THERMOCHEMICAL AND KINETIC ASPECTS
OF METAL PICRATES

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ABSTRACT

The standard enthalpies of formation of ammonium picrate, picric acid, 2,4-dinitrophenol, 2,6-dinitrophenol and methylurea have been determined by oxygen static bomb calorimetry as

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{ONH}_4 \right) \text{(c)} = -385.44 \pm 2.94 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH} \right) \text{(c)} = -217.88 \pm 1.99 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \right) \text{(c)(2,4)} = -235.5 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_3(\text{NO}_2)_2\text{OH} \right) \text{(c)(2,6)} = -209.64 \pm 3.27 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{CH}_3\text{NHCONH}_2 \right) \text{(c)} = -327.74 \pm 1.41 \text{ kJ mol}^{-1}
\]

From solution calorimetry, standard enthalpies of formation have been found for the potassium, rubidium, caesium, silver, tetramethylammonium and tetraethylammonium salts of picric acid.

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OK} \right) \text{(c)} = -508.02 \pm 3.05 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OHb} \right) \text{(c)} = -508.17 \pm 3.02 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCS} \right) \text{(c)} = -520.96 \pm 3.20 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OAe} \right) \text{(c)} = -136.29 \pm 3.01 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{ON(CH}_3)_4 \right) \text{(c)} = -543.70 \pm 4.30 \text{ kJ mol}^{-1}
\]

\[
\Delta H_{f}^{\circ} \left( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{ON(C}_2\text{H}_5)_4 \right) \text{(c)} = -488.14 \pm 5.80 \text{ kJ mol}^{-1}
\]

The thermochemical radius of the picrate ion has been found to be 0.26 nm. Lattice energies for picrate salts have been calculated.

The solubilities of these picrates in water have been determined as a function of temperature. Enthalpies of solution derived from the solubility data have been compared with calorimetric enthalpies of solution.
The standard enthalpy of formation of guanidine chloride, \( \text{CH}_6\text{N}_3\text{Cl}(c) \), has been determined as \(-366.71^{\pm}4.00\) kJ mol\(^{-1}\), using solution calorimetry.

Tentative values for the thermochemical radii of the 2,4- and 2,6-dinitrophenolate ions have been assigned. Lattice energies for some salts of these substituted phenols have been calculated.

Differential scanning calorimetric and thermogravimetric techniques have been used in an attempt to evaluate kinetic parameters for the decomposition of certain picrates.
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\( 0 < n < 2 \)
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CHAPTER I

INTRODUCTION
INTRODUCTION

I - 1 - a: Historical background and uses of picric acid

Picric acid (2,4,6-trinitrophenol, \((\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}\)) is a compound of great importance, and it has been known since the 17th Century. Glauber treated wool and horn with nitric acid and obtained picric acid in the form of its metal salts. Nitration was well known to the alchemists and reactions between nitric acid and a variety of organic substances were widely used. Picric acid was obtained from indigo, resins, silk etc.

Woulfe prepared picric acid from indigo in 1771. He termed the substance "indigo yellow" since he found it possessed dyeing properties. In 1788, Haussmann showed that it behaved like an acid. In the coming years many workers showed that it could be obtained by treating various organic materials such as silk and resins with nitric acid. In 1799 it was prepared by the action of nitric acid on silk—the source of the picric acid was the tyrosine units in the protein.

\[ \text{Picric acid} \quad \text{tyrosine} \]

\[ \text{Indigo} \]

\[ \text{Indigo yellow} \]
In 1809, Chevreul postulated that picric acid contained "certain constituents of nitric acid." Dumas in 1836 confirmed this idea when he established the composition by analysis, and introduced the present name for the compound, which derives from the Greek word \( \pi \lambda \kappa \rho \omega \sigma \) meaning bitter. Marchand substantiated Dumas' results and gave the empirical formula as \( \text{C}_{12}\text{H}_6\text{N}_2\text{O}_14 \), double the correct formula. Dumas is also reported to have prepared picric acid from phenol. Up until this time, the method of preparation involved treating nitric acid with indigo. Marchand put forward the idea that it was aniline, formed as an intermediate product in the decomposition of indigo, silk, etc., which yielded picric acid when treated with nitric. This view was subsequently shown to be true.

Laurent determined the constitution of picric acid in 1841. He prepared it by reacting phenol with nitric acid, and he was also able to isolate dinitrophenol, which is formed in an intermediate stage of the nitration. Schmidt and Glutz improved the method of preparation from phenol by sulphonating before nitrating.

Picric acid was found to stain proteins yellow, and in 1849 it was introduced as a dye for silk. This was the first use of an artificial dye. In the second half of the 19th century, it was widely used as a fast dye for silk and wool.

The explosive characteristics of salts of picric acid had been noted at an early stage, but it was not until 1830 that Welter suggested the possibility of applying picrates as explosives. Designolle suggested the use of potassium picrate as a propellant, and Brugère forwarded the idea that the ammonium salt could be used for the same purpose. Abel proposed the use of ammonium picrate as a high explosive in 1871. In Great Britain and the United States at that time, potassium picrate was already being used for filling shells.
The general consensus of opinion was that picric acid itself was not an explosive. Sprengel\textsuperscript{14} soon showed, however, that picric acid could be detonated with mercury fulminate, \((\text{CNO})_2\text{Hg}\). Turpin\textsuperscript{15} proposed applying this property of picric acid by using it as a shell filling.

It was first adopted for use as a military explosive by the French. Kitchener used the then novel explosive lyddite (picric acid) to great advantage at the Battle of Omdurman. He achieved victory at the cost of only 48 British lives. The First World War saw extensive use of picric acid, particularly by the French and Italians. It was known by various names; lyddite (Great Britain), melinite (France), pertite (Italy) and Shimose (Japan). The compound was melted and poured into shell cases. In Russia, Panpushko\textsuperscript{16} developed methods of preparation for picric acid and worked on its use as a shell filling.

Eventually it came to be accepted all over the world as the basic high explosive for military use. There were, however, disadvantages. It is quite strongly acidic and corrodes the metal surfaces of the shells into which it is poured, with the formation of highly-sensitive heavy metal picrates. The iron (III), nickel and chromium salts of picric acid are more sensitive to impact than tetryl (N-methyl-N,2,4,6-tetranitroaniline, \((\text{NO}_2)_2C_6H_2\text{N}(\text{CH}_3)(\text{NO}_2)_2\)), and are classed as detonators. Lead picrate is particularly dangerous owing to its sensitivity to heat or shock.

Another disadvantage in the use of picric acid is its high melting point, 120–122°C. The best method of loading shells is by melting and pouring, but because of the high melting point, there is a greater probability of explosion, leading to a decreased margin of safety in loading.

By the early 20th century, the useful properties of TNT(2,4,6-trinitrotoluene) as a shell filler had been recognised, and the
importance of picric acid diminished. However, it was still widely used because of the ease of preparation, but when the methods of manufacture of TNT improved (toluene became more readily available e.g. from petrochemicals), the importance of picric acid dwindled even further.

Cast picric acid requires a booster of the tetryl type. Pure picric acid is stable under normal storage conditions. It has about the same sensitivity to shock and friction as TNT. Using the Trauzl block and ballistic pendulum tests, its strength lies between that of TNT and tetryl. With equal loading densities, picric acid produces a greater number of fragments than TNT when the two are compared by shell fragmentation tests. Appendix I describes some of the common tests for explosives.

Urbanski has produced a very comprehensive review on explosives and treats picric acid in detail. He has reviewed the explosive, physical, chemical and thermochemical properties of the compound as well as its toxicity.

I - 1 - b Biological aspects

It is generally accepted that picric acid is more toxic than TNT, but less so than the nitrobenzenes. Koelsch and Lebedev have described the symptoms of picric acid poisoning. Saladin reported that small doses in man cause no ill-effects. Karplus found that in mammals picric acid is partially converted into the more toxic picramic acid \((\text{NO}_2)_2(\text{NH}_2)\text{C}_6\text{H}_2\text{OH})\). Similarly, Barral has described experiments in which stems bearing flowers of Achillea ptarmica and other common flowers were immersed in picric acid solutions of varying concentration. Changes in the odour and colour of the flowers were observed as the acid was absorbed. Analysis revealed the presence of picramic acid in the flowers. In man, ingestion or percutaneous absorption may cause nausea, vomiting,
diarrhoea, abdominal pain, oliguria, anuria, yellow staining of the skin, pruritus, skin eruptions, stupour, convulsions and death.

However, it has been used beneficially as an antiseptic, an astringent and as a stimulant for epithelization. Due to its bactericidal activity, it has been used in the treatment of burns.

Potassium picrate was used in the 18th century for "medical purposes" under the name of Tinctura nitri Glauberi. Ishiwara reported in 1924 that a 0.04% aqueous solution of picric acid exhibits bactericidal activity against typhoid bacteria, staphylococci, streptococci and gonococci.

I - 1 - c Preparation of picric acid

Phenol is sensitive to oxidation, so picric acid cannot be satisfactorily prepared by the direct action of nitric acid. It is manufactured by either

(a) sulphonating phenol prior to nitration

or

(b) nitrating dinitrophenol made by the hydrolysis of chlorodinitrobenzene.

(a) Phenol as the starting material.

This process occurs in two stages:

(i) sulphonation of phenol

(ii) nitration of the sulphonated product.

On a large scale, phenol (1 part) is treated with sulphuric acid (4 to 6 parts, S.G. 1.84). Concentrated nitric acid (7.5 parts, S.G. 1.38) is then added with stirring at 10°C. After the addition is complete, the mixture is gradually warmed to 80-90°C until gas evolution ceases. Picric acid will crystallise out upon cooling.
The unsaturated sulphonic acid groups stabilise the molecule and provide protection against the oxidising action of nitric acid. Sulphonation is a reversible process, and the acid groups are easily replaced by nitro\textsuperscript{55}.

**(b) Chlorobenzene as the starting material.**

Both 2,4,6-trinitrophenol and 2,6-dinitrophenol are prepared on a large scale by the alkaline hydrolysis of aryl halides containing strongly electron-withdrawing groups o and p to the halogen.
Chlorobenzene is a cheaper starting material than phenol.

Benzene can be nitrated in the presence of mercuric salts, and during the 1914-18 war attempts were made to apply industrially the Wolfenstein and Böters process. Desvergnes reviewed this method some years later and concluded that pure picric acid can be obtained by this process, but the yield is rather low. The nitration of tribromophenol has been used to prepare bromine and picric acid, and the latter may also be made by nitrating 2-tert-butyl-4,6-dinitrophenol.
I - 1 - d Physical properties of picric acid

Picric acid is a yellow crystalline solid, m.p. 122°C, which exists in two polymorphic forms. When crystallised from alcohol it takes the form of yellow, orthorhombic flattened rods, but from water it crystallises in bright yellow plates. From solutions in ligroin or strong HCl, it separates as nearly colourless crystals. These become yellow on the surface in contact with air or moisture. The yellow colour of solid picric acid has been attributed to impurities\(^{52}\), but Ives and Moseley\(^{22}\) disagree. They think that the colour is not due to impurities (although these may increase the depth of the colour), but to some structural feature (perhaps associated with internal hydrogen bonding) of the normal crystals. They do not elaborate upon this point. The orientation and intramolecular hydrogen bonding of the nitro groups in picric acid has been studied very recently.\(^{53}\) Crystals of picric acid are orthorhombic, space group P\(_{ca}\)\(^{2}\). The cell dimensions are 
\[a = 9.621\,\text{Å}, \quad b = 19.137\,\text{Å}, \quad c = 9.714\,\text{Å}.\]
There are eight molecules per unit cell. Similar results were obtained in an earlier determination.\(^{62}\)

Picric acid has a low solubility in cold water (1.4g/100g water at 25°C), but is more soluble in hot water (7g/100g water at 100°C) and organic solvents.\(^{63,64}\) A small amount of picric acid is sufficient to colour a large volume of water a distinct yellow colour. It possesses a persistent bitter taste and shows no tendency to absorb moisture from the atmosphere.

The three nitro groups in the molecule enhance the acidic properties of the phenolic group. The compound is quite strongly acid, but literature values for pK\(_a\) show some variation. Table I - 1 lists the pK\(_a\) values of some organic acids in aqueous solution — a typical value
for picric acid may be compared with values for other nitrophenols, phenol itself, and acetic and benzoic acids. Table I – 2 lists some of the reported values for picric acid. Ives and Moseley have reviewed the literature concerning methods for the determination of $pK_a$.

It has no resistence to strong oxidising agents: boiling with nitric acid yields oxalic acid, whilst treatment with boiling aqueous persulphate forms $\text{NO}_2$, $\text{NO}_3$, and HCN. Phosphoric acid is formed when picric acid is treated with a reducing agent with an oxidising sulphuric or fuming sulphuric. Boiling with concentrated nitric acid hydrosulphide may result in the decomposition of the ring.

It may also be decomposed by hypochlorite, leading to the formation of chloropicrin.

$$\text{C}_8\text{H}_3\text{(NO}_2\text{)}_3 \text{H}_3 \rightarrow \text{H}_3\text{CONO}_2\text{H}_2 \text{O} \rightarrow \text{C}_8\text{H}_2\text{(NO}_2\text{)}_3 \text{Cl}_3$$

When treated with chlorine, aqueous or potassium hypochlorite in the presence of hydrochloric acid, picric acid yields chloropicrin along with chloropicrin:

$$\text{C}_8\text{H}_3\text{(NO}_2\text{)}_3 \text{H}_3 \rightarrow \text{H}_3\text{CONO}_2\text{H}_2 \text{O} \rightarrow \text{C}_8\text{H}_2\text{(NO}_2\text{)}_3 \text{Cl}_3$$
I - 1 - e Reactions of picric acid

Picric acid will decompose carbonates and will readily form salts with metals or bases. Polynitro derivatives of phenol can form addition compounds with hydrocarbons and amines, and the picrates are often used for the identification of the parent compound.

It has no resistance to strong oxidizing agents – boiling with nitric acid yields oxalic acid, whilst treatment with boiling ammonium persulphate forms $\mathrm{CO}_2\cdot\mathrm{HNO}_3$ and HCN. Picramic acid is formed when picric acid is treated with a reducing agent such as sodium sulphide or ferrous sulphate. Boiling with concentrated sodium hydroxide may result in the decomposition of the ring.

It may also be decomposed by hypochlorites, leading to the formation of chloropicrin.

$$\ce{C_6H_2(NO_2)_3OH + 11HOCl \xrightarrow{85^\circ C} 3CCl_3.NO_2 + 3CO_2 + 6H_2O + 2HCl}$$

When treated with chlorine, aqua regia or potassium chlorate in the presence of hydrochloric acid, picric acid yields chloranil along with chloropicrin.

$$\ce{C_6H_2(NO_2)_3OH + Cl_2 \rightarrow CCl_3.NO_2 + Cl_2}$$
Sulphur will react with picric acid that has been heated to above its melting point. Addition of sulphur lowers the ignition temperature of \( \text{C}_6\text{H}_2(\text{NO}_2)_3 \text{OH} \).

Picryl chloride is formed when picric acid is treated with PCl\(_5\). The chlorine atom in picryl chloride is very reactive (due to the presence of three nitro groups in the ring), e.g.: when boiled with water it forms picric acid and when shaken with concentrated ammonia solution picramide results. Phenol itself gives a very poor yield of chlorobenzene with PCl\(_5\), but the more strongly acidic nitrophenols give fairly good yields of the nitrochloro-compounds.

The reactions of picric acid are summarised in fig. I - 1.
Fig. I-1 The reactions of picric acid.
Salts of picric acid

Metallic salts of picric acid are formed by its action on metals, their oxides, hydroxides and carbonates. They are crystalline substances, and are usually more sensitive to stimuli than the parent compound. Their explosive properties were known long before those of picric acid itself. Most picrates crystallise from aqueous solution as the hydrated salts — some heavily so; e.g.: the iron (III) salt has 10 molecules of water of crystallisation, whilst the aluminium salt has 16. Water of crystallisation desensitises the salts e.g: ferric picrate decahydrate is not sensitive to friction and impact whereas the anhydrous salt is exceptionally so. The salts used in this study however (potassium, rubidium, caesium, silver, ammonium, tetramethylammonium and tetraethylammonium) all crystallise from water in the anhydrous form.

The properties of picrates were the subject of several very comprehensive early investigations. Dupré listed several metal picrates in order of the violence of the explosion obtained when heated to explosion point. He reported that the picrates of calcium, lead and zinc, formed in situ, were capable of initiating explosion in molten picric acid. Will compared some of the more common picrates with other explosives by sensitiveness to impact tests. Silberrad and Phillips summarised the chemical properties of a large number of picrates, and reported explosion temperatures of the anhydrous forms. In 1911, Kast was the first to correlate the chemical and explosive properties of the salts, and he pointed out the effect of varying amounts of water of crystallisation on sensitiveness to impact. It was found that picrates free of whatever water of crystallisation that could be removed by drying at 100°C were more sensitive than the same salts dried in vacuo at room temperature. Taking into account water of crystallisation, he
concluded that the salts of picric acid, with the exception of those of ammonium and aluminium (basic), were more sensitive than the acid itself; heavy metal salts (e.g.: Pb, Fe, Cu, Ag) are the most sensitive, followed by the alkaline earth metals, and then the alkali metal salts. However, even the most sensitive, anhydrous lead, is, according to Kast, less sensitive than guncotton or dynamite. Vill^1^ placed lead, iron and copper picrates in the same class as mercury fulminate and nitroglycerin, whilst classing zinc, sodium and ammonium picrates with compounds of the TNT type. He reported that the alkaline earth picrates were less sensitive than picric acid. (Will had dried his samples at 40°C).

Hopper^3^ undertook an investigation to clarify this situation. He also reached the conclusion that the relative sensitivity depends upon the amounts of water of crystallisation present — highly hydrated forms being highly insensitive and anhydrous salts most sensitive. It was reported that anhydrous salts (with the exception of sodium, ammonium, aluminium and ferrous) were more sensitive to percussion than picric acid itself. Anhydrous copper, zinc and cadmium picrates are slightly more sensitive, whilst anhydrous nickel is especially so.

Răscănu^3^ lists all picrates prepared until 1939, including addition compounds as well as metallic salts. Aggarwal and Singh^3^ prepared some first-row transition metal picrates and characterised them by molar conductance, magnetic susceptibility, infra-red and electronic spectroscopy measurements.

Tucholski^3^ studied the thermal properties of many picrates, and determined dehydration temperatures, melting points and explosion temperatures for Groups I, II, III and transition metal salts. He found that in some respects they behaved like the triazides^3^7^. A special study was also made of the thermal decomposition of potassium picrate.

Other work dealing with the thermal analysis of picrates is reviewed.
more fully in Chapter III. Table I - 3 lists the properties of some picrate salts.

I - 2 - b: Ammonium picrate $C_6H_2(NO_2)_2\cdot ONH_4$

This has found extensive use as a military explosive, and is known as Explosive D and dunnite. It is less sensitive to shock than picric acid, and does not form dangerous metal salts. Explosive D is equal to TNT in power and brisance, but is, however, less sensitive, although it can be used satisfactorily with a tetryl booster. Were it not for the fact that it is a high melting solid ($265^\circ-271^\circ C$ with decomposition), it might be preferred to TNT as a general shell filling. Since it withstands the shock of impact better than TNT, it finds specific use as a charge for armour-piercing shells. First prepared by Marchand in 1841, it was formerly used by Brugère (in 1869) in a mixture with potassium nitrate as a substitute for black powder.

Ammonium picrate crystallises from water as the anhydrous salt and its solubility at $20^\circ C$ is $1.1g/100g$ of water and $74.8g/100g$ water at $100^\circ C$. Alkali will decompose ammonium picrate into picrate ion and ammonia. It has been reported that at $0^\circ C$ it absorbs one molecule of ammonia which is lost at $26^\circ C$.

Of particular interest is the fact that ammonium picrate exists in two modifications, a red form and a yellow one. No satisfactory explanation has been offered as to the difference between the two even though many detailed studies have been made. The existence of two forms was recognised as early as 1849 by Cahours. Dehn and Ball thought that the 2 forms were, as Hantzsch suggested, chromoisomers, and that the phenolic form should be assigned to the yellow modification, whilst the red one should be regarded as the quinonoid form. According to Hantzsch nitrophenols
exist in a phenolic, colourless form (I) and a quinonoid, coloured form (IIa, IIb). With picric acid, the forms are

\[
\begin{align*}
\text{OH} & \quad \text{NO-OH} \\
(\text{I}) & \\
\text{NO}_2 & \quad \text{O}_2\text{N} \\
(\text{IIa}) & \\
\text{NO}_2 & \quad \text{O}_2\text{N} \\
(\text{IIb}) & \\
\text{NOOH} & 
\end{align*}
\]

Mitchell and Bryant expressed the opinion that the red modification is not a distinct polymorph but a slightly contaminated form of the yellow salt. Stammler refutes the suggestion that phenolquinone tautomerism is responsible for the two colours. He thinks that the variation in colour may be due to a small excess of ammonium ions in the lattice, and this is compensated for electronically by localised hydroxyl or picryl ions. The two forms give the same spectrum in aqueous solution and exhibit identical X-ray powder patterns.

(The crystal structure of ammonium picrate has been determined (yellow form). The crystals are orthorhombic, space group Ibca (No. 73) and the cell dimensions are 13.45, 19.74, and 7.12 Å. The unit cell contains eight formula units. The phenoxide carbon-oxygen bond length is 1.23 Å, and the carbon-carbon bond lengths are 1.45 Å and 1.37 Å. The bond angle in the benzene ring at the carbon attached to the oxygen is 111°. The benzene ring is found to be planar within experimental error, but the nitro groups are not coplanar with the ring - the dihedral angles being 6° for the para group and 27° for
The method of preparation seems to dictate the form that is obtained. Hale found that the more concentrated the ammonia solution used to neutralise the picric acid, the darker (more red) the salt obtained. Urbanski, Hackel and Galas made similar findings—they state that the higher the pH of the solution in which the picric acid was neutralised, the more readily the red crystals formed. Neutralising picric acid with ammonium carbonate solution produces the yellow modification, whereas by using a 25% ammonia solution for neutralisation the red form results. Stammel produced red ammonium picrate by refluxing picric acid with concentrated ammonia solution for 24 hours.

Hale states that upon heating to 150°C, the red form changes into yellow. Stammel, however, found that ammonium picrate underwent a phase transition at 210°C; this was confirmed in the present work. This transition occurs in both the yellow and red forms, and it seems likely that both red and yellow room temperature modifications undergo transition to a high temperature yellow form. It is a reversible transition and results in the formation of the low temperature yellow form, regardless of the colour of the starting material. Many picrates exhibit phase transitions, and a convenient way of studying these is by Differential Scanning Calorimetry (D.S.C.) (see Chapter III). Chromoisomers are also known for thallium, barium (brown and yellow) and strontium (red and yellow) picrates.

Urbanski has reviewed the explosive properties of the two forms and concluded that there is little difference in the explosive properties. He also reviews the thermochemical properties of the red and yellow modifications—these are discussed more fully in Chapter II.

Ammonium picrate was manufactured by neutralising a hot aqueous solution of picric acid with aqueous ammonia. After the salt
had crystallised out, it was dried in a stream of warm air at 45°C for 8 hours. The dried crystals were then screened and packed.

Some authors state that ammonium picrate is hygroscopic and report that samples have been known to absorb 5% by weight of water during one month's storage in an atmosphere saturated with moisture. Explosive D is not markedly toxic, but it will discolour the skin and has been known to cause dermatitis. Alkyl substituted ammonium picrates are known, e.g. the tetramethylammonium and tetraethylammonium salts are soluble in water, the tetrabutylammonium salt is not so.

I - 2 - c: Silver picrate $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{OAg}$

Silver picrate, also known as pikratol or picragol, was prepared in 1809 by Chevreul, and recognised by Liebig as an explosive. Silberrad and Phillips established the formula and found that it exploded feebly at 336-44°C. It is used to combat granular vaginitis of cattle.

I - 2 - d: Potassium picrate $\text{C}_6\text{H}_2(\text{NO}_2)_2\text{OK}$

Potassium picrate exists as reddish or yellow rhombic crystals and was first prepared by Glauber. It was used as early as 1869 in explosives such as poudres Designolles (potassium picrate, potassium nitrate and charcoal) and poudres Fontaine (potassium picrate and potassium chlorate). Use has also been made of it in pyrotechnic whistle compositions, propellants such as Ballistite, and in some primer mixtures, i.e.: potassium picrate, lead picrate and potassium chlorate. Polymorphism in potassium picrate has been reported. These modifications are termed types A, B and C. Type A is the form obtained when picric acid in water/alcohol solution is neutralised using KOH solution. Type B results when using as solvent either methylated spirit at room temperature, or isopropyl or amyl alcohols at temperatures above 50°C. Water must be excluded from the system.
as B rapidly converts to A in its presence. The production of B is favoured by (i) use of alcoholic solvents (ii) elevated reaction temperatures and (iii) rapid mixing of solutions. Type C is obtained by heating type A to 260°C but Type B does not appear to show a transition to a high temperature form.

The crystal structure of potassium picrate (type A) has been determined by a number of authors. The crystals are orthorhombic, space group Ibca (No. 73) and the cell dimensions are a = 13.33, b = 19.09 and c = 7.14 Å. The unit cell contains eight formula units. The phenoxide carbon-oxygen bond length, and the bond lengths and bond angles are as for ammonium picrate.

Potassium picrate melts before it decomposes violently. The density of type A material is 1.95 g cm⁻³. It is slightly soluble in cold water (0.5g/100g of water at 15°C), more so in hot water (25g/100g at 100°C), and crystallises from water as the anhydrous salt.

I - 2 - e: Lead picrate

The lead salts of picric acid are amongst the most sensitive picrates known, and have found use as military explosives in the past. During the Second World War, the Germans employed, on a small scale, cap compositions containing lead picrate for the manufacture of electric fuses giving few gaseous products. Lead picrate monohydrate was patented in France in 1872 for use in caps and primers. Anhydrous lead picrate, \( \text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}_2\text{Pb} \), can be obtained by heating either the monohydrate or tetrahydrate to 150°C. The tetrahydrate is obtained in the form of silky yellow needles when an aqueous solution of picric acid is treated with lead carbonate. The German method of preparation involved adding picric acid to lead nitrate in ice water, maintaining the temperature below 10°C. Since the temperature rises with the precipitation of lead picrate, further ice-water must be
added. Many basic lead picrates are known, e.g., Pb(Pic)$_2$.2PbO, Pb(Pic)$_2$.PbO.$H_2$O, and Pb(Pic)$_4$.4PbO. The various forms are obtained using different methods of preparation. A basic form is also known for aluminium picrate: [C$_{6}$H$_{5}$NO$_{2}$)$_{3}$AlOH.7$H_2$O.

1 - 2 - f: Addition compounds

Like other polynitroaromatic compounds, picric acid readily forms addition compounds with other aromatics. Adducts with phenols, aromatic ketones and even with other nitro compounds are known. Table 1 - 4 lists some of the known 1:1 addition compounds. With m - cresol, picric acid forms a compound containing the two constituents in the molecular proportion of 1:2 that melts at 61.6°C. Two non-uniformly melting compounds are formed with salicylic aldehyde in the proportions of 1:1 (m.p. 55°C) and 1:2 (m.p. 55°C). A series of compounds containing the constituents in proportions from 1:1 to 1:5 are formed with m - hydroxybenzoic aldehyde.

1 - 2 - g: Amine picrates

Picrates are also yielded with amines. Some of them, such as quinine or quinoline picrates are insoluble in water. Guanidine picrate has been used in this work. It was prepared by treating a warm aqueous solution of ammonium picrate with aqueous guanidine nitrate. A yellow, crystalline substance that is insoluble in water, guanidine picrate melts at ca. 320°C with decomposition. Urbanski$^1$ reports that in the United States it has been suggested for use as a high explosive, being of exceptionally low sensitivity to impact and friction.
<table>
<thead>
<tr>
<th>Acid</th>
<th>Temp/°C</th>
<th>$K$</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic</td>
<td>25</td>
<td>1.76x10$^{-5}$</td>
<td>4.75</td>
</tr>
<tr>
<td>Benzoic</td>
<td>25</td>
<td>6.46x10$^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>Phenol</td>
<td>20</td>
<td>1.28x10$^{-10}$</td>
<td>9.89</td>
</tr>
<tr>
<td>o-nitrophenol</td>
<td>25</td>
<td>6.8x10$^{-8}$</td>
<td>7.17</td>
</tr>
<tr>
<td>m-nitrophenol</td>
<td>25</td>
<td>5.3x10$^{-9}$</td>
<td>8.28</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>25</td>
<td>7 x 10$^{-8}$</td>
<td>7.15</td>
</tr>
<tr>
<td>2,4-dinitrophenol</td>
<td>15</td>
<td>1.1x10$^{-4}$</td>
<td>3.96</td>
</tr>
<tr>
<td>3,6-dinitrophenol</td>
<td>15</td>
<td>7.1x10$^{-6}$</td>
<td>5.15</td>
</tr>
<tr>
<td>Picric acid</td>
<td>25</td>
<td>4.2x10$^{-1}$</td>
<td>0.38</td>
</tr>
</tbody>
</table>

All values taken from reference 69
### TABLE 1 - 2

**SOME $pK_a$ VALUES FOR PICRIC ACID (25°C)**

<table>
<thead>
<tr>
<th>$pK_a$</th>
<th>Reference</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>70</td>
<td>absorbance</td>
</tr>
<tr>
<td>0.27 ($20^\circ{C}$)</td>
<td>70</td>
<td>absorbance</td>
</tr>
<tr>
<td>0.37</td>
<td>70</td>
<td>absorbance</td>
</tr>
<tr>
<td>0.22</td>
<td>71</td>
<td>conductance</td>
</tr>
<tr>
<td>0.71</td>
<td>72</td>
<td>conductance</td>
</tr>
</tbody>
</table>

See also reference 73.
<table>
<thead>
<tr>
<th>M</th>
<th>WATER OF CRYSTALLISATION</th>
<th>TEMPERATURE OF DEHYDRATION TO NEXT LOWEST HYDRATE/ °C</th>
<th>EXPLOSION TEMP/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>H₂O</td>
<td>150</td>
<td>310-315</td>
</tr>
<tr>
<td></td>
<td>anhydrous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>anhydrous</td>
<td></td>
<td>311-316</td>
</tr>
<tr>
<td>NH₄</td>
<td>anhydrous</td>
<td></td>
<td>decomposes at ca.250 °C</td>
</tr>
<tr>
<td>Rb</td>
<td>anhydrous</td>
<td></td>
<td>300-315</td>
</tr>
<tr>
<td>Cs</td>
<td>anhydrous</td>
<td></td>
<td>272-277</td>
</tr>
<tr>
<td>Li</td>
<td>4H₂O</td>
<td>80</td>
<td>318-323</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anhydrous</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>anhydrous</td>
<td></td>
<td>336-341</td>
</tr>
<tr>
<td>Tl</td>
<td>anhydrous</td>
<td></td>
<td>273-275</td>
</tr>
<tr>
<td>Pb</td>
<td>4H₂O</td>
<td>80</td>
<td>270-275</td>
</tr>
<tr>
<td></td>
<td>H₂O</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>9H₂O</td>
<td>59</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6H₂O</td>
<td>82</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4H₂O</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2H₂O</td>
<td>208</td>
<td></td>
</tr>
<tr>
<td></td>
<td>anhydrous</td>
<td></td>
<td>368</td>
</tr>
</tbody>
</table>
### TABLE 1-4:

**SOME 1:1 ADDITION COMPOUNDS FORMED BY PICRIC ACID**

<table>
<thead>
<tr>
<th>Second Component</th>
<th>m.p./°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>ca. 141 (non uniform melting)</td>
</tr>
<tr>
<td>Benzene</td>
<td>84</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>150</td>
</tr>
<tr>
<td>Phenol</td>
<td>85</td>
</tr>
<tr>
<td>Resorcinol</td>
<td>100</td>
</tr>
<tr>
<td>o - cresol</td>
<td>89.8</td>
</tr>
<tr>
<td>p - cresol</td>
<td>ca. 65.6 (non uniform melting)</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>27 (readily dissociates)</td>
</tr>
<tr>
<td>Cinnamic acid</td>
<td>106.5</td>
</tr>
</tbody>
</table>

- a) 310°C (non uniform melting)
- b) 27 (readily dissociates)
REFERENCES - CHAPTER I

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   Ann., 43 (1842) 200.
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CHAPTER II

THERMOCHEMISTRY

II - 1: General Introduction

The thermochcmistry of picrates has not been neglected in the past. C. Ageron and Tscheltes in 1893 measured the heat of formation of solid picric acid and its salts (see Table II-2). The first attempt to undertake a combustion study of ammonium picrate appears to have been that of Assime and Pichl (1931). Both ammonium picrate and picric acid have since been burned on a number of occasions (Tables II-1 and II-2) and values for standard

enthalpies of formation of certain metal picrates have also been determined by reaction calorimetry. Why then is the present study so

doubted to be necessary?

Reference to Tables II-1 and II-2 shows that there is near agree-

ment between the reported values for the enthalpies of formation of both picric acid and its salts. The published figures for

sodium and potassium picrate do not appear to be correct. For the

sodium and potassium picrate, the figures for the salts have been interchanged. This error is in the original Russian paper, the

English translation and has found its way into the data books. It is

not a matter of interest to note that in the English translation, the

phrase is entitled "Standard Enthalpies of Formation of Picric Acid

and Certain Picrates" and several times in the course of this

translation, picrates are referred to as nitrate.

In this Russian paper (due to lapse or to the co-authored), the

following scheme was used:

1. $\text{C}_3\text{H}_7\text{NO}_3 \rightarrow \text{C}_3\text{H}_7\text{NO}_3$ (in $\Delta H$) $\text{Na}(\text{picrate}) \rightarrow \text{Na}(\text{NO}_3)$

2. $\text{C}_3\text{H}_7\text{NO}_3 \rightarrow \text{C}_3\text{H}_7\text{NO}_3$ (in $\Delta H$) $\rightarrow \text{Na}(\text{picrate}) \rightarrow \text{Na}(\text{NO}_3)$

$\text{C}_3\text{H}_7\text{NO}_3 \rightarrow \text{C}_3\text{H}_7\text{NO}_3$ (in $\Delta H$)
II - 1: General Introduction

The thermochemistry of picrates has not been neglected in the past — Berthelot\(^1\) in 1873 and Tschebitschow\(^2\) in 1886 measured enthalpies of solution in water of picric acid and its salts (see Table II - 28). The first attempt to undertake a combustion study of ammonium picrate appears to have been that of Sarrau and Vieille\(^3\) in 1881. Both ammonium picrate and picric acid have since been burned on a number of occasions (Tables II-1 and II-2) and values for standard enthalpies of formation of certain metal picrates\(^4\) have also been determined via reaction - calorimetry. Why then is the present study deemed to be necessary?

Reference to Tables II-1 and II-2 shows that there is poor agreement between the reported values for the enthalpies of formation of both picric acid and its ammonium salt. The published figures for sodium and potassium picrate\(^4\) do not appear to be correct. Due to, presumably, a printer's error, the figures for the salts have been interchanged. This error is in the original Russian paper, the English translation and has found its way into the data books.\(^5\) It is also of interest to note that in the English translation, the paper is entitled "Standard Enthalpies of Formation of Picric Acid and Certain Nitrates" and several times in the course of this translation, picrates are referred to as nitrates.

In this Russian paper (due to Vorob'ev\(^4\) and his co-workers), the following scheme was used

1. \[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}(\text{s}) + \text{XH}_2\cdot0 = \text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OM} \text{ soln. in XH}_2\cdot0 \]
\[\Delta H_1\]
2. \[\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}(\text{s}) + \text{MOH(\text{soln. in XH}_2\cdot0)}\]
\[= \text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OM(\text{soln. in XH}_2\cdot0)} \quad \Delta H_2\]
\[+ \text{H}_2\cdot0(\text{in soln. of C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OM})\]
3. \[ \text{6C(graphite)} + \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{N}_2(\text{g}) + 3\frac{1}{2} \text{O}_2(\text{g}) = \text{C}_6\text{H}_2(\text{NO}_2)_3 \text{OH(s)} \] \[ \Delta H_3 \]

4. \[ \text{M(s)} + \frac{1}{2} \text{O}_2(\text{g}) + \frac{1}{2} \text{H}_2(\text{g}) + \text{XH}_2\text{O} = \text{MOH(soln. of MOH in XH}_2\text{O)} \] \[ \Delta H_4 \]

5. \[ \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + \text{soln. of C}_6\text{H}_2(\text{NO}_2)_3 \text{OM in XH}_2\text{O} = \text{H}_2\text{O}(\text{soln. of C}_6\text{H}_2(\text{NO}_2)_3 \text{OM in XH}_2\text{O)} \] \[ \Delta H_5 \]

6. \[ \text{6C(graphite)} + \text{H}_2(\text{g}) + 1\frac{1}{2} \text{N}_2(\text{g}) + 3\frac{1}{2} \text{O}_2(\text{g}) + \text{M(s)} = \text{C}_6\text{H}_2(\text{NO}_2)_3 \text{OM(solid)} \] \[ \Delta H_6 \]

Hence \[ \Delta H_6 = \Delta H_2 + \Delta H_3 + \Delta H_4 - \Delta H_1 - \Delta H_5 \]

\[ \Delta H_1 \text{ = enthalpy of solution of picrate in water} \]

\[ \Delta H_2 \text{ = enthalpy of neutralisation of picric acid} \]

\[ \Delta H_3 \text{ = enthalpy of formation of picric acid} \]

\[ \Delta H_4 \text{ = enthalpy of formation of hydroxide solution} \]

\[ \Delta H_5 \text{ = enthalpy of formation of water} \]

\[ \Delta H_6 \text{ = enthalpy of formation of picrate} \]

Vorob'ev et al., tabulated their results as shown in Table II-3

<table>
<thead>
<tr>
<th>Cation</th>
<th>( \Delta H ) soln</th>
<th>( \Delta H ) neut</th>
<th>( \Delta H^o ) OH soln.</th>
<th>( \Delta H^o ) X soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>4.84</td>
<td>-8.32</td>
<td>-112.39</td>
<td>-118.45</td>
</tr>
<tr>
<td>K(^+)</td>
<td>12.17</td>
<td>-8.22</td>
<td>-115.24</td>
<td>-108.37</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>1.53</td>
<td>-8.19</td>
<td>-121.40</td>
<td>-113.94</td>
</tr>
<tr>
<td>NH(_4)(^+)</td>
<td>10.89</td>
<td>-7.07</td>
<td>-87.64</td>
<td>-88.42</td>
</tr>
</tbody>
</table>

(all values in kcal mol\(^{-1}\))

\[ \Delta H_3 = -51.14 \text{ kcal mol}^{-1} \]

\[ \Delta H_5 = -68.32 \text{ kcal mol}^{-1} \]
Using these values for $\Delta H_3$ and $\Delta H_5$ and substituting $\Delta H_1$, $\Delta H_2$ and $\Delta H_3$ as appropriate gives

$\Delta H_f^o$ Na picrate $\quad - 108.37$ kcal mol$^{-1}$

$\Delta H_f^o$ K picrate $\quad - 118.45$ kcal mol$^{-1}$

and not as published in the paper.

So, these results are based upon a combustion study of picric acid and if this combustion is wrong, then this will mean that the values for the metal picrates are also suspect.

The main aims of this work then were

(i) to establish standard enthalpies of formation, $\Delta H_f^o$, of ammonium picrate, picric acid and certain metal and alkyl-substituted ammonium picrates.

(ii) to calculate the "thermochemical radius", $r_{th}$, of the picrate ion, once values for the standard enthalpies of formation of at least two metal picrates were known (assuming data for $\Delta H_f^o (M^{n+}, g)$ and $r_{M^{n+}}$ are available).

(iii) to use the value of the thermochemical radius obtained to calculate lattice energies using the Kapustinskii equation.

(iv) to calculate the standard enthalpy of formation of the gaseous picrate ion, $\Delta H_f^o (Pic^-, g)$, using these calculated lattice energies. Knowing this quantity enables calculation of $\Delta H_f^o (MPic, c)$ for any M (provided $\Delta H_f^o (M^{n+}, g)$ and $r_{M^{n+}}$ are known).

The following cycle will be considered
The concept of the thermochemical radius, its calculation, and calculations involving the Kapustinskii equation are explained more fully in II-9.
II - 2: COMBUSTION CALORIMETRY

II - 2-a: Introduction

Combustion calorimetry is a well established process. As early as 1784 Lavoisier and Laplace obtained heats of combustion using an ice calorimeter. Later, in 1848, Andrews developed the first bomb calorimeter, and determined heats of combustion of hydrocarbons (methane and ethane), hydrogen, carbon monoxide, sulphur, phosphorus, carbon and many metals. His calorimeter was a thin copper vessel and he obtained a value for its water equivalent by summing the products of the masses of the component parts and their respective specific heats.

M.P.E. Berthelot in Paris made many contributions to the science of combustion calorimetry. His bomb was constructed of large amounts of platinum and steel (1300g of platinum and 2750g of steel) and hence proved to be very expensive. Mahler developed a bomb in which the platinum lining was replaced by enamel. Although this did make construction costs cheaper, the enamel was not as corrosion resistant as platinum. Parr designed a bomb made of a nickel-chromium alloy (illium) which had acceptable acid-resistant properties.

Modern innovations in combustion calorimetry include moving-bomb methods and fluorine combustion. A comprehensive review of combustion calorimetry and the contributions made by prominent workers in the field can be found in the book edited by Sunner and Mansson.

The bomb used throughout the course of this work was of the static oxygen type. Compounds containing carbon, hydrogen, oxygen and/or nitrogen are easily handled in this type of equipment. Halogen or sulphur containing compounds give corrosive products upon combustion and the bomb must be lined with an inert material, e.g.: platinum or tantalum. Another serious problem arising from the burning of halogen or sulphur
containing compounds in static bombs is the inhomogeneity of the final state. Development of the moving-bomb and rotating bomb\textsuperscript{15-18} ensured the homogeneity of the final state of the combustion products and opened up a whole new realm for the combustion calorimetrist.

\textbf{II -2-b: Background to a Combustion Experiment}

A combustion experiment essentially consists of two parts:

(a) chemical

and (b) calorimetric

In (a), the nature, Stoichiometry and extent of the bomb reaction must be established. Materials used for combustion must be very pure since the purity of the sample used can significantly influence the overall accuracy of the determination. Unless the impurities are isomeric with the host, the effective relative molecular mass will not be that calculated from tables and hence the number of moles of reaction will be in error. The impurities themselves may well undergo reaction and contribute to the energy change. Standard enthalpies of formation are obtained as the difference between two large quantities - the enthalpy of combustion and the enthalpy of formation of any carbon dioxide and water produced. The energy of combustion is obtained experimentally as the quantity per gramme and any errors in this (and not only those due to impurities) will of course be scaled up by the RMM to obtain the molar quantity, such that a small error in \(-\Delta H^o_c / \text{kJ g}^{-1}\) could amount to quite a significant one in \(-\Delta H^o_f\).

The thermodynamic state of the sample must be established—if it does exist in more than one form, the relative proportions must be found.

If the sample will be affected by a moist atmosphere of high pressure oxygen gas, then it must be encapsulated before being placed
in the bomb to ensure that no reaction prior to combustion occurs. The oxygen gas used to fill the bomb must be pure; possible impurities are water, nitrogen and hydrocarbons. Any hydrocarbons present would of course seriously influence the results.

Completeness of reaction must also be determined— is there any unburnt material left? The products of the reaction must be considered carefully. Their physical states must be characterised. The possibilities of side reactions and incomplete combustion to CO exist. For most combustion reactions of nitrogen-containing compounds, only about 90% of the nitrogen will finally remain as N2 gas—the remainder forms aqueous nitric acid and corrections must be made for this. The possibility of the formation of HNO2 must be considered.

In the case of C,H,0,N containing compounds, it is assumed that any carbon in the compound forms CO2(g), any hydrogen forms H2O(l) and the nitrogen behaves as discussed above. In more sophisticated apparatus, completeness of combustion is determined after the experiment by measuring the amount of CO2 produced by gravimetric procedures (using sodium hydroxide as absorbent). This method was not used in this work. Combustion was deemed to be good if the bomb had an 'ozone' smell when opened, and if there was no soot in the bottom. If either of these criteria were not met, the run was rejected. The amount of nitric acid formed is determined by titration against standard aqueous sodium hydroxide, using methyl orange as indicator.

The calorimetric part (b) of the experiment involves the determination of \( \Delta q (Jg^{-1}) \), the quantity of heat liberated in the bomb process. If \( \Delta m \) is the heat evolved in the burning of the compound of interest only, then this will refer to the following reaction.
\[ n_1 C_{10} H_{20} O_{24} (1 \text{ or } c) + r_1 O_2 (g) + m_1 H_2 O (g) + m_1' H_2 O (l) \]

\[ = (r_2 O_2 + s_2 N_2 + q_2 CO_2) (g) + m_2 H_2 O (g) + (q_2' CO_2 + m_2' H_2 O) \quad (1) \]

\[ \Delta \mu, \text{ the energy of combustion of an idealised (reduced) bomb process,} \]

will then refer to the following.

\[ n_1 \left[ C_{a b} H_{b c} O_{d e} (1 \text{ or } c) + (a + b/4 - c/2) O_2 (g) \right] \]

\[ = aCO_2 (g) + b/2 H_2 O (l) + d/2N_2 (g) \quad \quad (2) \]

i.e: (1) reduced to idealised conditions

Now, \[ \Delta u - \Delta u \]

\[ = q_w \quad \quad \quad (3) \]

Where \( q_w \) is the Washburn\(^1\) reduction (see later) and \( m_s \) is the mass of the sample.

Now, \( \Delta Q \) is the heat evolved in the actual bomb process

\[ (-m_s \Delta q) = (-m_s \Delta u) + q_i + q_n - q_c \quad \quad (4) \]

\( q_i \) is the correction for the ignition energy, i.e: the energy required to cause the platinum wire to glow plus the energy of combustion of the cotton fuse.

\[ q_i = 0.00183 + 17.49 m_f \quad (kJ) \]

0.00183\(kJ\) is the energy required to cause the wire to glow. (This figure comes from literature supplied with the bomb and only applies to wire of the stated diameter (0.0088cm)). 17.49\(kJg^{-1}\) is the energy of combustion of the cotton.

\( m_f \) is the mass of the cotton fuse

\( q_n \) is the correction for the nitric acid formed during combustion and was calculated using

\[ \Delta H_f^\circ (HNO_3, 500H_2O) = -59.72kJ \text{ mol}^{-1} \]

\( q_c \), the correction for the combustion of the unburnt soot residue was found by using

\[ q_c = 33 \times m_c \quad (kJ) \]
$m_c$ is the mass of the residue. The energy of combustion of soot is 33 kJ g$^{-1}$.

If $E_f$ is the energy equivalent of the final system (kJ K$^{-1}$), and $e_{sf}$ is the energy equivalent of standard final system, i.e.: the bomb less the oxygen and water charges, the combustion products, the platinum firing wire and the crucible, then combining (3) and (4) and

$$E_f = \frac{m \Delta q}{\Delta T} \quad e_f = e_{sf} + e_{cf}$$

Where $\Delta T$ is the corrected temperature rise, then

$$E_f = m_s (-\Delta u^o)_s^T + q_i + q_n + q_w - q_c \quad (5)$$

or

$$E_f = m_s (-\Delta u^o) + q_i + q_n - q_c \quad (6)$$

Calibration experiments are carried out using certified benzoic acid. Now, for this certified material, the figure supplied is $-\Delta u$ (kJ g$^{-1}$), i.e.: the heat evolved when the compound is burned under certain specified conditions.

Substitution of this value of $-\Delta u$ into (6) leads to calculation of $E_f$ and hence $e_{sf}$, i.e.: calibration experiments. McGlashan$^{20}$ writes, "It is much less expensive and, except in the most expert hands, more accurate to forego electrical calibration and to make bomb-calorimetric measurements relative to others made on benzoic acid in the same calorimeter". Once $e_{sf}$ is known, $\Delta u^o$ for unknown compounds may be found. It is worth noting that the Washburn correction is not needed for the calibration experiments but is required for the unknowns.

The specified conditions under which the benzoic acid must be burned for calibration experiments are:
(1) The sample is combusted in pure oxygen at a pressure of 30 atmospheres and initially at 25°C.

(2) \( \frac{m_s}{V} = 3 \)  
where \( \frac{m_s}{g} = \text{sample mass} \)  
\( V/\text{dm}^3 = \text{volume of bomb} \)

(3) \( \frac{m_w}{V} = 3 \)  
\( \frac{m}{g} = \text{mass of water originally in the bomb} \)

However, small departures from these certified conditions can be accommodated.

\[ \Delta u_{\text{non standard}} = \Delta u_{\text{standard}} \times f \]

where \( f = 1 + 10^{-6}(20(P-30)+42(m_s/3)+30(m_w/3)-45(T-25)) \)

\( T \) is the starting temperature of the experiment (°C).

'f' is only applicable in the ranges accompanying the following small deviations.

(1) \( 20 < P < 40 \)  (atmospheres)

(2) \( 2 < \frac{m_s}{V} < 4 \)  (g dm\(^{-3}\))

(3) \( 2 < \frac{m_w}{V} < 4 \)  (g dm\(^{-3}\))

(4) \( 20 < T < 30 \)

\( e_{cf} \) is the energy equivalent of the products of combustion and is calculated from the heat capacities of the crucible, oxygen, carbon dioxide, water and platinum wire.

\[ e_{cf} = 10^{-3}(21.04n_{O_2} + 4.18m_w + \Delta nm_s + 0.136m_{pt} + 0.76 \text{ J}) \]

21.04\( n_{O_2} \) is the energy equivalent of \( n \) moles of oxygen (here, \( n = 0.449395 \))

\( m_w \) = mass of water placed in the bomb originally (g). (This ensures that any solution is dilute enough to facilitate the Washburn correction)

4.18 = specific heat capacity (constant volume) of water (Jg\(^{-1}\)K\(^{-1}\)).

\( m_{pt} \) = mass of platinum firing wire (g)

0.136 = specific heat capacity of platinum (Jg\(^{-1}\)K\(^{-1}\)).
$s_c =$ mass of silica crucible (g)

0.76 = specific heat capacity of fused silica (J g$^{-1}$ K$^{-1}$)

$m_n =$ mass of the sample

$\Delta n$ is the difference in the heat capacities of the products and the oxygen gas for the burning of 1 g of the compound.

The corrected temperature rise, $\Delta T$, was calculated by back-extrapolation to a point corresponding to 0.65 of the observed temperature change.
This was evaluated using the abbreviated procedure of Prosen, whose method essentially follows that of Washburn.

It is essential to be able to define the exact process to which an energy change is referred, and if standard enthalpies of formation are to be derived from energies of combustion, then $\Delta U$ must refer to a well-defined standard reaction, i.e.: stoichiometric amounts of reactants yielding stoichiometric amounts of products - both reactants and products being in their standard states at the chosen temperature. Washburn in 1935 suggested that every bomb calorimetric experiment "should be corrected to give the value of $\Delta U$ for the pure isothermal reaction under the pressure condition of one normal atmosphere for both reactants and products". He restricted his account to CHO compounds only, but the discussion was later extended to CHON compounds by Prosen.

Previously, it was stated that the actual bomb process ($\Delta u^*$) may be represented by

$$n_1 \text{C}_a \text{H}_b \text{O}_c \text{N}_d \text{(1 or c)} + r_1 \text{O}_2(g) + m_1 \text{H}_2 \text{O}(g) + m_1 \text{H}_2 \text{O}(l)$$

$$= \left[r_2 \text{O}_2 + s_2 \text{N}_2 + q_2 \text{CO}_2\right](g) + m_2 \text{H}_2 \text{O}(g) + (q_2 \text{CO}_2 + m_3 \text{H}_2 \text{O})(l) \quad \ldots(1)$$

whereas the pure isothermal reaction (energy change $\Delta u^*$) is represented by

$$n_1 \text{C}_a \text{H}_b \text{O}_c \text{N}_d \text{(1 or c)} \text{ (a + b/4 - c/2)O}_2(g)$$

$$= a \text{CO}_2(g) + b/2 \text{H}_2 \text{O}(l) + d/2 \text{N}_2(g) \quad \ldots(2)$$

(Following the notation of Prosen.)

The Washburn correction is then
The initial states in the bomb are
(a) $n_l$ moles of $C_{a}H_{b}O_{c}N_{d}$ (1 or c) at pressure $P_1$.
(b) Gas phase- a mixture of oxygen, a small amount of nitrogen and water vapour. It is assumed that the mixture has the same energy content as pure oxygen and the water vapour separated from it, i.e: $1$ mole of $O_2(g)$ at pressure $P_1$ and $m_1$ moles of $H_2O(g)$ at pressure $P_w$.
(c) Liquid phase - this consists of water containing a negligible amount of dissolved oxygen (and nitrogen), so the liquid phase can be thought of as $m_1$ moles of $H_2O(l)$ at pressure $P_1$.

The final states in the bomb are
(a) Gas phase - a mixture of oxygen, nitrogen (ex combustion), carbon dioxide and water vapour, i.e: $m_2H_2O(g)$ at pressure $P_w$ and $[r_2CO_2+s_2N_2+q_2CO_2](g)$ at pressure $P_2$.
(b) Liquid phase - an aqueous solution of nitric acid containing dissolved CO$_2$, O$_2$ and N$_2$. The amounts of oxygen and nitrogen in solution may be ignored, but the CO$_2$ must be considered, so the liquid phase is $(q_2CO_2+m_2H_2O)(l)$ at pressure $P_2$.

Thus $q_w = \Delta u_1 + \Delta u_2 + \Delta u_3 + \Delta u_4$ (there are further terms in the correction but these are normally negligible).

$\Delta u_1$ is the energy change of $r_1$ moles of oxygen from zero pressure to $P_1$ atmospheres.
\[ \Delta u_1 = -6.59P_1r_1 \]

\( \Delta u_2 \) is the change in energy of a mixture of \( r_2 \) moles of oxygen, \( s_2 \) moles of nitrogen, \( q_2 \) moles of carbon dioxide from pressure \( P_2 \) to zero pressure.

\[ \Delta u_2 = \left[ 6.59r_2 + 6.04s_2 + 28.875q_2 - 11.15q_2(r_2 + s_2) \right] \times \frac{P_2(r_2 + s_2 + q_2)}{r_2 + s_2 + q_2} \]

where \( r_2 = r_2/(r_2 + s_2 + q_2) \) is the mole fraction of oxygen in the mixture, \( S_2 \) is that of nitrogen and \( Q_2 \) that of carbon dioxide.

\( \Delta u_3 \) is the energy of condensation of \( (m_2 - m_1) \) moles of water.

\[ \Delta u_3 = -41530(m_2 - m_1) \]

\( \Delta u_4 \) is the energy of vaporisation of \( q_2 \) moles of carbon dioxide from \( m_2 \) moles of water.

\[ \Delta u_4 = 17100q_2 \]

(All values of constants in the above equations are referred to 298.15K)

where

\[ V = 0.36 \text{ (the internal volume of the empty bomb in dm}^3)\]

\[ T = 298.15K \text{ (the temperature to which } \Delta u \text{ is referred)} \]

\[ n_1 = m_s/k \]

\( m \) = relative molecular mass of the sample

\[ P = 30 \text{ (the initial oxygen pressure, in atmospheres, at 298.15K)} \]

\[ m_1 \] = moles of water placed in the bomb

\( d_s \) = density of substance

\[ r_1 = P_1V_1/(RT(1 - 0.0006085P_1)) \]

\( R \) = gas constant

\[ V_1 = V - 0.018m_1 - m_s/(1000d_s) \]

\[ r_2 = r_1 - n_1(a + (b/4) - (c/2)) - 5/4(\text{moles HNO}_3) \]
\[ m_2 = m_1 + \left(\frac{b}{2}\right)n_1 \]
\[ s_2 = n_1\left(\frac{d}{2}\right) - \frac{n}{2}\text{(moles HNO}_3\text{)} \]
\[ \mu_2 = 0.0006085(1 + 3.21x(1 + 1.33x)) \]
\[ x = a_n_1/(r_2 + s_2 + a_n_1) \]
\[ V_2 = V - 0.018a_n_2 \]
\[ P_2^a = ((r_2 + s_2 + a_n_1)RT(1 - \mu_2P_1))/V_2 \] (the approximate final pressure)
\[ m_1 = (13.0375 + 0.04125P_1)10^{-4}V_1 \]
\[ m_2 = (13.0375 + (0.04125 + 0.21625)P_2^a)10^{-4}V_2 \]
\[ q_2' = 5.53m_2'.10^{-4}P_2^a \]
\[ q_2 = a_n_1 - q_2' \]
\[ P_2 = ((r_2 + s_2 + q_2)RT(1 - u_2P_2^a))/V_2 \]

All corrections are in J and apply to a temperature of 298.15K

A FORTRAN IV program was written to facilitate the evaluation of

\[ q_2' \]
II-2-c (1) Apparatus:

This was a commercial instrument (Gallenkamp Autobomb Automatic Adiabatic Bomb Calorimeter, Model CB-110), modified as follows.

(i) the thermometer supplied was replaced by a digital quartz thermometer (Hewlett Packard, Model 2801A)

(ii) the bomb supplied was replaced by a twin-valve bomb (Parr Instrument Company, Bomb No. 1101) of internal volume 360 cm$^3$.

(iii) the supplied stainless-steel calorimeter was replaced by a unit fabricated in copper (0.1 cm thick) to improve thermal response and a double stirrer was used within the calorimeter can.

The whole of the heat of the reaction must go into raising the calorimeter temperature and must not escape from the system. To ensure this adiabaticity, the temperature of the water bath on the outside is matched at every stage of the reaction to the temperature of the water in the calorimeter can.

This is achieved by using a pair of almost perfectly matched thermistors, one immersed in the calorimeter and the other in the water jacket. These constitute two arms of a bridge. The other arms consist of high stability resistors and a potentiometer. With the thermistors at the same temperature, the potentiometer is adjusted to balance the bridge. If the temperature of either thermistor then changes, its electrical resistance alters and puts the bridge out of the balance.

In operation, the jacket temperature normally becomes lower than the calorimeter temperature. This causes closure of the relay switch in the water jacket heater circuit, and the water jacket heats until its temperature again becomes equal to that of the calorimeter, and the bridge comes into balance. The relay switch in the heater circuit
opens until the water jacket temperature is again below that of the calorimeter.

II-2-c-(ii): Procedure

Suitable lengths of cotton fuse and platinum wire were weighed. The sample was then pelleted and left in a desiccator (the cotton fuse was incorporated in the pellet). After a silica crucible had been weighed, the pellet and fuse were then placed inside this crucible, and all three were weighed together. The platinum wire was strung across the bomb electrodes, and the crucible was placed in the support. The cotton fuse was tied to the platinum wire.

For the benzoic acid calibration experiments, 1.08 cm$^3$ of water were pipetted into the bottom of the bomb, but for the combustion of nitrogen containing compounds, 10.8 cm$^3$ were used. The firing circuit was then tested, after which the bomb was closed by screwing the cap down and then filled with oxygen to a pressure of 30 atmospheres. The pressure was then gently released and the bomb refilled with oxygen. The first filling with oxygen acts as a flushing operation. The charged bomb was placed in the copper calorimeter can and 1600 g of water at 25°C were added to the can. This ensemble was then placed within the calorimeter proper.

When the temperature had settled down, the initial period was begun, after which the bomb was fired. The run was stopped when the final period had been allowed to continue for about twenty minutes. The initial, firing and final periods were monitored on a chart recorder and a temperature print-out was obtained every 10 seconds. The bomb was removed from the calorimeter and the pressure gently released. As the gas was leaving the bomb, it was carefully sniffed. The smell of ozone indicated that the combustion was satisfactory. The electrodes, crucible, lid and walls of the bomb were washed with distilled water, and these washings titrated against 0.1M NaOH solution.
using methyl orange as indicator. The crucible was dried in an oven for several hours and then reweighed to determine the mass of soot.

II-2-c-(iii) Calibration and Test Materials

Calibration: Benzoic acid:—certified material (B.C.S. Thermochemical Standard No.190j, 99.97%) was used. The energy of combustion of this compound under the standard conditions mentioned before was given as 26435±5 [J g⁻¹] (sample weighed in vacuo).

Test Materials: Two test materials have been recommended for the combustion of CHON compounds. They are (i) acetanilide (for substances with a relatively low N content) and (ii) urea (for compounds with a relatively high N content). Urea suffers from the disadvantage that it does not burn easily and must be used with a combustion promoter (such as benzoic acid).

Johnson has measured the energy of combustion of acetanilide using an adiabatic rotating-bomb calorimeter. His sample was certified as being 99.99 mol% pure. The standard enthalpy of combustion was -(4224.88±0.93) [kJ mol⁻¹].

Cox states that there are no other reliable combustion studies to compare this with. However, a value for the standard enthalpy of formation of acetanilide may be calculated from some solution calorimetry of Wadsö. The mean of his results is

\[ \Delta H^\circ_f = -(209.37 \pm 0.69) \text{ [kJ mol}^{-1} \text{]} \]

giving

\[ \Delta H^\circ_c = -(4224.95 \pm 1.26) \text{ [kJ mol}^{-1} \text{]} \]

Combining this value with Johnson's gives

\[ \Delta H^\circ_c = -(4224.90 \pm 0.75) \text{ [kJ mol}^{-1} \text{]} \]

\[ \Delta n^\circ_c = -(31.2340 \pm 0.0056) \text{ [kJ g}^{-1} \text{]} \]
II-2-c-(iv) Materials

Certified benzoic acid (B.C.S.No.190j, Thermochemical standard, 99.97%) was used without further treatment, as recommended.

Acetanilide (B.D.H.Ltd., OAS grade) was used as supplied after drying overnight at 110°C. The purity was found by differential scanning calorimetry to be > 99.9%.

Ammonium picrate was prepared by neutralising a solution of picric acid (B.D.H. AnalaR grade, recrystallised once) with aqueous ammonium carbonate (B.D.H. Lab reagent grade). The yellow crystals were recrystallised four times from water and dried in air at ca.120°C for approximately 7 hours, and stored over anhydrous magnesium perchlorate (Anhydrone). The red modification is not formed under these conditions. The purity was determined by distillation from aqueous sodium carbonate into standard aqueous HCl, followed by titration using standard NaOH. Results were NH^+ = 6.91% (theoretical = 6.907%). A Karl Fischer titration indicated that the water content was negligible.

Picric acid (B.D.H. AnalaR grade) was recrystallised four times from ethanol and dried in air at ca.105-110°C for several hours. The melting point was 121.5-122°C. (Literature values range from 120-122°C).

II-2-d RESULTS

Table II-4 lists the results for the calibration experiments with benzoic acid:

\[ e_{sf} = 8.6186 \pm 0.0026 \text{ kJ K}^{-1} \]

Table II-5 contains the results for the combustion of the test compound, acetanilide.

\[ \Delta_h^c = -31.221 \pm 0.013 \text{ kJ g}^{-1} \]

This value is in satisfactory agreement with that of Johnson\(^{22}\) (-31.2300 \pm 0.0069 \text{ kJ g}^{-1}).
II. The results of the combustion experiments for ammonium picrate and picric acid are contained in Tables II-6 and II-7 respectively. Discussion of these results may be found in sections II-4 and II-5-a respectively.
II-3: SOLUTION CALORIMETRY

II-3-a Experimental

(i) Apparatus

Three solution calorimeters were employed in the course of this work. One is a commercial instrument while the other two were constructed in this Laboratory. All three are well documented, but a brief description of each is useful.

(a) The commercial instrument - the LKB. 8700-1 Precision Calorimetry System.

This was used to determine the enthalpy of solution of ammonium picrate in water and to investigate the neutralisation reaction between aqueous picric acid and sodium hydroxide solution. The calorimeter vessel is thin-walled Pyrex glass of volume 100cm$^3$. (A 25cm$^3$ vessel is also available). The calibration heater and thermistor are contained in oil-filled glass attached to the lid of the vessel. The stirrer consists of a stainless-steel spindle attached to a gold ampoule holder. The glass ampoules were broken by lowering the stirrer - ampoule holder onto a sapphire-tipped glass rod fixed to the bottom of the vessel.

The great disadvantage of this system is its poor stirring. The base of the vessel is flat. A PTFE paddle was fixed to the stirrer shaft, but this did not greatly improve the performance. The LKB system is excellent for very fast reactions e.g. acid-base neutralisations, but it cannot be used for slow reactions or those where precipitates form. In this work, it could not even be used for the solution of one of the more soluble picrates.

Full details of the construction and operation are available in the instrument manual.

(b) Precipitation reactions were investigated using a calorimeter constructed in this Laboratory. It operates in the partial differential
isoperibol mode.

The calorimeter vessels are of the glass Dewar type. They are thin-walled (1 mm) borosilicate glass and are available in two sizes, 100 cm³ and 200 cm³. The thermistors are contained in glass tubes fitted in the screw-top aluminium (100 cm³) or plastic (200 cm³) lids. The stirrer and ampoule holder are of precision-bore glass rod, and are fitted into precision tubing firmly adhered to the lids. The stirring of the calorimetric fluid in this instrument is far superior to that in the LKB - a glass propeller is attached to the end of the rod and a PTFE paddle is fixed to the shaft. There is also far more control over the speed of stirring than with the LKB.

The ampoules were glass blown from B5 sockets, and the two bulbs were broken against the stirrer paddles or the walls of the calorimeter to start the reaction. The calibration heaters are of nominal 100 J resistance PTFE encapsulated resistors of low thermal capacity with double leads. The thermistors are sealed into thin-walled tapered glass tubes containing a drop of silicone oil (for good heat transfer).

The twin vessels are immersed in a well-stirred water bath kept at 25°C. A proportional counter is used to control the temperature of the bath. The temperature changes in the calorimeter are detected by the thermistors, which are connected to an a.c. bridge. Full details of the construction of this calorimeter and its use are available elsewhere.

(c) A third calorimeter, also built in this department, was used to determine the enthalpies of solution of most of these picrates in water. This instrument has also been described in detail previously. It operates in duplicate in the isoperibol mode, and is of the all-glass Dewar type with vessel capacity 200 cm³.
II-3-a-(ii) Test Reactions in Solution Calorimetry

Test reactions are helpful in solution calorimetry, serving the dual purposes of checking both instrument performance and operator technique. The test reactions employed here were

(a) for EXOTHERMIC reactions — the neutralisation of tria(hydroxymethyl) aminomethane (THAM) in excess 0.1M aqueous hydrochloric acid.

\[ \text{Lit.value}^{27} = -29.79 \pm 0.031 \text{ kJ mol}^{-1} \]

(b) for ENDOTHERMIC reactions - the enthalpy of solution of THAM in excess 0.05M (and 0.1M) aqueous sodium hydroxide solution.

\[ \text{Lit.values}^{28} : 0.05M \text{ NaOH} = 17.189 \pm 0.005 \text{ kJ mol}^{-1} \]
\[ 0.10M \text{ NaOH} = 16.698 \text{ kJ mol}^{-1} \]

(This reaction is very dependent upon the hydroxide ion concentration).

(c) for PRECIPITATION reactions - the reaction between crystalline potassium bromide and excess silver nitrate solution.

\[ \text{KBr} \,(c) + \text{AgNO}_3 \,(aq) \rightarrow \text{KNO}_3 \,(aq) + \text{AgBr} \,(c) \]

\[ 0.15M \triangle H^\circ_{r}^{29} = -65.168 \pm 0.011 \text{ kJ mol}^{-1} \]

II-3-a-(iii) Preparations

Potassium picrate was prepared by neutralising a boiling 30% alcohol in water solution of picric acid with aqueous 1M potassium hydroxide solution\(^{30}\). The resulting yellow needles were recrystallised three times from water and dried at 120°C. Using sodium tetraphenylborate as the precipitating agent 14.58% K was found.

( theoretical for \( C_{6}H_{2}(NO_{2})_{3}K = 14.63\% \))

Silver picrate was obtained by adding small amounts of silver oxide to a 30% ethanol in water solution of picric acid\(^{31}\). The product was recrystallised three times from water and dried at 80°C to give yellow plates. Analysis by Volhard’s method gave 32.10% Ag

(Theoretical for \( C_{6}H_{2}(NO_{2})_{3}Ag = 32.11\% \text{ Ag} \))
The yellow form of ammonium picrate was prepared as described previously (see II-2-c-(iv)). Refluxing picric acid solution with concentrated ammonia for 24 hours gave the red form.

Rubidium, caesium, tetramethylammonium and tetraethylammonium picrates were prepared by treating a warm solution of silver picrate in water with the appropriate bromide. The precipitated silver bromide is filtered off whilst the picrate remains in the warm solution. All these salts were recrystallised thrice from water. (Treating picric acid with tetramethylammonium and tetraethylammonium hydroxides could possibly have resulted in the formation of the corresponding amine picrates, since these hydroxides decompose upon heating).

Guanidine picrate was obtained by adding aqueous guanidine nitrate to a picric acid solution. It is a very insoluble, dark yellow salt. All the salts mentioned above crystallise from water in the anhydrous form.

II-3-b: RESULTS

(i) Results for the test reactions may be found in tables II-8, II-9 and II-10.

Results for the enthalpies of solution in water of the picrates and picric acid may be found in tables II-11 to II-18 inclusive.

The results for the enthalpy changes for the precipitation reactions may be found in tables II-20 to II-25 inclusive.

(ii) Enthalpies of solution

Vorob'ev et al. measured, inter alia, the enthalpies of solution in water of potassium and ammonium picrates. Their values agree well with this work (see Table II-19). Ling has recently determined enthalpies of aqueous solution for sodium and tetramethylammonium picrates. His value for tetramethylammonium agrees well with the value found in this work, and his figure for sodium picrate is close to that of Vorob'ev's (Table II-19).
Enthalpies of solution in water for lithium and sodium picrates were also found by Askew. Unlike the salts studied here, lithium and sodium picrates both crystallise from water as the hydrates. Askew's values do not agree with those of Vorob'ev, (Table II-19) who attributes the discrepancy to the fact that Askew did not use the anhydrous salts.

Berthelot measured the enthalpies of solution in water of picric acid, potassium, sodium and ammonium picrates, inter al, in 1873, but his results are several kJ mol\(^{-1}\) different from those obtained here and by Vorob'ev and are dismissed as being merely of historical interest. The same must apply to the results of Tscheltzow, who measured solution enthalpies for a large number of anhydrous and hydrated salts of picric acid, including barium, lead and copper. Berthelot and Tscheltzow's results may be found in Table II-28.

II-4: AMMONIUM PICRATE

The energy of combustion at 298.15K of ammonium picrate was found to be
\[\Delta H^\circ \text{ at 298.15K} = -385.44 \pm 2.94 \text{kJ mol}^{-1}\]

Values of \(\Delta H^\circ \text{ CO}_2(g)\) and \(\Delta H^\circ \text{ H}_2O(1)\) are given in Table II-31.
Table II-1 lists the reported values of the standard enthalpy of formation of ammonium picrate. They range from ca. -325 to -400 kJ mol\(^{-1}\).

The very early (1884) result of Sarrau and Vieille\(^3\) can probably be discounted, as can the values of Tomioka and Takahashi\(^34\) and Urbanski and Soroka\(^35\), which seem lower than the others. There is also a difference of ca. 42 kJ mol\(^{-1}\) between the standard enthalpies of formation of the red and yellow forms as reported by Urbanski. This may be compared with a difference of only ca. 5 kJ mol\(^{-1}\) reported by Medard and Thomas\(^36\). This latter difference seems much more likely.

Recalculation of the results obtained by Medard and Thomas (\(\Delta u^e = -11.556 \text{ kJ g}^{-1}\)), using more recent values of \(\Delta H_f^\circ \text{CO}_2(g)\) and \(\Delta H_f^\circ \text{H}_2\text{O}(l)\), leads to a value which agrees, very satisfactorily within experimental error, with that reported here. The values Medard and Thomas used for \(\Delta H_f^\circ \text{CO}_2(g)\) and \(\Delta H_f^\circ \text{H}_2\text{O}(l)\) were -395.43 and -286.06 kJ mol\(^{-1}\) respectively. Their combustion was referred to 18\(^\circ\)C. It is not possible to correct Medard and Thomas' results for any change in the value of \(\Delta H_f^\circ \text{HNO}_3(aq)\) because their paper does not give any information about the amounts of nitric acid formed.

Hence the value obtained in this work for the standard enthalpy of formation of ammonium picrate is probably correct because of the excellent agreement with the French work. However, the considerable difference between these values and that of Vorob'ev et al. (ca. 16 kJ mol\(^{-1}\)) is not easily explained. Vorob'ev's procedure was based on a combustion study of picric acid and then solution calorimetry involving the enthalpies of neutralisation of picric acid by ammonium, lithium, sodium and potassium hydroxides. The Russian solution calorimetric results agree well with this work – see II-3-b(ii), so their combustion results must be questioned.
II-5-a: PICRIC ACID

Using the values obtained in this work for the standard enthalpies of formation of ammonium (see II-4) and potassium picrates (see II-6-a), their enthalpies of aqueous solution and Vorob'ev's enthalpy of neutralisation values, it has been possible to calculate a value for the standard enthalpy of formation of picric acid viz. -229.4 kJ mol\(^{-1}\) (ex ammonium) and -227.9 kJ mol\(^{-1}\) (ex potassium), giving a mean value of -228.7 kJ mol\(^{-1}\). Comparison of this with results from all reported combustion studies shows it to be anomalously high. A combustion study of picric acid carried out as part of this work thus seems to be justified.

The energy of combustion of picric acid at 298.15 K was found to be
\[-11.2717\pm 0.0076 \text{ kJ g}^{-1} \text { (mean of 6 runs)}\]

Using the equation
\[C_6H_3N_3O_7(c) + 13/4O_2(g) \rightarrow 6CO_2(g) + 3/2H_2O(l) + 3/2N_2(g)\]
since \(\Delta n = 17/4\)

the standard enthalpy of combustion at 298.15 K has been found to be
\[-2571.92\pm 1.92 \text{ kJ mol}^{-1}\]

This gives rise to a standard enthalpy of formation of \(-217.89\pm 1.99 \text{ kJ mol}^{-1}\). This value is coincidentally very close to the mean of the 4 earlier results, and the value of -211 kJ mol\(^{-1}\) is probably too low. Since the bomb system was satisfactorily checked using acetonilide, this gives some confidence in the value of -217.9\pm 2 kJ mol\(^{-1}\).

But this is still inconsistent with the value derived from solution-reaction experiments. The constitution of picric acid in aqueous solution is thought by some workers to be concentration dependent, and this will be discussed later.
II-5-b. Neutralisation Reactions

The value for the standard enthalpy of formation of picric acid based upon this burning of ammonium picrate and the solution calorimetric results from this work and from Vorob'ev is \(-229\text{kJ mol}^{-1}\), some 10–15kJ mol\(^{-1}\) more exothermic than values from combustion experiments. It was known that Vorob'ev's enthalpies of solution agreed very well with this work, but it was thought prudent to check the neutralisation results. This was done with solutions of ammonia and sodium hydroxide.

Solid picric acid was broken into ammonia solution and the results in table II-29 obtained. The scatter of these results is somewhat larger than would normally be acceptable, but they do compare quite favourably with those of Vorob'ev.

However, when picric acid was broken into sodium or potassium hydroxide solution, particles were still observed in the solution after a period of about 25 minutes. The nature of these particles is not clear. Possibly they were undissolved picric acid crystals which had been coated with potassium picrate, thus inhibiting further reaction.

This problem was overcome by breaking an ampoule containing a slight excess of sodium hydroxide solution into aqueous picric acid. This entailed measuring the enthalpy of solution of picric acid in water (table II-18). Table II-30 lists the results for the enthalpy of neutralisation of picric acid and sodium hydroxide solutions. These results (when corrected for the enthalpy of solution of picric acid) are in good agreement with those of Vorob'ev, and they certainly do not account for the discrepancy in the enthalpy of formation of picric acid.

The precipitate formed when sodium or potassium hydroxides are
When potassium hydroxide solution from a burette is run into picric acid solution, the titration curve shows a sharp peak, as would be expected for the neutralisation of a monobasic acid. After the equivalence point was reached, concentrated potassium hydroxide solution was added until a precipitate appeared (pH 12-13). This precipitate was filtered off and washed with water/ethanol/ether. The procedure was then repeated, except that KOH pellets were added after the neutralisation. The i.r. spectra of these precipitates were recorded. They were identical to each other and to spectra of potassium picrate samples prepared from potassium hydroxide and potassium carbonate neutralisations of picric acid. So there is no evidence that any product apart from picrate is formed.

If different products were formed upon neutralisation than those formed in solution, then this could have perhaps explained the difference between the enthalpies of formation. It has been suggested that in picrate solutions there are interactions involving ionic species other than the simple $\text{H}_3\text{O}^+$ and $\text{OH}^-$. 

Ives and Moseley's conductance data indicated the onset of these interactions at concentrations greater than $1.3 \times 10^{-3}\text{M}$. Moseley and Spiro explained the anomalous concentration dependence of picric acid solutions in terms of the formation of hydrogen-bonded triple ions of the type $\text{HPiC}_2^-$ or the dimerisation of picrate ions, viz. $\text{Pic}_2^{2-}$ - the structure of these dimers is unclear. The conductance and transference number data did not fit the triple-ion hypothesis. The transference number measurements of Moseley and Spiro in 0.02M solutions of potassium picrate confirmed the dimerisation hypothesis, and led to a dimerisation constant of $4.2 \text{mol}^{-1}\text{dm}^3$ at 25°C. Hence at a concentration of ca. $3 \times 10^{-3}\text{M}$, a concentration of $3.4 \times 10^{-5}\text{M}$ of picrate ion dimers should exist in potassium picrate solutions at
25°C. However, even if there were this concentration of 'dimers' present upon solution and not, for some reason, in the 'neutralised' solution, it seems very unlikely that a difference of ca. 10-15 kJ mol\(^{-1}\) would result.

The problem of the standard enthalpy of formation of picric acid has not been resolved. The good agreement between the values obtained in this work and the French work, and the solution calorimetry performed here and in the Soviet Union tend to lend confidence to the value of ca. 229 kJ mol\(^{-1}\) for \(\Delta H_f^\circ\) picric acid. The fact that there is poor agreement between the combustion studies would also support this. The values from combustion studies are all low compared with -229 kJ mol\(^{-1}\) which means that the enthalpies of combustion are all high. It may well be that there was an impurity of high energy of combustion present in all the samples burned, or that picric acid does not undergo complete combustion.
II-6-a: Standard Enthalpies of Formation of MPic

Knowing the standard enthalpy of formation of ammonium picrate and its enthalpy of solution, the enthalpy of formation of aqueous silver picrate may be calculated from the enthalpy change for the following reaction,

\[ \text{AgPic}(aq) + \text{NH}_4\text{Br}(c) \rightarrow \text{AgBr}(c) + \text{NH}_4\text{Pic}(aq) \]

(Ancillary data are contained in Table II-31)

The standard enthalpies of formation of the other picrates can now be obtained from their enthalpies of solution and the enthalpy changes for the following type of reaction,

\[ \text{AgPic}(aq) + M\text{Br}(c) \rightarrow \text{AgBr}(c) + M\text{Pic}(aq) \]

\[ M = K, \text{Rb, Cs, NMe}_4^-, \text{NET}_4^- \]

Values for the standard enthalpies of formation of these salts are listed in Table II-27.

II-6-b: Standard Enthalpy of Formation of the Aqueous Picrate Ion, \( \Delta H_f^{\circ} \text{Pic}^- (aq) \)

Consider the following cycle for the dissolution of a metal picrate, MPic(c), in water.

\[ \text{Elements (standard states)} \]

\[ \Delta H_f^{\circ} \text{Pic}^- (aq) = \Delta H_f^{\circ} \text{Pic}^{-}(aq) - \Delta H_f^{\circ} \text{H}^+(aq) + \Delta H_f^{\circ} \text{sol} \]

From the data in Table II-33, a mean value for the standard enthalpy of formation of the aqueous picrate ion may be calculated as \(-206.02 \text{ kJ mol}^{-1}\).
The enthalpy of solution of picric acid in water is \(21.67 \pm 0.38\) kJ mol\(^{-1}\), so this enables calculation of another value for the standard enthalpy of formation of picric acid, viz. \(-227.7\) kJ mol\(^{-1}\) in good agreement with the value based upon the burning of ammonium picrate and the neutralisation results.

II-7: Tetramethylammonium and tetraethylammonium picrates

The standard enthalpies of formation of these compounds have been calculated using the procedure outlined previously - solution calorimetry based upon a combustion study of ammonium picrate.

Since these two alkyl-substituted ammonium picrates contain only carbon, hydrogen, oxygen and nitrogen, combustion experiments were made. Four runs were attempted with each compound. However, neither of the compounds burned satisfactorily. Two of the tetraethylammonium and three of the tetramethylammonium runs had to be discounted because there was either a large mass of soot or a yellow solution (or both) in the bottom of the bomb when opened. Both of these salts have a very high carbon content. Enthalpies of formation have been calculated from the results of the 'successful' runs (see Table II-32). These values are not in particularly good agreement with those obtained from solution calorimetry, but in this case it would appear that the combustions are probably suspect.

\[
\begin{align*}
\Delta H_f^\circ/\text{kJ mol}^{-1} & \quad \text{(ex. solution)} & \Delta H_f^\circ/\text{kJ mol}^{-1} & \quad \text{(ex. combustion)} \\
\text{NMe}_4\text{Pic} & 343.7 & 330.9 \\
\text{NET}_4\text{Pic} & 488.1 & 445.8 & 450.4
\end{align*}
\]

Approximate densities for these compounds have also been determined. For both salts, \(\rho = 1.50\) g cm\(^{-3}\).
II-8-a: Guanidine salts

Guanidine \( \text{CH}_3\text{N}_2 \), is a strong base which forms crystalline salts with acids, e.g:

- guanidine chloride \( \text{CH}_3\text{N}_2\text{HCl} \)
- guanidine nitrate \( \text{CH}_3\text{N}_2\text{HNO}_3 \)
- guanidine perchlorate \( \text{CH}_3\text{N}_2\text{HClO}_4 \)
- guanidine picrate \( \text{CH}_3\text{N}_2\text{C}_6\text{H}_5\text{N}_3\text{O}_7 \)

Some studies have been made of the thermochemistry of guanidine salts, but no work appears to have been done on the picrate. Table II-34 shows some standard enthalpies of formation of salts of guanidine.

Krivtsov, Titova and Rosolovskii\(^5\) determined enthalpies of formation of the nitrate, perchlorate and sulphate.

\[
\Delta H_f^\circ (\text{CH}_3\text{N}_2\text{HNO}_3, c) = -389.11 \pm 3.9 \text{ kJ mol}^{-1}
\]

\[
\Delta H_f^\circ (\text{CH}_3\text{N}_2\text{HClO}_4, c) = -310.03 \pm 2.3 \text{ kJ mol}^{-1}
\]

\[
\Delta H_f^\circ (\text{CH}_3\text{N}_2\text{C}_6\text{H}_5\text{N}_3\text{O}_7, c) = -1200.81 \pm 7.53 \text{ kJ mol}^{-1}
\]

These figures were calculated from the results of solution calorimetric experiments. Krivtsov et al, measured the heat of reaction of aqueous \( \text{Ba(ClO}_4)_2 \) with guanidine carbonate \( \text{CH}_3\text{N}_2\text{H}_2\text{CO}_3 \) and guanidine sulphate \( \text{CH}_3\text{N}_2\text{H}_2\text{SO}_4 \) \((17.20 \pm 0.50 \text{ and } 0.402 \pm 0.29 \text{ kJ mol}^{-1} \) respectively\). They also found the enthalpies of solution of guanidine perchlorate and of anhydrous \( \text{Ba(ClO}_4)_2 \) in water at 1:1200 dilution \((43.58 \pm 0.38 \text{ and } 3.89 \pm 0.00 \text{ kJ mol}^{-1} \) respectively\). Other ancillary data required were the enthalpies of solution of guanidine nitrate in dilute perchloric acid and of guanidine perchlorate in dilute nitric acid \((40.93 \pm 0.17 \text{ and } 43.51 \pm 0.08 \text{ kJ mol}^{-1} \) respectively\).

These experiments enabled calculation of the afore mentioned enthalpies of formation.
In 1971, Lobanov and Karuianova measured the enthalpy of formation of crystalline guanidine nitrate by combustion calorimetry and obtained a value of \(-405.01 \pm 4.60 \text{kJ mol}^{-1}\). This is approximately 16 kJ mol\(^{-1}\) more exothermic than the other Russian work. However, Wagman et al. report a figure of \(-387.02 \text{kJ mol}^{-1}\) for \(\Delta H_f^{\circ}(\text{CH}_2\text{N}_3\text{HNO}_3, c)\) in good agreement with Krivtsov. Wagman's value for \(\Delta H_f^{\circ}(\text{CH}_2\text{N}_3\text{HC10}_4, c)(-312.96 \text{kJ mol}^{-1})\) also compares well with that of Krivtsov.

Ahluwalia, Subramanian, Sarma and Balasubramanian found the integral heat of solution of guanidine chloride at 25°C to be 18.87±0.04kJ mol\(^{-1}\).

To find the standard enthalpy of formation of guanidine picrate, several schemes were considered. An ampoule of crystalline guanidine nitrate was broken into an ammonium picrate solution, pre-saturated with guanidine picrate (highly insoluble). This method, however, gave very irreproducible results—the reaction appears to take place in two stages. The first is the endothermic dissolution of guanidine nitrate in water and the second is the formation of the guanidine picrate and ammonium nitrate.

\[
\text{CH}_2\text{N}_3\text{HNO}_3(c) + \text{NH}_4\text{Pic}(aq) \rightarrow \text{CH}_2\text{N}_3\text{Pic}(c) + \text{NH}_4\text{NO}_3(aq)
\]

Guanidine nitrate is not sufficiently soluble in water to be able to place a small amount of solution in an ampoule such that the solution would contain enough of the nitrate to give a reasonable temperature change.

The enthalpy of formation of guanidine chloride does not appear in the literature. However, this has been determined in this work by breaking an ampoule of guanidine chloride into silver nitrate solution. The enthalpy of solution of guanidine nitrate in water was determined and compared with the value in dilute perchloric acid.
Knowing the standard enthalpy of formation of guanidine chloride, it should have been possible to find the same quantity for guanidine picrate by studying the following reaction calorimetrically:

\[ \text{CH}_3\text{N}_2\text{HCl(c)} + \text{AgPic(aq)} \xrightarrow{\Delta H^\circ} \text{CH}_3\text{N}_2\text{Pic(c)} + \text{AgCl(c)} \]

This was indeed tried, but the results obtained for \( \Delta H^\circ \) were rather disappointing - ranging between -92 and -105 kJ mol\(^{-1}\). Unlike other precipitation reactions studied during the course of this work, two precipitates were formed here, but the stirring seemed adequate. There seemed to be no dependence of \( \Delta H^\circ \) on mass. The stoichiometry of the reaction was checked by precise analytical methods.

**II-8-b RESULTS**

The enthalpy of solution of crystalline guanidine nitrate in water was found to be 40.18 ± 0.50 kJ mol\(^{-1}\) (Table II-35). This compares with the value of Krivtsov\(^{51}\) et al. (in dilute perchloric acid) of 40.93 ± 0.17 kJ mol\(^{-1}\).

The enthalpy of reaction between crystalline guanidine chloride and excess silver nitrate solution was found to be -46.70 ± 0.22 kJ mol\(^{-1}\).

The results may be found in Table II-36.

This leads to a value for the standard enthalpy of formation of \( \text{CH}_3\text{N}_2\text{HCl(c)} \) of 366.71 ± 4.00 kJ mol\(^{-1}\).

A reliable value for the standard enthalpy of formation of guanidine picrate cannot be calculated from these results (see Table II-37), but it is probably of the order of -430 kJ mol\(^{-1}\).

Guanidine chloride was recrystallised three times from hot methanol, and diethyl ether was added. It is of interest to note that when a warm saturated solution of guanidine chloride (in a conical flask) was shaken very gently, the precipitate was caused to come down with such a force that some of it was projected over the
Guanidine nitrate (B.D.H. AnalR grade) was kindly donated by Woolwich Arsenal.

The specific heat of \( \Delta \) as a function of temperature is required to perform the integration. For the alkali metal and alkaline earth metal halides, the difference between \( U_a \) and \( U_{\text{polar}} \) is no more than about 13 kJ mol\(^{-1}\).

Consider the Born-Haber cycle for the compound \( MX_0(v) \).

\[
\begin{align*}
U_{\text{polar}}(MX_0) &= U_a + \sum \Delta H_{\text{fus}}(i) + \sum w_i \Delta H_{\text{elec}}(f) \\
\Delta H_{\text{fus}}(i) &= w_i (U_a - U_{\text{polar}}(MX_0)) \\
\Delta H_{\text{elec}}(f) &= 0
\end{align*}
\]

\( w_i \) denotes the weight fraction of each component, \( U_a \) is the lattice energy at 0 K, and \( U_{\text{polar}} \) is the lattice energy at 0 K.
II-9: Lattice Energies

The lattice energy, $U_0$, at $0^\circ K$, of an ionic crystal may be defined as the internal energy change when one mole of a compound is converted into the relevant ions, infinitely separated from each other. At $0^\circ K$, these ions are stationary. For the compound $MX_n$, it can be shown that the lattice energies at temperatures $T^\circ$ and $0^\circ K$ are related by

$$U_T(MX_n) - U_0(MX_n) = \frac{3}{2} RT(n+1) - \int_0^T C_p(MX_n) \, dT.$$

The specific heat of $MX_n$ as a function of temperature is required to perform this integration. (For the alkali metal and alkaline earth metal halides the difference between $U_0$ and $U_{298}$ is no more than about 12kJ mol$^{-1}$).

Consider the Born-Haber cycle for the compound $MX_n(c)$.

$$MX_n(c) \xrightarrow{U_{298}+(n+1)RT} M^{n+}(g) + nX^-(g)$$

$$H_I \quad \text{I} \quad E_a$$

$$M(c) + \frac{n}{2}X_2(g) \xrightarrow{H_{SUB}} M(g) + nX(g)$$

$\Delta H_{Diss}$

Then

$$U_{298}(MX_n) = \Delta H_{SUB} + \sum_{o} n_i I_{n_i} + \frac{n}{2} \Delta H_{Diss} - nE_a(X) - \Delta H^e_I(MX_n) - (n+1)RT$$

Hence

$$U_{298}(MX_n) = \Delta H^0_I M^{n+}(g) + n \Delta H^0_I X^-(g) - \Delta H^e_I(MX_n) - (n+1)RT$$
Hence, lattice energy values are available experimentally provided the other quantities in the cycle are known. This is not always the case, and a number of approaches have been developed to calculate lattice energies on a theoretical basis.

If it is assumed that the crystal consists of hard spheres and that the charges on the cation and the anion are $z_+$ and $z_-$, it is necessary to calculate

(i) the attractive (Coulombic) forces between the ions.

(ii) the repulsive forces due to interpenetration of the spherical charge clouds of the ions.

Born and Landé proposed the following equation for the calculation of lattice energies.

$$U = \frac{Nz_+z_-e^2}{r_0} \left( 1 - \frac{1}{n} \right) \ldots (1)$$

$N = \text{Avogadro's number}$

$A = \text{Madelung constant}$

$r_0 = \text{equilibrium internuclear distance}$

$n$: Born and Landé assumed the repulsive force to be proportional to $1/r^n$.

$r_0$ and $n$ may be determined experimentally.

Born and Mayer used a different expression for the repulsive energy. This leads to an expression for the lattice energy as

$$U_0 = \frac{Nz_+z_-e^2}{r_0} \left( 1 - \frac{f}{r_0} \right)$$

$f$ is a constant, taken for many crystals to be $0.345 \times 10^{-10}$ m.

For alkali and alkaline earth metal halides, the agreement between the calculated lattice energies and the Born-Haber cycle values is good.

These simple expressions do not take into account the contributions of the London forces or the zero-point energy of the crystal.
Kapustinskii Equations

The calculation of lattice energies from the Born–Landé and Born–Mayer expressions depends upon the Madelung constant. Kapustinskii\(^5\) showed that if the Madelung constants for a number of structures were divided by \(r\), the number of ions in one molecule, the values obtained were nearly constant. He also noted that the order of the values was approximately that of the average co-ordination number around the ions. This means that the proportional variations in \(A/r\) will be less than those in \(A/r^2\), since \(r\) increases slightly with co-ordination number. The value of \(A/r\) is hence almost constant regardless of structure.

For the 6:6 NaCl lattice, \(A/r^2\) is 0.874/\(r^2\). \(r\) may be replaced by \((r^++r^-)\) (the octahedral ionic radii).

Substitution into the Born–Landé equation gives

\[
U_0 = \frac{0.874N\cdot e^+ \cdot e^-}{(r^++r^-)} \left( \frac{1}{n} - \frac{1}{n} \right)
\]

Kapustinskii used an average value \(n = 9\).

Hence \(U_0 = 108.0 \frac{\mathcal{Q} e^+ \cdot e^-}{(r^++r^-)} \) kJ mol\(^{-1}\)

For sodium chloride structures, \(r\) is 0.0345nm.

\[
U_0 = 121.4 \frac{\mathcal{Q} e^+ \cdot e^-}{(r^++r^-)} \left( 1 - \frac{0.0345}{r^++r^-} \right) \text{ kJ mol}^{-1}
\]

The Kapustinskii equations have been used for lattice energy calculations in the absence of structural and compressibility data, and this leads on to the concept of the thermochemical radius. Kapustinskii defined the thermochemical radius of a non-spherical complex ion as being "the radius of the hypothetical spherical ion that can replace the given ion iso-energetically in the crystal lattice."
Suppose a complex anion, $X^-$, forms two salts, $M_1 X$ and $M_2 X$, with two different cations, $M_1^+$ and $M_2^+$ (this would also apply to a complex cation $M^+ \cdot X^-$ forming $MX_1$ and $MX_2$), it is easy to show that

$$U(M_1X) - U(M_2X) = \Delta H_f^e(M_1^+(g)) - \Delta H_f^e(M_2^+(g)) - \Delta H_f^e(M_1X) + \Delta H_f^e(M_2X)$$

If the enthalpies of formation of the salts and the gaseous cations are known, the difference in lattice energies may be found. If this difference is then equated to the difference in the Kapustinskii equations, the radius of $X^-$ may be calculated (if the radii of the cations are known), since it can be shown that, if

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

then

$$r^4 + 2r^3(m_1 + m_2) + r^2(m_1^2 + m_2^2 + 4m_1 m_2 + c(m_1 - m_2)) +$$

$$r(2m_1^2 m_2 + 2m_2^2 m_1 + c(m_1^2 - m_2^2) - 0.069c(m_1 - m_2)) +$$

$$(m_1 m_2^2 + c(m_1 m_2 - m_1^2) + 0.0345c(m_1^2 - m_2^2)) = 0$$

where $r$ is the thermochemical radius of the complex anion and $m_1$ and $m_2$ are the radii (nm) of the cations and $(U_1 - U_2)$ is in kJ mol$^{-1}$.

This is a quartic equation of the form

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

and was solved by an iterative method using a standard program supplied with the calculator, (Hewlett-Packard HP-65 calculator, program STD 14A) (see reference 25 for details of the program).

Knowing the thermochemical radius of $X^-$ it is then possible to substitute this value back into the Kapustinskii equation to calculate lattice energies, which may then be used to obtain a value for the enthalpy of formation of the gaseous anion.

Strictly, results from the Kapustinskii equation are lattice energies at 0 K and values used in the Born-Haber cycle are enthalpies at 298 K.
For MX

\[ U_{298} = U_0 + \frac{3}{2} RT(2) - \int_0^T C_P^0(MX) \, dT \]

\[ = U_0 + 3RT - \int_0^T C_P^0(MX) \, dT \]

\[ H_{298} = U_{298} + 2RT \]

\[ H_{298} = U_0 + 5RT - \int_0^{298} C_P(MX) \, dT \]

Therefore, to the U values calculated from the Kapustinskii equation, \((5RT - \int_0^{298} C_P^0(MX) \, dT)\) should be added to give values of the lattice enthalpy for use in the Born-Haber cycle to calculate \(\Delta H_f^{X^-}(g)\). \(\int_0^{298} C_P(MX) \, dT\) for \(X^-, \text{Pic}^-\) are unknown, and in view of the approximations made in the calculation of the lattice energy, the significance of making a correction of 5RT to the calculated value must be questioned.

For the picrate ion, the thermochemical radius was calculated from data for the potassium, rubidium and caesium salts, taking them in pairs.

<table>
<thead>
<tr>
<th>salts</th>
<th>(K, \text{Rb})</th>
<th>(K, \text{Cs})</th>
<th>(\text{Rb}, \text{Cs})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{th}/\text{nm})</td>
<td>0.199</td>
<td>0.264</td>
<td>0.328</td>
</tr>
</tbody>
</table>

The mean value was 0.264nm. (It is of interest to note that in 1948, Yatsimirskii published a value of 0.223nm for the thermochemical radius of the picrate ion. How this value was calculated is unknown since there appear to have been no enthalpy of formation data for metal picrates in the literature at that time.)

The thermochemical radius can then be used to calculate lattice energies from

\[ U_o = 242.8 \frac{(1-0.0345)}{r_{\text{th}^+ \text{Pic}}} \left( \frac{1}{r_{\text{th}^+ \text{Pic}}} \right) \]

Using the mean value of \(r_{th} = 0.264\text{nm}\), lattice energies for the alkali metal salts were calculated as
Substitution of these figures and enthalpies of formation for
MPic and $M^+(g)$ into the Born-Haber cycle

\[
\begin{align*}
\text{Elements} & \quad \Delta H^+_1(g) \\
\text{MPic} & \quad U_{298} + 2RT \\
\Delta H^+_1 & \quad H^+(g), Pic^-(g)
\end{align*}
\]

yields a value for the standard enthalpy of formation of the gaseous
picrate ion. (In these calculations it is assumed that $U_0 = U_{298}$)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$\Delta H^+_1 Pic^-(g)/kJ \ mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium picrate</td>
<td>459.3</td>
</tr>
<tr>
<td>Rubidium picrate</td>
<td>453.2</td>
</tr>
<tr>
<td>Caesium picrate</td>
<td>458.7</td>
</tr>
<tr>
<td>Mean</td>
<td>457.1</td>
</tr>
</tbody>
</table>

Using this mean value for $\Delta H^+_1 Pic^-(g)$ and $r_{th} = 0.264 nm$ it is
possible to predict enthalpies of formation for other picrates and
compare them with the experimental values (see Table II-38).

For the alkali metals (Na, K, Rb, Cs) and for the ammonium and
tetramethylammonium salts the agreement between the experimental
and calculated enthalpies of formation is good. For tetraethylammonium
and lithium picrates, the agreement is less good, although the
calculated values still give a reasonable idea of the magnitude of
$\Delta H^+_1$. For the silver salt, however, the agreement is poor. The
presence of the small, highly polarising $Ag^+$ ion ensures that there
will be a large deviation from ionic character in the bonding. The actual lattice energy will be greater than that calculated from the Kapustinskii equation because of these non-ionic interactions.

Some standard enthalpies of formation of anhydrous Group II metal picrates have also been calculated using \( r_{th} = 0.264 \text{nm} \) and \( \Delta H_{f}^{\ast} C_{6}H_{2}(NO_{2})_{3}O_{-}^{\ast} (g) = -457.1 \text{ kJ mol}^{-1} \) (see Table II-39).

0.264nm was the mean of the values calculated for the thermochemical radius of the picrate ion (it is also the value calculated from the potassium and caesium salts). From this result, lattice energies, the enthalpy of formation of the gaseous picrate ion and standard enthalpies of formation of salts have been calculated. How would these quantities be influenced, if at all, by using the two extreme values of \( r_{th} \) in the calculations, viz. 0.199 and 0.328nm?

Table II-40 shows the effect of the thermochemical radius upon the calculated lattice energies of the potassium, rubidium and caesium salts. It can be seen that the lattice energy is greatly influenced by the thermochemical radius (since \( U_{o} \propto \frac{1}{r_{c}+r_{a}} \)), and the \( U_{o} \) values are greatest when \( r_{c} = r_{K^{+}} \) and \( r_{a} = 0.199\text{nm} \). There is a difference of some 200 kJ mol\(^{-1}\) between the calculated \( U_{o} \) values for K (with \( r_{a}(r_{pic}) = 0.199\text{nm} \)) and Cs (with \( r_{pic} = 0.328\text{nm} \)).

Consider now the values calculated for \( \Delta H_{f}^{\ast} \text{Pic}^{-}(g) \) with varying thermochemical radius (Table II-41). The greatest mean value is that calculated from cycles assuming \( r_{pic} = 0.328\text{nm} \).

For each value of the thermochemical radius and its corresponding mean enthalpy of formation of the gaseous picrate anion,
enthalpies of formation of the salts may then be calculated (Table II-42). It is clear that although the lattice energy and enthalpy of formation of the gaseous anion are very sensitive to changes in the thermochemical radius, the effect on the enthalpies of formation of the salts is minimised because of the nature of their calculation.

To demonstrate this effect further, more calculations were made assuming values of 0.1, 0.2, 0.3, 0.4, 0.5 nm for $r_{\text{Pic}}$.

Tables II 43-45 inc. list the results obtained for the "lattice energies", "enthalpies of formation of the gaseous picrate anion" and "enthalpies of formation of salts". A graph has been made of the calculated enthalpies of formation against the thermochemical radius for potassium, rubidium and caesium picrates (Fig. II-1). This plot also shows the experimental values with their corresponding error limits.

The most noticeable features about this graph are

(i) for caesium picrate, the "standard enthalpy of formation" becomes more exothermic as $r_{\text{Pic}}$ increases.

(ii) for potassium picrate, the "standard enthalpy of formation" becomes less exothermic as $r_{\text{Pic}}$ increases.

(iii) for rubidium picrate, the "standard enthalpy of formation" shows little variation with $r_{\text{Pic}}$ (although all the calculated values lie just outside the limits on the experimental result).

For potassium picrate, values of $r_{\text{Pic}}$ lying between 0.2 and 0.3 nm give calculated values of the "standard enthalpy of formation" lying within the experimental limits, and for the caesium salt, $0.25 < r_{\text{Pic}} < 0.35$ gives acceptable results.
The relative constancy of the calculated rubidium results is readily explained by the fact that the mean value of $\Delta H_f^{\text{Pic}}(g)$ from the three cycles (K, Rb and Cs) was used in these calculations. These mean results were similar to those found from the rubidium cycles.

Similar calculations were made using sodium, ammonium and tetramethylammonium picrates (Table II-46). The sodium and tetramethylammonium results show a large variation with $r_{\text{Pic}}$ (similar to that exhibited by K and Cs). Ammonium picrate ($r_{\text{NH}_4^-} = 0.144\text{nm}$) is like rubidium picrate in behaviour ($r_{\text{Rb}^+} = 0.147\text{nm}$), i.e. there is very little variation in the calculated enthalpy of formation with $r_{\text{th}}$. This is easily explained in terms of the similarity of the radii of the cations and the use of the mean value of $\Delta H_f^{\text{Pic}}(g)$, calculated from the alkali-metal cycles.
FIG. II-1: Effect of the variation in the thermochemical radius of the picrate anion upon the calculated enthalpies of formation of the K, Rb and Cs salts.

- Solid horizontal lines - experimental values
- Dotted lines - error limits on experimental values

\[ -\Delta H_f / \text{kJ mol}^{-1} \]

\[ r_{th} / \text{nm} \]

K ———
Rb ———
Cs ———
II-10: Solubility

II-10-a: Introduction

Solubility may be defined as the amount of solute that will dissolve in a given volume of solvent to give a saturated solution at a particular temperature. It varies with temperature and the nature and extent of this variation depend on the system being studied. Solubility data have been used to calculate heats of solution.

Considering systems where the solute is a solid and the solvent is liquid, there are a number of ways of measuring solubility. While it is reasonably easy to obtain solubility data at room temperature with these methods, measuring the temperature dependence of solubility is difficult. Some of these methods involve withdrawing an aliquot of solution saturated at a given temperature and evaporating off the solvent and weighing the solid. Other methods are based on a spectrophotometric analysis of solutions. Both of these methods suffer from the disadvantage that a considerable period of time is required to saturate the solution, and that withdrawing an aliquot of solution at elevated temperatures and maintaining the solution at that temperature during the whole of the transfer and while it is being examined is very difficult.

In this work, a dynamic precipitation method was used to determine solubility curves for the potassium, rubidium, caesium, silver, ammonium, tetramethylammonium and tetraethylammonium salts of picric acid. This method suffers none of the disadvantages mentioned above, although a clear danger is that of supercooling.

II-10-b: Experimental

Dynamic precipitation method for solubility determination

A known mass of salt was weighed into a boiling tube and a measured aliquot of water was added from a burette. The mixture was warmed to
effect solution and the tube was then clamped in a large beaker to exclude draughts. The solution was then allowed to cool with constant stirring. A calibrated (N.P.L.) thermometer, graduated to 0.05°C was used to note the temperature at which crystals first appeared. The solution was re-heated to restore homogeneity, and the process repeated to obtain concordant results (± 0.1°C). A known volume of water was then added and the procedure repeated to obtain a further result. This process of successive dilution, warming and cooling was continued as far as was practical.

II-10-c: Results and Discussion

Tables II-47-53 inclusive list the solubility data for each of the salts. From these data, solubility curves of S vs. T were plotted (Fig. II-2) and graphs of ln S vs. 1/T made (Fig. II-3).

The solubility data were fitted to general equations of the form

\[ \ln S = A - 10^3 B/T \]

Table II-54 lists values of the constants A and B for each picrate and the correlation coefficients, \( r^2 \).

The solubilities of many picrates in water and in various organic solvents (notably methanol, ethanol and acetone) have been measured, e.g. hydrazine \(^61\), thallium in water \(^62\) and methanol, thorium in water \(^63\), sodium in water \(^64,65\), aqueous ethanol and aqueous salt solution \(^64\), barium in ethanol \(^66\), rubidium in acetonitrile \(^68\), and ammonium in alcohol \(^69\).

The solubility of potassium picrate in a variety of organic solvents has been measured: methanol \(^70,71\), acetonitrile \(^70,71,72,73\), dimethylformamide \(^70,71\), ethanol \(^71\), N-methyl acetamide \(^74\), water/H\(_2\)O mixtures \(^75\), and aqueous ethanol mixtures \(^76\).

In water, values are available for the solubility of potassium (see Table II-55), rubidium \(^67,79\), caesium \(^67,79\) and ammonium \(^69\) picrates. The solubility of picric acid itself was measured by Desvergnes \(^80\) (see Table II-56).
Solubilities of some salts of dinitrophenols have been determined by some authors. The solubility of sodium dinitrophenolate was found to decrease with increasing temperature in aqueous ethanol, methanol and acetone. Pastac and Lecrivain determined approximate solubilities for the ammonium, magnesium, calcium, potassium and barium salts of dinitrophenol (isomer not specified) by making up mixtures with water in varying proportions, heating until the salt had dissolved and then cooling to the desired temperature. By noting in which tubes there were no crystals and those in which there were, the solubility was known within limits (see Table II-57).

Reference to Table II-55 will show that values obtained in this work for the solubility of potassium picrate are somewhat higher than those found by other authors. This is disconcerting. A danger involved in the use of this method is that of supercooling which is an irreproducible but common phenomenon. Special care was taken to noting the maximum temperature readings at the crystallisation points, but the smoothness of solubility versus temperature plots and the linearity of the $\ln S = A - 10^B/T$ plots may be taken as supporting evidence for the reliability of the data. There may well be some sort of systematic error inherent in the method which gives rise to the discrepancy between this work and that of other authors using different methods. However, the order of the solubilities of these compounds and their variation with temperature, which is difficult to measure by other methods, are presumably sound.

From the solubility plots of $\ln S = A - 10^B/T$, "van't Hoff" enthalpies of solution may be calculated. Table II-19 lists these enthalpies of solution and compares them with the calorimetric ones. There is poor agreement between the two. This indicates the need for care in the interpretation of $\ln S = 1/T$ data uncorrected for activity and heat capacity effects. Caveat experimenter!
For a sparingly soluble salt

\[ MX(c) \rightarrow \Delta H^\circ_{\text{sol}} \rightarrow \text{M}^+(aq) + X^-(aq) \]

\[ \Delta H^\circ_{\text{sol}} = \Delta H^\circ_f M^+(aq) + \Delta H^\circ_f X^-(aq) - \Delta H^\circ_f MX(c) \]

The original idea behind this work had been that it might be possible to obtain estimates of enthalpies of formation from solubility data without having to resort to lengthy calorimetric experiments. Using the experimentally determined heats of formation and the van't Hoff enthalpies of solution, a value has been calculated for \( \Delta H^\circ_{\text{sol}} \), viz. \(-188.5\pm5\) kJ mol\(^{-1}\). This compares with the "calorimetric" value of \(-206\) kJ mol\(^{-1}\). Hence it would appear that approximate values for enthalpies of formation could be calculated from solubility data obtained in the manner described. Table II-59 compares the experimentally determined enthalpies of formation and values calculated using the "van't Hoff" enthalpies of solution. The agreement is reasonable.

II-10-d: Calculation of Heats of Solution from Solubility Data

The simplest, most precise and most accurate method of measuring an enthalpy of solution is usually via a direct calorimetric experiment except for sparingly soluble compounds. For these the solubility method is often appropriate.

For a sparingly soluble salt(MX) system containing crystalline salt and saturated solution, it can be shown that

\[ -\Delta G^\circ_{\text{sol}} = 2RT \ln S \] (1)

where \( \Delta G^\circ_{\text{sol}} \) is the free energy of solution and \( S \) is the solubility, assuming the salt is completely ionized into 2 ions.

It follows that

\[ \Delta H^\circ_{\text{sol}} = 2RT^2 \left( \frac{d\ln S}{dT} \right)_p \] (2)
However, with salts in water, it is often found that the saturated concentration is beyond the range for which the van't Hoff relationship applies. The free energy upon dissolving may then be found provided values are available for the mean ionic activity coefficient, \( \gamma \), at the concentration of the saturated solution. Then, assuming complete dissociation, we have, in terms of the molality of the saturated solution,

\[
- \Delta G_{\text{sol}}^\circ = 2RT \ln (m \gamma)_{\text{sat}}
\]

and

\[
- \Delta H_{\text{sol}}^\circ = 2RT^2 \left( \frac{d \ln (m \gamma)}{dT} \right)_{\text{sat}}
\]

(3) only really applies to ideal solutions in this form. However, Williamson has recalculated this by rigorous thermodynamic methods to make it suitable for non-ideal systems, and it has been shown that solutions of electrolytes must obey the relation

\[
\Delta H_{\text{sol}}^\circ = \gamma RT^2 \left( \frac{dm}{dT} \right)_{\text{sat}} \left( \frac{d \ln \gamma}{dm} \right)_{\text{sat}} \left( \frac{1}{m} \right)_{\text{sat}}
\]

and that non-electrolytes follow a formally similar expression in which \( \gamma = 1 \). In this precise equation, \( \Delta H_{\text{sol}}^\circ \) is the heat absorbed per mole of solute dissolved in the nearly saturated solution, or the heat evolved per mole on crystallisation. The molality, \( m \), is the value characteristic of the saturated solution, \( \gamma \) is the stoichiometric number of ions produced per mole of electrolyte, and \( \gamma \) is the mean ionic activity coefficient. Williamson used several examples from the data available at the time (1944), and his values of \( \Delta H_{\text{sol}}^\circ \) calculated from the exact equation show good agreement with those measured calorimetrically, e.g.: KCl, Ba\((NO_3)_2\), Na\(_2\)CO\(_3\)·10H\(_2\)O, NaOH and urea. The equation can be adapted for use with hydrated salts.
II-10-e: The Solubility of Ionic Salts

Because of the logarithmic dependence of $\Delta G_{\text{sol}}^*$ upon solubility, Johnson points out that the energetic differences between 'soluble' and 'insoluble' salts are small. He cites the examples of potassium nitrate and potassium perchlorate. The standard free energy of solution in water of KNO$_3$ is less than 13kJ mol$^{-1}$ more negative than KCIO$_4$. Johnson writes 'any treatment of solubilities based on a theoretical interpretation of $\Delta G_{\text{sol}}^*$ is thus exposed to considerable error even when small approximations are made.'

Consider the following cycle for the dissolution of an ionic salt, $M\text{a}X\text{b}_s$, in water.

\[
\begin{array}{c}
\text{M}_a\text{X}_b\quad \Delta G_{\text{sol}}^* \\
\xrightarrow{\text{sol}} \quad \text{aM}^{b+}(aq) + \text{bX}^{a-}(aq) \\
\Delta G_L^* \\
\Delta G_h^* \\
\end{array}
\]

$\Delta G_{\text{sol}}^*$ is the free energy of solution.

$\Delta G_L^*$ is the free energy change when the lattice is dissociated into the separate gaseous ions at one atmosphere pressure.

$\Delta G_h^*$ is the free energy of hydration of these gaseous ions.

In water, $\Delta G_L^*$ and $\Delta G_h^*$ are of similar magnitude but opposite sign, i.e: $\Delta G_{\text{sol}}^*$ is the small difference between two large quantities.

Johnson considers the free energy of sublimation of the lattice and the free energy of hydration of the ions and derives expressions for each, combining them to give a grand expression for $\Delta G_{\text{sol}}^*$. He then examines the change is the free energies of solution of a series of anhydrous salts, of the same anion and formula type, as the cation size is varied, by differentiating the expression for $\Delta G_{\text{sol}}^*$ with respect
to $r_+$. Further differentiation shows this to refer to a maximum.

It can be shown that a maximum in the free energy of solution occurs when

$$r_+ = r_+ \left( 1.25 \sqrt{\left( \frac{1 + \frac{e_-}{e_+} \right) - 1} + 0.90 \sqrt{\frac{1 + \frac{e_-}{e_+}}{1}} \right)$$

(1)

Because of the approximations made in its derivation (1) cannot be expected to predict accurately the cationic radius at which the maximum in $\Delta G_{sol}^\circ$ is achieved in a series of salts of the same anion and formula type. However, it is largely successful in predicting the qualitative variation in $\Delta G_{sol}^\circ$.

For an anion of minimum size 0.13nm, the equation predicts:

(i) For salts of the same anion and formula type, if $r_+$ is increased, $\Delta G_{sol}^\circ$ rises, reaches a maximum and then falls towards a limiting value. The series of experimentally observed free energies may only cover the increasing or decreasing portion of the curve.

(ii) If the size of the cation in a salt of a particular anion and formula type is increased, a fall in the free energy of solution should never be succeeded by a rise.

(iii) When two series of salts have different formula types but contain fixed anions of similar size, the free energy maximum should occur at a smaller cation radius in the series with the higher value of $e_-/e_+$.

Johnson's rules have been successfully applied to predict the solubilities of many series of salts. They hold for the alkali metal picrates. The maximum in $\Delta G_{sol}^\circ$ is probably observed at a cationic radius greater than that of caesium.

This suggests that tetramethylammonium and tetraethylammonium picrates would be less soluble than caesium picrate. It is hence surprising to find that the solubilities of $\text{NMMe}_4\text{Pic}$ and $\text{NMe}_4\text{Pic}$ are, respectively, greater than and comparable with that of potassium picrate.
Tetrabutylammonium picrate is insoluble in water, so the aqueous solubility of these tetraalkylammonium picrates seems to decrease with increasing size of the alkyl group.
The aqueous solubility of picrates.
InS vs. $1/T$ plots for picrates in water.
Another method for determining the standard enthalpy of formation of picric acid via solution calorimetry is outlined here. It is also based upon a neutralisation reaction but this time the use of carbonates is proposed. This presents problems not encountered with hydroxide neutralisation—namely concerning the evolution of \( \text{CO}_2 \).

Consider the following reaction carried out in a calorimeter:

\[
\text{an ampoule of solid sodium or potassium carbonate (of high purity (known))} \quad (\Delta H^\circ_f \text{ of these salts are well established}) \text{ is broken into a slight excess of picric acid solution. (The enthalpy of solution of picric acid in water is known.)}
\]

\[
\begin{align*}
2\text{HPic(aq)} + \text{Na}_2\text{CO}_3 & \quad \Delta H_1 \\
2\text{NaPic (aq)} + \left[ \text{H}_2\text{O}(l) + \text{CO}_2 \right] & \quad \ldots \quad (1)
\end{align*}
\]

The final state of the \( \text{CO}_2 \) formed must be known for this reaction to be calorimetrically useful. How much of the \( \text{CO}_2 \) will dissolve in the calorimetric fluid and how much will be evolved as gas?

If, for reaction (1)

\[
X = \Delta H^\circ_f \left[ \text{H}_2\text{O} + \text{CO}_2 \right]
\]

then

\[
\Delta H_1 = \Delta H^\circ_f \left[ 2\text{NaPic(aq)} \right] + X \quad \left[ \Delta H^\circ_f (2\text{HPic(aq)} + \Delta H^\circ_f \text{Na}_2\text{CO}_3(c)) \right]
\]

Since \( \Delta H^\circ_f \text{NaPic(aq)} \) and \( \Delta H^\circ_f \text{Na}_2\text{CO}_3(c) \) are known and \( \Delta H_1 \) may be found experimentally, \( X - \Delta H^\circ_f 2\text{HPic(aq)} \) may be calculated.

If the above procedure is now repeated using \( \text{K}_2\text{CO}_3 \) to give an enthalpy of reaction \( \Delta H_2 \), then another value for \( X - \Delta H^\circ_f 2\text{HPic(aq)} \) may be determined. (Amounts of reactants in the two sets of reactions could be adjusted to produce similar amounts of \( \text{CO}_2 \).) The two values of \( X - \Delta H^\circ_f 2\text{HPic(aq)} \) would hopefully be the same. (These two series of
experiments merely act as a 'double-check' on each other.)

If another acid whose standard enthalpy of formation is well known (and whose sodium and potassium salts are also well established) is now used to neutralise sodium carbonate, e.g:

\[
\begin{align*}
2\text{HCl(aq)} + \text{Na}_2\text{CO}_3(\text{c}) & \rightarrow 2\text{NaCl(aq)} + \text{H}_2\text{O(1)} + \text{CO}_2, \\
\Delta H_\text{f} & \rightarrow
\end{align*}
\]

a value for X may be found. (Comparable amounts of CO\textsubscript{2} as in picrate experiments).

Again, X may be checked by a second series of experiments using K\textsubscript{2}CO\textsubscript{3} (or employing another acid).

If the X values are the same, \(\Delta H_\text{f}^\text{HPic(c)}\) may then be calculated.

Further investigations of the constitution of picrate solutions should be made. In this work, it is assumed that, upon dissolution, picric acid undergoes complete dissociation thus:

\[
\begin{align*}
\text{HPic(c)} & \rightarrow \text{H}^+(\text{aq}) + \text{Pic}^-(\text{aq}), \\
\Delta H_\text{f} & \rightarrow
\end{align*}
\]

A very cursory investigation of the variation of the refractive index of dilute potassium picrate solution with temperature was made but these results (obtained using an Abbé refractometer) did not show any great discontinuity in r.i. between the solutions. However this study was very unsatisfactory and no conclusions may be drawn from it, but it is clearly an area where further work would be useful.
<table>
<thead>
<tr>
<th>$\Delta H_f^{\circ}/\text{kJ mol}^{-1}$</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>326.35</td>
<td>Combustion</td>
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</tr>
<tr>
<td>359.31</td>
<td>Combustion</td>
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</tr>
<tr>
<td>396.64±2.7</td>
<td>Combustion(y)</td>
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<td>399.15±2.5</td>
<td>Combustion(r)</td>
<td>37</td>
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<td>350.2</td>
<td>Combustion(y)</td>
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<td>392.04</td>
<td>Combustion(r)</td>
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<td>369.95</td>
<td>Solution(y)</td>
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<tr>
<td>384.1±2.7</td>
<td>y *</td>
<td></td>
</tr>
<tr>
<td>385.44±2.94</td>
<td>Combustion(y)</td>
<td>This work</td>
</tr>
</tbody>
</table>

r = Red form; y = yellow form

* = recalculated from ref. 36
TABLE II-2
ENTHALPIES OF COMBUSTION AND FORMATION OF PICRIC ACID AT 298.15K

<table>
<thead>
<tr>
<th>$\Delta H^\circ_c / kJ \text{ mol}^{-1}$</th>
<th>$\Delta H^\circ_f / kJ \text{ mol}^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>2575.46$\pm$1.34</td>
<td>214.35$\pm$1.38</td>
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<td>2569.10$\pm$2.55</td>
<td>220.71$\pm$2.59</td>
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<tr>
<td>2578.60$\pm$2.51</td>
<td>211.29$\pm$2.51</td>
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<tr>
<td>2567.64$\pm$2.51</td>
<td>222.17$\pm$2.59</td>
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<tr>
<td>2571.92$\pm$1.74</td>
<td>217.88$\pm$1.99</td>
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</tr>
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<td>B</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>m(sample)/g</td>
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<td>1.056907</td>
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<tr>
<td>m(fuse)/g</td>
<td>0.00483</td>
<td>0.00448</td>
</tr>
<tr>
<td>m(Pt wire)/g</td>
<td>0.00719</td>
<td>0.00916</td>
</tr>
<tr>
<td>m(silica crucible)/g</td>
<td>4.766044</td>
<td>4.638436</td>
</tr>
<tr>
<td>m(soot)/g</td>
<td>0.00003</td>
<td>0.00013</td>
</tr>
<tr>
<td>m(H₂O)/g</td>
<td>1.08</td>
<td>1.08</td>
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<tr>
<td>q;/kJ</td>
<td>0.086307</td>
<td>0.080185</td>
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<td>q₀/kJ</td>
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<tr>
<td>ΔT/K</td>
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<td>3.2438</td>
</tr>
<tr>
<td>f</td>
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<td>0.999990</td>
</tr>
<tr>
<td>eₙ/kJ K⁻¹</td>
<td>8.6424</td>
<td>8.6380</td>
</tr>
<tr>
<td>eₙ/kJ K⁻¹</td>
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<tr>
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<tr>
<td>Ref. No.</td>
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<td>H</td>
</tr>
<tr>
<td>--------------------------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>m(sample)/g</td>
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<td>1.195802</td>
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<td>m(fuse)/g</td>
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<td>0.00663</td>
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<tr>
<td>m(silica crucible)/g</td>
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<td>4.451490</td>
</tr>
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<td>m(H₂O)/g</td>
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<td>1.08</td>
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<td>0.063395</td>
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<td>q₃/kJ</td>
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<td>ΔT/K</td>
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<td>f</td>
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<tr>
<td>eᵢ/kJ K⁻¹</td>
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<td>8.6374</td>
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<td>eₑᵢ/kJ K⁻¹</td>
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<td>0.020042</td>
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Mean = 8.6186 ± 0.0026 kJ K⁻¹
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<tr>
<td>qᵣ/kJ</td>
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Mean = -11.5504 ± 0.0115 kJg⁻¹
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<td>m(soot)/g</td>
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<td>qc/kJ</td>
<td>0.000000</td>
<td>0.006600</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
<td>0.000000</td>
</tr>
<tr>
<td>qw/kJ</td>
<td>0.065324</td>
<td>0.050484</td>
<td>0.051188</td>
<td>0.063985</td>
<td>0.065718</td>
<td>0.062323</td>
</tr>
<tr>
<td>ΔT/K</td>
<td>3.2290</td>
<td>2.5421</td>
<td>2.5740</td>
<td>3.1541</td>
<td>3.2356</td>
<td>3.0829</td>
</tr>
<tr>
<td>e_f/kJ/K</td>
<td>8.6792</td>
<td>8.6786</td>
<td>8.6786</td>
<td>8.6791</td>
<td>8.6793</td>
<td>8.6790</td>
</tr>
<tr>
<td>e_cf/kJ/K</td>
<td>0.060636</td>
<td>0.059956</td>
<td>0.059980</td>
<td>0.060438</td>
<td>0.060643</td>
<td>0.060380</td>
</tr>
<tr>
<td>- Δu_c(298.15K)/kJ_g^{-1}</td>
<td>11.2701</td>
<td>11.2748</td>
<td>11.2817</td>
<td>11.2613</td>
<td>11.2754</td>
<td>11.2665</td>
</tr>
</tbody>
</table>

Mean = - 11.2716 ± 0.0076 kJ_g^{-1}
### TABLE II - 8

**SOLUTION CALORIMETRY TEST REACTION:** Enthalpy of neutralisation of THAM in excess 0.1M HCl

<table>
<thead>
<tr>
<th>Calorimeter</th>
<th>$\Delta H^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>29.81 ± 0.08</td>
</tr>
</tbody>
</table>

### TABLE II - 9

**SOLUTION CALORIMETRY TEST REACTION:** Enthalpy of solution of THAM in aqueous sodium hydroxide solution

<table>
<thead>
<tr>
<th>Calorimeter</th>
<th>$\Delta H^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>16.67 ± 0.05 (0.1M)</td>
</tr>
<tr>
<td>b</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>17.18 ± 0.04 (0.05M)</td>
</tr>
</tbody>
</table>

### TABLE II - 10

**REACTION CALORIMETRY TEST:** Enthalpy of reaction between crystalline KBr and excess AgNO$_3$ solution

<table>
<thead>
<tr>
<th>Calorimeter</th>
<th>$\Delta H^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-</td>
</tr>
<tr>
<td>b</td>
<td>65.17 ± 0.11</td>
</tr>
<tr>
<td>c</td>
<td>-</td>
</tr>
</tbody>
</table>

For calorimeter nomenclature and literature values for test reactions, see Sections II-3-a(i) and (ii).
### TABLE II-11

**ENTHALPY OF SOLUTION OF POTASSIUM PICRATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H_{\text{sol}}^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5230</td>
<td>5678</td>
<td>50.84</td>
</tr>
<tr>
<td>0.5142</td>
<td>5775</td>
<td>52.18</td>
</tr>
<tr>
<td>0.5133</td>
<td>5784</td>
<td>50.43</td>
</tr>
<tr>
<td>0.5109</td>
<td>5811</td>
<td>52.08</td>
</tr>
<tr>
<td>0.5035</td>
<td>5898</td>
<td>50.50</td>
</tr>
<tr>
<td>0.4459</td>
<td>6657</td>
<td>50.64</td>
</tr>
<tr>
<td>0.4161</td>
<td>7136</td>
<td>51.26</td>
</tr>
<tr>
<td>0.4118</td>
<td>7210</td>
<td>52.26</td>
</tr>
<tr>
<td>0.3614</td>
<td>8212</td>
<td>50.46</td>
</tr>
<tr>
<td>0.1177</td>
<td>25250</td>
<td>50.77</td>
</tr>
</tbody>
</table>

Mean = 51.14 ± 0.55$^b$

### TABLE II-12

**ENTHALPY OF SOLUTION OF RUBIDIUM PICRATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H_{\text{sol}}^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4751</td>
<td>7333</td>
<td>54.22</td>
</tr>
<tr>
<td>0.4691</td>
<td>7427</td>
<td>55.55</td>
</tr>
<tr>
<td>0.4568</td>
<td>7480</td>
<td>55.51</td>
</tr>
<tr>
<td>0.4389</td>
<td>7938</td>
<td>55.65</td>
</tr>
<tr>
<td>0.4239</td>
<td>8219</td>
<td>54.78</td>
</tr>
<tr>
<td>0.3857</td>
<td>9033</td>
<td>54.45</td>
</tr>
<tr>
<td>0.3591</td>
<td>9702</td>
<td>55.27</td>
</tr>
<tr>
<td>0.3438</td>
<td>10134</td>
<td>54.87</td>
</tr>
<tr>
<td>0.3056</td>
<td>11401</td>
<td>54.81</td>
</tr>
</tbody>
</table>

Mean = 55.01 ± 0.36$^b$

---

$a$ = mole ratio of compound to water

$b$ = uncertainties are 95% confidence limits calculated using the student's t distribution with the appropriate number of degrees of freedom.
### TABLE II-13
**ENTHALPY OF SOLUTION OF CAESIUM PICRATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n^a</th>
<th>( \Delta H^\circ_{\text{sol}} \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6767</td>
<td>5927</td>
<td>54.73</td>
</tr>
<tr>
<td>0.5830</td>
<td>6860</td>
<td>56.02</td>
</tr>
<tr>
<td>0.5817</td>
<td>6895</td>
<td>56.00</td>
</tr>
<tr>
<td>0.5096</td>
<td>7871</td>
<td>55.73</td>
</tr>
<tr>
<td>0.4390</td>
<td>9137</td>
<td>56.27</td>
</tr>
<tr>
<td>0.4382</td>
<td>9154</td>
<td>56.72</td>
</tr>
<tr>
<td>0.4332</td>
<td>9259</td>
<td>57.29</td>
</tr>
<tr>
<td>0.3959</td>
<td>10132</td>
<td>55.73</td>
</tr>
<tr>
<td>0.3627</td>
<td>11050</td>
<td>55.76</td>
</tr>
</tbody>
</table>

Mean = 56.03 ± 0.55

### TABLE II-14
**ENTHALPY OF SOLUTION OF TETRAMETHYLAMMONIUM PICRATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n^a</th>
<th>( \Delta H^\circ_{\text{sol}} \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38062</td>
<td>4411</td>
<td>31.54</td>
</tr>
<tr>
<td>0.32448</td>
<td>5175</td>
<td>31.62</td>
</tr>
<tr>
<td>0.28571</td>
<td>5877</td>
<td>32.08</td>
</tr>
<tr>
<td>0.20253</td>
<td>8291</td>
<td>31.90</td>
</tr>
<tr>
<td>0.20030</td>
<td>8383</td>
<td>31.97</td>
</tr>
<tr>
<td>0.19626</td>
<td>8555</td>
<td>32.36</td>
</tr>
<tr>
<td>0.12948</td>
<td>12968</td>
<td>31.42</td>
</tr>
</tbody>
</table>

Mean = 31.84 ± 0.31

### TABLE II-15
**ENTHALPY OF SOLUTION OF TETRAETHYLAMMONIUM PICRATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n^a</th>
<th>( \Delta H^\circ_{\text{sol}} \text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2214</td>
<td>8990</td>
<td>31.84</td>
</tr>
<tr>
<td>0.4342</td>
<td>9170</td>
<td>32.07</td>
</tr>
<tr>
<td>0.3415</td>
<td>11660</td>
<td>32.17</td>
</tr>
<tr>
<td>0.1656</td>
<td>12021</td>
<td>31.96</td>
</tr>
<tr>
<td>0.3054</td>
<td>13039</td>
<td>31.82</td>
</tr>
<tr>
<td>0.1384</td>
<td>14383</td>
<td>32.23</td>
</tr>
</tbody>
</table>

Mean = 32.02 ± 0.18
### Table II-16
**Enthalpy of Solution of Ammonium Picrate in Water**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H^{\circ}_{298}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33957</td>
<td>4027</td>
<td>45.81</td>
</tr>
<tr>
<td>0.31901</td>
<td>4287</td>
<td>46.40</td>
</tr>
<tr>
<td>0.30780</td>
<td>4443</td>
<td>45.86</td>
</tr>
<tr>
<td>0.25396</td>
<td>5384</td>
<td>46.13</td>
</tr>
<tr>
<td>0.24986</td>
<td>5473</td>
<td>45.43</td>
</tr>
<tr>
<td>0.24152</td>
<td>5662</td>
<td>45.44</td>
</tr>
<tr>
<td>0.22225</td>
<td>6153</td>
<td>46.30</td>
</tr>
<tr>
<td>0.21467</td>
<td>6370</td>
<td>46.24</td>
</tr>
<tr>
<td>0.20487</td>
<td>6675</td>
<td>45.20</td>
</tr>
<tr>
<td>0.17983</td>
<td>7604</td>
<td>44.88</td>
</tr>
<tr>
<td>0.15146</td>
<td>9028</td>
<td>46.23</td>
</tr>
</tbody>
</table>

Mean = 45.81 ± 0.35

### Table II-17
**Enthalpy of Solution of Silver Picrate in Water**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H^{\circ}_{298}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8569</td>
<td>4355</td>
<td>36.40</td>
</tr>
<tr>
<td>0.7855</td>
<td>4752</td>
<td>36.35</td>
</tr>
<tr>
<td>0.7602</td>
<td>4910</td>
<td>36.21</td>
</tr>
<tr>
<td>0.6754</td>
<td>5527</td>
<td>36.97</td>
</tr>
<tr>
<td>0.6279</td>
<td>5945</td>
<td>37.03</td>
</tr>
<tr>
<td>0.6201</td>
<td>6019</td>
<td>36.50</td>
</tr>
<tr>
<td>0.5775</td>
<td>6464</td>
<td>37.60</td>
</tr>
<tr>
<td>0.4682</td>
<td>7973</td>
<td>36.70</td>
</tr>
<tr>
<td>0.4147</td>
<td>9001</td>
<td>36.47</td>
</tr>
</tbody>
</table>

Mean = 36.69 ± 0.35
<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H^\circ$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2073</td>
<td>6140</td>
<td>21.65</td>
</tr>
<tr>
<td>0.2070</td>
<td>6149</td>
<td>21.74</td>
</tr>
<tr>
<td>0.1305</td>
<td>9754</td>
<td>22.71</td>
</tr>
<tr>
<td>0.1041</td>
<td>12227</td>
<td>21.99</td>
</tr>
<tr>
<td>0.0978</td>
<td>13015</td>
<td>21.04</td>
</tr>
<tr>
<td>0.0950</td>
<td>13398</td>
<td>21.03</td>
</tr>
<tr>
<td>0.0822</td>
<td>15485</td>
<td>21.69</td>
</tr>
<tr>
<td>0.0731</td>
<td>17412</td>
<td>21.96</td>
</tr>
<tr>
<td>0.0654</td>
<td>19462</td>
<td>21.04</td>
</tr>
<tr>
<td>0.0645</td>
<td>19734</td>
<td>21.78</td>
</tr>
</tbody>
</table>

Mean = 21.67 $^\pm$ 0.38
<table>
<thead>
<tr>
<th>M</th>
<th>$\Delta H^\circ$ /kJ mol$^{-1}$</th>
<th>$\Delta H^\circ$ /kJ mol$^{-1}$</th>
<th>$\Delta H^\circ$ /kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(calorimetric)</td>
<td>(calorimetric)</td>
<td>(solubility)</td>
</tr>
<tr>
<td>Li</td>
<td>6.40$\pm$0.04</td>
<td>15.80$^{33}$</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>20.25$\pm$0.17</td>
<td>21.16$^{32}$</td>
<td>32.05$^{33}$</td>
</tr>
<tr>
<td>K</td>
<td>51.14$\pm$0.55</td>
<td>50.92$\pm$0.21</td>
<td>62.65$\pm$1.42</td>
</tr>
<tr>
<td>Rb</td>
<td>55.01$\pm$0.36</td>
<td></td>
<td>73.74$\pm$1.18</td>
</tr>
<tr>
<td>Cs</td>
<td>56.03$\pm$0.55</td>
<td></td>
<td>72.40$\pm$1.86</td>
</tr>
<tr>
<td>Ag</td>
<td>36.69$\pm$0.35</td>
<td></td>
<td>54.32$\pm$0.85</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>45.81$\pm$0.35</td>
<td>45.46$\pm$0.30$^{34}$</td>
<td>71.88$\pm$1.27</td>
</tr>
<tr>
<td>NMe$_4$</td>
<td>31.84$\pm$0.31</td>
<td>31.97$^{32}$</td>
<td>42.75$\pm$0.76</td>
</tr>
<tr>
<td>NEt$_4$</td>
<td>32.02$\pm$0.18</td>
<td>30.39$^{33}$</td>
<td>52.66$\pm$1.53</td>
</tr>
</tbody>
</table>
### TABLE II-20

**ENTHALPY OF PRECIPITATION OF SILVER PICRATE AND AMMONIUM BROMIDE**

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^o_{ \text{aq} } / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0934</td>
<td>69.81</td>
</tr>
<tr>
<td>0.0942</td>
<td>70.67</td>
</tr>
<tr>
<td>0.1000</td>
<td>69.40</td>
</tr>
<tr>
<td>0.1151</td>
<td>70.01</td>
</tr>
<tr>
<td>0.1160</td>
<td>69.92</td>
</tr>
<tr>
<td>0.1247</td>
<td>69.77</td>
</tr>
<tr>
<td>0.1367</td>
<td>69.86</td>
</tr>
</tbody>
</table>

Mean = $-69.92 \pm 0.37^b$

### TABLE II-21

**ENTHALPY OF PRECIPITATION OF SILVER PICRATE AND POTASSIUM BROMIDE**

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^o_{ \text{aq} } / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0752</td>
<td>65.94</td>
</tr>
<tr>
<td>0.0691</td>
<td>65.22</td>
</tr>
<tr>
<td>0.1067</td>
<td>65.39</td>
</tr>
<tr>
<td>0.1130</td>
<td>65.65</td>
</tr>
<tr>
<td>0.1584</td>
<td>65.43</td>
</tr>
<tr>
<td>0.1777</td>
<td>65.59</td>
</tr>
<tr>
<td>0.2137</td>
<td>65.63</td>
</tr>
</tbody>
</table>

Mean = $-65.55 \pm 0.22^b$
### TABLE II-22
ENTHALPY OF PRECIPITATION OF SILVER PICRATE AND RUBIDIUM BROMIDE

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ /kJ \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1655</td>
<td>64.58</td>
</tr>
<tr>
<td>0.1945</td>
<td>64.20</td>
</tr>
<tr>
<td>0.2186</td>
<td>64.94</td>
</tr>
<tr>
<td>0.2201</td>
<td>64.74</td>
</tr>
<tr>
<td>0.3016</td>
<td>64.82</td>
</tr>
<tr>
<td>0.3254</td>
<td>64.87</td>
</tr>
<tr>
<td>0.3408</td>
<td>64.71</td>
</tr>
</tbody>
</table>

Mean $= -64.69 \pm 0.24^b$

### TABLE II-23
ENTHALPY OF PRECIPITATION OF SILVER PICRATE AND CAESIUM BROMIDE

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ /kJ \text{ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2031</td>
<td>58.97</td>
</tr>
<tr>
<td>0.2588</td>
<td>58.99</td>
</tr>
<tr>
<td>0.2691</td>
<td>59.33</td>
</tr>
<tr>
<td>0.2855</td>
<td>61.93</td>
</tr>
<tr>
<td>0.3015</td>
<td>60.55</td>
</tr>
<tr>
<td>0.3304</td>
<td>59.80</td>
</tr>
<tr>
<td>0.3504</td>
<td>59.17</td>
</tr>
<tr>
<td>0.3599</td>
<td>61.22</td>
</tr>
<tr>
<td>0.3661</td>
<td>61.69</td>
</tr>
</tbody>
</table>

Mean $= -60.18 \pm 0.94^b$
### Table II-24

**Enthalpy of Precipitation of Silver Picrate and Tetramethylammonium Bromide**

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ_{\text{pre}}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0803</td>
<td>61.23</td>
</tr>
<tr>
<td>0.0744</td>
<td>60.83</td>
</tr>
<tr>
<td>0.0834</td>
<td>61.85</td>
</tr>
<tr>
<td>0.0981</td>
<td>60.95</td>
</tr>
<tr>
<td>0.1041</td>
<td>60.86</td>
</tr>
<tr>
<td>0.1313</td>
<td>60.55</td>
</tr>
<tr>
<td>0.1472</td>
<td>61.44</td>
</tr>
<tr>
<td>0.1690</td>
<td>61.36</td>
</tr>
</tbody>
</table>

Mean = $-61.13 \pm 0.36^b$

### Table II-25

**Enthalpy of Precipitation of Silver Picrate and Tetraethylammonium Bromide**

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ_{\text{pre}}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0777</td>
<td>81.48</td>
</tr>
<tr>
<td>0.0837</td>
<td>79.82</td>
</tr>
<tr>
<td>0.1044</td>
<td>79.26</td>
</tr>
<tr>
<td>0.1062</td>
<td>79.28</td>
</tr>
<tr>
<td>0.1149</td>
<td>79.59</td>
</tr>
<tr>
<td>0.1277</td>
<td>79.77</td>
</tr>
<tr>
<td>0.1280</td>
<td>79.50</td>
</tr>
<tr>
<td>0.1344</td>
<td>80.43</td>
</tr>
</tbody>
</table>

Mean = $-79.89 \pm 0.64^b$
**TABLE II-26**

**COLLATED DATA**

**ENTHALPY OF PRECIPITATION OF SILVER PICRATE AND MBr.**

<table>
<thead>
<tr>
<th>M</th>
<th>$-\Delta H^\circ_{298}/kJ \text{ mol}^{-1}$ b</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_4$</td>
<td>69.92±0.37</td>
</tr>
<tr>
<td>K</td>
<td>65.55±0.22</td>
</tr>
<tr>
<td>Rb</td>
<td>64.69±0.24</td>
</tr>
<tr>
<td>Cs</td>
<td>60.18±0.94</td>
</tr>
<tr>
<td>NMe$_4$</td>
<td>61.13±0.36</td>
</tr>
<tr>
<td>NEt$_4$</td>
<td>79.89±0.64</td>
</tr>
</tbody>
</table>
TABLE II-27

STANDARD ENTHALPIES OF FORMATION OF PICRATES, $^{\text{MPic}}$

<table>
<thead>
<tr>
<th>M</th>
<th>$-\Delta H_f^*/\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_4$</td>
<td>385.44$^{\pm}$2.94</td>
</tr>
<tr>
<td>Ag</td>
<td>136.29$^{\pm}$3.01</td>
</tr>
<tr>
<td>K</td>
<td>508.09$^{\pm}$3.05</td>
</tr>
<tr>
<td>Rb</td>
<td>508.17$^{\pm}$3.02</td>
</tr>
<tr>
<td>Cs</td>
<td>520.96$^{\pm}$3.20</td>
</tr>
<tr>
<td>$\text{N(CH}_3)_4$</td>
<td>343.70$^{\pm}$4.30</td>
</tr>
<tr>
<td>$\text{N(C}_2\text{H}_5)_4$</td>
<td>488.14$^{\pm}$5.80</td>
</tr>
<tr>
<td>M</td>
<td>$\Delta H^\circ$/kJ mol$^{-1}$</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>H</td>
<td>29.7</td>
</tr>
<tr>
<td>Ba</td>
<td>19.7</td>
</tr>
<tr>
<td>Ba(H$_2$O)</td>
<td>39.3</td>
</tr>
<tr>
<td>Ba(6H$_2$O)</td>
<td>61.7</td>
</tr>
<tr>
<td>Ca</td>
<td>-9.2</td>
</tr>
<tr>
<td>Ca(6H$_2$O)</td>
<td>62.4</td>
</tr>
<tr>
<td>Cu</td>
<td>-13.8</td>
</tr>
<tr>
<td>Cu(8H$_2$O)</td>
<td>73.7</td>
</tr>
<tr>
<td>K</td>
<td>42</td>
</tr>
<tr>
<td>Mg</td>
<td>-61.5</td>
</tr>
<tr>
<td>Mg(8H$_2$O)</td>
<td>66.5</td>
</tr>
<tr>
<td>Na</td>
<td>26.95</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>36.4</td>
</tr>
<tr>
<td>Pb</td>
<td>29.7</td>
</tr>
<tr>
<td>Pb(2H$_2$O)</td>
<td>55.2</td>
</tr>
<tr>
<td>Sr</td>
<td>-3.3</td>
</tr>
<tr>
<td>Sr(6H$_2$O)</td>
<td>60.3</td>
</tr>
<tr>
<td>Zn</td>
<td>-48.1</td>
</tr>
<tr>
<td>Zn(8H$_2$O)</td>
<td>66.5</td>
</tr>
</tbody>
</table>
TABLE II-29

ENTHALPY OF NEUTRALISATION OF PICRIC ACID/AMMONIUM HYDROXIDE (298K)

<table>
<thead>
<tr>
<th>m/\text{g}</th>
<th>\Delta \text{H}^\circ /\text{kJ mol}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0582</td>
<td>29.20</td>
</tr>
<tr>
<td>0.0600</td>
<td>29.72</td>
</tr>
<tr>
<td>0.0761</td>
<td>30.69</td>
</tr>
<tr>
<td>0.0973</td>
<td>29.75</td>
</tr>
<tr>
<td>0.1862</td>
<td>29.87</td>
</tr>
<tr>
<td>0.2068</td>
<td>30.50</td>
</tr>
</tbody>
</table>

Mean = 29.95\pm 0.58
TABLE II-30

Enthalpy of neutralisation of picric acid/\textit{MOH} (M= Na,K)

with NaOH solution

\[ \Delta H_n = 56.65 \pm 0.6 \text{ kJ mol}^{-1} \]

(Vorob'ev's result: 56.48 kJ mol\(^{-1}\))

with KOH solution

\[ \Delta H_n = 56.61 \pm 0.9 \text{ kJ mol}^{-1} \]

(Vorob'ev's result: 56.06 kJ mol\(^{-1}\))

(The Soviet results have been corrected for the enthalpy of solution in water of picric acid = 21.67 kJ mol\(^{-1}\))
TABLE 11-31

ANCILLARY DATA

(a) Thermochemical Quantities

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta H^\circ_X/\text{kJ mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K^+(aq) )</td>
<td>( 251.21^{+5}, 46 )</td>
</tr>
<tr>
<td>( \text{NH}_{4}^+(aq) )</td>
<td>( 132.51^{+5} )</td>
</tr>
<tr>
<td>( \text{Rb}^+(aq) )</td>
<td>( 248.3^{+7} )</td>
</tr>
<tr>
<td>( \text{Cs}^+(aq) )</td>
<td>( 261.9^{+45} )</td>
</tr>
<tr>
<td>( \text{Ag}^+(aq) )</td>
<td>( -105.6^{+45} )</td>
</tr>
<tr>
<td>( \text{NMe}_4^+(aq) )</td>
<td>( 103.3^{+3.0}, 49 )</td>
</tr>
<tr>
<td>( \text{NEt}_4^+(aq) )</td>
<td>( 246.5^{+5.0}, 49 )</td>
</tr>
<tr>
<td>( \text{K}^+(g) )</td>
<td>( -514.63^{+7} )</td>
</tr>
<tr>
<td>( \text{Rb}^+(g) )</td>
<td>( -491.25^{+56} )</td>
</tr>
<tr>
<td>( \text{Cs}^+(g) )</td>
<td>( -459.82^{+56} )</td>
</tr>
<tr>
<td>( \text{NH}^+(g) )</td>
<td>( -618.8 )</td>
</tr>
<tr>
<td>( \text{NMe}_4^+(g) )</td>
<td>( -580.0 )</td>
</tr>
<tr>
<td>( \text{NEt}_4^+(g) )</td>
<td>( -462.0 )</td>
</tr>
<tr>
<td>( \text{Ag}^+(g) )</td>
<td>( -1021.7^{+47} )</td>
</tr>
<tr>
<td>( \text{KBr}(c) )</td>
<td>( 392.16^{+7} )</td>
</tr>
<tr>
<td>( \text{NH}_4\text{Br}(c) )</td>
<td>( 270.83^{+0.1}, 45 )</td>
</tr>
<tr>
<td>( \text{AgBr} )</td>
<td>( 100.37^{+0.1}, 83 )</td>
</tr>
<tr>
<td>( \text{RbBr} )</td>
<td>( 589.23^{+7} )</td>
</tr>
<tr>
<td>( \text{CsBr} )</td>
<td>( 405.68^{+0.4}, 86, 87, 88 )</td>
</tr>
<tr>
<td>( \text{NMe}_4\text{Br}(c) )</td>
<td>( 251.5^{+3.0} )</td>
</tr>
<tr>
<td>( \text{NEt}_4\text{Br}(c) )</td>
<td>( 377.0^{+5.0} )</td>
</tr>
<tr>
<td>( \text{AgCl}(c) )</td>
<td>( 127.0^{+0.1}, 83 )</td>
</tr>
<tr>
<td>( \text{H}_2\text{O}(1) )</td>
<td>( 285.850^{+0.042}, 85 )</td>
</tr>
</tbody>
</table>
### TABLE II-31
### ANCILLARY DATA

(a) Thermochemical Quantities contd.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\Delta H^\circ_X/\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CO}_2(g)$</td>
<td>$393 \pm 0.13^{85}$</td>
</tr>
<tr>
<td>$\text{AgNO}_3(2000\ \text{H}_2\text{O})$</td>
<td>$100.67^{47}$</td>
</tr>
<tr>
<td></td>
<td>$101.73 \pm 0.18^{3}$</td>
</tr>
</tbody>
</table>
### Table II-31

**ANCILLARY DATA**

(b) **Ionic radii**

<table>
<thead>
<tr>
<th>Ion</th>
<th>$r_{\text{Me}r}/\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}^+$</td>
<td>0.13366</td>
</tr>
<tr>
<td>$\text{NH}_4^+$</td>
<td>0.14456</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>0.10056</td>
</tr>
<tr>
<td>$\text{Rb}^+$</td>
<td>0.14756</td>
</tr>
<tr>
<td>$\text{Cs}^+$</td>
<td>0.16856</td>
</tr>
<tr>
<td>$\text{Mg}^{2+}$</td>
<td>0.06856</td>
</tr>
<tr>
<td>$\text{Ca}^{2+}$</td>
<td>0.09956</td>
</tr>
<tr>
<td>$\text{Sr}^{2+}$</td>
<td>0.11656</td>
</tr>
<tr>
<td>$\text{Ba}^{2+}$</td>
<td>0.13456</td>
</tr>
<tr>
<td>$\text{NH}_4^+$</td>
<td>0.14456</td>
</tr>
<tr>
<td>$\text{NMe}_4^+$</td>
<td>0.21050</td>
</tr>
<tr>
<td>$\text{NET}_4^+$</td>
<td>0.16050</td>
</tr>
<tr>
<td>$\text{Ag}^+$</td>
<td>0.11356</td>
</tr>
<tr>
<td>NEL_F (A)</td>
<td>NEL_F (B)</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
</tr>
<tr>
<td>1.117055</td>
<td>1.117055</td>
</tr>
<tr>
<td>86800.00</td>
<td>86800.00</td>
</tr>
<tr>
<td>6.69896</td>
<td>6.69869</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
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<tr>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>8.6805</td>
<td>8.6805</td>
</tr>
<tr>
<td>0.44194</td>
<td>0.44194</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>0.00000</td>
<td>0.00000</td>
</tr>
</tbody>
</table>
**TABLE II-33**

THE STANDARD ENTHALPY OF FORMATION OF THE AQUEOUS PICRATE ION

<table>
<thead>
<tr>
<th>M</th>
<th>$-\Delta H_f^{\circ}{\text{MPic}}(e)/\text{kJ mol}^{-1}$</th>
<th>$-\Delta H_f^{\circ}{\text{M}}^+(\text{aq})/\text{kJ mol}^{-1}$</th>
<th>$\Delta H_f^{\circ}{\text{MPic}}/\text{kJ mol}^{-1}$</th>
<th>$-\Delta H_f^{\circ}{\text{Pic}^-}(\text{aq})/\text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>508.1</td>
<td>252.5</td>
<td>51.1</td>
<td>204.5</td>
</tr>
<tr>
<td>Rb</td>
<td>508.2</td>
<td>248.3</td>
<td>55.0</td>
<td>204.9</td>
</tr>
<tr>
<td>Cs</td>
<td>521.0</td>
<td>261.9</td>
<td>56.0</td>
<td>203.0</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>385.4</td>
<td>132.2</td>
<td>45.5</td>
<td>207.8</td>
</tr>
<tr>
<td>NMe$_4$</td>
<td>343.7</td>
<td>103.3</td>
<td>51.8</td>
<td>208.5</td>
</tr>
<tr>
<td>NET$_4$</td>
<td>488.1</td>
<td>248.0</td>
<td>32.0</td>
<td>208.1</td>
</tr>
<tr>
<td>Ag</td>
<td>136.3</td>
<td>-105.6</td>
<td>36.7</td>
<td>205.2</td>
</tr>
</tbody>
</table>

$\Delta H_f^{\circ}{\text{Pic}^-}(\text{aq}) = -206\pm2\text{ kJ mol}^{-1}$
TABLE II-34

STANDARD ENTHALPIES OF FORMATION OF SOME SALTS OF GUANIDINE

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H^\circ_{f}/kJ\ mol^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$N$_3$.HNO$_3$</td>
<td>405.01$\pm$4.60</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>387.02</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>389.11$\pm$3.9</td>
<td>51</td>
</tr>
<tr>
<td>CH$_5$N$_3$.HClO$_4$</td>
<td>312.96</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>310.03$\pm$2.30</td>
<td>51</td>
</tr>
<tr>
<td>(CH$_5$N$_3$)$_2$.H$_2$SO$_4$</td>
<td>1200.81$\pm$7.53</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>1204.99</td>
<td>45</td>
</tr>
<tr>
<td>(CH$_5$N$_3$)$_2$.H$_2$CO$_3$</td>
<td>971.90$\pm$0.63</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>965.63$\pm$3.89</td>
<td>55</td>
</tr>
<tr>
<td>CH$_5$N$_3$.HCl</td>
<td>366.71$\pm$4.00</td>
<td>This work</td>
</tr>
</tbody>
</table>

Note: for CH$_5$N$_3$.HNO$_3$, the mean of the values from references 45 and 51 has been taken. Since no error limits were quoted in reference 45, the limits on the mean value have been arbitrarily assigned as $\pm$4 kJ mol$^{-1}$. Hence $\Delta H^\circ_{f}$ CH$_5$N$_3$.HNO$_3$ = -388.07 $\pm$4 kJ mol$^{-1}$ was used in calculations.

All these values are referred to 298.15K.
### Table II.35
**Enthalpy of Solution of Guanidine Nitrate in Water**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H^\circ_{\text{m}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2166</td>
<td>3129</td>
<td>40.03</td>
</tr>
<tr>
<td>0.2047</td>
<td>3311</td>
<td>40.14</td>
</tr>
<tr>
<td>0.1900</td>
<td>3567</td>
<td>40.81</td>
</tr>
<tr>
<td>0.1190</td>
<td>5696</td>
<td>39.20</td>
</tr>
<tr>
<td>0.0970</td>
<td>6987</td>
<td>39.94</td>
</tr>
<tr>
<td>0.0865</td>
<td>7836</td>
<td>40.87</td>
</tr>
<tr>
<td>0.0819</td>
<td>8276</td>
<td>39.27</td>
</tr>
</tbody>
</table>

Mean = 40.18 ± 0.50$^b$

### Table II.36
**Enthalpy of Precipitation of Silver Nitrate and Guanidine Chloride**

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ_{\text{m}}$ / kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2220</td>
<td>46.71</td>
</tr>
<tr>
<td>0.2151</td>
<td>46.44</td>
</tr>
<tr>
<td>0.1765</td>
<td>47.15</td>
</tr>
<tr>
<td>0.1736</td>
<td>47.03</td>
</tr>
<tr>
<td>0.1581</td>
<td>46.67</td>
</tr>
<tr>
<td>0.1556</td>
<td>46.45</td>
</tr>
<tr>
<td>0.1166</td>
<td>46.69</td>
</tr>
<tr>
<td>0.1131</td>
<td>46.46</td>
</tr>
</tbody>
</table>

Mean = -46.70 ± 0.22$^b$
**TABLE II-37**

RESULTS OBTAINED FOR THE REACTION BETWEEN GUANIDINE CHLORIDE AND SILVER PICRATE SOLUTION

<table>
<thead>
<tr>
<th>m/g</th>
<th>$-\Delta H^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0457</td>
<td>92.91</td>
</tr>
<tr>
<td>0.0485</td>
<td>92.12</td>
</tr>
<tr>
<td>0.0666</td>
<td>93.40</td>
</tr>
<tr>
<td>0.0694</td>
<td>96.51</td>
</tr>
<tr>
<td>0.0778</td>
<td>95.01</td>
</tr>
<tr>
<td>0.0794</td>
<td>100.25</td>
</tr>
<tr>
<td>0.0936</td>
<td>94.90</td>
</tr>
<tr>
<td>0.1085</td>
<td>103.29</td>
</tr>
<tr>
<td>0.1831</td>
<td>105.28</td>
</tr>
<tr>
<td>M</td>
<td>exp.</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>Li</td>
<td>491.4*</td>
</tr>
<tr>
<td>Na</td>
<td>468.1*</td>
</tr>
<tr>
<td>K</td>
<td>508.1</td>
</tr>
<tr>
<td>Rb</td>
<td>508.2</td>
</tr>
<tr>
<td>Cs</td>
<td>521.0</td>
</tr>
<tr>
<td>Ag</td>
<td>136.3</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>385.4</td>
</tr>
<tr>
<td>NMe₄⁻</td>
<td>343.7</td>
</tr>
<tr>
<td>NEt₃⁺</td>
<td>488.1</td>
</tr>
</tbody>
</table>

* calculated from results of Vorob'ev, using value of -228.7 kJ mol⁻¹ for $\Delta H^\circ$ picric acid.
### TABLE 11-39: CALCULATED ENTHALPIES OF FORMATION OF GROUP II METAL PICRATES $\text{MPic}_2$

<table>
<thead>
<tr>
<th>M</th>
<th>$U_e / \text{kJ mol}^{-1}$</th>
<th>$-\Delta H_f^\circ \text{MPic}_2 / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1966</td>
<td>539</td>
</tr>
<tr>
<td>Ca</td>
<td>1816</td>
<td>815</td>
</tr>
<tr>
<td>Sr</td>
<td>1743</td>
<td>875</td>
</tr>
<tr>
<td>Ba</td>
<td>1672</td>
<td>935</td>
</tr>
</tbody>
</table>
### Table II - 40

**Effect of Variation in the Thermochemical Radius of the Picrate Anion on the Calculated Lattice Energies, $U_0$**

<table>
<thead>
<tr>
<th>$r_{\text{th}}$/nm</th>
<th>$U_0$/kJ mol$^{-1}$</th>
<th>$0.199$</th>
<th>$0.264$</th>
<th>$0.328$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>655.3</td>
<td>558.4</td>
<td>487.3</td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>631.8</td>
<td>541.2</td>
<td>474.0</td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>599.4</td>
<td>517.2</td>
<td>455.5</td>
<td></td>
</tr>
</tbody>
</table>

### Table II - 41

**Effect of the Variation in the Thermochemical Radius of the Picrate Anion on the Calculated Enthalpy of Formation of the Gaseous Anion**

<table>
<thead>
<tr>
<th>$r_{\text{th}}$/nm</th>
<th>$-\Delta H_f^{\circ}$ Pic$^-$ (g)/kJ mol$^{-1}$</th>
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<th>$0.264$</th>
<th>$0.328$</th>
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<td>530.5</td>
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<tr>
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<td>458.7</td>
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TABLE II - 42
EFFECT OF THE VARIATION IN THE THERMOCHEMICAL RADIUS OF THE PICRATE ANION ON THE CALCULATED ENTHALPIES OF FORMATION OF ALKALI METAL PICRATES MPic

<table>
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<th>Cs</th>
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<td>Rb</td>
<td>Cs</td>
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### TABLE II - 44

**EFFECT OF THE VARIATION IN THE THERMOCHEMICAL RADIUS ON THE CALCULATED ENTHALPY OF FORMATION OF THE GASEOUS PICRATE ION Pic⁻(g)**

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TABLE II - 45

EFFECT OF THE VARIATION IN THE THERMOCHEMICAL RADIUS ON THE CALCULATED
ENTHALPIES OF FORMATION OF METAL PICRATES MPic

\[ \Delta H^\circ_{\text{MPic}}(c) / \text{kJ mol}^{-1} \]

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<th>Rb</th>
<th>Cs</th>
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### Table 11-46

**Effect of the Variation in the Thermochemical Radius of the Picrate Anion on the Calculated Enthalpies of Formation of Sodium, Ammonium, and Tetramethylammonium Picrates MPic**

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### POTASSIUM PICRATE SOLUBILITY

#### TABLE 11-47

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<th>T/K</th>
<th>10⁴ K/T</th>
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Note: All data is reported as triplicate measurements.
### RUBIDIUM PICRATE SOLUBILITY

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<th>10⁴ K/T</th>
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<td>ln S</td>
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<td>B&lt;sup&gt;a&lt;/sup&gt;</td>
<td>r&lt;sup&gt;2&lt;/sup&gt; &lt;sup&gt;b&lt;/sup&gt;</td>
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<td></td>
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<td>--------------</td>
<td>--------------</td>
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<td>0.998</td>
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<td>3.167</td>
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<sup>a</sup> See text

<sup>b</sup> Correlation coefficient
### TABLE II-55

**THE AQUEOUS SOLUBILITY OF POTASSIUM PICRATE**

<table>
<thead>
<tr>
<th>T/°C</th>
<th>10³ S/mol dm⁻³</th>
<th>Ref.</th>
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<tr>
<td>20</td>
<td>18.9</td>
<td>67</td>
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<td>25</td>
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<td>66</td>
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<tr>
<td>25</td>
<td>23.1</td>
<td>77</td>
</tr>
<tr>
<td>25</td>
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<td>25</td>
<td>23.3</td>
<td>76</td>
</tr>
<tr>
<td>25</td>
<td>26.7</td>
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<td>30</td>
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<td>65</td>
</tr>
<tr>
<td>30</td>
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<td>This work</td>
</tr>
</tbody>
</table>

### TABLE II-56

**THE AQUEOUS SOLUBILITY OF PICRIC ACID**

<table>
<thead>
<tr>
<th>T/°C</th>
<th>S(g/100g water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.98</td>
</tr>
<tr>
<td>25</td>
<td>1.40</td>
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<tr>
<td>50</td>
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<td>82</td>
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<tr>
<td>100</td>
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<td>Cation</td>
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</tr>
<tr>
<td>Ba^{2+}</td>
<td>1-2%</td>
</tr>
<tr>
<td>K^{+}</td>
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<tr>
<td>Ca^{2+}</td>
<td>0.5-1.0%</td>
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<tr>
<td>NH_{4}^{+}</td>
<td>0.25-0.5%</td>
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</table>
### TABLE II-58
THE STANDARD ENTHALPY OF FORMATION OF THE AQUEOUS PICRATE ION (FROM SOLUBILITY DATA)

<table>
<thead>
<tr>
<th>M</th>
<th>$\Delta H_f^{\circ}{\text{Pic}}(c)/\text{kJ mol}^{-1}$</th>
<th>$\Delta H_f^{\circ}{\text{M}}^{+}(\text{aq})/\text{kJ mol}^{-1}$</th>
<th>$\Delta H_f^{\circ}{\text{MPic}}/\text{kJ mol}^{-1}$</th>
<th>$\Delta H_f^{\circ}{\text{Pic}^-}(\text{aq})/\text{kJ mol}^{-1}$</th>
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<tbody>
<tr>
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<td>252.5$^{45,46}$</td>
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<td>248.3$^{47}$</td>
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<tr>
<td>Cs</td>
<td>521.0</td>
<td>261.9$^{45}$</td>
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<tr>
<td>$\text{NH}_4$</td>
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<td>132.2$^{45}$</td>
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<tr>
<td>$\text{NMe}_4$</td>
<td>343.7</td>
<td>103.3$^{49}$</td>
<td>42.8</td>
<td>197.6</td>
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<tr>
<td>$\text{NET}_4$</td>
<td>488.1</td>
<td>248.0$^{50}$</td>
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<td>187.4</td>
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<tr>
<td>Ag</td>
<td>136.3</td>
<td>-105.6$^{45}$</td>
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<td>187.6</td>
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</table>

$\Delta H_f^{\circ}{\text{Pic}^-}(\text{aq})(\text{sol}) = -188.5^{\pm}5 \text{ kJ mol}^{-1}$
<table>
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<tr>
<th>M</th>
<th>(\Delta H^\circ_{MPic(c)}/\text{kJ mol}^{-1}) (Experimental)</th>
<th>(\Delta H^\circ_{MPic(c)}/\text{kJ mol}^{-1}) (Calculated)</th>
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</thead>
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<tr>
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<td>508.1</td>
<td>503.7</td>
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<td>Ag</td>
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CHAPTER III

KINETIC ASPECTS OF PICRATES
KINETIC ASPECTS OF PICRATES

III-1-a: Introduction

Differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetric (TG) methods have been used to obtain kinetic parameters for various processes, e.g. decompositions, polymerisations, dehydrations, using materials as diverse as clays and explosives.

Both sample and reference are heated by the same source in a differential thermal analyser. Sensors placed in the sample and reference materials monitor the temperature. A plot is made of the temperature difference, $\Delta T = T_s - T_r$, between the sample and reference against time. However in a differential scanning calorimeter, the sample and reference are each provided with a heater. There is a control loop for average temperature control, so that the sample and reference temperature may be increased at a given rate, and a loop to ensure that if a temperature difference develops between the sample and reference, the power input is adjusted to remove this difference. Thus the sample holder is always kept at the same temperature as the reference holder by continuous adjustment of the heater power. A signal, proportional to the difference between the heat input to the sample and that to the reference, $dH/dt$, is fed into a recorder. In thermogravimetry, the weight of a sample with increasing temperature and/or time is recorded.

Many papers have been published concerning the evaluation of kinetic parameters from data obtained by thermal means. The earliest methods were developed for DTA, but these and other methods have been developed and/or adapted for use with DSC and TG. There are data analysis schemes for use when these instruments are operating in either the scanning (dynamic or non-isothermal) or isothermal modes.
In the following discussion, particular emphasis will be placed on those applications involving explosives.

III-1-b: Non-Isothermal Methods

Working with clays, Murray and White\(^1\) were able to show that a relationship exists between the peak temperature and heating rate for a first order reaction.

\[
Ae^{-\frac{E}{RT_m}} = \frac{E}{R T_m^2} \cdot \frac{dT}{dt} \quad \ldots \quad (1)
\]

- \(R\) = gas constant
- \(T\) = absolute temperature
- \(T_m\) = peak temperature
- \(dT/dt\) = heating rate
- \(E\) = activation energy for decomposition
- \(A\) = pre-exponential factor

(1) may be rewritten

\[
\ln \left(\frac{\rho}{T_m^2}\right) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT_m} \quad \ldots \quad (2)
\]

Hence, a plot of \(\ln(\rho/T_m^2)\) vs. \(1/T_m\) should give a straight line of slope \(-E/R\), thus enabling calculation of the activation energy.

Kissinger\(^2\) used this to study the decomposition of certain clays and found \(E\), and hence \(A\).

For an \(n^{th}\) order reaction, it may be shown that

\[
\frac{E\rho}{RT_m^2} \cdot \frac{(1-x)^n}{n!} \cdot e^{-\frac{E}{RT_m}} \quad \ldots \quad (3)
\]

in which \((1-x)_m\) is the fraction of material unreacted at the peak temperature, \(T_m\).

Kissinger\(^3\) later showed that \(n(1-x)_m^{n-1}\) is independent of \(\rho\) and is also very nearly equal to 1. Hence equation (3) reduces to (1). The Kissinger method would appear to be applicable regardless of the reaction order.
Patel and Chaudhri made plots of $\ln (\varphi/T^2_m)$ vs. $1/T_m$ for the decomposition of tetracene and lead azide.

Ozawa was able to show that a plot of $\ln \varnothing$ vs. $1/T_m$ is a straight line of slope $-0.457 E/R$. He originally developed his method for use with TG data, but Krien used it to interpret his DSC data for the decomposition of lead tetraazide. Patel and Chaudhri also used the Ozawa method for their lead azide and tetracene results, and there was good agreement with the Kissinger analysis figures (Table III-1).

Another method developed by Rogers and Morris may also be used to interpret some DSC data. Here the activation energy is found from

$$-E = R \ln \frac{d_1 - \ln d_2}{1/T_1 - 1/T_2}$$

where $d_1$ and $d_2$ are the distances between the points on the curve and the baseline corresponding to temperatures $T_1$ and $T_2$ respectively. Patel and Chaudhri used this equation to interpret their lead azide data and found that the activation energy was about three times greater than that derived from the Kissinger and Ozawa methods (see Table III-1). The Rogers and Morris method is only applicable to reactions governed by an equation of the form

$$\frac{d\alpha}{dt} = k$$

where $\alpha$ is the fractional decomposition at time $t$ and $k$ is the rate constant ($AE^{-E/RT}$). For a reaction obeying $\alpha = kt^n$ where $n > 1$, the equation does not hold.

Rogers and Morris applied their method to the decomposition of HMX, RDX, Tetryl and PETN.

The Kissinger and Ozawa methods both suffer from the disadvantage that they use only a single point ($T_m$) from a trace to produce one point on the activation energy plot. Thus, to obtain a reliable value
for E, several experiments are required.

Borchardt and Daniels proposed a method by which $E_A$ and $n$ are found from the shapes of DTA curves. They considered reactions in the liquid phase, having a single rate constant and an activation energy that does not vary with temperature. To obtain reaction parameters, they assumed a value for $n$. This enabled calculation of $k$. A plot of $\ln k$ vs $1/T$ yields a straight line only if the correct value of $n$ has been assumed — thus $E_A$ and $n$ can be found. The disadvantage is the large number of plots that must be made until all the points lie on a straight line.

Benin used computer programs

(i) to produce a thermogram given the reaction parameters $E_A$ and $n$.

(ii) to calculate $E_A$ and $n$ from an experimental thermogram

(iii) to determine the reaction parameters and the complex reaction mechanism from an experimental thermogram.

Benin's method, however, uses a lot of computer time.

Hauser and Field have developed a method based on the ideas of Borchardt and Daniels which can be applied to data obtained from a thermobalance and, in principle, a DSC.

They assume that the reaction can be described by

$$\frac{dw}{dt} = -A_i \exp\left(\frac{E_i}{RT}\right)f_i(w) \ldots \tag{6}$$

$w$ fractional residual weight at time $t$, $f_i(w)$ is the dependence of the reaction rate on the fractional residual weight i.e. $f_i(w)=w^n$.

The heating rate, $h(\text{deg min}^{-1})$ is constant

Since $$\frac{dT}{dt} = \frac{h}{60} \quad (\text{deg sec}^{-1})$$

Then $$\frac{-dw_i}{dt} \times \frac{h}{60} = A_i \exp\left(\frac{-E_i}{RT}\right)f_i(w) \ldots \tag{7}$$
Taking natural logarithms

\[ \ln(-dw_i) - \ln f_i(w) = \ln A_i x 60 - \frac{E_i}{RT} \quad \cdots (8) \]

Therefore, a plot of \( \frac{\ln(-dw_i) - \ln f_i(w)}{dt} \)

against \( 1/T \) will give a straight line only if \( f_i(w) \) has been chosen correctly. In the case of \( f_i(w) = w^n \) the reaction order \( n \) is varied until a straight line is found. The activation energy \( E \) may be found from the slope of the plot, \( A \) from the intercept on the ordinate and \( n \) from the straight line criterion.

The analysis can also be applied to DSC data. However, caution must be exercised.

\[ \frac{dQ}{dt} = \frac{\Delta H(w_i - w_r) A \exp(-E) f(w)}{R T} \quad \cdots (9) \]

The \( \frac{dQ}{dt} \) sign corresponds to an exothermic/endothermic change where \( Q \) is the heat given out by the sample (m cal), \( \Delta H \) is the enthalpy change (cal g\(^{-1}\)) for the reaction, \( w_i \) is the initial weight and \( w_r \) is the rest weight.

Taking logs

\[ \ln \left( \frac{dQ}{dt} - \ln f(w) \right) = \ln \Delta H(w_i - w_r) A - \frac{E}{RT} \]

Using differential scanning calorimetry, \( dQ/dt \) at temperature \( T \) is the quantity measured.

Since \( \frac{dQ}{dt} = \frac{\Delta H}{dt} \frac{dw}{dt} \)

\[ W_t = \frac{1}{\Delta H} \int_0^t \frac{dQ}{dt} \, dt \]

Hence the weight at time \( t \) may be calculated. A plot of

\( \left\{ \ln \left( \frac{dQ}{dt} - \ln f(w) \right) \right\} \) against \( 1/T \) produces \( E, A \) and \( n \) as for the TG curves.
Hauser and Field\textsuperscript{11} determined the kinetic parameters for the dehydration of calcium oxalate monohydrate using this method and obtained values in satisfactory agreement with others in the literature. Brown and Swallowe\textsuperscript{12} have studied silver nitrotetrazole decomposition using these programs.

However, it would appear that Hauser and Field's method, as it stands, cannot be satisfactorily applied to DSC data for compounds that undergo some melting immediately before decomposition. Modification of the programs to allow for this might be possible. Hauser and Field used their program to study the decomposition of PETN by DSC, but this melts at a somewhat lower temperature than that at which it decomposes.

\textbf{III-l-c: Isothermal Methods}

\textbf{DSC and DTA:} In the isothermal mode, the extent of reaction is measured directly as a function of temperature and time. Samples are held in the instrument at a given temperature but for varying lengths of time. They are then programmed through their decompositions. The decrease in the peak area per unit sample weight as a function of the previous isothermal exposure time is a measure of the reaction rate at the set temperature. This procedure is repeated at various temperatures and data can be obtained for the variation of the reaction rate with temperature. Duswalt\textsuperscript{13} used this method for studying some highly exothermic decompositions.

Alternatively, a sample can be placed in the instrument at ambient temperature and then the temperature of the sample holder is immediately raised at a very fast heating rate to the chosen temperature. This temperature is then kept constant until the sample has completely decomposed. The amount of fractional decomposition, $\alpha$, at time $t$, may be found by dividing the area under the curve up to $t$ by the total area. Patel and Chaudhri\textsuperscript{4} used this method to study the thermal
decomposition of tetracene and assumed that their sample had completely
decomposed when the trace came back to the baseline. Powder X-ray work
confirmed this. The $\alpha$–t curves were sigmoid shaped (see section
III-2.) An Arrhenius plot for the acceleratory period was a straight
line of slope $-E/R$, from which the activation energy for decomposition
may be found.

**Ignition Time Method**

A reactive material, suddenly raised to a high enough temperature,
will ignite after a time delay, $t_{\text{exp}}$. For various substances, a relationship
of the following type often exists

$$\ln t_{\text{exp}} = \frac{B}{E/RT}$$

$B$ is a constant.

Again, Patel and Chaudhri used this to study the decomposition
of tetracene. The $E$ value obtained was in good agreement with answers
found using the other methods. (see Table III-1).

**Thermogravimetric Methods**

Here the weight of a sample with time is monitored whilst the
sample is kept in an isothermal environment. $\alpha$–t curves at different
temperatures can then be constructed. From data obtained from the $\alpha$–t
curves, Arrhenius plots can usually be made. Knowing the shape of the
$\alpha$–t curves usually enables the data to be fitted to one of the
equations used to describe solid-state decompositions.

Complementary ESR and isothermal DSC studies have been made
of the thermal decomposition of TNT.

Tang and Chaudhri made critical reviews on the analysis
of isothermal and dynamic kinetic data from solid-state reactions.

Before describing the experimental methods and results obtained
therefrom, it is of interest to consider some of the modern views on
solid-state reactions and the interpretation of data in the form of
$\alpha$–t plots.
III-2 Solid State Reactions

III-2-a: Introduction

Reaction rates for homogeneous phase reactions e.g.; between two gases, are often proportional to the reactant concentration raised to a power (the order). This is not generally true for heterogeneous phase reactions (these include those of solids). Reactions involving solids usually occur at a reactant-product interface, and the rate of product formation depends upon

(i) the variation in the interfacial area during the progress of the reaction.

(ii) the rate of progress of the interface through the reactant.

As the reaction proceeds, a layer of inert products may be deposited – this would tend to lead to a decrease in reactivity as the contact area becomes smaller.

The reactivity of a solid often depends on the history of the crystal, and the rate of a process involving a solid is often controlled by the surface area of the solid. In reporting kinetic data for solid reactions, the sample form should always be stated.

General mathematical expressions have been developed for the kinetics of processes involving solids. Many simplifications have been made. Much attention has been focused on thermal decompositions.

Consider the following

\[ A(\text{solid}) \rightarrow B(\text{solid}) + C(\text{gas}) \] performed isothermally.

If \( \alpha \) is the fractional decomposition (this is easily measured from the product gas pressure or sample weight loss), then \( \alpha \)-time plots for some typical solid-state thermal decompositions are as shown in fig. III-1. (Page 181)

(a) is deceleratory throughout—the rate decreases as the reactant is consumed.

(b) shows a short initial acceleratory period, in which the rate
increases, and then becomes deceleratory
(c) has a more pronounced acceleratory period followed by
deceleratory behaviour
(d) exhibits a short initial deceleratory region followed by
a sigmoid shaped curve.

Sigmoid shaped $x$–time plots usually result from reactions occurring
at a reactant–product interface established initially on the surface of
the crystal (nuclei) by the formation of micro amounts of product. The
reaction will then proceed within the strained contact area of the
reactant – product interface. This area is small during the initial
formation of nuclei, and reaction is slow immediately following the
commencement of heating. The time between the reactant reaching
reaction temperature and the detection of significant quantities of
product is termed the induction period. This is quite significant
for many solids. During the induction time, germ nuclei of solid
product are established at a limited number of points on the
reactant surfaces.

For several solids, it has been shown experimentally, that there
is a constant rate of advance of the reaction interface through the
solid (for a reaction at constant temperature), once nuclei have been
established. Growth of nuclei results in an increase in the product
nuclei–reactant surface contact area. This leads to an increase in
the rate of product formation and the reaction is acceleratory.
These nuclei will continue to grow, and reaction interfaces from
different nuclei will begin to overlap. This reduces the rate of
interface expansion (and hence product formation) and the rate of
acceleration decreases. At a later stage, this factor becomes more
important and the rate becomes deceleratory.

Once the original surfaces of the reactant have been decomposed,
the remaining reaction interfaces may continue growing towards the
central, unreacted regions of the crystal. This leads to a progressive
decrease in interfacial area and the rate becomes deceleratory, until
the reactant has completely decomposed.

III-2-b: Nucleation

Nucleation may be defined as the conversion of a small volume of
reactant into stable particle products. It generally occurs on
crystal surfaces (here the product gases can easily escape and the
lattice units are not subjected to spherically symmetrical forces).
For many solids, nucleus formation can only occur at a limited
number of sites — these are believed to be regions of local disorder.
In these solids (assuming that nucleation involves a single surface
chemical reaction), the nucleation rate is proportional to the
number of sites at which nuclei can form.

\[
\frac{dN}{dt} = k(N_i - N)
\]

\(N_i\) is the number of possible sites at which nuclei may form
\(N\) is the number of nuclei present at time \(t\).

\[
\frac{dN}{dt} = kN_i e^{-kt}
\]

For reactions in solids where \(k\) is small, the rate of nucleus
formation is approximately constant during the initial periods of
the reaction (i.e: \(dN/dt \approx kN_i\)). If \(k\) is large, all possible nuclei
are formed at the beginning of the reaction and further nucleation
does not occur. The above expressions were obtained by assuming
that a single chemical reaction results in stable nucleus formation.
If more than a single step is required, expressions of the type
\(N = k_1 t^3\) are required, e.g: for barium azide decomposition \(N = k_1 t^3\).

Jacobs and Tompkins\(^1^8\) considered the geometry of nucleation.

For the general equation

\[
A \text{ (solid)} \rightarrow B \text{ (solid)} + C \text{ (gas)}
\]

they noted that the first formed units of \(B\) will initially conform
to the structure of and retain their former positions with reference to A. As greater quantities of B form, though, the consequent increase in total deformation strain energy will lead to the structural characteristics of B. In terms of free energy they expressed this

\[ \triangle G_1 = m \triangle G_B + \sigma \gamma \]

where each particle of B contains \( m \) molecules. \( \triangle G_B \) is the bulk free energy change per molecule. \( \sigma \) is a shape factor \( (4 \pi r^2 \) for a spherical interface).

\( \gamma \) is the strain energy per unit area of interface.

Jacobs and Tompkins were able to show that \( \triangle G_1 \) must pass through a maximum at a critical size, \( m_c \)

\[ m = m_c = \frac{32 \pi \sigma^3 V_m^2}{3(\triangle G_B)^3} \]

where \( m = \frac{4 \pi r^3}{3V_m} \)

where \( V_m \) is the volume of product per "molecule", and the nucleus attains equilibrium with its surroundings at

\[ \left( \frac{\delta \triangle G_1}{\delta m} \right)_m = m_c = 0 \]

When \( m < m_c \), the product is unstable and thermodynamics predicts that it will tend to revert to reactant. However, particles of \( B \rangle m_c \) are stable and further growth is possible. If \( m \rangle m_c \), the units are termed germ nuclei, and if \( m \rangle m_c \), growth nuclei.

A theoretical treatment can also be applied to disc-shaped nuclei, and here it is found that there is no critical size requirement for growth.
Growth may be defined as the movement of the reactant-product interface. For salts where the rate of interfacial progress through the reactant can be directly measured, the growth rate has been shown to be constant and to increase with increase in reaction temperature.

A general expression for the rate of a solid phase decomposition in which the nucleation rate obeys a power law and the nuclei grow in \( \lambda \) dimensions has been shown to be

\[ \propto = k_1 t^\lambda = k_1 t^n \]

This expression applies in the early stages of a reaction before appreciable overlap of nuclei occurs, and it has been shown to hold, at lower values of \( \alpha \), for the thermal decomposition of silver oxide \( n=3 \) and barium azide \( n=6 \).

Barium azide \(^\text{20}\) has been studied in great detail. For a large single crystal, it was shown experimentally that

\[ \alpha = k_1 t^n \]

where \( n=6 \), \( \beta = \lambda = 3 \)

(However, the thermal decomposition of very fine powder has been shown to obey first order kinetics)

From the \( \alpha \)-time measurements on the crystal, it has been shown that

(i) nucleation obeys the power law \( N=kt^3 \)(i.e. \( \beta = 3 \))

(ii) three-dimensional nuclei are formed \( (\lambda = 3) \).

(iii) the rate of reaction interface progression through the unreacted material is constant at constant temperature.

Thus, information about \( \beta \) and \( \lambda \) can be found from \( \alpha \)-time measurements. When these \( \alpha \)-t values are fitted to an equation of the form

\[ \alpha = k t^n \]

it is found that there is sometimes uncertainty about the moment when
t=0. This is because of thermal disturbances when the reactant is introduced into the heating zone. Also, it has been shown for many substances, that very small nuclei of product consisting of small numbers of molecules and being relatively unstable, grow at a rate slower than that subsequently attained when the product crystallite size has been increased. Allowances can be made for both of these effects in the kinetic expression by modifying the zero point on the time scale. If a time correction, \( t_1 \), is made to the measured time, \( t \), equations of the power law form may be expressed

\[ \alpha = k_1(t-t_1)^n \]

This holds well in the initial stages of many decompositions, but equations have been developed in which allowance is made for the overlap of nuclei. As nuclei grow, the overall rate of reaction may be reduced by

(i) the end of reaction at areas of contact formed by overlap of reaction interfaces where the growth of two adjoining nuclei have resulted in a common boundary.

(ii) the removal of potential nucleus-forming sites on the surface through their incorporation into the growth of existing nuclei.

A general equation to take into account these effects is of the form

\[ -\log(1 -\alpha) = (kt)^n \]

This is known as the Avrami-Erofeev equation \(^{21}\), and has been found to hold for, inter alia, ammonium perchlorate, nickel formate, nickel oxalate and sodium azide.

Prout-Tompkins Equation

In 1944, Prout and Tompkins\(^{22}\) were able to show that the thermal decomposition kinetics of \( \text{KMnO}_4 \) fitted the equation

\[ \log \left( \frac{\alpha}{1-\alpha} \right) = kt+c \]
and they suggested that the reaction in the solid took place by a mechanism similar to the chain-branching radical processes of gas-phase reactions. Their hypothesis was that nucleation formed an active species which could then react to give two or more active species which could, in turn, react to increase the number of active centres as the reaction progressed. However, against this chain-branching must be considered the possibility of terminating the chain by direct combination—the probability of this increasing with the concentration of the active species (the characterisation of the species involved in the chain process is not easily resolved).

The equation has been usefully applied in many decomposition studies which yield sigmoid $\alpha$–time curves. The reason for this may be seen by considering the differential form of the equation:

$$\frac{d\alpha}{dt} = k\alpha(1-\alpha)$$

i.e.: the reaction rate is proportional to the fraction of the solid which has decomposed, $\alpha$ (dominant in the early (acceleratory) parts of the reaction) and to the fraction which has not decomposed ($1-\alpha$) (more significant in the later stages of reaction). Thus the equation shows acceleratory and deceleratory behaviour—comparable to nucleation and growth processes.

$\alpha$–time measurements fit the Prout-Tompkins equation for nickel formate, silver oxalate and ammonium perchlorate.

The Avrami-Erofeev and Prout-Tompkins equations may be used when the substance shows an initial acceleratory period. Two equations found to hold for reactions that are deceleratory throughout are:

1. the contracting cube model, for which $1-(1-\alpha)^{1/3} = kt$ is fitted to the data
2. First Order Equation (unimolecular decay law)

$$-\log(1-\alpha) = kt$$
The kinetics of the decomposition of calcium carbonate and
of the dehydration of copper sulphate pentahydrate are best
described in terms of the contracting cube model.

Comprehensive reviews may be found in the books by Galwey\textsuperscript{25},
Garner\textsuperscript{26}(ed.) and Brown et al.\textsuperscript{27}
Typical fractional decomposition $\alpha$-time plots for solid phase thermal decomposition reactions\textsuperscript{25}.

See text (Section III-2-a) for explanation.
Many authors have studied the behaviour of picric acid and its salts during heating. Tucholski\textsuperscript{28-32} was amongst the earliest. He measured temperatures at which water of crystallisation was lost and temperatures of explosion. Special attention was paid to the thermal decomposition of potassium picrate.\textsuperscript{28} Below the minimum temperature of inflammation (287\degree C), Tucholski found that potassium picrate decomposed autocatalytically at the beginning of the reaction and then proceeded via a chain mechanism. There was a violent increase in rate above this temperature, but it was still a chain reaction. When the temperature of the substance became higher than that of the surrounding medium, the reaction became extremely fast and at 310-325\degree C ended with an explosion.

Previously, Tucholski\textsuperscript{29-32} had measured dehydration and explosive temperatures and melting points for many picrates. He was not able to find evidence for the existence of some hydrates that had been found by other authors.

Andreev and Pao-Feng Liu\textsuperscript{33,34} investigated the thermal decomposition of picric and styphnic acids and their potassium, ammonium and lead salts. These substances were decomposed isothermally in a closed system, and pressure changes and reaction times in the temperature range 183-270\degree C were recorded. For the vapour phase decomposition of picric acid\textsuperscript{33} they observed 5 stages, as distinguished by the rate of gas evolution. Using the first-order rate constants,\( k_3 \), of decomposition phase 3, in the temperature interval 183-250\degree C, an Arrhenius plot yielded the following temperature dependence

\[
k_3 = 10^{11.6} e^{-38.600/RT} \text{ (min}^{-1})
\]

The reaction products of this decomposition were not identified, but it is recorded that 4.8-5.4 moles of gaseous products were released per mole of picric acid.
The decomposition of ammonium picrate was studied between 200° and 270° C. In contrast to the picric acid decomposition, a black and brown residue was observed at the end of the experiment. The pressure-time curves for ammonium picrate showed a longer induction period than the parent acid, and this is followed by a first-order reaction. After approximately 50% decomposition, the gas evolution rate decreased abruptly and became deceleratory only. Between 5.6 and 5.8 moles of gaseous products (again unidentified) were produced per mole of ammonium picrate. For the initial first-order reaction (11-45% decomposition), \( E_{\text{act}} \) was found to be 239.3 kJ mol\(^{-1}\), whilst for the reaction occurring after 50% decomposition the activation energy was 134.7 kJ mol\(^{-1}\).

For potassium picrate, the pressure-time curves in the range 250-300°C were similar in shape to those of the ammonium salt. Here, a longer induction time was observed and the reaction stopped abruptly near 50% decomposition. Approximately 3.8 moles of gaseous products were formed per mole of potassium picrate. A black residue was observed at the end of the reaction. Activation energies were calculated from first-order rate constants and induction times and were found to be 172.4 and 175.7 kJ mol\(^{-1}\) respectively.

Szabó and Száva investigated the factors affecting the thermal decomposition of potassium picrate. They found that apart from such physical parameters as temperature, pressure and grain-size, certain chemical factors such as extraneous-gas atmosphere, impurities and decomposition (as a consequence of heat treatment) affected the decomposition kinetics.

As part of a systematic study of the thermal reactivities of nitro compounds, Hara, Eda and Osada used thermal and spectrometric methods for the decomposition of picric acid. They found that decomposition began at 160°C with evolution of NO\(_2\) and proceeded by
2 steps. 10% of the picric acid decomposed in the first step at 200–260°C and the remainder at 260–320°C. The first step was inhibited by the addition of radical chain inhibitors or by pre-heating the acid. For the second step, the activation energy was found to be 184 kJ mol⁻¹.

Elinkova, Maksimov and Orlova studied the behaviour of alkali and alkaline-earth metal picrates during heating by differential thermal analysis. They obtained DTA curves for picrates between 20° and 320°C and noted temperatures of dehydration, phase transitions and melting. Wendlandt and Hoiberg obtained DTA and TGA curves for, inter alia, picric acid.

Stammler prepared picrates of sodium, potassium, rubidium, caesium, ammonium, tetramethylammonium, tetraethylammonium and thallium and used DTA to determine temperatures of loss of water of crystallisation, phase transitions and melting points. Subsequently, he investigated the kinetics and mechanism of decomposition of alkali metal picrates. They were chosen because their low volatility permitted the use of thermogravimetric methods, and the presence of a relatively heavy alkali metal ion permitted the isolation of solid decomposition products which are of use in establishing a reaction path for the decomposition. Stammler studied the decompositions at heating rates of from 2–50°C min⁻¹ and isothermally in a helium atmosphere below 300°C. It was found that decomposition without melting (below 300°C) of the compounds studied produced a water-soluble (alcohol-insoluble) solid residue whose formula was believed to be \( \text{M(C}_2\text{NO}_3)_3, \text{M=Na,K,Rb,Cs.} \) The gaseous products formed were identical for all the picrates, but were different from those obtained when 2,6-dinitrophenoxides were studied.

Decomposition without melting (above 300°C) always resulted in the explosion of the picrates. The activation energy was found to be
125 kJ mol\(^{-1}\) for alkali metal picrates.

Isothermal decomposition without melting was studied at 250–300°C with 5–25 mg samples. The decomposition curves were characterised by an induction time which was followed by a first-order decomposition reaction coming to an abrupt stop after 39.4%, 45.3%, 52.1% and 53.0% weight loss for Cs, Rb, K and Na picrates respectively. A water-soluble, alcohol-insoluble, black residue remained which was hygroscopic. The empirical formula was found to be \(\text{M}(\text{C}_2\text{H}_2\text{NO})\text{)}\), where \(\text{M} = \text{Cs}, \text{Rb}, \text{K}\) and \(\text{Na}\).

Andreev et al. observed a similar decomposition-time curve for potassium and ammonium picrates.

The reaction essentially stopped after about 50% decomposition. (Stammler found 52.1% for potassium).

Stammler's most extensive isothermal studies were on caesium picrate. During the induction period he could find no detectable heat release or weight loss. Stammler explained this by assuming an intramolecular rearrangement into an intermediate compound which in turn decomposes, or catalyses the decomposition of unchanged picrate.

For the first-order region of the curve, an apparent activation energy of 350 kJ mol\(^{-1}\) was observed—about twice the value found by Andreev for potassium picrate (172 kJ mol\(^{-1}\)).

The decomposition products from the isothermal experiments were investigated by sweeping the gases into an absorption liquid (water or 0.1 M KOH) with helium. This liquid was tested for common ions, formaldehyde and formic acid. Only \(\text{CN}^-\) and \(\text{CO}_2\text{)}\text{)}\) were detected in relatively large amounts. The picrates were also decomposed in the mass spectrometer. The main products were \(\text{CO}_2\text{H}, \text{HCN}, \text{CN}^-\) and \(\text{H}_2\text{O}\).

The solid products were also analysed. Chemical tests and spectroscopy suggested that the end product was probably an oxynitrile derivative of oxalic acid.
For the scanning runs on caesium picrate (with decomposition in the melt), heating rates of between 2 and $50^\circ$C min$^{-1}$ were used. However, at heating rates below $4.5^\circ$C min$^{-1}$, it was found that slow decomposition without melting occurred and samples did not deflagrate. Therefore, only experiments where the heating rate was greater than $4.5^\circ$C min$^{-1}$ were considered. A different reaction path to that occurring in the isothermal experiments was assumed to operate here since different reaction products were formed, including elemental carbon, and the reaction resulted in an explosion. Experimentally it is very difficult, Stammelcr noted, to determine intermediate products for such fast reactions.

**III-4: Differential Scanning Calorimetry (Kissinger and Ozawa Methods)**

**III-4-a: Experimental**

The Perkin-Elmer Corp. DSC-2 was used for these runs, although preliminary scans to establish sample size and conditions were made on the Perkin-Elmer DSC-1B. Samples were sealed in aluminium pans and were temperature programmed at the desired rate. Peak temperatures from traces obtained at each of the heating rates were measured.

Only potassium and caesium picrates were studied by this method, using samples of mass 0.05–0.5mg. If larger samples were used, it was found that the aluminium pans were unable to contain the products of the decomposition. It is well known that the peak temperature depends partially on the sample size, but with the amounts used in these experiments, this effect is presumably negligible.
III-4-b: Results

For potassium picrate, two exotherms were observed. At some heating rates these exotherms were preceded by a small endotherm which would seem to indicate that perhaps the sample undergoes some melting before decomposition. The two exotherms might mean that perhaps the sample undergoes some decomposition, and then possibly that the products of this first decomposition catalyse the second stage of decomposition, i.e.: some sort of autocatalysis reaction.

A Kissinger-type plot was made from the potassium picrate data. The peak temperature for the exotherm that occurred at the lower temperature was taken since this indicates the onset of decomposition. From the slope of this graph, the activation energy was found to be \( 214.1 \pm 1.5 \text{ kJ mol}^{-1} \). This may be compared with a value of \( 223.3 \pm 1.5 \text{ kJ mol}^{-1} \) derived from an Ozawa treatment.

Results for potassium picrate may be found in Table III-2 and the Kissinger and Ozawa plots are shown in Fig. III-2.

For caesium picrate (see Table III-3 and Fig. III-3), the activation energy for decomposition was found by the Kissinger method to be \( 192 \pm 1.5 \text{ kJ mol}^{-1} \), and by the Ozawa treatment of the data to be \( 202.9 \pm 1.5 \text{ kJ mol}^{-1} \).

Discussion of these results may be found in Section III-7.
Kissinger (a) and Ozawa (b) plots for the decomposition of potassium picrate.
Kissinger (a) and Ozawa (b) plots for the decomposition of caesium picrate.
III-5: Thermogravimetry

III-5-a: Apparatus

The thermobalance system used in the Physics and Chemistry of Solids section of the Cavendish Laboratory, University of Cambridge was employed. A full description of the apparatus may be found elsewhere, but it may be useful to have an outline here. It is built around a Stanton-Hedcroft TG-750 and has a gas-handling system for controlling the atmospheric conditions around the experiment. The output from the thermobalance is via a DVM to a paper-tape punch. These tapes are processed on a Hewlett-Packard 9825A calculator and plotter.

The maximum sensitivity of the thermobalance is 1 g and the temperature range is from ambient to 1000°C. Samples down to below 1 mg may be used. The entire balance is encased in glass, allowing control of the atmosphere under which the experiments are to take place. A flow meter indicates the gas flow through the system.

The microbalance operates electrically. There is a coil around the pivot of the balance arm which produces a restoring couple whenever photocells indicate that the balance arm has drifted away from its horizontal position. The magnitude of the current needed to provide this restoring couple is proportional to the weight of the sample, and this is measured and displayed. When a new sample pan is used there is an electrical tare for zeroing.

One of the scales is suspended on a long hang-down wire and reaches into the furnace, which can be lowered to allow easy access to the scales for sample addition. The scales are surrounded completely when the furnace is raised. An alarm controlled water-cooled jacket fits around the furnace to prevent any part of it overheating.

The temperature controller of the balance gives a temperature rise with time at a variety of heating rates from 1 degree per minute to
100 degrees per minute. It can be set either to hold the preset maximum temperature or to cool automatically down to room temperature. Both heating and cooling of the sample can be programmed at rates from 1 to 100 deg min\(^{-1}\), provided the natural cooling rate of the sample is faster than that programmed.

A thermocouple (platinum to platinum plus 13\% rhodium) mounted just underneath the scales gives the temperature output in analog form (0–10mV).

The displayed sample weight is connected via a system which consists basically of a clock which outputs a pulse every X seconds (where X varies between \(\frac{1}{2}\) and several hundred). This pulse causes the paper-tape punch (Addo punch drive, LU 1718) to output the sample weight, thus enabling variation of the number of data points to suit the decomposition rate, length of run etc.

III-5-b: Procedure

For the containment of the sample, the aluminium pan bottoms supplied by the Perkin-Elmer Corporation for use with their differential scanning calorimeters were used. All handling of pans was done with tweezers. A pan bottom was carefully placed on the stirrup connected to the long hang-down wire, the furnace was raised and the balance zeroed, ensuring that the pan and stirrup were free of the furnace walls. The furnace was then lowered and a small amount of sample very carefully 'dropped' onto the pan.

III-5-b-(i) Scanning Runs

After the furnace had been raised to accommodate the pan and sample for a scanning run, a suitable time was allowed for the sample to come to thermal equilibrium with its surroundings and for the purge gas (argon, 50 cm\(^3\) min\(^{-1}\)) to remove all traces of air. The temperature programmer was then started at the desired heating rate and continued until the required temperature had been reached. The weight of the
sample was recorded on paper tape every X seconds. These tapes were analysed using the method of Hauser and Field, as described in section III-1-b. A Hewlett-Packard 9825A calculator/plotter was used.

For these dynamic runs, the dehydration of calcium oxalate monohydrate served as a test reaction.

III-5-b-(ii): Isothermal Runs

The furnace was allowed to reach the temperature required for the experiment. Then, as for the dynamic runs, the pan was zeroed and the sample carefully placed in position. This procedure helped to minimise the time required for the sample to reach the experimental temperature when the furnace is raised. Tapes from isothermal runs were also analysed using the Hewlett-Packard 9825A machine.

III-6: Results

III-6-a: Isothermal Runs

The decompositions of silver, potassium, guanidine and tetraethylammonium picrates were studied isothermally. Ammonium picrate was found to be too volatile for study. No attempts were made to characterise any of the decomposition products, solid or gaseous, except in the case of silver picrate, where the X-ray pattern of the residue confirmed it to be silver and not silver oxide. The results for potassium were inconclusive and will not be considered further.

After decomposition, the average % masses lost were:

Guanidine picrate 83.1%
Tetraethylammonium picrate 66.7%
Silver picrate 67.4%
(Potassium picrate) (between 58 and 70%) *

* This figure for potassium does not compare well with the mass losses reported by Stammler and Andreev. The other picrates do not appear to have been subjected to this treatment before.
The decomposition was studied at a series of temperatures between ca. 270° and 300°C. Using the calculator-plotter, a graph of $\alpha$ (fractional decomposition) versus $t$ (time) was made for each temperature. A typical $\alpha$-$t$ curve is shown in Fig. III-4. Curves like these (sigmoid) usually conform to the Avrami-Erofeev equation

$$\left(-\ln(1-\alpha)\right)^{1/n} = k_n(t-t_o)$$

($t_o$ is assumed to be zero) with an appropriate value of $n$, or to the Prout-Tompkins equation

$$\ln(\alpha/(1-\alpha)) = k(t-t_o).$$

No attempt was made to fit the data to the Prout-Tompkins equation.

Reduced-time scale plots were also made for each temperature, such that at $\alpha=0.5$, $t_{\text{red}} = 1.0$ (see Fig. III-5). These plots show a fairly good coincidence which indicates that the same mechanism probably operates at each of the temperatures studied.

For each temperature, an Avrami plot was made, using different values of $n$. The slope of the best straight line was found ($k_n$) and then a plot of $\ln k_n$ vs. $1/T$ was made, the activation energy being found from the slope of the graph. (It is not always easy to distinguish the best value of $n$.) For guanidine picrate, $n=2$ gave the best straight line.

Theoretical reduced-time curves for the Avrami model

$$\alpha = 1-\exp\left(-\left(k_0 t_{\text{red}}\right)^n\right)$$

using values of $n=1,2,3$ were plotted on the same graph as the experimental reduced plot (see Fig. III-5) and the theoretical $n=2$ curve did give better coincidence than $n=1$ or $3$. However, inspection of the graph indicates that the 'best' value of $n$ is probably between 1.5 and 2.0. (At one temperature, $n=1.5$ did give...
a better straight line than $n=2$ for the Avrami plot.)

The rate constants, $k_{n=2}$, for each temperature are listed in Table III-4. From the Arrhenius plot (Fig. III-6) a value of 245 kJ mol$^{-1}$ was calculated for the activation energy and the frequency factor, $A$ was estimated to be of the order of $10^{18}$.

Fig. III-7 shows an Avrami plot for guanidine picrate.

III-6-a-(ii): Silver picrate

The average mass loss during decomposition was 67.4%. The residue was shown to be silver metal by its X-ray powder pattern. Decomposition of silver picrate to silver oxide should result in a 65.5% mass loss, whilst decomposition to the metal should give a 67.9% loss. The latter figure is in reasonable agreement with the experimental figure.

The decomposition of silver picrate was studied at a series of temperatures in the range 280°-310°C. A series of $\alpha$-$t$ plots were made and up to ca. $\alpha=0.6$, the plots were linear and the slopes of these regions were used as estimates of the zero-order rate coefficients $k_1$

$$\frac{d\alpha}{dt} = k_1 \quad (0<\alpha<0.6)$$

A plot of $\ln k_1$ versus $1/T$ gives an estimate of the activation energy for this initial stage (Fig. III-8). The activation energy was found to be approx. 270 kJ mol$^{-1}$. Table III-5 lists the rate constants at the temperatures studied.

A reduced-time plot showed acceptable coincidence, demonstrating that the same mechanism probably operates at all the temperatures studied.
Analysis of the deceleratory portion of the curves was not attempted.

III-6-a-(iii): Tetraethylammonium picrate

This was decomposed isothermally at a series of temperatures over the range ca. 235-270°C. The slopes of the initial linear regions were used to estimate the zero-order rate coefficients. The reduced-time plot showed good coincidence for all temperatures. Table III-6 lists the rate constants and Figs. III-9 and III-10 respectively show a typical $\alpha$-t curve and the reduced-time plot. The activation energy for decomposition was found to be approx. 195 kJ mol$^{-1}$.

III-6-b: Scanning Runs

The decompositions of potassium, rubidium, caesium, tetramethylammonium, tetraethylammonium and guanidine picrates were studied by a dynamic method. The heating rate used for all these compounds, except for tetramethylammonium picrate, was 5°min$^{-1}$. For the tetramethylammonium salt, 15°min$^{-1}$ was used. Some of the scans were started at ambient temperature, but when this proved to be too time consuming, runs were commenced at 200°C.

For all of these scanning tapes, the method of Hauser and Field was used to obtain the kinetic parameters (see section III-1-b). Table III-7 shows the value of n for each run (the best straight line) and the calculated quantities E and A.

Fig. III-11 shows a plot of $(\ln \frac{dw}{dt} - n \ln w)$ vs. $1/T$ for caesium.
FIG. III -4

$\alpha$ - t curve for the decomposition of guanidine picrate at $315^\circ$C

$\alpha$ vs $t/10^2$ sec
FIG. III-5: Experimental (— — ) and theoretical
(— — ) reduced-time plots for guanidine picrate.
FIG. III-6: Plot of $\ln k$ vs. $1/T$ for the decomposition of guanidine picrate.
FIG. III-7: Plot of $(-\ln(1-\alpha))^1/n$ vs. $t$ for guanidine picrate (Avrami plot)
FIG. III-8: Plot of $\ln k$ vs. $1/T$ for the decomposition of silver picrate.
FIG. III - 9  $\alpha$-t plot for tetraethylammonium picrate decomposition.
FIG. III-10: Plot of $\ln k$ vs. $1/T$ for the decomposition of tetraethylammonium picrate.
FIG. III-11: Plot of \( \ln \left( \frac{dw}{dt} - n \ln w \right) \) vs. \( \frac{1}{T} \) for caesium (\( n < 2 \))
III-7: Results and Discussion

The results obtained by the non-isothermal TG method for the alkali-metal picrates are all in the region of 2 to 3 thousand kJ mol\(^{-1}\). These values seem very high for the activation energies of decomposition of explosive compounds. Compared with the results obtained in this work by DSC and those of Stammler\(^{40}\) and Andreev\(^{23}\) (see Section III-3), these figures would appear to be at least 10 times too large. Values of this magnitude are not readily explicable.

The result found for the dehydration of calcium oxalate monohydrate (98.5 kJ mol\(^{-1}\)) is slightly higher than the range of other values found in the literature (84-92 kJ mol\(^{-1}\)) (see ref 11) but it is certainly not 10 times greater, so there cannot be too much doubt that the techniques employed and the programs used were working properly. (Due to lack of time the test reaction was only performed once.)

The agreement between individual runs on the same compound is not particularly good and often the n value was different. Some runs showed evidence for decomposition taking place in several stages, but other experiments only seemed to show one stage. The ln A values are also extremely high. These alkali-metal picrates decompose very quickly - there was a sharp 'pop' and a very sudden decrease in mass. It must be concluded that this is not the best method for studying compounds which decompose as rapidly as the alkali-metal picrates.

Hauser\(^{41}\) used this procedure to study the decomposition of PETN and Brown\(^{12}\) and Swallowe worked with silver nitrotetrazole. Credible results were obtained in both cases.

No satisfactory conclusions may be drawn from the results obtained here but this field is clearly an area requiring more careful investigation. This work was performed in Cambridge and the
time spent there was limited and better results would no doubt have been obtained had more time been available.

Non-isothermal runs were attempted using tetramethylammonium picrate. Values of the activation energy of decomposition were determined as 565, 521 and 494 kJ mol$^{-1}$.

Guanidine picrate showed a one-stage decomposition, giving $E$ as 608 kJ mol$^{-1}$. This may be compared with 245 kJ mol$^{-1}$ from the isothermal runs.

Tetraethylammonium picrate showed good agreement between the two methods - the scanning runs gave $E$ values of 196 and 191 kJ mol$^{-1}$, whilst the isothermal run gave 195 kJ mol$^{-1}$.

The Kissinger and Ozawa treatment of the DSC data for potassium and caesium picrates gave values of 214(Kis.) and 223(Ozw.) for potassium and 192(Kis.) and 202(Ozw.) for caesium. These are comparable with Andreev$^{33}$ (ca. 175 for potassium, isothermally) but Stammler$^{30}$ found 350 for the apparent activation energy of the first-order region of the decomposition-curve of caesium picrate. (All values in kJ mol$^{-1}$.)

It is difficult to draw meaningful conclusions from any of these kinetic results, either isothermal or dynamic.

Ideally, analyses of the end products of reaction and of any gaseous products formed during the decomposition should be performed. This would confirm or otherwise Stammler's proposed mechanism and intermediates.
### TABLE III-1

**DECOMPOSITION OF EXPLOSIVES USING DSC: COMPARISON OF ACTIVATION ENERGY VALUES FOUND BY DIFFERENT METHODS**

<table>
<thead>
<tr>
<th>Compound:</th>
<th>Kissing</th>
<th>Ozawa</th>
<th>Rogers</th>
<th>Ignition Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetracene: Peak 1</td>
<td>$193^{±6}_{4}^{4}$</td>
<td>$200^{±6}_{4}^{4}$</td>
<td>–</td>
<td>$195^{4}_{4}$</td>
</tr>
<tr>
<td>Peak 2</td>
<td>$172^{±2}_{4}^{4}$</td>
<td>$184^{±2}_{4}^{4}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Peak 3</td>
<td>$109^{±11}_{4}^{4}$</td>
<td>$122^{±15}_{4}^{4}$</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Lead Azide</td>
<td>$163^{±8}_{5}^{5}$</td>
<td>$167^{±6}_{5}^{5}$</td>
<td>$460^{±25}_{5}^{5}$</td>
<td>–</td>
</tr>
<tr>
<td>Lead Tetraazolate</td>
<td>–</td>
<td>$129.5^{7}_{5}^{7}$</td>
<td>$169.7^{7}_{5}^{7}$</td>
<td>–</td>
</tr>
</tbody>
</table>

All values in kJ/mol$^{-1}$
TABLE III-2
DSC RESULTS FOR POTASSIUM PICRATE DECOMPOSITION

<table>
<thead>
<tr>
<th>$\dot{\phi}$/deg min$^{-1}$</th>
<th>$\ln \phi$</th>
<th>$T_m$/K</th>
<th>$-\ln(\phi/T_m^2)$</th>
<th>$10^4K/T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>0.2231</td>
<td>583.2</td>
<td>12.51</td>
<td>17.15</td>
</tr>
<tr>
<td>1.25</td>
<td>0.2231</td>
<td>583.5</td>
<td>12.51</td>
<td>17.14</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9163</td>
<td>594.4</td>
<td>11.86</td>
<td>16.82</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9163</td>
<td>591.3</td>
<td>11.85</td>
<td>16.91</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9163</td>
<td>594.2</td>
<td>11.86</td>
<td>16.83</td>
</tr>
<tr>
<td>2.5</td>
<td>0.9163</td>
<td>592.7</td>
<td>11.85</td>
<td>16.87</td>
</tr>
<tr>
<td>10.0</td>
<td>2.3025</td>
<td>609.0</td>
<td>10.52</td>
<td>16.42</td>
</tr>
<tr>
<td>10.0</td>
<td>2.3025</td>
<td>611.0</td>
<td>10.53</td>
<td>16.37</td>
</tr>
<tr>
<td>10.0</td>
<td>2.3025</td>
<td>608.0</td>
<td>10.52</td>
<td>16.45</td>
</tr>
<tr>
<td>19.0</td>
<td>2.3025</td>
<td>610.5</td>
<td>10.53</td>
<td>16.38</td>
</tr>
<tr>
<td>20.0</td>
<td>2.9957</td>
<td>619.0</td>
<td>9.86</td>
<td>16.16</td>
</tr>
<tr>
<td>20.0</td>
<td>2.9957</td>
<td>620.5</td>
<td>9.87</td>
<td>16.12</td>
</tr>
<tr>
<td>20.0</td>
<td>2.9957</td>
<td>620.0</td>
<td>9.86</td>
<td>16.13</td>
</tr>
<tr>
<td>20.0</td>
<td>2.9957</td>
<td>619.5</td>
<td>9.86</td>
<td>16.14</td>
</tr>
<tr>
<td>40.0</td>
<td>3.6888</td>
<td>633.0</td>
<td>9.21</td>
<td>15.80</td>
</tr>
<tr>
<td>40.0</td>
<td>3.6888</td>
<td>632.5</td>
<td>9.21</td>
<td>15.81</td>
</tr>
</tbody>
</table>

Kissinger plot: slope = $-2.574 \times 10^4$

Correlation coefficient = 0.99

Ozawa plot: slope = $-2.696 \times 10^4$

Correlation coefficient = 0.99
<table>
<thead>
<tr>
<th>$\dot{\phi}$ deg min$^{-1}$</th>
<th>$\ln \dot{\phi}$</th>
<th>$T_m/K$</th>
<th>$-\ln (\dot{\phi}/T_m^2)$</th>
<th>$10^4 K/T_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.6094</td>
<td>597.0</td>
<td>11.17</td>
<td>16.75</td>
</tr>
<tr>
<td>5</td>
<td>1.6094</td>
<td>597.5</td>
<td>11.18</td>
<td>16.76</td>
</tr>
<tr>
<td>10</td>
<td>2.3025</td>
<td>606.0</td>
<td>10.51</td>
<td>16.50</td>
</tr>
<tr>
<td>10</td>
<td>2.3025</td>
<td>605.5</td>
<td>10.51</td>
<td>16.51</td>
</tr>
<tr>
<td>40</td>
<td>3.6888</td>
<td>629.0</td>
<td>9.20</td>
<td>15.90</td>
</tr>
<tr>
<td>40</td>
<td>3.6888</td>
<td>628.0</td>
<td>9.20</td>
<td>15.92</td>
</tr>
<tr>
<td>40</td>
<td>3.6888</td>
<td>628.0</td>
<td>9.20</td>
<td>15.92</td>
</tr>
</tbody>
</table>

Kissinger plot: slope $= -2.315 \times 10^4$

   correlation coefficient = 0.99

Ozawa plot: slope $= -2.440 \times 10^4$

   correlation coefficient = 0.99
### TABLE III-4

Rate constants, $k_{m_{2}}$, for the decomposition of guanidine picrate.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^{3} K/T$</th>
<th>$10^{4} k_{s}^{-1}$</th>
<th>$\ln k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>547</td>
<td>1.828</td>
<td>2.446</td>
<td>-8.316</td>
</tr>
<tr>
<td>548</td>
<td>1.822</td>
<td>3.703</td>
<td>-7.901</td>
</tr>
<tr>
<td>558</td>
<td>1.792</td>
<td>9.285</td>
<td>-6.982</td>
</tr>
<tr>
<td>565</td>
<td>1.771</td>
<td>16.50</td>
<td>-6.407</td>
</tr>
</tbody>
</table>

### TABLE III-5

Rate constants, $k_{i}$, for the decomposition of silver picrate.

<table>
<thead>
<tr>
<th>T/K</th>
<th>$10^{3} K/T$</th>
<th>$10^{4} k_{s}^{-1}$</th>
<th>$\ln k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>557</td>
<td>1.795</td>
<td>2.420</td>
<td>-8.326</td>
</tr>
<tr>
<td>561</td>
<td>1.765</td>
<td>5.33</td>
<td>-7.537</td>
</tr>
<tr>
<td>567</td>
<td>1.763</td>
<td>5.886</td>
<td>-7.438</td>
</tr>
<tr>
<td>573</td>
<td>1.745</td>
<td>12.51</td>
<td>-6.684</td>
</tr>
<tr>
<td>576</td>
<td>1.736</td>
<td>13.42</td>
<td>-6.613</td>
</tr>
<tr>
<td>577</td>
<td>1.732</td>
<td>16.43</td>
<td>-6.411</td>
</tr>
<tr>
<td>580</td>
<td>1.724</td>
<td>14.17</td>
<td>-6.550</td>
</tr>
</tbody>
</table>
TABLE III-6

Rate constants, $k$ for the decomposition of tetraethylammonium picrate.

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$10^3 K/T$</th>
<th>$10^4 k_s^{-1}$</th>
<th>$\ln k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>1.954</td>
<td>1.689</td>
<td>-8.686</td>
</tr>
<tr>
<td>534</td>
<td>1.871</td>
<td>11.00</td>
<td>-6.812</td>
</tr>
<tr>
<td>543</td>
<td>1.842</td>
<td>24.40</td>
<td>-6.016</td>
</tr>
</tbody>
</table>
Results obtained by scanning TG method for the decomposition of certain picrates MPic.

<table>
<thead>
<tr>
<th>M</th>
<th>E/kJ mol⁻¹</th>
<th>n</th>
<th>ln A</th>
</tr>
</thead>
<tbody>
<tr>
<td>NET₄ A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td>199</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Stage II</td>
<td>404</td>
<td>1.0</td>
<td>84</td>
</tr>
<tr>
<td>NET₄ B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td>196</td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>Stage II</td>
<td>385</td>
<td>1.0</td>
<td>74</td>
</tr>
<tr>
<td>NMe₄ A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>565</td>
<td>1.0</td>
<td>108</td>
</tr>
<tr>
<td>NMe₄ B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>494</td>
<td>0.9</td>
<td>97</td>
</tr>
<tr>
<td>NMe₄ C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>521</td>
<td>1.0</td>
<td>106</td>
</tr>
<tr>
<td>Guanidine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td>608</td>
<td>1.4</td>
<td>110</td>
</tr>
<tr>
<td>Stage II</td>
<td>452</td>
<td>1.0</td>
<td>81</td>
</tr>
<tr>
<td>K A</td>
<td>2250</td>
<td>1.5</td>
<td>470</td>
</tr>
<tr>
<td>K B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td>1692</td>
<td></td>
<td>340</td>
</tr>
<tr>
<td>Stage II</td>
<td>3440</td>
<td>2.0</td>
<td>760</td>
</tr>
<tr>
<td>K C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage 1</td>
<td>2034</td>
<td>1.0</td>
<td>404</td>
</tr>
<tr>
<td>Stage II</td>
<td>3600</td>
<td>3.0</td>
<td>723</td>
</tr>
<tr>
<td>K D</td>
<td>2366</td>
<td>2.0</td>
<td>460</td>
</tr>
</tbody>
</table>
TABLE III-7: contd

<table>
<thead>
<tr>
<th>M</th>
<th>$E/\text{kJ mol}^{-1}$</th>
<th>n</th>
<th>$\ln A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs A</td>
<td>2255</td>
<td>1.2</td>
<td>460</td>
</tr>
<tr>
<td>Cs B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stage I</td>
<td>2870</td>
<td></td>
<td>460</td>
</tr>
<tr>
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<td>2240</td>
<td>2.0</td>
<td>360</td>
</tr>
<tr>
<td>Rb A</td>
<td>2123</td>
<td>1.0</td>
<td>430</td>
</tr>
<tr>
<td>Rb B</td>
<td>2015</td>
<td>1.0</td>
<td>430</td>
</tr>
</tbody>
</table>
REFERENCES - CHAPTER III

29. T. Tucholski, ibid., 13 (1933) 435.
30. T. Tucholski, ibid., 14 (1934) 125.
31. T. Tucholski, ibid., 14 (1934) 259.
32. T. Tucholski, ibid., 14 (1934) 430.
APPENDIX I

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Explosives Testing

The properties tested for in establishing the suitability of explosives for commercial or military use, or in the comparison of explosives are:

(i) stability
(ii) brisance
(iii) sensitivity
(iv) explosive - strength characteristics

Some of the more important of these tests are described briefly below.

Brisance (shattering power) is determined by the sand test. A small sample of explosive is pressed into a metal blasting cap under a pressure of some 3000 psi. Known charges of tetryl and lead azide are added under the same pressure, and a reinforcing cap is then pressed against the top charge. A length of miner's fuse is then inserted in the cap and clamped tightly in place. This detonator is then centred in a bomb containing sand – the particle size of this sand is such that it will pass through a no.20 sieve but not a no.30. The bomb is closed and the charge fired. The amount of sand crushed is determined by weighing the portion that will pass through a no.30 sieve, and this is corrected for the amount of tetryl and lead azide added.

Sensitivity to impact is determined by subjecting a small quantity of confined explosive to the transmitted shock of a falling weight and determining the minimum height of fall that will produce at least one explosion in ten.

Sensitivity to explosion when heat is applied is determined as the temperature required to produce explosion in either 5 seconds or in less than 1 second.
The Pendulum Friction Test determines the sensitivity to friction. A sample of explosive is spread evenly over a scored steel-base plate, and a heavy steel shoe suspended from about 1.5m is allowed to sweep back and forth pendulum-wise across the base plate.

The fall-hammer test was used to measure approximately the sensitiveness to shock of an explosive. The classification of explosives for transport on German railways many years ago was based upon the results of this test.

Explosive strength may be determined by the Ballistic Pendulum or Trauzl Lead-block tests. In the Lead-block test a charge is exploded in a cylindrical cavity (25mm in diameter and 125mm deep) in a cylindrical lead block, 200mm in height and diameter. The sample is wrapped in tin foil, with a detonator embedded in the charge and placed in the bottom of the cavity, which is stemmed with sand. After firing, the volume of the cavity is determined by pouring in water. (The volume caused by the detonator alone is subtracted).

In the ballistic pendulum test the sample is detonated in a heavy mortar suspended by a pendulum bar and closed by means of a loosely fitting steel cylinder. An adjacent scale shows the angular deflection of the mortar from its rest position when the steel plug is ejected in the opposite direction. The relative strength of an explosive is calculated by comparison with 10g of TNT.
APPENDIX II

THERMOCHEMISTRY OF MONOMETHYLUREA

Introduction

Combustion studies of mono-formic acid, mono-nitro and mono-nitro-substituted ureas have previously been made in this laboratory. The monomethyl substituted compound and urea, however, have been absent. Davis has calculated a value for the standard enthalpy of formation and a combustion study was undertaken to confirm this value.

Experimental

Monomethylurea (analysis 92.9%) was recrystallized from benzene from a litro suction/diethyl ether mixture. Using differential scanning calorimetry, the purity was found to be greater than 99.4%.

The experimental procedure was as described in Chapter II.

Table II-1 gives data on the energy for each experiment.

Results and Discussion

The energy of combustion of monomethylurea, $\Delta H_f$, was found to be $-1247.4 \pm 0.0171$ kJ mol$^{-1}$.

This gives rise to a standard enthalpy of combustion of monomethylurea, $\Delta H_c$, of $-1367.76 \pm 0.4$ kJ mol$^{-1}$ and a standard enthalpy of formation of $-1218.75 \pm 1.4$ kJ mol$^{-1}$.

There is excellent agreement between the value obtained experimentally and that predicted by Davis.

References

1. R. A. Davis, unpublished work.
APPENDIX II

THERMOCHEMISTRY OF MONOMETHYLUREA

Introduction:

Combustion studies on urea, urea nitrate and certain methyl-substituted ureas have previously been made in this Laboratory.\textsuperscript{1} The monomethyl substituted compound had not, however, been burned. Davies\textsuperscript{1} has calculated a value for its standard enthalpy of formation and a combustion study was undertaken to confirm this value.

Experimental

Monomethylurea (Aldrich, 97\%) was recrystallised four times from a 1:1 acetone/diethyl ether mixture. Using differential scanning calorimetry\textsuperscript{2}, the purity was found to be greater than 99.9\%.

The experimental procedure was as described in Chapter II.

Table AII-1 gives detailed results for each experiment.

Results and Discussion

The energy of combustion of monomethylurea, $\Delta u_{c}^0$, was found to be $-17.7749 \pm 0.0173 \text{ kJ g}^{-1}$.

This gives rise to a standard enthalpy of combustion, $\Delta h_{c}^0$, of $-1316.76 \pm 1.38 \text{ kJ mol}^{-1}$ and a standard enthalpy of formation of $-327.75 \pm 1.41 \text{ kJ mol}^{-1}$.

There is excellent agreement between the value obtained experimentally and that predicted by Davies.

References

1. R.H. Davies, unpublished work.
<table>
<thead>
<tr>
<th>Ref. No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
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<tbody>
<tr>
<td>m(sample)/g</td>
<td>1.400800</td>
<td>1.678509</td>
<td>1.847708</td>
<td>2.073653</td>
<td>1.685454</td>
<td>1.598743</td>
<td>1.404994</td>
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<td>m(fuse)/g</td>
<td>0.00386</td>
<td>0.00526</td>
<td>0.00379</td>
<td>0.00409</td>
<td>0.00465</td>
<td>0.00422</td>
<td>0.00519</td>
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<tr>
<td>m(Pt wire)/g</td>
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<td>0.00593</td>
<td>0.00607</td>
<td>0.00554</td>
<td>0.00559</td>
<td>0.00627</td>
<td>0.00657</td>
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<td>m(silica crucible)/g</td>
<td>4.450700</td>
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<td>4.450410</td>
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<td>4.450190</td>
<td>4.638766</td>
<td>4.449960</td>
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<tr>
<td>m(soot)/g</td>
<td>0.00001</td>
<td>0.00003</td>
<td>0.00000</td>
<td>0.00019</td>
<td>0.00008</td>
<td>0.00100</td>
<td>0.00000</td>
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<td>m(H₂O)/g</td>
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<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
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<tr>
<td>q_i/kJ</td>
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<td>0.093827</td>
<td>0.068117</td>
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<td>0.083158</td>
<td>0.075638</td>
<td>0.092603</td>
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<tr>
<td>q_a/kJ</td>
<td>0.123023</td>
<td>0.147389</td>
<td>0.160408</td>
<td>0.168112</td>
<td>0.144284</td>
<td>0.135863</td>
<td>0.124098</td>
</tr>
<tr>
<td>q_c/kJ</td>
<td>0.000330</td>
<td>0.000990</td>
<td>0.000000</td>
<td>0.006270</td>
<td>0.00264</td>
<td>0.03300</td>
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<td>q_w/kJ</td>
<td>0.025904</td>
<td>0.031534</td>
<td>0.035064</td>
<td>0.039989</td>
<td>0.031721</td>
<td>0.029954</td>
<td>0.025980</td>
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<td>ΔT/K</td>
<td>2.8945</td>
<td>3.4598</td>
<td>3.8158</td>
<td>4.2780</td>
<td>3.4805</td>
<td>3.2972</td>
<td>2.9057</td>
</tr>
<tr>
<td>e_f/kJ K⁻¹</td>
<td>8.6812</td>
<td>8.6822</td>
<td>8.6826</td>
<td>8.6835</td>
<td>8.6821</td>
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<td>e_cf/kJ K⁻¹</td>
<td>0.062535</td>
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<td>0.063987</td>
<td>0.064865</td>
<td>0.063460</td>
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<td>0.065801</td>
</tr>
<tr>
<td>- Δu_c/kJ g⁻¹ (298.15K)</td>
<td>17.7812</td>
<td>17.7341</td>
<td>17.7882</td>
<td>17.7815</td>
<td>17.7765</td>
<td>17.7750</td>
<td>17.7877</td>
</tr>
</tbody>
</table>

Mean = -17.7749 ± 0.0173 kJ g⁻¹
APPENDIX III

THERMOCHEMISTRY OF DINITROPHENOLS

Some thermochimical aspects of dinitrophenols have been investigated. Table III-I lists some values of the standard enthalpies of formation of these compounds and other aminophenols. There do not appear to have been any thermochimical studies made on the nitrates.

The 2,4- and 2,6-isomers were chosen for study in this work.

From Table III-I, there are the values in the literature for

\[ \begin{align*}
\Delta H_f^\circ & \text{2,4-dinitrophenol} \text{ and } \Delta H_f^\circ \text{2,6-dinitrophenol.}
\end{align*} \]

The aim of this work was to determine which of the values for the 2,4-nitrophenolate was correct, and to check the 2,6-nitrophenolate. The molecular and associate units of these ions have been reported, and no investigation of their thermal properties has reached. From any of these preliminary results, it was possible to determine thermochimical data for each of the nitrophenolate ion, and hence calculate relative
Thermochemistry of Dinitrophenols

AIII-at: Introduction

The direct nitration of phenol beyond the mononitro stage results in considerable loss by oxidation. Dinitrophenols may be prepared by treating phenol with sulphuric acid at 110°C to form phenol-sulphonic acid, and then diluting with an equal volume of water. Dilute nitric acid is then added slowly, the temperature being maintained below 50°C. They may also be prepared from dinitrobenzene by hydrolysis with NaOH, and treating with acid to liberate the dinitrophenols.

2,4-dinitrophenol can be detonated by a powerful initiator, but is deficient in oxygen for complete explosive decomposition. It forms explosive salts with most metals. The neutral lead salt \( \left( \text{C}_6\text{H}_3\!(\text{NO}_2)\!\text{O}\!\text{H}_\text{2}\!\text{O}\!\text{Pb}.\!\text{H}_\text{2}\!\text{O} \right)_\text{Pb}.\!\text{H}_\text{2}\!\text{O} \) detonates strongly.

Dinitrophenol forms stable compounds with aromatic amines and aromatic hydrocarbons. It is appreciably more poisonous than picric acid or TNT.

Some thermochemical aspects of dinitrophenols have been investigated. Table AIII-1 lists some values of the standard enthalpies of formation of these isomers and other nitrophenols. There do not appear to have been any thermochemical studies made on the salts.

The 2,4- and 2,6- isomers were chosen for study in this work. From Table AIII-1, there are two values in the literature for \( \Delta H^\circ_f \) 2,4-dinitrophenol and one for \( \Delta H^\circ_f \) 2,6-dinitrophenol.

The aim of this work was to determine which of the values for the 2,4-salt (if either) was correct, and to check the 2,6-value. The potassium and ammonium salts of these isomers have been prepared, and an investigation of their thermal properties has started. From some of these preliminary results, it has been possible to calculate thermochemical radii for each of the dinitrophenolate anions and hence calculate lattice
energies for some salts.

AIII-b: Experimental

The potassium and ammonium salts of 2,4- and 2,6-dinitrophenols were prepared by neutralising aqueous ethanolic solutions of the phenols with potassium and ammonium carbonates respectively. The salts were recrystallised twice from water and allowed to dry in an oven at 110°C.

The potassium salts of the 2,4- and 2,6-isomers are yellow and red respectively, whilst ammonium 2,4-dinitrophenol is yellow and the 2,6-salt is brown.

The parent dinitrophenols were given by Woolwich Arsenal and were made by P. Stansfield, ca. 1942.

For the combustion calorimetry, 2,4-dinitrophenol (B.D.H.Ltd., AnalaR grade) was recrystallised three times from ethanol (by Miss E.Y.T. Kao), m.p. = 112°C. There is some variation in the literature concerning the melting point of 2,4-dinitrophenol (see Table AIII-2). The purity of the 2,4-dinitrophenol was found to be > 99.9% by differential scanning calorimetry (by Miss E.Y.T. Kao).

The 2,6-dinitrophenol prepared at Woolwich Arsenal was used for the combustion calorimetry of this compound. It was recrystallised twice from ethanol and dried in vacuo over P₂O₅, m.p. = 64°C (Lit. = 64°C). Differential scanning calorimetry showed the purity of this compound to be greater than 99.9%.

The enthalpies of solution of the potassium and ammonium salts of these dinitrophenols in water were measured using a calorimeter constructed in this Laboratory.

An attempt was made to measure the enthalpy of solution of 2,4-dinitrophenol in water, but this did not prove to be successful owing to its low solubility in water.

The energies of combustion of 2,4- and 2,6-dinitrophenols were determined using static oxygen-bomb calorimetry.
Results and Discussion

Tables AIII-3-6 inclusive list the results for the enthalpies of solution in water of the dinitrophenol salts.

The mean values were found to be:

\[
\begin{align*}
2,4\text{-dinitrophenol} & : 33.27 \pm 0.71 \\
2,6\text{-dinitrophenol} & : 36.43 \pm 0.72
\end{align*}
\]

(all values in kJ mol\(^{-1}\))

The limits of error on these enthalpies of solution are unacceptably high. This may be due in part to the low solubility of these compounds, and the small number of determinations carried out with each.

Tables AIII-7 and AIII-8 list the combustion calorimetry results for 2,4- and 2,6-dinitrophenols respectively. (The results for 2,4-dinitrophenol were obtained with the aid of Miss E.Y.T. Kao).

The energies of combustion at 298.15K of 2,4- and 2,6-dinitrophenols were found to be -2703.42 and -2729.28 \pm 3.18\,kJ\,mol\(^{-1}\) respectively.

(For 2,4-dinitrophenol, only two experiments were performed; it is therefore inappropriate to calculate error limits).

Using

\[
\text{C}_6\text{H}_4\text{N}_2\text{O}_6(c) + 9/2\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 2\text{H}_2\text{O}(l) + \text{N}_2(g) \]

(\(\Delta n = 5/2\))

the standard enthalpies of combustion are -2697.22(2,4) and -2723.08 \pm 3.18\,(2,6)\,kJ\,mol\(^{-1}\), and hence standard enthalpies of formation for these compounds are:

\[
\begin{align*}
\Delta H_f^\circ/\text{kJ}\,\text{mol}^{-1} & \\
2,4\text{-dinitrophenol} & : 235.50 \\
2,6\text{-dinitrophenol} & : 209.64 \pm 3.27
\end{align*}
\]
These results compare favourably with those obtained in 1942 by Badoche \(^{2}\) for 2,4- and 2,6-dinitrophenol respectively).

From the enthalpies of solution, it has been possible to calculate very tentative values for the thermochemical radii of the 2,4- and 2,6-dinitrophenolate anions.

Consider the following cycle

\[
(DNP^-=C_6H_3(NO_2)_2O^-) 
\]

\[
\begin{align*}
& \text{U}+2\text{RT} \\
& \Delta H_{\text{hyd}} \text{M}^+ \\
& \Delta H \\
& \text{M}^+ (\text{aq}) + \text{DNP}^- (\text{aq}) \\
& \Delta H_{\text{hyd}} \text{DNP}^- 
\end{align*}
\]

\[
(\Delta H = \text{enthalpy of solution})
\]

Then

\[
\begin{align*}
\Delta H_1 &= \text{U}_1 + 2\text{RT} + \Delta H_{\text{hyd} \text{M}^+} + \Delta H_{\text{hyd} \text{DNP}^-} \\
\Delta H_2 &= \text{U}_2 + 2\text{RT} + \Delta H_{\text{hyd} \text{M}^{2+}} + \Delta H_{\text{hyd} \text{DNP}^-} 
\end{align*}
\]

Then

\[
(\text{U}_1 - \text{U}_2) = (\Delta H_1 - \Delta H_2) + (\Delta H_{\text{hyd} \text{M}^+} - \Delta H_{\text{hyd} \text{M}^{2+}})
\]

\[
\Delta H_{\text{hyd} \text{K}^+(\text{aq})} = \Delta H_{\text{hyd} \text{K}^+(\text{g})} - \Delta H_{\text{hyd} \text{K}^+(\text{aq})} = -765.84 \text{kJ mol}^{-1} \quad 15
\]

\[
\Delta H_{\text{hyd} \text{NH}_4^+(\text{aq})} = -751.32 \text{kJ mol}^{-1} \quad 15
\]

(Both based on \(\Delta H_{\text{hyd} \text{H}^+(\text{g})} = 0\))

Knowing \((\text{U}_1 - \text{U}_2)\), the thermochemical radius may then be calculated in a manner similar to that described for the picrate ion.
The thermochemical radii of the 2,4- and 2,6-dinitrophenolate anions have been calculated as 0.28 and 0.34 nm respectively. However it seems likely that at least one of these figures is wrong. It is unlikely that these two isomers would have thermochemical radii differing by such a large amount. Lattice energies have been calculated on the basis of both figures (Table AIII-9). These values are almost certainly wrong. A more complete investigation of the salts of 2,4- and 2,6-dinitrophenols is needed. The ammonium salt was probably a bad choice for this type of calculation. The rubidium or caesium salts would have been better.

AIII-d: Suggestions for further work

The rubidium and caesium salts of 2,4- and 2,6-dinitrophenol could be prepared and their enthalpies of solution measured. A further attempt to measure the enthalpy of solution of 2,4- and 2,6-dinitrophenols should be made. The solubility of the silver salts of these isomers may be worth investigating.

A combustion study of the ammonium salts might be fruitful, and the neutralisation of these dinitrophenols could also be studied by solution calorimetry. Values obtained by the two methods for $\Delta H_f$ of the ammonium dinitrophenolates could be compared. It would be interesting to see if the same problem exists with the dinitrophenols as with the trinitro compound i.e. a difference in the enthalpies of formation calculated from solution and combustion experiments. This seems to be unlikely in the case of the dinitrophenols since this combustion work has essentially confirmed that of Badoche in 1942. The problem with picric acid is that no only do the solution and combustion calorimetric results disagree, but also that all of the combustion studies are in poor agreement with each other (Badoche also burned picric acid in 1942 in the same investigation as the dinitrophenols). The combustion of picric acid is probably incomplete...
under the conditions used in all the combustion studies, including this one.

Other nitrophenols could also be usefully investigated calorimetrically. The mononitrophenols were burned over 50 years ago by Kharasch1. These values may be worth checking. Other di- and tri-nitro isomers exist and also a tetranitrocompound (Table AIII-10), and none of these compounds appear to have been studied previously.

It might be of interest to see how the enthalpy of formation varies with the pattern of substitution, and how this compares with other substituted phenols e.g: halophenols (if data are available). Heats of nitration could also be calculated for a series of nitro compounds.

Other substituted nitrophenols may also be of interest; the mono, di- and tri-nitro resorcinols (e.g: styphnic acid) and the amino-nitrophenols (e.g: picramic acid).
**TABLE AIII-1**

**THERMOCHEMICAL DATA FOR NITROPHENOLS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>$\Delta H_f^\circ$/kJ mol$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-nitrophenol</td>
<td>C$_6$H$_5$NO$_3$</td>
<td>210.45</td>
<td>1</td>
</tr>
<tr>
<td>o-nitrophenol</td>
<td>C$_6$H$_5$NO$_3$</td>
<td>194.14</td>
<td>1</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>C$_6$H$_5$NO$_3$</td>
<td>194.14</td>
<td>1</td>
</tr>
<tr>
<td>2,4-dinitrophenol</td>
<td>C$_6$H$_4$N$_2$O$_5$</td>
<td>235.81±2.72</td>
<td>2</td>
</tr>
<tr>
<td>2,6-dinitrophenol</td>
<td>C$_6$H$_4$N$_2$O$_5$</td>
<td>209.91±2.76</td>
<td>2</td>
</tr>
<tr>
<td>2,4,6-trinitrophenol</td>
<td>C$_6$H$_3$N$_3$O$_7$</td>
<td>217.88±1.99</td>
<td>This work</td>
</tr>
<tr>
<td>(picric acid)</td>
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<td>214.35±1.38</td>
<td>4</td>
</tr>
<tr>
<td>(added for</td>
<td></td>
<td>220.71±2.59</td>
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</tr>
<tr>
<td>completeness)</td>
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<td>211.29±2.51</td>
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<td></td>
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<td>222.17±2.59</td>
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<td>2,4-dinitroresorcinol</td>
<td>C$_6$H$_4$N$_2$O$_6$</td>
<td>415.64±2.55</td>
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<td>4,6-dinitroresorcinol</td>
<td>C$_6$H$_4$N$_2$O$_6$</td>
<td>439.61±2.55</td>
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<td>2-amino-4,6-dinitrophenol</td>
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<td>(picramic acid)</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE AIII-2

THE MELTING POINT OF 2,4-DINITROPHENOL

<table>
<thead>
<tr>
<th>m.p./°C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>112.8</td>
<td>8</td>
</tr>
<tr>
<td>112.8</td>
<td>9</td>
</tr>
<tr>
<td>112.9</td>
<td>10</td>
</tr>
<tr>
<td>113.0</td>
<td>11</td>
</tr>
<tr>
<td>114.0</td>
<td>12</td>
</tr>
<tr>
<td>112.0</td>
<td>This work</td>
</tr>
</tbody>
</table>
### TABLE AIII-3

**ENTHALPY OF SOLUTION OF POTASSIUM 2,4-DINITROPHENOLATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H_{298}^o / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1005</td>
<td>12283</td>
<td>32.57</td>
</tr>
<tr>
<td>0.1108</td>
<td>11140</td>
<td>33.93</td>
</tr>
<tr>
<td>0.1281</td>
<td>9656</td>
<td>33.02</td>
</tr>
<tr>
<td>0.1308</td>
<td>9437</td>
<td>33.79</td>
</tr>
<tr>
<td>0.1431</td>
<td>8626</td>
<td>33.06</td>
</tr>
</tbody>
</table>

Mean = 33.27 ± 0.71

**a** = mole ratio of compound to water  
**b** = uncertainties are 95% confidence limits calculated using the student's t distribution with the appropriate number of degrees of freedom.

### TABLE AIII-4

**ENTHALPY OF SOLUTION OF AMMONIUM 2,4-DINITROPHENOLATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n</th>
<th>$\Delta H_{298}^o / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0953</td>
<td>11725</td>
<td>34.76</td>
</tr>
<tr>
<td>0.0966</td>
<td>11560</td>
<td>34.08</td>
</tr>
<tr>
<td>0.1107</td>
<td>10094</td>
<td>34.52</td>
</tr>
<tr>
<td>0.1174</td>
<td>9517</td>
<td>34.43</td>
</tr>
<tr>
<td>0.1362</td>
<td>8204</td>
<td>34.26</td>
</tr>
</tbody>
</table>

Mean = 34.41 ± 0.32

**a** = mole ratio of compound to water  
**b** = uncertainties are 95% confidence limits calculated using the student's t distribution with the appropriate number of degrees of freedom.
TABLE AIII-5

**ENTHALPY OF SOLUTION OF POTASSIUM 2,6-DINITROPHENOLATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n^a</th>
<th>$\Delta H^\circ_{298}/kJ \ mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0952</td>
<td>12966</td>
<td>36.02</td>
</tr>
<tr>
<td>0.0987</td>
<td>12506</td>
<td>37.30</td>
</tr>
<tr>
<td>0.1025</td>
<td>12042</td>
<td>36.00</td>
</tr>
<tr>
<td>0.1160</td>
<td>10641</td>
<td>36.62</td>
</tr>
<tr>
<td>0.1299</td>
<td>9502</td>
<td>37.09</td>
</tr>
<tr>
<td>0.1387</td>
<td>8899</td>
<td>35.53</td>
</tr>
</tbody>
</table>

Mean = 36.43$^{\pm}$0.72

TABLE AIII-6

**ENTHALPY OF SOLUTION OF AMMONIUM 2,6-DINITROPHENOLATE IN WATER**

<table>
<thead>
<tr>
<th>m/g</th>
<th>n^a</th>
<th>$\Delta H^\circ_{298}/kJ \ mol^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0828</td>
<td>13494</td>
<td>41.53</td>
</tr>
<tr>
<td>0.0984</td>
<td>11356</td>
<td>40.41</td>
</tr>
<tr>
<td>0.1013</td>
<td>11031</td>
<td>40.25</td>
</tr>
<tr>
<td>0.1155</td>
<td>9675</td>
<td>41.99</td>
</tr>
<tr>
<td>0.1162</td>
<td>9616</td>
<td>39.96</td>
</tr>
<tr>
<td>0.1207</td>
<td>9257</td>
<td>41.06</td>
</tr>
<tr>
<td>0.1215</td>
<td>9196</td>
<td>40.46</td>
</tr>
</tbody>
</table>

Mean = 40.81$^{\pm}$0.69
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<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>9.6771</td>
<td>5.0675</td>
<td>8.6794</td>
<td>8.6794</td>
<td></td>
</tr>
<tr>
<td>9.5000</td>
<td>3.6380</td>
<td>5.9000</td>
<td>5.9000</td>
<td></td>
</tr>
<tr>
<td>6.6900</td>
<td>5.6737</td>
<td>6.6900</td>
<td>6.6900</td>
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</tr>
<tr>
<td>0.6930</td>
<td>3.0500</td>
<td>0.6930</td>
<td>0.6930</td>
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</tr>
<tr>
<td>0.4820</td>
<td>1.7500</td>
<td>0.4820</td>
<td>0.4820</td>
<td></td>
</tr>
<tr>
<td>0.4850</td>
<td>1.7500</td>
<td>0.4850</td>
<td>0.4850</td>
<td></td>
</tr>
<tr>
<td>0.1450</td>
<td>1.3517</td>
<td>1.2116</td>
<td>2.1171</td>
<td></td>
</tr>
</tbody>
</table>

**Table IVII-8**

(Continued)

Composition calorimetry results for 2,6-Dinitrophenol (P-1,688 cm⁻³)
### TABLE AIII-9

**CALCULATED LATTICE ENERGIES FOR**

**2,4- and 2,6-DINITROPHENOL SALTS**

<table>
<thead>
<tr>
<th>Cation</th>
<th>2,4 isomer $U_0$/kJ mol$^{-1}$</th>
<th>2,6 isomer $U_0$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>586</td>
<td>510</td>
</tr>
<tr>
<td>K</td>
<td>544</td>
<td>477</td>
</tr>
<tr>
<td>Rb</td>
<td>527</td>
<td>464</td>
</tr>
<tr>
<td>Cs</td>
<td>504</td>
<td>446</td>
</tr>
<tr>
<td>Mg</td>
<td>1905</td>
<td>1638</td>
</tr>
<tr>
<td>Ca</td>
<td>1764</td>
<td>1532</td>
</tr>
<tr>
<td>Sr</td>
<td>1695</td>
<td>1480</td>
</tr>
<tr>
<td>Ba</td>
<td>1627</td>
<td>1428</td>
</tr>
</tbody>
</table>
TABLE AIII-10

**OTHER NITROPHENOLS**

<table>
<thead>
<tr>
<th>isomer</th>
<th>m.p./(^{\circ})C(^{14})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3-di</td>
<td>144.5</td>
</tr>
<tr>
<td>2,5-di</td>
<td>108</td>
</tr>
<tr>
<td>3,4-di</td>
<td>134</td>
</tr>
<tr>
<td>3,5-di</td>
<td>126.1</td>
</tr>
<tr>
<td>2,3,6-tri</td>
<td>119</td>
</tr>
<tr>
<td>2,4,5-tri</td>
<td>96</td>
</tr>
<tr>
<td>2,3,4,6-tetra</td>
<td>140 (decomposes)</td>
</tr>
</tbody>
</table>
REFERENCES - APPENDIX III

4. A.F. Vorobiev, N.M. Privalova, L.V. Storozhenko and
15. Handbook of Chemistry and Physics, ed. R.C. Weast, Chemical
   Rubber Co., Cleveland, Ohio.
TO WHOM IT MAY Concern:

This is to certify that

Ann Elizabeth SMITH

has been registered as a full-time postgraduate student at Royal Holloway College (University of London) from 9th January 1979 to 31st December 1981.

Whilst enrolled as a postgraduate student, Miss Smith took and passed the following courses:

Courses taken and passed in June 1980:

<table>
<thead>
<tr>
<th>Course Code</th>
<th>Course Title</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM301</td>
<td>Nuclear and Radiochemistry</td>
<td>½ course unit</td>
</tr>
<tr>
<td>S111</td>
<td>Fundamentals of Programming</td>
<td>½ course unit</td>
</tr>
</tbody>
</table>

Courses taken and passed in June 1981:

<table>
<thead>
<tr>
<th>Course Code</th>
<th>Course Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>S130</td>
<td>Statistics for Scientists</td>
</tr>
</tbody>
</table>

It is not the policy of the University of London to divulge the marks or grades obtained by candidates in individual courses.
THERMOCHEMISTRY OF PICRATES. I. THE STANDARD ENTHALPY
OF FORMATION OF AMMONIUM PICRATE

ARTHUR FINCH, PETER J. GARDNER and ANN E. SMITH

The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey
(Gt. Britain)

(Received 22 April 1981)

ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion at
298.15 K of the yellow crystalline modification of ammonium picrate has been deter­
mined as $-2833.11 \pm 2.83$ kJ mole$^{-1}$. The standard enthalpy of formation is $-385.44 \pm$
2.94 kJ mole$^{-1}$. These results are discussed in relation to previous values and also in con­
exion with solution calorimetric studies involving picric acid and metal picrates.

INTRODUCTION

Ammonium picrate $[2,4,6-(\text{NO}_2)_3\text{C}_6\text{H}_2\text{ONH}_4]$, long known and with an
extensive history in the explosives industry [1], is a key compound in the
thermochemistry of metal picrates. For these compounds, consistent and
reliable values of standard enthalpies of formation may be calculated from
solution-reaction calorimetric measurements. An essential input datum is a
value for the standard enthalpy of formation of the aqueous picrate ion,
which derives from precise enthalpy of solution experiments involving either
picric acid or ammonium picrate. Surprisingly, agreed values of standard
enthalpies of formation for neither of these compounds are apparently
available [2—9]. Since ammonium picrate is far more easily soluble in aque­
oun media than is picric acid, and is hence more suitable for solution-reaction
experiments, we have measured its enthalpy of combustion using conven­
tional static-bomb oxygen calorimetry.

EXPERIMENTAL

Materials and synthesis

Ammonium picrate

Picric acid (B.D.H., AnalaR grade) in an acetone—water mixture (1:1)
was carefully neutralised using aqueous ammonium carbonate (B.D.H.,
AnalaR grade). The yellow product was recrystallised four times from water,
dried in air at ca. 120°C for ca. 7 h, and stored over anhydrous magnesium
perchlorate. Under these conditions the red modification is not formed [10]. Analysis was based on distillation from aqueous sodium carbonate into standard aqueous HCl to collect NH₃, followed by titration using standard NaOH. Results were: NH₃, 6.91% (calcd. 6.907%). A Karl Fischer titration indicated that the water content was negligible.

**Acetanilide**
A commercial sample (B.D.H., OAS grade) was used as supplied after drying overnight at ca. 110°C. A purity of ca. 99.95% was indicated using differential scanning calorimetry [11].

**Benzoic acid**
Certified material (B.C.S. Thermochemical Standard No. 190j, 99.97%) was used directly, as recommended, without further treatment.

**Combustion calorimeter**
This was a commercial instrument (Gallenkamp Automatic Bomb Calorimeter, Model CB-110) modified as follows: the thermometer supplied was replaced by a digital quartz thermometer (Hewlett-Packard, Model 2801 A); the bomb supplied was replaced by a twin-valve bomb (Parr Instrument Company, Bomb No. 1101) of internal volume 360 cm³; the supplied stainless-steel calorimeter can was replaced by a unit fabricated in copper (0.1 cm thick) to improve thermal response and a double stirrer was used within the calorimeter can.

**TABLE 1**
Combustion calorimetry results for ammonium picrate

<table>
<thead>
<tr>
<th>Ref. No.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>m(sample)(g) *</td>
<td>2.738639</td>
<td>1.104000</td>
<td>2.45520</td>
<td>2.451683</td>
<td>2.597862</td>
</tr>
<tr>
<td>m(fuse)(g)</td>
<td>0.00447</td>
<td>0.00430</td>
<td>0.00381</td>
<td>0.00326</td>
<td>0.00427</td>
</tr>
<tr>
<td>m(Pt wire)(g)</td>
<td>0.00622</td>
<td>0.00555</td>
<td>0.00642</td>
<td>0.00575</td>
<td>0.00512</td>
</tr>
<tr>
<td>m(silica crucible)(g)</td>
<td>4.651442</td>
<td>4.638626</td>
<td>4.638466</td>
<td>4.638726</td>
<td>4.638616</td>
</tr>
<tr>
<td>m(soot)(g)</td>
<td>0.00000</td>
<td>0.00020</td>
<td>0.00022</td>
<td>0.00021</td>
<td>0.00003</td>
</tr>
<tr>
<td>m(H₂O)(g)</td>
<td>10.80000</td>
<td>10.80000</td>
<td>10.80000</td>
<td>10.80000</td>
<td>10.80000</td>
</tr>
<tr>
<td>q₁(kJ)</td>
<td>0.080010</td>
<td>0.077037</td>
<td>0.068470</td>
<td>0.058847</td>
<td>0.076512</td>
</tr>
<tr>
<td>q₂(kJ)</td>
<td>0.099016</td>
<td>0.073754</td>
<td>0.097821</td>
<td>0.073336</td>
<td>0.101404</td>
</tr>
<tr>
<td>q₃(kJ)</td>
<td>0.00000</td>
<td>0.00060</td>
<td>0.00759</td>
<td>0.00698</td>
<td>0.00099</td>
</tr>
<tr>
<td>q₄(kJ)</td>
<td>0.066904</td>
<td>0.025039</td>
<td>0.059280</td>
<td>0.059511</td>
<td>0.063061</td>
</tr>
<tr>
<td>Δθ(K)</td>
<td>3.6677</td>
<td>1.4854</td>
<td>3.2919</td>
<td>3.2795</td>
<td>3.4839</td>
</tr>
<tr>
<td>ε₁(KJ K⁻¹)</td>
<td>8.6804</td>
<td>8.6782</td>
<td>8.6801</td>
<td>8.6801</td>
<td>8.6802</td>
</tr>
<tr>
<td>ε₂(KJ K⁻¹)</td>
<td>0.061849</td>
<td>0.059627</td>
<td>0.061464</td>
<td>0.061460</td>
<td>0.061658</td>
</tr>
<tr>
<td>-Δu₂⁽298.15 K⁾ (kJ g⁻¹)</td>
<td>11.5354</td>
<td>11.5230</td>
<td>11.5493</td>
<td>11.5356</td>
<td>11.5484</td>
</tr>
</tbody>
</table>

Mean = -11.5504 ± 0.0115 kJ g⁻¹.
* Density of ammonium picrate was taken as 1.72 g cm⁻³ for buoyancy correction purposes.
The system was calibrated using benzoic acid, and the performance checked using acetanilide as a test material: detailed results are given below. All samples were pelleted, contained in a silica crucible, and fired by a weighed cotton fuse (ca. 3—4 mg) ignited electrically by a weighed platinum wire (ca. 6 mg, diameter 0.0089 cm, electrical energy input 0.0018 kJ). Weighings were buoyancy corrected, and accurate to ±0.5 × 10⁻⁵ g.

Using the notation of Coops et al. [14] values for the internal energy change on combustion were calculated from

\[-\Delta u^\circ_c = \left[ (\varepsilon_{sf} + \varepsilon_{cf}) \Delta \theta - q_i - q_n - q_w + q_e \right]/m_s\]

where \(\varepsilon_{sf}\) is the energy equivalent of the standard final system, i.e. the bomb less the oxygen and water charges, the combustion products, the platinum firing wire and the crucible. The energy equivalent of these components is contained in the \(\varepsilon_{cf}\) term. The correction for nitric acid formed during combustion, \(q_n\), was calculated using \(\Delta u^\circ_c(HNO_3, 500 H_2O) = -59.72\) kJ mole⁻¹ [12] and for the combustion of the unburnt soot residue, 33 kJ g⁻¹ was used. The abbreviated procedure of Prosen [13] was used to evaluate the Washburn correction, \(q_w\). The fore and after periods are not exactly parallel (as would be the case in a perfect adiabatic system) and the corrected temperature rise, \(\Delta \theta\), was calculated by back-extrapolation to a point corresponding to 0.63 of the observed temperature change.

The mean of 11 calibration experiments using benzoic acid gave the energy equivalent of the uncharged calorimeter as \(\varepsilon_{sf} = 8.6186 ± 0.0026\) kJ K⁻¹, and the mean of six experiments using acetanilide as a test substance gave a value of \(\Delta u^\circ_c = -31.218 ± 0.011\) kJ g⁻¹, in satisfactory agreement with the recommended value, viz. \(-31.2300 ± 0.0069\) kJ g⁻¹ [15]. Uncertainty intervals are quoted as 95% confidence limits throughout.

<table>
<thead>
<tr>
<th></th>
<th>G</th>
<th>H</th>
<th>I</th>
<th>J</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>2.514827</td>
<td>2.239838</td>
<td>2.491305</td>
<td>2.330267</td>
<td>2.019368</td>
</tr>
<tr>
<td></td>
<td>0.00433</td>
<td>0.00382</td>
<td>0.00357</td>
<td>0.00380</td>
<td>0.00432</td>
</tr>
<tr>
<td></td>
<td>0.00632</td>
<td>0.00642</td>
<td>0.00604</td>
<td>0.00683</td>
<td>0.00625</td>
</tr>
<tr>
<td></td>
<td>0.00018</td>
<td>0.00020</td>
<td>0.00021</td>
<td>0.00012</td>
<td>0.00016</td>
</tr>
<tr>
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<td>10.80000</td>
<td>10.80000</td>
<td>10.80000</td>
<td>10.80000</td>
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<tr>
<td></td>
<td>0.077737</td>
<td>0.08642</td>
<td>0.064269</td>
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<tr>
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<td>0.091312</td>
</tr>
<tr>
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<tr>
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<td>3.1311</td>
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</tr>
<tr>
<td></td>
<td>8.6802</td>
<td>8.6797</td>
<td>8.6801</td>
<td>8.6800</td>
<td>8.6795</td>
</tr>
<tr>
<td></td>
<td>0.061546</td>
<td>0.061172</td>
<td>0.061514</td>
<td>0.061391</td>
<td>0.060872</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSION

The energy of combustion at 298.15 K of ammonium picrate was found to be $-11.5504 \pm 0.0115$ kJ mol$^{-1}$. Using the equation

$$C_6H_6N_4O_7(c) + 4 O_2(g) = 6 CO_2(g) + 2 N_2(g) + 3 H_2O(l)$$

the standard enthalpy of combustion is hence $-2833.11 \pm 2.83$ kJ mol$^{-1}$ and the standard enthalpy of formation, $\Delta H_f^\circ [2,4,6-(NO_2)_3C_6H_2ONH_4, c]$ at 298.15 K is $-385.44 \pm 2.94$ kJ mol$^{-1}$. Detailed experimental results are collated in Table 1.

Ammonium picrate may be prepared in either of two coloured modifications, red or yellow, at ambient temperatures. However, the red form is metastable with respect to the yellow, and is not expected to result from the procedure adopted here.

Table 2 lists reported values of $\Delta H_f^\circ [C_6H_2(NO_2)_3ONH_4, c]$ with values ranging from ca. $-350$ kJ mol$^{-1}$ to $-399$ kJ mol$^{-1}$. The value reported by Urbanski and Soroka in 1938 [9], besides being much lower than any other, is coupled with a difference of ca. 42 kJ mol$^{-1}$ between the standard enthalpies of formation of the red and yellow forms. This may be compared with a difference of only ca. 5 kJ mol$^{-1}$ reported by Médard and Thomas [6]. This latter difference seems very much more likely, and is consistent with exploratory differential scanning calorimetric (DSC) measurements made in this laboratory although it is not possible to quantify the DSC results.

Recalculation of the results obtained by Médard and Thomas, using more recent values of $\Delta H_f^\circ [CO_2, g]$ and $\Delta H_f^\circ [H_2O, g]$ leads to a value which agrees very satisfactorily within experimental error to that reported here. The considerable difference between these values, and that of Vorob'ev et al. [2], viz. ca. 16 kJ mol$^{-1}$ is difficult to explain. Vorob'ev's procedure is based on solution calorimetry involving enthalpies of neutralisation of picric acid by ammonium, lithium, sodium and potassium hydroxides. Calculation of a value of $\Delta H_f^\circ [C_6H_2(NO_2)_3ONH_4, c]$ from these measurements

<table>
<thead>
<tr>
<th>$-\Delta H_f^\circ$ (kJ mol$^{-1}$)</th>
<th>Method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>396.64 ± 2.7</td>
<td>Combustion (y)</td>
<td>6</td>
</tr>
<tr>
<td>399.15 ± 2.5</td>
<td>Combustion (r)</td>
<td>7</td>
</tr>
<tr>
<td>384.1 ± 2.7</td>
<td>y *</td>
<td></td>
</tr>
<tr>
<td>350.2</td>
<td>Combustion (y)</td>
<td>9</td>
</tr>
<tr>
<td>392.04</td>
<td>Combustion (r)</td>
<td>9</td>
</tr>
<tr>
<td>369.95</td>
<td>Solution (y)</td>
<td>2</td>
</tr>
<tr>
<td>385.44 ± 2.94</td>
<td>Combustion (y)</td>
<td>This work</td>
</tr>
</tbody>
</table>

r = Red form; y = yellow form.
* Recalculated from ref. 6.
depends upon a value for the standard enthalpy of formation of picric acid, derived from combustion experiments. The agreement between the independent, collated combustion values of Médard and Thomas, and Clift and Féderoff [8], with those reported here suggest that a re-examination of the value for the standard enthalpy of formation of picric acid may be appropriate.

ACKNOWLEDGEMENTS

Financial support from the Procurement Executive, Ministry of Defence (A.E.S.) and helpful discussions with Mr. K. Holloway, Dr. P. Collins and Dr. R. McGuchan, are gratefully acknowledged.

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THERMOCHEMISTRY OF PICRATES. II. THE STANDARD ENTHALPY OF FORMATION OF PICRIC ACID

ARTHUR FINCH and ANN E. SMITH
The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey (Gre. Britain)
(Received 29 July 1981)

ABSTRACT

Using a static, oxygen-bomb calorimeter, the standard enthalpy of combustion at 298.15 K of picric acid has been determined as \(-2571.92 \pm 1.74\) kJ mole\(^{-1}\). This gives rise to a value for the standard enthalpy of formation of \(-217.88 \pm 1.99\) kJ mole\(^{-1}\). These results are compared with previous combustion values and also with values calculated from solution calorimetric studies.

INTRODUCTION

Although picric acid [2,4,6-trinitrophenol, \(C_6H_2(NO_2)_3OH\)] is an important commercial compound readily available in a state of purity, reported thermodynamic properties are surprisingly discrepant. In particular, the standard enthalpy of formation derived from combustion experiments apparently differs from values calculated from solution-reaction processes; literature combustion experiments themselves exhibit poor precision. In this paper we report a re-determination of enthalpies of combustion and formation.

EXPERIMENTAL

Materials and synthesis

Picric acid
Picric acid (B.D.H., AnalAR grade) was recrystallised four times from ethanol and dried in air at ca. 105–110°C for several hours. The melting point was 121.5–122°C; literature values range from 120 to 122°C.

Acetanilide
A commercial sample (B.D.H., OAS grade) was used as supplied after drying overnight at 110°C.

Benzoic acid
Certified material (B.C.S. Thermochemical Standard No. 190j, 99.97%) was used without further treatment.
Combustion calorimeter

A commercial instrument (Gallenkamp Automatic Bomb Calorimeter Model CB-110) was used with modifications given in detail in a previous paper [6]. The system was calibrated using benzoic acid and the performance checked using acetanilide as a test substance. Experimental details and the calculation procedure are as given before [6].

\( \epsilon_{sf} \) value and acetanilide

The mean of 11 calibration experiments using benzoic acid gave the energy equivalent of the uncharged calorimeter as \( 8.6186 \pm 0.0026 \text{kJ K}^{-1} \) and the mean of seven experiments using acetanilide as a test substance gave a value of \( \Delta u^\circ_f = -31.221 \pm 0.013 \text{kJ g}^{-1} \), in very good agreement with the recommended value, viz. \(-31.2300 \pm 0.0069 \text{kJ g}^{-1} \) [5].

RESULTS AND DISCUSSION

The energy of combustion of picric acid at 298.15 K was found to be \(-11.2717 \pm 0.0076 \text{kJ g}^{-1} \). Using the equation

\[
C_6H_3N_3O_7(c) + 13/4 O_2(g) = 6 CO_2(g) + 3/2 H_2O(l) + 3/2 N_2(g)
\]

the standard enthalpy of formation, \( \Delta H_f^0 [C_6H_3(NO_2)_3OH, (c)] \) at 298 K = \(-217.88 \pm 1.91 \text{kJ mole}^{-1} \). Relevant details of the combustion experiments are listed in Table 1.

<p>| TABLE 1 |
| Combustion calorimetry results for picric acid |
|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Ref. no.</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>( m ) (sample) (g)*</td>
<td>2.465541</td>
<td>1.939664</td>
<td>1.962406</td>
<td>2.412313</td>
<td>2.472575</td>
<td>2.355853</td>
</tr>
<tr>
<td>( m ) (fuse) (g)</td>
<td>0.00511</td>
<td>0.00474</td>
<td>0.00499</td>
<td>0.00439</td>
<td>0.00388</td>
<td>0.00469</td>
</tr>
<tr>
<td>( m ) (Pt wire) (g)</td>
<td>0.00619</td>
<td>0.00563</td>
<td>0.00615</td>
<td>0.00620</td>
<td>0.00647</td>
<td>0.00594</td>
</tr>
<tr>
<td>( m ) (silica crucible) (g)</td>
<td>4.638936</td>
<td>4.449560</td>
<td>4.449830</td>
<td>4.449730</td>
<td>4.638856</td>
<td>4.449650</td>
</tr>
<tr>
<td>( m ) (soot) (g)</td>
<td>0.00000</td>
<td>0.00020</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>( m ) (H(_2)O) (g)</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
<td>10.8</td>
</tr>
<tr>
<td>( q_f ) (kJ)</td>
<td>0.091204</td>
<td>0.084732</td>
<td>0.089105</td>
<td>0.078611</td>
<td>0.069691</td>
<td>0.083858</td>
</tr>
<tr>
<td>( q_a ) (kJ)</td>
<td>0.081816</td>
<td>0.063900</td>
<td>0.059123</td>
<td>0.066289</td>
<td>0.067842</td>
<td>0.068081</td>
</tr>
<tr>
<td>( q_o ) (kJ)</td>
<td>0.00000</td>
<td>0.000660</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
<td>0.00000</td>
</tr>
<tr>
<td>( q_w ) (kJ)</td>
<td>0.065324</td>
<td>0.050484</td>
<td>0.051188</td>
<td>0.063985</td>
<td>0.065718</td>
<td>0.062323</td>
</tr>
<tr>
<td>( \Delta \theta ) (K)</td>
<td>3.2290</td>
<td>2.5421</td>
<td>2.5740</td>
<td>3.1541</td>
<td>3.2356</td>
<td>3.0829</td>
</tr>
<tr>
<td>( \epsilon_f ) (kJ K(^{-1}))</td>
<td>8.6792</td>
<td>8.6786</td>
<td>8.6786</td>
<td>8.6790</td>
<td>8.6793</td>
<td>8.6790</td>
</tr>
<tr>
<td>( \epsilon_{cf} ) (kJ K(^{-1}))</td>
<td>0.060636</td>
<td>0.059956</td>
<td>0.059980</td>
<td>0.060438</td>
<td>0.060643</td>
<td>0.060380</td>
</tr>
<tr>
<td>( -\Delta u^\circ_f ) (298.15 K) (kJ g(^{-1}))</td>
<td>11.2701</td>
<td>11.2748</td>
<td>11.2817</td>
<td>11.2613</td>
<td>11.2754</td>
<td>11.2665</td>
</tr>
</tbody>
</table>

Mean = \(-11.2717 \pm 0.0076 \text{kJ g}^{-1} \).

* Density of picric acid taken as 1.76 g cm\(^{-3}\) for buoyancy correction purposes.
Table 2 summarises values of $\Delta H^0_\text{f}[^{\text{C}_6\text{H}_2(\text{NO}_2)_3}\text{OH}, (c)]$, ranging from ca. $-211$ to ca. $-222$ kJ mole$^{-1}$. The value reported in this work, ca. $-218.0$ kJ mole$^{-1}$, is coincidentally very close to the mean of all four values and the early value of ca. $-211$ kJ mole$^{-1}$ is clearly too low. Since the bomb system used was satisfactorily checked using acetanilide, we have additional confidence in the value of $-217.9 \pm 2$ kJ mole$^{-1}$.

However, this is apparently inconsistent with a value derived from solution-reaction experiments. A very recent [6] combustion study of ammonium picrate essentially confirms an earlier study. Combination of a value of the standard enthalpy of formation, calculated from these results, with precision enthalpy of solution and enthalpies of neutralisation measurements appear to suggest a value of $\Delta H^0_\text{f}[^{\text{C}_6\text{H}_2(\text{NO}_2)_3}\text{OH}, (c)] = -229$ kJ mole$^{-1}$. This is not only well outside the experimental error of this study, but is anomalously high compared with results from all reported combustion studies. However, the constitution of picric acid in aqueous solution is known to be concentration-dependent and further solution-calorimetric studies will be reported later.

**Acknowledgements**

Financial support from the Procurement Executive, Ministry of Defence (A.E.S.) and helpful discussions with Mr. K. Holloway, Dr. P. Collins and Dr. R. McGuchan, are gratefully acknowledged.

**References**

THERMOCHEMISTRY OF PICRATES. III. ENTHALPIES OF SOLUTION AND SOLUBILITIES OF PICRATE SALTS

ARTHUR FINCH and ANN E. SMITH
The Bourne Laboratory, Royal Holloway College, University of London, Egham, Surrey (Gt. Britain)
(Received 17 September 1981)

ABSTRACT

Using isoperibol solution-reaction calorimeters, the aqueous enthalpies of solution at 298.15 K of ammonium, caesium, potassium, silver, rubidium, tetramethylammonium and tetraethylammonium picrates have been determined as 45.81±0.35, 56.03±0.55, 51.14±0.55, 36.69±0.35, 55.01±0.36, 31.84±0.31 and 32.02±0.18 kJ mole⁻¹, respectively. Aqueous solubility data, as a function of temperature, have been measured for potassium, silver, ammonium, rubidium and caesium picrates by a precipitation method.

INTRODUCTION

Values of enthalpies of solution, ΔH°ₘ, of picrate salts are important: the standard enthalpy of formation of the aqueous picrate ion, ΔH°ₘ(C₆H₅(NO₂)₃O⁻ (aq)), for example, is a key datum in the estimation of lattice energies, U°ₚ and standard enthalpies of formation of ionic picrates. Reliable data both for ΔH°ₘ and for solubilities are sparse; determinations for several 1:1 picrates were hence made as part of a systematic investigation of thermochemical properties of nitroaromatic compounds.

EXPERIMENTAL

Materials and synthesis

C₆H₅(NO₂)₃OK
Stammler's [1] method was used, viz. neutralisation of a hot, 30% ethanol: water solution of picric acid by aqueous KOH.

C₆H₅(NO₂)₃OAg
This was prepared by the established method of addition of silver oxide to an ethanol/water solution of picric acid.
The more thermodynamically stable (yellow) modification was prepared as described recently from ammonium carbonate and picric acid.

This was prepared by adding a small excess of tetramethylammonium bromide solution to silver picrate solution, filtering off the precipitated silver bromide. This was found to be preferable to the neutralisation method. Tetraethylammonium, caesium and rubidium picrates were similarly prepared from silver picrate and the appropriate bromides.

All picrates were recrystallised thrice from water, dried appropriately, and stored in desiccators until used.

**CALORIMETRY**

Either of two isoperibol calorimeters were used. For NH$_4$Pic, Me$_4$NPic and Et$_4$NPic a commercial system (LKB, Model 8700) was operated; for AgPic, KPic, CsPic and RbPic a calorimeter constructed in the department and described elsewhere was employed. The performance of each calorimeter was checked periodically, using the enthalpy of dissolution, $\Delta H_{\text{diss}}^\circ$, of 2-amino-2-hydroxy-propane-1,3 diol (THAM) in NaOH as a test reaction. Typical results were

- LKB calorimeter, 16.67 ± 0.05 kJ mol$^{-1}$ (0.10 M NaOH) (Lit. [2]: 16.698 ± 0.005 kJ mol$^{-1}$);
- RHC calorimeter 17.18 ± 0.04 kJ mol$^{-1}$ (0.05 M NaOH) (Lit. [2]: 17.189 ± 0.005 kJ mol$^{-1}$)

**SOLUBILITY MEASUREMENTS**

A dynamic precipitation method was used. A picrate salt was weighed into a boiling tube and 10.00 cm$^3$ of distilled water added. The mixture was warmed to effect solution and then placed inside a transparent enclosure to exclude draughts. The solution was allowed to cool with constant stirring. A calibrated (N.P.L.) thermometer graduated to 0.05°C was used to note the temperature at which crystals first appeared. The solution was re-heated to restore homogeneity, and the process repeated to obtain concordant results (±0.1°C). From a burette, a measured aliquot of water was then added, and the procedure repeated to obtain a further result. This process of successive dilution, warming and cooling was continued as far as was practical.

A clear danger in this method is that of supercooling, which is irreproducible but common. Hence attention was directed to noting maximum temperature readings at crystallisation points, and to repetition to concordance. The smoothness of solubility, $S$, vs. temperature, $T$, plots and the linearity of ln $S$ vs. $1/T$ plots were taken as further evidence of reliability.
RESULTS AND DISCUSSION

The calorimetric enthalpies of solution of these compounds in water are shown in Tables 1 and 2. Table 3 collates these results with those of other authors [3,8], and with values obtained using solubility data, fitted to general equations of the form $\ln S = A - 10^3 \frac{B}{T}$; “van’t Hoff” enthalpies of solution are calculated using these plots. Table 4 lists values of the constants $A$ and $B$ for each picrate, as well as correlation coefficients.

There is good agreement between the independent calorimetric determinations for sodium, potassium, ammonium and tetramethylammonium picrates, but concordance between the calorimetric and van’t Hoff enthalpies of solution is poor. This indicates the need for care in the interpretation of $\ln S$ vs. $1/T$ data uncorrected for activity and heat capacity effects.

Results of measurements of the aqueous solubility of potassium picrate are listed in Table 5. Values obtained in this work are somewhat higher than the others; this may be due to a systematic error. However, the order of solubilities of these compounds and their variation with temperature, which is difficult to determine by other methods, is presumably sound (see Fig. 1).

Johnson [7] has formulated rules for predicting the solubilities of some series of salts. Briefly, he states that for compounds of the same anion and formula type, as the radius of the cation is increased, the standard free energy of solution rises (i.e. the solubility decreases), reaches a maximum and then falls steadily towards a limiting value. For some salts, however, the series of experimentally observed free

![Fig. 1. Aqueous solubilities of picrates.](image-url)
### TABLE 1
Enthalpies of solution of ammonium, rubidium, tetramethylammonium and tetaethylammonium picrate in water at 298.15 K

<table>
<thead>
<tr>
<th>Mass NH₄Pic (g)</th>
<th>n*</th>
<th>ΔH°ₚ (kJ mole⁻¹)</th>
<th>Mass RbPic (g)</th>
<th>n*</th>
<th>ΔH°ₚ (kJ mole⁻¹)</th>
<th>Mass Me₄NPic (g)</th>
<th>n*</th>
<th>ΔH°ₚ (kJ mole⁻¹)</th>
<th>Mass Et₄NPic (g)</th>
<th>n*</th>
<th>ΔH°ₚ (kJ mole⁻¹)</th>
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<tbody>
<tr>
<td>0.33957</td>
<td>4027</td>
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<td>0.4751</td>
<td>7333</td>
<td>54.22</td>
<td>0.38062</td>
<td>4411</td>
<td>31.54</td>
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<tr>
<td>0.31901</td>
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<td>0.32448</td>
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<td>11660</td>
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<td>0.3054</td>
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<td>0.3857</td>
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<td>0.20487</td>
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</tbody>
</table>

Mean ΔH°ₚ = 45.81 ± 0.35 kJ mole⁻¹  
Mean ΔH°ₚ = 55.01 ± 0.36 kJ mole⁻¹  
Mean ΔH°ₚ = 31.84 ± 0.32 kJ mole⁻¹  
Mean ΔH°ₚ = 32.02 ± 0.19 kJ mole⁻¹
<table>
<thead>
<tr>
<th>Mass ( \text{AgPic} ) (g)</th>
<th>( n^* )</th>
<th>( \Delta H_{c}^\circ ) (kJ mole(^{-1}))</th>
<th>Mass ( \text{KPic} ) (g)</th>
<th>( n^* )</th>
<th>( \Delta H_{c}^\circ ) (kJ mole(^{-1}))</th>
<th>Mass ( \text{CsPic} ) (g)</th>
<th>( n^* )</th>
<th>( \Delta H_{c}^\circ ) (kJ mole(^{-1}))</th>
</tr>
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<tbody>
<tr>
<td>0.8569</td>
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<td>0.5142</td>
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<td>5898</td>
<td>50.50</td>
<td>0.4390</td>
<td>9137</td>
<td>56.27</td>
</tr>
<tr>
<td>0.6201</td>
<td>6019</td>
<td>36.50</td>
<td>0.4459</td>
<td>6657</td>
<td>50.64</td>
<td>0.4382</td>
<td>9154</td>
<td>56.72</td>
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<td>0.5775</td>
<td>6464</td>
<td>37.60</td>
<td>0.4161</td>
<td>7136</td>
<td>51.26</td>
<td>0.4332</td>
<td>9259</td>
<td>57.29</td>
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<tr>
<td>0.4682</td>
<td>7973</td>
<td>36.70</td>
<td>0.4118</td>
<td>7210</td>
<td>52.26</td>
<td>0.3959</td>
<td>10132</td>
<td>55.73</td>
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<tr>
<td>0.4147</td>
<td>9001</td>
<td>36.47</td>
<td>0.3614</td>
<td>8212</td>
<td>50.46</td>
<td>0.3627</td>
<td>11050</td>
<td>55.76</td>
</tr>
</tbody>
</table>

\[ \text{Mean } \Delta H_{c}^\circ = 36.69 \pm 0.35 \text{ kJ mole}^{-1} \]

\[ \text{Mean } \Delta H_{c}^\circ = 51.14 \pm 0.55 \text{ kJ mole}^{-1} \]

\[ \text{Mean } \Delta H_{c}^\circ = 56.03 \pm 0.56 \text{ kJ mole}^{-1} \]
### TABLE 3
Enthalpies of solution in water of picrates (M Pic)

<table>
<thead>
<tr>
<th>M</th>
<th>$\Delta H^\circ_1$ (kJ mole$^{-1}$)$^a$</th>
<th>$\Delta H^\circ_2$ (kJ mole$^{-1}$)$^a$</th>
<th>$\Delta H^\circ_3$ (kJ mole$^{-1}$)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>6.40 ± 0.04$^1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>20.25 ± 0.17$^2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>51.14 ± 0.55</td>
<td>50.92 ± 0.21$^3$</td>
<td>62.65 ± 1.42</td>
</tr>
<tr>
<td>Rb</td>
<td>55.01 ± 0.36</td>
<td></td>
<td>73.74 ± 1.18</td>
</tr>
<tr>
<td>Cs</td>
<td>56.03 ± 0.55</td>
<td></td>
<td>72.40 ± 1.86</td>
</tr>
<tr>
<td>Ag</td>
<td>36.69 ± 0.35</td>
<td></td>
<td>54.32 ± 0.85</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>45.81 ± 0.35</td>
<td>45.46 ± 0.30$^3$</td>
<td>71.88 ± 1.27</td>
</tr>
<tr>
<td>NMe$_4$</td>
<td>31.84 ± 0.31</td>
<td>31.97$^8$</td>
<td>42.75 ± 0.76</td>
</tr>
<tr>
<td>NEt$_4$</td>
<td>32.02 ± 0.18</td>
<td></td>
<td>52.66 ± 1.53</td>
</tr>
</tbody>
</table>

$^a$ Calorimetric method.

$^b$ Solubility method.

### TABLE 4
Aqueous solubility data for picrates (M Pic)

<table>
<thead>
<tr>
<th>M</th>
<th>K</th>
<th>Rb</th>
<th>Cs</th>
<th>Ag</th>
<th>NH$_4$</th>
<th>NMe$_4$</th>
<th>NEt$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r^2$</td>
<td>$^b$</td>
<td>0.996</td>
<td>0.998</td>
<td>0.995</td>
<td>0.995</td>
<td>0.997</td>
<td>0.998</td>
</tr>
</tbody>
</table>

$^a$ See text.

$^b$ Correlation coefficient.

### TABLE 5
Solubility of potassium picrate

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$10^3 S$ (mole dm$^{-3}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>18.9</td>
<td>9</td>
</tr>
<tr>
<td>25</td>
<td>24.1</td>
<td>10, 11</td>
</tr>
<tr>
<td>25</td>
<td>23.1</td>
<td>12</td>
</tr>
<tr>
<td>25</td>
<td>24.2</td>
<td>13</td>
</tr>
<tr>
<td>25</td>
<td>23.3</td>
<td>14</td>
</tr>
<tr>
<td>30</td>
<td>26.7</td>
<td>This work</td>
</tr>
<tr>
<td>30</td>
<td>28.2</td>
<td>15</td>
</tr>
<tr>
<td>30</td>
<td>33.2</td>
<td>This work</td>
</tr>
</tbody>
</table>

This work
energies may only cover the increasing or decreasing portion of the curve. One consequence is that, if the size of the cation in a salt of a particular anion and formula type is increased, a fall in the free energy of solution should never be succeeded by a rise.

Johnson's rules seem to hold for the solubilities of the alkali metal picrates. The maximum in the free energy of solution is probably observed at a cationic radius less than that of potassium, and the solubility of the picrates decreases from potassium to rubidium to caesium. This suggests that tetramethylammonium and tetraethylammonium picrates would be less soluble than caesium picrate. It is hence surprising to find that the solubilities of NMe\textsubscript{4}Pic and NEt\textsubscript{4}Pic are, respectively, greater than and comparable with that of potassium picrate. Tetrabutylammonium picrate is insoluble in water, so the aqueous solubility of these tetraalkylammonium picrates seems to decrease with increasing size of the alkyl group. Johnson's rules have been successfully applied to predicting the solubilities of some tetraalkylammonium salts e.g. iodides and perchlorates, but fail for some simple salts, e.g. alkali metal bromides and nitrates. They are not applicable to salts of cations such as silver, where there is considerable deviation from ionic character.

Calorimetric enthalpies of solution for lithium and sodium picrates were reported in 1934 [4] as 32.05 and 34.89 kJ mole\textsuperscript{-1}, respectively, but Vorob'ev et al. [3] account for the discrepancy with their work by explaining that these values are consistent with those obtained by using the hydrated salts. Lithium and sodium picrates, unlike the others mentioned here, which are anhydrous, crystallise from water as the monohydrate.

From our results, and some unpublished standard enthalpies of formation for these salts, an approximate value for the standard enthalpy of formation of the aqueous picrate ion, $\Delta H^\circ_{f} \text{Pic}^- (aq)$, is calculated as $-206$ kJ mole\textsuperscript{-1}.

The constitutions of picric acid and potassium picrate solutions have been investigated by Moseley and Spiro [5], who suggested that, due to the anomalous concentration dependence of conductance in picric acid solutions [6], the possibility of the formation of hydrogen-bonded triple ions of type HPic\textsubscript{2} or picrate-ion dimers Pic\textsubscript{2} cannot be overlooked. Later experiments involving 0.02 M potassium picrate solution confirmed that dimerisation occurred. At a concentration of ca. $3 \times 10^{-3}$ M, it has been calculated that a concentration of ca. $3.4 \times 10^{-5}$ M of picrate-ion dimers, Pic\textsubscript{2}\textsuperscript{-}, should exist in aqueous potassium picrate at 25°C. In the solution calorimetry results reported here, the concentration of potassium picrate in the final solution varied between $4.4 \times 10^{-3}$ M and $9.8 \times 10^{-3}$ M.

ACKNOWLEDGMENTS

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