hg. The purity found by chloride determination was 100·1%(3)

Tetraethyl Ammonium Perchlorate

This was prepared by neutralising tetraethyl ammonium hydroxide solution (25% in water) with perchloric acid at 0°C, using bromothymol blue as an indicator. The purification was similar to that described for tetramethyl ammonium perchlorate. The sample was found to be 99·6%(2) pure by chloride analysis.

Ethylenediamine Diperchlorate (anhydrous)

Perchloric acid was slowly added to ethylenediamine until the bromothymol blue indicator showed excess acid was present. The solution was evaporated to dryness and the residue was recrystallised twice from isopropanol. This procedure yields the hemi-hydrate (Stammler et al, 1966). The anhydrous compound was obtained by drying at 120°C for 18 hours and analyses were carried out on this sample. Chloride determination showed the sample to be 99.8%(2) pure.

Analysis:	C	H	N	Cl
Calculated for $C_2H_{10}N_2Cl_2O_8$	9.20%	3.86%	10.72%	27.16%
Found	9.35%	4.00%	10.62%	27.11%

n-Propyl Ammonium Perchlorate

n-Propylamine was neutralised with perchloric acid at 0°C, using bromothymol blue as an indicator, and the solution evaporated to dryness. The residue was twice recrystallised from isopropanol and the product dried over anhydrous calcium sulphate at ambient temperature and 0.5mm.Hg. The purity found by chloride determination was 99.8%(2).

Analysis	C	H	N	Cl
Calculated for $C_3H_{10}NClO_4$	22.59%	6.32%	8.78%	22.22%
Found	22.74%	6.48%	8.95%	22.18%

Tri-n-propyl Ammonium Perchlorate

Tri-n-propyl ammonium perchlorate was prepared in a similar manner to n-propyl ammonium perchlorate, from tri-n-propylamine and perchloric acid. After two recrystallisations and drying, the following analytical data were obtained.

Analysis:	C	H	N	Cl
Calculated for $C_9H_{22}NClO_4$	44.35%	9.09%	5.75%	14.58%
Found	44.24%	8.98%	5.60%	14.49%

Dimethyl Ammonium Chloride

This compound was prepared by neutralising dimethylamine solution (40% in water) with concentrated hydrochloric acid at 0°C, using bromothymol blue as an indicator. The sample was twice recrystallised from isopropanol and dried over anhydrous calcium sulphate at ambient temperature and 0.5mm.Hg. The purity of this compound was found to be 99.1%(2) based on chloride determination. Handling of this compound was carried out in a dry-nitrogen-filled glove-bag, in view of its hydroscopic nature.

Dimethyl Ammonium Bromide

Dimethylamine solution (40% in water) was neutralised with hydrobromic acid (48% aqueous) at 0°C, using bromothymol blue as an indicator. The solid product, after evaporating off the water, was twice recrystallised from ethanol and dried over anhydrous calcium sulphate at ambient temperature and 0.5mm.Hg in a desiccator, m.p.134°C, lit.133-134°C (Heilbron et al, 1965).

Diethyl Ammonium Bromide

This compound was prepared in a similar manner to dimethyl ammonium bromide, from diethylamine and aqueous hydrobromic acid.

The sample was twice recrystallised from isopropanol before drying over anhydrous calcium sulphate at ambient temperature and 0.5mm.Hg. The purity was found to be 99.9%(2) using a standard argentimetric technique for bromide determination.

Methyl Ammonium Nitrate

Concentrated nitric acid was neutralised with aqueous methylamine solution at 0°C, using bromothymol blue as an indicator. The solid product, after evaporating off the water, was twice recrystallised from ethanol and dried at ambient temperature and 0.2mm.Hg over P_2O_5.

Analysis:	C	H	N
Calculated for $CH_6N_2O_3$	12.77%	6.43%	29.78%
Found	13.01%	6.46%	29.61%

Trimethyl Ammonium Nitrate

The preparation, from aqueous trimethylamine solution and concentrated nitric acid, and purification were similar to those described for methyl ammonium nitrate.

Analysis:	C	H	N
Calculated for $C_3H_{10}N_2O_3$	29.50%	8.25%	22.93%
Found	29.70%	8.22%	22.79%

Tri(p-tolyl)methanol (Mothwurf, 1904)

p-Bromotoluene (54g, 0.316 mole) and magnesium turnings (8.5g, 0.354 mole) were used to form p-tolyl magnesium bromide (Newman and Deno, 1951) in dry ether as solvent. Methyl p-toluate (20.5g, 0.137 mole), in dry ether, was slowly added to the Grignard complex and the mixture refluxed for 30 min. The resulting solution was hydrolysed with dilute hydrochloric acid and the etherial layer separated. Steam distillation of the etherial layer resulted in an orange oily residue. Crystals were obtained from the oil by recrystallising from 60°- 80° petroleum ether. A further recrystallisation gave colourless crystals (20g, 48% based on p-bromotoluene), m.p.92°C, lit.97°C (Davis et al, 1956) and 94°- 96°C (Gatzke and Stewart, 1961).

Analysis:	C	H
Calculated for $C_{22}H_{22}O$	87.42%	7.29%
Found	87.25%	7.28%

Tri(p-tolyl)methyl Chloride (Davis et al, 1956)

Tri(p-tolyl)methanol (10g, 0.033 mole) was refluxed for 20 mins. with acetyl chloride (7ml, 7.7g, 0.098 mole) in 60°- 80° petroleum ether (40ml). The product deposited on cooling and was recrystallised from 60°- 80° petroleum ether. The resulting crystals of tri(p-tolyl)-methyl chloride (7.5g, 70% based on tri(p-tolyl)methanol) were slightly yellow, m.p.171°C, lit.171°- 172°C (Marvel et al, 1939).

Tri(p-tolyl)methyl Perchlorate (Longworth and Mason, 1966)

Tri(p-tolyl)methyl chloride (7.5g, 0.023 mole) in dichloromethane (25ml) and nitromethane (2ml) was refluxed with silver perchlorate (7.5g, 0.036 mole) for 20 mins. The silver perchlorate was dried at 120°C for 2 hrs. prior to use. The reaction mixture was filtered to remove silver chloride and then evaporated to dryness. The residue was recrystallised from acetonitrile to give green crystals (1.5g, 17% based on tri(p-tolyl)methyl chloride), m.p.169°- 170°C, lit.187°C (Gomberg and Cone, 1909). The purity was determined by reducing the perchlorate to chloride with sodium peroxide (microanalytical grade) in a Parr bomb. The chloride can then be determined by a standard argentimetric technique. The purity of the sample was found to be 99.9%(6).

Tri(p-nitrophenyl)methane (Montagne, 1905)

Triphenylmethane (90g, 0.368 mole) was slowly added to stirred fuming nitric acid at -65°C. After the addition, the mixture was vigorously stirred and allowed to reach room temperature. The reaction mixture was poured into 3 l. of ice and water, and the precipitate filtered off. The precipitate was boiled with glacial acetic acid, to remove partially nitrated products, and filtered hot. The residue was recrystallised from toluene to yield a colourless product, (70g, 50% based on triphenylmethane), m.p.204°C, lit.206°C (Schwartz, 1909).

Tri(p-nitrophenyl)methanol (Fischer and Fischer, 1878)

Tri(p-nitrophenyl)methane (94g, 0.248 mole) in glacial acetic acid (1500ml) was heated to 50°C and Chromium(III) trioxide (80g, 0.800 mole) was stirred in. The oxidation was allowed to continue at 50°C for 1 hr., then stopped by pouring into 3½ l. of ice and water. The precipitate was filtered off and recrystallised from glacial acetic acid to give the final product (72g, 73% based on tri(p-nitrophenyl)methane), m.p.178°C, lit.180°- 183°C (Hawthorne,1955).

Analysis:	C	H	N
Calculated for $C_{19}H_{13}N_3O_7$	57.72%	3.29%	10.63%
Found	57.76%	3.28%	10.56%

Tri(p-nitrophenyl)methyl Chloride (Bosshard et al, 1959)

Tri(p-nitrophenyl)methanol (5g, 0.012 mole) was refluxed with thionyl chloride (45ml) and dimethylformamide (1ml) for 4 hrs. The reaction mixture was poured onto ice (3l) and filtered. The residue was twice recrystallised from toluene to give the final product (3.8g, 76% based on tri(p-nitrophenyl)methanol), m.p.200°C, lit.196°- 198°C (from benzene) or 208°C (from acetone)(Patai and Zabricky, 1961).

Analysis:	C	H	N	Cl
Calculated for $C_{19}H_{12}N_3O_6Cl$	55.13%	2.90%	10.15%	8.59%
Found	55.26%	3.09%	10.00%	8.41%

The method described above gives a considerably improved yield compared with that of Patai and Zabricky, 1961 (20%).

Reaction of Tri(p-nitrophenyl)methyl Chloride with silver perchlorate

Tri(p-nitrophenyl)methyl chloride (1g, 0.002 mole) and silver perchlorate (0.5g, 0.002 mole) were refluxed together in dichloromethane (10ml) and nitromethane (1ml) for 30 mins. No precipitate of silver chloride was formed and it was concluded that no reaction had taken place.

Triphenylmethyl Perchlorate

Method A (Dauben et al, 1960)

Perchloric acid (12.5ml, 21.3g, 0.211 mole) was slowly added to a vigorously stirred mixture of triphenylmethanol (10g, 0.038 mole) in dry redistilled acetic anhydride (200ml) cooled to 0°C. Small yellow crystals were deposited and these were separated by decanting the mother liquor. The final product (10g, 76% based on triphenylmethanol) was obtained by washing these crystals with dry ether and drying at ambient temperature and 0.5mm.Hg over calcium chloride, m.p.143°C, lit.143°C (Dauben et al, 1960) and 150°C (Longworth and Mason, 1966).

Extreme difficulty was encountered in attempting to remove quantitatively occluded acetic anhydride and so method B is preferred.

Method B

Triphenylmethyl chloride (18g, 0.068 mole) was dissolved in dichloromethane (150ml) and nitromethane (6ml) and added to a solution of silver perchlorate (16g, 0.077 mole) in dichloromethane (100ml). The mixture was refluxed for 5 min., cooled, and filtered to remove silver chloride. The filtrate was evaporated to dryness and the residue recrystallised for dichloromethane. The final product (15g, 70% based on triphenylmethyl chloride) was dried as before, m.p.142°C.

Analysis:	C	H
Calculated for $C_{19}H_{15}ClO_4$	66.56%	4.38%
Found	66.26%	4.50%

An independent analysis was effected by hydrolysing the sample by refluxing for 4 hrs. with distilled water, and titrating the liberated perchloric acid with N/10 sodium hydroxide. The presence of triphenylmethanol did not affect the endpoint. The mean percentage purity was found to be 99.34 ± 0.42% (6).

Tri(p-methoxyphenyl)methyl Perchlorate

Tri(p-methoxyphenyl)methyl chloride (9g, 0.024 mole), supplied by Schuchard, in acetonitrile (50ml) and nitromethane (3ml), was refluxed for 15 mins. with silver perchlorate (5g, 0.024 mole). The precipitated silver chloride was filtered off and the filtrate evaporated to dryness. The residue was recrystallised from a 1:1 mixture of chloroform and petroleum ether (60°- 80°) to give crimson needles (7.5g, 72% based on tri(p-methoxyphenyl)methyl chloride), m.p.191°C, lit.192°- 193°C (Dilthey and Alfuss, 1929) and 193°- 195°C (Burton and Cheeseman, 1953).

Analysis:	C	H	Cl
Calculated for $C_{22}H_{21}ClO_7$	61.04%	4.91%	8.19%
Found	60.79%	4.85%	8.39%

(The author wishes to thank Dr. Cheeseman for an authentic sample of this compound.)

SECTION 3

Calorimetry

3a. Differential Scanning Calorimetry

Introduction

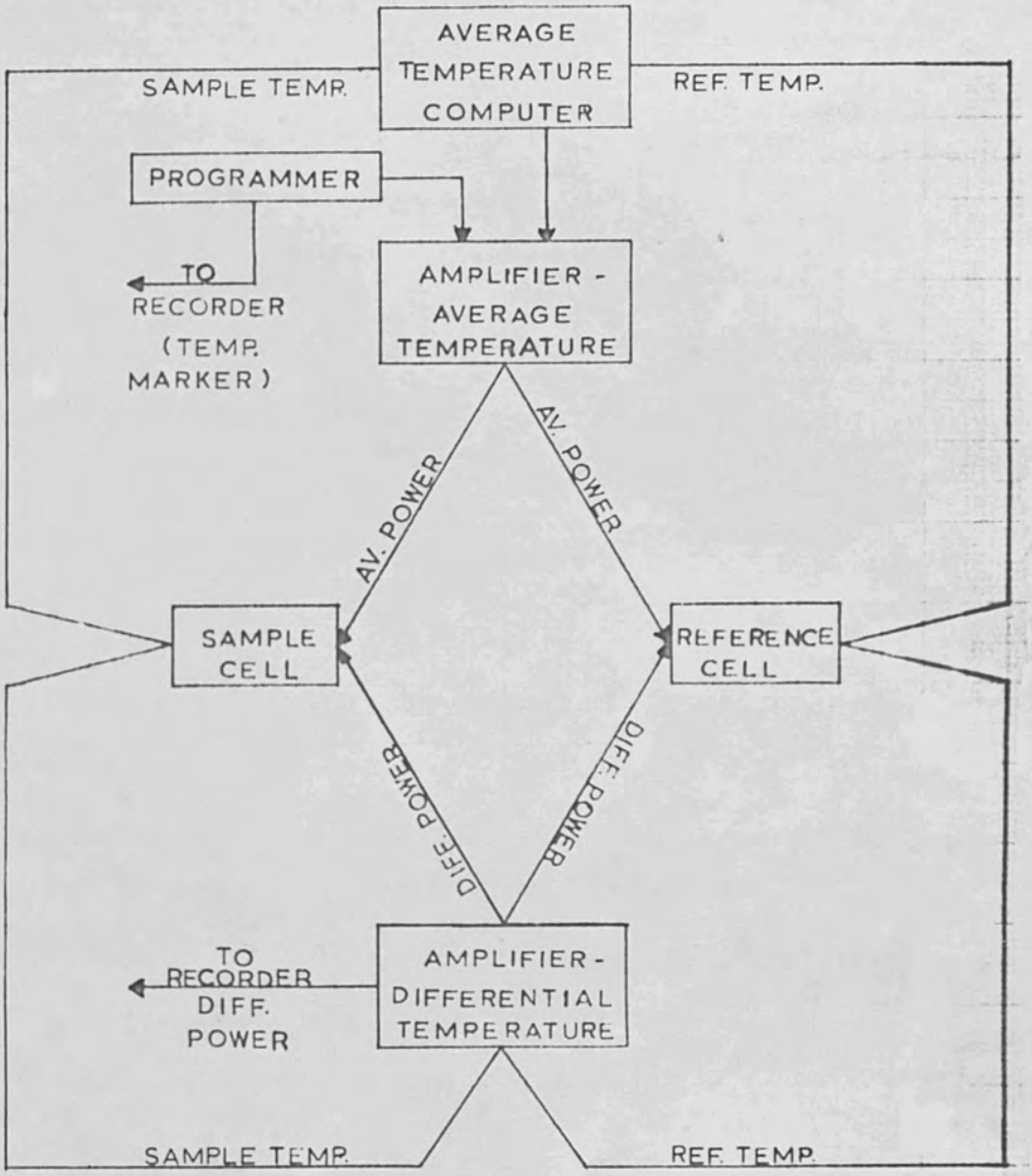
Differential Scanning Calorimetry (D.S.C.) is a rapid technique for studying the thermal properties of milligram quantities of a substance. The technique involves subjecting the substance to a linear heating programme and continuously monitoring the rate of heat flow into the substance, relative to an inert reference substance. This rate of heat flow is proportional to the instantaneous specific heat of the substance and a signal, proportional to the heat flow rate, is visually displayed on a chart recorder. Calibration of the equipment allows heat capacities and transition enthalpies to be determined. The capabilities of the D.S.C. have been previously described by Watson et al, 1964.

The Calorimeter

A Perkin-Elmer D.S.C.-1B calorimeter with a Leeds and Northrup Speedomax W recorder was used in this work. An effluent analyser attachment was connected to the calorimeter gas line; however, it was not used during the heat of transition or fusion determinations. The sensing head of the D.S.C. consists of two matched calorimeter cells which are enclosed in the same temperature-controlled environment. These are programmed simultaneously with a reference substance in the right-hand cell and the sample in the left-hand cell. The calorimeter can be calibrated to accept an empty sample pan as a reference substance, and an empty sample pan was used in the reference cell in all the present heat of fusion and transition determinations. The temperatures of the two cells are measured with platinum resistance thermometers, and heaters beneath each cell provide constant thermal control. The electronic circuitry is shown in block diagram form, Fig.3.1.

In operation, the D.S.C. is alternately controlled by two separate circuits. The upper half of the circuitry in Fig. 3.1 represents the average temperature loop, and the lower half represents the differential temperature loop. In the average temperature loop, into which the heating rate is programmed, the two thermometers are read, their readings are averaged and compared with the programmed temperature, and sufficient power is supplied to the cells to enable them to follow the temperature programme. This section of the circuit also operates the temperature event pen on the recorder.

Fig. 3·1



Block Diagram of the

Differential Scanning Calorimeter

When the differential temperature loop is in control of the instrument, the two thermometers are read and differential power applied to the cell with the lower temperature, in order to maintain a zero temperature differential between the sample and the reference. The differential power is recorded as millicalories per second, and thus the area under a peak is a quantitative measure of the heat evolved or absorbed during a transition. The direction of the peak indicates whether it is exo- or endothermic.

Samples were weighed into shallow aluminium pans and covered with aluminium lids before introducing into the apparatus. The type of sample pan used depends on the nature of the sample. Volatile samples, or those which sublime, were hermetically sealed into volatile sample pans; other samples were placed in ordinary sample pans and the lids fitted by means of a crimping press. This process only loosely seals the pans and thus allows decomposition products to escape.

When the sample and reference pans are placed in their respective cells, they are covered with a cylindrical jacket. For operation in the region 173°K to 300°K, a jacket fitted with a Dewar vessel was used. Liquid nitrogen was used as a coolant for all low-temperature studies.

Above 300°K a jacket with a glass window for viewing the cells was used. Nitrogen, dried by passing through a silica gel drying tower, was used as a purge gas in the present work.

The calibration procedures adopted for the slope, differential temperature and average temperature controls, were those reported by Watson et al, 1964. Area calibration of the chart paper was obtained by measuring the area of the peak corresponding to the melting of a weighed sample of Indium (99.999%, m.p.429.7°K (McClaren and Murdock, 1964), heat of fusion = 780 cal.mole^{-1} (Hultgren et al, 1963)). Heats of transition or fusion, of weighed samples, were obtained by comparing their peak areas to that of Indium. The temperature scale was calibrated using the melting points of Indium and Lead as fixed points. The accuracy of the temperature scale, calibrated using these two points, is ± 1°K. The precision of heats of transition and fusion, measured by D.S.C., is ± 2% (Tsau and Gilson, 1968).

Determination of Heats of Transition and Fusion

The D.S.C. was used to measure the heats of transition and fusion of some of the amine salts studied in this work. A sample was heated at 8°K min^{-1} through the temperature range to be studied, in order to find the transition regions. An empty pan was used in the reference cell. Heats of transition were then obtained from three weighed samples, sealed into appropriate sample pans and heated at $1^{o}K\ min^{-1}$ through the transition regions. During the crimping process, the bottom of the sample pan sometimes became distorted, and so to obtain good thermal contact between the pan and the cell, the base of the pan was flattened by rubbing on a clean piece of card before introducing into the calorimeter.

Samples were ground in an agate mortar before sealing into the pans. This eliminates 'bumps' in the fusion peaks due to the melting of large crystals. Sample sizes of the order of 1-5 mg were usually sufficient to give a reasonably sized peak, and the samples were weighed on a Cahn Electrobalance (0.00001 to 1 g).

The transition temperatures recorded are when the pen begins to deviate from the baseline, i.e. the beginning of the transition. The maximum peak height corresponds to the point when the transition is proceeding at a maximum rate. The various methods which exist for manually determining the area of the transition peaks are:

1) A triangle can be drawn to fit the shape of the peak and the area obtained from the base and height measurements. This method is useful for a rough approximation, but it has a limited use in D.S.C. work since the low and high temperature peak boundaries are better represented by curves than by straight lines.

2) The area representing the transition energy can be cut out and weighed. Comparison of this weight with the weight of a known area of the chart paper yields the area of the peak. Merrifield, 1970, reported that the variations in weight of 10 cm^2 areas of chart paper were less than 1%. This method suffers from the disadvantage that the thermogram is destroyed in measuring the area.

3) The area can be measured using a planimeter. This was the method adopted in the present work. The chart paper was taped to stiff paper or cardboard, to prevent it moving, and the area of the transition peak was measured by tracing the peak with the planimeter. The peak area can be read directly from the planimeter. Peak areas were measured three times and quoted to a precision of $\pm$ 0.1 cm^2.

The heats of transition and fusion are recorded in Section 4b.

Determination of Specific Heat

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

$$\frac{dH}{dt} = m.C.\frac{dT}{dt}$$

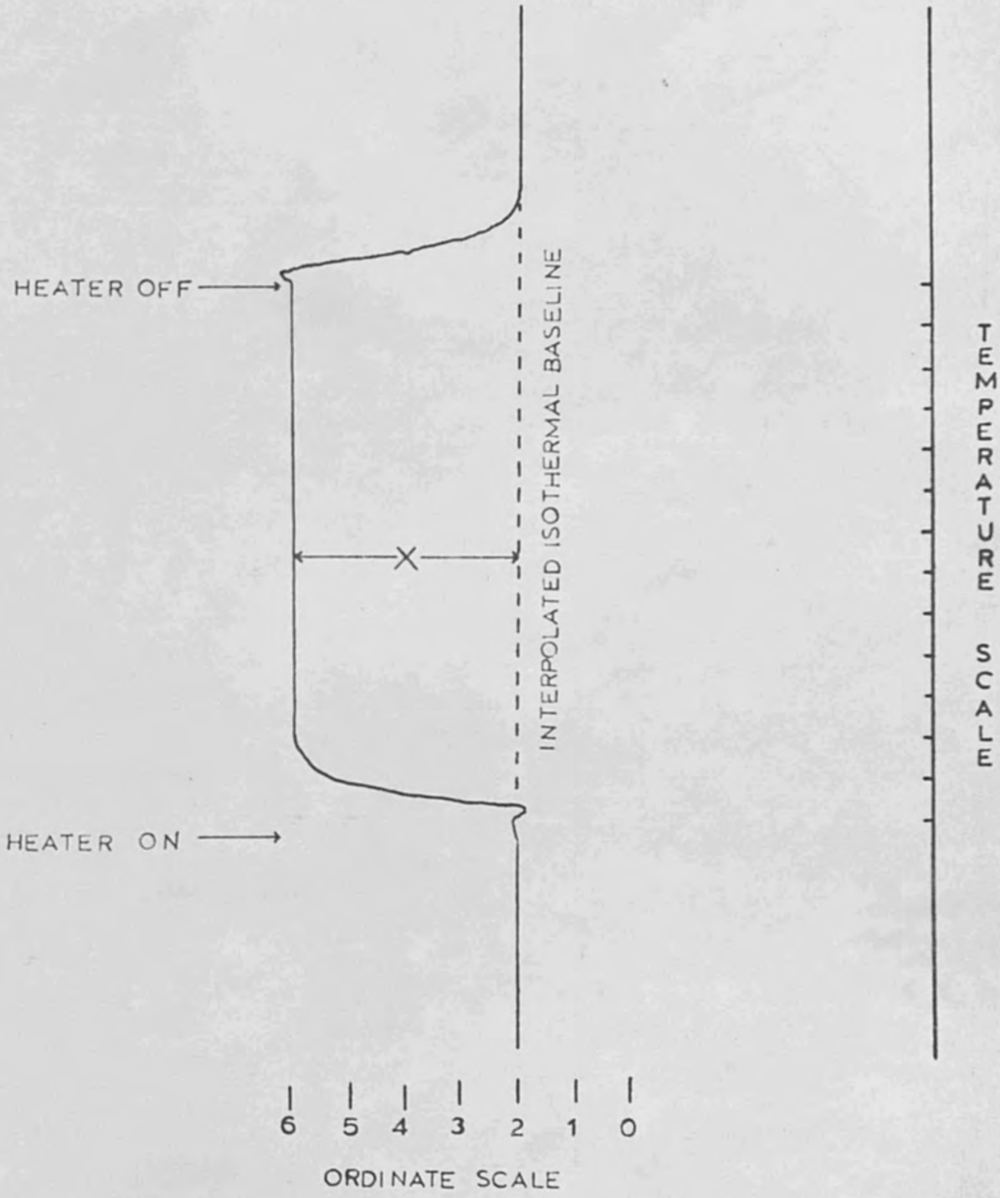
where dH/dt is the rate of heat flow (cal.sec^{-1}), m is the sample weight (g), C is the instantaneous specific heat (cal. deg^{-1} g^{-1}) and dT/dt is the programmed heating rate (deg. sec^{-1}).

The rate of heat flow into the sample is proportional to the ordinate deflection on the chart paper, from the interpolated isothermal baseline (see Fig. 3.2).

Thus
$$\frac{dH}{dt} = Q.x$$

where Q is the ordinate calibration factor and x is the ordinate deflection. In order to obtain values for the specific heat of a sample, Q and dT/dt must be known. However, these two factors can be eliminated if a material of known specific heat is used to calibrate the instrument, using identical conditions.

Fig. 3·2



Specific Heat Trace

At any temperature, $T^{o}K$

$$Q.x_1 = m_1.c.\frac{dT}{dt}$$

and $$Q.x_s = m_s.C_s.\frac{dT}{dt}$$

where x_1 and x_s are the ordinate deflections due to the sample and the standard, and m_s and C_s represent the mass and specific heat of the standard. Combining and rearranging these two equations

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

Thus the specific heat of a weighed sample can be obtained directly by comparing its ordinate deflection with that of a weighed standard. Sapphire discs were used as a standard and the values of the specific heat of sapphire were taken from Ginnings and Furukawa, 1953.

The experimental procedure adopted was described in the maker's handbook (Perkin-Elmer, 1968). Sample weights should be as large as possible in order to obtain large ordinate deflections. Large sample weights were obtained by fusing the sample into the pan and then allowing sufficient time for the sample to cool down. Volatile sample pans were used in the case of benzoic acid in order to suppress sublimation. A typical specific heat trace is shown in Fig. 3.2.

The results of the specific heat measurements are presented in section 4c.

Reliability of Specific Heat Measurements

The values of specific heats measured using a D.S.C. are subject to certain inherent sources of error. The more important of these are:

(a) random noise on the ordinate deflection,

(b) slope control setting,

(c) reproducibility of the temperature programme.

The measurement of the ordinate deflection is also subject to a certain amount of error. This can, however, be reduced by making the ordinate deflection as large as possible, i.e., by using a large sample. The magnitude of the ordinate deflection, for a given sample weight, can also be increased by increasing the sensitivity of the D.S.C. However, this was found to increase (a). This random noise is due to dirt on the cells from sample spillage or decomposition and it can be reduced by the procedure suggested by Plato and Glasgow, 1969.

The slope control is used to adjust the power supply to each cell and hence to minimise the difference in thermal capacity between sample cell and reference cell. The correct slope setting is evidenced by a vertical baseline on the chart paper. The slope control requires setting for each temperature range used for specific heat measurements, in order to compensate for variations in the thermal capacity withrespect to temperature.

The magnitude of these errors is discussed and summarised by Merrifield, 1970. Values of the specific heat in a transition region are considered to be accurate to ± 3% and in non-transition regions to ± 2%. Present studies using benzoic acid as a test material confirm the value of ± 2% for specific heat values in a non-transition region; however, within 5°K of a transition temperature, ± 4-5% is probably a more realistic estimate of the error.

3b. Solution Reaction Calorimetry

Calorimetry involves the measurement of the temperature change when a known amount of sample undergoes a known chemical reaction or dissolution. The enthalpy change associated with this reaction can be determined by introducing a known amount of heat, and again measuring the temperature change. The enthalpy change is then a direct proportionation between the two temperature changes.

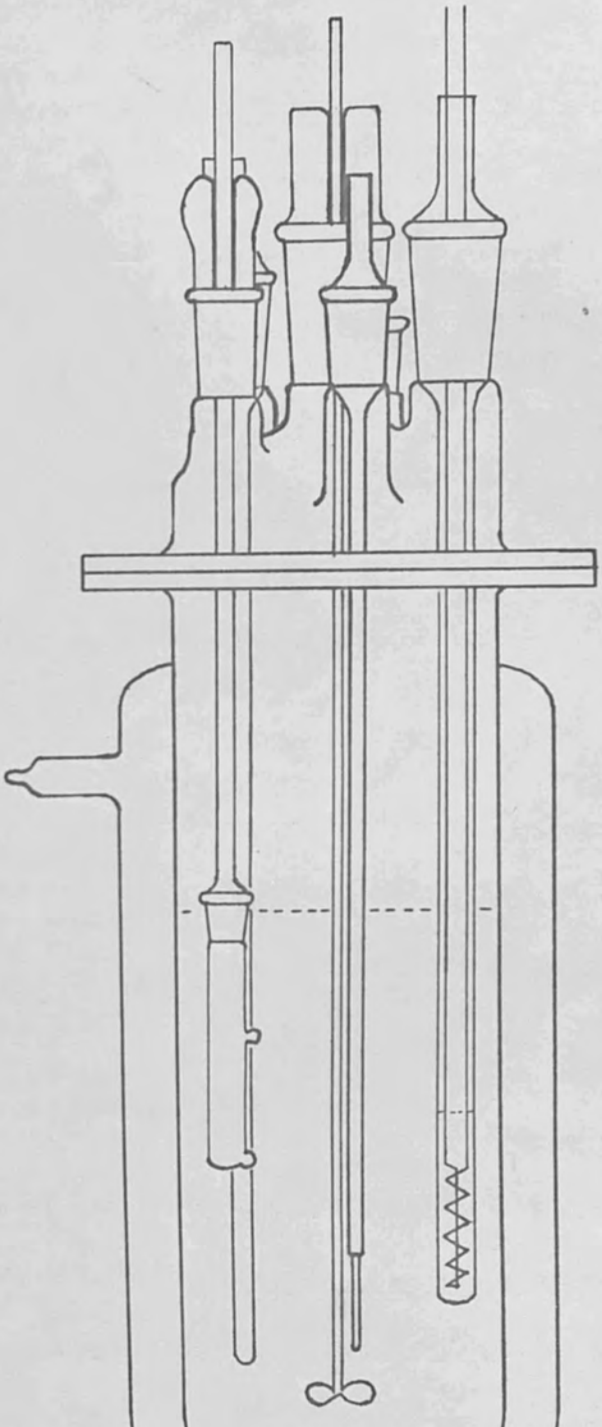
The Calorimeter

The calorimeter was of the Constant Temperature Environment (C.T.E.) type and the operating procedure was similar to that adopted in this laboratory over the past few years (Gardner, 1963).

The calorimeter consists of a 250 ml. round-bottomed Dewar vessel, approximately 2" internal diameter, with a glass flange and a flanged lid with several 'Quickfit' sockets, through which the various inserts were introduced into the calorimeter (Fig. 3.3). The ampoule holder and stirrer were made from precision glass rod which fitted through a corresponding precision-bore glass sleeve mounted on B 10 and B 14 cones respectively. The stirrer was driven by a constant speed 1/30 hp. motor (Parvalux Electric Motors Ltd., Model SD 8) via a flexible drive. The ampoules, which contain the sample were constructed from B 7 sockets which had two small fragile glass bulbs, and were attached to the ampoule rod via a B 7/B 5 adaptor. The lower bulb was broken by lowering the ampoule into the stirrer blades and the upper one was broken on the side of the calorimeter. This type of ampoule was preferred to the older single bulb ampoule blown on a B 5 socket because

(a) fewer fragments of glass were introduced into the calorimetric fluid. Fragments of glass cause irregularities in the post reaction and calibration

Fig. 3·3



C.T.E. Calorimeter

lines due to collision with the thermistor.

(b) the calorimetric fluid can flow through the ampoule and wash all the sample into solution.

The design and construction procedure of these ampoules is explained by Wellum, 1969.

The heater element was constructed from 'Karma' wire (British Driver Harris, 42 S.W.G., 52 ohms/ft.) wound non-inductively onto an alumina former. This former was mounted on two insulated copper support rods (20 S.W.G.), which were also used to connect the heater element to the stranded wire leads. The whole of the heater unit was immersed in light paraffin oil in a thin glass sheath attached to an extended B 14 cone. The oil acted as a medium for heat flow from the heater element to the calorimeter. The heater current was supplied from a mains powered constant potential source (Ether Ltd., Model AA 100, 6 volts D.C.).

The cooling tube was constructed from an extended B 10 cone. Liquid nitrogen or solid carbon dioxide could be introduced into the tube to cool the calorimeter between reaction and calibration.

Temperature changes were detected using a thermistor (F 53, Standard Telephone and Cable Ltd.) mounted on a B 10 socket. The thermistor constitutes one arm of a Wheatstone bridge circuit (Fig. 3.4) and temperature changes were recorded as changes in resistance. The temperature-resistance relationship is given approximately by the equation

$$R = A.\exp \frac{B}{T}$$

where R is the resistance in ohms

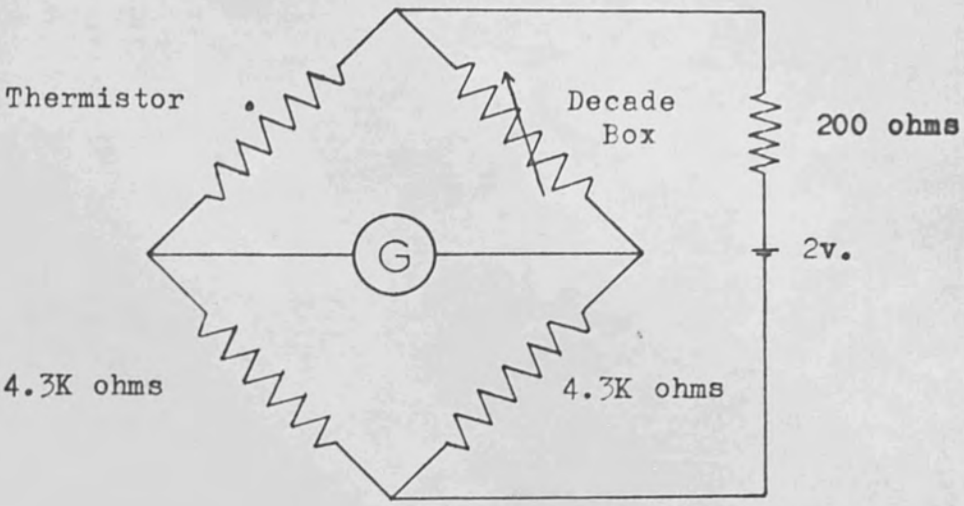
T is the absolute temperature

A and B are thermistor constants.

The ratio arms of the Wheatstone bridge consisted of two fixed resistors (4.3 K.ohms) and the variable arm was a decade box (Muirhead, 0 to 10^4 ohms). A Scalamp galvanometer (W. G. Pye and Co. Ltd., R = 1400 ohms, Cat. No. 7904/T) was used to detect the out of balance bridge current.

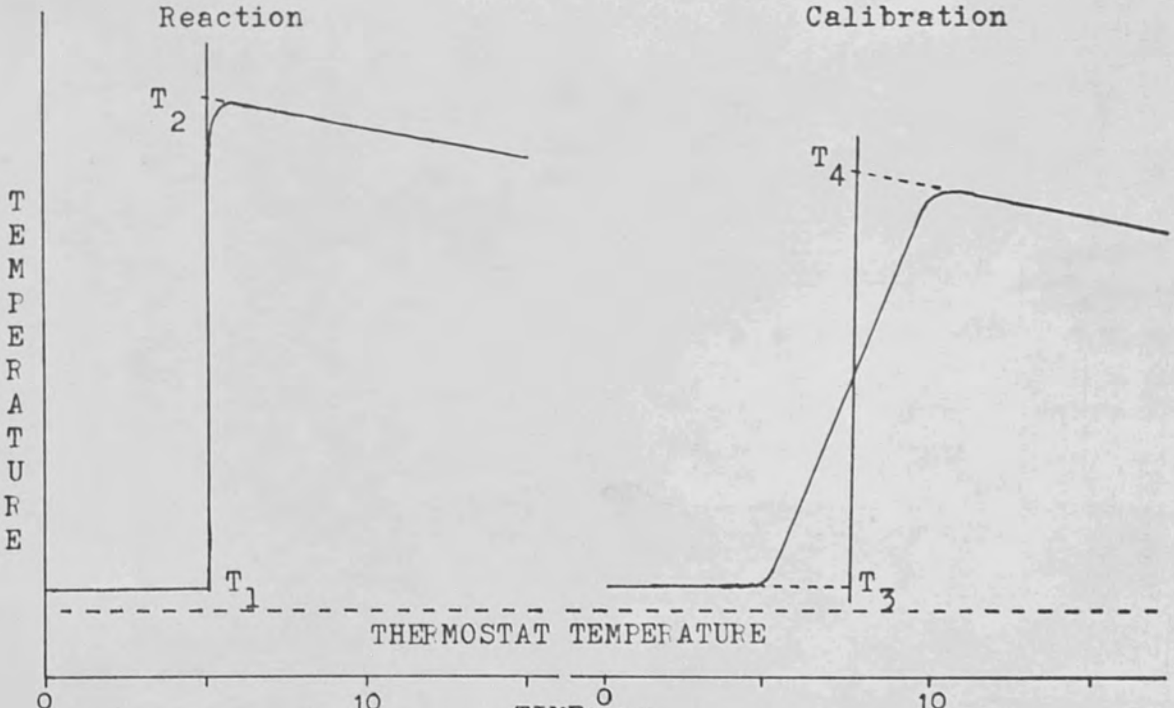
Actual temperatures were not calculated in this work and the following procedure was used to obtain the temperature differences. Fig. 3.5 represents the temperature-time profiles for an exothermic reaction and its calibration. For the reaction graph, T_1 represents the temperature when the ampoule was broken and T_2 represents the corrected temperature, so that $T_2 - T_1$ is the temperature change due to the reaction process. The resistance values corresponding to temperatures T_1 and T_2 are R_1 and R_2.

Fig. 3.4



Temperature Detection Wheatstone Bridge

Fig. 3.5



Reaction and Calibration Temperature-Time Profiles

$$\Delta Tr = T_2 - T_1 = \frac{B.\ln(R_1/R_2)}{\ln(R_1.R_2/A^2)}$$

Similarly for the calibration graph, T_4-T_3 represents the corrected temperature rise for the electrical calibration, where temperatures T_3 and T_4 have corresponding resistance values R_3 and R_4. Temperature correction methods are outlined in Appendix I .

$$\Delta Tc = T_4 - T_3 = \frac{B.\ln(R_3/R_4)}{\ln(R_3.R_4/A^2)}$$

Then
$$\frac{\Delta Tr}{\Delta Tc} = \frac{\ln(R_1/R_2).\ln(R_3.R_4/A^2)}{\ln(R_3/R_4).\ln(R_1.R_2/A^2)}$$

Now if R_1 and R_3 are approximately the same and heat is applied during the calibration such that Tr and Tc are approximately equal, then the previous equation simplifies to

$$\frac{\Delta Tr}{\Delta Tc} = \frac{\ln(R_1/R_2)}{\ln(R_3/R_4)} = \frac{\log R_1 - \log R_2}{\log R_3 - \log, R_4}$$

This approximation is valid to within 0.1% as long as the initial and final resistances during the calibration are both within 40 ohms of the initial and final resistances during the reaction (Wellum, 1969).

The heater circuit diagram is shown in Fig. 3.6. The heater is wired in parallel with a potential divider comprising a 10 ohm resistance and a 100 ohm resistance (Croydon Precision Resistors, 2w., 0.025% tolerance) and in series with a standard resistance (W.G. Pye and Co. Ltd., 0.99996 ohms).

The power dissipated by the heater was given by

$$P = 11.V_2 (V_1 - 0.1 V_2) \quad \text{watts}$$

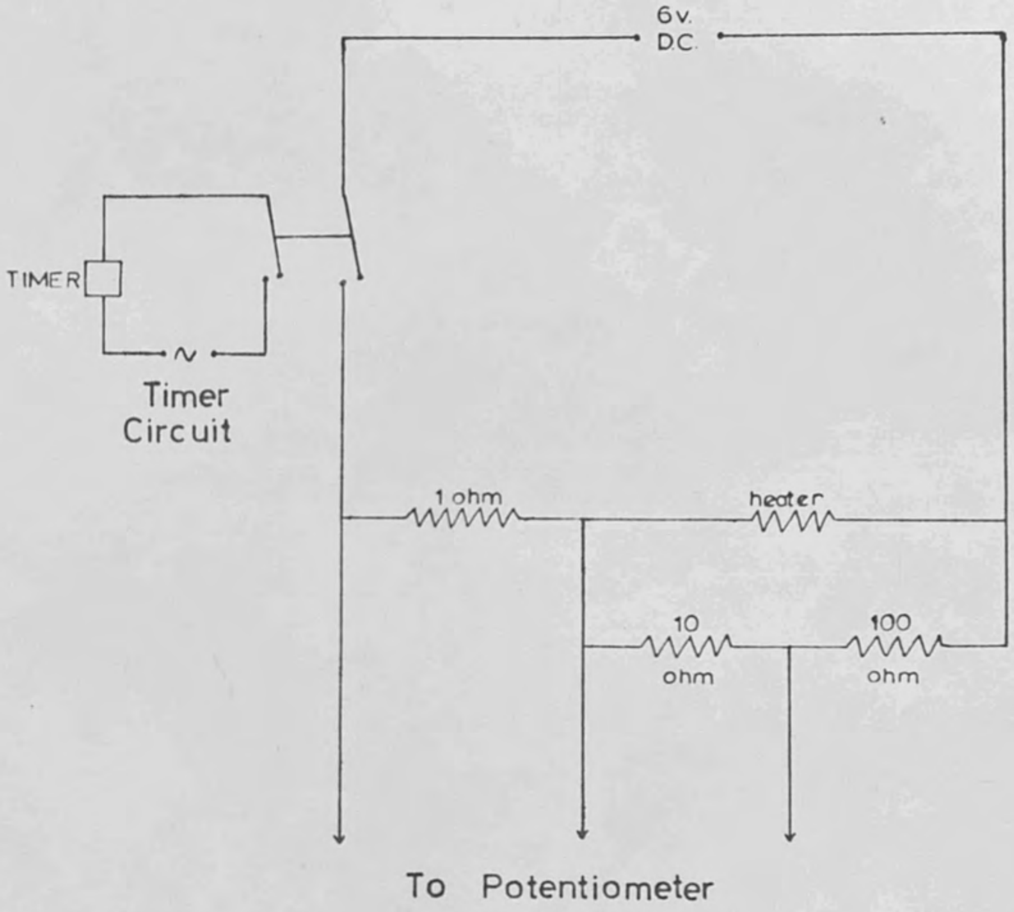
where V_1 is the potential across the standard resistance (in volts);

and V_2 is the potential across the 10 ohm resistance of the divider (in volts).

The potentials V_1 and V_2 were measured on a potentiometer (Tinsley, type 3387B, ± 0.00005 volts) which was used in conjunction with a Scalamp galvanometer. The potentiometer was calibrated before use with a Weston Standard Cell (Cambridge Instuments Co. Ltd.). The heating period was timed using an electric timer (J. Hengster and Co., Model FO 43.4) coupled to the heating circuit by a two way switch. The timer was accurate to 0.02 sec.

The equation used to determine the enthalpy change of a reaction was

Fig. 3·6



Circuit used to measure power input to the heater

$$\Delta H = \frac{f \times P \times \text{time(secs)} \times \text{molecular wt.} \times \Delta Tr}{4184.0 \times \text{sample wt.} \times \Delta Tc} \text{ Kcal.mole}^{-1}$$

The factor f accounts for the heat dissipated in the heater leads and is obtained from

$$f = R_g/_R$$

where R_g is the resistance of the heater element

and R = resistance of heater element and leads

$= 11.V_2/(V_1 - 0.1V_2)$

In operation the calorimeter was submerged in a thermostat tank at 25 ± 0.01°C.

The accuracy of the calorimeter was checked by studying the neutralisation of tris(hydroxymethyl)aminomethane (THAM) in excess N/10 hydrochloric acid.

$$(CH_2OH)_3NH_2 + (m + 1)HClnH_2O \longrightarrow ((CH_2OH)_3NH_3^+ + Cl^-)mHClnH_2O$$

where m and n represent the moles of HCl and water respectively. This was proposed as a test reaction for solution calorimeters by Irving and Wadsö in 1964. The literature values for the enthalpy of this reaction, ΔH, are recorded in table 3.1

Table 3.1

Literature Values of ΔH for the Neutralisation of THAM with excess N/10 HCl

Reference	Dilution, n	ΔH	
		Kcal.mole^{-1}	Kj.mole^{-1}
Gunn, 1965	373 - 1120	-7.107 ± 0.001	-29.736 ± 0.004
Sunner and Wadsö, 1966	1138 - 1462	-7.111 ± 0.001	-29.752 ± 0.004
Ojelund and Wadsö, 1967	1320 - 1390	-7.112 ± 0.002	-29.757 ± 0.008
Hill et al, 1969	1170 - 1574	-7.109 ± 0.001	-29.744 ± 0.003

Table 3.2 gives values of ΔH obtained in the present work, which are in good agreement with the literature values. Aristar grade THAM was used for these measurements. It was dried at 100°C, for 24 hours, before loading into the calorimeter.

Table 3.2

Values of ΔH for the Neutralisation of THAM with excess N/10 HCl

Exp.	Dilution, n	ΔH Kcal.mole^{-1}
1	726.1	-7.16
2	745.5	-7.08
3	749.9	-7.16
4	761.3	-7.13
5	765.9	-7.11
6	766.2	-7.08
7	773.9	-7.12
8	778.6	-7.13
9	783.9	-7.16
10	821.5	-7.13

Mean value of ΔH = -7.13 ± 0.02 Kcal.mole^{-1}

SECTION 4

Results

4a Standard Heats of Formation

This section deals with the derivation of the standard heats of formation from the experimentally determined heats of solution and heats of reaction, which are recorded in Appendix III. The values quoted for the standard heats of formation, and for all ancillary data, are all at 298°K.

The majority of the standard heats of formation reported in this work can be obtained directly from the heats of solution, and the procedure of calculation is illustrated for methyl ammonium perchlorate. The remainder of the calculations, for those compounds whose standard heat of formation cannot be obtained directly from a heat of solution measurement, are listed under the individual compound.

Methyl Ammonium Perchlorate

The heat of solution of the following reaction was measured

$$MeNH_3ClO_{4(c)} + nH_2O \longrightarrow (MeNH_3^+ + ClO_4^-)nH_2O \quad \ldots \quad \Delta H_s$$

where n represents the ratio of the number of moles of water per mole of solute, and is thus a dilution factor.

As n tends to infinity then the above reaction becomes

$$MeNH_3ClO_4(c) + \infty H_2O \longrightarrow MeNH_3^+ \text{ aq} + ClO_4^- \text{ aq} \quad \ldots \quad \Delta H_s^o$$

A series of experiments were conducted to study the variation of ΔH_s with dilution. However, the precision of the equipment was found to be such, that no significant variation of ΔH_s with respect to dilution could be detected for any salt. Thus ΔH_s^o is set equal to the mean of the ΔH_s data. The standard heat of formation of methyl ammonium perchlorate, $\Delta H_f^o(MeNH_3ClO_4,c)$, can be obtained from the following equation

$$\Delta H_f^o(MeNH_3ClO_4,c) = \Delta H_f^o(MeNH_3^+,aq) + \Delta H_f^o(ClO_4^-,aq) - \Delta H_s^o$$

where $\Delta H_f^o(MeNH_3^+,aq)$ and $\Delta H_f^o(ClO_4^-,aq)$ represent the standard heats of formation of the aqueous methyl ammonium and the aqueous perchlorate ion. The standard heats of formation of these aqueous ions are listed in table 4.1, and the value of ΔH_s^o, from Appendix III, is listed in table 4.2. These values can be combined to give the standard heat of formation of crystalline methyl ammonium perchlorate.

$$\Delta H_f^o(MeNH_3ClO_4,c) = -67.82 \pm 0.03 \text{ Kcal.mole}^{-1} (-283.75 \pm 0.12 \text{ Kj.mole}^{-1})$$

Table 4.1

Standard Heats of Formation of Aqueous Ions at Infinite Dilution

Aqueous Ion	ΔH_f^o	
	Kcal.mole^{-1}	Kj.mole^{-1}
NH_4^+	-31.67	-132.51
$MeNH_3^+$	-29.86	-124.93
$Me_2NH_2^+$	-28.74	-120.25
Me_3NH^+	-26.99	-112.93
$EtNH_3^+$	-37.3	-156.06
$Et_2NH_2^+$	-45.1	-188.70
Et_3NH^+ (a)	-49.2	-205.85
$(CH_2NH_3^+)_2$	-36.0	-150.62
ClO_4^-	-30.91	-129.33
NO_3^-	-49.56	-207.36
Cl^-	-39.95	-167.15
Br^-	-29.05	-121.55
I^-	-13.19	-55.19

(a) Value updated from Cox and Pilcher, 1970

The compounds whose standard heats of formation can be calculated in a similar manner are listed in table 4.3. The uncertainty intervals (Section 6) quoted for these compounds are based on uncertainty intervals of ± 0.01 Kcal.mole^{-1} for values in table 4.1 quoted to two decimal places, and ± 0.05 Kcal.mole^{-1} for values quoted to one decimal place.

Table 4.2

Heats of Solution, ΔH_s°

Compound	ΔH_s°	
	Kcal.mole^{-1}	Kj.mole^{-1}
$MeNH_3ClO_4$	7.05 ± 0.03	29.49 ± 0.10
$Me_2NH_2ClO_4$	6.94 ± 0.03	29.03 ± 0.11
Me_3NHClO_4	8.04 ± 0.05	33.65 ± 0.22
Me_4NClO_4	10.35 ± 0.01	43.28 ± 0.01
$EtNH_3ClO_4$	3.88 ± 0.02	16.23 ± 0.11
$Et_2NH_2ClO_4$	4.55 ± 0.02	19.02 ± 0.08
Et_3NHClO_4	4.63 ± 0.03	19.39 ± 0.12
Et_4NClO_4	7.41 ± 0.02	31.02 ± 0.11
$PrNH_3ClO_4$	3.91 ± 0.03	16.34 ± 0.14
$(CH_2NH_3)_2(ClO_4)_2$	12.79 ± 0.08	53.52 ± 0.33
Me_2NH_2Cl	0.47 ± 0.02	1.96 ± 0.09
$EtNH_3Cl$	2.02 ± 0.04	8.43 ± 0.16
Me_2NH_2Br	3.25 ± 0.05	13.63 ± 0.20
Et_2NH_2Br	1.92 ± 0.02	8.04 ± 0.10
$MeNH_3NO_3$	5.27 ± 0.02	22.06 ± 0.09
Me_3NHNO_3	5.70 ± 0.03	23.86 ± 0.14

Table 4.3

Standard Heats of Formation of Amine Salts

Compound	ΔH_f°	
	Kcal.mole^{-1}	Kj.mole^{-1}
$MeNH_3ClO_4$	-67.83 ± 0.03	-283.75 ± 0.12
$Me_2NH_2ClO_4$	-66.59 ± 0.03	-278.61 ± 0.12
Me_3NHClO_4	-65.91 ± 0.05	-275.91 ± 0.23
Me_4NClO_4	-70.79 ± 0.52	-296.24 ± 2.17
$EtNH_3ClO_4$	-72.10 ± 0.06	-301.62 ± 0.24
$Et_2NH_2ClO_4$	-80.56 ± 0.06	-337.05 ± 0.23
Et_3NHClO_4	-84.76 ± 0.06	-334.63 ± 0.24
Et_4NClO_4	-70.81 ± 0.54	-296.27 ± 2.25
$(CH_2NH_3)_2(ClO_4)_2$	-110.61 ± 0.10	-462.80 ± 0.40
$Pr^nNH_3ClO_4$	-71.08 ± 0.18	-297.40 ± 0.75
$Pr^n{}_3NHClO_4$	-102.42 ± 0.56	-428.53 ± 2.34
Me_2NH_2Cl	-69.16 ± 0.03	-289.36 ± 0.09
$EtNH_3Cl$	-79.27 ± 0.07	-331.64 ± 0.26
Me_2NH_2Br	-61.04 ± 0.05	-255.43 ± 0.20
Et_2NH_2Br	-76.07 ± 0.05	-318.29 ± 0.23
$MeNH_3NO_3$	-84.69 ± 0.03	-354.35 ± 0.10
Me_3NHNO_3	-82.25 ± 0.04	-344.15 ± 0.15

The standard heats of formation of methyl ammonium nitrate and trimethyl ammonium nitrate are compared with the literature values in table 4.4. The standard heats of formation of these compounds were originally determined by Cottrell and Gill in 1951. The literature values in table 4.4 are the updated values quoted by Wagman et al, 1968.

Table 4.4

Standard Heats of Formation of Methyl and Trimethyl Ammonium Nitrates

	ΔH_f^o Kcal.mole^{-1}	
	Present work	Literature
$MeNH_3NO_3$	-84.69 ± 0.03	-84.7
Me_3NHNO_3	-82.25 ± 0.04	-82.2

Tetramethyl Ammonium Perchlorate

The standard heat of formation of tetramethyl ammonium iodide was first determined from the following reactions:

$$MeI(\ell) + (x+1)Me_3NyH_2O \longrightarrow (Me_4N^+ + I^-)xMe_3NyH_2O \quad \ldots \Delta H_1$$

$$Me_4NI(c) + (x+1)Me_3NyH_2O \longrightarrow (Me_4N^+ + I^-)(x+1)Me_3NyH_2O \quad \ldots \Delta H_2$$

$$(Me_4N^+ + I^-)xMe_3NyH_2O + Me_3N(\ell) \longrightarrow (Me_4N^+ + I^-)(x+1)Me_3NyH_2O \quad \ldots \Delta H_3$$

where x and y represent the mole ratios of trimethylamine and water per mole of methyl iodide (the concentration of trimethylamine corresponding to the ratio $(x + 1)/y$ is 25% $^{w}/_{v}$). The nomenclature used for describing the trimethylamine solution does not mean $(x + 1)$ moles of trimethylamine solution per mole of methyl iodide.

The reaction between methyl iodide and trimethylamine solution was chosen because it was fast (main period of the reaction was less than 1 minute) and because the final thermodynamic state was easily reproducible.

The methyl iodide was distilled into an ampoule under vacuum, and the ampoule sealed to prevent loss of methyl iodide. The volume of the ampoule was determined before filling and this allowed a correction to be made for the gaseous methyl iodide when calculating ΔH_1. A post-calorimetric iodide determination of the calorimetric fluid showed that there had been no loss of iodide during the reaction.

The second reaction represents the heat of solution of tetramethyl ammonium iodide in aqueous trimethylamine solution. The values of ΔH_1 and ΔH_2 are:

$$\Delta H_1 = -22.55 \pm 0.30 \text{ Kcal.mole}^{-1} \ (-94.41 \pm 1.26 \text{ Kj.mole}^{-1})$$

$$\Delta H_2 = 9.75 + 0.04 \text{ Kcal.mole}^{-1} \ (40.80 + 0.16 \text{ Kj.mole}^{-1})$$

The third reaction represents a correction term which is applied so that the final thermodynamic state in the previous two reactions is the same. Assuming that the tetramethyl ammonium and iodide ions have little effect on the dilution, then equation 3 becomes

$$x\ Me_3NyH_2O \ + \ Me_3N\ (l) \longrightarrow (x+1)Me_3NyH_2O \qquad \ldots \ \Delta H_3$$

or $$x(Me_3N\ y/x\ H_2O) + Me_3N\ (l) \longrightarrow (x+1)(Me_3N\ y/(x+1)H_2O) \ \ldots \ \Delta H_3$$

The mole ratio $y/(x + 1)$ corresponds to 7.74 for the aqueous trimethylamine used. The value of $\Delta H_f^o(Me_3N\ 7.74H_2O)$ was obtained from the following dilution.

$$Me_3N\ 7.74\ H_2O \ + \ (z - 7.74)H_2O \longrightarrow Me_3N\ zH_2O \quad \ldots \quad \Delta H_d$$

The values of ΔH_d are listed in table 4.5.

Table 4.5

Exp.	Dilution, z	ΔH_d Kcal.mole^{-1}
1	815.7	-1.38
2	872.5	-1.36

The values of $\Delta H_f^o(Me_3N\ zH_2O)$ were obtained by interpolation from the literature (Wagman et al, 1968).

Thus $\Delta H_f^o(Me_3N\ 7.74H_2O) = -17.19 \pm 0.03$ Kcal.mole^{-1}

$(-71.92 \pm 0.13$ Kj.mole$^{-1})$

The precision of the calorimeter is such that it was impossible to distinguish between $\Delta H_f^o(Me_3N\ y/x\ H_2O)$ and $\Delta H_f^o(Me_3N\ y/(x+1)\ H_2O)$ and so these were taken to have the same value. The error introduced in this way is probably within the error quoted for ΔH_3

The standard heats of formation of trimethylamine are given in table 4.6 below

Table 4.6

Standard Heats of Formation of Trimethylamine (liquid)

ΔH_f^o Kcal.mole^{-1}	Reference
-11.7 ± 0.5	Issoire and van Long, 1960
-12.0 ± 0.5	Issoire and van Long, 1960
-11.0	Wagman et al, 1968
-10.93 ± 0.17	Cox and Pilcher, 1970

Using the value of $\Delta H_f^o(Me_3N,l) = -10.93 \pm 0.17$ Kcal.mole^{-1}, then the correction term

$$\Delta H_3 = -6.26 \pm 0.17 \text{ Kcal.mole}^{-1}\ (-26.19 \pm 0.71 \text{ Kj.mole}^{-1})$$

The standard heat of formation of crystalline tetramethyl ammonium iodide can be obtained from the reaction

$$\mathrm{MeI}\ (1)\ +\ \mathrm{Me_3N}\ (1)\ =\ \mathrm{Me_4NI}\ (c) \qquad \ldots\ \Delta H$$

where $\Delta H = \Delta H_1 - \Delta H_2 + \Delta H_3$

$= -38.56 \pm 0.35\ \mathrm{Kcal.mole^{-1}}\ (-161.40 \pm 1.46\ \mathrm{Kj.mole^{-1}})$

and $\Delta H_f^o(\mathrm{Me_4NI,c}) = \Delta H + \Delta H_f^o(\mathrm{MeI,l}) + \Delta H_f^o(\mathrm{Me_3N,l})$

The standard heats of formation of methyl iodide are listed in table 4.7 below.

Table 4.7

Standard Heats of Formation of Methyl Iodide

ΔH_f^o Kcal.mole^{-1}	Reference
-3.6 ± 1.2	Carson et al, 1949
-2.9 ± 0.3	Carson et al, 1961
-3.4 ± 0.4	Golden et al, 1965
-3.32 ± 0.35	Goy and Pritchard, 1965

The value for $\Delta H_f^o(\mathrm{MeI,l}) = -3.3 \pm 0.3\ \mathrm{Kcal.mole^{-1}}$ was proposed by Cox and Pilcher, 1970, and this gives a standard heat of formation of crystalline tetramethyl ammonium iodide of $-52.79 \pm 0.49\ \mathrm{Kcal.mole^{-1}}\ (-220.94 \pm 2.05\ \mathrm{Kj.mole^{-1}})$

The standard heat of formation of the aqueous tetramethyl ammonium ion was obtained from the reaction

$$Me_4NI\ (c) + \infty H_2O \quad Me_4N^+\ aq + I^-\ aq \qquad ..\Delta H_s^\circ$$

where $\Delta H_f^\circ\ (Me_4N^+, aq) = \Delta H_s^\circ - \Delta H_f^\circ\ (I^-, aq) + \Delta H_f^\circ\ (Me_4NI, c)$

The available data for ΔH_s° are listed in table 4.8.

Table 4.8

Heats of Solution of Tetramethyl Ammonium Iodide

ΔH_s° Kcal.mole^{-1}	Reference
10.05 ± 0.02	Coulter et al, 1940
10.08	Wu and Friedman, 1966
10.13	Boyd and Wang, 1968
9.99 ± 0.05	Bhatnagar and Criss, 1969
10.07 ± 0.17	This work

Using the value of $\Delta H_s^\circ = 10.07 \pm 0.17$ Kcal.mole^{-1}, the value obtained for

$$\Delta H_f^\circ\ (Me_4N^+, aq) = -29.53 \pm 0.52\ \text{Kcal.mole}^{-1}$$
$$(-123.63 \pm 2.17\ \text{Kj.mole}^{-1})$$

The standard heat of formation of tetramethyl ammonium perchlorate can now be obtained directly from its heat of solution.

Thus $\quad Me_4NClO_4\ (c) + \infty H_2O \quad Me_4N^+ aq + ClO_4^- aq \quad \ldots.\ \Delta H_{sn}$

and $\Delta H_f^{\circ}\ (Me_4NClO_4, c) = \Delta H_f^{\circ}\ (Me_4N^+, aq) + \Delta H_f^{\circ}\ (ClO_4^-, aq) - \Delta H_{sn}$

From Appendix III

$$\Delta H^{\circ}_{sn} = 10.35 \pm 0.01\ Kcal.mole^{-1}\ (43.28 \pm 0.01\ Kj.mole^{-1})$$

and thus the value obtained for the standard heat of formation of crystalline tetramethyl ammonium perchlorate is

$$\Delta H_f^{\circ}\ (Me_4NClO_4, c) = -70.79 \pm 0.52\ Kcal.mole^{-1}$$
$$(-296.24 \pm 2.17\ Kj.mole^{-1})$$

The standard heat of formation of the aqueous tetramethyl ammonium ion also allows the calculation of the standard heats of formation of the other tetramethyl ammonium halides from their heats of solution. These heats of solutionand the standard heats of formation are

$\Delta H_s^{\circ}(Me_4NCl, c) = 0.98 \pm 0.08\ Kcal.mole^{-1}$ (Askew et al, 1934)

$\Delta H_f^{\circ}(Me_4NCl, c) = -70.46 \pm 0.53\ Kcal.mole^{-1}$

$\Delta H_s^{\circ}(Me_4NBr, c) = 5.92 \pm 0.05\ Kcal.mole^{-1}$ (Wu and Friedman,1966)

$\Delta H_f^{\circ}(Me_4NBr, c) = -64.50 \pm 0.52\ Kcal.mole^{-1}$

Tetraethyl Ammonium Perchlorate

The standard heat of formation of the aqueous tetraethyl ammonium ion was obtained by measuring the heat of reaction of triethylamine with aqueous ethyl iodide. This reaction was found to be slower than the corresponding reaction between methyl iodide and trimethylamine; the main period for the ethyl iodide reaction being between 6 and 9 minutes (Appendix III). The 'equal area' procedure (Appendix I) was used to obtain the corrected resistance change for this reaction. The reaction between ethyl iodide and triethylamine was found to be too slow at 25°C to be a suitable calorimetric reaction.

The aqueous ethyl iodide was prepared by shaking ethyl iodide (4 ml., 6.1 g, 0.042 mole) with distilled water (21, 111.0 mole) for 48 hours. (The solubility of ethyl iodide in water is 0.388 g ethyl iodide per 100 g water at 22.5°C and 0.402 g ethyl iodide per 100 g water at 30°C (Stephen and Stephen, 1963.))

Thus $$\mathrm{EtI\ n\ H_2O + (x + 1)\ Et_3N \longrightarrow (Et_4N^+ + I^-)x\ Et_3N.n\ H_2O}$$

where n and (x+1) represent the moles of water and trimethylamine with respect to 1 mole of ethyl iodide.

The measured heat change, Q cals, is related to the component reactions by the equation

$$Q = n_1 . \Delta H_1 + (n_2-n_1) . \Delta H_2 + n_1 . \Delta H_3$$

where n_1 and n_2 are the moles of ethyl iodide and trimethylamine respectively, and

ΔH_1 is the molar heat of dissolution of ethyl iodide from water,

ΔH_2 is the molar heat of dilution of the excess triethylamine,

ΔH_3 is the molar heat of reaction of ethyl iodide with triethylamine.

The heat of dissolution of ethyl iodide from water was obtained using the 'Second Law' method. A graph of ln Kx vs. $^1/_T$ was drawn using solubility data from Stephen and Stephen, 1963, where Kx represents the mole fraction of ethyl iodide soluble in water at T^oK. The slope of the graph yields the heat of solution of ethyl iodide in water.

The value of ΔH_1 obtained is -0.81 ± 0.03 Kcal.mole^{-1}. The heat of dilution of triethylamine, from liquid to infinite dilution was taken from Wagman et al, 1968.

$$\Delta H_2 = -9.50 \pm 0.05 \text{ Kcal.mole}^{-1}$$

Using this ancillary data the value of ΔH_3 was obtained

$$\Delta H_3 = -5.56 \pm 0.32 \text{ Kcal.mole}^{-1} \ (-23.24 \pm 1.35 \text{ Kj.mole}^{-1})$$

The molar excess of triethylamine is small and, neglecting the dilution term to infinite dilution, the original equation becomes

$$EtI(l) + Et_3N(l) + \alpha H_2O \longrightarrow Et_4N^+aq + I^-aq \quad \ldots \quad \Delta H_3$$

and $$\Delta H_f^o(Et_4N^+,aq) = \Delta H_3 - \Delta H_f^o(I^-,aq) + \Delta H_f^o(EtI,l) + \Delta H_f^o(Et_3N,l)$$

The ancillary data for the last equation are

$$\Delta H_f^o(EtI,l) = -9.6 \pm 0.4 \text{ Kcal.mole}^{-1} \text{ (Ashcroft et al, 1965)}$$
$$\Delta H_f^o(Et_3N,l) = -30.52 \pm 0.16 \text{ Kcal.mole}^{-1} \text{ (Lebedeva, 1966)}$$

and hence the standard heat of formation of the aqueous tetraethyl ammonium ion

$$\Delta H_f^o(Et_4N^+,aq) = -32.49 \pm 0.54 \text{ Kcal.mole}^{-1} \ (-135.92 \pm 2.25 \text{ Kj.mole}^{-1})$$

The heat of solution of tetraethyl ammonium perchlorate leads to its standard heat of formation directly

$$Et_4NClO_4(c) + \alpha H_2O \longrightarrow Et_4N^+aq + ClO_4^- aq \quad \ldots \quad \Delta H_s^o$$

and $$\Delta H_f^o(Et_4NClO_4,c) = \Delta H_f^o(Et_4N^+,aq) + \Delta H_f^o(ClO_4^-,aq) - \Delta H_s^o$$

Using $\Delta H_s^{\circ} = 7.41 \pm 0.02$ Kcal.mole^{-1} (31.02 ± 0.11 Kj.mole^{-1})

then $\Delta H_f^{\circ}(Et_4NClO_4, c) = -70.81 \pm 0.54$ Kcal.mole^{-1}

(-296.27 ± 2.25 Kj.mole^{-1})

Askew et al, 1934, reported the value 7.18 Kcal.mole^{-1} for the value of ΔH_s at 20°C.

The heat of dilution of triethylamine in water was measured

$$Et_3N(l) + n\ H_2O \longrightarrow Et_3N.n\ H_2O \qquad .... \Delta H_4$$

and from two experiments the value $\Delta H_4 = 7.71 \pm 0.32$ Kcal.mde^{-1} (n = 1589 and 1679) was obtained. Using this value for the heat of dilution then

$\Delta H_3 = -6.34 \pm 0.32$ Kcal.mole^{-1}

$\Delta H_f^{\circ}(Et_4N^+, aq) = -33.47 \pm 0.54$ Kcal.mole^{-1}

$\Delta H_f^{\circ}(Et_4NClO_4, c) = -71.59 \pm 0.54$ Kcal.mole^{-1}

Using the standard heat of formation of the aqueous tetraethylammonium ion (-32.49 ± 0.54 Kcal.mole^{-1}), the standard heatsof formation of the other tetraethyl ammonium halides can be obtained from their heats of solution.

$\Delta H_s^{\circ}(Et_4NCl, c) = -3.07 \pm 0.05$ Kcal.mole^{-1} (Wu and Friedman,1966)

$\Delta H_f^{\circ}(Et_4NCl, c) = -69.37 \pm 0.54$ Kcal.mole^{-1}

$\Delta H_s^{\circ}(Et_4NBr, c) = 1.49 \pm 0.02$ Kcal.mole^{-1}(Wu and Friedman,1966)

$\Delta H_f^{\circ}(Et_4NBr, c) = -63.03 \pm 0.54$ Kcal.mole^{-1}

n-Propyl Ammonium Perchlorate

The standard heat of formation of the aqueous propyl ammonium ion was obtained by measuring the following heat of reaction

$$PrNH_2(l) + (x+1)HClO_4yH_2O \longrightarrow (PrNH_3^+ + ClO_4^-)xHClO_4yH_2O \quad \ldots \; \Delta H_1$$

where x and y represent the moles of perchloric acid and water respectively, and the ratio (x+1)/y corresponds to 3% aqueous perchloric acid.

No significant trend in the value of ΔH_1 with dilution could be detected, so ΔH_1 was set equal to ΔH_1^o, where ΔH_1^o is the heat of the following reaction

$$PrNH_2(l) + HClO_4aq \longrightarrow PrNH_3^+aq + ClO_4^-aq \quad \ldots \; \Delta H_1^o$$

and $\Delta H_f^o(PrNH_3^+,aq) = \Delta H_1^o + \Delta H_f^o(PrNH_2,l)$

$\Delta H_f^o(HClO_4,aq) = \Delta H_f^o(ClO_4^-,aq)$

Now $\Delta H_1^o = -19.49 \pm 0.10$ Kcal.mole^{-1} (-81.56 ± 0.40 Kj.mole^{-1})

and $\Delta H_f^o(PrNH_2,l) = -16.77 \pm 0.13$ Kcal.mole^{-1}

(Smith and Good, 1967)

Thus $\Delta H_f^o(PrNH_3^+,aq) = -36.26 \pm 0.17$ Kcal.mole^{-1}

(-151.71 ± 0.71 Kj.mole^{-1})

Using the heat of solution of the reaction

$$PrNH_3ClO_4(c) + \alpha H_2O \longrightarrow PrNH_3^+\ aq + ClO_4^-\ aq \quad \ldots \quad \Delta H_s^o$$

then $\Delta H_f^o(PrNH_3ClO_4, c) = \Delta H_f^o(PrNH_3^+, aq) + \Delta H_f^o(ClO_4^-, aq) - \Delta H_s^o$

$$= -71.08 \pm 0.18\ Kcal.mole^{-1}$$

$$(-297.40 \pm 0.75\ Kj.mole^{-1})$$

Tri-n-Propyl Ammonium Perchlorate

The standard heat of formation of crystalline tri-n-propyl ammonium perchlorate was obtained by studying the reactions

$$Pr_3N(l) + (m+1)HClO_4nH_2O \longrightarrow (Pr_3NH^+ + ClO_4^-)mHClO_4nH_2O \quad \ldots \quad \Delta H_1$$

$$Pr_3NHClO_4(c) + (m+1)HClO_4nH_2O \longrightarrow (Pr_3NH^+ + ClO_4^-)(m+1)HClO_4nH_2O \quad \ldots \quad \Delta H_2$$

where m and n represent the moles of perchloric acid and water respectively and the ratio $(m+1)/n$ corresponds to 72% perchloric acid.

From Appendix III

$\Delta H_1 = -30.14 \pm 0.13\ Kcal.mole^{-1}\ (-126.10 \pm 0.68\ Kj.mole^{-1})$

$\Delta H_2 = 1.99 \pm 0.14\ Kcal.mole^{-1}\ (8.32 \pm 0.57\ Kj.mole^{-1})$

A correction term must be applied to the two equations above so that the final thermodynamic state in both cases is the same. The correction term is expressed by the equation

$$(Pr_3NH^+ + ClO_4^-)mHClO_4nH_2O + HClO_4(l) \longrightarrow (Pr_3NH^+ + ClO_4^-)(m+1)HClO_4nH_2O \quad \ldots \quad \Delta H_3$$

Assuming that the ions present have a negligible effect on this reaction, then the equation can be written

$$mHClO_4\ nH_2O + HClO_4\ (l) \longrightarrow (m+1)HClO_4\ nH_2O \qquad \ldots \Delta H_3$$

The value of ΔH_3 was obtained from perchloric acid dilution tables (Wagman et al, 1968), and

$$\Delta H_3 = -11.08 \pm 0.42\ \text{Kcal.mole}^{-1}$$

The equation from which the standard heat of formation can be obtained is

$$Pr_3N\ (l) + HClO_4\ (l) \longrightarrow Pr_3NHClO_4\ (c) \qquad \ldots \Delta H$$

where $\Delta H = \Delta H_1 - \Delta H_2 + \Delta H_3$

$= -43.21 \pm 0.50\ \text{Kcal.mole}^{-1}\ (-180.79 \pm 2.09\ \text{Kj.mole}^{-1})$

and $\Delta H_f^{\circ}(Pr_3NHClO_4,c) = \Delta H + \Delta H_f^{\circ}(HClO_4,l) + \Delta H_f^{\circ}(Pr_3N,l)$

$\Delta H_f^{\circ}(HClO_4,l) = -9.70 \pm 0.02\ \text{Kcal.mole}^{-1}$ (Wagman, et al,1968)

$\Delta H_f^{\circ}(Pr_3N,l) = -49.51 \pm 0.24\ \text{Kcal.mole}^{-1}$ (Lebedeva, 1966)

Thus $\Delta H_f^{\circ}(Pr_3NHClO_4,c) = -102.42 \pm 0.56\ \text{Kcal.mole}^{-1}$

$(-428.53 \pm 2.34\ \text{Kj.mole}^{-1})$

The standard heat of formation of the aqueous tri-n-propyl ammonium ion was obtained in a similar manner to the standard heat of formation of the aqueous n-propyl ammonium ion.

Thus

$$Pr_3N(l) + (p+1)HClO_4\ qH_2O \longrightarrow (Pr_3NH^+ + ClO_4^-)pHClO_4\ qH_2O \quad \ldots \Delta H_s^o$$

where p and q represent the moles of perchloric acid and water respectively and the ratio (p+1)/q corresponds to 3% perchloric acid.

Then $\Delta H_f^o(Pr_3NH^+,aq) = \Delta H_s^o + \Delta H_f^o(Pr_3N,l)$

$= -65.92 \pm 0.29$ Kcal.mole^{-1}

This reaction had a main period in the range 6 to 10 minutes and so the 'equal area' technique (Appendix I) was used to obtain the corrected resistance change for the reaction period.

Triphenylmethyl Perchlorate

The following two reactions were used to obtain the standard heat of formation of triphenylmethyl perchlorate

$$Ph_3COH\ (c) + (m+1)HClO_4nH_2O \longrightarrow (Ph_3C^+ + ClO_4^-)mHClO_4(n+1)H_2O \quad \ldots \Delta H_1$$

$$Ph_3CClO_4\ (c) + (m+1)HClO_4nH_2O \longrightarrow (Ph_3C^+ + ClO_4^-)(m+1)HClO_4nH_2O \quad \ldots \Delta H_2$$

Two different samples of triphenylmethanol were used to study the first reaction. Sample A was recrystallised from ethanol and sample B was recrystallised from toluene. The value of ΔH_1 is taken as the mean of ΔH_a and ΔH_b

Thus $\Delta H_1 = -2.90 \pm 0.13$ Kcal.mole^{-1} (-12.13 ± 0.54 Kj.mole^{-1})

and $\Delta H_2 = 3.09 \pm 0.02$ Kcal.mole^{-1} (12.93 ± 0.11 Kj.mole^{-1})

Two dilution terms must be used in order to obtain the final thermodynamic state in both reactions

$$(m+1)HClO_4\ nH_2O + H_2O \longrightarrow (m+1)HClO_4(n+1)HClO_4 \quad \ldots .\ \Delta H_3$$

$$(m+1)HClO_4(n+1)H_2O \longrightarrow m\ HClO_4(n+1)H_2O + HClO_4(l) \quad \ldots\ \Delta H_4$$

The effect of the triphenyl methyl and perchlorate ions on these dilution terms are assumed to be negligible. The mean value of $\Delta H_3 + \Delta H_4$ was determined by considering variations of m and n with respect to experimental quantities of triphenyl methanol, using perchloric acid dilution tables (Wagman et al, 1968).

$$\Delta H_3 + \Delta H_4 = 6.70 \pm 0.02\ \text{Kcal.mole}^{-1}$$

The standard heat of formation of triphenyl methyl perchlorate can be obtained from

$$Ph_3COH\ (c) + HClO_4\ (l) \longrightarrow Ph_3CClO_4\ (c) + H_2O \quad \ldots .\ \Delta H$$

where $\Delta H = \Delta H_1 = \Delta H_2 - (\Delta H_3 + \Delta H_4)$

$$= -12.71 \pm 0.13\ \text{Kcal.mole}^{-1}\ (-53.18 \pm 0.54\ \text{Kj.mole}^{-1})$$

and $\Delta H_f^{\circ}(Ph_3CClO_4, c) = \Delta H - \Delta H_f^{\circ}(H_2O, l) + \Delta H_f^{\circ}(HClO_4, l) + \Delta H_f^{\circ}(Ph_3COH, c)$

$$\Delta H_f^{\circ}(H_2O, l) = -68.32 \pm 0.01\ \text{Kcal.mole}^{-1}\ \text{(Wagman et al,1968)}$$

$$\Delta H_f^{\circ}(Ph_3COH, c) = -0.80 \pm 0.60\ \text{Kcal.mole}^{-1}\ \text{(Parks et al,1954)}$$

Thus $\Delta H_f^{\circ}(Ph_3CClO_4, c) = 46.71 \pm 0.62\ \text{Kcal.mole}^{-1}(195.43 \pm 2.59\ \text{Kj.mole}^{-1})$

Tri(p-tolyl)methyl Perchlorate

The low solubility of tri(p-tolyl)methanol and tri(p-tolyl)-methyl perchlorate in perchloric acid prevented similar reactions to those of triphenylmethyl perchlorate being used to obtain the standard heat of formation. The hydrolysis of tri(p-tolyl)-methyl perchlorate proved to be too slow for calorimetric study.

A series of reactions involving the alkaline hydrolysis of a solution of tri(p-tolyl)methyl perchlorate in acetonitrile were carried out. However, the results were inconsistent. This may hav been due to a reaction between acetonitrile and sodium hydroxide.

The calorimetric reaction finally chosen was the hydrolysis of a solution of tri(p-tolyl)methyl perchlorate in glacial acetic acid.

$$Ar_3C.ClO_4 \text{ m AcOH} + (n+1)\ H_2O \longrightarrow Ar_3COH(c) + HClO_4\text{mAcOH n } H_2O$$

where m and n represent the mole ratios of acetic acid and water respectively.

The measured heat change, Q cals, is related to the two reactions which occur by the equation

$$Q = n_1.\Delta H_1 + n_2.\Delta H_2$$

where n_1 and n_2 represent the moles of acetic acid and perchlorate respectively, and ΔH_1 is the heat of solution of acetic acid, and ΔH_2 the heat of hydrolysis of tri(p-tolyl)methyl perchlorate.

The value obtained for $\Delta H_2 = -5.58 \pm 0.03$ Kcal.mole^{-1} (-23.33 ± 0.14 Kj.mole^{-1})

In this reaction the tri(p-tolyl)methanol is assumed to be precipitated out quantitatively and since the amount of acetic acid is small, the final liquid state is considered to be infinitely dilute perchloric acid. Thus the previous equation becomes

$$Ar_3CClO_4\ mAcOH + \infty H_2O \longrightarrow Ar_3COH\ (c) + HClO_4 \infty H_2O \quad \ldots \Delta H_2$$

The heat of solution of tri(p-tolyl)methyl perchlorate in glacial acetic acid was also measured

$$Ar_3CClO_4\ (c) + mAcOH \longrightarrow Ar_3CClO_4\ mACOH \quad \ldots \Delta H_s^{o}$$

$$\Delta H_s^{o} = 6.23 \pm 0.09\ \text{Kcal.mole}^{-1}\ (26.07 \pm 0.39\ \text{Kj.mole}^{-1})$$

The standard heat of formation of tri(p-tolyl)methyl perchlorate can be obtained from

$$Ar_3CClO_4 + H_2O\ (l) \qquad Ar_3COH + HClO_4\ (l) \quad \ldots \Delta H$$

where $\Delta H = \Delta H_2 + \Delta H_s^{o} - \Delta H_3$

ΔH_3 is the heat of dilution of liquid perchloric acid to infinite dilution

$$HClO_4\ (l) + \infty H_2O \longrightarrow HClO_4 \infty H_2O \quad \ldots \Delta H_3$$

and $\Delta H_3 = -21.21$ Kcal.mole^{-1} (Wagman et al, 1968)

Thus $\Delta H = 21.86 \pm 0.10$ Kcal.mole^{-1}

and
$$\Delta H_f^{\circ}(Ar_3CClO_4,c) = \Delta H_f^{\circ}(Ar_3COH,c) + \Delta H_f^{\circ}(HClO_4,l) - \Delta H_f^{\circ}(H_2O,l) - \Delta H$$

$$\Delta H_f^{\circ}(Ar_3COH,c) = -26.2 \pm 1.2 \text{ Kcal.mole}^{-1} \text{ (cf. Appendix II)}$$

and hence $\Delta H_f^{\circ}(Ar_3CClO_4,c) = 10.6 \pm 1.2 \text{ Kcal.mole}^{-1}$ ($44.4 \pm 5.4 \text{ Kj.mole}^{-1}$)

Tri(p-methoxyphenyl)methyl Perchlorate

The procedure for obtaining the standard heat of formation of tri(p-methoxyphenyl)methyl perchlorate is exactly analogous to that for tri(p-tolyl)methyl perchlorate. The data used are listed below

$$\Delta H_2 = 2.60 \pm 0.25 \text{ Kcal.mole}^{-1} \ (10.88 \pm 1.05 \text{ Kj.mole}^{-1})$$

$$\Delta H_s^{\circ} = 7.78 \pm 0.11 \text{ Kcal.mole}^{-1} \ (32.55 \pm 0.46 \text{ Kj.mole}^{-1})$$

$$\Delta H = 31.59 \pm 0.27 \text{ Kcal.mole}^{-1} \ (132.17 \pm 1.13 \text{ Kj.mole}^{-1})$$

$$\Delta H_f^{\circ}(Ar_3COH,c) = -117.2 \pm 5.5 \text{ Kcal.mole}^{-1} \text{ (Appendix II)}$$

$$\Delta H_f^{\circ}(Ar_3CClO_4,c) = -90.2 \pm 5.5 \text{ Kcal.mole}^{-1}(377.4 \pm 23.0\text{Kj.mole}^{-1})$$

Tetrapropyl Ammonium Bromide and Tetrabutyl Ammonium Bromide

The heats of solution of these two compounds were measured in order to complete the series of heats of solution for the tetraalkylammonium halides. However, the values of these two heats of solution were found to have been reported (Krishnan and Friedman, 1969). Present values are compared with the literature values in table 4.9.

Table 4.9

Heats of Solution of Tetra-alkyl Ammonium Bromides

Compound	ΔH_s° Kcal.mole^{-1}	
	Present work	Literature
Pr_4N Br	-1.17 ± 0.04	-1.03 (a) -1.10 (b)
Bu_4N Br	-2.20 ± 0.15	-2.02 (a)

(a) Krishnan and Friedman, 1969

(b) Boyd and Wang, 1968

The standard heats of formation of these compounds cannot be calculated since the standard heats of formation of the aqueous tetra-alkyl ammonium ions are not available in the literature.

4b Heats of Transition and Fusion

The measured transition temperatures and the endothermic enthalpies of transition (T) and fusion (F), for the amine salts studied in this work, are recorded in table 4.10. Fusions were distinguished from transitions by observing the samples through the glass window, in the cylindrical jacket. The results presented, except for ammonium perchlorate, are the mean values of three separate runs for each sample. The uncertainty interval quoted for these results is the range. The enthalpy of transition of ammonium perchlorate was obtained from the mean of six runs and the uncertainty interval was determined as in section 6.

Transition energies are recorded in $\mathrm{Kcal.mole^{-1}}$ and transition temperatures in degrees C. An error of ± 1°C is placed on the transition temperatures. No transitions were detected for tetramethyl ammonium perchlorate and tri-n-propyl ammonium perchlorate in the temperature range -90°C to 360°C. A very small peak was consistently detected at 100°C for tetrabutyl ammonium bromide but its area was not measured. Typical thermograms for transition and fusion are recorded in Fig. 4.1.

Fig. 4·1

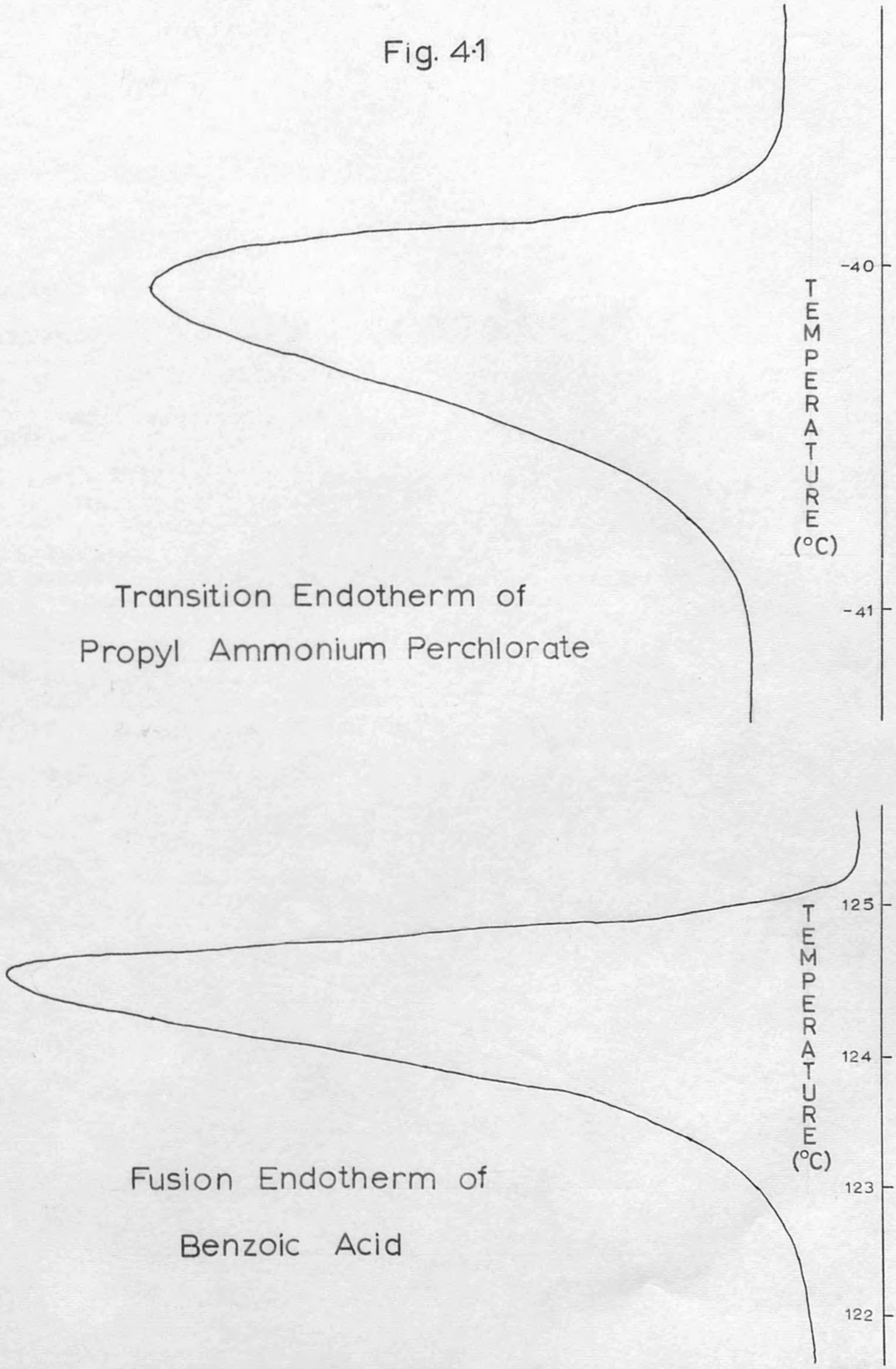

Transition Endotherm of Propyl Ammonium Perchlorate
TEMPERATURE (°C)
-40
-41
Fusion Endotherm of Benzoic Acid
TEMPERATURE (°C)
125
124
123
122

Table 4.10

Heats of Transition and Fusion in the range -90°C to 250°C

	Temperature	Energy
NH_4ClO_4	242	2.24 ± 0.32(T)
$MeNH_3ClO_4$	37	1.69 ± 0.01(T)
	178	1.97 ± 0.02(T)
$Me_2NH_2ClO_4$	39	1.81 ± 0.04(T)
	41	0.79 ± 0.05(T)
	180	0.57 ± 0.05(F)
Me_3NHClO_4	119	0.22 ± 0.01(T)
	209	0.99 ± 0.01(T)
$EtNH_3ClO_4$	4	2.90 ± 0.04(T)
	149	2.31 ± 0.06(T)
$Et_2NH_2ClO_4$	- 56	0.40 ± 0.01(T)
	158	2.33 ± 0.05(F)
Et_4NClO_4	93	2.79 ± 0.22(T)
$PrNH_3ClO_4$	- 41	0.88 ± 0.02(T)
	170	2.46 ± 0.03(F)
Pr_4NBr	100	3.72 ± 0.20(T)
	118	0.07 ± 0.02(T)
Bu_4NBr	83	0.50 ± 0.07(T)
	92	3.23 ± 0.12(T)
	113	2.84 ± 0.15(F)

4c Specific Heats

The specific heat of dimethyl ammonium perchlorate was determined in the range 275° to 350°K in order to resolve the apparent divergence of opinion about the crystal phase transformations of this compound. Stammler et al, 1966, report the transition from monoclinic to tetragonal at 311°K (38°C) and Duke , 1970, suggests that the lower temperature phase is cubic. Present D.S.C. studies, however, show that there are two phase changes in the 303° to 313°K (30° - 40°C) range

The accuracy of the D.S.C. for specific heat determinations was checked by measuring the specific heat of a standard substance. Thermochemically pure benzoic acid (Bureau of Analysed Samples, Middlesborough, England) was chosen as a standard, since precise data are available (Furukawa et al, 1951) in the range 0° to 410°K.

The results obtained for benzoic acid are presented in tables 4.11 and 4.12. The values in table 4.11, in the range 320° to 340° represent measurements in a non-transition region. Data in table 4.12 represent specific heat measurements through the melting point of benzoic acid. Data for this transition region were obtained from separate runs in the temperature ranges 372° - 395°K and 400° to 420°K.

The raw data were fitted to an equation of the form

$$C_p = A + BT$$

using a least-mean-square computer programme, in order to minimise random noise effects on the trace. The smoothed data are presented in tables 4.11 and 4.12, and Fig. 4.2 shows these values compared graphically with the literature values.

Table 4.10

Specific Heat of Benzoic Acid (320° - $340^{\circ}K$)

$T^{\circ}K$	Specific Heat cal.$^{\circ}K^{-1}.g^{-1}$	
	Measured	Literature
320	0.3009	0.3071
325	0.3095	0.3116
330	0.3181	0.3162
335	0.3267	0.3207
340	0.3352	0.3301

The specific heat of dimethyl ammonium perchlorate was determined in the range 275° to $350^{\circ}K$ and the values are recorded in table 4.12. The values in the pre- and post-transition regions, 275° to $295^{\circ}K$ and 320° to $350^{\circ}K$ are the mean of five separate experiments.

Table 4.11

Specific Heat of Benzoic Acid (372° - 420°K)

T°K	Specific Heat cal. g^{-1}. $^{o}K^{-1}$	
	Measured	Literature
372	0.3685	0.3601
374	0.3711	0.3620
376	0.3737	0.3644
378	0.3764	0.3659
380	0.3790	0.3678
382	0.3816	0.3698
384	0.3842	0.3716
385	0.3855	0.3726
386	0.3868	0.3736
388	0.3894	0.3755
390	0.3920	0.3774
400	0.4816	0.5031
402	0.4858	0.5057
404	0.4900	0.5082
405	0.4921	0.5095
406	0.4942	0.5108
408	0.4983	0.5134
410	0.5025	0.5160
412	0.5067	0.5186
414	0.5109	0.5212
416	0.5150	0.5238
418	0.5192	0.5264
420	0.5234	0.5290

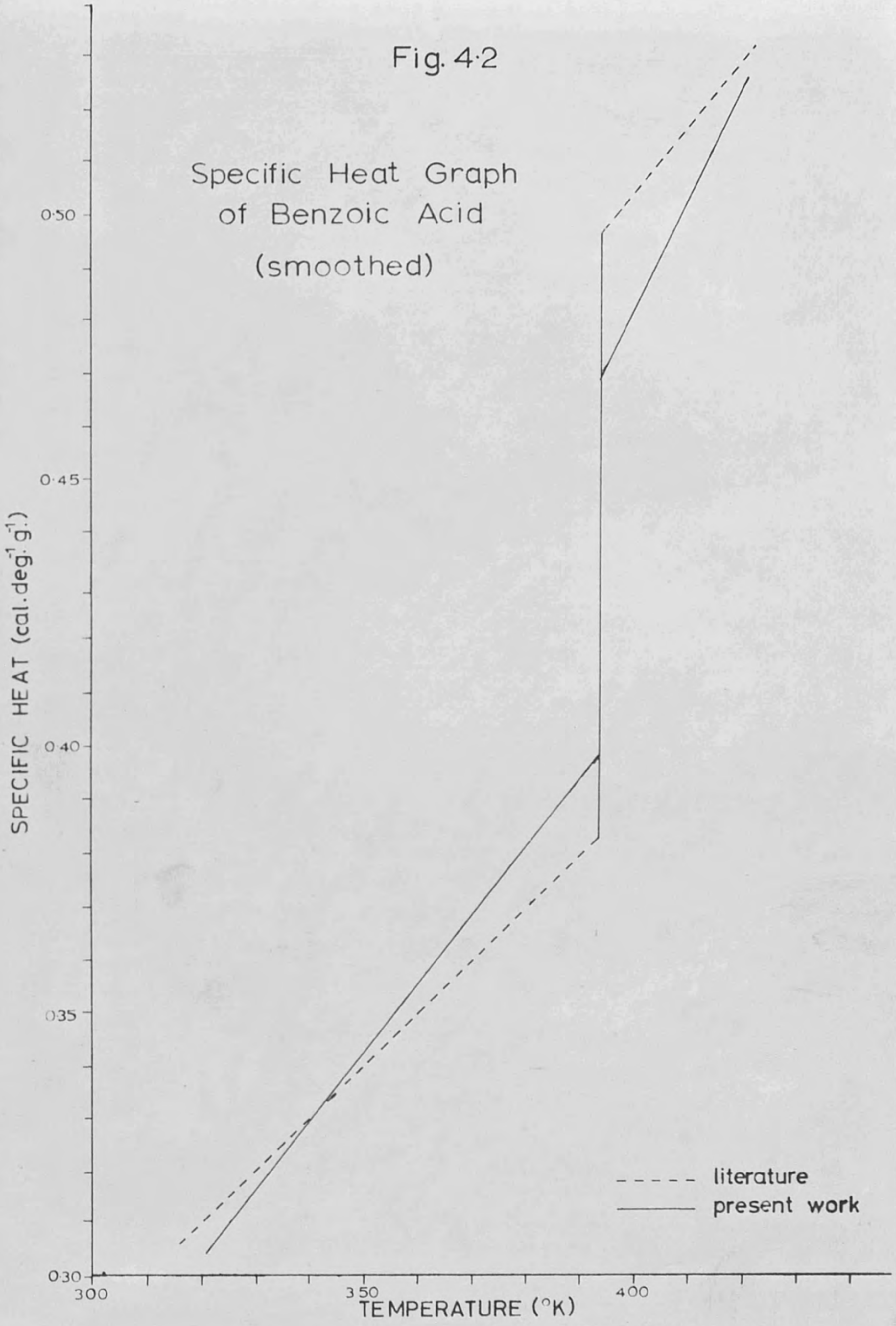


Fig. 4·2

Specific Heat Graph of Benzoic Acid (smoothed)

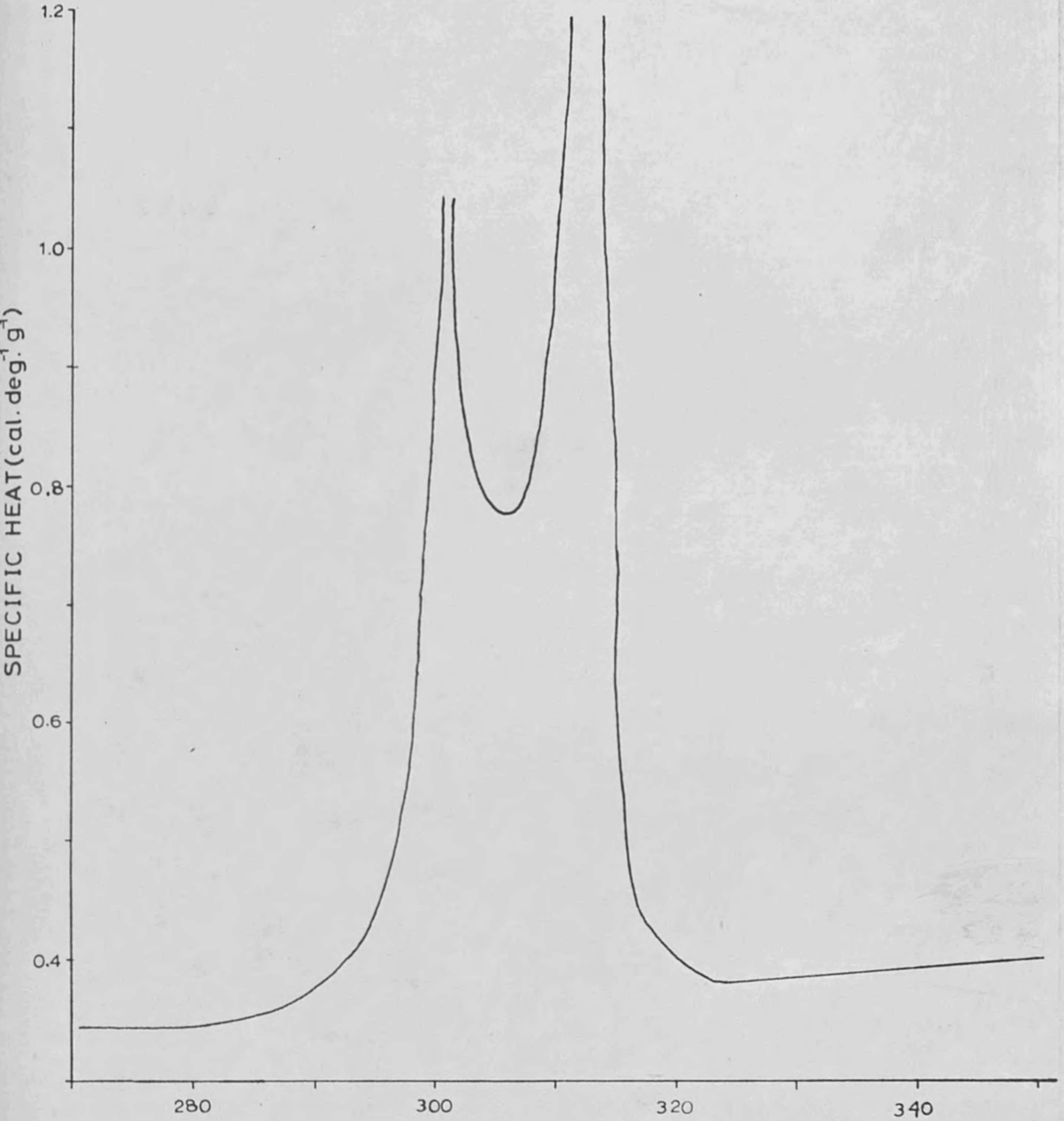
Table 4.12

Specific Heat of Dimethyl Ammonium Perchlorate (275^{o}- $350^{o}K$)

$T^{o}K$	C_p cal.$^{o}K^{-1}$. g^{-1}.	$T^{o}K$	C_p cal.$^{o}K^{-1}$.g^{-1}.
275	0.3428	304	0.8084
280	0.3452	306	0.7361
285	0.3537	308	0.8295
290	0.3734	310	1.0664
294	0.4259	316	0.4930
295	0.4354	320	0.3812
296	0.4826	325	0.3849
297	0.5358	330	0.3886
298	0.6393	335	0.3923
299	0.7328	340	0.3960
300	0.9174	345	0.3997
301	0.9971	350	0.4034
302	0.8956		

The values in the transition region were obtained from two experiments in the range 290° to 320°K. The values for the specific heat in table 4.12 are presented graphically in Fig. 4.3.

Fig. 4·3



Specific Heat Graph of $Me_2NH_2ClO_4$

SECTION 5

Discussion

This section is concerned with the discussion of the results in Section 4 and with thermodynamic quantities derived from these results.

5a Lattice Energies

Lattice energies have been derived for the substituted alkyl amine salts of the general formula

$$R_nNH_{4-n}X$$

where $n = 1-4$,

R = Me and Et,

and X = Cl, Br, NO_3, and ClO_4.

These lattice energies have been calculated using the modified (Yatsimirskii, 1961) Kapustinskii equation (Section 1).

$$U^o_y = \frac{287.2\ v\ z^+\ z^-(r_c + r_a - 0.345)}{(r_c + r_a)^2} + 2.5\ v\ z^+\ z^- \quad \text{Kcal.mole}^{-1} \qquad \ldots.\ 5.1$$

where v is the number of ions per molecule, z^+ and z^- are the cationic and anionic charges, and r_c and r_a are the cationic and anionic radii. For a uni- univalent salt equation 5.1 simplifies to

$$U^o_y = \frac{574.4\,(r_c + r_a - 0.345)}{(r_c + r_a)^2} + 5.0 \quad \text{Kcal.mole}^{-1}$$

The assumptions involved in developing the above equations have been outlined in Section 1.

The above equations only require a knowledge of the thermochemical radii of the cation (r_c) and anion (r_a) in order to calculate the lattice energies. The thermochemical radii used for the halogen ions were the Goldschmidt radii and the thermochemical radii of the complex anions were obtained by Yatsimirskii in 1947 (cf. Section 1).

$$r_{NO_3^-} = 1.89\ \text{Å}$$

$$r_{ClO_4^-} = 2.36\ \text{Å}$$

Yatsimirskii's method can be modified to give the thermochemical radii of complex cations, by considering two salts with a common cation. Consider two methyl ammonium salts as an example

$$MeNH_3ClO_4\ (c) \longrightarrow MeNH_3^+\ (g) + ClO_4^-\ (g) \qquad \dots\ \Delta H_{L1}$$

$$MeNH_3NO_3\ (c) \longrightarrow MeNH_3^+\ (g) + NO_3^-\ (g) \qquad \dots;\ \Delta H_{L_2}$$

$$\Delta H_{L1} - \Delta H_{L2} = U_1^{\circ} - U_2^{\circ}$$

$$= \Delta H_f^{\circ}(ClO_4^-, g) - \Delta H_f^{\circ}(MeNH_3ClO_4, c) - \Delta H_f^{\circ}(NO_3^-, g)$$

$$+ \Delta H_f^{\circ}(MeNH_3NO_3, c) \qquad \ldots\ 1$$

Using the Kapustinskii equation

$$U_1^{\circ} - U_2^{\circ} = 574.4 \left[\frac{1}{(r^+ + r_1^-)} \left[1 - \frac{0.345}{(r^+ + r_1^-)} \right] - \frac{1}{(r^+ + r_2^-)} \left[1 - \frac{0.345}{(r^+ + r_2^-)} \right] \right] \qquad \ldots\ 2$$

where r^+ is the radius of the cation,

r_1^- is the radius of the perchlorate ion,

and r_2^- is the radius of the nitrate ion

Equations 1 and 2 can be equated and rearranged to give an equation for the cation radius r^+. Similar equations can also be written for combinations involving chlorides, bromides, nitrates, and perchlorates, and the general equation is as follows,

$$r^4 + (2f + 2d)r^3 + (f^2 + 4fd + d^2)r^2 + (2f^2d + 2d^2f)r + d^2f^2 = \frac{574.4}{\Delta H_{L1} - \Delta H_{L2}} \left[(2f + c - 2d - e)r^2 + (f^2 + 2cf - d^2 - 2ed)r + f^2c - ed^2 \right] \qquad \ldots\ 3$$

In this equation r = cation radius

$c = r_1^- - 0.345$

$$d = r_1^-$$

$$e = r_2^- - 0.345$$

$$f = r_2^-$$

The standard heats of formation of the gaseous halide anions and the crystalline alkyl ammonium chlorides and nitrates were taken from Wagman et al, 1968. The standard heats of formation of the gaseous nitrate and perchlorate ion were obtained in the following manner.

Consider sodium perchlorate

$$NaClO_4\ (c) \ = \ Na^+\ (g) + ClO_4^-\ (g) \qquad \ldots.\ H_L$$

$$\Delta H_f^\circ(ClO_4^-, g) \ = \ \Delta H_L + \Delta H_f^\circ\ (NaClO_4, c) - \Delta H_f^\circ(Na^+, g)$$

From the modified Kapustinskii equation

$$\Delta H_L - 2RT = U_y^\circ = \frac{574.4(r_{Na^+} + r_{Cl^-} - 0.345)}{(r_{Na^+} + r_{Cl^-})^2} + 5.0 \ \ \text{Kcal.mole}^{-1}$$

Thus the value of $\Delta H_f^\circ(ClO_4^-, g)$ can be evaluated. Similar calculations can also be performed for potassium, rubidium and caesium perchlorates. The standard heats of formation of the gaseous perchlorate ion obtained by the above procedure are recorded in table 5.1. The standard heats of formation of the crystalline perchlorates and gaseous metal ions were taken from Rossini et al, 1952.

Table 5.1

Standard Heats of Formation of the gaseous Perchlorate Ion

	$\Delta H_f^o(ClO_4^-,g)$ Kcal.g ion^{-1}
$NaClO_4$	-77.81
$KClO_4$	-79.38
$RbClO_4$	-79.85
$CsClO_4$	-77.43

The mean of the values in table 5.1 for the standard heat of formation of the gaseous perchlorate ion is -78.12 ± 1.18 Kcal.g ion^{-1}. (The uncertainty interval is quoted as twice the standard deviation from the mean; cf, Section 6).

The standard heat of formation of the gaseous nitrate ion was obtained in a similar manner

$$\Delta H_f^o(NO_3^-,g) = -75.79 \pm 0.52 \text{ Kcal.g ion}^{-1}$$

Substituting the value of $\Delta H_{L1} - \Delta H_{L2}$ into equation 3, this equation can then be arranged into the form

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

Solutions to this equation were obtained by feeding the coefficients

A to D into an ExCHLF computer programme for the solution of polynomial equations. (Muller Subroutine No. 881, Atlas Computing Service, University of London). The roots of the above equation usually had 1 positive and 3 negative values. The positive roots for the different combinations of salts used are listed in table 5.2. The values in parenthesis in table 5.2 were not used in calculating the mean value. The method used to calculate the uncertainty interval is outlined in Section 6. The asterisk in the NO_3^-/Br^- list indicates that one of the roots of the quartic equation was complex and the other two had negative real values. C indicates that three of the roots were complex (of the order $10^{-12} - 10^{-14}$) and the other was real and negative. The real portions of the complex roots were also negative. Odd numbers of partially complex roots may be due to a minor anomaly in the computer programme. Complex roots would be expected to occur in pairs since a complex root will have its complex conjugate.

The lattice energies were calculated for the alkyl ammonium perchlorates, nitrates, chlorides and bromides using equation 5.1 and the mean thermochemical radii in table 5.2. The lattice energy values are recorded in tables 5.3 to 5.6.

Table 5.2

Thermochemical Ionic Radii

Ion	ClO_4^-/ NO_3^-	ClO_4^-/ Cl^-	ClO_4^-/ Br^-	ClO_4^-/ I^-	NO_3^-/ Cl^-	NO_3^-/ Br^-	Cl^-/ Br^-	Cl^-/ I^-	Br^-/ I^-	Mean
NH_4^+	1.10	1.00	1.10	(0.29)C	0.79	1.38*	1.10	1.39	1.67	1.18±0.06
$MeNH_3^+$	1.21	1.34	-	-	1.09	-	-	-	-	1.21±0.12
$Me_2NH_2^+$	1.07	1.14	1.07	-	1.59	1.34*	1.81	-	-	1.34±0.22
Me_3NH^+	1.27	1.49	-	-	1.81	-	-	-	-	1.52±0.27
Me_4N^+	-	1.39	1.16	C	-	-	3.01	3.77	4.56	2.78±1.08
$EtNH_3^+$	1.34	1.03	-	-	C	-	-	-	-	1.19±0.16
$Et_2NH_2^+$	0.97	1.18	0.98	-	1.56	(0.61)*	1.34	-	-	1.21±0.18
Et_3NH^+	1.61	1.79	-	-	1.73	-	-	-	-	1.71±0.09
Et_4N^+	-	1.50	1.30	C	-	-	2.84	4.22	6.32	3.23±1.52

* 1 complex root

C 3 complex roots

Table 5.3

Lattice Energies of Alkyl Ammonium Perchlorate

	U_y^o Kcal.mole^{-1}		U_y^o Kcal.mole^{-1}
NH_4ClO_4	151.4 ± 2.3		
$MeNH_3ClO_4$	150.3 ± 4.5	$EtNH_3ClO_4$	151.1 ± 6.1
$Me_2NH_2ClO_4$	145.8 ± 7.9	$Et_2NH_2ClO_4$	150.3 ± 6.9
Me_3NHClO_4	139.9 ± 9.0	Et_3NHClO_4	134.2 ± 2.6
Me_4NClO_4	109.3 ± 25.2	Et_4NClO_4	101.4 ± 32.8

Table 5.4

Lattice Energies of Alkyl Ammonium Nitrates

	U_y^o Kcal.mole^{-1}		U_y^o Kcal.mole^{-1}
NH_4NO_3	171.1 ± 2.9		
$MeNH_3NO_3$	169.7 ± 5.7	$EtNH_3NO_3$	170.6 ± 7.9
$Me_2NH_2NO_3$	163.8 ± 10.2	$Et_2NH_2NO_3$	169.7 ± 8.8
Me_3NHNO_3	156.4 ± 11.4	Et_3NHNO_3	149.3 ± 3.3
Me_4NNO_3	118.9 ± 30.7	Et_4NNO_3	109.6 ± 39.7

Table 5.5

Lattice Energies of Alkyl Ammonium Chlorides

	U_y^{o} Kcal.mole^{-1}		U_y^{o} Kcal.mole^{-1}
NH_4Cl	174.9 ± 3.1		
$MeNH_3Cl$	173.4 ± 6.1	$EtNH_3Cl$	174.4 ± 8.3
Me_2NH_2Cl	167.4 ± 10.6	Et_2NH_2Cl	173.5 ± 9.2
Me_3NHCl	159.6 ± 11.9	Et_3NHCl	152.2 ± 3.4
Me_4NCl	120.7 ± 31.9	Et_4NCl	111.2 ± 41.0

Table 5.6

Lattice Energies of Alkyl Ammonium Bromides

	U_y^{o} Kcal.mole^{-1}		U_y^{o} Kcal.mole^{-1}
NH_4Br	167.8 ± 2.8		
$MeNH_3Br$	166.5 ± 5.5	$EtNH_3Br$	167.4 ± 7.5
Me_2NH_2Br	160.9 ± 9.7	Et_2NH_2Br	166.5 ± 8.4
Me_3NHBr	153.7 ± 11.0	Et_3NHBr	146.8 ± 3.2
Me_4NBr	117.4 ± 29.7	Et_4NBr	108.3 ± 38.5

The uncertainty intervals quoted in the tables 5.3 to 5.6 are derived from the uncertainty interval quoted for the thermochemical cation radii, assuming a zero error in the anion radius. The accuracy of this method of calculation can be estimated by comparing the present values of lattice energies to lattice energies obtained by extended Born-Mayer calculations (Waddington, 1959). Bleick in 1934 used the Born-Mayer method to calculate the lattice energies of ammonium chloride, bromide and iodide. Similar calculations have recently been carried out by Ladd, 1970, for ammonium chloride and bromide and these values are compared in table 5.7.

Table 5.7

Lattice Energies of Ammonium Halides

	Lattice Energy Kcal.mole^{-1}		
	Present Work	Bleick	Ladd
NH_4Cl	174.9 ± 3.1	161.6	157.3 ± 0.5
NH_4Br	167.8 ± 2.8	154.0	151.2 ± 0.5
NH_4I	159.2 ± 2.5	145.5	-

Bleick's values of lattice energy were calculated at 0°K, and the correction to 298°K is given by

$$U_{298} - U_0 = \frac{3}{2} R.T.(n+1) - \int_0^{298} C_p(NH_4X)\, dT$$

The correction factor is approximately 6 ± 1 Kcal.mole^{-1}

Comparison of the lattice energies obtained in the present work, with values obtained by extended calculations, indicate that the value of the thermochemical radius of the ammonium cation in table 5.2 is too low. If Ladd's values of the lattice energies of ammonium chloride and bromide are used as the solution of the modified Kapustinskii equation, then the value of the thermochemical radius for the ammonium cation would be of the order of 1.58 - 1.59 Å. Steadman, 1967 and Halliwell and Nyberg, 1963, have reported lattice energies for tetramethyl and tetraethyl ammonium halides. These values are compared with present values in table 5.8.

Table 5.8

Lattice Energies of Tetraalkyl Ammonium Halides

	Present work	Steadman	Halliwell
Me_4NCl	120.7 ± 31.9	140.2	118.8
Me_4NBr	117.4 ± 29.7	138.4	115.7
Me_4NI	113.2 ± 27.3	132.9	111.2
Et_4NCl	111.2 ± 41.0	129.3	-
Et_4NBr	108.3 ± 38.5	127.2	-
Et_4NI	104.7 ± 30.5	122.7	-

Steadman's lattice energies were obtained from a knowledge of experimental heats of solution and the solvation energies of the constituent ions (calculated). Ionic radii were obtained from a semi-empirical equation derived by Conway et al, 1965, and from these radii, estimates of the solvation energies were. derived. Finally, substitution into the equation

$$\Delta H_s^{o} = \Delta H_L + \Phi$$

where ΔH_s^{o} = heat of solution

ΔH_L = lattice enthalpy

Φ = combined ion hydration enthalpy

gives an estimate of the lattice energy.

Halliwell and Nyberg, 1963, calculated their values from the Kapustinskii equation using a value of the cationic radius of the tetramethyl ammonium ion of 3.0 Å (Yatsimirskii, 1956).

The values obtained for the lattice energies of tetra-alkyl ammonium halides using thermochemical radii are in quite good agreement, however, the margin of error could equally well include Steadman's values. In view of the large uncertainty intervals, the lattice energies must be considered to be only approximate.

In formulating the equation for lattice energies, Kapustinskii assumed that it was possible to replace the interatomic distance(r_a) by the sum of the cationic and anionic radii ($r_c + r_a$) (Section 1). This substitution assumes that the unlike ions are 'touching', which is incorrect for compounds possessing large ions. The lattice spacing in sodium iodide, for example, is governed by $I^- - I^-$ contacts. The lattice spacing in the perchlorate compounds with small cations is also likely to be governed by perchlorate-perchlorate contacts. Thus the Kapustinskii equation will probably not yield reliable results for these compounds. The lattice energies calculated for compounds with non-spherically-symmetric cations are also likely to be inaccurate, since Yatsimirskii's method of obtaining thermochemical radii assumes that the cation is spherical. This problem also occurs in extended calculation methods, but only in the repulsive term, U_R, which is an order of magnitude less than the Madelung term, U_M. In the Kapustinskii equation the difficulty occurs in both the U_M and the U_R terms. In spite of these deficiencies in the Kapustinskii equation, it is the only method of obtaining lattice energy estimates where insufficient data are available for extended calculations.

5b Proton Affinities

Waddington in 1959 determined the proton affinity of ammonia and suggested that the method could be extended to measure the proton affinities of the alkyl substituted amines. Using the standard heats of formation measured in this work, such calculations are possible. The derivation of proton affinities is outlined in Section 1.

$$NH_4^+ \ (g) \ = \ NH_3^+ \ (g) + H^+ \ (g) \qquad \ldots\ldots \ P_{NH_3}$$

$$\therefore \qquad P_{NH_3} = - \Delta H_L + \Delta H_f^\circ \ (H^+, g) + \Delta H_f^\circ (NH_3, g) + \Delta H_f^\circ \ (x^-, g) - \Delta H_f^\circ \ (NH_4X, c)$$

Similar equations can also be written for the proton affinities of the other amines. Values of the proton affinities calculated from the above equation are listed in table 5.9. The standard heats of formation of the amine gases were taken from Cox and Pilcher, 1970 and the standard heat of formation of the gaseous proton from Wagman et al, 1968.

Table 5.9

Proton Affinities of Substituted Amines (Kcal. mole^{-1})

	From Perchlorate	From Nitrate	From Chloride	From Bromide	Mean
NH_3	193.9	194.7	197.3	196.0	195.5±3.4
$MeNH_2$	197.7	198.9	200.4	-	199.0±5.6
Me_2NH	202.1	204.9	205.4	205.8	204.6±9.8
Me_3N	206.0	209.5	210.1	-	208.5±11.0
$EtNH_2$	195.3	195.2	201.6	-	197.4±8.1
Et_2NH	198.8	202.7	203.0	202.5	201.8±8.6
Et_3N	214.2	225.0	226.0	-	221.7±67

The lattice energies in table 5.7 can be used to calculate the proton affinities of ammonia, and these values are compared with other data in table 5.10. The values obtained from Bleick's and Ladd's lattice energies are the mean values from calculations involving the individual ammonium halides.

Table 5.10

Proton Affinities of Ammonia

Reference	P_{NH_3} Kcal.mole^{-1}
Bleick, 1934	210.3
Price et al, 1963	206.2
Ladd, 1970	213.3
Present work	195.5

The values of the proton affinities of ammonia derived from extended lattice energy calculations should be considered as the most accurate. The value obtained by Price et al, 1963, was obtained from work on bond dissociation energies. The low value obtained in the present work reflects the deviation in the lattice energy values of ammonium halides obtained by the Kapustinskii equation, compared to those obtained by more rigorous calculations.

The ionisation reaction, from which proton affinities are obtained

$$NH_4^+(g) = NH_3(g) + H^+(g) \qquad \ldots\ldots P_{NH_3}$$

has an analogous reaction in solution

$$NH_4^+(aq) = NH_3(aq) + H^+(aq) \qquad \ldots\ldots \Delta H_{ion}$$

Similar reactions can also be written for the other alkyl substituted ammonium ions. A graph of proton affinity vs. ΔH_{ion} is shown in Fig. 5.1. The interesting feature about this graph is the nearly linear relationship between mono-, di- and trialkyl amines. This line may possibly become exactly linear if more accurate data for calculating proton affinities become available. The equations mentioned previously can be combined in the following manner

$$R_3NH^+ \text{ aq} = R_3N \text{ aq} + H^+ \text{ aq} \qquad \ldots\ldots \Delta H_{ion}$$

$$R_3NH^+ (g) = R_3N(g) + H^+(g) \qquad \ldots\ldots P$$

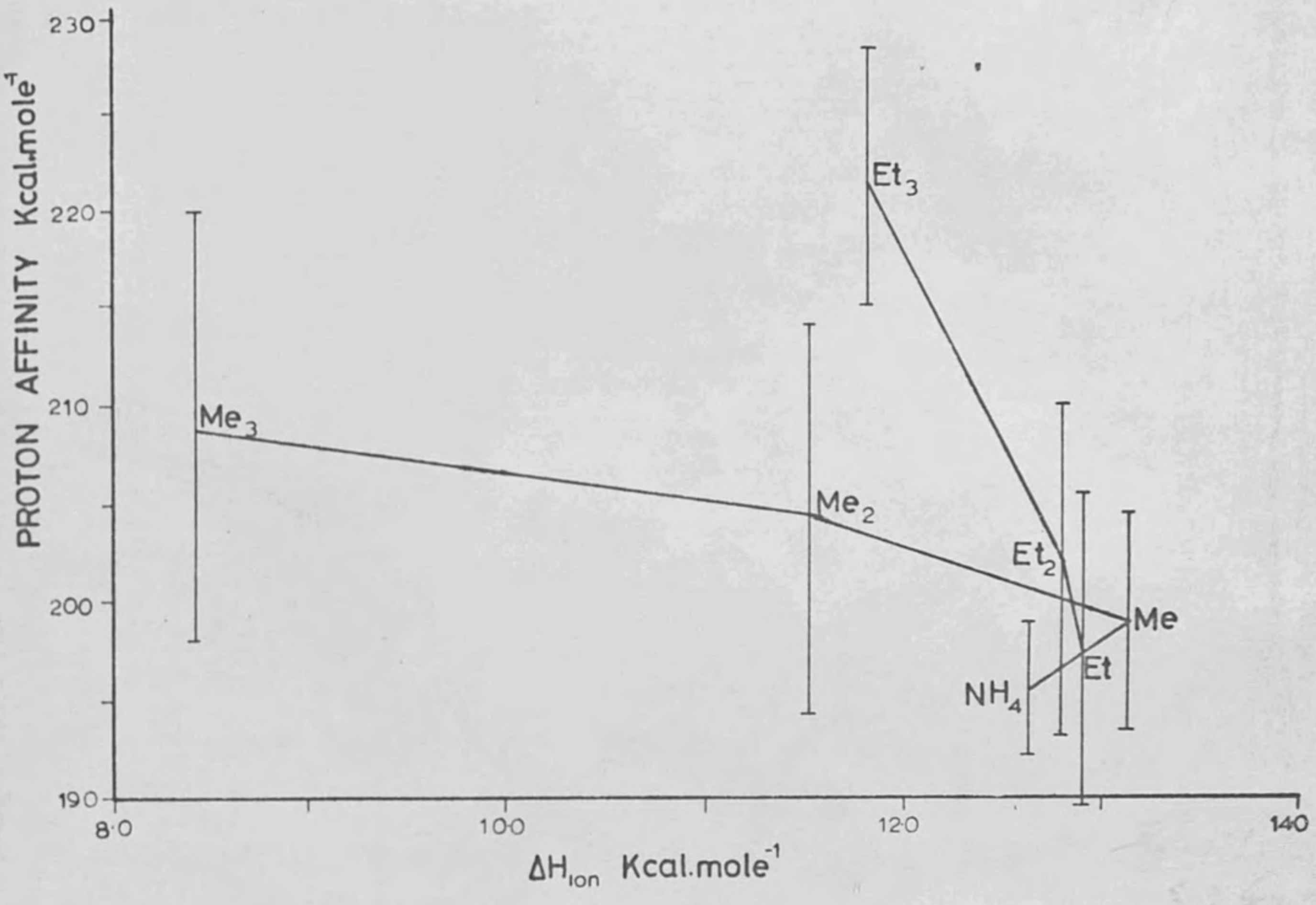
$$\begin{aligned}\Delta(\Delta H) = \Delta H_{ion} - P = {} & \Delta H_f^o(R_3N,aq) - \Delta H_f^o(R_3N,g) \\ & + \Delta H_f^o(H^+,aq) - \Delta H_f^o(H^+,g) \\ & - \Delta H_f^o(R_3NH^+,aq) + \Delta H_f^o(R_3NH^+,g)\end{aligned}$$

Now $\quad R_3N(g) + \text{xs } H_2O = R_3N \text{ aq} \qquad \ldots\ldots \Delta H_s$

$$\Delta H_s = \Delta H_f^o(R_3N,aq) - \Delta H_f^o(R_3N,g)$$

i.e. the heat of solution of the gaseous amine to an aqueous infinitely dilute solution

Fig. 5·1



Graph of Proton Affinity

vs. ΔH(ionisation)

for

Alkyl Ammonium Ions

and $$H^+\,(g) + xs\,H_2O = H^+\,aq \qquad \ldots W_{H^+}$$

$$W_{H^+} = \Delta H_f^o(H^+,aq) - \Delta H_f^o(H^+,g)$$

i.e. the absolute enthalpy of hydration of the proton.

$$Y = \Delta(\Delta H) - \Delta H_s = W_{H^+} - \Delta H_f^o(R_3NH^+,aq) + \Delta H_f^o(R_3NH^+,g)$$

The latter two terms on the right hand side of the equation correspond to the enthalpy of solvation of the substituted ammonium ion. The enthalpy of solvation is given by the Born-Bjerrum equation (Bjerrum and Larsson, 1927)

$$\Delta H_{solv} = \frac{N\,z^2\,e^2}{2r}\left[1 - \frac{1}{D} - \frac{T}{D^2}\left(\frac{dD}{dT}\right)_p\right]$$

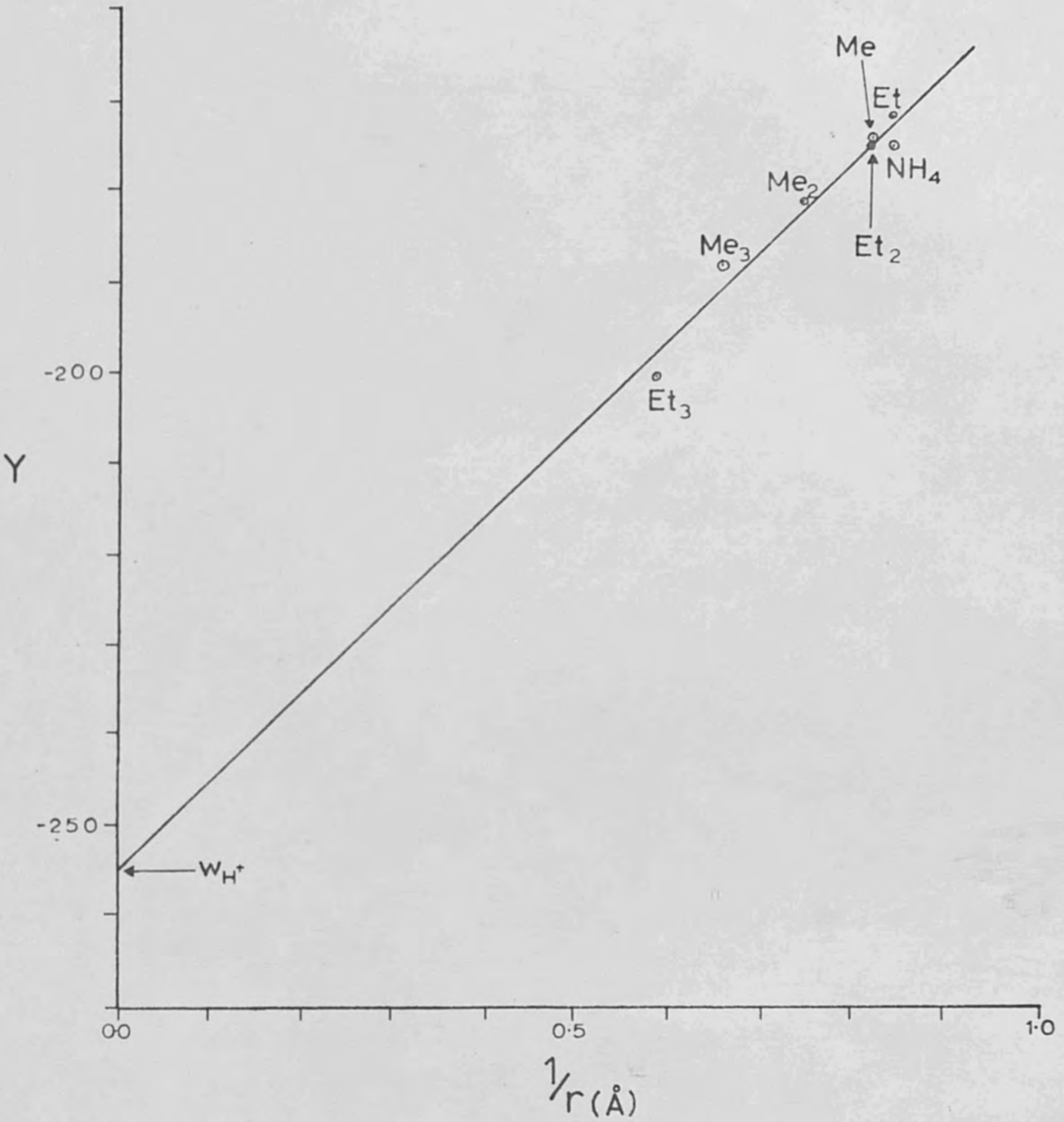
Therefore an inverse dependence of Y upon r might be expected.

Fig. 5.2 is a graph of Y vs. reciprocal (thermochemical) cation radius for the different substituted ammonium cations. A least-mean-square computer programme was used to obtain the 'best' straight line through the points. The equation obtained was

$$Y = -254.08 + \frac{96.74}{r}$$

The absolute enthalpy of hydration of the proton is the constant term in the above equation, so

Fig. 5·2



Y vs. Reciprocal Cationic Radius

for Alkyl Substituted Amines

$$W_{H^+} = -254.1 \pm 3.5 \text{ Kcal.mole}^{-1}$$

In view of the uncertainty in the ionic radii and the calculated proton affinities, this value is considered to be in good agreement with absolute enthalpies of hydration quoted by Halliwell and Nyberg, 1963, (-260.7 ± 2.5 Kcal.mole^{-1}) and Morris, 1968 (-263.7 ± 3.0 Kcal.mole^{-1}). When $Y = 0$

$$W_{H^+} = -\frac{96.74}{r}$$

Therefore $r = 0.38$ Å

This value of r is the hydrated radius of the proton.

5c. Standard Heats of Formation

Karapet'yants, 1954, constructed graphs of the lattice enthalpies of complete series of salts (e.g. alkali metal chlorides) against incomplete series. Unknown values can then be obtained by extrapolation or interpolation. Finch and Gardner, 1965, have used this method to estimate the lattice enthalpies of rubidium and caesium iodates.

A similar type of Karapet'yants graph is shown in Fig 5.3 in which standard heats of formation of allyl ammonium nitrates and chlorides are plotted against the standard heats of formation of alkyl ammonium perchlorates. The NO_3^-/ClO_4^- and Cl^-/ClO_4^- points can be fitted to two straight lines which have the same slope. Lines with exactly the same slope are now drawn through the available data for alkyl ammonium bromides and iodides. The unknown standard heats of formation can then be read directly from the graph and these values are recorded in table 5.11.

The standard heats of formation of propyl ammonium perchlorate and tripropyl ammonium perchlorate are reported in Section 4a, and substituting these values into Fig. 5.3 allows an estimation of the standard heats of formation of the other propyl and tripropyl ammonium salts to be made.

The standard heats of formation of the tetramethyl and tetraethyl ammonium salts do not fit onto the straight line, and so they have been omitted from the graph for clarity. This casts doubt upon the values reported for the standard heats of formation of the tetramethyl and tetraethyl ammonium perchlorates.

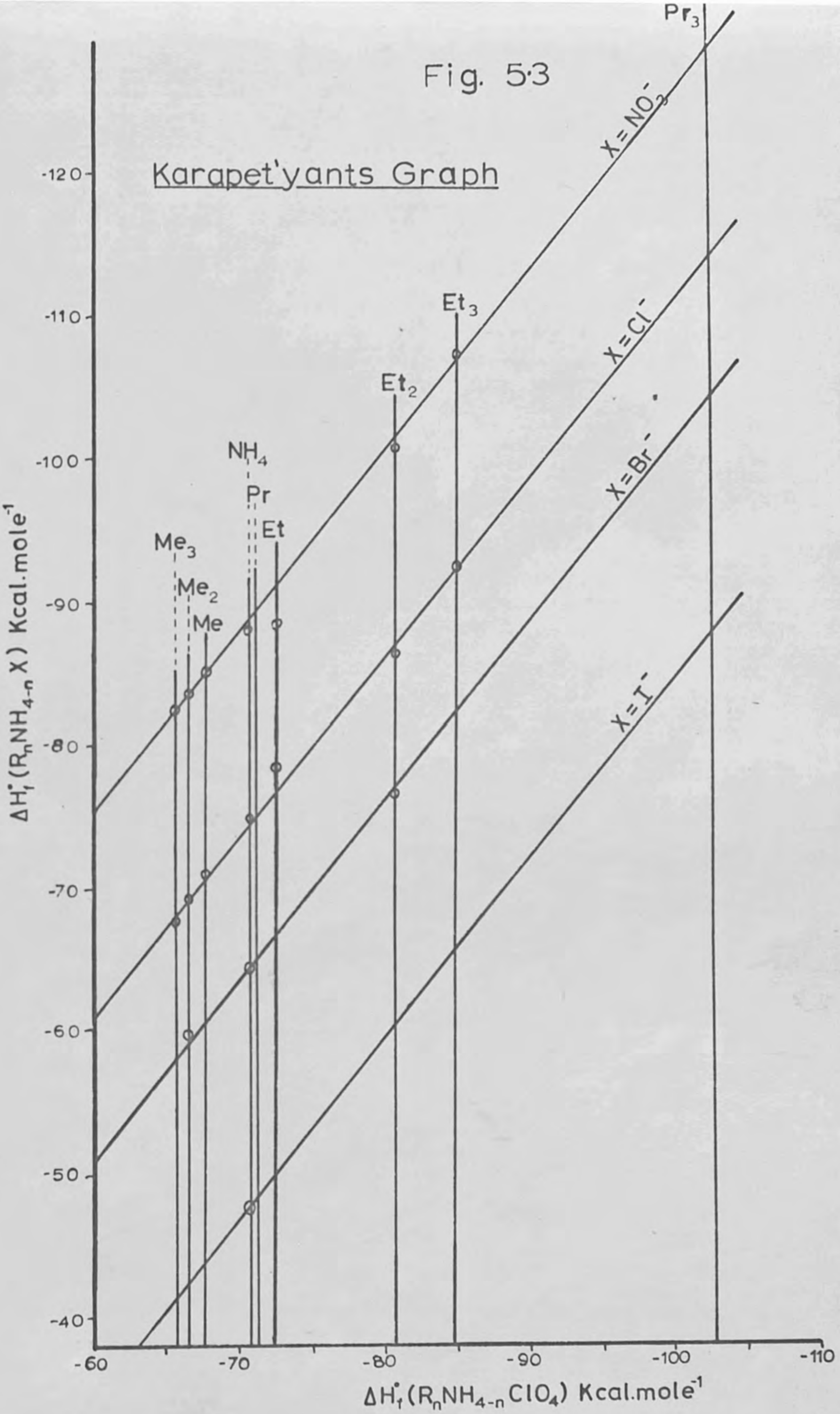


Fig. 5·3

Karapet'yants Graph

Table 5.11

Estimated Standard Heats of Formation from Karapet'yants Graph

Compound	ΔH_f° Kcal.mole^{-1}
$MeNH_3Br$	-61.1
Me_3NHBr	-58.6
$EtNH_3Br$	-66.8
Et_3NHBr	-82.1
$MeNH_3I$	-44.3
Me_2NH_2I	-43.1
Me_3NHI	-41.9
$EtNH_3I$	-50.7
Et_2NH_2I	-60.6
Et_3NHI	-65.4
$PrNH_3NO_3$	-89.2
$PrNH_3Cl$	-74.9
$PrNH_3Br$	-65.3
$PrNH_3I$	-48.8
Pr_3NHNO_3	-129.1
Pr_3NHCl	-113.5
Pr_3NHBr	-103.9
Pr_3NHI	-86.9

The error in these data is approximately ±5 Kcal.mole^{-1}

A further method of determining the standard heats of formation of these, and other tetra-alkyl ammonium salts, would be via combustion of the tetra-alkyl ammonium nitrate in a bomb calorimeter. This would yield the standard heat of formation of the tetra-alkyl ammonium nitrate. Heat of solution determinations of the tetra-alkyl ammonium nitrate would check the standard heat of formation of the aqueous tetra-alkyl ammonium ion, and thus the standard heats of formation of the other tetra-alkyl ammonium salts.

It was originally hoped to be able to measure the standard heats of formation of more of the tri-p-substituted aryl perchlorates. Synthetic problems and the lack of suitable calorimetric reactions made this impossible. However, it is possible to estimate the standard heats of formation of these compounds from a knowledge of the standard heat of formation of triphenylmethyl perchlorate ($C_{19}H_{15}ClO_4$) using method 2 of Appendix II, e.g. for tri(p-nitrophenyl)methyl perchlorate ($C_{19}H_{12}N_3ClO_{10}$)

$$\Delta H_f^o(C_{19}H_{12}N_3ClO_{10}) = \Delta H_f^o(C_{19}H_{15}ClO_4) + 3(\Delta H_f^o(C_6H_5NO_2) - \Delta H_f^o(C_6H_6))$$

This method assumes that

a) there is no alteration in the crystal forces between tri(p-nitrophenyl)methyl perchlorate and triphenylmethyl perchlorate;

b) the difference term compensates for the different resonance bonding between the two triarylmethyl cations.

Standard heats of formation estimated in this manner are listed in table 5.12.

Table 5.12

Estimated Standard Heats of Formation of Triaryl Perchlorates

	ΔH_f^o Kcal.mole^{-1}
Tri(p-tolyl)methyl perchlorate	20.0 (10.6±1.2)[a]
Tri(p-methoxyphenyl)methyl perchlorate	-74.1 (-90.2±5.5)[a]
Tri(p-nitrophenyl)methyl perchlorate	73.6
Tri(p-chlorophenyl)methyl perchlorate	19.0
Tri(p-bromophenyl)methyl perchlorate	54.8
Tri(p-iodophenyl)methyl perchlorate	94.4

(a) Values reported in Section 4.

In view of the fact that all the values in table 5.12 are estimates, no further discussion of these results is presented.

Future work in this field might involve a measurement of the standard heats of formation of tri(p-tolyl)methanol, tri(p-methoxyphenyl)-methanol and tri(p-nitrophenyl)methanol by bomb calorimetry. Two possible routes are also proposed by which tri(p-nitrophenyl)-methyl perchlorate might be synthesised.

a) $(p\text{-}NO_2Ph)_3C\ Br + AgClO_4 \xrightarrow{CH_2Cl_2} (p\text{-}NO_2Ph)_3CClO_4 + AgBr$

The greater polarisability of the C-Br linkage compared with the C-Cl linkage might facilitate the preparation of tri(p-nitrophenyl)-methyl perchlorate. The preparation of tri(p-nitrophenyl)-methyl bromide was described by Boyle and Ziegler, 1927 and Lewis et al, 1944.

b) The reaction between chlorine perchlorate and metal chlorides yields metal perchlorates and gaseous chlorine (Schack and Pilipovich, 1970). The reaction between chlorine perchlorate and tri(p-nitrophenyl)methyl chloride might yield tri(p-nitrophenyl)methyl perchlorate.

$$(p\text{-}NO_2Ph)_3CCl + Cl\text{-}OClO_3 \longrightarrow (p\text{-}NO_2Ph)_3CClO_4 + Cl_2$$

5d Heats of Transition and Specific Heat Values

Stammler et al reported in 1966 the polymorphic phase transitions of methyl substituted ammonium perchlorates obtained from Differential Thermal Analysis (D.T.A.). The transitions found in this work and reported in table 4.10 confirm Stammler's results. The effect of ethyl and propyl groups on the crystal phases has also been examined in the present work. Stammler complemented his D.T.A. results with X-ray powder patterns of the different polymorphic forms and in this respect the present work must be viewed as incomplete. A visual study of the sample during a phase transition allows a differentiation between fusion and change in crystal habit.

Ammonium Perchlorate

Ammonium perchlorate exists in three crystal modifications

$$NH_4ClO_4\ \text{(III)} \xrightleftharpoons{-190^\circ C} NH_4ClO_4\ \text{(II)} \xrightleftharpoons{c.240^\circ C} NH_4ClO_4\ \text{(I}$$

The number in parentheses is used to differentiate the different crystal modifications (Phase III is the lowest temperature form).

Phase III was first reported by Stammler et al in 1962. However, the nature of this phase is unknown and it does not appear to have been investigated since that time.

The room temperature modification, phase II, has a $BaSO_4$ structure (orthorhombic) which is stable up to approximately 240°C. (Bussem and Herrmann, 1928; Smith and Levy, 1962). Venkatesan, 1957, found the chlorine atom to be tetrahedrally surrounded by four oxygen atoms at a mean distance of 1.46 Å. The four hydrogen atoms were found to encompass each nitrogen atom, and the ammonium ion was surrounded by twelve oxygen atoms. The distance between the ammonium ion and eight of these oxygen atoms was reported to be 2.94 - 3.08 Å; the remaining four are separated from the ammonium ion by 3.25 - 3.52 Å. The change II - I has been ascribed to the onset of free rotation of the perchlorate anion (Vorlaender and Kaascht, 1923; Finbak and Hassel, 1936).

X-ray determinations at 270°C show that phase I crystals possess a structure resembling a sodium chloride lattice (Brakken and Harang, 1930; Herrmann and Ilge, 1930). The II - I phase transition has a marked effect on the rate maximum in the thermal decomposition (Bircumshaw and Newman, 1954). The maximum gradually rises with temperature, reaching a peak at ca. 240°C, then falling to a minimum at 250°C and finally rising again with temperature. This phenomenum has been attributed to crystal volume modifications (Bircumshaw and Newman, 1954) and alteration of the crystal imperfections (Galwey and Jacobs, 1960). This rate of decomposition is, however, sufficiently slow for the phase change to be sensibly examined.

The enthalpy of the II-I transition has been calculated from D.T.A. and specific heat data, and these values are compared with the present D.S.C. results in table 5.13.

Table 5.13

Transition Enthalpy from Phase II to Phase I for Ammonium Perchlorate

Reference	Method	ΔH_t Kcal.mole^{-1}
Markowitz and Boryta, 1962	D.T.A.	2.3 ± 0.2
Evans et al, 1964	Calorimetry	2.7
Present work	D.S.C.*	2.24 ± 0.32

* air-tight sample pan

During the phase change two other processes are occurring simultaneously:

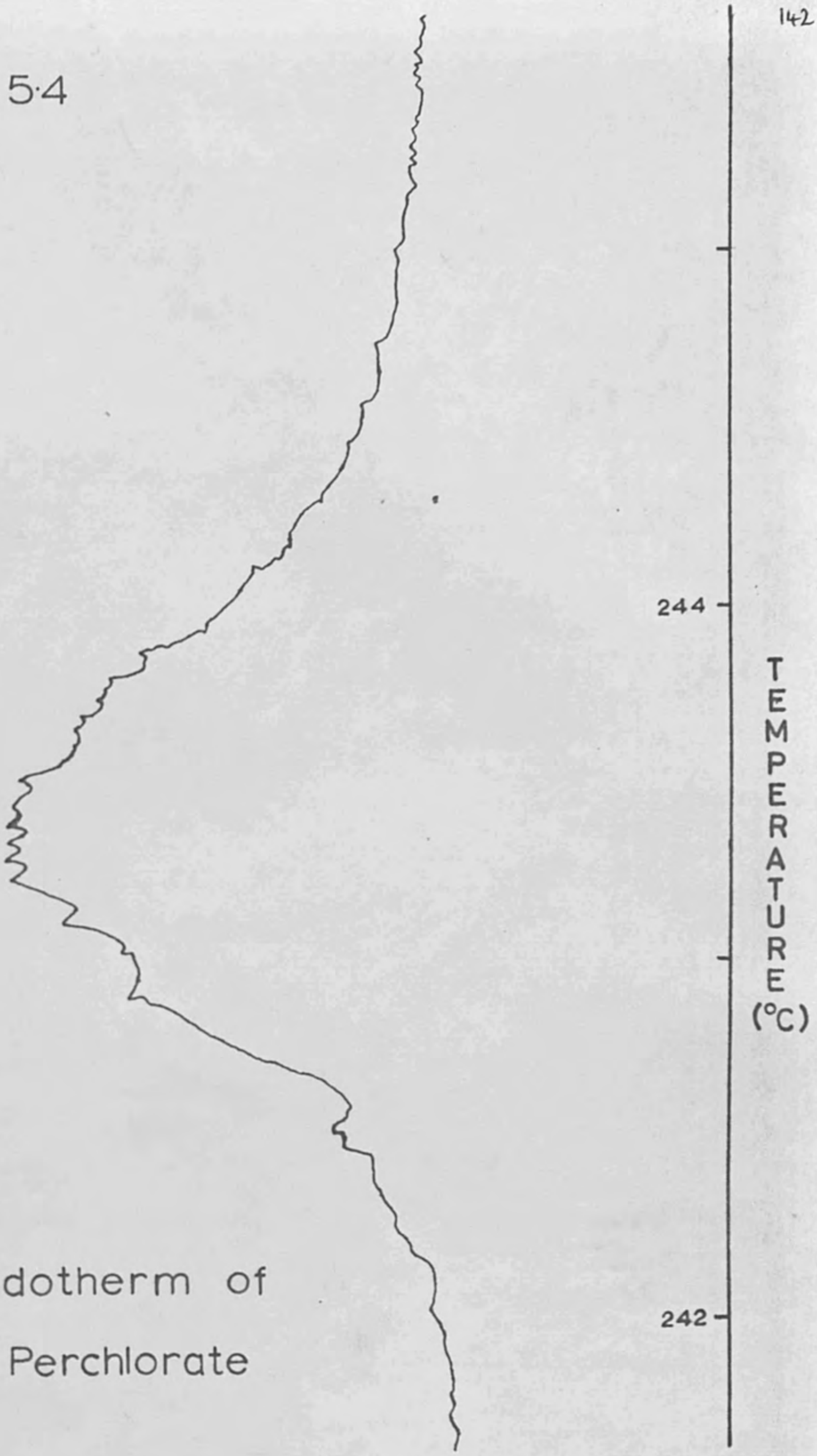
a) endothermic dissociative sublimation;

b) exothermic dissociative decomposition.

These processes give rise to an uneven or 'noise' trace for the II-I transition of ammonium perchlorate (Fig. 5.4) compared with normal peaks (Fig. 4.1).

Markowitz and Boryta, 1962, suppressed the sublimation and decomposition processes by heating the sample under an atmosphere

Fig. 5·4



Transition Endotherm of Ammonium Perchlorate of ammonia. No such precautions were taken by Evans et al, 1964. In the present work the sublimation was suppressed by sealing the sample into an air-tight sample pan and sample decomposition was kept to a minimum by programming the D.S.C. from only 4°C below the transition temperature. In view of these difficulties, the enthalpy values for the II-I phase change reported by Markowitz and that reported in the present work are in good agreement.

The temperature of the II-I phase transition, 242° ± 1°C is also in good agreement with the literature value of 240° ± 1°C (Gordon and Campbell, 1955).

Methyl Ammonium Perchlorate

Stammler et al, 1966, report that methyl ammonium perchlorate exists in the following phases

$$\mathrm{MeNH_3ClO_4\ (III)} \xrightleftharpoons{48^\circ C} \mathrm{MeNH_3ClO_4\ (II)} \xrightleftharpoons{178^\circ} \mathrm{MeNH_3ClO_4\ (I)}$$

X-ray patterns of phase I at 200°C indicate cubic symmetry and for phase II at 77°C, tetragonal symmetry. Phase III is stable below 48°C and has monoclinic or triclinic symmetry. The existence of three polymorphs is confirmed in the present work and no further transitions were detected between -90°C and ambient temperature. Methyl ammonium perchlorate begins to decompose above its melting point (255°C). The enthalpies for the phase transitions are

$$MeNH_3ClO_4\ (III) \longrightarrow MeNH_3ClO_4\ (II) \quad .... \Delta H_t = 1.69 \pm 0.01\ Kcal.mole^{-1}$$

$$MeNH_3ClO_4(II) \longrightarrow MeNH_3ClO_4\ (I) \quad .... \Delta H_t = 1.97 \pm 0.02\ Kcal.mole^{-1}$$

A discrepancy exists between the III-II transition temperature reported in this work (37°C) and that found by Stammler (48°C). Differences between the two investigations include:

a) the heating rate. Stammler's D.T.A. heating rate was 20-30°C/min. compared to 1°C/min. used in the D.S.C. measurements. With heating rates of the order of 30°C/min., the temperature of the sample will be lower than the programmed temperature, and hence transitions will occur at slightly higher temperatures. This, however, should not account for a difference of 11°C;

b) recrystallising solvent. Stammler's samples were 'twice recrystallised from isopropanol and dried over anhydrous calcium sulphate in a vacuum desiccator'. The sample used in this work was twice recrystallised from ethanol and dried at 70°C and 0.2 mm Hg over P_2O_5. Analytical data on the dried sample indicated a purity of 98.6%. Duke, 1971, reports that occluded solvent is likely to stabilise a crystal modification and thus cause a higher transition temperature. Drying the sample above the III-II transition temperature would be more likely to dislodge any occluded solvent. In view of this, we are confident of the lower transition temperature. Stammler reports that methyl ammonium perchlorate melts at 255°C and in this region decomposition begins.

Dimethyl Ammonium Perchlorate

The D.T.A. thermogram obtained by Stammler et al, 1966, has two reversible endothermic phase transitions and is shown in Fig. 5.5. The endotherm occuring at 180°C is due to melting of the sample and is confirmed in the present work. The enthalpy of fusion

$$\Delta H(c \rightarrow l) = 0.57 \pm 0.05 \text{ Kcal.mole}^{-1}$$

and the entropy of fusion is given by

$$\Delta S = \frac{\Delta H(c \rightarrow l)}{T^{o}K}$$

$$= 1.32 \text{ cal.mole}^{-1} \text{ deg}^{-1}$$

No further transitions were found in the range -90° to 20°C and using a heating rate of $8^{o}C \text{ min}^{-1}$, the single endotherm at 40°C was reproduced. However, using a heating rate of $1^{o}C \text{ min}^{-1}$ this peak was resolved into two. The existence of a third crystal

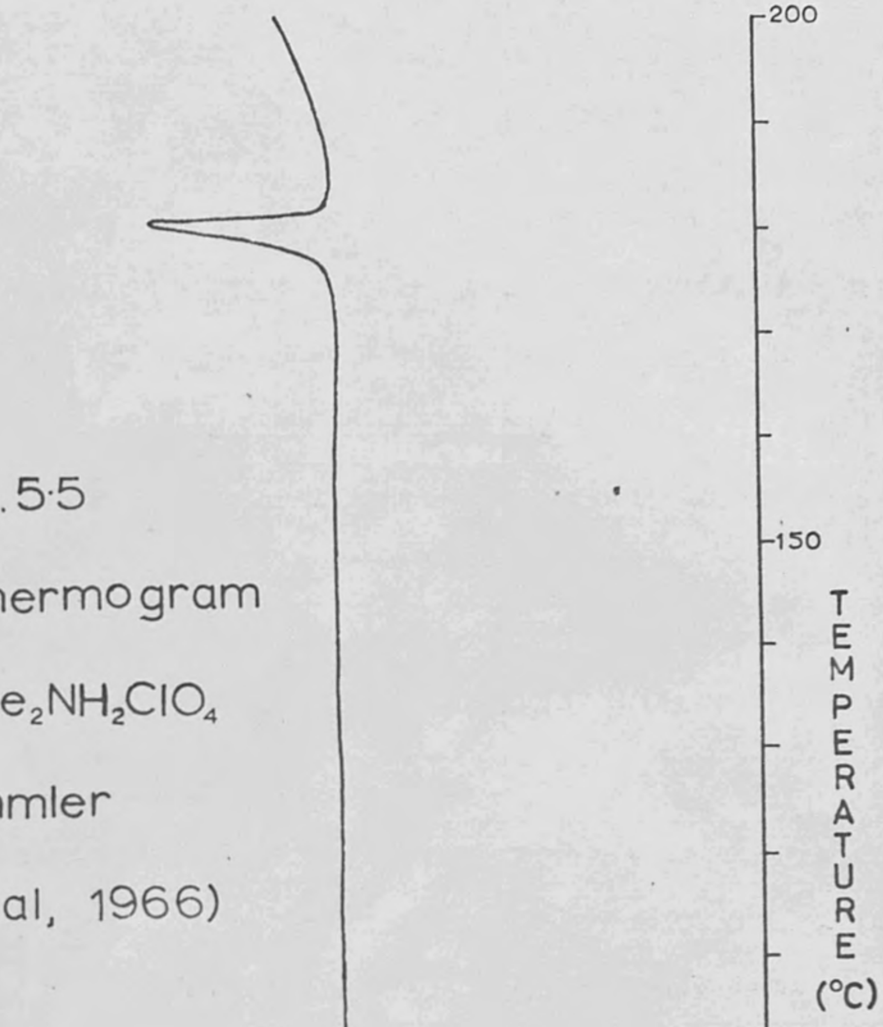


Fig. 5·5

D.T.A. Thermogram of $Me_2NH_2ClO_4$ (Stammler et al, 1966) form has been confirmed by Duke, 1971, and although the transition temperature has not been determined accurately, Duke suggests a value of about 25°C. Batty, 1971, has examined dimethylammonium perchlorate with a polarising microscope and has detected a phase change in the range 25° - 30°C. The specific heat experiments on dimethyl ammonium perchlorate (Fig. 4.3) indicate that there is a transition at 30° ± 1°C. The absence of a second phase transition in Stammler's work may be due to either

a) the D.T.A. thermogram was initiated above the transition temperature or

b) the heating rate of 20° - 30°C min^{-1} was too rapid and the peak at 40°C was not resolved.

A sample of dimethyl ammonium perchlorate was thermally cycled between 22°C and 43°C and the thermograms produced are shown in Fig. 5.6. During the cooling periods, supercooling takes place as evidenced by the displacement of the peaks towards lower temperatures. The areas of the peaks in Fig. 5.6 are recorded in table 5.14, the figures in parentheses indicate the transition temperatures.

Fig. 5·6

Thermograms showing thermal cycles of $Me_2NH_2ClO_4$ between 22°C and 43°C

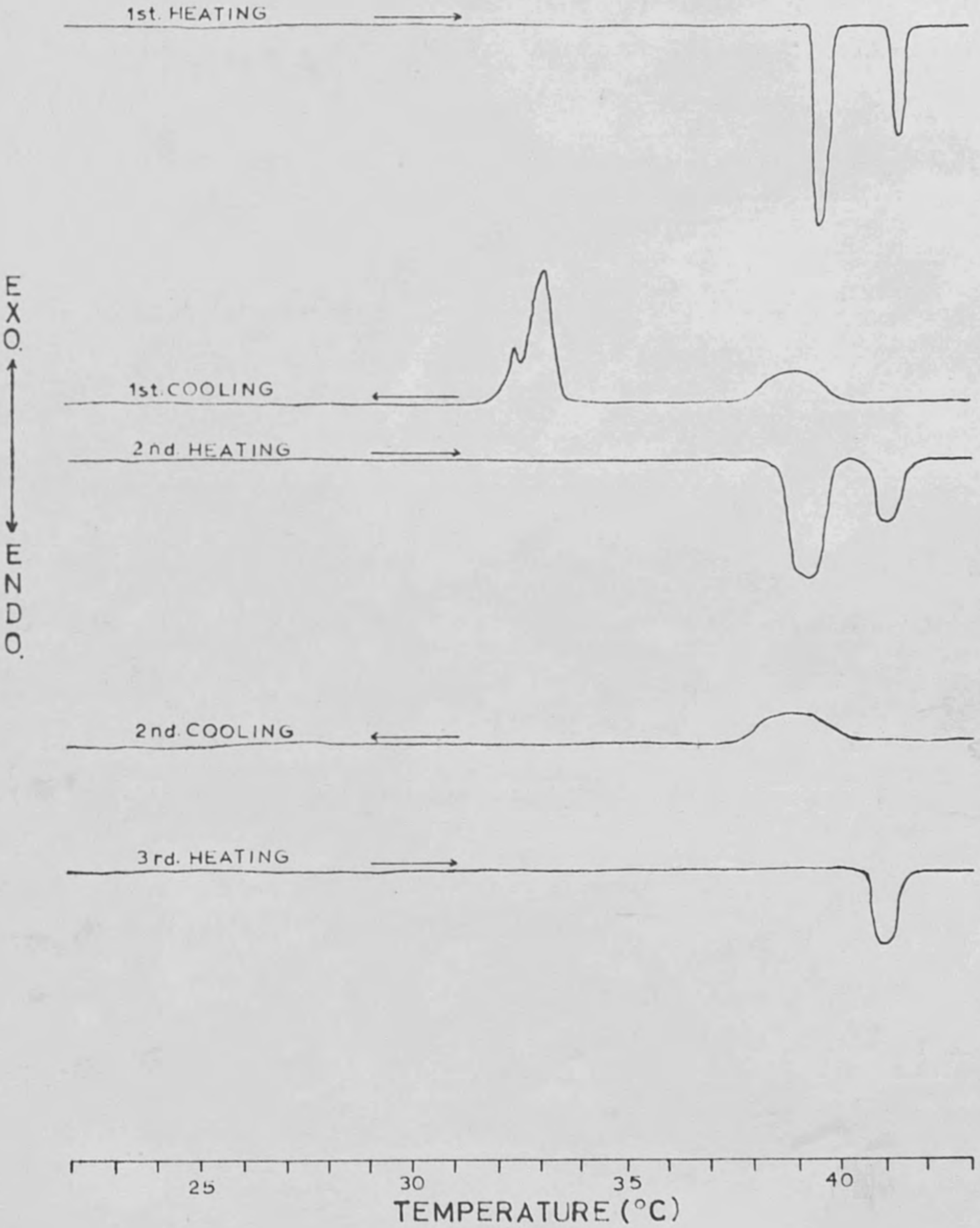


Table 5.14

Peak areas (cm^2) obtained during thermal cycles of $Me_2NH_2ClO_4$

1st Heating	12.5 (39)	4.5 (41)
1st Cooling	10.3 (33)	4.4 (39)
2nd Heating	10.3 (39)	4.4 (41)
2nd Cooling	-	4.3 (39)
3rd Heating	-	4.1 (41)

During the second cooling period, the transition characterised by the peak of larger area did not occur on cooling to 22°C. There are two possible explanations.

1. The sample of dimethyl ammonium perchlorate was recrystallised from isopropanol and dried in a manner similar to that described for methyl ammonium perchlorate by Stammler et al, 1966. Thus, there is the possibility that the dimethyl ammonium perchlorate lattice contained occluded isopropanol, causing the transition to occur at a higher temperature. Heating the sample through the phase transition would cause some of the trapped solvent to be expelled, with the result that the reverse transition would occur at a lower temperature than for the portion of the sample which still contained some solvent. There is a reduction of 20% in the area of the lower temperature endotherm on cooling, compared with heating, during the

first thermal cycle. The remainder of the occluded solvent could be dislodged during the second heating period resulting in the absence of the corresponding endotherm during the second cooling period. If supercooling of this transition occurred during the second cooling period, then the transition possibly occurred below 22°C and thus remains undetected.

2. Another possible explanation can be formulated in terms of a new phase (labelled III) which can exist in metastable equilibrium with phase II. The transitions could then be represented as follows:

$$Me_2NH_2ClO_4\ (III) \xrightleftharpoons{39^\circ C} Me_2NH_2ClO_4\ (II) \xrightleftharpoons{41^\circ C} Me_2NH_2ClO_4\ (I)$$

The temperatures are those obtained from the D.S.C. traces.

The X-ray diffraction patterns for dimethyl ammonium perchlorate were first reported by Stammler et al in 1966. The lower temperature X-ray pattern (presumably II) was recorded at 25°C and is described as 'a fairly complex lattice of monoclinic or lower symmetry'. Duke, 1970, confirms Stammler's basic X-ray pattern for phase II; however, the discovery of extra lines in the X-ray spectrum favours a cubic rather than a monoclinic lattice. The experimental temperature for this latter determination was thought to be in the range 24° - 28°C. Duke reports that the phase II lattice has a unit cell of side 32 Å which contains 192 molecules. He also reports that the X-ray pattern of phase II remains the same between 32° and 41.5°C. Both Stammler and Duke agree that phase I is tetragonal and that the transition temperature (II-I) is 41°C.

Duke, 1971, has recorded a distinct X-ray pattern for a low temperature polymorph (presumably III) below 20°C. This phase has been indexed as orthorhombic. Duke's work can be summarised by the following:

$$\underset{\text{orthorhombic}}{Me_2NH_2ClO_4\ (III)} \overset{c\ 25^{\circ}C}{\rightleftarrows} \underset{\text{cubic}}{Me_2NH_2ClO_4} \overset{41^{\circ}C}{\rightleftarrows} \underset{\text{tetragonal}}{Me_2NH_2ClO_4\ (I)}$$

In view of the specific heat experiments and the X-ray evidence the III-II transition temperature is likely to be 30° ± 1°C. Prior to the specific heat experiments, the samples were melted into the pans, thus expelling occluded solvent. This would eliminate the possibility that in these experiments the transition temperatures are artificially elevated. This precaution was not observed in the D.S.C. experiments. The polymorphic forms of dimethyl ammonium perchlorate can be summarised by

$$\underset{\text{orthorhombic}}{Me_2NH_2ClO_4\ (III)} \overset{30^{\circ}C}{\rightleftarrows} \underset{\text{cubic}}{Me_2NH_2ClO_4(II)} \overset{41^{\circ}C}{\rightleftarrows} \underset{\text{tetragonal}}{Me_2NH_2ClO_4\ (I)}$$

and the transition enthalpies by

$Me_2NH_2ClO_4$ (III) $\longrightarrow$ $Me_2NH_2ClO_4$ (II) $\Delta H_t=1.81\pm0.04$ Kcal.mole^{-1}

$Me_2NH_2ClO_4$ (II) $\longrightarrow$ $Me_2NH_2ClO_4$ (I) $\Delta H_t=0.79\pm0.05$ Kcal.mole^{-1}

Trimethyl Ammonium Perchlorate

The phase changes for this compound, detected by Stammler et al, 1966, are summarised by

$$Me_3NHClO_4 \text{ (III)} \overset{116^\circ C}{\rightleftharpoons} Me_3NHClO_4 \text{ (II)} \overset{207^\circ C}{\rightleftharpoons} \underset{\text{tetragonal}}{Me_3NHClO_4 \text{ (I)}}$$

Stammler lists the X-ray reflections for phase III and phase II, but no attempt was made to interpret them. The reason quoted is that the sample had a large thermal expansion coefficient which made it difficult to obtain unequivocal diffraction patterns.

Two crystal phase changes are confirmed in the present work and transition temperatures are in good agreement with those quoted above. No further transitions were detected in the temperature range-90° to 30°C. The enthalpies of transition are

Me_3NHClO_4 (III) $\longrightarrow$ Me_3NHClO_4(II) $\Delta H_t=0.22\pm0.01$ Kcal.mole^{-1}

Me_3NHClO_4 (II) $\longrightarrow$ Me_3NHClO_4 (I) $\Delta H_t=0.99\pm0.01$ Kcal.mole^{-1}

Tetramethyl Ammonium Perchlorate

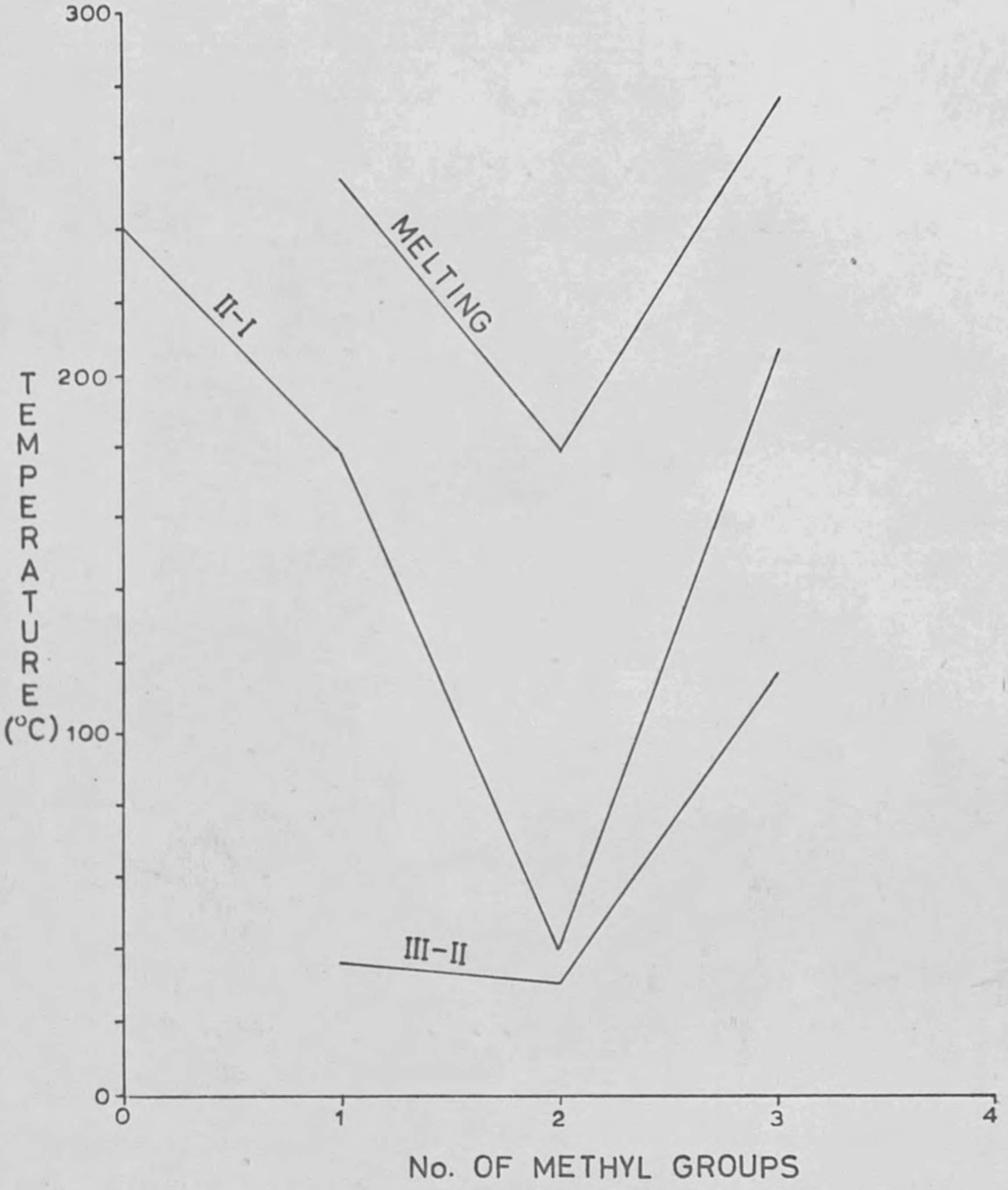
Stammler et al, 1966, report that this compound has a crystal phase change at 340°C. This, however, was only detected using a ten-fold increase in sensitivity of the D.T.A. equipment. This transition was not detected in the present work and thus it is concluded that, if this transition exists, it has a very low transition enthalpy. No further transitions were detected in the temperature range -90° to 30°C.

Stammler reports the X-ray diffraction patterns for both tetramethyl ammonium perchlorate and tetramethyl ammonium fluoroborate at 25°C, which indicate that these salts both have tetragonal lattices. These salts are isostructural with tetramethyl ammonium permanganate which is also tetragonal at 25°C (Hermann and Ilge, 1930).

The transition temperatures are summarised for the methyl series of compounds in Fig. 5.7. Several features can be noted from this graph.

1. Addition of methyl groups to the cation causes a reduction in the symmetry of the cation and an increase in the number of polymorphic forms. The number of polymorphic forms is reduced to one on reaching the symmetrical tetramethyl system.

Fig. 5·7



Transition Temperatures of Methyl Substituted Ammonium Perchlorates

2. There is a transition temperature minimum at dimethyl ammonium perchlorate for both polymorphic phase changes and for fusion.

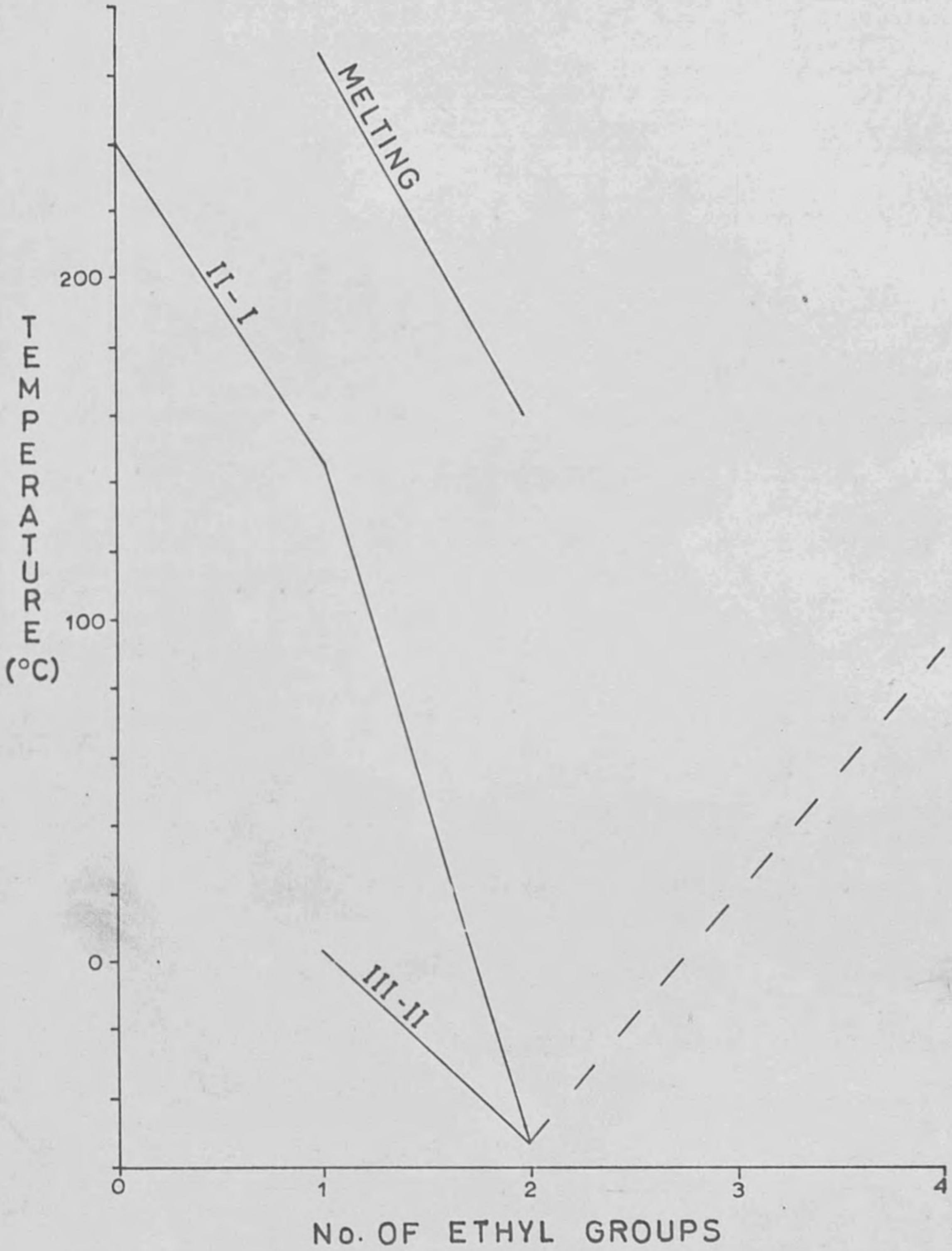
3. The symmetrical ammonium and tetramethyl ammonium perchlorates decompose before melting.

The only similarity between the results in Fig. 5.7 and the results of Stammler, 1967, for a series of methyl ammonium chlorides (Fig. 1.4) is the melting point minimum for dimethyl ammonium salts. The available data for the ethyl ammonium series are similarly plotted in Fig. 5.8. The absence of transition data for triethyl ammonium perchlorate is due to difficulties encountered in preparing a further sample of this compound. Attempted preparations resulted in a syrup which could not be induced to crystallise. Ethyl ammonium perchlorate melts with decomposition at 267°C and thus the enthalpy of transition is not recorded in Section 4b.

The transition temperatures for the ethyl series follow closely to the methyl series for the mono- and di- substituted compounds, except that there is only one polymorphic transformation in diethyl ammonium perchlorate. The other feature is the appearance of a polymorphic transformation for tetraethyl ammonium perchlorate.

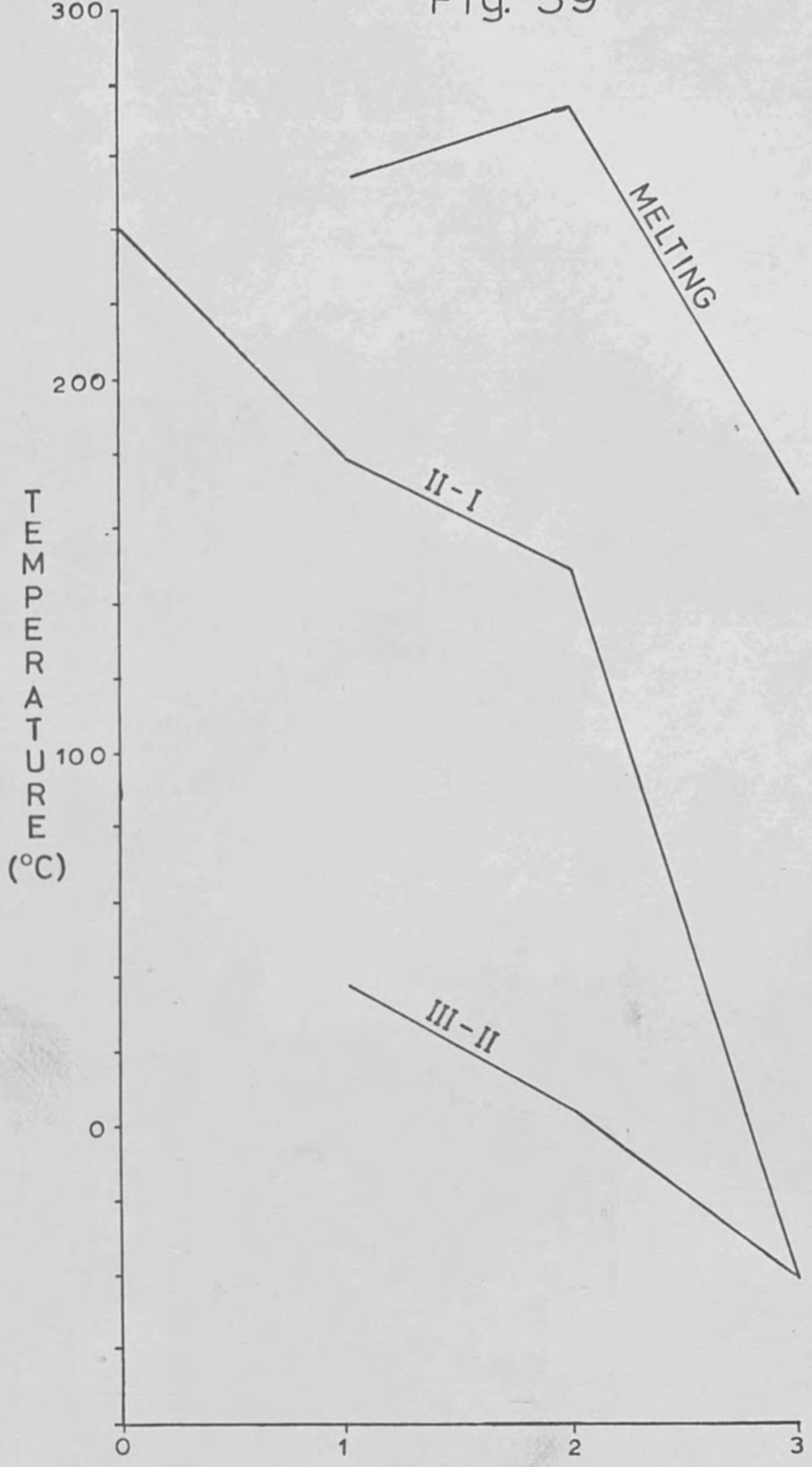
The effect of increasing the size of the alkyl substituent on the transition temperatures of mono-alkyl ammonium perchlorates is shown in Fig. 5.9. The transition temperatures in general tend

Fig. 5·8



Transition Temperatures of Ethyl Substituted Ammonium Perchlorates

Fig. 5·9



Transition Temperatures of Mono-Alkyl Ammonium Perchlorates to decrease as the alkyl substituent gets larger and only one phase transition was detected for propyl ammonium perchlorate. This trend can also be seen by comparing the transition temperatures of dimethyl and diethyl ammonium perchlorates. Insufficient data were available to plot a more extensive graph for the alkyl ammonium perchlorates similar to that constructed from Tsau and Gilson's, 1968, data for the alkyl ammonium chlorides and bromides.

5e Thermal Decomposition of Amine Salts

In general terms, good propellant fuels and oxidisers should possess endothermic standard heats of formation and decompose to give products with large exothermic standard heats of formation. The standard heats of formation of some present day fuels and oxidisers are listed in table 5.15. The values were taken from Holtzmann, 1969.

Decomposition products which have exothermic standard heats of formation, and are possibly formed in the decompositions considered later are:

H_2O ; $\Delta H_f^{\circ}(H_2O, g) = -57.80$ Kcal.mole^{-1}

CO ; $\Delta H_f^{\circ}(CO, g) = -26.42$ Kcal.mole^{-1}

CO_2 ; $\Delta H_f^{\circ}(CO_2, g) = -94.05$ Kcal.mole^{-1}

HCl ; $\Delta H_f^{\circ}(HCl, g) = -22.06$ Kcal.mole^{-1}

CH_4 ; $\Delta H_f^{\circ}(CH_4, g) = -17.88$ Kcal.mole^{-1}

C_2H_6; $\Delta H_f^{\circ}(C_2H_6, g) = -20.24$ Kcal.mole^{-1}

Table= 5.15

Standard Heats of Formation of Fuels and Oxidisers at 25°C

Fuels	ΔH_f^o Kcal.mole^{-1}
Liquid hydrogen	-1.89
Liquid hydrazine	12.05
1,1-Dimethyl hydrazine (l)	12.74
Dicyanoacetylene (g)	118.0
Aluminium hydride (c)	10.0
Oxidisers	
Liquid oxygen	-3.08
Liquid fluorine	-3.47
Oxygen difluoride (g)	3.6
Nitrogen trifluoride (g)	-32.2
Nitronium perchlorate (c)	88.0
Ammonium perchlorate (c)	-70.58

The values of the standard heats of formation are taken from Wagman et al, 1968. Throughout this section the decomposition products are considered to be gaseous and enthalpies of decomposition are per mole of decomposing solid.

The thermal decomposition of ammonium perchlorate has been thoroughly investigated and the results of these investigations have been reviewed recently by Jacobs and Whitehead, 1969, and Keenan and Siegmund, 1969. Escales, 1910, proposed the following decomposition of ammonium perchlorate in a closed constant pressure system

$$4NH_4ClO_4 = 6H_2O + 5O_2 + 4HCl + 2N_2 \qquad \Delta H(\text{from data above} = -38.2\ \text{Kcal.mole}^{-1}$$

Ammonium perchlorate has two decomposition modes at atmospheric pressure in two distinct temperature regions (below 300°C and above 350°C). Low temperature decomposition:

$$4NH_4ClO_4 = 8H_2O + 2Cl_2 + 3O_2 + 2N_2O \qquad \Delta H= -31.1\ \text{Kcal.mole}^{-1}$$

The enthalpy of decomposition was calculated for the above reaction by estimating the standard heats of formation of the decomposition products at 250°C from specific heat data.

High temperature decomposition:

$$2NH_4ClO_4 = 4H2O + Cl2 + 2O2 + N2 \qquad \Delta H= -33.6\ \text{Kcal.mole}^{-1}$$

The enthalpy of decomposition of this reaction was calculated at 400°C. The enthalpy of decomposition for the low and high temperature decomposition modes is thus roughly constant.

Ammonium nitrate begins to decompose above its melting point and the nature of the decomposition is outlinediin Section 1. The major decomposition products are nitrous oxide and water, thus

$$NH_4NO_3 = N_2O + 2H_2O$$

$$\Delta H = -8.6 \ \text{Kcal.mole}^{-1}$$

Nitrogen has also been detected among the decomposition products and this can be accounted for by the reaction

$$2NH_4NO_3 = 2N_2 + 4H_2O + O_2$$

$$\Delta H = -28.2 \ \text{Kcal.mole}^{-1}$$

Cawthon and Taylor, 1954 b, proposed a general mechanism for the decomposition of primary aliphatic amine nitrates. They proposed mechanisms which account for the formation of nitrous oxide and nitrogen. Their decomposition reactions can be summarised, for methyl ammonium nitrate, by

$$2MeNH_3NO_3 = MeONO_2 + MeNH_2 + N_2O + 2H_2O$$
$$\Delta H = 19.4 \ \text{Kcal.mole}^{-1}$$

and

$$8MeNH_3NO_3 = 5MeONO_2 + 3MeNH_2 + 4N_2 + 9H_2O$$
$$\Delta H = -0.6 \ \text{Kcal.mole}^{-1}$$

The standard heats of formation of methyl nitrate and methylamine were taken from Cox and Pilcher, 1970.

The latter equation was written in order to account for the decomposition products reported by Cawthon and was not taken from his work. Methyl nitrate and methylamine seem to be unreasonable decomposition products, and during a decomposition reaction these would probably decompose further. Solid carbon, carbon monoxide or carbon dioxide would be better decomposition products for decompositions in a closed constant pressure system. The amount of oxygen in the alkyl ammonium nitrates is limited and so carbon is more likely to be formed. There are more atoms of hydrogen present than carbon atoms and so water is to be preferred as the decomposition product containing oxygen. Based on this scheme the following decomposition reactions are proposed for the alkyl ammonium nitrates.

$$MeNH_3NO_3 = C + N_2 + 3H_2O \qquad \Delta H = -88.7 \text{ Kcal.mole}^{-1}$$

$$Me_2NH_2NO_3 = 2C + N_2 + 3H_2O + H_2 \qquad \Delta H = -89.7 \text{ Kcal.mole}^{-1}$$

$$Me_3NHNO_3 = 3C + N_2 + 3H_2O + 2H_2 \qquad \Delta H = -91.2 \text{ Kcal.mole}^{-1}$$

$$EtNH_3NO_3 = 2C + N_2 + 3H_2O + H_2 \qquad \Delta H = -85.7 \text{ Kcal.mole}^{-1}$$

$$Et_2NH_2NO_3 = 4C + N_2 + 3H_2O + 3H_2 \qquad \Delta H = -73.3 \text{ Kcal.mole}^{-1}$$

$$Et_3NHNO_3 = 6C + N_2 + 3H_2O + 5H_2 \qquad \Delta H = -66.4 \text{ Kcal.mole}^{-1}$$

The thermal decomposition of methyl substituted ammonium perchlorates has been studied by Guillory and King, 1969, using mass spectrometry. The three methyl ammonium salts considered principally decompose via

$$Me_nNH_{4-n}ClO_4 = Me_nNH_{3-n} + HClO_4$$

where n = 1-3

Present D.S.C. thermograms and the D.T.A. thermograms of Stammler et al, 1966, show that these compounds begin to decompose above their melting points. The decomposition products reported by Guillory and King, 1969, are probably an inaccurate guide to the decomposition reactions, since their samples were not heated much above the melting points. Consequently all possibilitiem have been considered for the decomposition of the alkyl ammonium perchlorates.

Methyl Ammonium Perchlorate

Guillory and King, 1969, detected small amounts of N_2O, H_2O, O_2 and N_2, so these products have been considered in formulating decomposition reactions

$$2MeNH_3ClO_4 = 2C + N_2 + 6H_2O + O_2 + Cl_2 \qquad \Delta H = -105.6 \text{ Kcal.mole}^{-1}$$

$$4MeNH_3ClO_4 = 4C + 2N_2O + 12H_2O + O_2 + Cl_2 \qquad \Delta H = -95.8 \text{ Kcal.mole}^{-1}$$

The standard heat of formation of hydrogen chloride is exothermic (-22.1 Kcal.mole^{-1}) and so reactions resulting in hydrogen chloride were considered.

$$4MeNH_3ClO_4 = 4C + 2N_2 + 4HCl + 10H_2O + 3O_2 \qquad \Delta H = -98.8 \text{ Kcal.mole}^{-1}$$

$$2MeNH_3ClO_4 = 2C + N_2O + 2HCl + 5H_2O + O_2 \qquad \Delta H = -89.0 \text{ Kcal.mole}^{-1}$$

In the above reactions oxygen is produced which could be used to burn the carbon. The reactions which are possible are:

$$C\ (s) + \tfrac{1}{2}O_2 = CO \qquad \Delta H = -26.41 \text{ Kcal.mole}^{-1}$$

$$C\ (s) + O_2 = CO_2 \qquad \Delta H = -94.05 \text{ Kcal.mole}^{-1}$$

The reaction to form carbon dioxide has the largest exothermic enthalpy change and this was chosen as route by which the carbon burns

$$2MeNH_3ClO_4 = C + CO_2 + N_2 + 6H_2O + Cl_2 \qquad \Delta H = -152.6 \text{ Kcal.mole}^{-1}$$

$$4MeNH_3ClO_4 = C + CO_2 + 2N_2O + 12H_2O + Cl_2 \qquad \Delta H = -119.3 \text{ Kcal.mole}^{-1}$$

$$2MeNH_3ClO_4 = CO_2 + CO + N_2 + 2HCl + 5H_2O \qquad \Delta H = -159.1 \text{ Kcal.mole}^{-1}$$

$$2MeNH_3ClO_4 = C + CO_2 + N_2O + 2HCl + 5H_2O \qquad \Delta H = -136.0 \text{ Kcal.mole}^{-1}$$

Dimethyl Ammonium Perchlorate

Guillory and King, 1969, have detected the following decomposition species: H_2O, O_2, N_2, HCl and H_2O

Possible decomposition reactions are thus:

$$2Me_2NH_2ClO_4 = 4C + N_2 + 8H_2O + Cl_2 \qquad \Delta H = -164.6\ Kcal.mole^{-1}$$

$$2Me_2NH_2ClO_4 = 4C + N_2O + 7H_2O + 2HCl \qquad \Delta H = -148.0\ Kcal.mole^{-1}$$

$$2Me_2NH_2ClO_4 = 3C + CO + N_2 + 7H_2O + 2HCl \ \Delta H = -171.0\ Kcal.mole^{-1}$$

$$4Me_2NH_2ClO_4 = 8C + 2N_2 + 14H_2O + 4HCl + O_2 \ \Delta H = -157.8\ Kcal.mole^{-1}$$

Trimethyl Ammonium Perchlorates

Guillory and King, 1969, report the following decomposition products: H_2O, O_2, N_2, HCl and N_2O. Possible decomposition reactions which give rise to these products are:

$$2Me_3NHClO_4 = 6C + N_2 + 2HCl + 8H_2O + H_2 \qquad \Delta H = -187.4\ Kcal.mole^{-1}$$

$$2Me_3NHClO_4 = 6C + N_2O + 2HCl + 7H_2O + 2H_2 \ \Delta H = -148.7\ Kcal.mole^{-1}$$

Thermal decompositions of the remaining methyl and the ethyl substituted ammonium perchlorates do not appear to have been reported in the literature. The decomposition reactions for these other perchlorates are based on the previous reactions, where H_2O, N_2, N_2O and HCl appear to be the usual decomposition products.

$$2Me_4NClO_4 = 8C + N_2 + 8H_2O + 2HCl + 3H_2 \qquad \Delta H = -182.5\ Kcal.mole^{-1}$$

$$2Me_4NClO_4 = 8C + N_2O + 7H_2O + 2HCl + 4H_2 \qquad \Delta H = -143.8\ Kcal.mole^{-1}$$

$$2EtNH_3ClO_4 = 4C + N_2 + 8H_2O + Cl_2 \qquad \Delta H = -159.1\ Kcal.mole^{-1}$$

$$2EtNH_3ClO_4 = 4C + N_2O + 7H_2O + 2HCl \qquad \Delta H = -142.5\ Kcal.mole^{-1}$$

$$2EtNH_3ClO_4 = 3C + CO + N_2 + 7H_2O + 2HCl \qquad \Delta H = -165.5\ Kcal.mole^{-1}$$

$$2Et_2NH_2ClO_4 = 8C + N_2 + 8H_2O + 2HCl + 3H_2 \qquad \Delta H = -172.7\ Kcal.mole^{-1}$$

$$2Et_2NH_2ClO_4 = 8C + N_2O + 7H_2O + 2HCl + 4H_2 \qquad \Delta H = -134.0\ Kcal.mole^{-1}$$

$$2Et_3NHClO_4 = 12C + N_2 + 8H_2O + 2HCl + 7H_2 \qquad \Delta H = -168.5\ Kcal.mole^{-1}$$

$$2Et_3NHClO_4 = 12C + N_2O + 7H_2O + 2HCl + 8H_2 \qquad \Delta H = -129.8\ Kcal.mole^{-1}$$

$$2Et_4NClO_4 = 16C + N_2 + 8H_2O + 2HCl + 11H_2 \qquad \Delta H = -182.5\ Kcal.mole^{-1}$$

$$2Et_4NClO_4 = 16C + N_2O + 7H_2O + 2HCl + 12H_2 \qquad \Delta H = -143.8\ Kcal.mole^{-1}$$

The previous reactions have been for the decomposition of the solid in a closed constant pressure system. Decompositions have also been considered where the sample decomposes in an atmosphere of oxygen so that complete combustion can take place. These decomposition reactions are generalised into the forms:

$$(C_nH_{2n-1})_yNH_{4-y}NO_3 + x\ O_2 = nyCO_2 + N_2 + \frac{(2n-1)y + 4-y}{2}H_2O$$

$$2(C_nH_{2n-1})yNH_{4-y}ClO_4 + x\ O_2 = 2nyCO_2 + N_2 + 2HCl + \frac{(2n-1)y + 2-y}{2} H_2O$$

The decomposition enthalpies, ΔH, for the alkyl ammonium nitrates and perchlorates are listed in table 5.16.

Table 5.16

Compound	ΔH Kcal.mole^{-1}
$MeNH_3NO_3$	- 182.8
$Me_2NH_2NO_3$	- 335.7
Me_3NHNO_3	- 571.3
$EtNH_3NO_3$	- 331.7
$Et_2NH_2NO_3$	- 723.2
Et_3NHNO_3	-1027.0
$MeNH_3ClO_4$	- 192.9
$Me_2NH_2ClO_4$	- 346.0
Me_3NHClO_4	- 498.6
Me_4NClO_4	- 645.6
$EtNH_3ClO_4$	-340.5
$Et_2NH_2ClO_4$	- 635.8
Et_3NHClO_4	- 935.4
Et_4NHClO_4	-1253.2

Although the decomposition reactions reported in this section are hypothetical, the enthalpies of decomposition indicate that these compounds possess considerable potential as explosives.

SECTION 6

Errors

The uncertainty interval associated with the experimentally determined heats of solution and reaction is that proposed by Rossini and Deming, 1939. The uncertainty interval is defined as twice the standard deviation of the mean, $\bar{s}$, where

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

n represents the number of observations of which the arithmetic mean is $\bar{x}$ and x represents an individual value. For this method of calculating the uncertainty interval, the probability that the mean value lies within the range is 67%. Rossini recommends the above method for values of n between 4 and 12. For two or three observations the uncertainty interval is quoted as the range.

If $\Delta H = \Delta H_1 + \Delta H_2 + \dots \Delta H_n$

where ΔH_i has an uncertainty interval $\pm x_i$

Then the uncertainty interval for ΔH is

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

APPENDIX I

Determination of ΔTr for Moderate Reactions

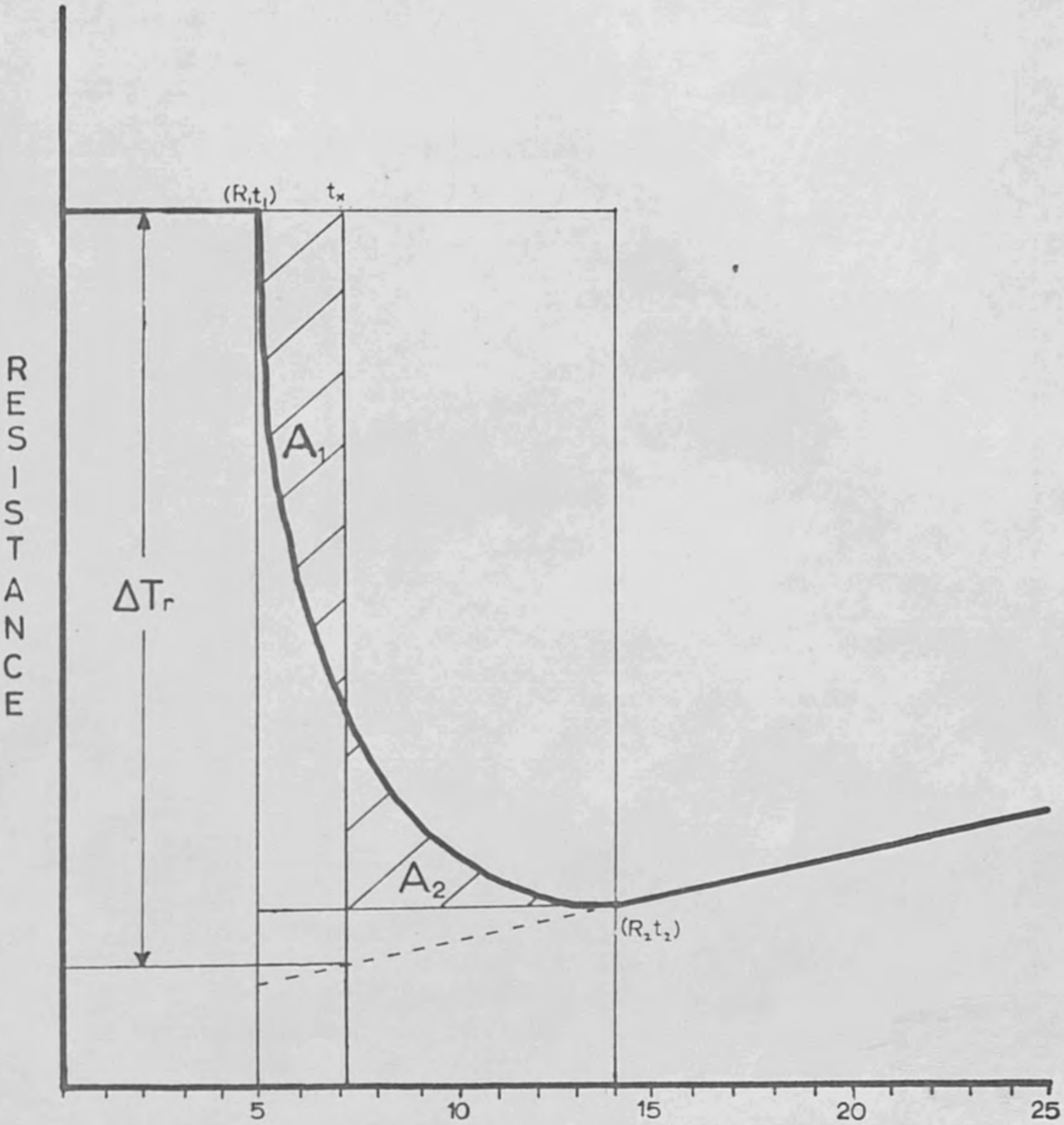
In the present work moderate reactions are arbitrarily defined as those having a main reaction period of between three and fifteen minutes. The "equal-area" technique described by Dickinson in 1915 was used to obtain the corrected resistance change, expressed by ΔTr. In a review (Macleod, 1967) of temperature correction methods in calorimetry, Macleod recommends Dickinson's method where a precision of about 0.2% is acceptable.

Fig. I.1 represents a resistance-time profile for a moderate exothermic reaction and Dickinson's method, used in the present work, defines a time (t_x) such that the shaded areas A_1 and A_2 are equal. The point (R_1, t_1) represents the resistance R_1, at time t_1, when the reaction was started, and (R_2, t_2) represents the corresponding quantities when the thermal output from the reaction balances the thermal leakage from the calorimeter. This point is the minimum in the resistance-time profile.

The resistance-time points for the reaction period between t_1 and t_2 were used to compute a 'best fit' curve represented by the general equation

$$R = a_o + a_1 t + a_2 t^2 + \quad \ldots\ldots \quad a_i t^i$$

Fig. I·1



Resistance-Time Profile for a Moderate Exothermic Reaction

Comparison of input R values with computed R values showed that a 'best fit' was obtained when $i = 9$ and so a ten-term equation was used in all calculations.

The upper shaded area, A_1, is given by

$$A_1 = (t_x - t_1)\ R_1 - \int_{t_1}^{t_x} f\ (t)\ dt$$

and the lower shaded area, A_2, by

$$A_2 = \int_{t_x}^{t_2} f\ (t)\ dt - (t_2 - t_x)\ R_2$$

Equating A_1 with A_2 and rearranging

$$t_x = \frac{\int_{t_1}^{t_2} f(t)\ dt + t_1 R_1 - t_2 R_2}{(R_1 - R_2)}$$

The integration and hence the t_x calculations are carried out using a computer, as an additional part of the curve fitting programme (see Appendix IV). The points for calculating ΔT_f are then obtained from where the extrapolated pre- and post-reaction lines cut the line $t = t_x$. The pre- and post-reaction lines were extrapolated manually.

For reactions which are faster than three minutes, a graphical technique was used to obtain the value of ΔT_r. This involves drawing 'aid-of-eye' straight lines through the pre- and post-reaction data and obtaining T_r from the points where these lines intercept a line representing the start of the reaction, usually $t = 5$ min.

In the present work no reactions with a main period longer than fifteen minutes were encountered. For such reactions, an adiabatic calorimeter would give better results than a C.T.E. calorimeter.

In table I.1 a comparison of the results of the heat of solution of tetramethyl ammonium perchlorate in water are presented. ΔH_a represents the heat of solution values obtained by 'aid-of-eye', assuming that the reaction is fast and ΔH_c represents the values obtained by using the 'equal-area' computer technique. All ΔH values are in Kcal.mole^{-1} at 298°K.

The table indicates the greater consistency in the results obtained by using the 'equal-area' computer technique which, therefore, is preferred for moderate reactions.

Table I.1

Heat of Solution of Tetramethyl Ammonium Perchlorate

Exp.	ΔH_a	ΔH_c	$\Delta H_a - \Delta H_c$
1	10.44	10.35	0.09
2	10.42	10.33	0.09
3	10.40	10.34	0.06
4	10.42	10.35	0.07
5	10.39	10.35	0.04
6	10.41	10.35	0.06

Mean value of $\Delta H_a = 10.41 \pm 0.02$ Kcal.mole^{-1}

Mean value of $\Delta H_c = 10.35 \pm 0.01$ Kcal.mole^{-1}

In the remainder of this section a method is outlined by which the enthalpy of solution or reaction could be calculated entirely by computer. The method outlined is applied to fast reactions; however, the 'equal-area' moderate-reaction procedure could be easily incorporated.

The resistance-time data for the pre- and post-reaction, pre-calibration, electrical heating and post-calibration periods can be expressed by straight lines (Fig. 3.5). The slope (m) and constant (c) terms for each of these straight lines can be obtained by inputting the resistance-time data, for each period, into a least-mean-square-fit programme. The individual straight lines can be expressed by

$$R = m_1 . t + c_1 \qquad \text{(pre-reaction)}$$

$$R = m_2 . t + c_2 \qquad \text{(post-reaction)}$$

$$R = m_3 . t + c_3 \qquad \text{(pre-calibration)}$$

$$R = m_4 . t + c_4 \qquad \text{(electrical heating)}$$

$$R = m_5 . t + c_5 \qquad \text{(post-calibration)}$$

The resistance change for the reaction, expressed by ΔTr is given by

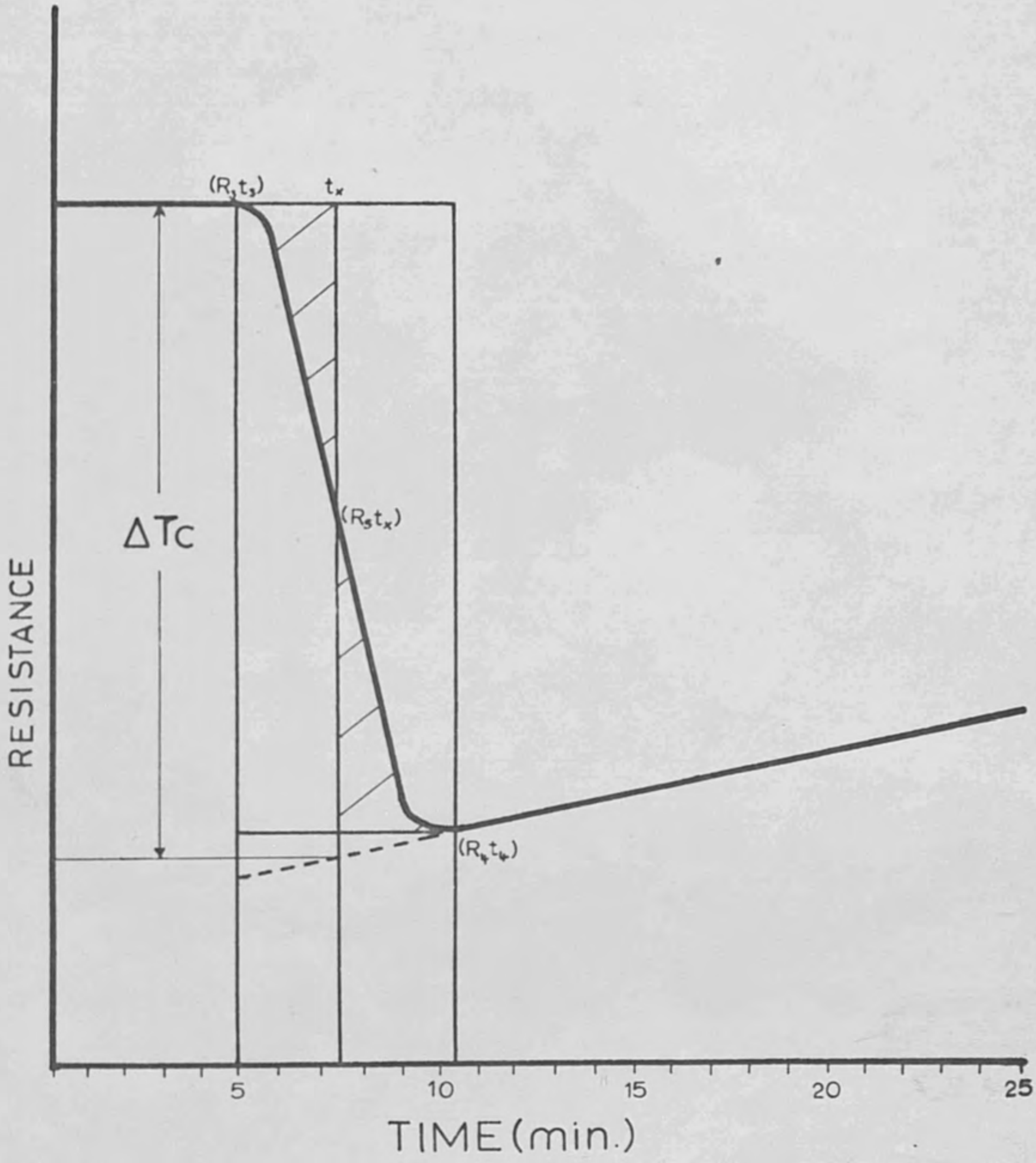
$$\Delta Tr = \log R_1 - \log R_2$$

where $\qquad R_1 = 5.0 m_1 + c_1$

and $\qquad R_2 = 5.0 m_2 + c_2$

Fig. I.2 represents the resistance-time profile for the calibration part of the experiment. Dickinson's 'equal-area' technique is again employed to obtain a time (t_x), such that the shaded areas are equal. The points (R_3, t_3) and (R_4, t_4) correspond to where the heating line cuts the pre- and post-calibration lines.

Fig. I·2



Resistance-Time Profile for

a Calibration Period

Upper area, $A_3 = \frac{1}{2}(t_x - t_3)(R_3 - R_5)$

Lower area, $A_4 = \frac{1}{2}(t_4 - t_x)(R_s - R_4)$

Equating and rearranging

$$t_x = \frac{t_4(R_5 - R_4) + t_3(R_3 - R_5)}{(R_3 - R_4)}$$

Now
$$R_3 = m_3\ t_3 + c_3$$
$$R_4 = m_5\ t_4 + c_5$$
$$R_5 = m_4\ t_x + c_4$$

Substituting these values into the above equation

$$t_x = \frac{t_4(c_4 - m_5t_4 - c_5) + t_3(m_3t_3 + c_3 - c_4)}{(m_3t_3 + c_3 - m_5t_4 - c_5 - m_4t_4 + m_4t_3)}$$

The resistance change for the calibration, expressed by ΔT_c is obtained from

$$\Delta T_c = \log(m_3t_x + c_3) - \log(m_5t_x + c_5)$$

In 'aid-of-eye' processing of the thermal correction during the heating period, t_x was taken as the mean time of the heating period so that

$$t_x = t_3 + \tfrac{1}{2}(t_4 - t_3)$$

A computer programme based on the above method was developed and tested. The comparison of computer and graphical results for the heat of neutralisation of THAM in excess $N/_{10}$ HCl is given in table II.2. Values recorded are in Kcal.mole^{-1}.

Table II.2

Exp.	ΔH (computer)	ΔH (graphical)
A	7.21	7.20
B	7.26	7.27

These two examples show the good agreement between computer and graphical methods of determining the enthalpy of reaction. However, the use of a computer programme to calculate enthalpy changes, would only be advantageous, at the present time, if all the resistance-time data were recorded on punched paper tape.

APPENDIX II

Estimation of Standard Heats of Formation of Triarylmethanols

The absence of the standard heats of formation of tri(p-tolyl)-methanol and tri(p-methoxyphenyl)methanol in the literature necessitated the estimation of these data. Three methods of estimation were used:

Method 1

Standard heats of formation of gaseous compounds can be obtained by the group contribution method developed by Franklin (1949). Franklin extended the method of Pitzer (1940) to account for branched hydrocarbon and non-hydrocarbon substances.

Pitzer has shown that the heat content and free energy functions of gaseous straight chain paraffins can be expressed as additive functions of the number of carbon atoms and constants characteristic of temperature, molecular motions and the symmetry number of the molecule.

The principle of this method can be summarised by the equation $G(x) = \sum$ contributions of structural groups of the complex molecule $+ R.T.\ln \sigma + \sum$ correction terms

Where G can be $(G^o - H^o_o)$, $(H^o - H^o_o)$, ΔG^o_f and ΔH^o_f for the complex molecule X. The symmetry number, σ, only enters into estimations involving free energy terms. Allowance for the interaction of groups on adjacent carbon atoms in benzene structures can be made by applying correction terms. These correction terms, together with the structural contributions, are listed in Franklin's paper. The correction and symmetry terms do not apply in the estimations of standard heats of formation of the compounds mentioned in this section. The estimated values of the thermodynamic properties of hydrocarbons are accurate to within 1 $\mathrm{Kcal.mole^{-1}}$. However, the error for non-hydrocarbons is higher, due to the tentative nature of the values of the non-hydrocarbon group increments. The principle of this method is illustrated for benzene and ethanol: Benzene can be considered to be composed of 6 groups which are given the symbol $\overset{\nwarrow}{\underset{\swarrow}{>}}\mathrm{CH}$

$$\Delta H_f^o(C_6H_6,g) = 6 \text{ X the contribution from a } \overset{\nwarrow}{\underset{\swarrow}{>}}\mathrm{CH} \text{ group}$$
$$= 19.80 \text{ Kcal.mole}^{-1}$$

The ethanol molecule can be broken down into the following groups

$$CH_3 \ldots CH_2 \ldots OH$$

i.e., a methyl group, CH_3-; a methylene group, $-CH_2-$; and a primary hydroxyl group, -OH.

$$\Delta H_f^o(C_2H_5OH,g) = \text{the contribution from a } CH_3- \text{ group } + \text{ the contribution from a } -CH_2- \text{ group } + \text{ the contribution from an } -OH \text{ group}$$
$$= -56.95 \text{ Kcal.mole}^{-1}$$

In table II.1 a series of estimated standard heats of formation are compared with literature values from Cox and Pilcher(1970). All values are in $\mathrm{Kcal.mole^{-1}}$ at 298°K.

TABLE II.1

Estimated and Literature ΔH_f^o's for some organic compounds in the gas phase

Compound	ΔH_f^o(est)	ΔH_f^o(lit)	ΔH_f^o(lit)-ΔH_f^o(est)
Benzene	19·80	19·81	0·01
Toluene	11·95	11·99	0·04
Anisole	-15·25	-17·27	-2·02
Phenol	-24·83	-23·04	1·79
Methanol	-52·02	-48·07	3·95
Ethanol	-56·95	-56·24	0·71

The mean error associated with the four non-hydrocarbon compounds for the estimated standard heats of formation is of the order of 7%. This method gives the values for the triphenylmethanol, tri(p-tolyl)methanol and tri(p-methoxyphenyl)methanol as

ΔH_f^o $(C_{19}H_{16}O,g)$ = 17·8 Kcal.mole^{-1}

ΔH_f^o $(C_{22}H_{22}O,g)$ = -6·9 Kcal.mole^{-1}

ΔH_f^o $(C_{22}H_{22}O_4,g)$ = -88·5 Kcal.mole^{-1}

The standard heat of formation of crystalline triphenylmethanol is 0·8± 0·60 Kcal.mole^{-1} (Parks et al, 1954) and so an estimated heat of sublimation of triphenylmethanol is 17·0± 1·3 Kcal.mole^{-1}. The error for the heat of sublimation of triphenylmethanol was based on a 7% error in the standard heat of formation.

The heats of sublimation for tri(p-tolyl)methanol and tri(p-methoxyphenyl)methanol were estimated from the heat of sublimation of triphenylmethanol using the respective ratios of molecular weights as a correction factor.

$\Delta H_{sub}\ (C_{22}H_{22}O) = 19{\cdot}7 \pm 1{\cdot}3$ Kcal.mole^{-1}

$\Delta H_{sub}(C_{22}H_{22}O) = 22{\cdot}9 \pm 1{\cdot}3$ Kcal.mole^{-1}

Thus the standard heats of formation of the crystalline compounds were estimated to be

$\Delta H_f^o\ (C_{22}H_{22}O,c) = -26{\cdot}6 \pm 1{\cdot}4$ Kcal.mole^{-1}

$\Delta H_f^o\ (C_{22}H_{22}O_4,c) = -111{\cdot}4 \pm 6{\cdot}3$ Kcal.mole^{-1}

The uncertainty interval quoted for the standard heats of formation of the crystalline compounds is based on a 7% error in the standard heats of formation of the gaseous substances.

Method 2

In this method the difference in the standard heats of formation between tri(p-tolyl)methanol and triphenylmethanol was considered as three times the difference in the standard heats of formation of toluene and benzene.

Thus

$$\begin{aligned}\Delta H_f^o\ (C_{22}H_{22}O,c) &= \Delta H_f^o\ (C_{19}H_{16}O,c) + 3(\Delta H_f^o(C_7H_8,l) - \Delta H_f^o(C_6H_6,l)\\ &= 0{\cdot}80 + 3x(-8{\cdot}81)\\ &= -25{\cdot}63 \pm 1{\cdot}03\ \text{Kcal.mole}^{-1}\end{aligned}$$

Similarly the standard heat of formation of tri(p-methoxyphenyl)methanol was found to be

$\Delta H_f^o\ (C_{22}H_{22}O_4,c) = -119{\cdot}71 \pm 4{\cdot}79$ Kcal.mole^{-1}

The uncertainty interval is based on the mean error of 4% obtained by using this method to estimate the standard heats of formation of the compounds in table II.2. The literature values are taken from Cox and Pilcher (1970) and all values quoted are Kcal.mole^{-1} at 298^{o}K.

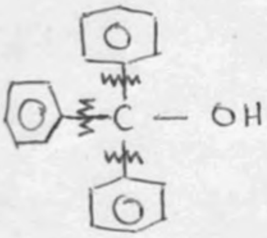
TABLE II.2

Estimated and Literature Standard Heats of Formation using Method 2

Compound	ΔH_f^0(lit)	ΔH_f^0(est)	ΔH_f^0(lit) - ΔH_f^0(est)
p-Cresol	-47.63	-48.26	0.63
Toluic acid	-102.39	-100.80	-1.59
Salicylic acid	-141.00	-124.31	-16.69
p-Ethyl phenol	-53.63	-54.72	1.09

Method 3

This method considers triphenylmethanol to be built up from three benzene molecules and one methanol molecule, thus



An estimation of the standard heat of formation of trophenylmethanol was made in terms of the standard heats of formation of benzene and methanol

$$\Delta H_f^0(C_{19}H_{16}O,c)est = 3X\Delta H_f^0(C_6H_6,l) + \Delta H_f^0(CH_4O,l)$$

A correction factor, B, can be obtained from the difference between this estimated value and the literature value.

$$B = \Delta H_f^0(C_{19}H_{16}O,c)est - \Delta H_f^0(C_{19}H_{16}O,c)lit$$

Tri(p-tolyl)methanol was considered, in a similar manner to triphenylmethanol, to be built up from three toluene molecules and a methanol molecule. The estimated standard heat of formation was given by

$$\Delta H_f^o(C_{22}H_{22}O,c) = 3x\Delta H_f^o(C_7H_8,l) + \Delta H_f^o(CH_4O,l) + B$$
$$= -26.4 \text{ Kcal.mole}^{-1}$$

Similarly the standard heat of formation of tri(p-methoxyphenyl)-methanol was estimated to be -120.5 Kcal.mole^{-1}.

Summary

The estimated standard heats of formation of tri(p-tolyl)methanol and tri(p-methoxyphenyl)methanol were taken as the mean of the results of all three methods.

$$\Delta H_f^o(C_{22}H_{22}O,c) = -26.2 \pm 1.2 \text{ Kcal.mole}^{-1}$$
$$\Delta H_f^o(C_{22}H_{22}O_4,c) = -117.2 \pm 5.5 \text{ Kcal.mole}^{-1}$$

The uncertainty interval quoted is the mean value obtained from methods 1 and 2.

APPENDIX III

HEAT OF SOLUTION DATA

Heat of Solution of Methyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$CH_3NH_3ClO_4(c) + nH_2O \longrightarrow [CH_3\overset{+}{NH_3} + \overset{-}{ClO_4}]nH_2O \ldots \Delta H_s$$

are recorded in table III.1. Throughout this section, the duration of the main period of the solution or the reaction is expressed by the symbol t.

Table III.1

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	747.9	7.06	29.54
2	837.9	6.99	29.25
3	1197	7.08	29.62
4	1253	7.03	29.41
5	1443	7.08	29.62
6	1501	7.09	29.66
7	1656	7.03	29.41
8	1791	7.02	29.37

Mean value of ΔH = 7.05 ± 0.03 Kcal.mole^{-1}(29.49 ± 0.10 Kj.mole^{-1})

Heat of Solution of Dimethyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$(CH_3)_2NH_2ClO_4(c) + nH_2O \longrightarrow [(CH_3)_2NH_2^+ + ClO_4^-]nH_2O \ \ldots \ \Delta H_s$$

are recorded in table III.2.

Table III.2

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	917.1	6.94	29.04
2	1247	6.91	28.91
3	1382	6.90	28.87
4	1544	6.99	29.25
5	1919	6.95	29.08
6	2525	6.93	29.00

Mean value of $\Delta H_s = 6.94 \pm 0.03$ Kcal.mole^{-1} (29.03 ± 0.11 Kj.mole^{-1})

Heat of Solution of Trimethyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$(CH_3)_3NHClO_4(c) + nH_2O \longrightarrow [(CH_3)_3NH^+ + ClO_4^-]nH_2O \ \ldots \ \Delta H_s$$

are recorded in table III.3.

Table III.3

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1288	7.95	33.26
2	1457	8.07	33.76
3	1572	7.98	33.39
4	2136	8.05	33.68
5	2218	8.19	34.27
6	2387	8.00	33.47
7	3955	8.05	33.68
8	4092	8.06	33.72

Mean value of $\Delta H_s = 8.04 \pm 0.05$ Kcal.mole^{-1} (33.65 ± 0.22 Kj.mole^{-1})

Heat of Reaction of Methyl Iodide with aqueous Trimethylamine solution

The enthalpy data for the reaction

$$MeI(l) + (x+1)Me_3NyH_2O \longrightarrow [Me_4N^+ + I^-]xMe_3NyH_2O \quad \ldots \quad \Delta H_1$$

are recorded in table III.4.

Table III.4

t< 1 min.

Exp.	Dilution, (x+1)	ΔH_1	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	194.7	-22.55	-94.35
2	267.4	-22.68	-94.89
3	275.9	-22.07	-92.34
4	289.9	-22.66	-94.81
5	419.4	-22.96	-96.06
6	712.5	-22.02	-92.13
7	998.8	-23.02	-96.32

Mean value of $\Delta H_1 = -22.55 \pm 0.30$ Kcal.mole^{-1} (-94.41 ± 1.26 Kj.mole^{-1})

Heat of Solution of Tetramethyl Ammonium Iodide in aqueous Trimethylamine solution

The heat of solution data for the reaction

$$Me_4NI(c) + (x+1)\ Me_3NyH_2O \longrightarrow [Me_4N^+ + I^-](x+1)Me_3N.yH_2O \quad \ldots \quad \Delta H_2$$

are recorded in table III.5.

Table III.5

t = 1-3 min.

Exp.	Dilution, (x+1)	ΔH_2	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	150.9	9.78	40.92
2	161.5	9.72	40.67
3	164.1	9.73	40.71
4	166.5	9.71	40.63
5	207.0	9.81	41.05

Mean value of ΔH_2 = 9.75 ± 0.04 Kcal.mole^{-1} (40.80 ± 0.16 Kj.mole^{-1})

Heat of Solution of Tetramethyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$(CH_3)_4NClO_4(c) + nH_2O \longrightarrow ((CH_3)_4N^+ + ClO_4^-)nH_2O \;\ldots\; \Delta H_{sn}$$

are recorded in table III.6

Table III.6

t = 3-5 min.

Exp.	Dilution, n	ΔH_{sn}	
		$Kcal.mole^{-1}$	$Kj.mole^{-1}$
1	1573	10.35	43.30
2	2271	10.33	43.22
3	2211	10.34	43.26
4	3144	10.35	43.30
5	3359	10.35	43.30
6	5311	10.35	43.30

Mean value of $\Delta H_{sn} = 10.35 \pm 0.01$ $Kcal.mole^{-1}$ (43.28 ± 0.01 $Kj.mole^{-1}$)

Heat of Solution of Tetramethyl Ammonium Iodide in Water

The heat of solution data for the reaction

$$(CH_3)_4NClO_4(c) + nH_2O \longrightarrow ((CH_3)_4N^+ + ClO_4^-)nH_2O \;...\; \Delta H_s$$

are recorded in table III.7

Table III.7

$t < 1$ min.

Exp.	Dilution	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1610	10.13	42.38
2	1823	10.18	42.59
3	2135	10.07	42.13
4	2706	9.75	40.79
5	3213	10.21	42.72

Mean value of ΔH_s = 10.07 ± 0.17 Kcal.mole^{-1} (42.12 ± 0.70 Kj.mole^{-1})

Heat of Solution of Ethyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$C_2H_5NH_3ClO_4(c) + nH_2O \longrightarrow [C_2H_5NH_3^+ + ClO_4^-]nH_2O \; \ldots \; \Delta H_s$$

are recorded in table III.8.

Table III.8

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	725.4	3.92	16.40
2	1064	3.79	15.86
3	1069	3.92	16.40
4	1092	3.87	16.19
5	1096	3.86	16.15
6	1137	3.86	16.15
7	1160	3.85	16.11
8	1228	3.91	16.36
9	1310	3.92	16.40
10	1716	3.90	16.32

Mean value of $\Delta H_s = 3.88 \pm 0.02$ Kcal.mole^{-1} (16.23 ± 0.11 Kj.mole^{-1})

Heat of Solution of Diethyl Ammonium Perchlorate

The heat of solution data for the reaction

$$(C_2H_5)_2NH_2ClO_4(c) + nH_2O \longrightarrow [(C_2H_5)_2NH_2^{+} + ClO_4^{-}]nH_2O \quad \ldots \quad \Delta H_s$$

are recorded in table III.9.

Table III.9

t < 1 min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1200	4.57	19.12
2	1264	4.52	18.91
3	1388	4.58	19.16
4	1434	4.55	19.04
5	1477	4.52	18.91
6	1498	4.53	18.95
7	1609	4.52	18.91
8	2093	4.57	19.12

Mean value of ΔH_s = 4.55 ± 0.02 Kcal.mole^{-1} (19.02 ± 0.08 Kj.mole^{-1})

Heat of Solution of Triethyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$(C_2H_5)_3NHClO_4(c) + nH_2O \longrightarrow [(C_2H_5)_3NH^+ + ClO_4^-]nH_2O \;\ldots\; \Delta H_s$$

are recorded in table III.10.

Table III.10

t <1 min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1050	4.69	19.62
2	1161	4.62	19.33
3	1847	4.66	19.50
4	1870	4.57	19.12
5	1932	4.67	19.54
6	2068	4.63	19.37
7	2106	4.58	19.16
8	2129	4.69	19.62
9	2257	4.59	19.20
10	2437	4.64	19.41

Mean value of $\Delta H_s = 4.63 \pm 0.03$ Kcal.mole^{-1} (19.39 ± 0.12 Kj.mole^{-1})

Heat of Reaction of aqueous Ethyl Iodide with Triethylamine

$$\text{EtInH}_2\text{O} + (x+1)\text{Et}_3\text{N} \longrightarrow (\text{Et}_4\text{N}^+ + \text{I}^-)x\text{Et}_3\text{NnH}_2\text{O}$$

The enthalpy data for the above reaction are recorded in table III.11.

Table III.11

t = 6-9 min.

Exp.	Qcals	moles of Et I $\times 10^3$, n_1	moles of Et_3N $\times 10^3$, n_2	ΔH_3	
				$Kcal.mole^{-1}$	$Kj.mole^{-1}$
1	-50.962	4.93	7.04	-5.46	-22.84
2	-52.892	4.93	7.17	-5.60	-23.43
3	-48.992	4.93	7.17	-4.82	-20.17
4	-54.573	4.93	7.19	-5.90	-24.69
5	-50.632	4.93	6.81	-5.84	-24.43
6	-53.804	4.93	7.21	-5.71	-23.89

Mean value of $\Delta H_3 = -5.56 \pm 0.32\ Kcal.mole^{-1}$ ($-23.24 \pm 1.35\ Kj.mole^{-1}$)

Heat of Solution of Tetraethyl Ammonium Perchlorate

The heat of solution data for the reaction

$$(C_2H_5)_4NClO_4(c) + nH_2O \longrightarrow [(C_2H_5)_4N^+ + ClO_4^-]nH_2O \ldots \Delta H_s$$

are recorded in table III.12.

Table III.12

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1968	7.43	31.07
2	2159	7.43	31.07
3	2876	7.45	31.17
4	3327	7.40	30.96
5	3772	7.37	30.82
6	5123	7.41	30.99

Mean value of $\Delta H_s = 7.41 \pm 0.02$ Kcal.mole^{-1} (31.02 ± 0.11 Kj.mole^{-1})

Heat of Reaction of n-Propylamine with dilute aqueous Perchloric Acid

The enthalpy data for the reaction

$$PrNH_2(l) + (x+1)HClO_4yH_2O \longrightarrow (PrNH_3^+ + ClO_4^-)xHClO_4yH_2O \;\ldots\; \Delta H_1$$

are recorded in table III.13

Table III.13

$t < 1$ min.

Exp.	Dilution, y	ΔH_1	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	961.6	-19.46	-81.42
2	1784	-19.47	-81.46
3	4975	-19.63	-82.13
4	6277	-19.41	-81.21

Mean value of $\Delta H_1 = -19.49 \pm 0.10$ Kcal.mole^{-1} (-81.56 ± 0.40 Kj.mole^{-1})

Heat of Solution of n-Propyl Ammonium Perchlorate in Water

The heat of solution data for the reaction

$$C_3H_7NH_3ClO_4(c) + nH_2O \longrightarrow [C_3H_7NH_3^+ + ClO_4^-]nH_2O \;\ldots\; \Delta H_s$$

are recorded in table III.14.

Table III.14

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	781.4	3.92	16.40
2	1247	3.87	16.19
3	1366	3.92	16.40
4	2019	3.84	16.07
5	2042	3.93	16.44
6	2623	3.95	16.53

Mean value of $\Delta H_s = 3.91 \pm 0.03$ Kcal.mole (16.34 ± 0.14 Kj.mole^{-1})

Heat of Reaction of Tri-n-propylamine with 72% Perchloric Acid

The enthalpy data for the reaction

$Pr_3N(l) + (m+1)HClO_4 \longrightarrow (Pr_3NH^+ + ClO_4)mHClO_4nH_2O$ ... ΔH_1

are recorded in table III.15.

Table III.15

t <1 min.

Exp.	Dilution, m+1	ΔH_1	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	2291	-30.08	-125.85
2	2332	-30.06	-125.77
3	2369	-30.08	-125.85
4	2448	-30.53	-127.74
5	2611	-29.97	-125.39
6	2736	-30.12	-126.02

Mean value of ΔH_1 = -30.14 ± 0.13 Kcal.mole^{-1} (-126.10 ± 0.68 Kj.mole^{-1})

Heat of Solution of Tri-n-Propyl Ammonium Perchlorate in 72% Perchloric Acid

The heat of solution data for the reaction

$$Pr_3NHClO_4(c) + (m+1)HClO_4nH_2O \longrightarrow [Pr_3NH^+ + ClO_4^-](m+1)HClO_4nH_2O \quad \ldots \Delta H_2$$

are recorded in table III.16.

Table III.16

t < 1 min.

Exp.	Dilution, m+1	ΔH_2	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	783.4	1.91	7.99
2	814.1	2.17	9.08
3	816.4	1.70	7.11
4	818.7	2.08	8.70
5	857.4	1.99	8.33
6	880.0	2.08	8.70

Mean value of ΔH_2 = 1.99 ± 0.14 Kcal.mole^{-1} (8.32 ± 0.57 Kj.mole^{-1})

Heat of Reaction of Tri-n-propylamine with dilute aqueous Perchloric Acid

The enthalpy data for the reaction

$$Pr_3N(l) + (p+1)HClO_4qH_2O \longrightarrow (Pr_3NH^+ + ClO_4^-)pHClO_4qH_2O \quad \ldots \Delta H_s$$

are recorded in table III.17.

Table III.17

t = 6-10 min.

Exp.	Dilution, q	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	4179	-16.47	-68.91
2	5327	-16.60	-69.45
3	6186	-16.36	-68.45
4	11492	-16.19	-67.74

Mean value of ΔH_s = -16.41 ± 0.17 Kcal.mole^{-1} (-68.66 ± 0.71 Kj.mole^{-1})

Heat of Solution of Ethylenediamine Diperchlorate (anhydrous) in Water

The heat of solution data for the reaction

$$(CH_2NH_3)_2(ClO_4)_2(c) + nH_2O \longrightarrow ((CH_2NH_3^+)_2 + 2ClO_4^-)nH_2O \ldots \Delta H_s$$

are recorded in table III.18.

Table III.18

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1484	12.63	52.84
2	2287	12.88	53.89
3	2303	12.88	53.89
4	2855	12.70	53.14
5	3050	12.84	53.72
6	4524	12.89	53.93
7	5108	12.72	53.22

Mean value of $\Delta H_s = 12.79 \pm 0.08$ Kcal.mole^{-1} (53.52 ± 0.33 Kj.mole^{-1})

Heat of Solution of Dimethyl Ammonium Chloride in Water

The heat of solution data for the reaction

$$(CH_3)_2NH_2Cl(c) + nH_2O \longrightarrow [(CH_3)_2\overset{+}{N}H_2 + Cl^-]nH_2O \;\ldots\; \Delta H_s$$

are recorded in table III.19.

Table III. 19

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	959.2	0.49	2.05
2	1099	0.48	2.01
3	1265	0.45	1.88
4	1476	0.45	1.88

Mean value of $\Delta H_s = 0.47 \pm 0.02$ Kcal.mole^{-1} (1.96 ± 0.09 Kj.mole^{-1})

Heat of Solution of Ethyl Ammonium Chloride in Water

The heat of solution data for the reaction

$$C_2H_5NH_3Cl(c) + nH_2O \longrightarrow [C_2H_5NH_3^+ + Cl^-]nH_2O \quad \ldots \Delta H_s$$

are recorded in table III. 20.

Table III. 20

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	979.5	1.97	8.24
2	1003	2.06	8.62
3	1330	2.01	8.41
4	1567	2.02	8.45

Mean value of $\Delta H_s = 2.02 \pm 0.04$ Kcal.mole^{-1} (8.43 ± 0.16 Kj.mole^{-1})

Heat of Solution of Dimethyl Ammonium Bromide in Water

The heat of solution data for the reaction

$$(CH_3)_2NH_2Br(c) + nH_2O \longrightarrow [(CH_3)_2\overset{+}{N}H_2 + Br^-]nH_2O \; \ldots \; \Delta H_s$$

are recorded in table III. 21.

Table III.21

t < 1 min.

Exp.	Dilution , n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1391	3.26	13.64
2	1827	3.28	13.72
3	1853	3.19	13.35
4	2306	3.30	13.81

Mean value of $\Delta H_s = 3.25 \pm 0.05$ Kcal.mole^{-1} (13.63 ± 0.20 Kj.mole^{-1})

Heat of Solution of Diethyl Ammonium Bromide

The heat of solution data for the reaction

$$(C_2H_5)_2NH_2Br(c) + nH_2O \longrightarrow [(C_2H_5)_2\overset{+}{N}H_2 + Br^-]nH_2O \; \ldots \; \Delta H_s$$

are recorded in table III. 22.

Table III.22

t < 1 min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1316	1.93	8.08
2	1539	1.90	7.95
3	1595	1.90	7.95
4	2289	1.95	8.16

Mean value of ΔH_s = 1.92 ± 0.02 Kcal.mole^{-1} (8.04 ± 0.10 Kj.mole^{-1})

Heat of Solution of Methyl Ammonium Nitrate

The heat of solution data for the reaction

$$CH_3NH_3NO_3(c) + nH_2O \longrightarrow [CH_3\overset{+}{NH_3} + \overset{-}{NO_3}]nH_2O \quad \ldots \quad \Delta H_s$$

are recorded in table III.23.

Table III.23

t < 1 min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1590	5.25	21.97
2	1901	5.29	22.13
3	2603	5.28	22.09

Mean value of ΔH_s = 5.27 ± 0.02 Kcal.mole^{-1} (22.06 ± 0.09 Kj.mole^{-1})

Heat of Solution of Trimethyl Ammonium Nitrate

The heat of solution data for the reaction

$$(CH_3)_3NHNO_3(c) + nH_2O \longrightarrow [(CH_3)_3NH^+ + NO_3^-]nH_2O \;\ldots\; \Delta H_s$$

are recorded in table III. 24.

Table III. 24

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1088	5.75	24.06
2	1645	5.67	23.72
3	1687	5.69	23.81
4	2196	5.70	23.85

Mean value of ΔH_s = 5.70 ± 0.03 Kcal.mole^{-1} (23.86 ± 0.14 Kj.mole^{-1})

Heat of Reaction of Triphenylmethanol with 72% Perchloric Acid

Sample A (c.f. Section 4a)

The enthalpy data for the reaction

$$Ph_3COH(c) + (m+1)HClO_4nH_2O \longrightarrow [Ph_3C^+ + ClO_4^-]mHClO_4(n+1)H_2O \;\ldots\; \Delta H_a$$

are recorded in table III. 25.

Table III. 25

t = 1-3 min.

Exp.	Dilution, m+1	ΔH_a	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	416.2	-2.81	-11.76
2	460.8	-2.70	-11.30
3	467.2	-2.65	-11.09
4	468.8	-2.74	-11.46
5	499.1	-2.94	-12.30
6	514.3	-2.98	-12.47

Mean value of ΔH_a = -2.80 ± 0.10 Kcal.mole^{-1} (-11.73 ± 0.46 Kj.mole^{-1})

The enthalpy data for sample B are recorded in table III. 26.

Table III. 26

Exp.	Dilution, m+1	ΔH_b	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	387.9	-3.13	-13.10
2	397.0	-2.86	-11.97
3	413.3	-2.99	-12.51
4	414.0	-3.06	-12.80
5	428.0	-3.06	-12.80
6	457.9	-2.93	-12.26
7	474.7	-2.88	-12.05

Mean value of ΔH_b = -2.99 ± 0.08 Kcal.mole^{-1} (-12.50 ± 0.36 Kj.mole^{-1})

Heat of Solution of Triphenylmethyl Perchlorate in 72% Perchloric Acid

The heat of solution data for the reaction

$$Ph_3CClO_4(c) + (m+1)HClO_4nH_2O \longrightarrow [Ph_3C^+ + \bar{ClO_4}](m+1)HClO_4nH_2O \quad \ldots \Delta H_2$$

are recorded in table III.27.

Table III.27

t = 3-6 min.

Exp.	Dilution, m+1	ΔH_2	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	669.6	3.15	13.17
2	1008	3.09	12.93
3	1126	3.07	12.84
4	1143	3.08	12.89
5	1159	3.06	12.80
6	1226	3.09	12.93

Mean value of $\Delta H_2 = 3.09 \pm 0.02$ Kcal.mole^{-1} (12.93 ± 0.11 Kj.mole^{-1})

Heat of Solution of Tri(p-tolyl)methyl Perchlorate in Glacial Acetic Acid

The heat of solution data for the reaction

$$Ar_3C\,ClO_4(c) + mAcOH \longrightarrow [ArC\,ClO_4]\,mAcOH \quad \ldots \Delta H_s$$

are recorded in table III.28.

Table III.28

t = 3 min.

Exp.	Dilution, m	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	7614	6.19	25.90
2	8442	6.38	26.69
3	9833	6.13	25.65
4	10411	6.30	26.36
5	11856	6.16	25.77

Mean value of ΔH_s = 6.23 ± 0.09 Kcal.mole^{-1} (26.07 ± 0.39 Kj.mole^{-1})

Heat of Hydrolysis of Tri(p-tolyl)methyl Perchlorate solution in Water

The heat of hydrolysis data for the reaction

$$(Ar_3CClO_4)mAcOH + (n+1)H_2O \longrightarrow Ar_3COH(c) + HClO_4mAcOHnH_2O$$

are recorded in table III.29

Table III.29

$t < 1$ min.

Exp.	Q (cals)	$10^2 n_1$	$10^4 n_2$	ΔH_2	
				Kcal.mole^{-1}	Kj.mole^{-1}
1	-12.479	4.030	2.29	-5.57	-23.30
2	-12.634	4.074	2.31	-5.66	-23.68
3	-12.850	4.145	2.35	-5.65	-23.64
4	-12.864	4.155	2.36	-5.56	-23.26
5	-12.901	4.169	2.37	-5.53	-23.14
6	-13.105	4.232	2.40	-5.58	-23.35
7	-13.194	4.267	2.42	-5.50	-23.01
8	-13.283	4.289	2.44	-5.57	-23.30
9	-13.358	4.314	2.45	-5.57	-23.30

Mean value of $\Delta H_2 = -5.58 \pm 0.03$ Kcal.mole^{-1} (-23.33 ± 0.14 Kj.mole^{-1})

Heat of Solution of Tri(p-methoxyphenyl)methyl Perchlorate in Glacial Acetic Acid

The heat of solution data for the reaction

$$ArCClO_4(c) + mAcOH \longrightarrow [Ar\,C\,ClO_4]mAcOH \quad \ldots \quad \Delta H_s$$

are recorded in table III.30.

Table III.30

t = 4-6 min.

Exp.	Dilution, m	ΔH_s	
		$Kcal.mole^{-1}$	$Kj.mole^{-1}$
1	7235	7.78	32.55
2	8482	7.72	32.30
3	8624	7.61	31.84
4	8691	7.92	33.14
5	8733	7.87	32.93

Mean value of $\Delta H_s = 7.78 \pm 0.11$ $Kcal.mole^{-1}$ (32.55 ± 0.46 $Kj.mole^{-1}$)

Heat of Hydrolysis of Tri(p-methoxyphenyl)methyl Perchlorate in Water

$(Ar_3CClO_4)mAcOH + (n+1)H_2O \longrightarrow Ar_3COH(c) + HClO_4mAcOHnH_2O$

The heat of hydrolysis data for the above reaction are recorded in table III.31.

Table III.31

$t < 1$ min.

Exp.	Q cals	$10^2 n_1$	$10^8 n_2$	ΔH_2	
				Kcal.mole^{-1}	Kj.mole^{-1}
1	-11.551	4.185	3.45	2.42	10.13
2	-11.548	4.192	3.46	3.05	12.76
3	-11.746	4.274	3.53	2.64	11.05
4	-11.955	4.293	3.54	2.34	9.79
5	-11.812	4.300	3.55	2.76	11.55
6	-11.882	4.328	3.57	2.44	10.21
7	-12.213	4.447	3.67	2.02	8.45
8	-12.342	4.495	3.71	2.22	9.29
9	-12.437	4.544	3.75	2.75	11.51
10	-15.528	5.836	4.82	2.87	12.01
11	-16.178	6.072	5.01	3.09	12.93

Mean value of $\Delta H_2 = 2.60 \pm 0.25$ Kcal.mole^{-1} (10.88 ± 1.05 Kj.mole^{-1})

Heat of Solution of Tetra-n-propyl Ammonium Bromide in Water

The heat of solution data for the reaction

$$(C_3H_7)_4NBr(c) + nH_2O \longrightarrow [(C_3H_7)_4N^+ + Br^-]nH_2O \;\ldots\; \Delta H_s$$

are reported in table III.32.

Table III.32

$t < 1$ min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	1542	-1.13	-4.73
2	2128	-1.16	-4.85
3	2338	-1.22	-5.10
4	2918	-1.16	-4.85

Mean value of $\Delta H_s = -1.17 \pm 0.04$ Kcal.mole^{-1} (-4.88 ± 0.17 Kj.mole^{-1})

Heat of Solution of Tetra-n-butyl Ammonium Bromide

The heat of solution data for the reaction

$$(C_4H_9)_4N\ Br(c) + nH_2O \longrightarrow [(C_4H_9)_4N^+ + Br^-]nH_2O \ \ldots \ \Delta H_s$$

are reported in table III.32.

Table III.33

t 1 min.

Exp.	Dilution, n	ΔH_s	
		Kcal.mole^{-1}	Kj.mole^{-1}
1	2902	-2.43	-10.17
2	3097	-2.12	-8.87
3	3579	-2.32	-9.71
4	3627	-2.03	-8.49
5	4504	-2.10	-8.79

Mean value of $\Delta H_s = -2.20 \pm 0.15$ Kcal.mole^{-1} (9.21 ± 0.63 Kj.mole^{-1})

APPENDIX IV

Computer Programme used to obtain the Temperature Change for a Moderate Reaction using the Equal Area assumption

The Fortran IV computer programme listed overleaf was used to obtain a 'best fit' curve for the resistance-time data of the reaction period in moderate reactions. A time XREQ, was calculated so that the shaded areas in Fig. I.1 were equal.(c.f. Appendix I)

In this programme N (integer) is the number of coefficients, up to a maximum of 10 and K (integer) is the number of points (maximum of 50). X(1) (real) is the time at which the reaction was started and the resistance value at this time is Y(1) (real). The input resistance values are compared with the computed resistance values (W) and the difference between these two values is shown by DIFF.

```
          DIMENSION F(10,10,10), G(10,10),B(10),X(50),Y(50)
          READ 100, N,K
100       FORMAT (2I5)
          READ 101, X(1)
101       FORMAT (F4.1)
          DO 20 I = 2,K
20        X(I) = X(I-1) + 0.5
          READ 102, (Y(I), I = 1,K)
102       FORMAT (6F8.3)
          DO 9 M = 1,N
          DO 9 I = 1,N
          DO 9 L = 1,N
9         F(M,I,L) = 0
          DO 10 M = 1,N
          DO 10 I = 1,N
          DO 10 J = 1,K
10        F(M,I,1) = F(M,I,1) + A(X,J,M-1)*A(X,J,I-1)
          DO 21 M = 1,N
          DO 21 L = 1,N
21        G(M,L) = 0
          DO 11 M = 1,N
          DO 11  J = 1, K
11        G(M,1) = G(M,1) + Y(J)*A(X,J,M-1)
          NA = N
          NB = N - 1
```

```
      DO 13 L = 2,NA
      DO 12 M = 1,NB
      DO 12 I = 1,NB
12    F(M,I,L) = F(M,I,L-1) - F(NB+1,I,L-1)*
     1F(M,NB+1,L-1)/F(NB+1,NB+1,L-1)
13    NB = NB - 1
      N = NA
      NB = N - 1
      DO 14 L = 2,NA
      DO 15 M = 1,NB
15    G(M,L) = G(M,L-1)-G(NB+1,L-1)*F(M,NB+1,L-1)/
     1F(NB+1,NB+1,L-1)
14    NB = NB - 1
      N = NA
C     BACK SUBSTITUTION BEGINS
      PRINT 200,
200   FORMAT(1H1,50X,21HCOEFFICIENTS A1 TO AN)
      B(1) = G(1,N)/F(1,1,N)
      PRINT 201, B(1)
      DO 16 J = 2,N
      L = N - J + 1
      SUM = 0.0
      JA = J - 1
      DO 17 I = 1,JA
17    SUM = SUM + B(I)*F(1,I,L)
```

```
            B(J) = (G(1,L) - SUM)/F(1,J,L)
            PRINT 201, B(J)
201         FORMAT(56X,F12.5)
16          CONTINUE
            PRINT 202,
202         FORMAT(//70X,32HTEST EQUATION WITH ORIGINAL
           1DATA//70X,1HX,6X,6HCALC Y,6X,7HINPUT Y,6X,
           24HDIFF)
            DO 18 J = 1,K
            W = 0.0
            DO 19 I = 1,N
19          W = W + B(I)*A(X,J,I-1)
            DIFF = Y(J) - W
            PRINT 203, X(J),W,Y(J),DIFF
203         FORMAT(67X,F4.1,4X,F8.3,4X,F8.3,4X,F8.3)
            IF(J.EQ.1) YMIN = W
            IF(J.EQ.1) XMIN = X(J)
18          CONTINUE
            YMAX = W
            XMAX = X(J)
            AREA = 0.0
            DO 50 LT = 1,N
50          AREA = AREA+(B(LT)*(XMAX**LT-XMIN**LT))/LT
            XREQ=(AREA-(YMAX*XMAX-YMIN*XMIN))/(YMIN-YMAX)
            PRINT 204, XREQ
```

```
204        FORMAT(30X,41HREQUIRED VALUE OF X TO GIVE
          1EQUAL AREAS =, F10.3)
           STOP
           END

           FUNCTION A(X,KC,L)
           DIMENSION X(50)
           IF(X.EQ.0) GO TO 1
           A = X(KC)**L
           RETURN
1          A = 1.0
           RETURN
           END
```

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