141

THERMOCHEMICAL INVESTIGATIONS OF NITRORESORCINOLS AND RELEVANT METAL SALTS

A thesis submitted by JOHN ROLAND PAYNE
in candidature for the degree of Doctor of
Philosophy of the University of London.

The Bourne Laboratory,
(Department of Chemistry),
Royal Holloway College,
University of London,
Egham Hill,
Egham,
Surrey TW20 0EX

February 1986.

THERMOCHEMICAL INVESTIGATIONS OF NITRORESORCINOLS AND RELEVANT METAL SALTS.

ABSTRACT

The standard enthalpies of formation of 2,4-dihydroxy-1,3,5-trinitrobenzene (styphnic acid), 2,4-dihydroxy-3,5-dinitrobenzene (4,6-DNR), 2,4-dihydroxy-1,5-dinitrobenzene (2,4-DNR), 2,6-dinitrotoluene (two crystal forms) have been determined by oxygen static bomb calorimetry.

An isoperibol solution reaction calorimeter has been constructed. By the determination of various enthalpies of reaction and solution, the enthalpies of formation of various synthesised polymorphs of lead styphnate, lead 2,4-dinitroresorcinol, and lead 4,6-dinitroresorcinol, thallous styphnate and barium styphnate were found. From these data, enthalpies of decomposition were calculated. By use of a group additivity scheme for solids, the enthalpies of formation for a further five lead polynitroresorcinols was determined.

The integral enthalpy of solution for lead nitrate was determined. A differential enthalpy of solution for lead nitrate was determined and an activity correction applied.

The enthalpy of transition between the two crystal forms of 2,6-dinitrotoluene was determined and heat capacities of the respective forms in the solid and liquid phase measured. Powder X-ray crystallographic study of the two forms was made.

TABLE OF CONTENTS

Chapter I-Introduction

Chapter II- Purification of Raw Materials, and Preparations

Chapter III- Combustion Calorimetry

Chapter IV- Solution Calorimetry

Chapter V - Solubility and Enthalpy of Solution by the Dynamic Precipitation Method

Chapter VI- Differential Scanning Calorimetry

Chapter VII- X-Ray Crystallography

Chapter VIII- Further Work

Appendix I- Computer Programs

Appendix II- Buoyancy Correction

Appendix III- Lead Analysis

Appendix IV- Density measurements

Appendix V- Statistical Analysis

LIST OF TABLES

LIST OF FIGURES

ACKNOWLEDGEMENTS

I wish to express thanks to Professor A. Finch my supervisor, and Dr. P.J. Gardner for his useful advice. I would also like to say thank you to any member of staff at Royal Holloway College who have helped my studies, especially Dr. A.M. Moore, J.P.B. Sandall and Mr R. Lane.

I would also like to thank the Procurement Executive, Ministry of Defence, for financing this work and special thanks are due to Mr L. Bates, and Drs. P. Collins and M.J. Healey of PERME(RARDE), Waltham Abbey for helpful discussions and the supply of raw materials.

I am also grateful to Miss J. Diggens for her very prompt and skilful typing of this thesis.

DEDICATION

To my parents.

Chapter I

INTRODUCTION

INTRODUCTION

I-AI: Historical background of Explosives

Many compounds exhibit explosive properties, even though they are not used for mining or military purposes. They include, e.g., organic peroxide catalysts and gas-liberating agents used in the polymer industry.

Explosives are solid or liquid substances, alone or mixed with one another, which are in a metastable state and are capable, for this reason, of undergoing a rapid chemical reaction without the participation of external reactants such as atmospheric oxygen[1]. The first compound to be fully recognised as an explosive was black powder,(potassium nitrate, sulphur and charcoal) and was used by Chinese alchemists to amuse their Emperor. This was in the early eleventh century, and it was not until the mid thirteenth century that black-powder (later known as gunpowder) reached the west. The Arabs invented the gun in 1300, and in 1346 the first recorded use of gunpowder for military purposes was in the battle of Crècy. Table I-1 lists a brief history of the development of explosives and some explosive devices. Several definitions of what constitutes an explosive have been made. Berthelot in 1883 stated that an explosive is "the sudden expansion of gases into a volume much greater than the initial one, accompanied by noise and violent mechanical effects". Sarrau in 1885 gave a more concise definition of an explosive as "any body capable of being transformed into gas at a high temperature". The legal definition in the United Kingdom is given in the Explosives Act of 1875, as any substance used or manufactured with a view to produce a practical effect by explosion[23]. It is interesting to note that explosions are generally regarded by the research chemist as highly undesirable intrusions into the course of preparative chemistry, for example nitroglycerine, discovered

by Sobrero in 1846. Sobrero's interest waned through his experience of its explosive properties. The birth of the modern explosives industry has been attributed to Immanuel Nobel and his son Alfred. It was during the Crimean War that two Russian scientists, Sirion and Trapp, approached Immanuel Nobel in Stockholm and suggested the large scale manufacture of nitroglycerine for military purposes, and Nobel's first small plant at Heleneborg near Stockholm began operations in 1862. The rest of the Nobel story is now history, if not somewhat tragic. But it is from intense research at that time that three major inventions, which can be said to have formulated the pattern of the high explosives industry for the next hundred years or so, were first noted. These are,
(a) dynamite (Alfred Nobel patent, discovery in 1867); (b) detonators (Alfred Nobel invents blasting cap in 1865); and (c) gelatinous explosives (Alfred Nobel invents gelatinous dynamite in 1875).

I-AII: Explosive classifications

Three main classes of explosives are now recognised: primary (or initiating), secondary, and tertiary explosives. The latter two are also known as high explosives. The former covers compounds which in quite small quantity are capable of ready ignition by flame, spark or precussion, rapidly increasing their reaction velocity to full detonation, and can then generate detonation in an adjacent mass of high explosive. The method of initiating a high explosive is more complicated than this. For example, if a time lapse is required between initiation and final detonation of the tertiary explosive, then a dense secondary charge with a slow detonation propagation rate (deflagration) will be used. There is a problem here, in that the energy produced in the detonation chain in the secondary charge is often not sufficient to initiate the tertiary explosive. To solve this problem a substance known as a booster charge is sandwiched between the secondary and tertiary explosives. This booster charge will increase the

Table I-1

Condensed Early History of Explosives and Explosive Devices[69]

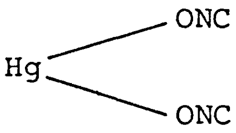
C 11th century:	Chinese use explosive black powder.
C 13th century:	Black powder reaches West.
1242:	Roger Bacon describes gun/black powder.
C1300:	Arabs invent guns.
1376:	Explosive shells used by Venetians.
1618-1648:	Rifles and cannon used regularly in English Civil War, etc.
1800:	Henry Shrapnel invents Shrapnel shell for British Army.
1831:	William Bickford invents safety fuse.
1845:	Guncotton discovered by Christian Schoenbein.
1846:	Ascanio Sobrero discovers nitroglycerine.
1854-1856:	Immanuel Nobel's mines used by Russians in Crimean War.
1855-1866:	Nitroglycerine used to blast Hoosac railway tunnel, Massachusetts.
1863:	Trinitrotoluene (TNT) discovered by J. Wilbrand.
1864:	Emil Nobel killed with three other workers by nitroglycerine explosion.
1865:	Alfred Nobel's first explosive factory outside Sweden, near Hambury, Germany.
1865:	Alfred Nobel invents blasting cap.
1866:	German nitroglycerine factory explodes.
1867:	Alfred Nobel patents discovery of dynamite.
1871:	Hermann Sprengel demonstrates that picric acid can be detonated.
1872:	Immanuel Nobel dies.
1875:	Alfred Nobel invents water resistant gelatinous dynamite.
1884:	Paul Vieille invents smokeless powder for riflemen and artillery.
1885:	Eugene Turpin shows that picric acid can be used in explosive shells.
1887:	Alfred Nobel invents cartridge propellant called ballistite.
1895:	Car von Linde invents liquid oxygen explosive (LOX).
1898:	Henning prepared cyclonite (RDX).

detonation velocity and, if correctly applied, initiate the tertiary explosive.

I-AIII: Primary explosives

It would be quite correct to say that the study of detonation reactions is a post-Second World War science, and has even acquired the title of 'detonics'. The traditional type-member of the class of primary explosives is mercury fulminate (mercuric isocyanate), since its first use by Nobel.

$C_2N_2O_2Hg$;



Mercury Fulminate

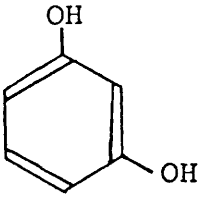
In 1630 the first initiator ever to be prepared was mercury fulminate[24,25,26]. It was not until the early nineteenth century that percussion compositions and the whole chemistry of igniting powders were considered seriously[27,28]. In comparison, the metal-salt of the polynitroresorcinols are relatively recent compounds, and by far the most important is lead styphnate.

I-AIV: Lead Styphnate

Lead styphnate (also known under the names of Bleitrizinat, Trizinat in Germany and Teneres in the U.S.S.R.) has found extensive commercial and military use as an initiator for explosive charges. Unfortunately the information relating to them is confined mostly to the patent literature, or is classified, and is concerned almost totally to commercial preparation methods, with very little effort being devoted to a better understanding of their chemical nature. Three polymorphs of lead styphnate are known, and three monobasic lead salts with some higher basic salts[9]. The first preparation of a lead styphnate has never been substantiated but it is thought that it could have been by Griess[29] in 1874. The first preparation of anhydrous normal lead styphnate was by Herz[30] in 1919. It has since been questioned whether the anhydrous salt may be prepared directly from aqueous solution as claimed[31]. Since then various preparations have been recorded, e.g. [32,33,34,35,36] but essentually the method is the addition of a solution containing lead acetate to a solution of sodium or magnesium styphnate to precipitate the lead styphnate. Lead styphnate is considered a relatively poor initiating agent, but because of its sensitivity to ignition, it is used to some extent as a cover charge for lead azide and as an ingredient of priming compositions[37]. This is also true of normal lead dinitroresorcinate[38], thallium styphnate[39], silver styphnate[40], and potassium copper styphnate•copper hypophosphite[41]. Lead styphnate is unaffected by sodium or ammonium hydroxide, but is decomposed by concentrated sulphuric or nitric acid. The metal salt used industrially is not always the most efficient, as its ease of preparation will influence its choice. The availability of polynitroresorcinols has certainly influenced the development of primary explosives currently used.

I-BI: Nitro Derivatives of Polyhydric Phenols

Several polyhydric phenols exist, and the nitro derivatives of resorcinol have found use in the explosives industry.

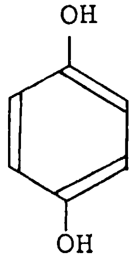


$C_6H_6O_2$

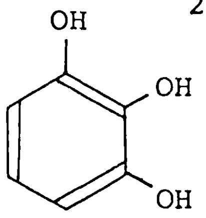
Resorcinol; 1,3-dihydroxybenzene

Resorcinol may be obtained by a potassium hydroxide fusion of many resins. It is industrially prepared by fusion of m-benzenedisulphonic acid with caustic soda.

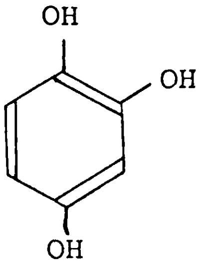
Other polyhydric phenols are Quinol (hydroquinone; p-dihydroxylbenzene); Pyrogallol (vic-trihydroxybenzene); Hydroxyquinol, and Phloroglucinol.



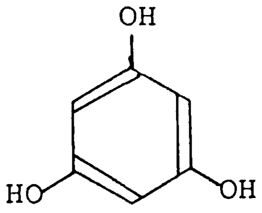
Quinol



Pyrogallol

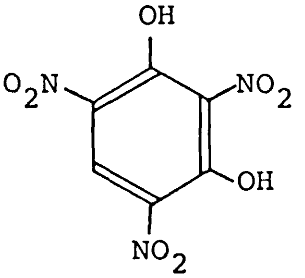


Hydroxyquinol



Phloroglucinol

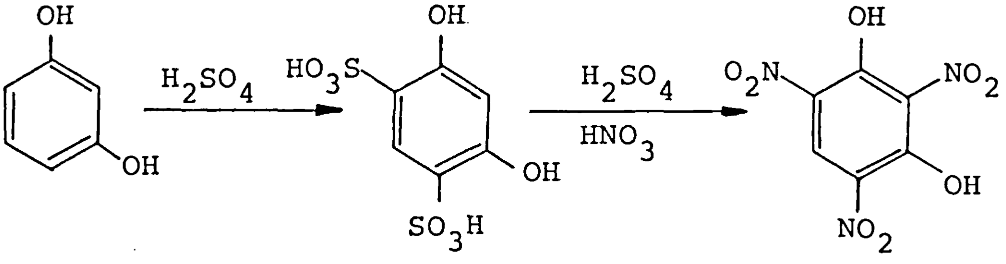
Resorcinols are very easy to nitrate, due to the presence of the hydroxyl groups in the ring. In fact the nitration process is so easy that preparation of resorcinols with less than three nitro groups requires the application of special methods.



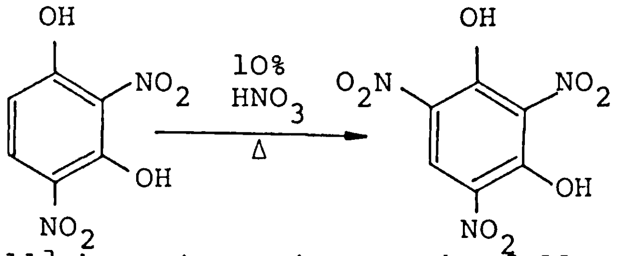
Styphnic Acid; $C_6H_3N_3O_8$

I-BII: Preparation of Styphnic Acid

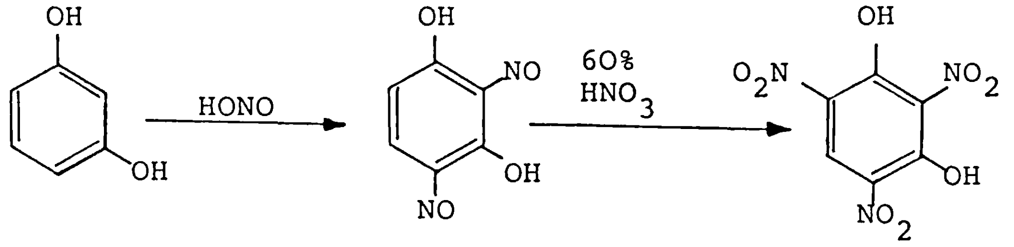
Trinitroresorcinol; (2,4,6-trinitro-1,3-dihydroxybenzene; styphnic acid; TNR), is usually prepared by a method which consists in the sulphonation of resorcinol to disulphonic acid, which is then nitrated. Thus a two-stage reaction takes place,[2].



Difficulty of stirring the pasty sulphonate mixture, and the tendency of foaming made this preparation unsuitable for large scale use. Further work was carried out on the synthesis [3,4,5,6,7,8], and in a subsequent investigation[9] it was found that styphnic acid could be formed by simply boiling 2,4-dinitroresorcinol (2,4-DNR) with dilute nitric acid[10], and thus overcoming the above problems in the sulphonation process.



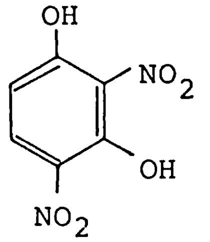
Further work[11] has given rise to the following reaction,



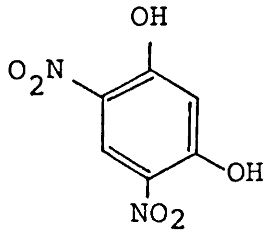
Which eliminates the process of isolating the DNR by a lengthy filtration. It is now possible to prepare styphnic acid in quantities up to 400kg. Styphnic acid will sublime at a constant temperature of 179-180^{o}C.

I-BIII: Preparation of Dinitroresorcinols

Another polyhydric phenol of important industrial use is dinitroresorcinol. Two isomers exist, 2,4- and 4,6-DNR.



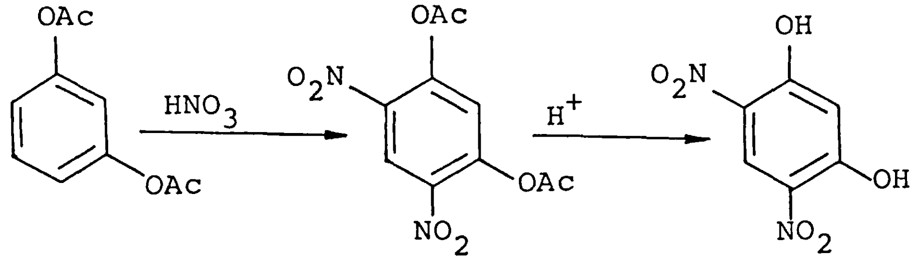
2,4-Dinitroresorcinol



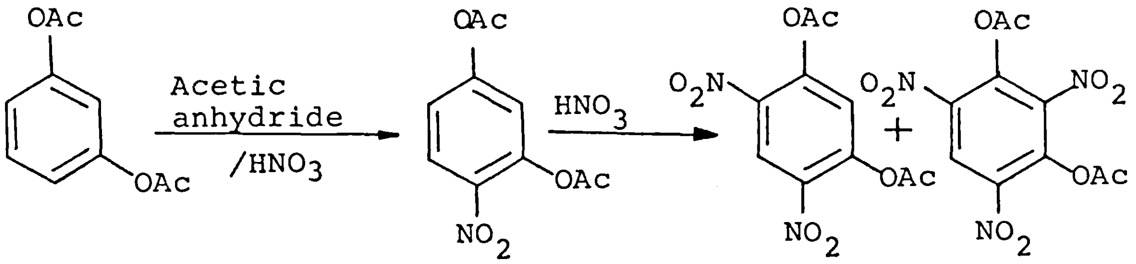
4,6-Dinitroresorcinol

The 4,6-DNR isomer has always been the lesser important of the two as it cannot be directly synthesised, though it may be prepared by the nitration of diacetylresorcinol.

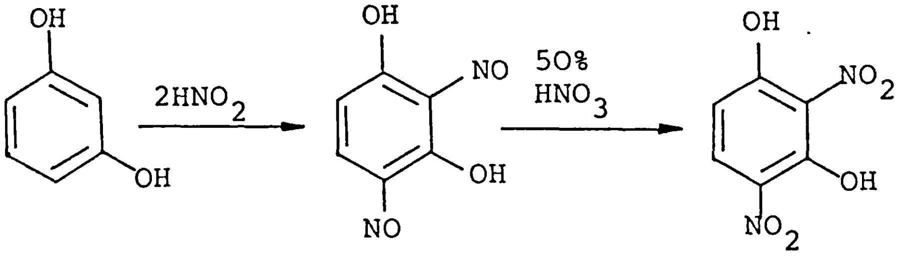
The first reported preparation of 4,6-DNR was in 1883 by Typke[12]. The method of synthesis consisted of treating diacetoxybenzene with cold nitric acid, followed by hydrolysis of the acetate group with hot hydrochloric acid[13,14,15,16]. Three other methods for the preparation of 4,6-DNR have been recorded,[10,17,18,19] but none was found to be suitable for large scale work. The most common method of preparation is the one mentioned above[12].



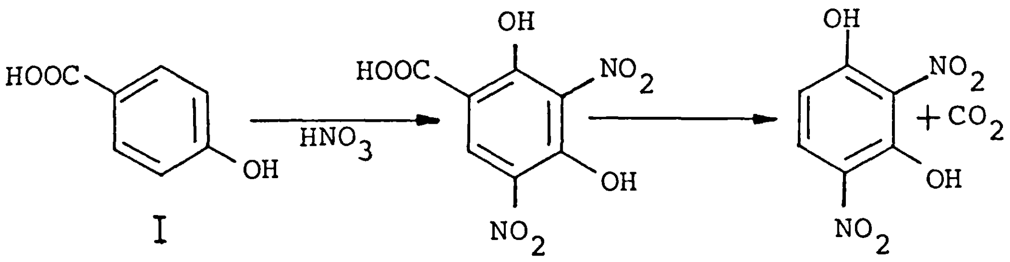
Attempts have been made to change the nitrating conditions, but with little success. Acetic anhydride/nitric acid is too mild, while sulphuric acid/nitric acid is too strong and yields styphnic acid.



The preparation of 2,4-DNR has proved to be much easier. According to Kostanecki and Feinstein[20], the following reactions take place,

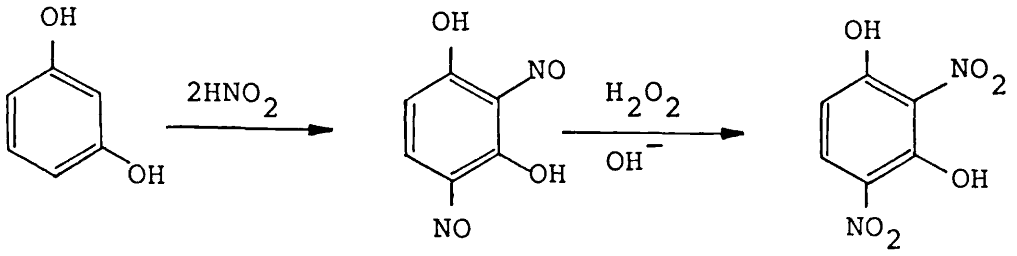


Another synthesis involved nitration of resorcylic acid I, and its subsequent decarboxylation[21].



I

The best preparation of 2,4-DNR has been found to be by dinitrosation of resorcinol by alkaline oxidation[22].



It is this synthesis that is used in the preparation of styphnic acid by the addition of ice cold dilute nitric acid to the 2,4-DNR. It is interesting to note that in the above synthesis, no 4,6-DNR is formed.

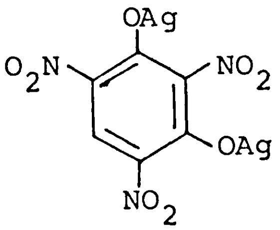
I-BIV: Properties of the Polynitroresorcinols

Styphnic acid is a slightly hygroscopic crystalline compound with two crystal modifications, stable form, m.pt. 176°-177°C, and unstable form m.pt. 165°-166°C. It is slightly soluble in water (9.45g of styphnic acid dissolves in 100cm^3 of water at 15°C, and 0.68-0.69 at 15°C). It is readily soluble in glycol diacetate (13g in 100cm^3 at room temperature), and slightly soluble in nitric and sulphuric acid, but practically insoluble in their mixtures[70]. Other properties include an oxygen balance of -38.8%[1]. (The amount of oxygen, expressed in weight percent in excess of that needed for complete oxidation of all elements in a compound is designated the oxygen balance. If the oxygen content of the explosive is insufficient for complete oxidation, the deficit amount of oxygen needed to complete the reaction is reported as negative). It ignites at 203°C (rate of heating, 5°C/min.), has a density of 1.84g cm^{-3} at 20°C, an RMM 257.1g, and a 2/3 water of crystallisation.

2,4-Dinitroresorcinol has a melting point of 147-148°C, and deflagrates on rapid heating, while 4,6-dinitroresorcinol has a much higher melting point at 212-215°C.

I-CI: Other metal salts of Polynitroresorcinols

Other metal salts of styphnic acid have been made, but as these are generally of little industrial interest, subsequently very few literature reports exist. Silver styphnate was first prepared in 1846 by Böttger and Will[43]. The product formed was described as a golden-yellow, palm-like crystal aggregate, for which the formula $Ag_2C_6HO_8N_3.H_2O$ was given.



Silver Styphnate
$C_6H(NO_2)_3(OAg)_2$

Small golden-yellow plates were later obtained by treating a hot ammonical solution of styphnic acid with a solution of silver nitrate[44]. The use of more concentrated solutions gave brownish-red crystals. Further work was carried out by Taylor[45] in 1926. Silver styphnate explodes at 305°C, decomposes at lower temperatures and darkens in sunlight. This compound has found extensive use in priming mixtures and in many respects is superior to normal lead styphnate[40].

I-CII: Priming Compositions

A typical example of an ammunition priming composition for silver styphnate is,

	% by mass
Guanylnitrosamino-guanyltetrazene	2
Silver styphnate	38
Barium nitrate	39
Lead peroxide	5
Antimony sulphide	5
Calcium silicide	11

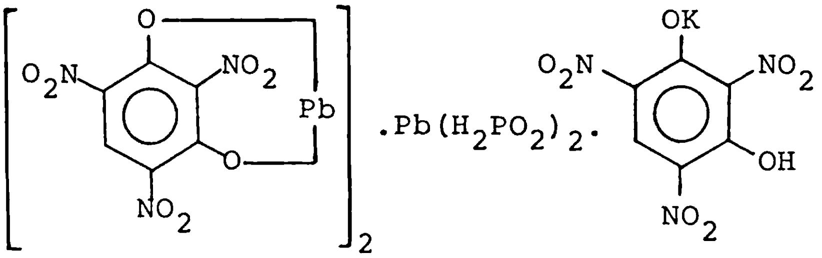
Other examples of priming mixtures include ferric styphnate-ferric hypophosphite, $[C_6H(NO_2)_3O_2]_3Fe_2.4Fe(H_2PO_2)_3$[37].

	% by mass
Ferric styphnate-ferric hypophosphite	5
Normal lead styphnate	41
Tetrazene	4
Barium nitrate	50

For potassium copper styphnate-copper hypophosphite, $[C_6H(NO_2)_3OK.O]_2Cu.Cu(H_2PO_2)_2$[41].

	% by mass
Potassium copper styphnate-copper hypophosphite	38
Tetrazene	4
Barium nitrate	25
Glass	33

For potassium styphnate-lead styphnate-lead hypophosphite, $[C_6H(NO_2)_3O_2Pb]_2.Pb(H_2PO_2)_2.\ C_6H(NO_2)_3OKOH\ .H_2O$ [35].



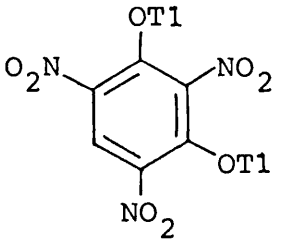
	% by mass
Potassium styphnate-lead styphnate-lead hypophosphite	10
Normal lead styphnate	36
Tetrazene	4
Barium nitrate	50

Thallium styphnate is another of these type of compounds which are used in priming compositions[39].

	% by mass
Mercury fulminate	20
Thallium styphnate	20
Antimony sulphide	9

	% by mass
Calcium silicide	7
Lead peroxide	7
Barium nitrate	37

An early preparation is by Langhans[46], in which the half-acid salt is produced. A subsequent investigation[47] has produced the full thallous salt.



Thallium Styphnate
$C_6H(NO_2)_3(OTl)_2$

Thallous styphnate explodes at 242°C with a moderate 'crack'. Priming compositions for rimfire cartridges of the double metal salts of styphnic acid shown above have good handling properties, and the toxic residues such as free or combined lead, which are especially undesirable in indoor ranges, do not occur. Other styphnates that have been noted include barium styphnate monohydrate[48], dilithium styphnate[9], copper styphnate[49], mercury styphnate[49], cobalt styphnate[49], cadmium styphnate[49], nickel styphnate[49], and zinc styphnate[49].

I-CIII: Uses

Metal styphnates have been found to be applicable to a wide range of military uses due to their sensitivity to percussion and static electricity (bridgewire fuse head). For example for potassium styphnate-lead styphnate-lead hypophosphite, 100% detonations are secured by a discharge of a 300μμF condenser at 500 volts[35]. This sensitivity to static electricity can also prove to be a problem as static electricity naturally builds up in many compounds on storage and transportation, giving rise to the triboelectric effect, which may cause the ammunition to detonate prematurely. This problem was found to be greatly alleviated by the addition of finely divided boron (90-92% pure; particle size average = 4 microns) during the synthesis of the initiator. Normal lead styphnate prepared with 10% by weight of boron, has a threshold energy for ignition by electrostatic spark of 5×10^{-4}J as opposed to 8×10^{-6}J without the boron[50].

I-CIV: Industrial Purification of Lead Styphnate

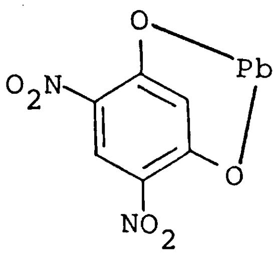
Purification of lead styphnate has long been a problem, as the compound readily decomposes in solution. One method for purification[51] employs glycerol and water. This method was not adopted for this investigation owing to the danger of glycerol being occluded in the final lead styphnate crystal structure.

I-CV: Metal Salts of Dinitroresorcinol

A similar situation exists for the dinitroresorcinols as that of the styphnates with regard to published preparative procedures[34,52,53,54,55,56,57,38]. As might be expected, lead-DNR is a less powerful explosive, and less efficient initiator than lead styphnate. The metal salts of 2,4-DNR are far more commonly found amongst the 2,4- and 4,6-isomers, because of the problems already described in the preparation of 4,6-DNR. The preparation of the lead salt is generally via the sodium salt of the dinitroresorcinol, the sodium being introduced as sodium carbonate and the lead as lead nitrate. The metal dinitroresorcinols have only been used to any extent since 1940, and like the styphnates, their uses are as primary composites.

I-CVI: Structures

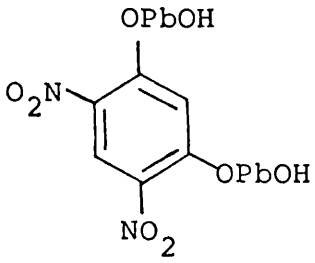
Structural determination of these complex metal compounds has never been easy. From X-ray crystallography and analytical work[9,47], the following structures have been postulated.



Normal lead 4,6-DNR (not isolated) [47]

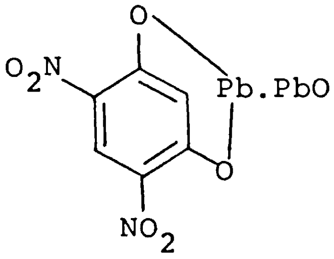
$C_6H_2(NO_2)_2O_2Pb$

Attempts to prepare yield mixture of acid and basic salts.



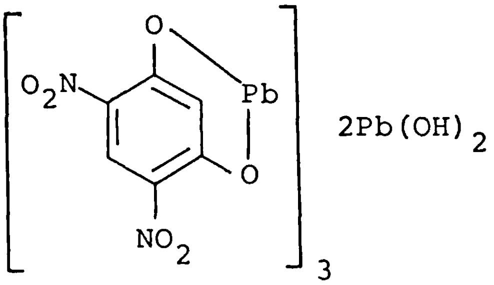
Monobasic lead 4,6-DNR (not isolated) [47]

$C_6H_2(NO_2)_2(OPbOH)_2$



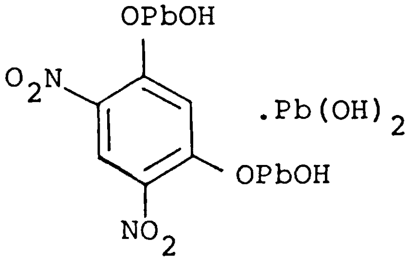
Monobasic lead 4,6-DNR (not isolated) [47]

$C_6H_2(NO_2)_2O_2Pb.PbO$



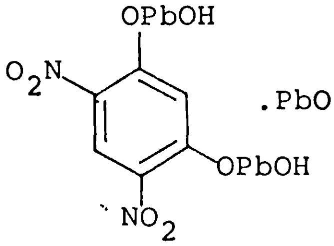
2/3 Basic lead 4,6-DNR [47]

$[C_6H_2(NO_2)_2O_2Pb]_3 2Pb(OH)_2$



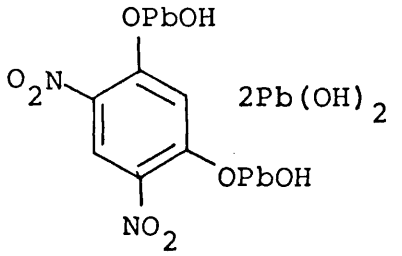
Dibasic lead 4,6-DNR (Probable structure)

$C_6H_2(NO_2)_2(OPbOH)_2.Pb(OH)_2$

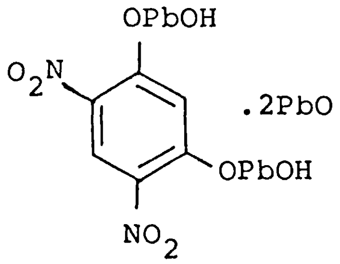


Dibasic lead 4,6-DNR

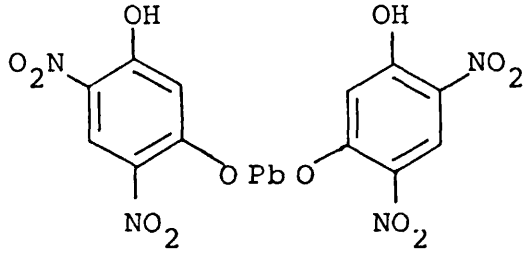
$C_6H_2(NO_2)_2(OPbOH)_2 \cdot PbO$



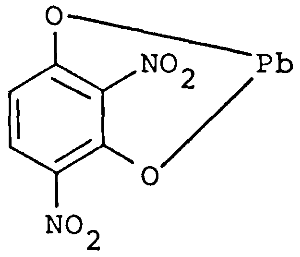
Tribasic lead 4,6-DNR
$C_6H_2(NO_2)_2(OPbOH)_2 2Pb(OH)_2$



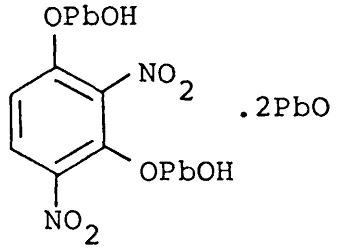
Tribasic lead 4,6-DNR
$C_6H_2(NO_2)_2(OPbOH)_2.2PbO$



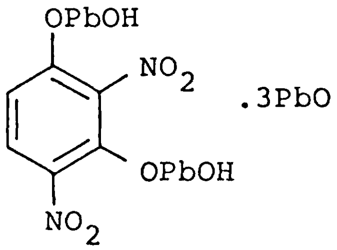
Acid lead 4,6-DNR
$[C_6H_2(NO_2)_2OH]_2O_2Pb$



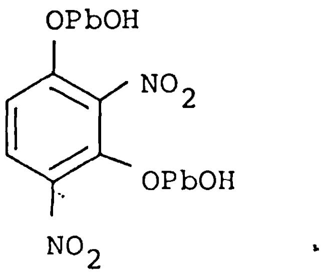
Normal lead 2,4-DNR[38]
$C_6H_2(NO_2)_2O_2Pb$



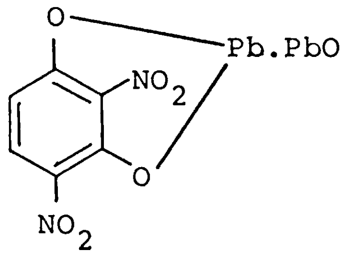
Tribasic lead 2,4-DNR[34]
$C_6H_2(NO_2)_2(OPbOH)_2 2PbO$



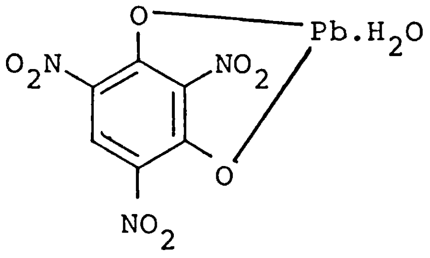
Quadrabasic lead 2,4-DNR[34]
$C_6H_2(NO_2)_2(OPbOH)_2\cdot 3PbO$



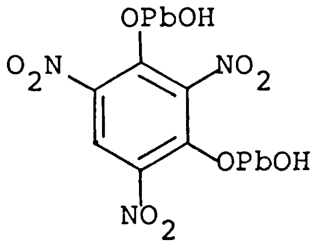
Monobasic lead 2,4-DNR[56]
$C_6H_2(NO_2)_2(OPbOH)_2$



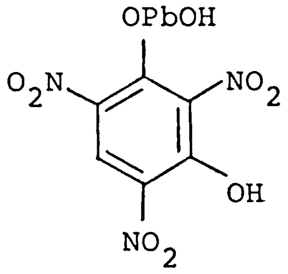
Monobasic lead 2,4-DNR[56]
$C_6H_2(NO_2)_2O_2Pb.PbO$



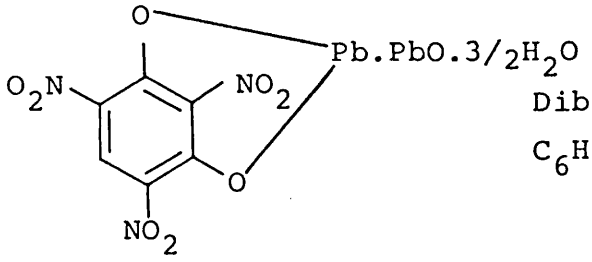
Normal lead styphnate[31]
$C_6H(NO_2)_3O_2Pb.H_2O$
$[M-O] \sim 2.38\,\text{Å}$ to $2.77\,\text{Å}$



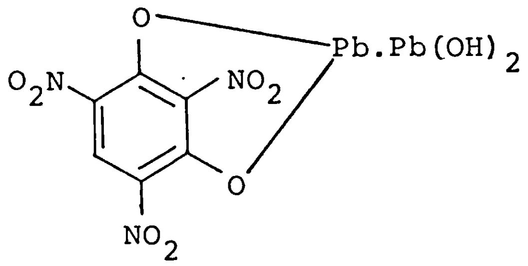
Dibasic lead styphnate[31]
$C_6H(NO_2)_3(OPbOH)_2$



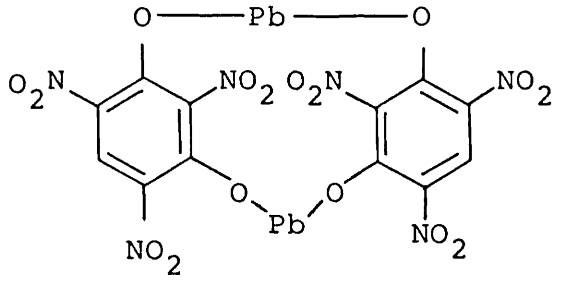
Monobasic lead styphnate[42]
$C_6H(NO_2)_3OH(OPbOH)$



Dibasic lead styphnate[29]
$C_6H(NO_2)_3O_2Pb.PbO.3/2H_2O$



Dibasic lead styphnate[31]
$C_6H(NO_2)_3O_2Pb.Pb(OH)_2$



Di-plumbic di-tri-nitro-resorcinol[71]

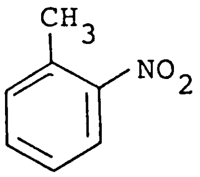
$Pb_2O_4C_{12}H_2(NO_2)_6$

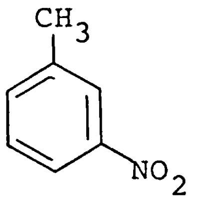
Table I-2 gives a summary of some of the properties already known about the metal polynitroresorcinols. To further the understanding of the explosive nature of these compounds, thermochemical data, in particular $\Delta_f H^\theta$ values are needed. It is to this object that this investigation is directed.

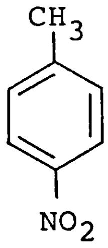
I-DI: Nitrotoluenes

Trinitrotoluene (TNT) is by far the most important, and the best known explosive. First discovered in 1863 by J. Wilbrand, TNT has become one of the most widely-used explosives for both peaceful and military purposes. Yet TNT is by no means the only nitrotoluene of interest. One, two or three nitro groups can be introduced by direct nitration of toluene to give a range of compounds.

I-DII: Mononitrotoluene (MNT)





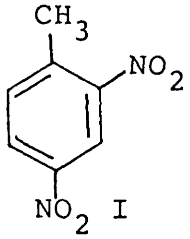


Three isomers are known, namely ortho-, meta-,and para-. The ortho-isomer has two melting points, depending on which form exists.

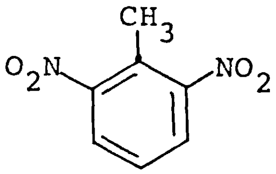
α-form melting point - 10.5°C
β-form melting point - 4.1°C

The meta-isomer melts at 16°C and the para-isomer at 52°C.

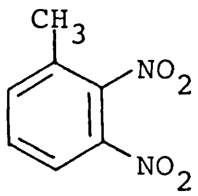
I-DIII: Dinitrotoluene (DNT)



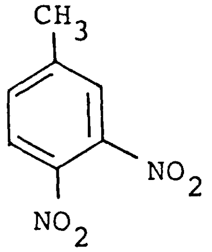
I



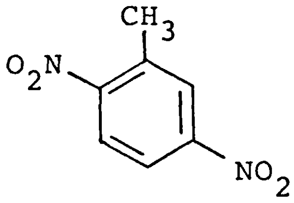
II



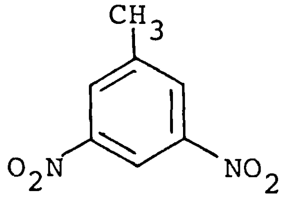
III



IV



V



VI

Six isomeric forms of dinitrotoluene exist; their form and commonly quoted melting points are shown in Table I-3.

Table I-3

	M.pt(common) °C	$\Delta_f H^\theta$ kJ mol^{-1}	Reference
2,4-DNT	71	-68.20	[57]
2,6-DNT	65.5	-43.93	[58]
2,3-DNT	63	-15.90	[57]
3,4-DNT	60	-14.64	[59]
3,6-(or 2,5-)DNT	52.5	-34.31	[57]
3,5-DNT	91	-43.51	[57]

I-DIV: Historical background to Dinitrotoluene

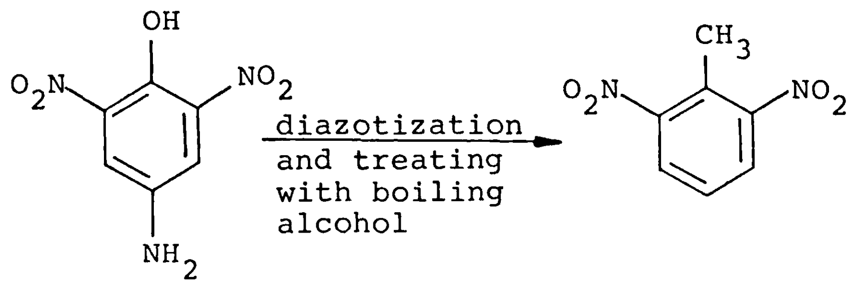
The first discovery of the existance of several isomeric forms of DNT was by Limpricht in 1885[60], who isolated the products of the 3,6-; 2,4-; and the 2,6- isomers from a nitration mixture. There is some speculation concerning the first preparation of a DNT. The first conclusive preparation was in 1870 by Beilstein and Kuhlberg[61] who obtained the 2,4-DNT isomer. Yet in 1841 St. Claire Deville[62] prepared a compound from "nitrobenzene" with a melting point of 71°C and called it "dinitrobenzene". The "nitrobenzene" had been prepared from light oil, and subsequent studies have shown that the product was dinitrotoluene. In 1903 the aromatic fraction of Galicia oil was nitrated and the 2,4-; and 3,6-DNT isolated. In the early 1870's it was realised that nitration of certain isomers of mononitrotoluenes would yield specific isomers of dinitrotoluenes. As found by Rosenstiel[63] in 1872, para-nitrotoluene yielded only the 2,4-DNT isomer, while ortho-nitrotoluene gave two isomers. Meta-nitrotoluene was nitrated in 1873[61] and the 3,4-DNT isomer obtained. Confusion remained about the existance of such isomers. In 1894, Häussermann and Grell[64] confirmed all the above preparations and also stated the existance of a 3,5-isomer. Sirks[65] nitrated meta-nitrotoluene and reproved that the 3,5-isomer did not exist. Further studies by Gibson, Duckham and Fairbairn[66] also did not yield conclusive evidence for the 3,5-isomer from meta-nitrotoluene nitration, and it was not until 1933 that its existance was again reported[67]. An extensive study of the nitration of ortho- and para- nitrotoluenes was carried out in 1955[68] and the following principal reaction products in the nitration process were confirmed.

$$\text{para-nitrotoluene} \xrightarrow{\text{Nitration}} \text{2,4-DNT}$$

$$\text{ortho-nitrotoluene} \xrightarrow{\text{Nitration}} \text{2,4-; and 2,6-DNT}$$

$$\text{meta-nitrotoluene} \xrightarrow{\text{Nitration}} \text{2,3-; 3,4-; and 3,6-DNT}$$

The formation of the 3,5-isomer by direct nitration of meta-nitrotoluene has not been definitely proven. Preparation of the 2,6-DNT isomer is obtainable from 2,6-dinitrotoluidine.



I-DV: Uses

Owing to its negative oxygen balance, DNT is primarily used as a carbon carrier, in both gelatinous and powdery commercial explosives. It is miscible with nitroglycerine and gelatinizes with soluble guncotton. DNT also finds a use in solid propellant systems. DNT is also used for the preparation of the corresponding mono- and di-amino- compounds, the latter compound being the precursor of toluene -2,4- di-isocyanate which is used in polyurethane formation.

TABLE I-2

Some properties of the metal polynitro resorcinols

NAME OF COMPOUND	Degree of Hydration	Physical Form	Water Solubility g/100cm^3 Sol^N(25°C)	% Oxygen Balance	Thermal T of I (5° C/min)	Electrostatic E(μJ), C(pJ) metal/metal or rubber/metal	Density gcm^{-3} at 20°C	Molecular Weight	Cell Volume (Å^3)	Crystal Type
Styphnic Acid	2/3 H_2O Variable	Pale Yellow Cryst. Solid	Slightly Soluble (Far less than Picric Acid)	-38.8	Flame at 203	M/M No ignition at 4.5J	1.84	257.1	1392.5	Trigonal
Lithium Styphnate	2.5 H_2O	Orange-Yellow Cryst.Solid	-	-34.4	322	M/M E = 0.45J No ignition E = 4.5 J gives ign.	1.79	302.0	560.1	Triclinic
Calcium Styphnate	$2H_2O$	Yellow Cryst. Solid	-	-35.5	321	M/M E = 0.45J No ignition E = 4.5J gives ign.	1.85	319.2	1143.3	Monoclinic
Cupric Styphnate	$4H_2O$	Green Cryst. Solid	-	-31.4	273	M/M No ignition at E=4.5J	2.02	378.7	1244.5	Orthorhombic
Barium Styphnate	$1H_2O$	Yellow Cryst. Solid	0.197	-37.9	296	M/M E = 1430, C = 520 r/M E = 250, C = 300	2.58	398.4	511.7	Monoclinic
α Lead Styphnate	$1H_2O$	Yellow Cryst. Solid	0.089	-33.3	257	M/M E = 25 C = 520 r/M E = 15, C = 60	3.08	468.3	1009.3	Monoclinic
β Lead Styphnate	$1H_2O$	Yellow Cryst. Solid	0.093	-33.3	255	M/M E = 13, C = 520	3.22	468.3	483.7	Monoclinic
β Monobasic Lead Styphnate	Anhydrous	Dark Red Cryst. Solid	0.0008	-25.9	240	M/M E = 4.5, C = 520 r/M E = 5.5, C = 35	4.09	689.5	4482.8	Monoclinic
Thallous Styphnate	Anhydrous	Yellow Cryst. Solid	-	-	242	-	-	-	-	-
Silver Styphnate		Orange platelike Cryst. Solid								

I-EI: References

1. MEYER,R.,Explosives,2nd Ed.,P136,Verlag Chemie, Basel,(1981).
2. MERTZ,V.,and ZETTER,G.,Ber.12,681,2037,(1879).
3. VERMEULEW,M.H.,Recueil des Travaux Chimiques des Pays Bas.38,107,(1919).
4. KAMETANI,T.,and OGASAWARA,K.,Chem. Pharm.Bull.15, 893,(1967).
5. FIESER,M.,and FIESER,L.F.,Reagents for Organic Synthesis. 3,212,Wiley-Interscience,New York,(1972).
6. WILKINSON,J.W.,U.S.Pat.2 246 936,(July 1941).
7. AUBERTEIN,P.,and EMEURY,J.M.,Mém, Poudres.39,7,(1957).
8. SAH,P.P.T.,Science Repts.Natl. Tsung Hua Univ.Ser.A, 1,197,(1932).
9. COLLINS,P.H.,Private Commun.
10. BENEDIKT,R.,and HÜBL,A.F.V.,Monatsh,2,323,(1881).
11. JONES,D.R.,and ROBERTS,C.L.,U.S. Pat.2 301 912,(Nov 1942).
12. TYPKE,P.G.W.,Chem. Ber.16,551,(1883).
13. SCHIAPARELLI,C.,and ABELLI,M.,Chem. Ber.16,872,(1883)
14. MUKERJI,D.N.,J. Chem. Soc.,545,(1922).
15. GILBERT,F.L.,LAXTON,F.C.,and PRIDEAUX,E.B.R.,J. Chem. Soc.2295,(1927).
16. BORSCHE,W.,and FESKE,E.,Chem.Ber.61,690,(1928).
17. JACKSON,C.L.,and KOCH,W.,Am. Chem. J.21,510,(1899).
18. BLANKSMA,J.J.,Rec. Trav. Chim.,21,286,(1902).
19. HODGSON,H.H.,and MOORE,F.H.,J. Chem. Soc.630,(1927).
20. KOSTANECKI,St.V.,and FEINSTEIN,B.,Chem.Ber.21,3119,(1888).
21. HEMMELMAYER,F.,Monatsh,26,190,(1905).
22. FICHEROULLE,H.,and SOULE,R.,Mém. Poudres,37,339,(1955).
23. WATTS,H.E.,The Law Relating to Explosives.Griffen & Co. Ltd.Lond.,(1954).
24. HOWARD, .,Phil. Trans.90,I,204,(1800).

25. KUNKEL,Laboratorium Chymicium,Hamburg,(1690).

26. ROMOCKI,S.J.V.,Geschichte der Sprengstoffchemie,Bd.I, Oppenheim (Schmidt),Berlin,(1895).

27. KAST,H.,Spreng-u. Zündstoffe,Vieweg & Sohn,Braunschweig, (1921).

28. WRIGHT,Phil.Mag,62,203,(1823).

29. GRIESS,P.,Ber.7,1224,(1874).

30. HERZ,E.v.,U.S. Pat.1 443 328,(1919).

31. ZINGARO,R.A.,J. Am. Chem. Soc.,76,1,816,(1954).

32. GRZESIEK,J.,GUGA,J., and PIECUCH,J.,Canadian Pat. 1080732,(June 1976).

33. TAYLOR,G.W.C., and NAPIER,S.E.,Brit. Pat. 1375531, (Nov. 1974).

34. HOLLOWAY,K.J.,TAYLOR,G.W.C.,and THOMAS,A.T., Brit. Pat. 1407733,(Sept. 1975).

35. KENNEY,J.F.,U.S. Pat. 2 702 745,(Feb. 1955).

36. TAUSON,H.,U.S. Pat. 2 020 665,(Nov. 1935).

37. KENNEY,J.F.,U.S. Pat. 2 689 788,(Sept. 1954).

38. HALE,G.C.,and RINKENBACH,W.M.,U.S. Pat. 2116514,(May 1938).

39. BRÜN,W.,U.S. Pat. 2099293,(Nov. 1937).

40. BRÜN,W.,U.S. Pat. 2097510,(Nov. 1937).

41. KENNEY,J.F., U.S. Pat. 2 663 627,(Dec. 1953).

42. URBAŃSKI,T.,'Chemistry and Technology of Explosives', 1,Pergamon Press,Oxford,(1983).

43. BÖTTGER,R.,and WILL,H.,Annalen.58,298,(1846).

44. HEMMELMAYR,F.,Monatsh,25,573,(1904),&26,185,(1905).

45. TAYLOR,C.A.,and BUXTON,E.P.,Army Ordnance, 7,68,(1926).

46. LANGHANS,V.,Zeit. Fuer. das. Gesamtes Schiess Und Sprengstoffwesen,31,359,402,(1936).

47. BATES,L.,Private Commun.

48. TAYLOR,G.W.C.,NAPIER,S.E.,and STANSFIELD,F.,Brit. Pat. 1 094 981,(Dec. 1967).

49. MAJRICH,A.,Chemicky Obzor,2,225,(1927).

50. TAYLOR,G.W.C.,MILLER,C.H.,and WHITE,J.R.,Brit. Pat. 1 086 861,(Oct. 1967).

51. KOMARMY,J.M.,U.S. Pat. 2 988 561,(June 1961).

52. TAYLOR,G.W.C.,and WHITE,J.R.,U.S. Pat. 3 301 882, (Jan. 1967).

53. JONES,D.T.,and RUBENSTEIN,L.,Brit. Pat. 582976,(Dec. 1946).

54. RUBENSTEIN,L.,U.S. Pat. 2 493 550,(Jan. 1950).

55. RUBENSTEIN,L.,Brit. Pat. 616454,(Jan. 1949).

56. RUBENSTEIN,L.,U.S. Pat. 2 493 549,(Jan. 1950).

57. RUBENSTEIN,L.,U.S. Pat. 2 493 551,(Jan. 1951).

58. KHARASCH,M.S.,J. Res. Natl. Bur. Std.2,359,(1929).

59. BADOCHE,M.,Bull. Soc. Chim. France,6,570,(1939).

60. LIMPRICHT,H.,Ber.18,1402,(1885).

61. BEILSTEIN,F.K.,and KUHLBERG,A.,Ann,155,1,(1870),&156, 81,206,(1870),&169,81,(1873).

62. DEVILLE,St.C.,Ann.Chim,3,3,151,(1841),&44,304,(1842).

63. ROSENSTIEL, .,Ann. Chim,4,27,433,(1872).

64. HÄUSSERMANN,C.,and GRELL,E.,Ber.27,2209,(1894).

65. SIRKS,H.A.,Rec.trav. Chim,27,209,(1908).

66. GIBSON,W.H.,DUCKHAM,R.,and FAIRBAIRN,R.,J. Chem.Soc., 121,270,(1922).

67. DE BEULE,E.,Bull. Soc. Chim,Belge,42,27,(1933).

68. KOBE,K.A.,SKINNER,C.G.,and PRINDLE,H.B.,Ind.Eng.Chem., 47,785,(1955).

69. JONES,G.,New Scientist,P189,(20th Oct. 1983).

70. FEDOROFF,B.T.,and SHEFFIELD,O.E.,Encyclopedia of Explosives and Related items,PATR 2700,5,P D1276, New Jersey,(1972).

71. PECK,H.T.,Brit.Pat. 165069,(12th June 1920).

Chapter II

PURIFICATION OF RAW MATERIALS, AND PREPARATIONS

II-A: Purification of Raw Materials

II-AI: Styphnic Acid

A sizable quantity of styphnic acid (∿20g) was purified as follows. It was first recrystallised[1,2] fives times from sodium-dried benzene (A.R.). The dry compound was then added to fuming nitric acid and stirred vigorously for 30 min. while a temperature of ca. 20°C was maintained in the mixture. The mixture was filtered, and the nitric acid wash repeated prior to washing the product with distilled water (6 x 200 cm^3). The pH of the final washing was checked for any noticable acidity. The compound was air-dried before storage in a vacuum desiccator over silica gel. The purified material had a very light yellow colour with no noticable nitric acid odour.

II-AII: Analysis

Micro-analysis of the purified styphnic acid gave satisfactory results, Table II-2, and a melting point of 176.5°C {lit. 176-179°C[3]} was obtained.

A further measurement of purity was performed using a Perkin-Elmer Differential Scanning Calorimeter (DSC2)[4]. An indium standard (N.P.L., 99.9999% pure) was used to check the DSC-2 calibration and reference for calculation. This method of analysis gave the purity of styphnic acid as >99.98%.

II-AIII: 2,4-Dinitroresorcinol

A sizable quantity of 2,4-Dinitroresorcinol (2,4-DNR) was needed (∿ 20g) for combuston calorimetry and further experimental work.

Problems were experienced in the finding of a suitable solvent for recrystallisation. A range of non-polar and polar solvents were tried, the most satisfactory results being obtained using chloroform (A.R.). The 2,4-DNR was recrystallised from this eight times prior to drying in air, then dried in a low-temperature oven ($\sim 40^{\circ}C$) and finally in a vacuum desiccator over silica gel. The crystals obtained had a light golden brown/orange colour.

II-AIV: Analysis

Micro-analysis results of the purified 2,4-DNR are collected in Table II-2; a melting point of $147^{\circ}C$ {lit. $146-149^{\circ}C$[3]} was obtained. Differential scanning calorimetry gave the purity of 2,4-DNR as >99.98%.

II-AV: 4,6-Dinitroresorcinol

4,6-Dinitroresorcinol, $\sim$ 20g, (4,6-DNR) was purified for combustion calorimetry and further experimental work, as follows[3]:

This consisted of recrystallising the crude 4,6-DNR by dissolving in sodium hydroxide (M), then precipitating by the addition of acetic acid (M) up to a pH of 4.4. Like 2,4-DNR, the major contaminant is styphnic acid which is also formed during the synthesis of the parent compound. In this purification process great care was taken not to increase the acidity of the mother liquor to avoid precipitation of styphnic acid.

The recrystallisation was repeated four times prior to drying the purified material first in air, then in a low-temperature oven ($\sim 40^{\circ}C$) and finally in a vacuum desiccator over silica gel. The crystals obtained were of a light sand colour.

II-AVI: Analysis

Micro-analysis of the purified 4,6-DNR gave satisfacotry results, Table II-2, and a melting point of $217^{\circ}C$ {lit. $215-218^{\circ}C$[3]} was obtained.

Thin-layer chromatography was also tried for this compound using an activated silica gel plate, and benzene (A.R.)/ methanol (A.R.)/acetic acid (A.R.) as solvent in the ratio 90/16/8. Only one spot was noticable at Rf 0.7[3] under visible and U.V. light. Differential scanning calorimetry gave the purity of 4,6-DNR as >99.98%.

II-AVl1: 2,6-Dinitrotoluene

A sizable quantity of 2,6-dinitrotoluene (2,6-DNT), ∿53g was purified for combustion calorimetry and further experimental work. It was recrystallised five times from sodium-dried benzene (A.R.). The produce (36.58g; yield 69%) was air-dried, and stored in a vacuum desiccator over silica gel in the dark. The purified material had a very light yellow colour with no noticable odour.

II-AVIII: Analysis

Micro-analysis of the purified 2,6-DNT gave satisfactory results, Table II-2, and a melting point of 58°C was obtained. Differential scanning calorimetry gave the purity of 2,6-DNT as >99.93%.

II-B: Preparations & Analyses

II-BI: Preparation of Normal Lead Styphnate Monohydrate (a),[5]

To a solution of styphnic acid (1.23g) in ethanol (25 cm^3), aqueous lead nitrate (25 cm^3; 0.20M) was added and the mixture heated to 70°C. Ethanolamine was then added dropwise with stirring, allowing the precipitate which formed after the addition of each drop to redissolve. The addition was continued until the pH, tested with Hydrion test paper, was ca. 3.5. A further amount of ethanol (25 cm^3, Abs.) was then added and the reaction mixture brought back to temperature. A solution of ethanolamine (4.0M) in ethanol was then prepared and added dropwise to the reaction mixture until a pH 4.8 was obtained. The orange precipitate formed was filtered off and washed with water and alcohol before drying.

II-BII: Analysis

The analysis for lead in the lead styphnate was performed according to the method described in Appendix III.

Theoretical lead content of $C_6H(NO_2)_3O_2Pb.H_2O$ = 44.24%
Found, 1. 44.34%, 2. 44.28%.

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BIII: Preparation of Monobasic Lead Styphnate, (b),[3]

A solution of lead nitrate (2.5g in 62.5 cm^3 water) was prepared and added to an agitated solution of sodium styphnate (0.62g styphnic acid, 0.4g sodium hydroxide, 37.5 cm^3 water), pre-heated to 95°C. The precipitate was filtered hot, and the product was subsequently washed with water and then alcohol before being further dried under vacuum in a silica gel desiccator for at least 25h.

II-BIV: Analysis

The analysis for lead in the lead styphnate was performed according to the method described in Appendix III.

Theoretical lead content of $C_6H(NO_2)_3O_2Pb.Pb(OH)_2$=59.93%
Found, 1, 58.82%. 2. 59.94%.

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BV: Preparation of Tribasic Lead Styphnate, (c),[3]

Ammonium styphnate was prepared (0.6g styphnic acid, 0.5 cm^3 .880 ammonia water in 37.5 cm^3 of water) at 95°C and added rapidly to a lead acetate solution (3.93g lead acetate in 75 cm^3 of water) also at 95°C. The mixture was stirred for a further 3 min. before hot filtration and washing of the product with water and alcohol prior to drying.

II-BVI: Analysis

The analysis for lead in the lead styphnate was performed according to the method described in Appendix III.
Theoretical lead content of $C_6H(NO_2)_3(OPbOH)_22PbO$ = 74.81%
Found (RHC), 1, 59.6%, 2, 59.69%.
Found (PERME), 59.5%.

From the analysis results it seems as if this method produces the monobasic lead styphnate only.

II-BVII: Another Preparation of Tribasic Lead Styphnate, (d),[6]

$$C_6H(NO_2)_3(ONa)_{2,aq} + 4Pb(NO_3)_{2,aq} + 6NaOH_{,aq} \longrightarrow C_6H(NO_2)_3(OPbOH)_2 2PbO\downarrow + 8NaNO_{3,aq} + 2H_2O_{,\ell}$$

To an aqueous, basic solution of disodium styphnate [25.0 cm^3; containing 0.96g styphnic acid, and 0.40g anhydrous sodium carbonate] was added with stirring a solution of lead nitrate [20.0 cm^3; containing 4.96g lead nitrate (A.R.)], simultaneously with a solution of sodium hydroxide [20.0 cm^3; containing 0.90g sodium hydroxide]. The two solutions were added very slowly with stirring while the reaction mixture was maintained at 85°C. Stirring was continued for 5 min. before the product was decanted hot. The orange coloured precipitate was washed and filtered under gravity before washing with methylated spirits and dried in a 60°C oven. The product was finally stored in a vacuum desiccator over silica gel.

II-BVIII: Analysis

The analysis for lead in the lead styphnate was performed according to the method described in Appendix III.

Theoretical lead content of $C_6H(NO_2)_3(OPbOH)_2 2PbO$=74.81%
Found Pb. 1, 72.34%, 2, 72.18% (Mean 72.26%)

Therefore prepared compound is $C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O$

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BIX: Preparation of Pentabasic Lead Styphnate, (e),[6]

$$C_6H(NO_2)_3(ONa)_{2,aq} + 6Pb(NO_3)_{2,aq} + 10NaOH_{,aq} \longrightarrow C_6H(NO_2)_3(OPbOH)_2 4PbO\downarrow + 12NaNO_{3,aq} + 4H_2O_{,\ell}$$

To an aqueous, basic solution of disodium styphnate [25.0 cm^3; containing 0.96g styphnic acid, and 0.40g anhydrous sodium carbonate] was added with stirring a solution of lead nitrate [20.0 cm^3; containing 7.45g lead nitrate(A.R.)], simultaneously with a solution of sodium hydroxide [20.0 cm^3; containing 1.5g sodium hydroxide]. The two solutions were added very slowly with stirring while the reaction mixture was maintained at 85°C. Stirring was continued for 5 min. before the product was decanted hot. The orange coloured precipitate was washed and filtered under gravity before washing with methylated spirits and dried in a 60°C oven. The product was finally stored in a vacuum desiccator over silica gel.

II-BX: Analysis

The analysis for lead in the lead styphnate was performed according to the method described in Appendix III.

Theoretical lead content of $C_6H(NO_2)_3(OPbOH)_24PbO.2H_2O$=76.72%
Found Pb. 1, 76.95%, 2, 76.83% (mean 76.89%).

Therefore prepared compound is $C_6H(NO_2)_3(OPbOH)_24PbO.2H_2O$

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BXI: Preparation of Silver Styphnate, (f), [7]

Glacial acetic acid (2.5 cm^3) was added to a boiling solution of styphnic acid (6.12g) and anhydrous sodium carbonate (2.65g) in water (320 cm^3). After effervescence had ceased, a boiling solution of silver nitrate (17g) in water (40 cm^3) was added with stirring. A dense orange precipitate suddenly formed and was filtered off and washed successively with distilled water, methanol, and petroleum spirit before being air-dried. The precipitate obtained weighed <u>ca</u>. 10g (yield <u>ca</u>. 87%). The crystals were deep orange in colour and of a fibrous nature with a metallic lustre.

II-BXII: Physical Properties

On heating, the crystals blackened at 325°C and exploded at 330°C. On addition to a stirred solution of hydrochloric acid (0.1M), rapid precipitation of silver chloride occurred.

II-BXIII: Analysis

The analysis of silver in silver styphnate was done gravimetrically.

An aqueous solution (200 cm^3) of silver styphnate (0.20g) containing nitric acid (2 cm^3) was heated to 70°C and hydrochloric acid (0.2m) was slowly added with stirring until no further precipitation was noticed. The mixture was then cooled to 25°C and the precipitate allowed to settle for several hours in the dark. The silver chloride was then filtered on a sinter-glass crucible (No. 4) which had been dried to constant weight. The solid was then washed with distilled water and air-dried. The crucible plus contents were then heated in an oven, set at 125°C for *ca.* one h and cooled in a desiccator to constant weight. Results are shown below.

Table II-1

Wt. of Silver Styphnate/g	Wt. of Silver Chloride/g	Silver expected /Wt. %	Silver found /Wt. %
0.0224	0.0141	47.02	47.04
	0.0140		
	0.0141		
0.0174	0.0108	47.02	46.72
	0.0108		
	0.0108		

Suggested formulae $C_6H(NO_2)_3(OAg)_2$

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BXIV: Preparation of Thallous Styphnate, (g), [8]

$$C_6H(NO_2)_3(OH)_{2,aq}+TlNO_{3,aq}\rightarrow C_6H(NO_2)_3OHOTl\downarrow+HNO_{3,aq}$$

Thallium nitrate (2.17g, Aldrich Gold Label 99.999%) was dissolved in distilled water (86.8 cm^3), and this aqueous solution was added to another consisting of styphnic acid (2.0g) dissolved in ice cold acetone (260 cm^3).

The mixture was stirred for 10 min., then allowed to settle. Upon evaporation of the acetone, golden-yellow crystals of the thallous styphnate were precipitated (yield ca. 98%).

The product was recrystallised from hot water (150 cm^3). The mixture was stirred, and allowed to settle. The product was filtered off and dried first in air, then in a warm oven ($\sim 35^oC$) and finally in a vacuum desiccator over silica gel.

II-BXV: Analysis

The analysis for thallium(I) was carried out according to the method described[9].

$$IO_3^-+2Tl^++6H^++Cl^-=ICl+2Tl^{3+}+3H_2O.$$

$$KIO_3\equiv 2Tl.$$

A solution of potassium iodate (0.025M) was prepared and used to titrate a solution containing hydrochloric acid (60 cm^3; conc.) and the thallium styphnate ($\sim 0.30g$).

Theoretical thallium content of $C_6H(NO_2)_3OHOTl=45.57\%$.
Found, Tl, 1. 45.41%, 2. 45.71%. (mean 45.56%).

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BXVI: Another preparation of Thallous Styphnate, (h),[10]

$C_6H(NO_2)_3(OH)_{2,aq}+CH_3CO_2Tl_{,aq}\rightarrow C_6H(NO_2)_3(OTl)_2\downarrow+2CH_3CO_2H_{,aq}$

To an aqueous solution of magnesium styphnate [50 cm^3; containing 0.625g styphnic acid, and 0.103g of magnesium oxide], a solution of thallium(I) acetate [50 cm^3, containing 6.57g of thallium(I) acetate (Aldrich Gold Label 99.99%)], was added. Both solutions were pre-heated to 70°C and this temperature was maintained throughout the reaction. The yellow precipitate was filtered hot under gravity and the product was washed with water and desiccated over silica gel.

II-BXVII: Analysis

The analysis for thallium(I) was carried out according to the method described[9].

$IO_3^-+2Tl^++6H^++Cl^-=ICl+2Tl^{3+}+3H_2O$

$KIO_3\equiv 2Tl.$

A solution of potassium iodate (0.025m) was prepared and used to titrate a solution containing hydrochloric acid (60 cm^3, conc.) and the thallium styphnate (∿0.30g).

Theoretical thallium(I) content of $C_6H(NO_2)_3(OTl)_2$=62.71%.
Found, Tl, 1. 62.65%, 2. 62.69%. (mean 62.67%).

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

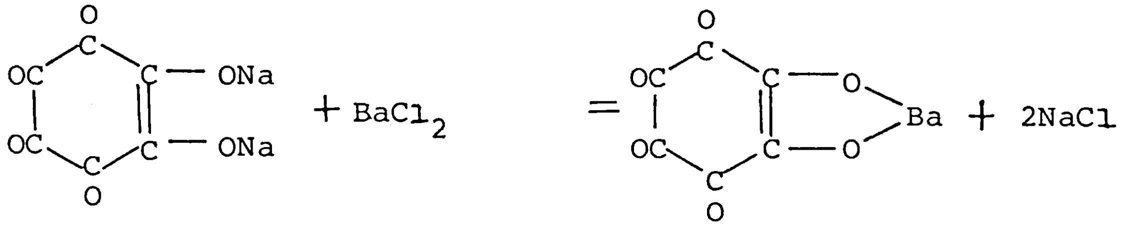
II-BXVIII: Preparation of Barium Styphnate Monohydrate, (i),[14]

To 11.72 cm^3 of an aqueous solution of magnesium styphnate [18.75 cm^3; containing 5.0g styphnic acid, and 1.83g magnesium carbonate], 3.91 cm^3 of dilute nitric acid [2.3 cm^3 of nitric acid (S.G. 1.42) added to 7.7 cm^3 of water] was added with stirring at 55°C. This solution was added to a second solution of barium acetate [15.65 cm^3; containing 9.37g barium acetate (B.D.H., A.R., purity > 99.5%)] with stirring at 75°C. After stirring for a further 10 min., and cooling, the mother liquor was removed by decantation and the product washed with water and dried in a warm oven (∿40°C). The yellow coloured precipitate was then placed in a vacuum desiccator over silica gel.

II-BXIX: Analysis

The analysis of barium in barium styphnate was done titrimetrically[13].

To an aqueous solution of barium styphnate [∿0.1g barium styphnate in 10 cm^3 deionised distilled water and 5 cm^3 of 0.1M hydrochloric acid], 10 drops of a freshly prepared solution of sodium rhodizonate indicator [15 mg sodium rhodizonate in 5 cm^3 of deionised distilled water] was added with 2cm^3 of absolute ethanol. With extremely vigorous shaking, the solution was titrated from a red to neutral colour with sulphuric acid (0.2N).



sodium rhodizonate

Theoretical barium(II) content of $C_6H(NO_2)_3O_2Ba.H_2O$=34.47%
Found, Ba, 1. 34.34%, 2. 33.49%. (mean 33.92%).

Results obtained from micro-analysis for C,H and N are recorded in Table II-2.

II-BXX: Preparation of Monobasic Lead 4,6-Dinitroresorcinol, (j),[11]

$C_6H_2(NO_2)_2(OH)_{2,aq} + 2Pb(OH)_{2,aq} \rightarrow C_6H_2(NO_2)_2(OPbOH)_2\downarrow + 2H_2O,_{\ell}$

To an aqueous solution of 4,6-dinitroresorcinol [1.4g of 4,6-DNR in 67.5 cm^3 of distilled water] heated to 90°C and vigorously stirred, was added a freshly made slurry of lead hydroxide, prepared as follows: 4.74g of lead acetate trihydrate (A.R.), and 1.0g of sodium hydroxide (A.R.), was added to 35 cm^3 of distilled water at room temperature. The mixture was stirred and gently warmed for ca. 5 min., then allowed to cool to room temperature and the white precipitate of lead hydroxide to settle. The precipitate was washed by decantation three times with 30 cm^3 of distilled water. The brick-red precipitate formed was agitated for 1h while the temperature was maintained at 90°C. The resulting precipitate was then filtered off and washed with distilled water and alcohol. The basic lead-DNR was stored in a vacuum desiccator over silica gel for several days before analysis.

II-BXXI: Analysis

The analysis for lead was performed as described in Appendix III. The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2(OPbOH)_2$ =64.1%
Found, Pb, 1. 64.15%, 2. 64.05%. (mean 64.1%).

Results obtained from micro-analysis are shown in Table II-2.

II-BXXII: Preparation of Dibasic Lead 4,6-Dinitroresorcinol, (k),[6]

$$C_6H_2(NO_2)_2(ONa)_{2,aq}+3Pb(NO_3)_{2,aq}+4NaOH_{,aq}$$
$$\longrightarrow C_6H_2(NO_2)_2(OPbOH)_2PbO\downarrow+6NaNO_{3,aq}$$

To an aqueous, basic solution of sodium 4,6-dinitroresorcinate [60 cm^3; containing 1g 4,6-DNR, and 0.5g sodium carbonate] was added with stirring a solution of lead nitrate [1.5 cm^3; containing 1.656g lead nitrate (A.R.)]. A solution of sodium hydroxide and lead nitrate [30 cm^3; containing 3.313g lead nitrate and 0.8g sodium hydroxide] was then added slowly with stirring while the reaction mixture was maintained at 90°C. Stirring was continued for *ca.* 5 min. before the mixture was allowed to cool and settle. The mother liquor was then decanted off, and the product washed with water before being first air-dried, then heated in a warm oven (∿45°C) and finally stored in a vacuum desiccator over silica gel (yield *ca.* 92%). The crystals were dark red in colour.

II-BXXIII: Analysis

The analysis of the product for lead was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2(OPbOH)_2PbO$=71.4%
Found, Pb, 1. 72.4%, 2. 71.0%. (mean 71.7%).

Results obtained from micro-analysis are shown in Table II-2.

II-BXXIV: Preparation of Tribasic Lead 4,6-Dinitroresorcinol, (l),[6]

$$C_6H_2(NO_2)_2(ONa)_{2,aq}+4Pb(NO_3)_{2,aq}+6NaOH_{,aq}$$
$$\longrightarrow C_6H_2(NO_2)_2(OPbOH)_22PbO\downarrow+8NaNO_{2,aq}$$

The disodium 4,6-dinitroresorcinate was prepared [60 cm^3; containing 1g 4,6-DNR and 0.5g sodium carbonate] and added with stirring to an aqueous lead nitrate solution [7.5 cm^3; 1.656g lead nitrate (A.R.)]. Upon completion of addition, the mixture was stirred for several min. before a second aqueous solution containing lead nitrate (A.R.) and sodium hydroxide [45 cm^3; 4.969g lead nitrate and 1.2g sodium hydroxide] was slowly added. The stirring was continued for 10 min. before the product was allowed to settle and isolated by decantation of the mother liquor. The product being washed with water before being first air-dried, then heated in a warm oven (∿45^{o}C) and finally stored in a vacuum desiccator over silica gel. The crystals were a deep orange colour.

II-BXXV: Analysis

Analysis for lead content was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2(OPbOH)_2 2PbO$=75.84%
Found, Pb, 1. 75.63%, 2. 75.38%. (mean 75.5%).

Results obtained from micro-analysis are shown in Table II-2.

II-BXXVI: Preparation of Normal Lead 2,4-Dinitroresorcinol, (m), [11]

$$C_6H_2(NO_2)_2(ONa)_{2,aq}+Pb(NO_3)_{2,aq} \longrightarrow C_6H_2(NO_2)_2O_2Pb\downarrow+2NaNO_{3,aq}$$

To a boiling aqueous solution of sodium 2,4-dinitroresorcinol [250 cm^3; containing 2.5g 2,4-DNR and 1.33g anhydrous sodium carbonate], a second boiling solution of lead nitrate [30 cm^3; containing 5g lead nitrate (B.D.H., A.R.)] was slowly added with stirring. Upon completion of addition, the mixture was stirred for a further 20 min. while cooling. The orange coloured precipitate was then filtered under gravity and washed with water, alcohol and finally petroleum ether (30-40°C). The product was put in a warm oven ($\sim$40°C) for several h, and finally stored in a vacuum desiccator over silica gel.

II-BXXVII: Analysis

The analysis for lead was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2O_2Pb$=51.12%.
Found, Pb, 1. 52.41%, 2. 50.19%. (mean 51.3%).

Results obtained from micro-analysis are shown in Table II-2.

II-BXXVIII: Preparation of Monobasic Lead 2,4-Dinitroresorcinol (n),[14]

$$C_6H_2(NO_2)_2(ONa)_{2,aq}+2Pb(NO_3)_{2,aq} \rightarrow C_6H_2(NO_2)_2O_2Pb.PbO\downarrow+2HNO_{3,aq} +2NaNO_{3,aq}$$

To an aqueous solution of sodium 2,4-dinitroresorcinol, [40 cm^3; containing 1g 2,4-DNR and 20 cm^3 (N) sodium hydroxide] heated with stirring to 75°C, a solution of lead nitrate [33 cm^3; containing 3.3g lead nitrate] also heated to 75°C was added. The temperature of the mixture was maintained at 75°C with constant stirring for 20 min. During this period the precipitate changed to a red tinge in colour from the initial orange colour. The product was filtered off under gravity and the precipitate was washed with water, alcohol and finally ether. The lead-DNR was placed in a warm oven ($\sim$40°C) for several h. and finally stored in a vacuum desiccator over silica gel.

II-BXXIX: Analysis

The analysis for lead was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead–DNR.

Theoretical lead content of $C_6H_2(NO_2)_2O_2Pb.PbO=65.9\%$
Found Pb, 1. 65.78%, 2. 65.75%. (mean 65.77%).

Results obtained from micro-analysis for C,H and N are shown in Table II-2.

II-BXXX: Preparation of Tribasic Lead 2,4-Dinitroresorcinol, (o),[6]

$$C_6H_2(NO_2)_2(ONa)_{2,aq}+4Pb(NO_3)_{2,aq}+6NaOH_{,aq}$$
$$\longrightarrow C_6H_2(NO_2)_2(OPbOH)_2 2PbO\downarrow+8NaNO_{3,aq}$$

The disodium 2,4-dinitroresorcinate was prepared [60 cm^3; containing 1g 2,4-DNR and 0.5g sodium carbonate]. To this solution was added with stirring an aqueous lead nitrate solution [7.5 cm^3, 1.65g lead nitrate (A.R.)]. Upon completion of addition, the mixture was stirred for several min. before a second aqueous solution containing lead nitrate (A.R.) and sodium hydroxide [45 cm^3; 4.97g lead nitrate and 1.2g sodium hydroxide] were slowly added. The stirring was continued for 10 min. before the product was allowed to settle and isolated as for (4,6-)lead-DNR. The temperature of the reaction mixture was maintained at 90°C throughout the preparation, (yield ca. 88%). The orange coloured compound was stored under vacuum in a desiccator over silica gel.

II-BXXXI: Analysis

The analysis was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2(OPbOH)_2 2PbO$=75.83%
Found,Pb, 1. 75.98%, 2. 75.09%. (mean 75.5%).

Results obtained from mirco-analysis for C,H and N are shown in Table II-2.

II-BXXXII: Preparation of Quadrabasic Lead 2,4-Dinitroresorcinol, (p),[6]

$$C_6H_2(NO_2)_2(ONa)_{2,aq} + 5Pb(NO_3)_{2,aq} + 8NaOH_{,aq} \longrightarrow C_6H_2(NO_2)_2(OPbOH)_2 3PbO\downarrow + 10NaNO_{3,aq}$$

The disodium 2,4-dinitroresorcinate was prepared [60 cm^3; containing 1g 2,4-DNR and 0.5g sodium carbonate]. To this solution was added with stirring an aqueous lead nitrate solution [7.5 cm^3, 1.66g lead nitrate(A.R.)]. Upon completion of addition, the mixture was stirred for several min. before a second aqueous solution containing lead nitrate (A.R.) and sodium hydroxide [60 cm^3; 6.626g lead nitrate and 1.6g sodium hydroxide] was slowly added. The stirring was continued for 10 min. before the product was allowed to settle and isolated as for (4,6-) lead-DNR. The crystals were a sand colour (yield *ca.* 91%).

II-BXXXIII: Analysis

The analysis was performed as described in Appendix III.

The acidity had to be increased to dissolve the lead-DNR.

Theoretical lead content of $C_6H_2(NO_2)_2(OPbOH)_2 3PbO$=78.42%
Found, Pb, 1. 79.23%, 2. 78.67%. (mean 78.9%).

Results obtained from micro-analysis for C,H and N are shown in Table II-2.

TABLE II-2

II-BXXXIV: Micro-Analysis Results

Compound Name (Index Letter) [Molecular Wt.]	CARBON		HYDROGEN		NITROGEN	
	Expected %	Found %	Expected %	Found %	Expected %	Found %
Styphnic Acid [245.106]	29.39	28.61	1.23	1.47	17.14	17.02
2,4-Dinitroresorcinol [200.112]	36.00	36.10	2.01	2.04	14.00	14.06
4,6-Dinitroresorcinol [200.112]	36.00	35.86	2.01	2.02	14.00	14.14
2,6-Dinitrotoluene [182.138]	46.16	46.33	3.32	3.30	15.38	15.47
Normal Lead Styphnate Monohydrate (a), [468.29]	15.39	15.63	0.65	0.60	8.97	8.76
Monobasic Lead Styphnate, (b) [691.48]	10.42	10.40	0.44	0.42	6.08	5.97
Tribasic Lead Styphnate, (c) [———]	-	-	-	-	-	-
Tribasic Lead Styphnate, (d) [1146.969]	6.28	6.15	0.62	0.55	3.66	3.59
Pentabasic Lead Styphnate, (e) [1620.27]	4.45	4.42	0.44	0.46	2.59	2.29
Silver Styphnate, (f) [458.828]	15.71	15.84 15.88	0.22	0.21 0.20	9.16	8.27 8.94
Thallous Styphnate, (g) [448.47]	16.07	16.35	0.45	0.42	9.37	8.96
Thallous Styphnate, (h) [651.828]	11.05	10.89	0.15	0.24	6.45	6.32
Barium Styphnate Monohydrate (i), [398.448]	18.08	18.18	0.76	0.78	10.55	10.65
Monobasic Lead 4,6-Dinitroresorcinol, (j), [646.512]	11.15	11.07	0.62	0.67	4.33	4.58
Dibasic Lead 4,6-Dinitroresorcinol (k), [869.682]	8.28	8.25	0.46	0.39	3.22	3.27
Dibasic Lead 4,6-Dinitroresorcinol (l), [1092.872]	6.59	6.61	0.37	0.39	2.56	2.63
Normal Lead 2,4-Dinitroresorcinol (m), [405.296]	17.78	17.70	0.50	0.53	6.91	6.94
Monobasic Lead 2,4-Dinitroresorcinol (n), [628.476]	11.47	11.52	0.32	0.25	4.46	4.38
Tribasic Lead 2,4-Dinitroresorcinol (o), [1092.872]	6.59	6.64	0.37	0.35	2.56	2.49
Quadrabasic Lead 2,4-Dinitroresorcinol (p), [1316.109]	5.47	5.25	0.31	0.32	2.13	2.15

II-BXXXV: References

1. MITRA,B.N.and SRINIVASON,M.,Science and Culture,12, 502,(1947).
2. KAMETANI,T.,and OGASAWARA, K.,Chem. Pharm. Bull,15, 893,(1967).
3. COLLINS,P.H.,Private Commun.
4. PLATO,C.,and GLASGOW,A.R.,Anal. Chem,41,1,(1969).
5. HERZ,E.v.,U.S. Pat.,1 443 328,(Jan 1923).
6. TAYLOR,G.W.C.,and NAPIER,S.E.,Brit. Pat,1 375 531,(Nov. 1974).
7. TAYLOR,C.A.,and BUXTON,E.P.,Army Ordnance,7,68,(1926).
8. LANGHANS,V.,Zeit. Fuer. das. Gesamte Schiess Und. Sprengstoffwesen,31,359,402,(1936).
9. VOGEL,A.,Textbook of Quantitative Inorganic Analysis, 4th Ed.,Longman,London,(1978).
10. BATES,L.,Private Commun.
11. FEDOROFF,B.T.,and SHEFFIELD,O.E.,Picatinny Arsenal Technical Report,2700,5,D1275,(1972).
12. TAYLOR,G.W.C.,NAPIER,S.E.,and STANSFIELD,F.,Brit. Pat. 1 094 981,(1967).
13. VOGEL,A.,Textbook of Quantitative Inorganic Analysis, 3rd Ed.,P275,Longman,London,(1961).
14. RUBENSTEIN,L.,U.S. Pat.2 493 550,(Jan.1950).

Chapter III

COMBUSTION CALORIMETRY

III-A: COMBUSTION CALORIMETRY

An adiabatic static oxygen bomb calorimeter was used. This has the capability of complete combustion only for compounds containing carbon, hydrogen, oxygen and/or nitrogen. The system used is based on a commercially available calorimeter (Gallenkamp Autobomb Automatic Adiabatic Bomb Calorimeter, Model CB-110). The only parts of this system used were the adiabatic jacket, ignition circuit, thermistor bridge and stirrer. The original bomb vessel was discarded in preference for a nickel-chromium (illium) alloy vessel (Parr Instruments Co. Illinois No.1101)[1]. The original can thermometer was removed and replaced with a quartz thermometer, (Hewlett-Packard Model 2801A). Signals from the quartz thermometer were fed to an analog output digital recorder system (Hewlett-Packard Model 523 562A). This in turn was connected to a chart recorder (Sunvic Controls Ltd. (AEI) type 10S) via an analog to digital converter, Figure III-1. The stainless-steel calorimeter can was substituted by a similar vessel fabricated in copper (0.1 cm thick) to improve thermal response.

The principle of the adiabatic bomb calorimeter is that the total heat of the reaction goes into raising the temperature of the can contents, and none escapes from the system, Figure III-2. Once a combustion has been initiated, the contents of the can will rise in temperature. The can is surrounded by an air baffle to give even heating to the outer jacket tank that contains water which is constantly circulated throughout the jacket. Adiabatic conditions are maintained by use of a Wheatstone bridge circuit. One arm of the bridge contains a thermistor immersed in water contained in the can, while the other arm of the bridge contains another thermistor immersed in water contained in the outer jacket. During combustion of the sample compound, the can water temperature increases with respect to that of the outer jacket water temperature. This causes the Wheatstone bridge to go off-balance. To regain

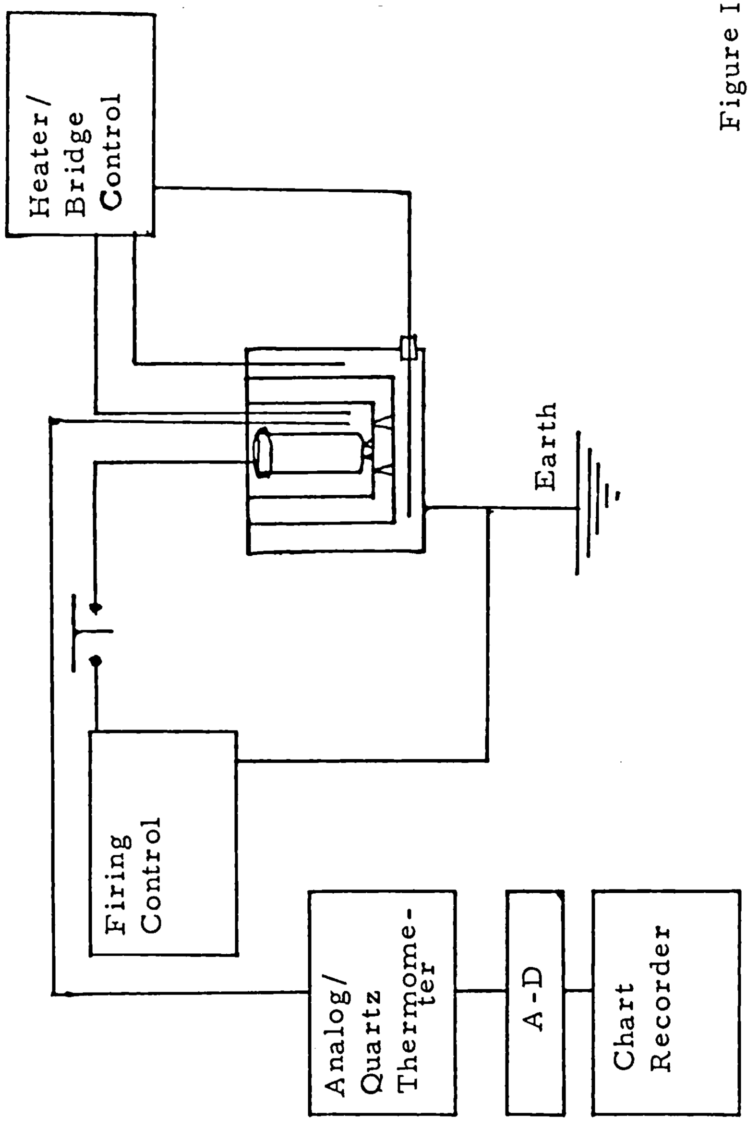
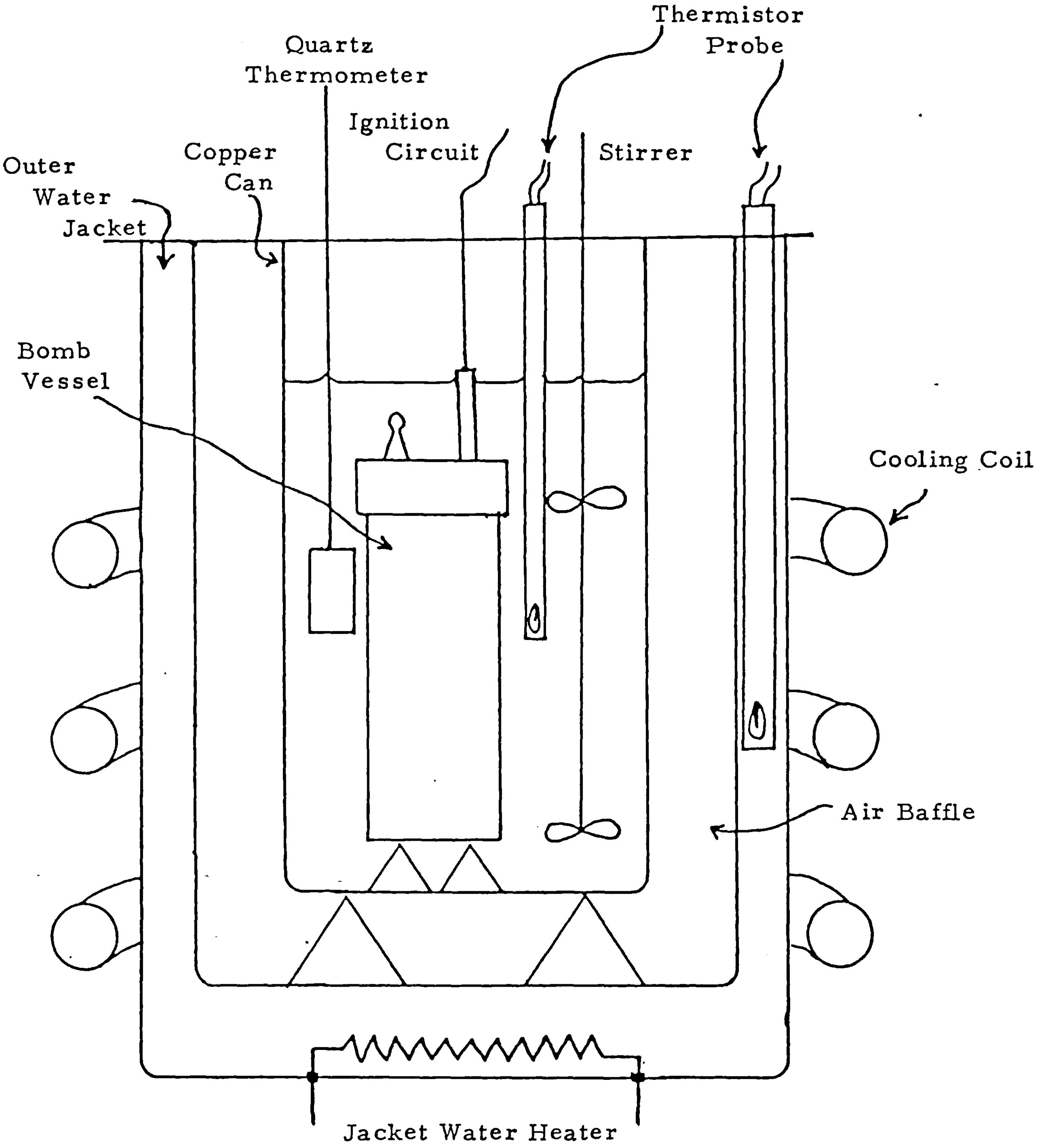

Heater/ Bridge Control
Earth
Firing Control
Analog/ Quartz Thermometer
A-D
Chart Recorder

Figure III-1

Figure III-2


Thermistor
Probe
Quartz
Thermometer
Ignition
Circuit
Stirrer
Outer
Water
Jacket
Copper
Can
Bomb
Vessel
Cooling Coil
Air Baffle
Jacket Water Heater

bridge balance and thus maintain an adiabatic condition, the water in the outer jacket is electrically heated. A cooling circuit is also fitted to the outer jacket to eliminate overheating of the jacket water. Figure III-3 gives an illustration of how the jacket temperature, T_j, follows the can temperature T_c. It is of crucial importance to (a), have the thermistors accuratly balanced for the working temperature (25.0°C) and, (b) ensure that the energy equivalent of the system is accurately known.

The shape and size of the silica crucible has been found to affect the efficiency of compound burning. If the crucible is very thin-walled, with sloping sides, efficient burning (clean) is usually observed. If a thick-walled crucible was used, especially with straight-side walls, then poor burning was observed, with severe 'sooting' and possibly splattering of the compound. The reason for this observation is that the crucible acts as a heat-sink which inhibits marginally complete combustion.

III-B: Procedure

A sample of the desiccated purified compound to be combusted was approximately weighed prior to pelleting. A length of cotton fuse and platinum wire, previously stored under desiccation, was cut off and weighed accurately to $\pm 0.5 \times 10^{-5}$ g (Oertling, Model No. 146). A dried silica glass crucible was then weighed, firstly empty, and then with the pellet. The crucible and pellet were then placed in the support within the bomb vessel, and the platinum wire fixed across the bomb electrodes. The cotton fuse was tied to the platinum wire and gently located under the pellet, Figure III-4.

If a benzoic acid calibration experiment was being performed, 1.08 cm^3 of water were added to the bomb vessel. Otherwise, as nitrogen-containing compounds were used in this investigation, 10.80 cm^3 of water,[7] were added. Continuity of the firing

Figure III-3

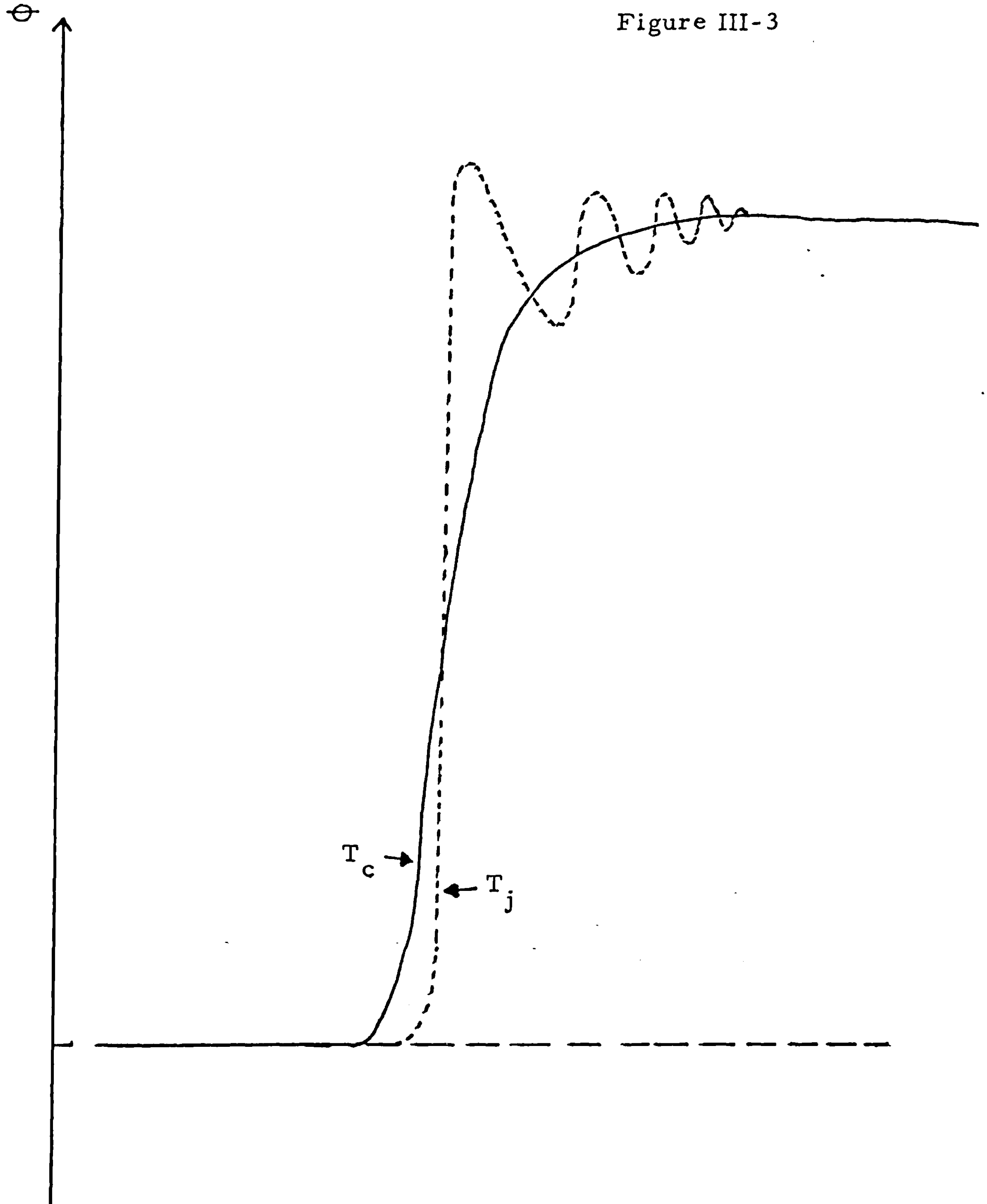


Figure III-4

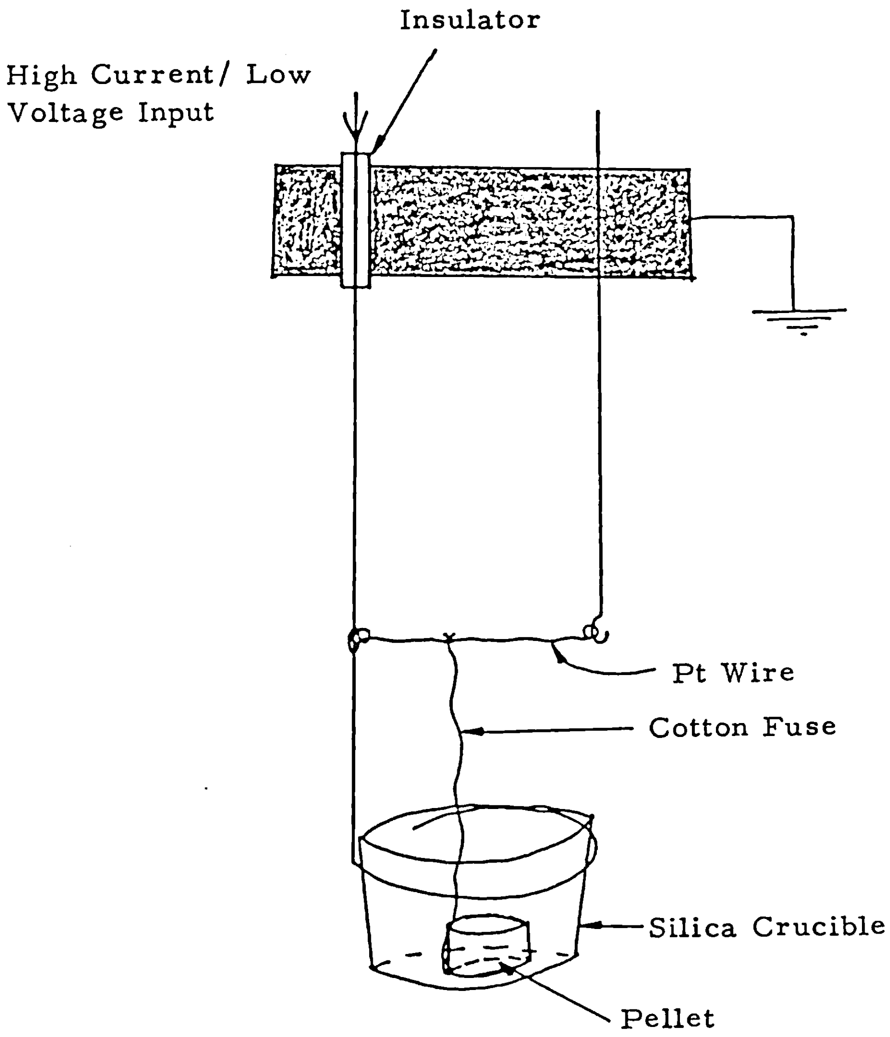
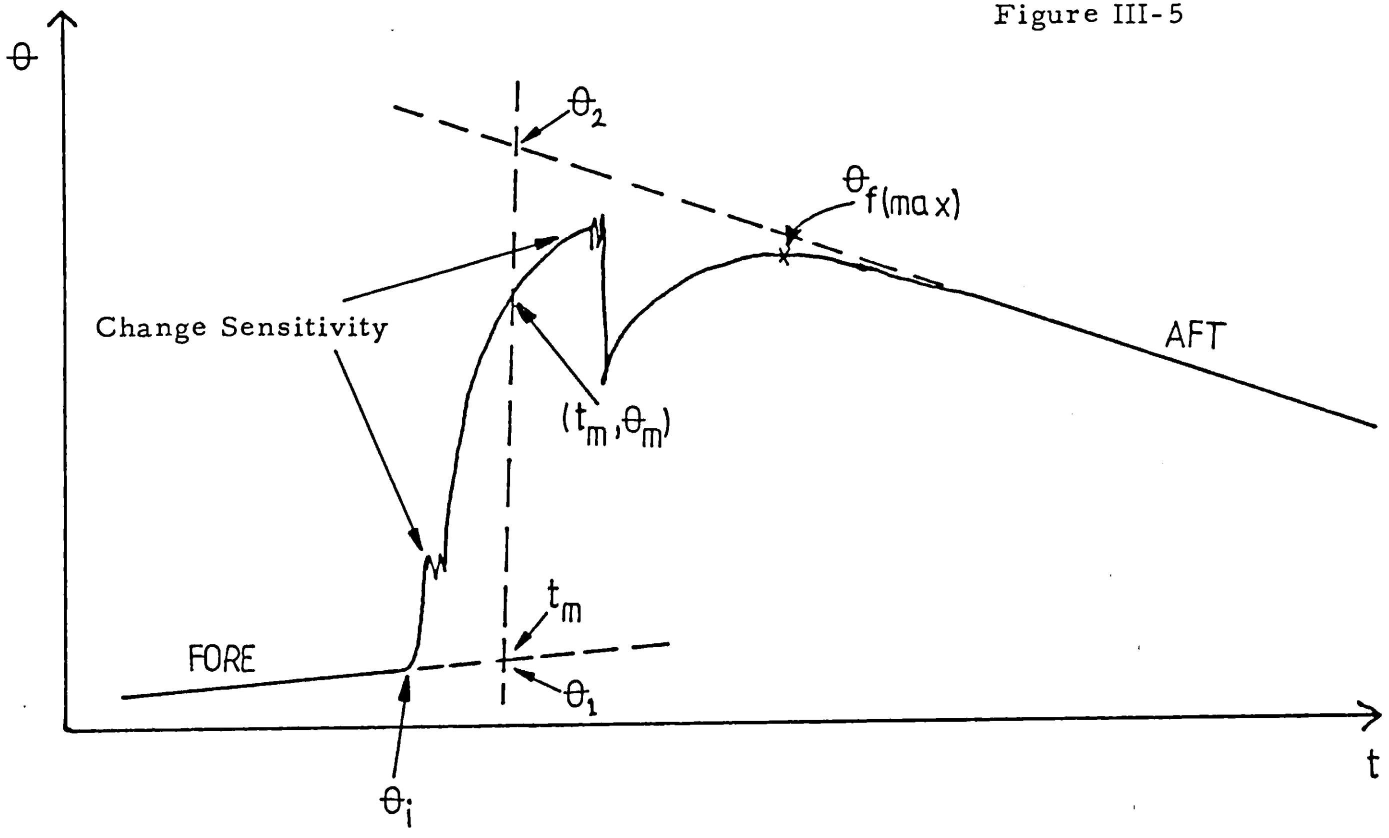

Insulator
High Current/ Low
Voltage Input
Pt Wire
Cotton Fuse
Silica Crucible
Pellet

Figure III-5



circuit was then checked, after which the bomb was closed and the cap screwed down. The bomb vessel was then purged from nitrogen by a repeated process of filling with oxygen to a pressure of thirty atmospheres and gently venting. The oxygen pressure was accurately gauged by weighing the bomb at one atmosphere, and then thirty atmospheres[2], the oxygen was then gently bled off to give a weight difference of 14.49g. The bomb was then placed in the calorimeter can and both it and the can weighed. Distilled water, pre-heated to 25°C, was then added to the can plus contents to give a weight rise of 1600.0g. The assembled bomb and can were placed in the abiabatic jacket and the lid, plus thermistor probe, etc. put in place, Figure III-2. All heater, cooler, thermometer, etc. circuits were then switched on and left for thirty minutes to allow the calorimeter to reach equilibrium at 25°C. The thermometer was switched to range 0.0001 (i.e. 25.1234, reading every 10 sec.) and the chart started in the chart recorder. If a reasonable trace was recorded after 15 minutes, then the fire button was depressed and the range setting on the thermometer switched to .1 (25.0° in .1 second), when the pen first deviated. When the heat evolved appeared to be reaching a climax, the range setting was switched back to 0.0001 to record the maximum temperature and the relaxation period, Figure III-5.

The instrument was then switched off and the bomb dismantled. As the bomb was opened, the contents were first checked for an acrid smell, and secondly, inspected for any signs of soot other than within the crucible. (These two faults result in error, due to incomplete combustion). The water contents of the bomb were carefully emptied into a conical flask and titrated with sodium hydroxide (0.1M) using methyl orange indicator.

Combustion was assumed to be good if the bomb had an 'ozone' smell when opened, and if no soot was observed. As the compounds used contained only C,H,O,N, it is assumed that any carbon in the compound forms $CO_2(g)$, hydrogen forms $H_2O(\ell)$ and that 90% of the nitrogen forms $N_2(g)$, the remainder of the nitrogen forming aqueous nitric acid.

$$C_xH_yO_zN_w \longrightarrow XCO_2+\frac{Y}{2}H_2O+\frac{W}{Z}N_2 \quad (\approx 90\%)$$

$$(\approx 10\%)\ \tfrac{1}{2}N_{2,g} + 5/4\,O_{2,g} + \tfrac{1}{2}H_2O,_{\ell} = HNO_{3,aq}$$

It is thus important that the extent of the bomb reaction be established to account, (a), for any unburnt material being left, (b), possible side reactions, and, (c), any incomplete combustion to CO.

The measurement of ΔU for the reaction is based on the relationship of ΔU being equal to q_v. The observed temperature change is converted into the q_v value by knowing the total heat capacity of the calorimeter.

$$\Delta U_T = -C_v^f\theta \qquad \text{(IIIA)}$$

where $C_v^f\theta$ = heat capacity at constant volume of final state (ref diag. below) and ΔU_T = internal energy change from initial starting temperature T. This comes from the application of the Kirchhoff formula[3] to the system.

$$\begin{tikzcd}
T+\theta[\text{Initial}] \arrow[r] & {[\text{Final}]} \\
T[\text{Initial}] \arrow[u, "C_v^i\theta"', "A"] \arrow[ur, "B"'] \arrow[r] & {[\text{Final}]} \arrow[u, "C_v^f\theta"'] \\
\text{30 atmos.} &
\end{tikzcd}$$

A. $\Delta U_{T+\theta} = -C_v^i\theta$ (IIIB)

B. $\Delta U_T = -C_v^f\theta$ (IIIA)

B is used, where a reaction is referenced to 25°C.

Equation IIIA gives rise to the expression for the energy equivalent of the final system ε_f/J K^{-1}

$$\varepsilon_f = \frac{m_s \, \Delta Q_{25}}{\Delta\theta} \qquad \text{(IIIC)}$$

where

m_s = mass of the sample/g, and
ΔQ = heat evolved in the actual bomb process/J g^{-1}.

Thus

$$(-m_s\Delta Q) = (-m_s\Delta U) + q_i + q_n - q_c \qquad \text{(IIID)}$$

where

q_i = heat of ignition (fuse + firing wire)/J.
q_n = heat evolved in forming $HNO_{3,aq}$/J.
$-q_c$ = heat correction for soot/J, and
ΔU = heat of combustion of compound only in system.

$$n_1C_xH_yO_zN_{w,\ell \text{ or } s} + r_1O_{2,g} + m_1H_2O_{,g} + m_1'H_2O_{,\ell}$$

$$= [r_2O_2+s_2N_2+q_2CO_2]_{,g}+m_2H_2O_{,g}+(q_2' \, CO_2+m_2'H_2O)_{,\ell} \qquad \text{(IIIE)}$$

For an idealised (reduced) bomb process, the energy of combustion ΔU^θ will refer to the pure isothermal reaction,

$$n_1[C_xH_yO_zN_{w,\ell \text{ or } s} + (x + y/4 + z/2)\,O_{2,g}$$

$$= xCO_{2,g} + y/2\ H_2O_{,\ell} + w/2\ N_{2,g}] \qquad \text{(IIIF)}$$

To be able to calculate the standard enthalpies of formation from combustion calorimetry, it is important that the same rigorous conditions are applied to the calculations as those applied to the experimental. It was suggested that every bomb calorimetric process "should be corrected to give the value of ΔU for the pure isothermal reaction under the pressure condition of one normal atmosphere for both reactants and products,"[4]. The account by Washburn only covered compounds containing C,H and O. Prosen[5] later expanded the argument to cover compounds of C,H,O and N. The number needed to correct the calculations is referred to as the Washburn correction, q_w.

For the difference between Equations IIIE and IIIF, the following relationship has been derived.

$$\Delta U^{\theta} - \Delta U = \frac{q_w}{m_s} \qquad \text{(IIIG)}$$

where

$$q_w = \Delta u_1 + \Delta u_2 + \Delta u_3 + \Delta u_4 + \Delta u_5 + \Delta u_6$$

Δu_1 = energy change of r_1 moles of oxygen from zero to P_1 atmospheres pressure, $(-6.59P_1r_1)$.

Δu_2 = energy change of r_2 moles of oxygen, q_2 moles of CO_2 and s_2 moles of N_2 from P_2 to zero atmospheres pressure. $([6.59R_2 + 6.04S_2 + 28.875Q_2 - 11.15Q_2(R_2+S_2)]P_2(r_2+s_2+q_2))$.

where $R_2 = r_2/(r_2 + s_2 + q_2)$, S_2 = mole fraction of oxygen and Q_2 the mole fraction of carbon dioxide.

$\Delta u_3 = -41530(m_2-m_1)$, the energy of condensation of (m_2-m_1) moles of H_2O.

$\Delta u_4 = 17100q_2'$, energy of vaporisation of q_2' moles CO_2 from m_2' moles H_2O.

$\Delta u_5 = (\partial U/\partial P)_v$, compressibility.

Δu_6 = volatility in O_2 when burnt.

Equating equations IIIC, IIID, and IIIG.

$$\varepsilon_f = \frac{-m_s\Delta U^\theta + q_i + q_n + q_w - q_c}{\Delta\Theta} \qquad \text{(IIIH)}$$

or

$$\varepsilon_f = \frac{-m_s\Delta U_B + q_i + q_n - q_c}{\Delta\Theta} \qquad \text{(IIII)}$$

Substitution of $-\Delta U_B$ into equation IIIH leads to the calculation of ε_f for calibration experiments.

(Certified benzoic acid supplied, with $-\Delta U_B/\text{kJ g}^{-1}$)

$$\varepsilon_f = \varepsilon_{sf} + \varepsilon_{cf} \qquad \text{(IIIJ)}$$

ε_{sf} = energy equivalent of the final system/kJ K^{-1}.

$\varepsilon_{cf} = 10^{-3}(20.96n_{O2} + 4.18m_w + 2.28m_s + 0.136m_{pt} + 0.76m_c)$, the energy equivalent of the products of combustion.

where

$20.96 = C_v(O_2)/\text{J mol}^{-1}\text{K}^{-1}$.

$n_{O2} = \left[\frac{PV}{0.08206T}\right](1 + (890-11.30\theta)10^{-6}P)$, nō of moles of oxygen initially.

$4.18 = C_v(H_2O)/\text{J K}^{-1}\text{g}^{-1}$.

m_w = mass of water originally in bomb/g.

2.28 = combustion product of benzoic acid.

$0.136 = C_v(Pt)/\text{J K}^{-1}\text{g}^{-1}$.

m_{Pt} = mass of Pt firing wire/g.

$0.76 = C_v(SiO_2)/\text{J g}^{-1}\text{K}^{-1}$.

m_c = mass of crucible/g.

Substituting for ε_f and ε_{cf} in equation IIIJ the following expression is derived.

$$\varepsilon_{sf} = \frac{-m_s\Delta U^\theta + \Sigma_i qi}{\Delta\Theta} - 10^{-3}\left[\Sigma_j \varepsilon_j\right] \qquad \text{(IIIK)}$$

where

$q_i = 0.00183 + (17.49 \times m_{cotton})$

0.00183 = electric energy for heating Pt wire calculated theoretically for R.H.C. bomb only.
17.49 = energy of combustion of cotton/kJ g^{-1}.
m_{cotton} = mass of cotton fuse/g.

From equation IIIK it can be seen that once ε_{sf} has been found from calibration experiments, it is possible to find ΔU^θ for unknown compounds.

Once a value for ΔU^θ has been established it can be transposed to give a figure for $\Delta_f H^\theta$ as follows

$$\Delta_c U^\theta \longrightarrow \Delta_c H^\theta \longrightarrow \Delta_f H^\theta$$

$$\Delta_c H^\theta = \Delta_c U^\theta + \Delta_c(PV) \qquad \text{(IIIL)}$$

$$= \Delta_c U^\theta + \Delta_c(nRT) \qquad \text{(IIIM)}$$

$$= \Delta_c U^\theta + RT\Delta n \qquad \text{(IIIN)}$$

where c = combustion.

To evaluate $\Delta_f H^\theta$, the standard heats of formation of water and carbon dioxide need to be known[6], and these values subtracted from that of $\Delta_c H^\theta$. This is where large errors of up to 2%

deviation in $\Delta_f H^\theta$ can result from as little as 0.1% error in $\Delta_c H^\theta$ as both $\Delta_c H^\theta$ and $\Sigma \Delta_f H^{CO_2}_{H_2O}$ are large negative numbers. It is thus of paramount importance that the combustion material be of the highest purity. If not, the relative molecular mass (RMM) will not be that calculated, and hence the number of moles of reaction will be in error. The impurities will also themselves undergo reaction and hence contribute to the energy change of the system.

For the calculation of the experimental data, a comprehensive computer program was written and is listed in Appendix 1.

III-C: Conditions of Experimental Work

1. $V = 0.36$, internal volume of empty bomb in dm^3.

2. $T = 298.15K$.

3. $P = 30$, internal oxygen pressure at 298.15K in atmospheres.

4. $\varepsilon_{sf} = 8.6286 \pm 0.0013$ kJ K^{-1}.

5. ΔU_B applied under conditions
   i) 298.15K
   ii) Burnt in pure O_2 at 30 atmospheres (O_2 hydrocarbon content < 20 vapour parts per million [BOC])
   iii) $m_s/V \approx 3$.
   iv) m_w (prior)$/V \approx 3$.

   for departure from non-standard conditions.

   $\Delta U_{non-standard} = \Delta U_{standard} \times f$

   where

   $f = 1 + 10^{-6}[20(P-30)+42((m_s/V)-3)+30((m_w/V)-3)-45(\theta-25)]$

   valid only if

   $20<P/atm<40;\ 2<(m_s/V)<4;\ 2<(m_w/V)<4;\ 20<\theta/^{o}C<30$.

6. The performance of the calorimeter was checked by the combustion of a secondary standard. Acetanilide (B.D.H., O.A.S. grade) was used, as values of $\Delta_c H^\theta$ and $\Delta_f H^\theta$ are

accurately known[7], and the nitrogen content of the compound is of a comparable order of magnitude to that of the investigation materials.

7. Buoyancy correction of weighings; this is shown in Appendix II.

III-D: Combustion Experiments

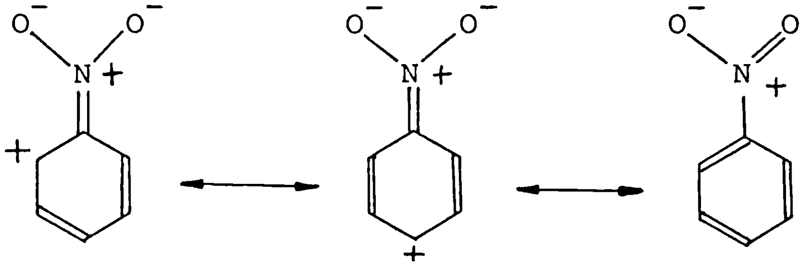
Combustion calorimetry was carried out on four compounds: styphnic acid; 2,4-dinitroresorcinol; 4,6-dinitroresorcinol, and 2,6-dinitrotoluene (two forms). The compounds were purified according to the methods described in Chapter II. All combustion work was carried out by the author except for that of the dinitrotoluenes which was carried out by Dr. A. Barakat; all subsequent calculations and statistical analysis were by the author. The results obtained are tabulated in Tables III-1 to III-6. Acetanilide was combusted to check efficient performance of the calorimeter. The computer program listed in Appendix I was used to calculate the enthalpies of formation, and Table III-7 give an overall summary of these results. Some of the densities used in the calculations were found using the method listed in Appendix IV.

III-E: Discussion

As these compounds are all complex aromatics, it is not possible to apply Hammett[13] numbers to the individual groups. To examine the enthalpies of formation constructively it is necessary to consider the steric inhibition of resonance, conjugation effects, and hydrogen bonding.

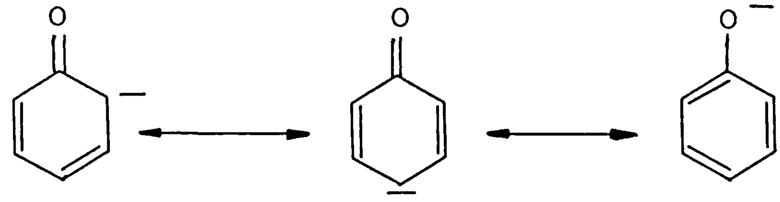
By convention, groups which are more powerful electron attractors than the hydrogen atom are said to show negative inductive (-I) effects, while those which are poorer electron attractors than hydrogen display positive inductive (+I) effects. Both the nitro and hydroxy groups show negative effects. This then leads to the mesomeric effect in aromatics.

For nitrobenzene, several resonance structures exist, I, II and III

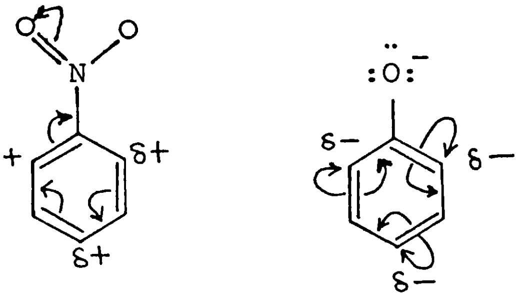


I II III

For structures I and II, the result of the introduction of a nitro group to the benzene ring is the withdrawal of Π-electron density from the ring, especially from ortho and para positions. Similarly for hydroxyl group introduction

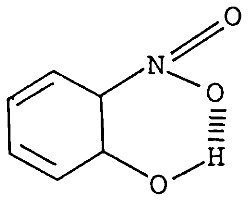


By consideration of what is happening within the ring system, the following two diagrams can be drawn.



(From a) combination of these resonance structures, a picture can be drawn to understand why the polynitroresorcinols are kinetically unstable structures, but before making a comparative judgement, several other effects need to be considered.

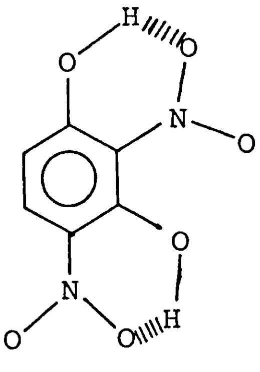
Some intramolecular bonding can take place between the hydroxyl and nitro groups.



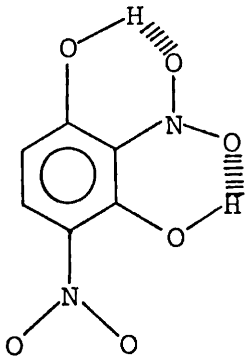
This hydrogen bonding will in turn cause some rigidity in the molecule, and increase its stability. As a price, this also increases the internal strain of the molecule from steric interference between the p-electrons of the hydroxyl oxygen and the p-electrons of the free oxygen atom of the nitro group, and causes structural instability. This is what is thought to cause the structure of 2,4-dinitroresorcinol to be more energetic than that of 4,6-DNR, and it is this that is reflected in their enthalpies of formation.

From infrared spectroscopy, the most stable structures have been found to be as follows[14].

2,4-Dinitroresorcinol has the most stable structures of I, and II in benzene,

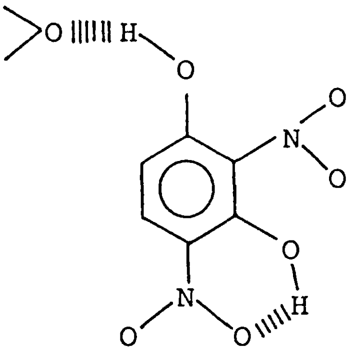


I



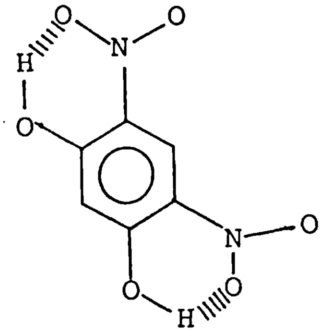
II

and in dioxane III



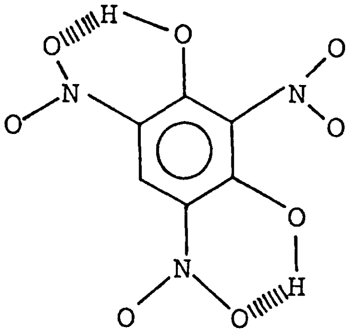
III

4,6-Dinitroresorcinol has the structure IV in benzene



IV

Styphnic acid has structure V in benzene



V

Table III-1

Acetanilide. $C_8H_9N_1O_1$ Density = 1.22 g cm^{-3} [7]

Ref. No.	1	2	3	4
M(sample)(g)(air)	1.05099	1.04474	0.98938	0.96108
M(sample)(g)(vacuo)	1.051862	1.045607	0.990201	0.961877
M(fuse)(g)	0.002605	0.00222	0.00242	0.00228
M(Pt wire)(g)	0.008075	0.00825	0.009199	0.00918
M(Silica Crucible)(g)	3.57983	3.18398	3.57969	3.57982
M(soot)(g)	0.00023	0.00000	0.000355	0.00017
$M(H_2O)$(g)	10.8	10.8	10.8	10.8
q_1(kJ)	0.04739	0.04066	0.04416	0.04171
q_n(kJ)	0.06599	0.06927	0.06062	0.06092
q_c(kJ)	0.00023	0.00000	0.00561	0.00561
q_w(kJ)	0.04055	0.04025	0.03684	0.03684
$\Delta\Theta$(K)	3.79885	3.78045	3.5755	3.47375
ε_{cf}(kJ K^{-1})	0.060207	0.059889	0.060036	0.05996
$-\Delta U_c^\theta$(kJ g^{-1})	31.24091	31.27009	31.23894	31.47375

$-\Lambda U/298.15K = 31.2478$
2 sdm = 0.0149

Table III-2

Styphnic Acid. $C_6H_3N_3O_8$ Density = 1.84 g cm^{-3} at 20°C

Ref. No.	1	2	3	4	5	6
M(sample)(g)(air)	0.93904	0.98578	0.98276	0.89546	0.92974	1.01028
M(sample)(g)(vacuo)	0.93951	0.98627	0.98325	0.89591	0.93021	1.01079
M(fuse)(g)	0.00279	0.00280	0.00291	0.00262	0.00326	0.002835
M(Pt wire)(g)	0.00898	0.00760	0.00845	0.00876	0.00923	0.00783
M(Silica Crucible)(g)	3.57988	3.18378	3.18390	3.57350	3.18376	3.57982
M(soot)(g)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
M(H_2O)(g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i(kJ)	0.50627	0.050802	0.052726	0.047654	0.0588474	0.051414
q_n(kJ)	0.04658	0.05076	0.05016	0.04795	0.04927	0.05198
q_c(kJ)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
q_w(kJ)	0.022602	0.023744	0.023674	0.021477	0.022333	0.024356
$\Delta\Theta$(K)	1.0434	1.09315	1.0973	0.99225	1.0346	1.12465
ε_{cf}(kJ K^{-1})	0.058279	0.058028	0.058025	0.058229	0.057969	0.058355
$-\Delta U_c^\theta$(kJ g^{-1})	9.51996	9.50091	9.56549	9.49030	9.52117	9.53915

$-\Delta U/298.15K = 9.52283$
2 sdm $= 2.20178 \times 10^{-2}$

Table III-3

2,4-Dinitroresorcinol. $C_6H_4N_2O_6$

Density = 1.81 g cm^{-3} at 25°C

Ref. No.	1	2	3	4	5	6
M(sample)(g){air}	0.94125	0.96103	0.85786	0.97978	0.949675	0.93491
M(sample)(g){vacuo}	0.94173	0.96152	0.85829	0.98028	0.95016	0.93538
M(fuse)(g)	0.00257	0.00260	0.00324	0.00313	0.002785	0.00239
M(pt wire)(g)	0.01044	0.00798	0.00812	0.00752	0.00740	0.00836
M(Silica Crucible)	3.58047	3.18385	3.58695	3.18386	3.57968	3.18381
M(soot)(g)	0.00000	0.00033	0.00000	0.00000	0.00080	0.00033
M(H_2O)(g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i(kJ)	0.04678	0.04730	0.05849	0.05657	0.05054	0.04363
q_n(kJ)	0.05882	0.05464	0.05196	0.05554	0.05285	0.05327
q_c(kJ)	0.00000	0.01089	0.00000	0.00000	0.0264	0.01089
q_w(kJ)	2.46×10^{-2}	2.52154×10^{-2}	2.2379×10^{-2}	2.5728×10^{-2}	2.4920×10^{-2}	2.4504×10^{-2}
$\Delta\Theta$(K)	1.3837	1.4163	1.2715	1.42115	1.37915	1.35975
ε_{cf}(kJ K^{-1})	5.8512×10^{-2}	5.8236×10^{-2}	5.8408×10^{-2}	5.82604×10^{-2}	5.85219×10^{-2}	5.8202×10^{-2}
$-\Delta U_c^{\theta}$(kJ g^{-1})	12.62586	12.67462	12.71436	12.45308	12.50205	12.50966

$-\Delta U/298.15K = 12.57994$

2 sdm = 0.08659

Table III-4

4,6-Dinitroresorcinol. $C_6H_4N_2O_6$ Density = 1.85 g cm^{-3} at 25^oC

Ref. No.	1	2	3	4	5	6
M(sample)(g){air}	0.81772	0.86392	1.00673	0.95807	0.93580	0.93743
M(sample)(g){vacuo}	0.81812	0.86435	1.00723	0.95854	0.93626	0.93789
M(fust)(g)	0.00334	0.00258	0.002705	0.00222	0.00256	0.00246
M(Pt wire)(g)	0.010785	0.00781	0.009065	0.00784	0.00716	0.00698
M(Silica Crucible)(g)	3.18386	3.18384	3.18388	3.18379	3.18386	3.18389
M(soot)(g)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
$M(H_2O)$(g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i(kJ)	0.06025	0.04695	0.04914	0.04066	0.04660	0.04486
q_n(kJ)	0.043297	0.048075	0.054644	0.051956	0.053151	0.052255
q_c(kJ)	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
q_w(kJ)	$2.1376x10^{-2}$	$2.2597x10^{-2}$	$2.64969x10^{-2}$	$2.51687x10^{-2}$	$2.45332x10^{-2}$	$2.4589x10^{-2}$
$\Delta\Theta$(K)	1.19005	1.25435	1.4604	1.3907	1.3578	1.3633
$\varepsilon_{cf}(kJ\ K^{-1})$	$5.8049x10^{-2}$	$5.8109x10^{-2}$	$5.82957x10^{-2}$	$5.82321x10^{-2}$	$5.8203x10^{-2}$	$5.82052x10^{-2}$
$-\Delta U_c^\theta(kJ\ g^{-1})$	12.48297	12.47016	12.46596	12.48038	12.46514	12.49717

- U/298.15K = 12.47696
2 sdm = 0.010089

Table III-5

2,6-Dinitrotoluene. $C_7H_6N_2O_4$. M.Pt. 56°C Density = 1.51 g cm^{-3} at 25°C

Ref. No.	1	2	3	4	5	6
M(sample)(g)(vacuo)	1.075269	0.9924756	0.9903342	0.9533105	1.002842	1.050023
M(fuse)(g)	0.00486	0.00384	0.00468	0.00454	0.00458	0.00516
M(Pt. wire)(g)	0.00718	0.00908	0.00777	0.00776	0.00668	0.008859
M(Silica crucible)(g)	7.31934	2.79518	3.42786	2.79520	3.42792	3.42794
M(soot)(g)	0.00084	0.00060	0.00120	0.00044	0.0005	0.00060
M(H_2O)(g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i(kJ)	0.08683139	0.0689916	0.0836832	0.0812346	0.08193419	0.09207839
q_n(kJ)	0.0734556	0.0668864	0.062706	0.0609144	0.0677822	0.0722612
q_c(kJ)	0.02772	0.0198	0.0396	0.01452	0.0165	0.0198
q_w(kJ)	0.0319343	0.0293722	0.0293547	0.0282013	0.02969109	0.03114128
$\Delta\Theta$(K)	2.4407	2.2547	2.2503	2.1626	2.2795	2.3873
ε_{cf}(kJ K^{-1})	0.0619706	0.0583905	0.0588675	0.0583232	0.05888884	0.05897004
$-\Delta U_c^\theta$(298.15K)(kJ g^{-1})	19.57331	19.5885	19.60274	19.54296	19.588888	19.58448

$-\Delta U/298.15K = 19.57943$
2 sdm = 0.016513

Table III-6

2,6-Dinitrotoluene. $C_7H_6N_2O_4$. M.pt. 66°C

Density = 1.49 g cm^{-3} at 25°C

Ref. No.	7	8	9	10	11	12
M(sample)(g)(vacuo)	1.013057	1.014838	1.136117	1.007264	1.02243	0.9404102
M(fuse)(g)	0.00428	0.00260	0.00476	0.00527	0.00450	0.00444
M(Pt. wire)(g)	0.0078	0.00652	0.00574	0.00781	0.00702	0.00824
M(Silica crucible)(g)	7.31920	3.42786	3.42782	7.31912	3.42784	7.3191
M(soot)(g)	0.00040	0.00050	0.00036	0.0006	0.000879	0.00080
M(H_2O)(g)	10.8	10.8	10.8	10.8	10.8	10.8
q_i(kJ)	0.0766872	0.047304	0.08508239	0.09400229	0.080535	0.0794856
q_n(kJ)	0.0680808	0.0677822	0.07465	0.0674836	0.0680808	0.05972
q_c(kJ)	0.0132	0.0165	0.01188	0.0198	0.029007	0.0264
q_w(kJ)	0.03000968	0.0300700	0.0387079	0.02983306	0.03030299	0.02780495
$\Delta\Theta$(K)	2.2970	2.3000	2.5803	2.2887	2.3155	2.1342
ε_{cf}(kJ K^{-1})	0.06186388	0.05890934	0.05911714	0.06185388	0.05892209	0.06173931
$-\Delta U_c^\theta$(298.15K)(kJ g^{-1})	19.54522	19.56235	19.57122	19.57612	19.52803	19.57264

$-\Delta U/298.15K = 19.55926$
2 sdm = 0.0154425

Table III-7

III-E: Bomb Calorimetry Results

Acetanilide	This work	Wadsö[8]	Johnson[7]
$-\Delta U_c^\theta$(kJ mol^{-1})	4223.67±0.024		4221.26
$-\Delta H_c^\theta$(kJ mol^{-1})	4220.57±0.024	4223.75	4224.88
$-\Delta H_f^\theta$(kJ mol^{-1})	213.74±1.06		209.44±1.00
Styphnic Acid	This work	Médard[9,11]	
$-\Delta U_c^\theta$(kJ mol^{-1})	2334.10±0.028		
$-\Delta H_c^\theta$(kJ mol^{-1})	2345.88±0.028		
$-\Delta H_f^\theta$(kJ mol^{-1})	443.93±0.78	434.72	
2,4-Dinitroresorcinol	This work	Médard[10,11]	
$-\Delta U_c^\theta$(kJ mol^{-1})	2517.35±0.111		
$-\Delta H_c^\theta$(kJ mol^{-1})	2524.79±0.111		
$-\Delta H_f^\theta$(kJ mol^{-1})	407.93±0.79	438.90	
4,6-Dinitroresorcinol	This work	Médard[10,11]	
$-\Delta U_c^\theta$(kJ mol^{-1})	2496.75±0.013		
$-\Delta h_c^\theta$(kJ mol^{-1})	2504.18±0.013		
$-\Delta H_f^\theta$(kJ mol^{-1})	428.54±0.78	463.17	
2,6-Dinitrotoluene (56°C)	This work	Médard[9]	Shaw[12]*
$-\Delta U_c^\theta$(kJ mol^{-1})	3566.13±0.021		
$-\Delta H_c^\theta$(kJ mol^{-1})	3569.85±0·021		
$-\Delta H_f^\theta$(kJ mol^{-1})	42.21±0.92		
2,6-Dinitrotoluene (66°C)	This work		
$-\Delta U_c^\theta$(kJ mol^{-1})	3562.463±0.020		
$-\Delta H_c^\theta$(kJ mol^{-1})	3566.181±0.020		
$-\Delta H_f^\theta$(kJ mol^{-1})	45.88±0.92	43.93	50.208

* By Group Additivity.

Earlier combustion work on nitroresorcinols[9,10] reference a temperature of 18°C. The values quoted in the table above have been recalculated to 25°C,[11].

III-F: References

1. PARR,S.W.,J. Ind. Eng. Chem.,4,746,(1912).
2. SVETLOV,B.S.,Trudy Moskovokogo Khimiko Tekhnologicheskogo, 53,328,(1967).
3. KIRCHHOFF,G.,Ann. Physik,103,(2),177,(1858).
4. WASHBURN,E.W.,J. Res. Natl. Bur. Std.,10,525,(1933).
5. PROSEN,G.J.,in F.D. Rossini(Ed.) Experimental Thermochemistry,Interscience,(1956).
6. CODATA Bulletin 28,ICSU CODATA,Paris,(1978).
7. JOHNSON,W.H.,J. Res. Natl. Bur. Std.,79A,3,487,(1975).
8. WADSÖ,I.,Acta Chem. Scand.,16,471,(1962).
9. MÉDARD,L.and THOMAS,M.,Mém. Poudres,31,173,(1949).
10. MÉDARD,L.and THOMAS,M.,Mém. Poudres,36,97,(1954).
11. WESTRUM,E.F.,STULL,D.R.,and SINKE,G.C.,The Chemical Thermodynamics of Organic Compounds.,J.Wiley & Sons Inc. N.Y.,(1969).
12. SHAW,R.,J. of Phys. Chem,75,26,4047,(1971).
13. HAMMETT,Physical Organic Chemistry,McGraw-Hill Book Co., Inc.,N.Y.,p. 184-199,(1940).
14. GRANZHAN,V.A.,SAVENKO,L.M.,SEMENENKO,S.V.,and LAKTIONOVA, S.K.,J. Structural Chem.,12,5,742,(1971).

Chapter IV

SOLUTION CALORIMETRY

IV-A: SOLUTION CALORIMETRY

IV-AI: Introduction

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

(1) An L.K.B. 8700-1 Precision Calorimetry System was employed to measure the enthalpy of solution/reaction of lead nitrate in various aqueous solutions.
(2) Enthalpies of reaction for metallo trinitroresorcinates and dinitroresorcinates were determined using a calorimeter constructed in this laboratory by the author.

IV-AII: L.K.B. 8700-1 Precision Calorimetry System

Details of the construction and operating procedures for the L.K.B. 8700-1 are given in the instruction manual. A block diagram of the calorimeter is shown in Figure IV-1. The calorimeter vessel is a thin-walled Pyrex cylinder of 100 cm^3 capacity. The thermistor and calibration heater are contained in glass oil-filled tubes supported from the lid of the vessel. Stirring within the calorimeter vessel is via a PTFE paddle and gold ampoule holder attached to a stainless-steel spindle. The solid sample is contained in a glass ampoule which is broken when required by lowering the stirrer/ampoule assembly vertically onto a sapphire-tipped glass rod located in the base of the vessel.

For calibration, a 500 mW heater was selected to give the most suitable heating time. The out-of-balance potential from the Wheatstone bridge, Figure IV-2, was monitored with a chart recorder (Bryans Ltd., model 2700). The sensitivities of the null-potentiometer and chart recorder were set to give $0.1\Omega \equiv 1$ cm of chart paper.

BLOCK DIAGRAM OF LKB 8700 CALORIMETRY SYSTEM

Figure IV-1

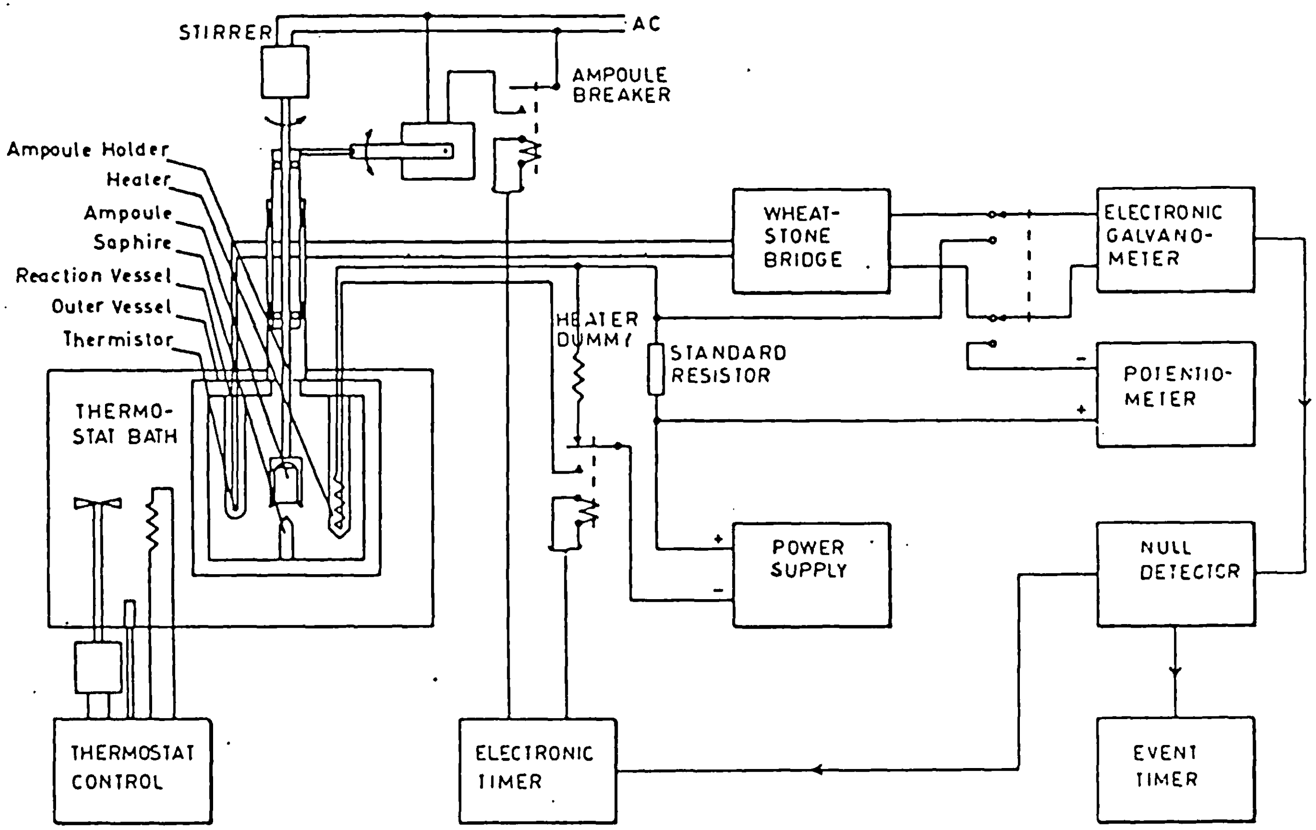


Figure IV-2

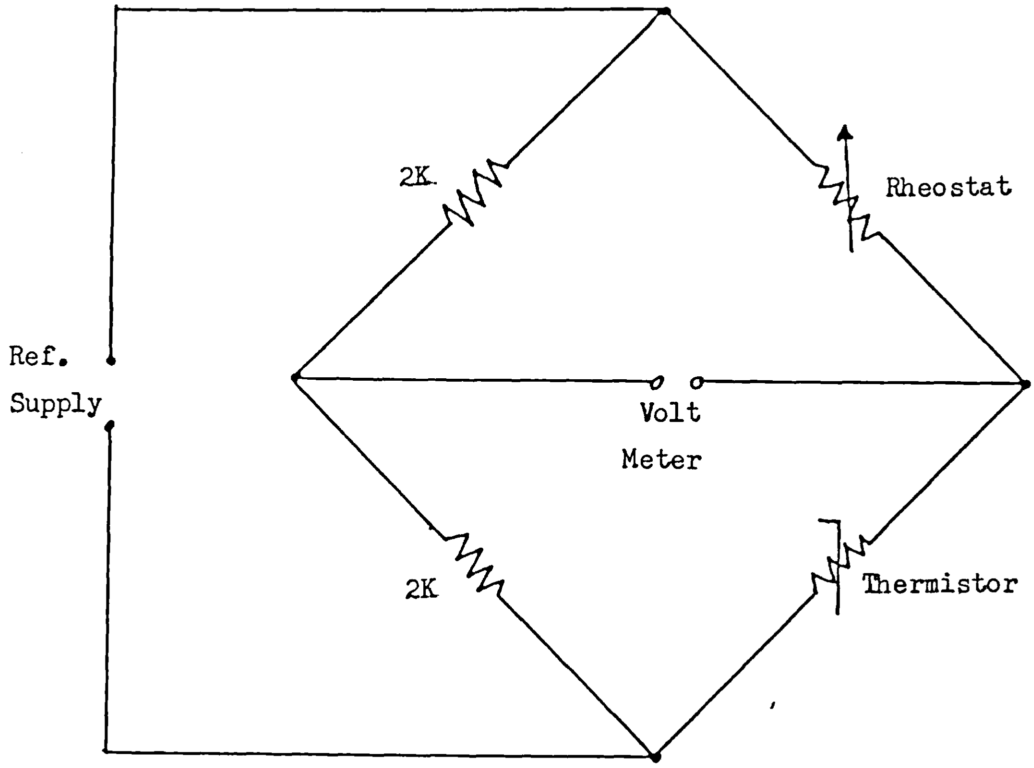


Figure IV-3

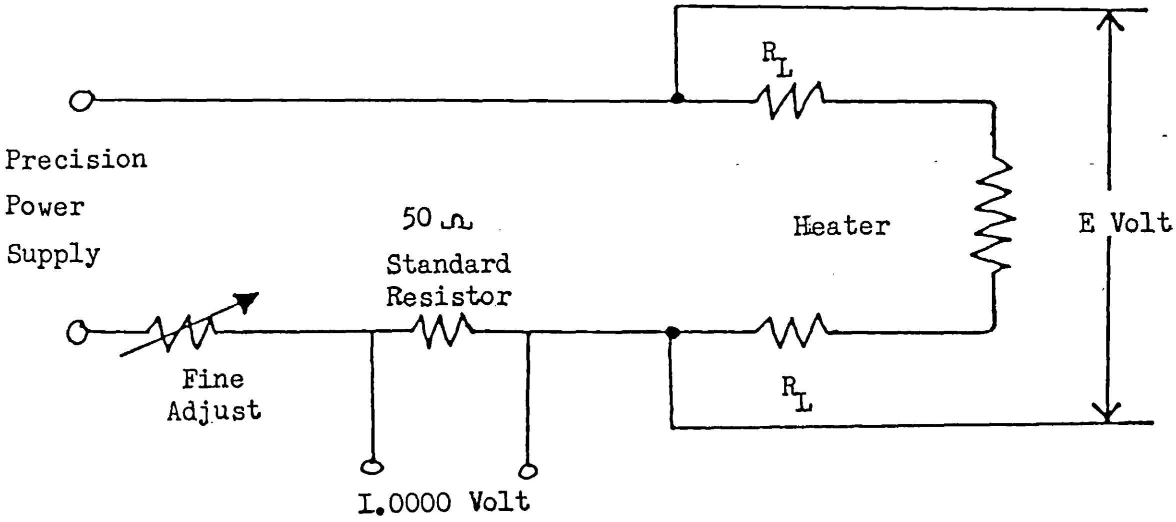


Figure IV-4

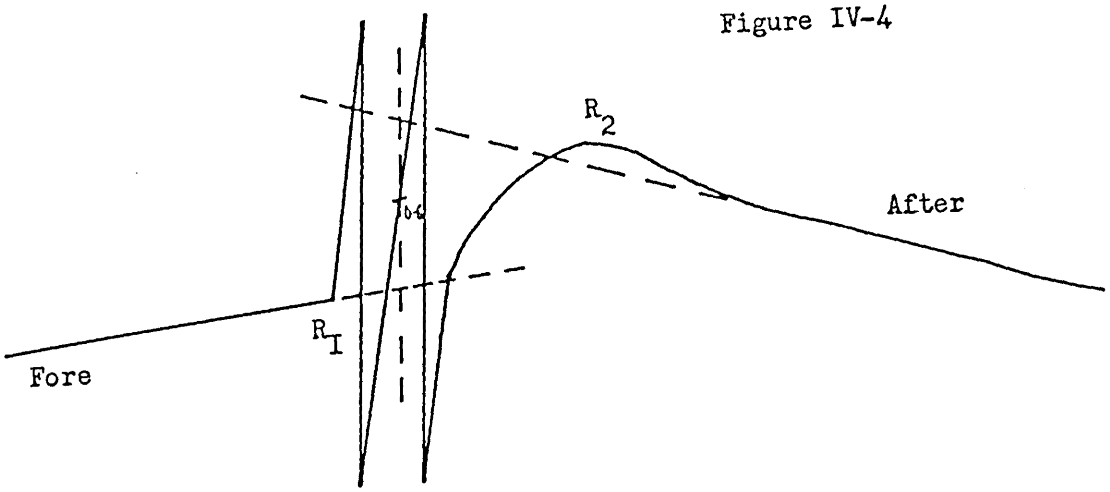
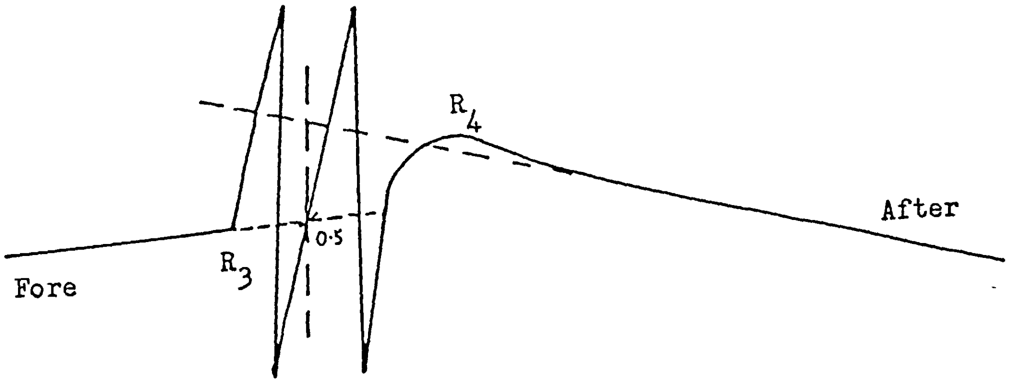


Figure IV-5



The L.K.B. 8700-1 is limited to non-precipitation reactions because of problems arising from relatively inefficient stirring within the reaction vessel. This is caused by the limitations in speed of rotation of the ampoule holder/stirrer, the flat bottomed cylindrical shape of the vessel, and the shape of the stirrer.

Figure IV-4 shows a typical results trace. To obtain a calibration trace, one of two procedures must be carried out. For a reaction giving an endothermic enthalpy change, the calibration heating is carried out after the initial reaction has taken place. For reactions yielding exothermic enthalpy changes, the calorimeter vessel content is first cooled to the initial starting temperature and then the calibration heating is performed.

The resistance of the heater was found by using the circuit shown in Figure IV-3. The current was altered to give a 1.0000 volt drop across the standard 50.00Ω resistor. Measurement of the potential drop across the heater allowed its resistance to be calculated.

For the interpretation of the output traces, Figure IV-4 and 5, two methods exist, namely the Regnault-Pfaundler method[1] and the Dickinson (Graphical) method[1,2,3,4].

IV-AIII: Dickinson's Method

This method was first developed for adiabatic systems, e.g. bomb calorimetry, but has subsequently found application with other systems, such as an isoperibol calorimeter. Application to such a system was first demonstrated by Dickenson[2], and is currently applied to such systems as the L.K.B. 8700-1 and R.H.C./J.R.P. calorimeter. In an isoperibol system, e.g. as with the solution calorimeters employed, the heat exchange with the surroundings follows Newton's cooling Law (the rate at which a body loses heat to its surroundings is proportional to the temperature difference between the body and its surroundings). The observed enthalpy change is thus not the total heat evolved from a reaction, but a fractional amount. Dickinson found that the mean temperature, T_m, for a given process would occur at 0.6 of the total enthalpy evolved, Figure IV-6. The fundamental equation on which the Dickinson correction is based is

$$\Delta T_{corr} = \Delta T_{obs} + k\int_{t_i}^{t_f} (T+T_{\infty})\,dt \qquad \text{(IV 1)}$$

where

t_i = time before start of reaction.
t_f = time after end of reaction.
T_{∞} is the equilibrium temperature of the calorimeter.
k is the cooling constant in $sec.^{-1}$

To eliminate the integral from equation IV 1, the areas of the reaction equal at a time t_m,[4].

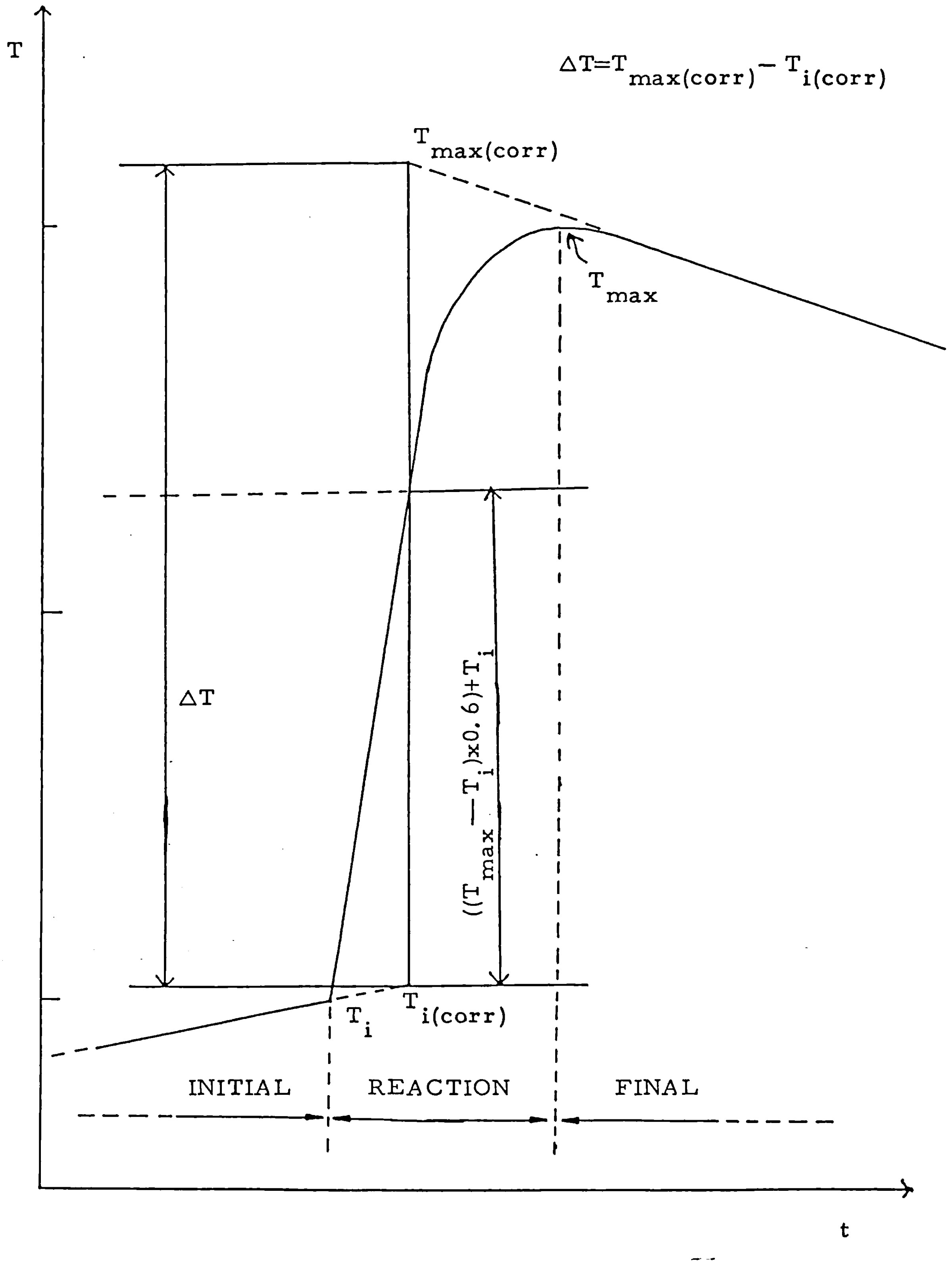
$$\int_{t_i}^{t_m} (T-T_i)\,dt = \int_{t_m}^{t_f} (T-T_f)\,dt \qquad \text{(IV 2)}$$

where

T = temperature in the main period of the reactions.
T_i= temperature at time t_i.
T_f= temperature at time t_f.

Thus when the tangents to the lines at t_i and t_f are extrapolated to t_m, the actual temperature rise is the temperature difference between the two interceptions of the tangents with the line through t_m. For the calibration, t_m is assumed to be halfway (0.5) through the heating period, as the heating process

Figure IV-6


T
$\Delta T = T_{max(corr)} - T_{i(corr)}$
$T_{max(corr)}$
T_{max}
ΔT
$((T_{max} - T_i) \times 0.6) + T_i$
T_i
$T_{i(corr)}$
INITIAL
REACTION
FINAL
t

being very nearly linear with time except for some effects of thermal lag within the system.

This method is prefered over the Regnault-Pfaundler method as it is much quicker and easier to use.

IV-AIV: Calculation Method used with L.K.B. 8700-1 Calorimeter

A more complete explanation is given by Wadsö[1]. The equation used to determine the enthalpy change during the reaction is,

$$\Delta_r H^\theta (\text{kJ mol}^{-1}) = \frac{t.M.R'_{mc}.\Delta R_c.((50\text{x}E)-0.013)}{W.R_{mc}.\Delta R'_c\text{x}10^5} \qquad \text{(IV 3)}$$

where

E = Potential drop over heater/volts.

t = Heating time/sec.

ΔR_c = Corrected resistance change of reaction (process)/ohms.

$\Delta R'_c$ = Corrected resistance change of calibration/ohms.

R_{mc} = Corrected mean resistance of reaction (process)/ohms.

R'_{mc} = Corrected mean resistance of calibration/ohms.

W = Weight of compound/g.

M = Molecular weight of compound/g.

Linearity of the thermistor resistance with temperature is assumed over small spans such as 0.2°C[4].

IV-AV: Calculation Method used with R.H.C./J.R.P. calorimeter

Unlike the L.K.B. 8700-1, this system is a twin-dewar calorimeter. The calculations are therefore somewhat different as a manual resistance change to balance the Wheatstone bridge is not required. For large enthalpy changes, the milli-volt unit is used to add a reverse voltage to oppose the bridge amplifier output. This reverse voltage has to be taken into account when calculating the corrected temperatures. The equation used to determine the enthalpy change during the reaction is

$$\Delta_r H^\theta (\text{kJ mol}^{-1}) = \frac{t.M.E.(v/10).\Delta_r T}{W.1000.\ \Delta_c T} \qquad \text{(IV 4)}$$

where

t = Heating time/sec.

M = Molecular weight of compound/g.

E = Potential drop over heater/volts.

W = Weight of compound/g.

v = Potential drop across 10Ω standard resistor/volts.

$\Delta_r T$ = Corrected output potential change of reaction/volts.

$\Delta_c T$ = Corrected output potential change of Calibration/volts.

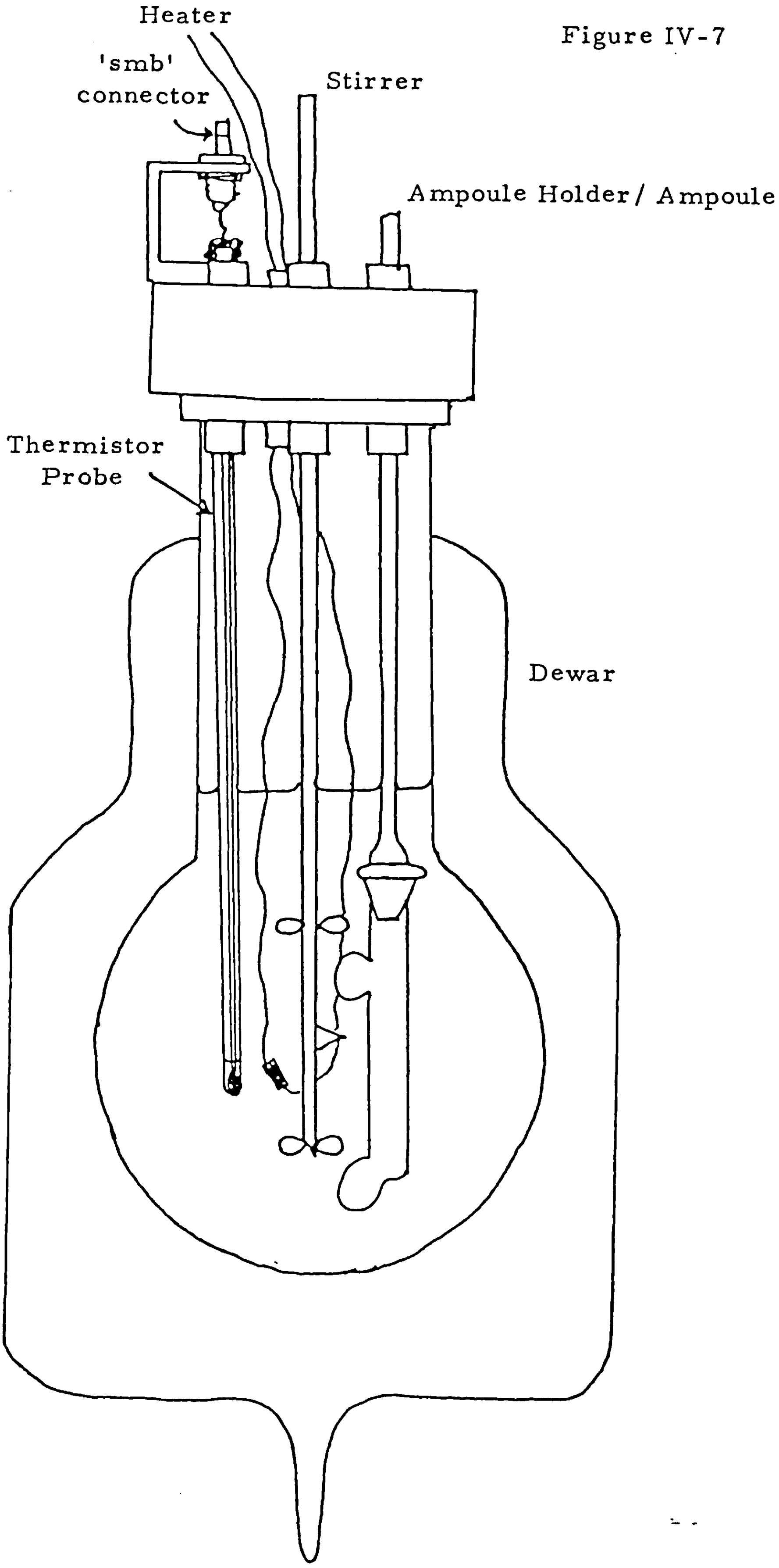
IV-AVI: Twin-dewar Calorimetry System (R.H.C./J.R.P.)

For precipitation reactions involving the metallo salts of TNR and DNR, a calorimeter was constructed by the author. The basic design of this is that used by Peake[5]. The precision of the results obtainable from the original-design was improved by re-designing and installation of more advanced technology systems. A brief explanation of the calorimeter system and improvements over the original design follows.

IV-AVIa: Calorimeter Vessel

The calorimeter vessel is of a borosilicate glass Dewar type construction[6] of internal capacity 100 cm^3, Figure IV-7. An aluminium screw fitted cap is located on the top of the vessel via threaded aluminium flange bonded to the neck of the vessel. This cap not only allows access to the vessel contents, but also acts as holder for the thermistor phrobe, vessel contents stirrer and sample ampoule. The cap has further been modified with an insulated bracket to hold the thermistor leads and eliminate earth loops on the Wheatstone bridge pick-ups. Stirring of the vessel contents is via a precision-bore glass tube and rod (3mm diameter). Two sets of contrary-pitch propeller blades and ampoule breaking spike are attached to the rod. Rotation of the shaft at a constant speed was

Figure IV-7


Heater
'smb'
connector
Stirrer
Ampoule Holder/ Ampoule
Thermistor
Probe
Dewar

achieved by a pair of a servo-controlled motors, (Electrocraft Corporation type E552-MG with E552-U Control unit; E550-MG and E550-O motor and control box was used for reference vessel). The reaction vessel and reference stirring rotation were synchronised using the control units and a stroboscope.

The stroboscope was later replaced by a device designed and constructed by the author, Figure IV-8, that worked on the principal of counting the reflections from an infrared probe with a phototransistor. The current which flows when the transistor gate is opened triggers a set of three digital integrators and displays, which record the number of reflections. The sample time-span is measured using a single monolithic integrated circuit (ZN1034) which utilises a digital technique of an internal oscillator and external resistor/capacitor (high tolerance components) to provide a precise timing interval of one minute. After one minute the timer deactivates the light emitting diode and thus freezes the counting sequence. Care has to be taken to shield the detector (phototransitor) as this is still active. The timer and counter are reset by a single low pulse via a push button. Selection of the components for the external timing circuit of ZN1034 was via use of the equation:

$$T=K.R_tC_t \qquad (IV\ 5)$$

where

T = time period/seconds.
R_t = External resistor/ohms.
C_t = External capacitor/farads.
K = 2727.273

A good reflective surface was made by painting half the end of the motor shaft white and, to contrast this, the other half black.

The thermistors (YSI44011, 100KΩ @ 25^oC) were immersed in

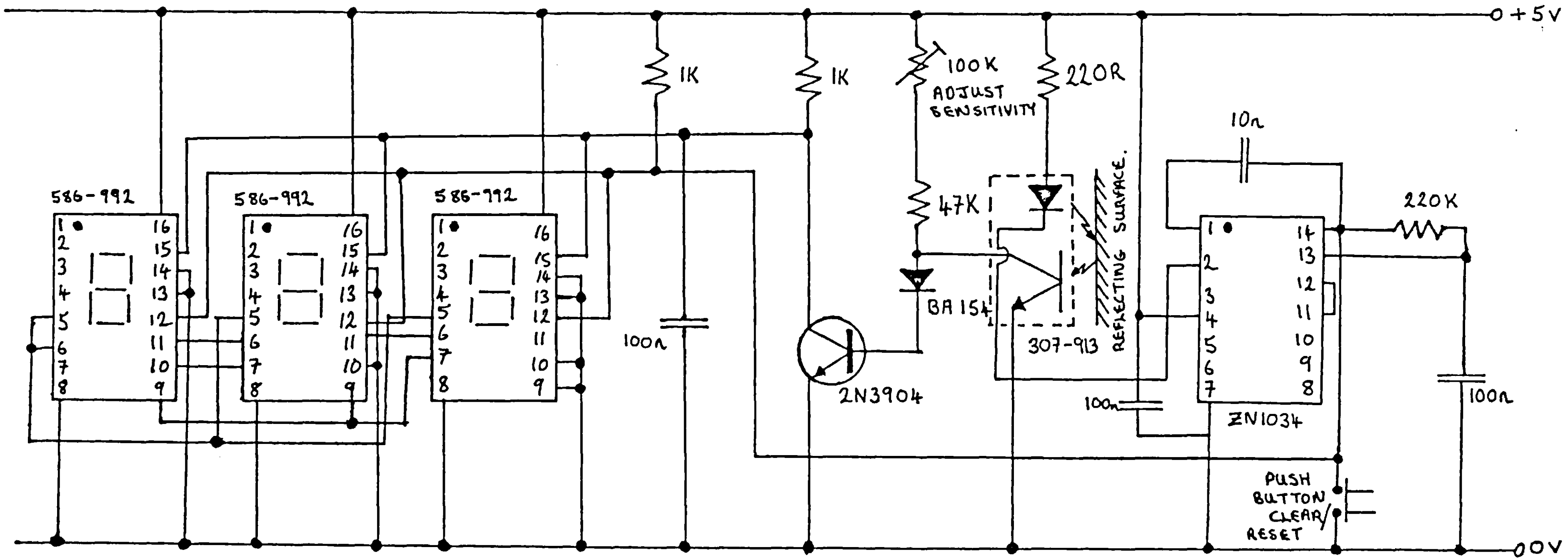

+5V
0V
586-992
586-992
586-992
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
1K
1K
100n
100K
ADJUST SENSITIVITY
220R
47K
BA 154
2N3904
307-913
REFLECTING SURFACE.
10n
100n
ZN1034
220K
100n
PUSH BUTTON CLEAR/RESET

Figure IV-8

a drop of silicone oil (MS200) contained in a very thin-walled glass tube. The thermistor connections were soldered to 'smb' bulkhead connectors (Radio Spares (RS) components 456-324) which were fitted via insulated collars to the bracket. The thermistor tubes were sealed with a silicone rubber compound (RS 555-588).

The ampoule and ampoule-holder assembly consisted of a rod (3mm precision glass) fitted with a B5 cone joint. The ampoules had two fracture bulbs, both being formed on the same side of the ampoule to aid vessel loading.

The reaction vessel and the reference vessel were immersed in a thermostatically-controlled tank, with baffled corners to eliminate hot spots.

IV-AVIb: Water Bath

The water contents of the tank was maintained at 25.0°C by use of a proportional heater control (Tronac Inc., Provo, Utah, model PTC-1000), with 5A mains filter (RS 238-390) and a chiller circulator unit (Churchill).

IV-AVIc: Heater Calibration Circuit

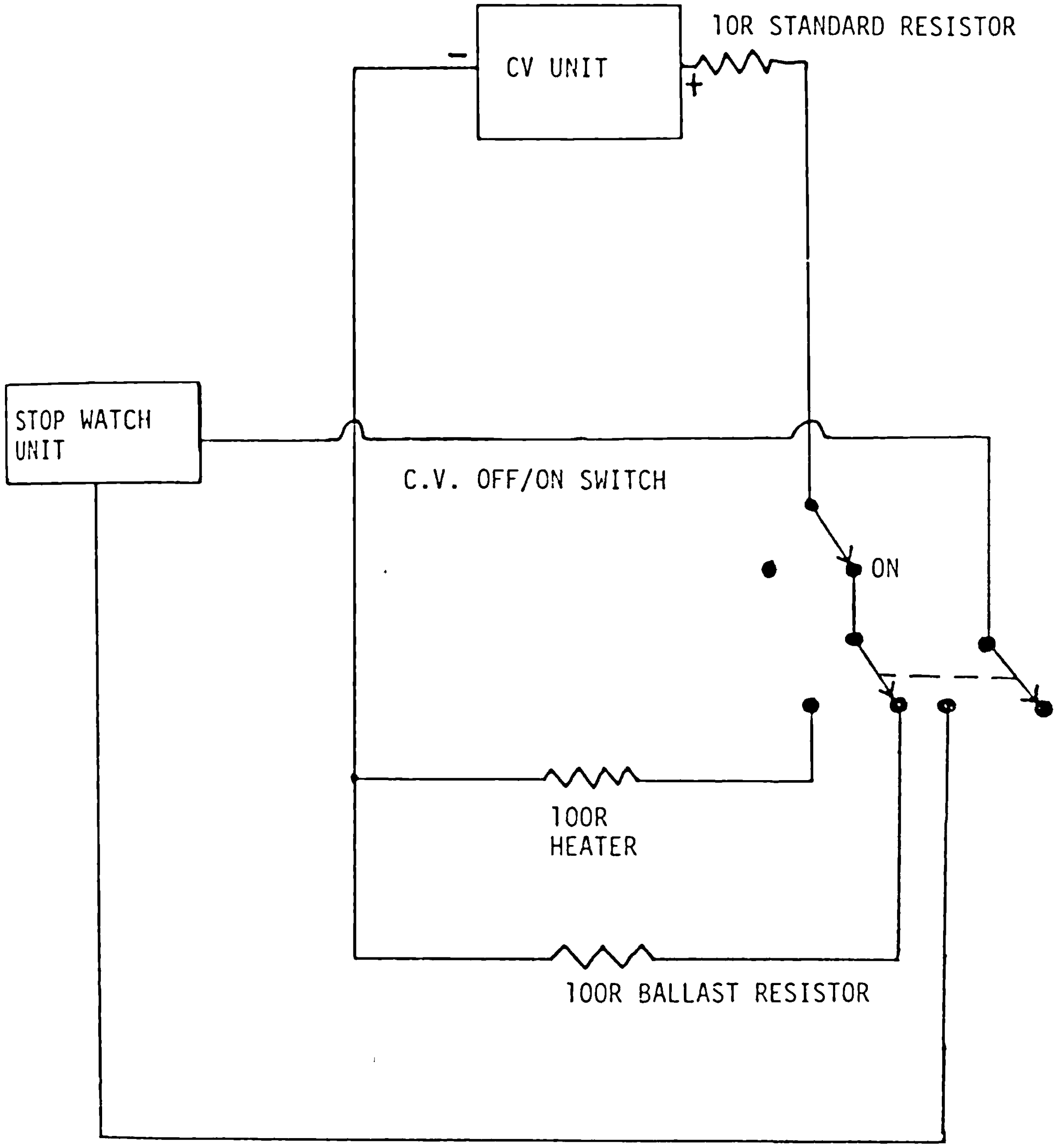
The vessel calibration heater circuit was totally re-designed to remove mains switch spikes which could cause noise in the differential A.C. bridge circuits in the previous design of mechanical timer switches. The clock circuit consists of three sections. The ballast resistor (100Ω) was a novel introduction to the system. A slight fault inherent in the previous design was that when the heater was activated, a current was suddenly drawn from the constant voltage unit (Ether Ltd.,6V.) resulting in a slight momentary drop in the voltage supplied. This problem was eliminated by having the ballast resistor act as a dummy heater. The resistor used was carefully selected to be of the highest tolerance and nearest resistance to that of the heater. Thus the constant voltage unit delivered the same current and voltage irrespective of the heater or ballast resistor being selected. The general lay-out of the heater circuit is shown in Figure IV-9. All the parts of this circuit are contained in one box, except the chip heater (Tronac R24, 100Ω) and the constant voltage unit. A separate power supply unit suitable for the C-MOS working voltage was designed, Figure IV-10.

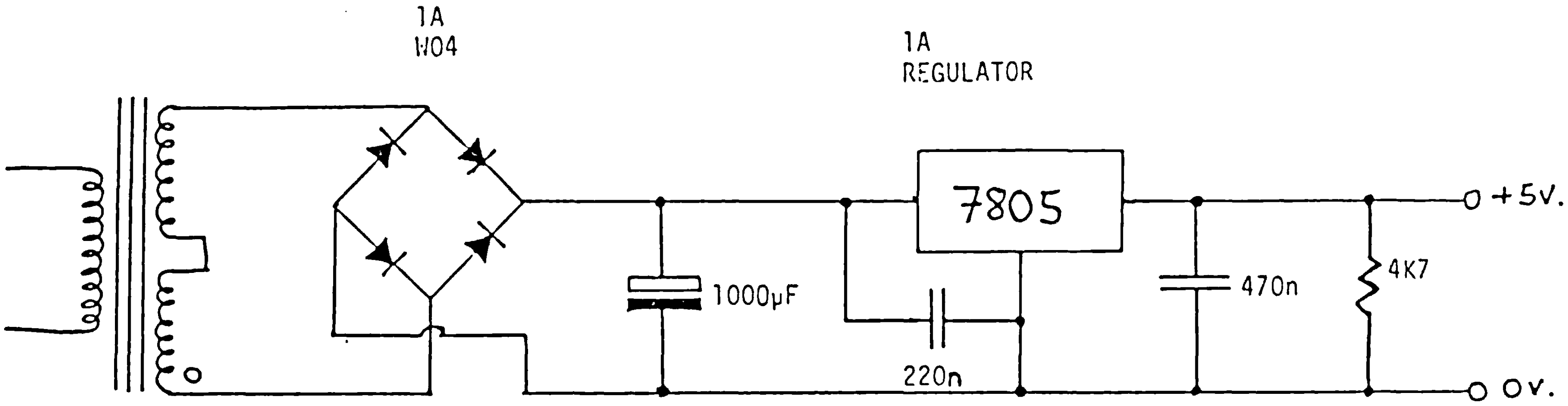
For the latching of the clock circuit, Figure IV-11, the original idea was to use a single 74LS123 integrated circuit, Figure IV-12. The problem experienced with this system was contact-bounce on the activation switch. The clock latch needed a high-low-high sequence to stop or start, and a suitable output was finally obtained by using a pair of SN74121 integrated circuits, and one SN7400, Figure IV-13. The first SN74121 is set to activate on a positive input, and the second on a negative input. The SN7400 NAD gate combines the output of the two SN74121's to give one pulse. The C-MOS and the 74 series integrated circuits were all de-coupled to earth.

IV-AVId: Bridge Circuit

Temperature changes within the vessels were detected by the thermistors, which are connected to a differential A.C. thermistor bridge (Carwyn Instruments type 401B)[7,8] via double-screened miniature co-axial leads (RS 367-280). The design has been further changed such that the voltage is measured through screened leads with a digital voltmeter (Solatron), across the heater plus the lengths of fine connecting wires. This has been done as the connecting wires have also a heating effect on the calorimeter contents. For the output stage of the bridge, it was found necessary to design and build a back-off unity gain amplifier, Figure IV-14, to insert between the thermistor bridge and chart recorder (Philips PM8251); The back-off is made possible by using

Heater Circuit Figure IV-9



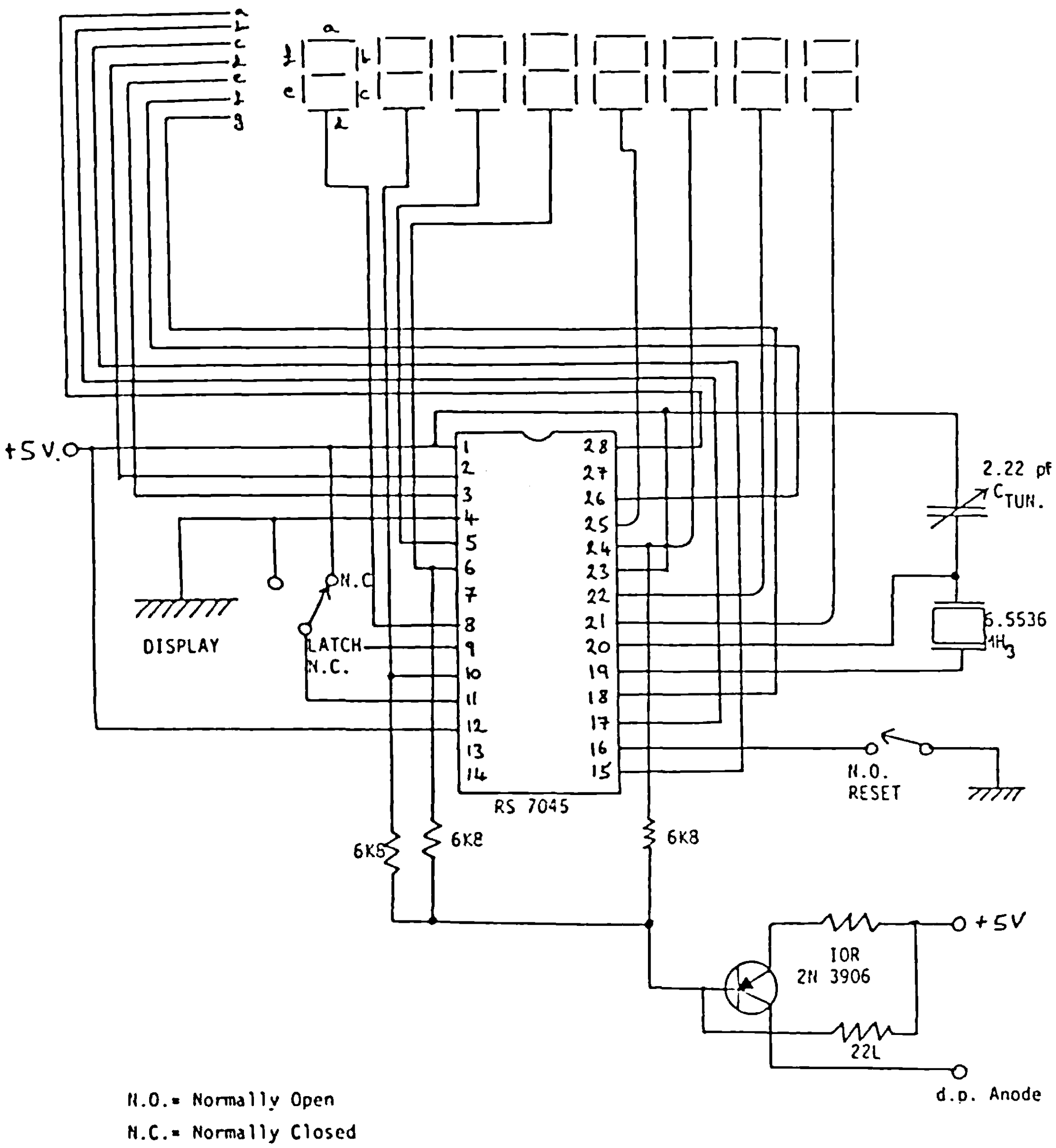


+5v Regulated Power supply unit

Figure IV-10

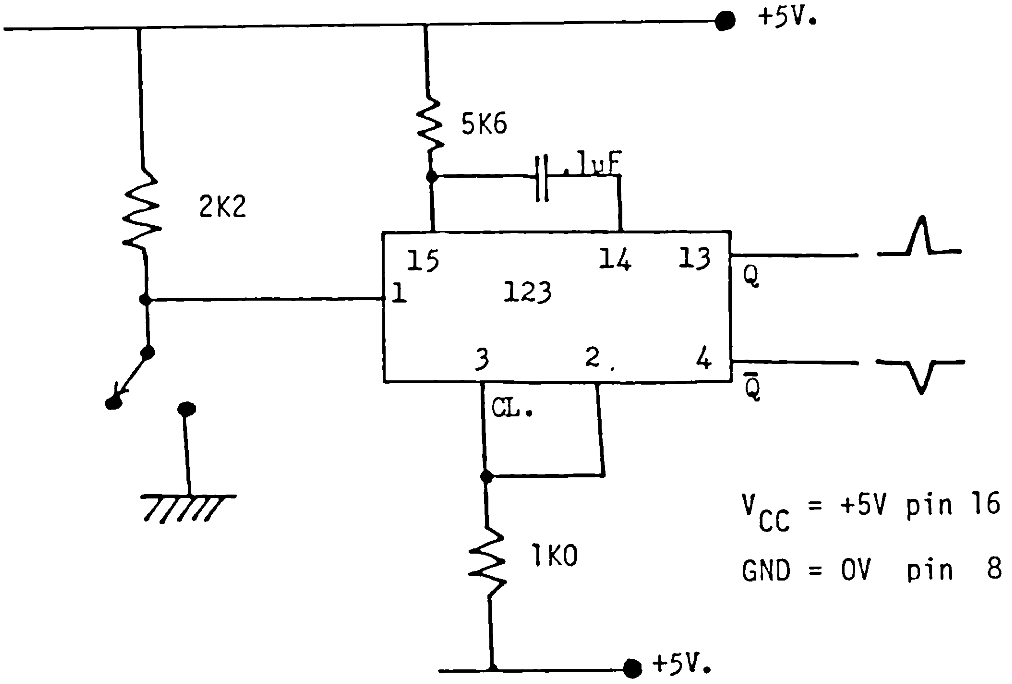
Figure IV-11

The Clock circuit Common Cathode LED's



Clock Latch Circuits

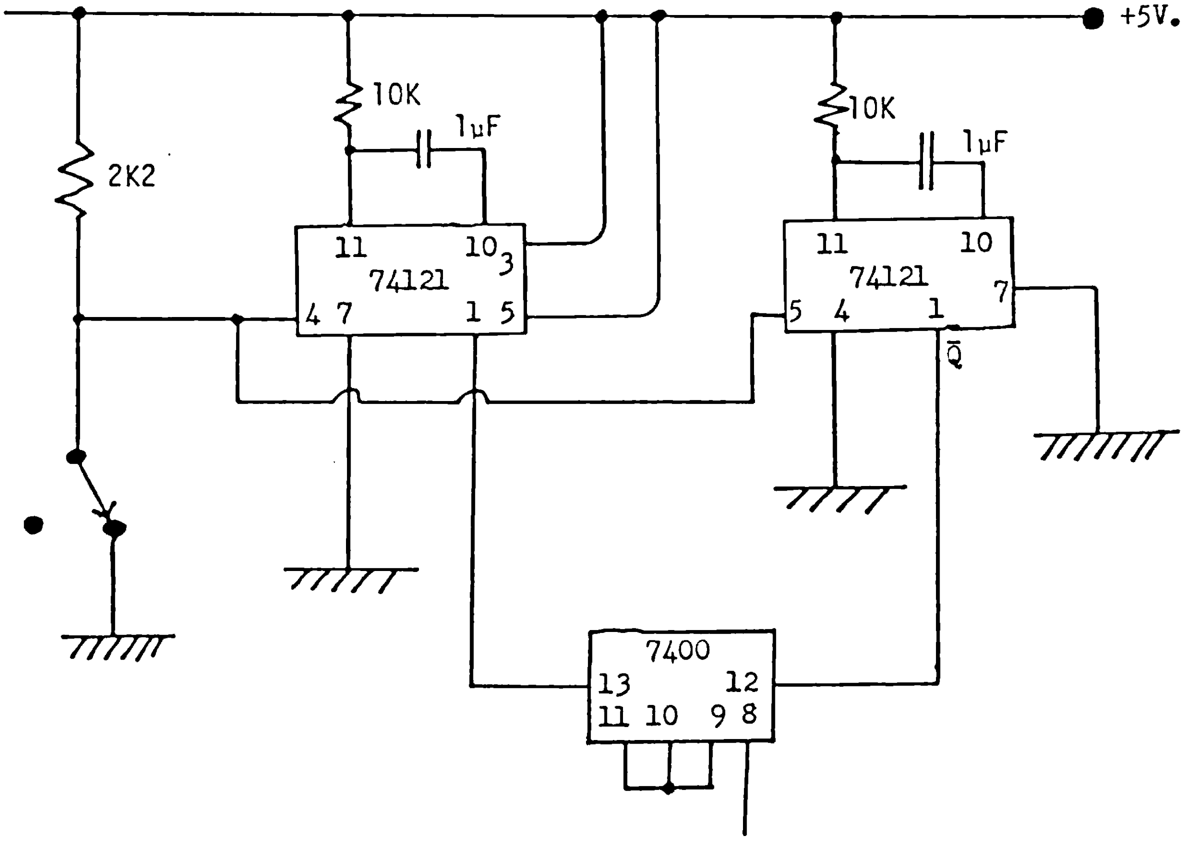
Figure IV-12



V_{CC} = +5V pin 16

GND = 0V pin 8

Figure IV-13



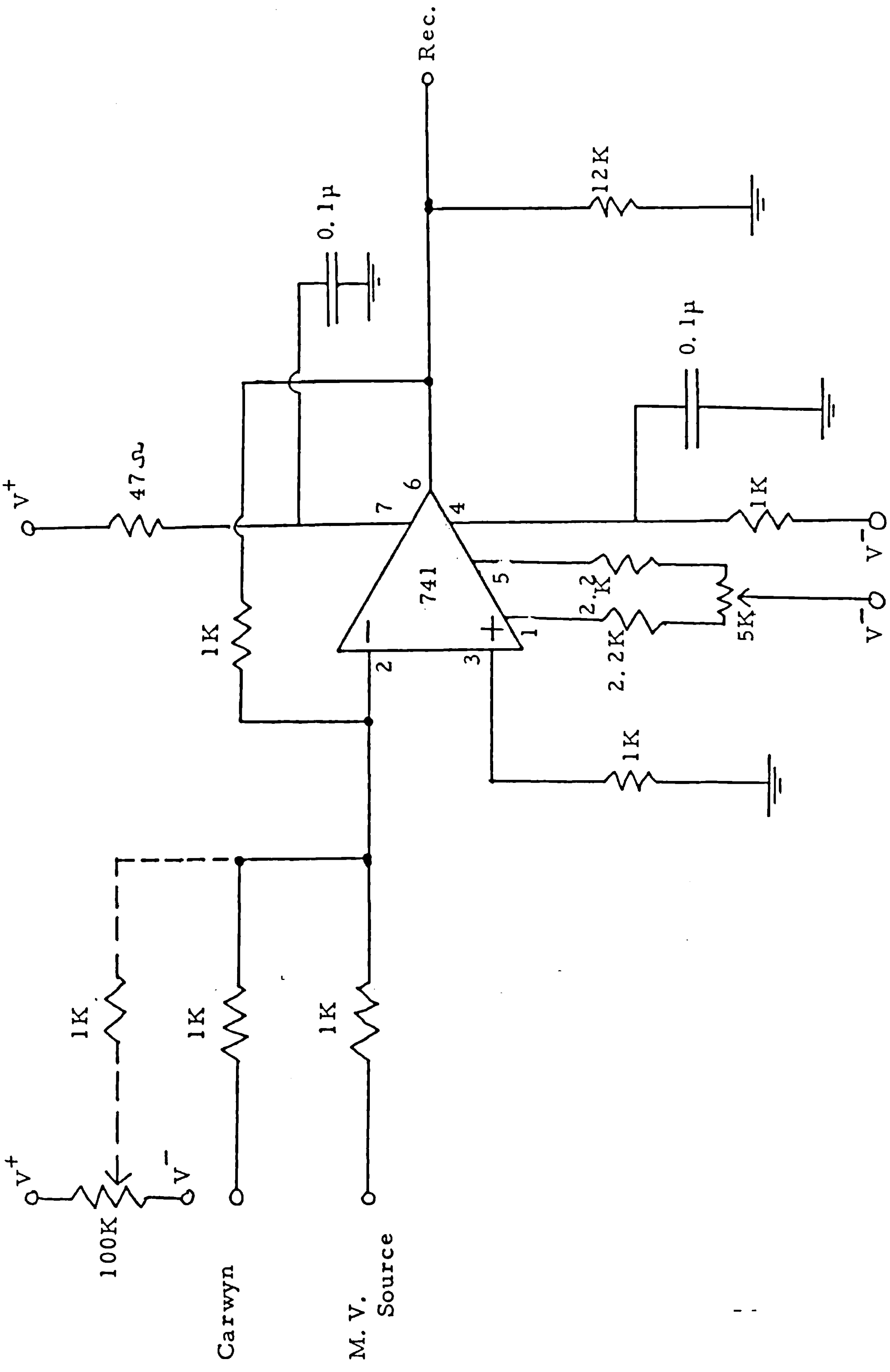

Rec.
12K
0.1μ
0.1μ
V^+
47Ω
7
6
4
1K
V^-
741
5
2.2K
2.2K
5K
V^-
1
2
3
1K
1K
1K
1K
1K
V^+
V^-
100K
Carwyn
M. V. Source

Figure IV-14

a multi-volt (mV) source (Time Electronics Ltd. 404S), and the option of a 100KΩ potentiometer on the input stage allows a further back-off if needed. A separate power supply unit was designed and built for the amplifier, Figure IV-15. The thermistor bridge, amplifier power supply unit and chart recorder, were all fitted with mains filters (RS 238-407).

The other major component used in the system was an oil-filled 10Ω standard resistor (Croydon Precision Instruments Co., type R.S.I. ±0.005%) which provided a potential to measure the total current flow in the circuit.

The process being studied was initiated by breaking the two-bulb ampoule on the stirrer spike and the bottom of the vessel, the process being monitored on the chart recorder and any back-off being added and noted as required.

IV-AVII: Test Reaction

The normal procedure for checking satisfactory operation of the calorimeter is to measure the heat of solution of tris (hydroxymethyl)methylamine (THAM or TRIS, B.D.H. Aristar grade, Min. 99.9%) $(HOCH_2)_3CNH_2$ in an excess of either aqueous hydrochloric acid (0.100M, B.D.H.;A.V.S.) for an exothermic change, or aqueous sodium hydroxide (0.050M, B.D.H.;A.V.S.) for an endothermic change. The use of THAM as an analytical standard was first proposed by Fossum et al[9], and the use as a test reaction in a solution calorimeter proposed by Irving and Wadsö[10] in 1964. Prior to use, the THAM was ground to a very fine powder using an agate mortar. The THAM was then annealed for 3h in an oven at $80^{o}C$ before being allowed to cool in a vacuum desiccator over silica gel. This annealing has been found necessary[11] to release significant amounts of energy (40 to 90 J mol^{-1}) stored in the solid as a result of crushing and grinding. The enthalpy of solution of THAM in hydrochloric acid (0.1M), or in sodium hydroxide

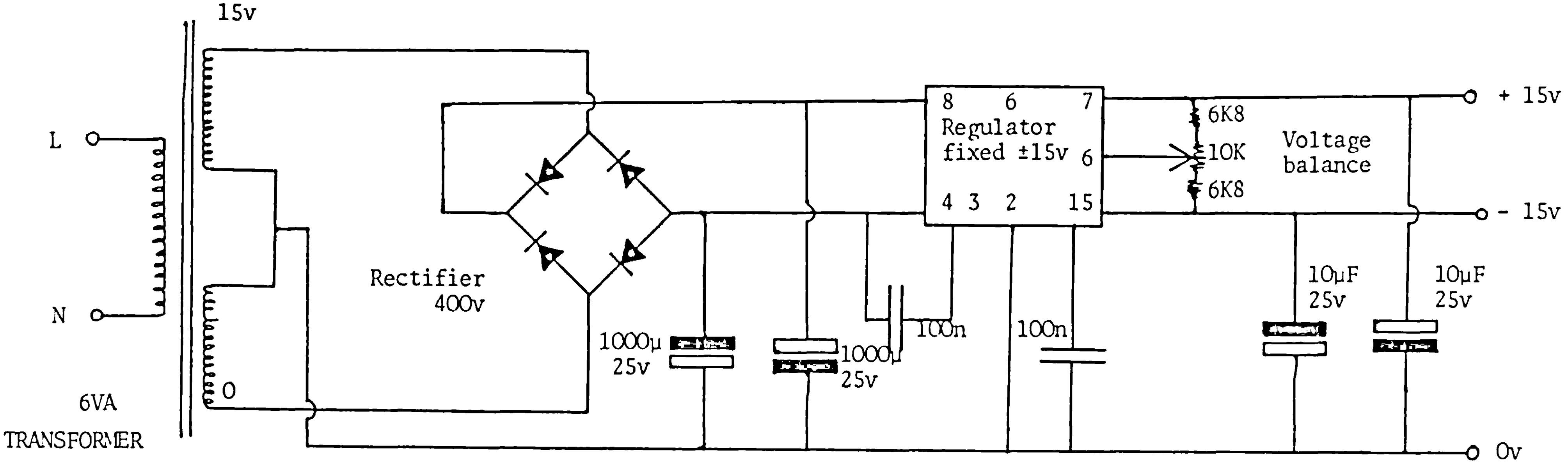


Figure IV-15 ± 15 volt Power Supply Unit.

(0.05M), was then determined using the calorimeter, and the results obtained were compared with literature results[12]. The results obtained are shown in Tables IV-3 and IV-4.

According to the specification of the A.C. bridge circuit a temperature discrimination of better than 2 x 10^{-5} ^{o}C is obtainable. It was found that a temperature difference of upto 1.0 x 10^{-4} ^{o}C could be recorded on the chart recorder. A temperature change of $\sim$5 x 10^{-3} ^{o}C for a reaction is normal.

IV-AVIII: Enthalpy of Solution of Lead Nitrate in Water

The enthalpy of solution, $\Delta_{sol}H^{\theta}$, of lead nitrate (B.D.H., A.R., re-crystallised from water) was measured using the L.K.B. 8700-1 calorimetric system, the performance of which was checked using the enthalpy of neutralisation, $\Delta_{N}H^{\theta}$, of tris (hydroxymethyl)methylamine (THAM) in excess of HCl(0.1 mol dm^{-3}) and in NaOH (0.05 mol dm^{-3}) as test reactions. THAM in 0.1M HCl $\Delta_{N}H^{\theta}= -29.88\pm0.014$ kJ mol^{-1}(lit.[12] $\Delta_{N}H^{\theta}= -29.790 \pm0.031$ kJ mol^{-1}

THAM in 0.05M NaOH $\Delta_{N}H^{\theta}= +17.185\pm0.005$ kJ mol^{-1}.

(lit.[13] $\Delta_{N}H^{\theta}= +17.189\pm0.005$ kJ mol^{-1}).

The calorimetric results obtained are shown in Table IV-5.

IV-BI: Solution Calorimetry of Lead Styphnate

A suitable reaction had to be found which would be fast and give rise to a reasonable change in enthalpy. Several common acids were used to try and find a suitable reaction condition. Nitric and perchloric acids were found to be most favourable. A range of dilutions of nitric acid was considered, but due to the limited solubility of styphnic acid in acidic media, (ca. $<3\times10^{-3}$ mol dm^{-3}) a more dilute concentration was used. This use of dilute nitric acid (0.05M) did reduce the rate of the reaction with the lead styphnate, but did allow for the solubility of styphnic acid.

The following reaction [A] was tried,

$$\begin{tikzcd}
(C_6H(NO_2)_3O_2)Pb.Pb(OH)_{2,s}+(n+4)HNO_{3,aq} \arrow[r, "{[A]}"] & {[C_6H(NO_2)_3+2Pb(NO_3)_2+2H_2O+HNO_3]_{n,aq}} \\
C_6H(NO_2)_3(OH)_{2,s}+2Pb(NO_3)_{2,aq}+HNO_{3,aq} \arrow[u, "{[C]}"] \arrow[ur, "{[B]}"'] &
\end{tikzcd}$$

The ultra-violet absorption spectrum (400 to 240 nm) of the chemical products from the reactions [A] and [B] was measured; the results indicated that the aqueous solutions obtained were identical.

Reaction [A] gave a satisfactory enthalpy change (−33.95 ±1.68 kJ mol^{-1}), although when the enthalpy of solution of styphnic acid in an aqueous lead nitrate/nitric acid solution was measured [B], the enthalpy was found to be too small to be accurately measured. The concentration of the styphnic acid could not be increased due to solubility problems, and the sensitivity of the instrument could not be increased due to noise problems. So the reaction was abandoned in preference to another.

This new reaction consists of using a pre-saturated solution of styphnic acid in nitric acid, the styphnate being placed in an ampoule which is broken at the relevent time.

$$HNO_{3,aq}+\text{Normal Lead Styphnate}_{,s} \xrightarrow{\Delta_r H^\theta} Pb(NO_3)_{2,aq}+\text{Styphnic Acid}_{,s}$$

A quantitative analysis was performed on the products to confirm complete reaction. This was done by extracting twice with chloroform (A.R.; 100 cm^3) the product mixture. The resulting nitric acid solution was then tested for the metal ion. The results are shown in Table IV-1.

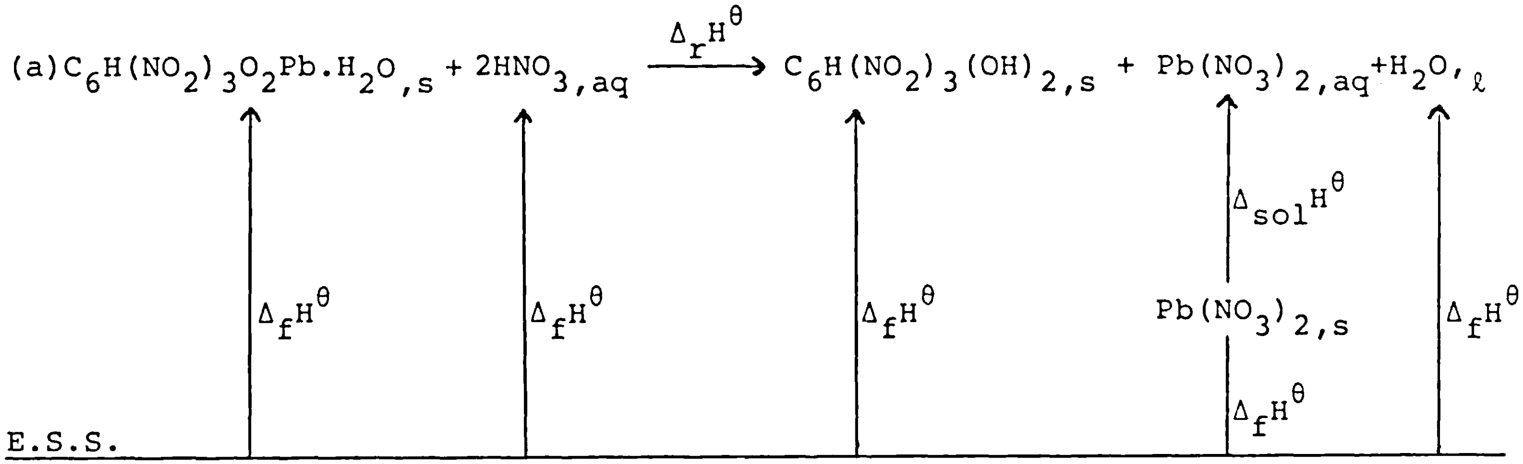
IV-BII: Enthalpy of Reaction of Normal Lead Styphnate (a)

The enthalpy of reaction, $\Delta_r H^\theta$, of normal lead styphnate monohydrate was measured using the R.H.C./J.R.P. calorimeter. Only one mole of aqueous lead nitrate is produced, unlike monobasic lead styphnate, which gives rise to two moles of aqueous lead nitrate. Tribasic lead styphnate produces four moles, and pentabasic lead styphnate produces six moles of lead nitrate.

The reaction for normal lead styphnate gave a small exothermic enthalpy change; results are shown in Table IV-6. For the calculation of the enthalpy of formation of the styphnate, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and enthalpies of formation of water, styphnic acid, and (0.1N) nitric acid.

IV-BIII: Direct measurement of the enthalpy of solution of Lead Nitrate in Nitric Acid/Styphnic Acid mixture

The enthalpy of solution, $\Delta_{sol}H^\theta$, of lead nitrate (B.D.H.,A.R., re-crystallised from water) was measured using the L.K.B. 8700-1



E.S.S. = Elemental Standard State

Table IV-1

Analysis results for the metal ion produced in various calorimetric reactions

	Calc. %	Found %
Normal lead styphnate monohydrate	44.24	(a) 44.22 (b) 44.24
Monobasic lead styphnate	59.93	(a) 59.85 (b) 59.90
Tribasic lead styphnate dihydrate	74.81	(a) 74.79 (b) 74.89
Pentabasic lead styphnate dihydrate	76.72	(a) 76.77 (b) 76.70
Silver styphnate	45.24	(a) 45.20 (b) 45.28
Thallous styphnate	37.50	(a) 37.47 (b) 37.55
Thallous styphnate	62.71	(a) 62.70 (b) 62.75
Barium styphnate monohydrate	34.47	(a) 34.40 (b) 34.45

Analysed metal ion underlined[17,18,19].

calorimeter. A solution of nitric acid (B.D.H.,0.1M A.V.S.) saturated with styphnic acid was made, the ampoule contained the lead nitrate, $[\mathrm{HNO_3} + \text{styphnic acid (sat)}]_{,aq} + \mathrm{Pb(NO_3)_{2,s}}$

$$\xrightarrow{\Delta_{sol}H^{\theta}} [\mathrm{HNO_3} + \text{styphnic acid (sat)} + \mathrm{Pb(NO_3)_2}]_{,aq}$$

The calorimetric results obtained are shown in Table IV-7.

IV-BIV: Enthalpy of Formation of Normal Lead Styphnate Monohydrate

From the enthalpies of reaction obtained for normal lead styphnate monohydrate, and using appropriate ancillary data, the enthalpy of formation was calculated.

Ancillary data: The following data were used.

$\Delta_f H^{\theta}[\mathrm{H_2O}_{,\ell}] = -285.83 \pm 0.04$ kJ mol^{-1} [14]

$\Delta_f H^{\theta}[\mathrm{C_6H(NO_2)_3(OH)_{2,s}}] = -443.93 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^{\theta}[\mathrm{Pb(NO_3)_{2,s}}] = -440.66 \pm 0.84$ kJ mol^{-1} [15]

$\Delta_{sol} H^{\theta}[\mathrm{Pb(NO_3)_{2,aq}}] = 24.49 \pm 0.09$ kJ mol^{-1} [Section IV-BIII]

$\Delta_f H^{\theta}[\mathrm{(0.1M)HNO_{3,aq}}] = -206.97 \pm 0.04$ kJ mol^{-1} [16]

Thermochemical equation,

$$\text{(a)} \quad \Delta_f H^{\theta}[\mathrm{C_6H(NO_2)_3O_2Pb.H_2O_{,s}}] = \Delta_f H^{\theta}[\mathrm{C_6H(NO_2)_3(OH)_{2,s}}] + \Delta_{sol} H^{\theta}[\mathrm{Pb(NO_3)_{2,aq}}] + \Delta_f H^{\theta}[\mathrm{Pb(NO_3)_{2,s}}] - \Delta_f H^{\theta}[\mathrm{HNO_{3,aq}}] + \Delta_f H^{\theta}[\mathrm{H_2O}_{,\ell}] - \Delta_r H^{\theta}$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3O_2Pb.H_2O_{,s}]$

$= [-443.93] + [24.49] + [-440.66] + [-285.83]$

$- [-206.97]$

$= \underline{\underline{-714.70\pm1.17 \text{ kJ mol}^{-1}}}$

IV-BV: Enthalpy of Reaction of Monobasic Lead Styphnate (b)

The enthalpy of reaction, $\Delta_r H^\theta$, of monobasic lead styphnate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction was the same as that for normal lead styphnate monohydrate. This gave rise to an exothermic enthalpy change, the results of which are shown in Table IV-8. For the calculation of the enthalpy of formation of the monobasic lead styphnate, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of styphnic acid; water, and (0.1N) nitric acid.

IV-BVI: Enthalpy of Formation of Monobasic Lead Styphnate

From the enthalpy of reaction of monobasic lead styphnate, and various ancillary data, the enthalpy of formation of the styphnate was calculated.

Ancillary data: The following data were used.

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83\pm0.04 \text{ kJ mol}^{-1}$[14]

$\Delta_f H^\theta[(0.1N)HNO_{3,aq}] = 206.97\pm0.04 \text{ kJ mol}^{-1}$[16]

$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] = -443.93\pm0.78 \text{ kJ mol}^{-1}$[Section III-E]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66\pm0.84 \text{ kJ mol}^{-1}$[15]

$\Delta_{sol}H^{\theta}[Pb(NO_3)_{2,aq}] = +24.49 \pm 0.09$ kJ mol^{-1}[Section IV-BIII]

Thermochemical equation,

$$\begin{aligned}(b)\quad \Delta_f H^{\theta}[C_6H(NO_2)_3(OPbOH)_{2,s}] &= \Delta_f H^{\theta}[C_6H(NO_2)_3(OH)_{2,s}] \\ &+ 2\Delta_f H^{\theta}[Pb(NO_3)_{2,s}] + 2\Delta_{sol}H^{\theta}[Pb(NO_3)_{2,aq}] \\ &+ 2\Delta_f H^{\theta}[H_2O_{,\ell}] - \Delta_r H^{\theta} - 4\Delta_f H^{\theta}[HNO_{3,aq}]\end{aligned}$$

Calculation of $\Delta_f H^{\theta}[C_6H(NO_2)_3(OPbOH)_{2,s}]$

$$= [-443.93] + 2[24.49] + 2[-285.83] - [-61.92] - 4[-206.97]$$

$$= -957.53 \pm 1.87 \text{ kJ mol}^{-1}$$

IV-BVII: Enthalpy of Reaction of Tribasic Lead Styphnate (c & d)

The enthalpy of reaction of tribasic lead styphnate dihydrate (d) was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for normal lead styphnate. This gave rise to an exothermic enthalpy change, the results of which are shown in Tables IV-9 and IV-10. Compound (c) was suspected of being monobasic lead styphnate from analysis results both by PERME and RHC. For the calculation of the enthalpy of formation of the tribasic lead styphnate (d), the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpies of formation of styphnic acid, water (1.0N) nitric acid.

IV-BVIII: Enthalpy of Formation of Tribasic Lead Styphnate

From the enthalpy of reaction of tribasic lead styphnate and various ancillary data, the enthalpy of formation of the metal styphnate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O,_\ell] = -285.83\pm0.04$ kJ mol^{-1} [14]

$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] = -443.93\pm0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66\pm0.84$ kJ mol^{-1} [15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.49\pm0.09$ kJ mol^{-1}[Section IV-BIII]

$\Delta_f H^\theta[(0.1N)HNO_{3,aq}] =-206.97\pm0.04$ kJ mol^{-1} [16]

$\Delta_f H^\theta[(1.0N)HNO_{3,aq}] =-206.85\pm0.03$ kJ mol^{-1} [16]

Thermochemical equations.

(c) $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_{2,s}] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$

$+ 2\Delta_f H^\theta[Pb(NO_3)_{2,s}] + 2\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}]$

$+ 2\Delta_f H^\theta[H_2O,_\ell] - \Delta_r H^\theta - 4\Delta_f H^\theta[HNO_{3,aq}]$

(d) $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O,_s] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$

$+ 4\Delta_f H^\theta[Pb(NO_3)_{2,s}] + 4\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}]$

$+ 6\Delta_f H^\theta[H_2O,_\ell] - \Delta_r H^\theta - 8\Delta_f H^\theta[HNO_{3,aq}]$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_{2,s}]$

$= [-443.93] + 2[24.49] + 2[-285.83] - [-60.52]$

$- 4[-206.97] + 2[-440.66]$

$= \underline{\underline{-958.13\pm1.95 \text{ kJ mol}^{-1}}}.$

($\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_{2,s}] = -957.53 \pm 1.87$ kJ mol^{-1}
[Section IV-BVI])

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O_{,s}]$

$$= [-443.93] + 6[-285.83] + 4[24.49] + 4[-440.66]$$

$$- 8[206.85] - [-196.37]$$

$$= \underline{\underline{-1972.42 \pm 3.48 \text{ kJ mol}^{-1}}}$$

Calorimetry of compound (c) confirms the analysis results that the preparation gave monobasic lead styphnate only.

IV-BIX: Enthalpy of Reaction of Pentabasic Lead Styphnate Dihydrate (e)

The enthalpy of reaction of pentabasic lead styphnate dihydrate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for the normal lead styphnate. This gave rise to an exothermic enthalpy change, the results of which are shown in Table IV-11. For the calculation of the enthalpy of formation of the lead styphnate, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of styphnic acid, water and (1.0N) nitric acid.

IV-BX: Enthalpy of Formation of Pentabasic Lead Styphnate

From the enthalpy of reaction of pentabasic lead styphnate dihydrate and various ancillary data, the enthalpy of formation of the styphnate was calculated.

Ancillary data: The following data were used.

$\Delta_f H^\theta[H_2O,_\ell] = -285.83 \pm 0.04$ kJ mol^{-1} [14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66 \pm 0.84$ kJ mol^{-1} [15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.49 \pm 0.09$ kJ mol^{-1} [Section IV-BIII]

$\Delta_f H^\theta[C_6H(NO_3)_2(OH)_{2,s}] = -443.93 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[(1.ON)HNO_{3,aq}] = -206.85 \pm 0.03$ kJ mol^{-1} [16]

Thermochemical equation,

(e) $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_2 4PbO.2H_2O_{,s}] =$

$$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] + 6\Delta_f H^\theta[Pb(NO_3)_{2,s}]$$

$$+ 6\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] + 8\Delta_f H^\theta[H_2O_{,\ell}]$$

$$- \Delta_r H^\theta - 12\Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3(OPbOH)_2 4PbO.2H_2O_{,s}]$

$$= [-443.93] + 8[-285.83] - 12[-206.85] + 6[-440.66]$$

$$+ 6[24.49] - [-281.12]$$

$$= \underline{\underline{-2464.27 \pm 5.19 \text{ kJ mol}^{-1}}}$$

IV-BXI: Enthalpy of Reaction of Silver Styphnate (f)

The enthalpy of reaction of silver styphnate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for the lead styphnates. This gave rise to a small endothermic enthalpy change, the results of which are shown in Table IV-12. For the calculation of the enthalpy of formation of the silver styphnate, the relevant ancillary data are the enthalpies of solution and formation of silver nitrate, and the enthalpy of formation of styphnic acid, water, and (1.0N) nitric acid.

IV-BXII: Enthalpy of Solution of Silver Nitrate in a Nitric Acid/Styphnic Acid Solution

The enthalpy of solution, $\Delta_{sol}H^{\theta}$, of silver nitrate (B.D.H.; A.R.) was measured using the L.K.B. 8700 calorimeter. A solution of nitric acid (B.D.H.; 1.0M A.V.S.) saturated with styphnic acid was made, and the ampoule contained the silver nitrate.

$$[HNO_3 + \text{Styphnic Acid (sat)}]_{,aq} + AgNO_{3,s} \xrightarrow{\Delta_{sol}H^{\theta}} [HNO_3 + \text{Styphnic Acid (sat)} + AgNO_3]_{,aq}$$

The calorimetric results obtained are shown in Table IV-13. Literature value of silver nitrate in (5000) water $\Delta_{sol}H^{\theta}=22.68\pm0.01$ kJ mol^{-1} [16].

IV-BXIII: Enthalpy of Formation of Silver Styphnate

From the enthalpy of reaction of silver styphnate and various ancillary data, the enthalpy of formation of the silver styphnate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^{\theta}[C_6H(NO_2)_3(OH)_{2,s}] = -443.93\pm0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^{\theta}[AgNO_{3,s}] = -124.39\pm0.9$ kJ mol^{-1} [16]

$\Delta_f H^{\theta}[(1.0N)HNO_{3,aq}] = -206.85\pm0.03$ kJ mol^{-1} [16]

$\Delta_{sol}H^{\theta}[AgNO_{3,aq}] = +20.81\pm0.16$ kJ mol^{-1} [Section IV-BXII]

Thermochemical equation,

$$\Delta_f H^\theta[C_6H(NO_2)_3(OAg)_{2,s}] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$$

$$+ \Delta_{sol} H^\theta[AgNO_{3,aq}] + \Delta_f H^\theta[AgNO_{3,s}]$$

$$- \Delta_f H^\theta[HNO_{3,aq}] - \Delta_r H^\theta$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3(OAg)_{2,s}]$

$$= [-443.93] + 2[-124.39] + 2[20.81] - 2[-206.85]$$

$$- [14.17]$$

$$= \underline{\underline{-251.56 \pm 2.06 \text{ kJ mol}^{-1}}}$$

IV-BXIV: Enthalpy of Reaction of Thallous Styphnate (g)

The enthalpy of reaction of the thallous styphnate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for the lead styphnates. This reaction gave rise to an endothermic enthalpy change, the results of which are shown in Table IV-14. For the calculation of the enthalpy of formation of the thallous styphnate, the relevant ancillary data are the enthalpies of solution and formation of thallous styphnate, and the enthalpy of formation of styphnic acid, and (0.1N) nitric acid.

IV-BXV: Enthalpy of Formation of [½ Acid] Thallous Styphnate

From the enthalpy of reaction of thallous styphnate and various ancillary data, the enthalpy of formation of the styphnate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83 \pm 0.04$ kJ mol^{-1} [14]

$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] = -443.93 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[TlNO_{3,s}] = -243.93 \pm 0.3$ kJ mol^{-1} [16]

$\Delta_{sol} H^\theta[TlNO_{3,aq}] = +39.21 \pm 0.1$ kJ mol^{-1} [16]

$\Delta_f H^\theta[(0.1N)HNO_{3,aq}] = -206.97 \pm 0.04$ kJ mol^{-1} [16]

Thermochemical equation,

$$\Delta_f H^\theta[C_6H(NO_2)_3OHOTl_{,s}] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$$
$$+ \Delta_f H^\theta[TlNO_{3,s}] + \Delta_{sol} H^\theta[TlNO_{3,aq}]$$
$$- \Delta_r H^\theta - \Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3OHOTl_{,s}]$

$$= [-443.93] + [-243.93] + [+39.21] - [-206.97]$$
$$- [+26.80]$$
$$= \underline{\underline{-468.48 \pm 0.86 \text{ kJ mol}^{-1}}}$$

IV-BXVI: Enthalpy of Reaction of Thallous Styphnate (h)

The enthalpy of reaction of thallous styphnate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for the lead styphnates.
This reaction gave rise to an endothermic enthalpy change, the

results of which are shown in Table IV-15. For the calculation of the enthalpy of formation of the thallous styphnate, the relevant ancillary data are the enthalpies of solution and formation of thallous nitrate, and the enthalpy of formation of styphnic acid, and (0.1N) nitric acid.

IV-BXVII: Enthalpy of Formation of Thallous Styphnate

From the enthalpy of reaction of thallous styphnate and various ancillary data, the enthalpy of formation of the styphnate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] = -443.93 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[TlNO_{3,s}] = -243.93 \pm 0.3$ kJ mol^{-1} [16]

$\Delta_{sol} H^\theta[TlNO_{3,aq}] = +39.21 \pm 0.1$ kJ mol^{-1} [16]

$\Delta_f H^\theta[(0.1N)HNO_{3,aq}] = -206.97 \pm 0.04$ kJ mol^{-1} [16]

Thermochemical equation,

$$\text{(h)}\quad \Delta_f H^\theta[C_6H(NO_2)_3(OTl)_{2,s}] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$$

$$+ \Delta_{sol} H^\theta[TlNO_{3,aq}] + \Delta_f H^\theta[TlNO_{3,s}] - \Delta_r H^\theta$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3(OTl)_{2,s}]$

$$= [-443.93] + 2[-243.93] + 2[+39.21] - 2[-206.97]$$

$$- [+64.56]$$

$$= \underline{\underline{-503.99 \pm 1.03 \text{ kJ mol}^{-1}}}$$

IV-BXVIII: Enthalpy of Reaction of Barium Styphnate Monohydrate (i)

The enthalpy of reaction of barium styphnate monohydrate was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that used for the lead styphnates. This reaction gave rise to an endothermic enthalpy change, the results of which are shown in Table IV-16. For the calculation of the enthalpy of formation of the barium styphnate, the relevant ancillary data are the enthalpies of solution and formation of barium nitrate, and the enthalpy of formation of styphnic acid, water, and (0.1N) nitric acid.

IV-BXIX: Enthalpy of Solution of Barium Nitrate in a Nitric Acid/Styphnic Acid solution

The enthalpy of solution, $\Delta_{sol}H^{\theta}$, of barium nitrate (B.D.H.; A.R.(99.5%)) was measured using the L.K.B. 8700-1 calorimeter. A solution of nitric acid (B.D.H.; 0.1M A.V.S.) saturated with styphnic acid was made, and the ampoule contained the barium nitrate.

$$[HNO_3 + \text{Styphnic Acid (sat)}]_{,aq} + Ba(NO_3)_{2,s} \xrightarrow{\Delta_{sol}H^{\theta}} [HNO_3 + \text{Styphnic Acid (sat)} + Ba(NO_3)_2]_{,aq}$$

The calorimetric results obtained are shown in Table IV-17. Literature value of barium nitrate into (10000) water, $\Delta_{sol}H^{\theta}=40.02 \pm 0.02$ kJ mol^{-1} [16]

IV-BXX: Enthalpy of Formation of Barium Styphnate Monohydrate

From the enthalpy of reaction of barium styphnate and various ancillary data, the enthalpy of formation of the styphnate was calculated.

Ancillary data: The following data were used.

$\Delta_f H^\theta[H_2O,_\ell] = -285.83 \pm 0.04$ kJ mol^{-1} [14]

$\Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}] = -443.93 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[Ba(NO_3)_{2,s}] = -992.07 \pm 0.7$ kJ mol^{-1} [16]

$\Delta_{sol} H^\theta[Ba(NO_3)_{2,aq}] = +39.69 \pm 0.18$ kJ mol^{-1} [Section IV-BXIX]

$\Delta_f H^\theta[(0.1N)HNO_{3,aq}] = -206.97 \pm 0.04$ kJ mol^{-1} [16]

Thermochemical equation,

$$\text{(i)} \quad \Delta_f H^\theta[C_6H(NO_2)_3O_2Ba.H_2O,_s] = \Delta_f H^\theta[C_6H(NO_2)_3(OH)_{2,s}]$$

$$+ \Delta_{sol} H^\theta[Ba(NO_3)_{2,aq}] + \Delta_f H^\theta[Ba(NO_3)_{2,s}]$$

$$- \Delta_f H^\theta[HNO_{3,aq}] + \Delta_f H^\theta[H_2O,_\ell] - \Delta_r H^\theta$$

Calculation of $\Delta_f H^\theta[C_6H(NO_2)_3O_2Ba.H_2O,_s]$

$$= [-992.01] + [39.69] + [-285.83] + [-443.93]$$

$$- [+17.12] - 2[-206.97]$$

$$= \underline{\underline{-1285.31 \pm 1.24 \text{ kJ mol}^{-1}}}$$

IV-BXXI: Direct measurement of the enthalpy of Solution of Lead Nitrate in Nitric Acid/(4,6- or 2,4-) DNR mixture

The enthalpy of solution, $\Delta_{sol}H^\theta$, of lead nitrate (B.D.H.; A.R.; re-crystallised from water) was measured using the L.K.B.

8700-1 calorimeter. A solution of nitric acid (B.D.H., 1.0M A.V.S.) saturated with the DNR was made, and the ampoule contained the lead nitrate.

$$[HNO_3 + DNR\ (sat)]_{,aq} + Pb(NO_3)_{2,s} \xrightarrow{\Delta_{sol}H^{\theta}} [HNO_3 + DNR\ (sat) + Pb(NO_3)_2]_{,aq}$$

The calorimetric results obtained are shown in Tables IV-18 and IV-19. Literature value for lead nitrate into (10000) water, $\Delta_{sol}H^{\theta} = -33.50 \pm 0.05$ kJ mol^{-1} [16].

Table IV-2

Analysis results for lead(II) cation in various calorimetric reactions

	Calc. %	Found %
Monobasic Lead 4,6-Dinitroresorcinol	64.10	(a) 64.13 (b) 64.17
Dibasic Lead 4,6-Dinitroresorcinol	71.47	(a) 72.07 (b) 71.56
Tribasic Lead 4,6-Dinitroresorcinol	75.84	(a) 75.65 (b) 75.82
Normal Lead 2,4-Dinitroresorcinol	51.12	(a) 51.10 (b) 51.11
Monobasic Lead 2,4-Dinitroresorcinol	65.94	(a) 65.85 (b) 66.01
Tribasic Lead 2,4-Dinitroresorcinol	75.83	(a) 75.95 (b) 75.90
Quadrabasic Lead 2,4-Dinitroresorcinol	78.42	(a) 78.53 (b) 78.40

IV-CI: Solution Calorimetry of Lead Dinitroresorcinols

For the calorimetry of the lead-dinitroresorcinols it seemed feasible to use a suitably modified reaction of that used for the lead styphnates. The acidity of the solution was increased to enhance the rate of reaction. Two points of concern were that during the process of making the solution saturated with the DNR, styphnic acid could be formed as the mixture was heated. It was found that styphnic acid only formed if the solution was boiled. Secondly, that no styphnic acid was formed in the calorimeter vessel. This was checked by filtering off the precipitate and then measuring its melting point. It was found that only DNR was formed.

To check that the reaction had gone to completion, the reaction was carried out quantitatively. The DNR precipitated was extracted twice using chloroform (A.R.; 100 cm^3). The resulting nitric acid solution was then tested for Pb^{2+}[17]. The results are shown in Table IV-2.

IV-CII: Enthalpy of Reaction of Monobasic Lead 4,6-Dinitroresorcinol, (j)

The enthalpy of reaction, $\Delta_r H^\theta$, of monobasic lead 4,6-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for normal lead styphnate except that the nitric acid was pre-saturated in 4,6-DNR. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table IV-20. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 4,6-DNR, water, and (1.0N) nitric acid.

IV-CIII: Enthalpy of Formation of Monobasic Lead 4,6-Dinitroresorcinol

From the enthalpy of reaction of monobasic lead-DNR, and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O,_\ell] = -285.83\pm0.04$ kJ mol^{-1}[14]

$\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -428.54\pm0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66\pm0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.32\pm0.09$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[(1.ON)HNO_{3,aq}] = -206.85\pm0.03$ kJ mol^{-1}[16]

Thermochemical equation,

(j) $\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_{2,s}] = 2\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}]$

$+ 2\Delta_f H^\theta[Pb(NO_3)_{2,s}] + 2\Delta_f H\ [H_2O,_\ell]$

$+ \Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}]$

$- \Delta_r H^\theta - 4\Delta_f H^\theta[HNO_{3,aq}]$

Calculation of $\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_{2,s}]$

$= 2[-440.66] + 2[24.32] + [-428.54] + 2[-285.83]$

$- [-92.62] - 4[-206.85]$

$= -912.87\pm1.87$ kJ mol^{-1}

IV-CIV: Enthalpy of Reaction of Dibasic Lead 4,6-Dinitroresorcinol (k)

The enthalpy of reaction of dibasic lead 4,6-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for monobasic lead DNR. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table IV-21. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 4,6-DNR, water, and (1.0N) nitric acid.

IV-CV: Enthalpy of Formation of Dibasic Lead 4,6-Dinitroresorcinol

From the enthalpy of reaction of dibasic lead 4,6-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83 \pm 0.04$ kJ mol^{-1}[14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66 \pm 0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.32 \pm 0.09$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[\ 4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -428.54 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[(1.0N)HNO_{3,aq}] = -206.85 \pm 0.03$ kJ mol^{-1}[16]

Thermochemical equation,

$$\text{(k)}\quad \Delta_f H^\theta[\,4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2PbO_{,s}]$$

$$= \Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] + 3\Delta_f H^\theta[Pb(NO_3)_{2,s}]$$

$$+ 3\Delta_f H^\theta[H_2O_{,\ell}] + 3\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] - \Delta_r H^\theta$$

$$- 6\Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2PbO_{,s}]$

$$= [-428.54] + 3[-440.66] + 3[-285.83] + 3[24.32]$$

$$- [-175.88] - 6[-206.85]$$

$$= \underline{\underline{-1118.08 \pm 2.69 \text{ kJ mol}^{-1}}}$$

IV-CVI: Enthalpy of Reaction of Tribasic Lead 4,6-Dinitroresorcinol (1)

The enthalpy of reaction of tribasic lead 4,6-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for monobasic lead DNR. This reaction gave rise to an exothermic enthalpy change, the results of which are shown in Table IV-22. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 4,6-DNR, water, and (1.0N) nitric acid.

IV-CVII: Enthalpy of Formation of Tribasic Lead 4,6-Dinitroresorcinol

From the enthalpy of reaction of tribasic lead 4,6-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83 \pm 0.04$ kJ mol^{-1}[14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66 \pm 0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.32 \pm 0.09$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -428.54 \pm 0.78$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[(1.ON)HNO_{3,aq}] = -206.85 \pm 0.03$ kJ mol^{-1}[16]

Thermochemical equation,

(1) $$\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s}] = \Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] + 4\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] + 4\Delta_f H^\theta[H_2O_{,\ell}] - 8\Delta_f H^\theta[HNO_{3,aq}] - \Delta_r H^\theta + 4\Delta_f H^\theta[Pb(NO_3)_{2,s}]$$

Calculation of $\Delta_f H^\theta[4,6\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s}]$

$$= [-428.54] + 4[-440.66] + 4[-285.83] + 4[24.32] - [-162.47] - 8[-206.85]$$

$$= \underline{\underline{-1419.96 \pm 3.50 \text{ kJ mol}^{-1}}}$$

IV-CVIII: Enthalpy of Reaction of Normal Lead 2,4-Dinitroresorcinol (m)

The enthalpy of reaction of normal lead 2,4-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for monobasic lead

4,6-DNR except that the nitric acid was pre-saturated with 2,4-DNR. This reaction gave rise to a small exothermic change, the results of which are shown in Table IV-23. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 2,4-DNR, and (1.0N) nitric acid.

IV-CIX: Enthalpy of Formation of Normal Lead 2,4-Dinitroresorcinol

From the enthalpy of reaction of normal lead 2,4-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[\mathrm{Pb(NO_3)_{2,s}}] = -440.66 \pm 0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[\mathrm{Pb(NO_3)_{2,aq}}] = +24.36 \pm 0.06$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[\mathrm{2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}}] = -407.93 \pm 0.79$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[\mathrm{(1.0N)HNO_{3,aq}}] = -206.85 \pm 0.03$ kJ mol^{-1}[16]

Thermochemical equation,

$$(m)\quad \Delta_f H^\theta[\mathrm{2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s}}] = \Delta_f H^\theta[\mathrm{2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}}] + \Delta_f H^\theta[\mathrm{Pb(NO_3)_{2,s}}] + \Delta_{sol} H^\theta[\mathrm{Pb(NO_3)_{2,aq}}] - \Delta_r H^\theta - 2\Delta_f H^\theta[\mathrm{HNO_{3,aq}}]$$

Calculation of $\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s}]$

$$= [-407.93] + [-440.66] + [+24.36] - [-29.36] - 2[-206.85]$$

$$= \underline{\underline{-381.17 \pm 1.17 \text{ kJ mol}^{-1}}}$$

IV-CX: Enthalpy of Reaction of Monobasic Lead 2,4-Dinitroresorcinol (n)

The enthalpy of reaction of Monobasic lead 2,4-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for normal lead 2,4-DNR. This reaction gave an exothermic enthalpy change, the results of which are shown in Table IV-24. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 2,4-DNR, water, and (1.ON) nitric acid.

IV-CXI: Enthalpy of Formation of Monobasic Lead 2,4-Dinitroresorcinol

From the enthalpy of reaction of monobasic lead 2,4-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83 \pm 0.03 \text{ kJ mol}^{-1}$[14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66 \pm 0.84 \text{ kJ mol}^{-1}$[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.36 \pm 0.06 \text{ kJ mol}^{-1}$[Section IV-BXXI]

$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -407.93 \pm 0.79 \text{ kJ mol}^{-1}$ [Section III-E]

$\Delta_f H^\theta[(1.ON)HNO_{3,aq}] = -206.85 \pm 0.03 \text{ kJ mol}^{-1}$[16]

Thermochemical equation,

$$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2O_2Pb.PbO_{,s}] = \Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}]$$
$$+ 2\Delta_f H^\theta[Pb(NO_3)_{2,s}] + 2\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}]$$
$$+ \Delta_f H^\theta[H_2O_{,\ell}] - \Delta_r H^\theta - 4\Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2O_2Pb.PbO_{,s}]$ =

$$[-407.93] + 2[-440.66] + 2[24.36] - [-85.34] - 4[-206.85]$$
$$+ [-285.83]$$
$$= \underline{\underline{-613.62 \pm 1.94 \text{ kJ mol}^{-1}}}$$

IV-CXII: Enthalpy of Reaction of Tribasic Lead 2,4-Dinitroresorcinol (o)

The enthalpy of reaction of tribasic lead 2,4-dinitroresorcinol was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for normal lead 2,4-DNR. This reaction gave an exothermic enthalpy change, the results of which are shown in Table IV-25. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data needed are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 2,4-DNR, water, and (1.0N) nitric acid.

IV-CXIII: Enthalpy of Formation of Tribasic Lead 2,4-Dinitroresorcinol

From the enthalpy of reaction of tribasic lead 2,4-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83 \pm 0.03$ kJ mol^{-1}[14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66 \pm 0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.36 \pm 0.06$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -407.93 \pm 0.79$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[(1.0N)HNO_{3,aq}] = -206.85 \pm 0.03$ kJ mol^{-1}[16]

Thermochemical equation,

$$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s}] = \Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}]$$
$$+ 4\Delta_f H^\theta[Pb(NO_3)_{2,s}] + 4\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}]$$
$$+ 4\Delta_f H^\theta[H_2O_{,\ell}] - \Delta_r H^\theta - 8\Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s}]$

$$= [-407.93] + 4[-440.66] + 4[24.36] - 8[-206.85]$$
$$+ 4[-285.83] - [-179.12]$$
$$= \underline{\underline{-1382.53 \pm 3.50 \text{ kJ mol}^{-1}}}$$

IV-CXIV: Enthalpy of Reaction of Quadrabasic Lead, 2,4-Dinitroresorcinol (p)

The enthalpy of reaction of quadrabasic lead 2,4-DNR was measured using the R.H.C./J.R.P. twin calorimeter system. The reaction used was the same as that for normal lead 2,4-DNR. This reaction gave an exothermic enthalpy change, the results of which are shown in Table IV-26. For the calculation of the enthalpy of formation of the lead-DNR, the relevant ancillary data are the enthalpies of solution and formation of lead nitrate, and the enthalpy of formation of 2,4-DNR, water, and (1.0N) nitric acid.

IV-CXV: Enthalpy of Formation of Quadrabasic Lead 2,4-Dinitroresorcinol

From the enthalpy of reaction of quadrabasic lead 2,4-DNR and various ancillary data, the enthalpy of formation of the dinitroresorcinate was calculated.

Ancillary data: The following data were used,

$\Delta_f H^\theta[H_2O_{,\ell}] = -285.83\pm0.03$ kJ mol^{-1}[14]

$\Delta_f H^\theta[Pb(NO_3)_{2,s}] = -440.66\pm0.84$ kJ mol^{-1}[15]

$\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] = +24.36\pm0.06$ kJ mol^{-1}[Section IV-BXXI]

$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] = -407.93\pm0.79$ kJ mol^{-1} [Section III-E]

$\Delta_f H^\theta[(1.0N)HNO_{3,aq}] = -206.85\pm0.03$ kJ mol^{-1}[16]

Thermochemical equation,

$$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 3PbO_{,s}] =$$

$$\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OH)_{2,s}] + 5\Delta_f H^\theta[Pb(NO_3)_{2,s}]$$

$$+ 5\Delta_{sol} H^\theta[Pb(NO_3)_{2,aq}] + 5\Delta_f H^\theta[H_2O_{,\ell}]$$

$$- \Delta_r H^\theta - 10\Delta_f H^\theta[HNO_{3,aq}]$$

Calculation of $\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2(OPbOH)_2 3PbO_{,s}]$

$= [-407.93] + 5[-285.83] + 5[-440.66] + 5[24.36]$

$- 10[-206.85] - [-227.37]$

$= \underline{\underline{-1622.71 \pm 4.45 \text{ kJ mol}^{-1}}}$

Table IV-3

Enthalpy of Solution of THAM in excess 0.1M HCl

W/g	dilution/n*	$-\Delta_N H^\theta$/kJ mol^{-1}
0.23095	2884.8	29.88
0.24712	2696.1	29.88
0.23508	2834.2	29.87

$\Delta_N H^\theta$(mean) = -29.88±0.01 kJ mol^{-1}(lit[12],$\Delta_N H^\theta$-29.790 ±0.031 kJ mol^{-1})

n* = Mole ratio of THAM to water.

Table IV-4

Enthalpy of Solution of THAM in excess 0.05M NaOH

W/g	dilution/n*	$+\Delta_N H^\theta$/kJ mol^{-1}
0.07737	8611.5	17.185
0.08195	8130.2	17.183
0.07863	8473.5	17.187

$\Delta_N H^\theta$ (mean) = 17.185±0.005 kJ mol^{-1}(lit[13],$\Delta_N H^\theta$+17.189 ±0.005 kJ mol^{-1})

n* = Mole ratio of THAM to water.

Table IV-5

Enthalpy of Solution of Lead Nitrate in Water

W/g	dilution /n*	$\Delta_{sol}H^{\theta}$/kJ mol^{-1}
0.10019	18181.5	33.73
0.11734	15523.5	34.00
0.12049	15118.3	34.00
0.20125	9051.2	33.69
0.24062	7570.3	33.71
0.18893	9641.4	33.64
0.13422	13571.7	33.64
0.24188	7531.0	33.67

$\Delta_{sol}H^{\theta}$(mean) = 33.76 ± 0.13 kJ mol^{-1}

n = molar ratio of lead nitrate to water.

Literature [16] $\Delta_{sol}H^{\theta}$ = 33.47 ± 0.7 kJ mol^{-1}. [10000 H_2O]

Table IV-6

Enthalpy of Reaction of Normal Lead Styphnate (a)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.13224	17.08
0.18164	17.38
0.08151	17.21
0.14352	17.18
0.06766	17.30
0.24786	17.56

$\Delta_r H^\theta$ (mean) = -17.29 + 0.18 kJ mol^{-1}

Table IV-7

Enthalpy of Solution of Lead Nitrate in aqueous Nitric Acid/Styphnic Acid

W/g	dilution /n*	$\Delta_{sol} H^\theta$/kJ mol^{-1}
0.16259	11204.0	24.46
0.12595	14463.9	24.49
0.31646	5756.2	24.71
0.19693	9250.2	24.45
0.20648	8822.4	24.42
0.19856	9174.3	24.43
0.15923	11440.4	24.47

$\Delta_{sol} H^\theta$(mean) = 24.49 ± 0.09 kJ mol^{-1}

n = molar ratio of lead nitrate to water.

Table IV-8

Enthalpy of Reaction of Monobasic Lead Styphnate (b)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.13895	61.901
0.11012	62.150
0.10006	62.072
0.08281	61.858
0.06749	61.920
0.03179	61.611

$\Delta_r H^\theta$ (mean) = -61.92 ± 0.20 kJ mol^{-1}

Table IV-9

Enthalpy of Reaction of Monobasic Lead Styphnate (c)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.07752	60.167
0.06036	60.527
0.06124	60.486
0.07322	60.486
0.06599	60.702
0.06332	60.794

$\Delta_r H^\theta$ (mean) = -60.52 ± 0.57 kJ mol^{-1}

Table IV-10

Enthalpy of Reaction of Tribasic Lead Styphnate (d)

W/g	$-\Delta_r H^\theta/\mathrm{kJ\ mol^{-1}}$
0.08140	196.591
0.23295	196.398
0.20671	196.058
0.17427	196.320
0.17479	196.334
0.12541	196.519

$\Delta_r H^\theta$ (mean) = -196.37 ± 0.19 kJ $\mathrm{mol^{-1}}$

Table IV-11

Enthalpy of Reaction of Pentabasic Lead Styphnate (e)

W/g	$-\Delta_r H^\theta/\mathrm{kJ\ mol^{-1}}$
0.30192	282.057
0.19705	281.998
0.13374	280.143
0.17605	280.815
0.20512	280.877
0.17968	280.837

$\Delta_r H^\theta$ (mean) = -281.12 ± 0.79 kJ $\mathrm{mol^{-1}}$

Table IV-12

Enthalpy of Reaction of Silver Styphnate (f)

W/g	$+\Delta_r H^\theta$/kJ mol^{-1}
0.12093	14.193
0.11474	14.491
0.09245	13.663
0.16518	14.347
0.10800	14.847
0.15354	13.490

$\Delta_r H^\theta$ (mean) = +14.17 ± 0.54 kJ mol^{-1}

Table IV-13

Enthalpy of Solution of Silver Nitrate in a Nitric Acid/ Styphnic Acid solution

W/g	$+\Delta_{sol} H^\theta$/kJ mol^{-1}
0.20493	20.78
0.26946	20.812
0.16055	21.06
0.21686	20.74
0.30798	20.85
0.16714	20.60

$\Delta_{sol} H^\theta$ (mean) = +20.81 ± 0.16 kJ mol^{-1}

Table IV-14

Enthalpy of Reaction of [½ Acid] Thallous Styphnate (g)

W/g	$+\Delta_r H^\ominus$/kJ mol^{-1}
0.06314	26.909
0.06563	26.815
0.07984	26.957
0.07878	26.812
0.08198	26.495
0.07934	26.803

$\Delta_r H^\theta$ (mean) = +26.80 ± 0.17 kJ mol^{-1}

Table IV-15

Enthalpy of Reaction of Thallous Styphnate (h)

W/g	$+\Delta_r H^\theta$/kJ mol^{-1}
0.03118	64.516
0.03553	64.421
0.03109	64.956
0.02791	64.511
0.05314	64.626
0.04121	64.300

$\Delta_r H^\theta$ (mean) = +64.56 ± 0.24 kJ mol^{-1}

Table IV-16

Enthalpy of Reaction of Barium Styphnate Monohydrate (i)

W/g	$+\Delta_r H^\theta$/kJ mol^{-1}
0.08514	16.851
0.09724	17.06
0.10416	17.306
0.10225	17.492
0.09290	17.108
0.10690	16.906

$\Delta_r H^\theta$ (mean) = +17.12 ± 0.62 kJ mol^{-1}

Table IV-17

Enthalpy of Solution of Barium Nitrate in a Nitric Acid/ Styphnic Acid solution

W/g	$+\Delta_{sol} H^\theta$/kJ mol^{-1}
0.16197	39.757
0.16827	39.702
0.19671	39.736
0.26002	39.569
0.19143	39.660
0.18402	39.748

$\Delta_{sol} H^\theta$ (mean) = 39.69 ± 0.18 kJ mol^{-1}

Table IV-18

The Enthalpy of Solution of Lead Nitrate in a Nitric Acid/4,6-DNR solution

W/g	$+\Delta_{sol}H^{\theta}$/kJ mol^{-1}
0.53373	24.20
0.51657	24.18
0.35832	24.35
0.41816	24.31
0.44935	24.44
0.35724	24.42

$\Delta_{sol}H^{\theta}$ (mean) = 24.32 ± 0.09 kJ mol^{-1}

Table IV-19

The Enthalpy of Solution of Lead Nitrate in a Nitric Acid/2,4-DNR solution

W/g	$+\Delta_{sol}H^{\theta}$/kJ mol^{-1}
0.50842	24.34
0.26581	24.34
0.40006	24.37
0.14732	24.39
0.24219	24.38
0.31689	24.33

$\Delta_{sol}H^{\theta}$ (mean) = 24.36 ± 0.06 kJ mol^{-1}

Table IV-20

The Enthalpy of Reaction of Monobasic Lead 4,6-Dinitroresorcinol, (j)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.14543	92.701
0.08829	92.692
0.08176	92.767
0.07089	92.572
0.07714	92.542
0.05440	92.413

$\Delta_r H^\theta$ (mean) = -96.62 ± 0.14 kJ mol^{-1}

Table IV-21

The Enthalpy of Reaction of Dibasic Lead 4,6-Dinitroresorcinol, (k)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.16898	175.609
0.09795	175.286
0.17040	176.125
0.09920	176.489
0.14927	176.035
0.16552	175.711

$\Delta_r H^\theta$ (mean) = -175.88 ± 0.45 kJ mol^{-1}

Table IV-22

The Enthalpy of Reaction of Tribasic Lead 4,6-Dinitroresorcinol (ℓ)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.14122	161.88
0.09929	162.31
0.10645	162.93
0.15174	162.94
0.13862	161.91
0.23212	162.83

$\Delta_r H^\theta$(mean) = -162.47 ± 0.53 kJ mol^{-1}

Table IV-23

The Enthalpy of Reaction of Normal Lead 2,4-Dinitroresorcinol (m)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.05652	29.44
0.05652	29.12
0.04920	29.38
0.07061	29.58
0.06813	29.23
0.07328	29.39

$\Delta_r H^\theta$ (mean) = -29.36 ± 0.17 kJ mol^{-1}

Table IV-24

The Enthalpy of Reaction of Monobasic Lead 2,4-Dinitroresorcinol (n)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.04256	86.069
0.06159	85.478
0.07222	85.257
0.05200	84.649
0.06471	85.613
0.06178	84.960

$\Delta_r H^\theta$ (mean) = -85.34 ± 0.53 kJ mol^{-1}

Table IV-25

The Enthalpy of Reaction of Tribasic Lead 2,4-Dinitroresorcinol (o)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.10260	178.40
0.14644	179.34
0.15036	179.24
0.14211	179.57
0.13159	179.15
0.12978	179.03

$\Delta_r H^\theta$ (mean) = -179.12 ± 0.42 kJ mol^{-1}

Table IV-26

The Enthalpy of Reaction of Quadrabasic Lead 2,4-Dinitroresorcinol (p)

W/g	$-\Delta_r H^\theta$/kJ mol^{-1}
0.12534	227.01
0.07677	226.78
0.11020	226.51
0.11740	228.68
0.10070	226.97
0.12095	228.25

$\Delta_r H^\theta$ (mean) = -227.37 ± 0.92 kJ mol^{-1}

IV-DI: Enthalpy of Breaking an Ampoule

A possible source of error is that associated with the enthalpy of mechanical breaking of the ampoule containing the solid. Other investigators[20] have found that this gives rise to a significant ($\sim$0.05J) enthalpy change. This is largely due to the enthalpy of evaporation caused by the gas trapped in the vapour space of the ampoule when the glass bulb is shattered being released and allowed to percolate up through the calorimeter contents. As the compounds used in this investigation are non-volatile, and account for a large volume of the ampoule, this correction becomes minimal. To check this, several ampoules were filled with the same approximate volume of styphnic acid as the lead salts, and the same calorimetric procedure observed as before with the metal styphnates. It was noted that a baseline deviation equivalent to a temperature change of less than 5.0×10^{-4}°C was observed. This deviation was hardly noticable above the baseline noise, and impossible to record with any degree of accuracy.

IV-DII: Enthalpy of Formation of Metallo Polynitroresorcinols by Group Additivity for Solids

Group additivity theory is a method for estimating heats of formation for any compound. For solids the usual approach is to use values for ideal gas groups together with heats of sublimation. Shaw[21] has produced a method which consists in the addition of values for various groups to give an estimated $\Delta_f H^\theta$ value. It is upon this that a further study was made. To make a comprehensive study of the compounds concerned in this investigation a great many more enthalpies of formation would need to be known.

Table IV-29 contains a list of the lead salts investigated and their enthalpies of formation. From inspection of the structures and subtraction of the relevant values of $\Delta_f H^\theta$, rudimentary calculations can be made to estimate enthalpies of formation. For example, subtraction of $\Delta_f H^\theta$ values for compounds 3 and 4, 5 and 6, 9 and 10, 10 and 11, and taking the mean of the resultants will give the estimate

$\Delta_f H^\theta[PbO_{,s}] = \underline{-246.37\ \text{kJ mol}^{-1}}$

To estimate the enthalpy of formation of occluded water the following two calculations, (a) and (b) were adopted, e.g.
(a) $\Delta_f H^\theta[H_2O_{,s}] = \Delta_f H^\theta[\text{Compound 3}] - \Delta_f H^\theta[\text{Compound 2}] - 2\Delta_f H^\theta[\text{Estimated PbO}_{,s}] = -[1972.4 - 957.53 - (2\text{x}246.37)] = -261.07\ \text{kJ mol}^{-1}$.

Similarly, (b)
$= \Delta_f H^\theta[\text{Compound 4}] - \Delta_f H^\theta[\text{Compound 2}] - 4\Delta_f H^\theta[\text{Estimated PbO}_{,s}] = -[2464.3 - 957.53 - (4\text{x}246.37)] = -260.65\ \text{kJ mol}^{-1}$.

$\therefore \Delta_f H^\theta[H_2O_{,s}] = -(260.65 + 261.07)/2 = \underline{-260.86\ \text{kJ mol}^{-1}}$.

$\Delta_f H^\theta[H_2O_{,s}] = -279.81 \pm 0.08\ \text{kJ mol}^{-1}$ [14,30].

The usefulness of this scheme is that it allows for the estimation of other compounds for which no experimental data exist. For example, the enthalpy of formation of the compounds in Table IV-30, are all estimated. The limitations with this method are two-fold. One, the accuracy of each estimation is only as good as the number of pieces of data used. Two, estimation of the enthalpies of formation of the aromatic structures (TNR & DNR) are not easy, and a study of many such structures would be needed before an accurate result could be estimated.

IV-DIII: Enthalpy of Decomposition

The decomposition of such compounds as the metallo-dinitroresorcinols and trinitroresorcinols has always proved difficult to follow, and to suggest a comprehensive mechanism for decomposition has so far proved impossible, as during explosive decomposition extremes of temperature and pressure are inherent within the compound. From various studies [22,23,24,25] some activation energies have been found.

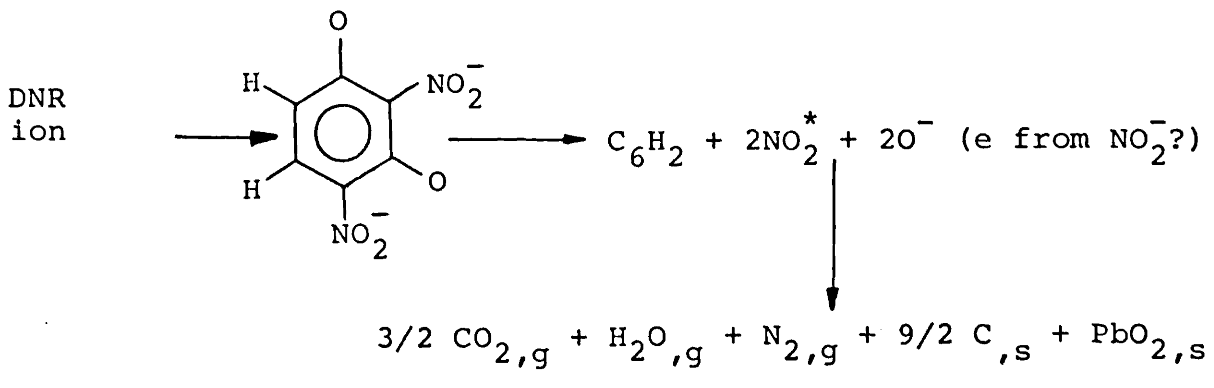
Compound	E_a; Activation Energy/ kJ mol^{-1}	
Barium styphnate monohydrate	195.39	[22]
Lead styphnate monohydrate	138.07	[23]
Lead styphnate monohydrate	315.43	[25]
Basic lead styphnate	315.47	[25]
Normal lead styphnate	156.90	[24]

No enthalpies of formation or decomposition exist except for the enthalpy of formation of normal lead styphnate, yet here again extreme discrepancies exist between sources, and no method has been quoted to how these values were derived.

Compound	$\Delta_f H^\theta$/kJ mol^{-1}	
Normal lead styphnate	-180.26	[25]
Normal lead styphnate	+200.00	†[26]
Normal lead styphnate	-386.18	[26]
Normal lead styphnate	-854.48	[27]
Normal lead styphnate monohydrate	-714.70±1.17	[Section IV-BIV]

† Assumed transcription error in original publication.

For lead 2,4-DNR, Tang[28] has postulated decomposition as



$$C_6H_2 + 2NO_2^* + 2O^- \text{ (e from } NO_2^-?)$$

$$\downarrow$$

$$3/2\ CO_{2,g} + H_2O_{,g} + N_{2,g} + 9/2\ C_{,s} + PbO_{2,s}$$

This decomposition path was suggested following combination of thermogravimetry, microscopy, differential scanning calorimetry and time-resolved mass spectroscopy. In principle the experiment was a solid-state decomposition of lead DNR under the action of heat. For the overall reaction,

$$2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s} \xrightarrow{\Delta_r H^\theta} 3/2\ CO_{2,g} + H_2O_{,g} + N_{2,g} + PbO_{2,s} + 9/2\ C_{,s}$$

and using the following ancillary data, an enthalpy of decomposition can be calculated.

Ancillary Data: The following data were used,

$\Delta_f H^\theta[H_2O_{,g}] = -241.814 \pm 0.042$ kJ mol^{-1}[14]

$\Delta_f H^\theta[CO_{2,g}] = -393.51 \pm 0.13$ kJ mol^{-1}[14]

$\Delta_f H^\theta[PbO_{2,s}] = -277.40 \pm 0.80$ kJ mol^{-1}[29]

$$\Delta_r H^\theta = \Delta_f H^\theta[PbO_{2,s}] + 3/2\Delta_f H^\theta[CO_{2,g}] + \Delta_f H^\theta[H_2O_{,g}]$$

$$-\Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s}]$$

$$= [-277.40] + 3/2\ [-393.51] + [-241.814] - [-381.17]$$

$$= \underline{\underline{-728.31 \pm 1.43\ \text{kJ mol}^{-1}}}$$

The assumption is made that only the oxygen within the compound is used to form the products. The following enthalpies of decomposition were calculated

Monobasic lead 2,4-DNR

$$C_6H_2(NO_2)_2O_2Pb.PbO_{,s} \xrightarrow{\Delta_r H^\theta} 2PbO_{2,s} + CO_{2,g} + H_2O_{,g} + N_{2,g} + 5C_{,s}$$

$$\Delta_r H^\theta = 2[-277.40] + [-393.51] + [-241.814] - [-613.622]$$

$$= \underline{\underline{-576.50 \pm 2.52\ \text{kJ mol}^{-1}}}$$

Tribasic lead 2,4-DNR

$$C_6H_2(NO_2)_2(OPbOH)_22PbO_{,s} \xrightarrow{\Delta_r H^\theta} 4PbO_{2,s}+2H_2O_{,g}+CO_{2,g}+N_{2,g}+5C_{,s}$$

$$\Delta_r H^\theta = 4[-277.40] + 2[-241.814] + [-393.51] - [-1382.5]$$

$$= \underline{\underline{-604.24\pm3.83\ \text{kJ mol}^{-1}}}$$

Quadrabasic lead 2,4-DNR

Insufficient oxygen exist in this compound for complete reaction. As molecular hydrogen is not going to be liberated, a secondary reaction would need to be considered.

Monobasic lead 4,6-DNR

$$C_6H_2(NO_2)_2(OPbOH)_{2,s} \xrightarrow{\Delta_r H^\theta} 2PbO_{2,s}+CO_{2,g}+2H_2O_{,g}+N_{2,g}+5C_{,s}$$

$$\Delta_r H^\theta = 2[-277.40] + [-393.51] + 2[-241.814] - [-912.87]$$

$$= \underline{\underline{-519.07\pm2.47\ \text{kJ mol}^{-1}}}$$

Dibasic lead 4,6-DNR

$$C_6H_2(NO_2)_2(OPbOH)_2PbO_{,s} \xrightarrow{\Delta_r H^\theta} 3PbO_{2,s}+2H_2O_{,g}+N_{2,g}+\tfrac{1}{2}CO_{2,g}+5\tfrac{1}{2}C_{,s}$$

$$\Delta_r H^\theta = 3[-277.40] + 2[-241.814] + \tfrac{1}{2}[-393.51] - [-1118.08]$$

$$= \underline{\underline{-394.50\pm3.61\ \text{kJ mol}^{-1}}}$$

Tribasic lead 4,6-DNR

$$C_6H_2(NO_2)_2(OPbOH)_22PbO_{,s} \xrightarrow{\Delta_r H^\theta} 4PbO_{2,s}+2H_2O_{,g}+CO_{2,g}+N_{2,g}+5C_{,s}$$

$$\Delta_r H^\theta = 4[-277.40] + 2[-241.814] + [-393.51] - [-1419.96]$$

$$= \underline{\underline{-566.77\pm4.74\ \text{kJ mol}^{-1}}}$$

Normal lead styphnate

$$C_6H(NO_2)_3O_2Pb.H_2O_{,s} \xrightarrow{\Delta_r H^\theta} PbO_{2,s}+1\frac{1}{2}H_2O_{,g}+1\frac{1}{2}N_{2,g}+2\ 3/4CO_{2,g}+3\frac{1}{4}C_{,s}$$

$$\Delta_r H^\theta = 2\ 3/4[-393.51] + [-277.40] + 1\frac{1}{2}[-241.814] - [-714.70]$$

$$= \underline{\underline{-1007.57 \pm 1.46\ \text{kJ mol}^{-1}}}$$

Monobasic lead styphnate

$$C_6H(NO_2)_3(OPbOH)_{2,s} \xrightarrow{\Delta_r H^\theta} 2PbO_{2,s}+1\frac{1}{2}H_2O_{,g}+1\frac{1}{2}N_{2,g}+2\frac{1}{4}CO_{2,g}+3\ 3/4C_{,s}$$

$$\Delta_r H^\theta = 2[-277.40] + 1\frac{1}{2}[-241.814] + 2\frac{1}{4}[-393.51] - [-957.53]$$

$$= \underline{\underline{-845.39 \pm 2.48\ \text{kJ mol}^{-1}}}$$

Tribasic lead styphnate

$$C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 4PbO_{2,s}+3\frac{1}{2}H_2O_{,g}+1\frac{1}{2}N_{2,g}$$
$$+1\frac{1}{4}CO_{2,g}+4\ 3/4C_{,s}$$

$$\Delta_r H^\theta = 4[-277.40] + 3\frac{1}{2}[-241.814] + 1\frac{1}{4}[-393.51] - [-1972.4]$$

$$= \underline{\underline{-475.44 \pm 4.75\ \text{kJ mol}^{-1}}}$$

Pentabasic lead styphnate

$$C_6H(NO_2)_3(OPbOH)_2 4PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 6PbO_{2,s}+3\frac{1}{2}H_2O_{,g}+\frac{1}{4}CO_{2,g}$$
$$+1\frac{1}{2}N_{2,g}+5\ 3/4C_{,s}$$

$$\Delta_r H^\theta = 6[-277.40] + 3\frac{1}{2}[-241.814] + \frac{1}{4}[-393.51] - [-2464.3]$$

$$= \underline{\underline{-144.82 \pm 7.08\ \text{kJ mol}^{-1}}}$$

Continuing the same method of decomposition for metal styphnates other than those of lead.

Ancillary data

$\Delta_f H^\theta[Tl_2O_{,s}]$ = -178.66±0.5 kJ mol^{-1}[29]

$\Delta_f H^\theta[BaO_{2,s}]$ = -634.3±0.7 kJ mol^{-1}[16]

$\Delta_f H^\theta[Ag_2O_{,s}]$ = -31.05±1.0 kJ mol^{-1}[16]

Thallous styphnate

$$C_6H(NO_2)_3(OTl)_{2,s} \xrightarrow{\Delta_r H^\theta} Tl_2O_{,s} + \tfrac{1}{2}H_2O_{,g} + 3\tfrac{1}{4}CO_{2,g} + 1\tfrac{1}{2}N_{2,g} + 2.3/4C_{,s}$$

$$= [-178.66] + \tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-503.99]$$

$$= \underline{\underline{-1074.48 \pm 1.22 \text{ kJ mol}^{-1}}}$$

Thallous styphnate (½ Acid)

$$C_6H(NO_2)_3OTlOH_{,s} \xrightarrow{\Delta_r H^\theta} \tfrac{1}{2}Tl_2O_{,s} + H_2O_{,g} + 3\tfrac{1}{4}CO_{2,g} + 1\tfrac{1}{2}N_{2,g} + 2.3/4C_{,s}$$

$$= \tfrac{1}{2}[-178.66] + [-241.814] + 3\tfrac{1}{4}[-393.51] - [-468.48]$$

$$= \underline{\underline{-1141.57 \pm 0.99 \text{ kJ mol}^{-1}}}$$

Barium styphnate

$$C_6H(NO_2)_3O_2Ba.H_2O_{,s} \xrightarrow{\Delta_r H^\theta} BaO_{2,s} + 1\tfrac{1}{2}H_2O_{,g} + 2.3/4CO_{2,g} + 1\tfrac{1}{2}N_{2,g} + 3\tfrac{1}{4}C_{,s}$$

$$= [-634.3] + 1\tfrac{1}{2}[-241.814] + 2\ 3/4[-393.51] - [-1285.31]$$

$$= \underline{\underline{-793.86 \pm 1.34 \text{ kJ mol}^{-1}}}$$

Silver styphnate

$$C_6H(NO_2)_3(OAg)_{2,s} \xrightarrow{\Delta_r H^\theta} Ag_2O_{,s}+\tfrac{1}{2}H_2O_{,g}+3\tfrac{1}{4}CO_{2,g}+1\tfrac{1}{2}N_{2,g}+2\tfrac{1}{2}C_{,s}$$

$$= [-31.05] + \tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-251.56]$$

$$= \underline{\underline{-1179.30 \pm 2.33 \text{ kJ mol}^{-1}}}$$

The decomposition reactions written out above all follow the example given by Tang[28]. If an explosive decomposition is considered, with the same assumption that only the oxygen within the compound is used to form the products, then the formation of lead monoxide or lead is more probable than lead dioxide, e.g.

$$\text{I,} \quad 2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s} \xrightarrow{\Delta_r H^\theta} 2CO_{2,g}+H_2O_{,g}+N_{2,g}+PbO_{,s}+4C_{,s}$$

$$\text{II,} \quad 2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s} \xrightarrow{\Delta_r H^\theta} 2\tfrac{1}{2}CO_{2,g}+H_2O_{,g}+N_{2,g}+Pb_{,s}+3\tfrac{1}{2}C_{,s}$$

Using the following ancillary data and that given before for carbon dioxide and water the enthalpy of each decomposition can be calculated.

Ancillary Data: The following data were used,

$$\Delta_f H^\theta[PbO_{,s(RED)}] = -218.99 \pm 1.0 \text{ kJ mol}^{-1}[29]$$

$$\text{I,} \quad \Delta_r H^\theta = \Delta_f H^\theta[PbO_{,s}]+2\Delta_f H^\theta[CO_{2,g}]+\Delta_f H^\theta[H_2O_{,g}]$$

$$- \Delta_f H^\theta[2,4\text{-}C_6H_2(NO_2)_2O_2Pb_{,s}]$$

$$= [-218.99] + 2[-393.51] + [-241.814] - [-318.17]$$

$$= \underline{\underline{-718.65 \pm 1.56 \text{ kJ mol}^{-1}}}$$

$$\text{II,}\quad \Delta_r H^{\theta} = 2\tfrac{1}{2}\Delta_f H^{\theta}[CO_{2,g}]+\Delta_f H^{\theta}[H_2O_{,g}] - \Delta_f H^{\theta}[2,4\text{-}C_6H_2(NO_3)_2O_2Pb_{,s}]$$

$$= 2\tfrac{1}{2}[-393.51] + [-241.814] - [-381.17]$$

$$= \underline{\underline{-844.42 \pm 1.22 \text{ kJ mol}^{-1}}}$$

Considering this decomposition for the same series of compounds as above, the following calculations were made.

<u>Monobasic lead 2,4-DNR</u>

$$\text{Ia,}\quad C_6H_2(NO_2)_2O_2Pb.PbO_{,s} \xrightarrow{\Delta_r H^{\theta}} 2PbO_{,s}+2CO_{2,g}+H_2O_{,g}+N_{2,g}+4C_{,s}$$

$$\Delta_r H^{\theta} = 2[-218.99] + 2[-393.51] + [-241.814] - [-613.622]$$

$$= \underline{\underline{-853.19 \pm 2.80 \text{ kJ mol}^{-1}}}$$

$$\text{IIa,}\quad C_6H_2(NO_2)_2O_2Pb.PbO_{,s} \xrightarrow{\Delta_r H^{\theta}} 3CO_{2,g}+H_2O_{,g}+N_{2,g}+3C_{,s}+2Pb_{,s}$$

$$\Delta_r H^{\theta} = 3[-393.51] + [-241.814] - [-613.622]$$

$$= \underline{\underline{-808.72 \pm 1.98 \text{ kJ mol}^{-1}}}$$

<u>Tribasic lead 2,4-DNR</u>

$$\text{Ib,}\quad C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s} \xrightarrow{\Delta_r H^{\theta}} 4PbO_{,s}+2H_2O_{,g}+2CO_{2,g}+N_{2,g}+4C_{,s}$$

$$= 4[-218.99] + 2[-393.51] + 2[-241.814] - [-1382.5]$$

$$= \underline{\underline{-764.11 \pm 4.53 \text{ kJ mol}^{-1}}}$$

IIb, $C_6H_2(NO_2)_2(OPbOH)_22PbO_{,s} \xrightarrow{\Delta_r H^\theta} 4Pb_{,s}+2H_2O_{,g}+4CO_{2,g}$

$+N_{2,g}+2C_{,s}$

$= 4[-393.51] + 2[-241.814] - [-1382.5]$

$= \underline{\underline{-675.17\pm2.17\ \text{kJ mol}^{-1}}}$

Quadrabasic lead 2,4-DNR

Ic, $C_6H_2(NO_2)_2(OPbOH)_23PbO_{,s} \xrightarrow{\Delta_r H^\theta} 5PbO_{,s}+2H_2O_{,g}+2CO_{2,g}$

$+N_{2,g}+4C_{,s}$

$\Delta_r H^\theta = 5[-218.99] + 2[-241.814] + 2[-393.51] - [-1622.7]$

$= \underline{\underline{-742.90\pm6.73\ \text{kJ mol}^{-1}}}$

IIc, $C_6H_2(NO_2)_2(OPbOH)_23PbO_{,s} \xrightarrow{\Delta_r H^\theta} 5Pb_{,s}+2H_2O_{,g}+4\tfrac{1}{2}CO_{2,g}$

$+N_{2,g}+1\tfrac{1}{2}C_{,s}$

$\Delta_r H^\theta = 2[-241.814] + 4\tfrac{1}{2}[-393.51] - [-1622.7]$

$= \underline{\underline{-631.72\pm4.54\ \text{kJ mol}^{-1}}}$

Monobasic lead 4,6-DNR

Id, $C_6H_2(NO_2)_2(OPbOH)_{2,s} \xrightarrow{\Delta_r H^\theta} 2PbO_{,s}+2H_2O_{,g}+2CO_{2,g}+N_{2,g}+4C_{,s}$

$\Delta_r H^\theta = 2[-218.99] + 2[-241.814] + 2[-393.51] - [-912.87]$

$= \underline{\underline{-795.76\pm2.75\ \text{kJ mol}^{-1}}}$

$$\text{IId,}\quad C_6H_2(NO_2)_2(OPbOH)_{2,s} \xrightarrow{\Delta_r H^\theta} 2Pb_{,s}+2H_2O_{,g}+3CO_{2,g}+N_{2,g}+3C_{,s}$$

$$\Delta_r H^\theta = 2[-241.814] + 3[393.51] - [-912.87]$$

$$= \underline{\underline{-751.29\pm1.91\ \text{kJ mol}^{-1}}}$$

Dibasic lead 4,6-DNR

$$\text{Ie,}\quad C_6H_2(NO_2)_2(OPbOH)_2PbO_{,s} \xrightarrow{\Delta_r H^\theta} 3PbO_{,s}+2H_2O_{,g}+N_{2,g}$$

$$+2CO_{2,g}+4C_{,s}$$

$$\Delta_r H^\theta = 3[-218.99] + 2[-241.814] + 2[-393.51] - [-1118.08]$$

$$= \underline{\underline{-809.54\pm4.04\ \text{kJ mol}^{-1}}}$$

$$\text{IIe,}\quad C_6H_2(NO_2)_2(OPbOH)_2PbO_{,s} \xrightarrow{\Delta_r H^\theta} 3Pb_{,s}+2H_2O_{,g}+N_{2,g}+3\tfrac{1}{2}CO_{2,g}$$

$$+2\tfrac{1}{2}C_{,s}$$

$$\Delta_r H^\theta = 2[-241.814] + 3\tfrac{1}{2}[-393.51] - [-1118.08]$$

$$= \underline{\underline{-742.83\pm2.73\ \text{kJ mol}^{-1}}}$$

Tribasic lead 4,6-DNR

$$\text{If,}\quad C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s} \xrightarrow{\Delta_r H^\theta} 4PbO_{,s}+2H_2O_{,g}+N_{2,g}$$

$$+2CO_{2,g}+3C_{,s}$$

$$\Delta_r H^\theta = 4[-218.99] + 2[-241.814] + 2[-393.51] - [-1419.96]$$

$$= \underline{\underline{-726.65\pm5.32\ \text{kJ mol}^{-1}}}$$

IIf, $C_6H_2(NO_2)_2(OPbOH)_2 2PbO_{,s} \xrightarrow{\Delta_rH^\theta} 4Pb_{,s} + 2H_2O_{,g} + N_{2,g} + 4CO_{2,g}$

$+2C_{,s}$

$$\Delta_rH^\theta = 2[-241.814] + 4[-393.51] - [-1419.96]$$

$$= \underline{\underline{-637.71 \pm 3.54 \text{ kJ mol}^{-1}}}$$

Normal lead styphnate

Ig, $C_6H(NO_2)_3O_2Pb.H_2O_{,s} \xrightarrow{\Delta_rH^\theta} PbO_{,s} + 1\tfrac{1}{2}H_2O_{,g} + 1\tfrac{1}{2}N_{2,g} + 3\tfrac{1}{4}CO_{2,g}$

$+2\ 3/4C_{,s}$

$$\Delta_rH^\theta = [-218.99] + 1\tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-714.70]$$

$$= \underline{\underline{-1145.92 \pm 1.60 \text{ kJ mol}^{-1}}}$$

IIg, $C_6H(NO_2)_3O_2Pb.H_2O_{,s} \xrightarrow{\Delta_rH^\theta} Pb_{,s} + 1\tfrac{1}{2}H_2O_{,g} + 1\tfrac{1}{2}N_{2,g} + 3.3/4CO_{2,g}$

$+2\tfrac{1}{4}C_{,s}$

$$\Delta_rH^\theta = 1\tfrac{1}{2}[-241.814] + 3\ 3/4[-393.51] - [-714.70]$$

$$= \underline{\underline{-1123.68 \pm 1.27 \text{ kJ mol}^{-1}}}$$

Monobasic lead styphnate

Ih, $C_6H(NO_2)_3(OPbOH)_{2,s} \xrightarrow{\Delta_rH^\theta} 2PbO_{,s} + 1\tfrac{1}{2}H_2O_{,g} + 1\tfrac{1}{2}N_{2,g} + 3\tfrac{1}{4}CO_{2,g}$

$+2\ 3/4C_{,s}$

$$\Delta_rH^\theta = 2[-218.99] + 1\tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-957.53]$$

$$= \underline{\underline{-1122.08 \pm 2.77 \text{ kJ mol}^{-1}}}$$

$$\text{IIh, } C_6H(NO_2)_3(OPbOH)_{2,s} \xrightarrow{\Delta_r H^\theta} 2Pb_{,s}+1\tfrac{1}{2}H_2O_{,g}+1\tfrac{1}{2}N_{2,g}+4\tfrac{1}{4}CO_{2,g}$$

$$+1\ 3/4C_{,s}$$

$$\Delta_r H^\theta = 1\tfrac{1}{2}[-241.814] + 4\tfrac{1}{4}[-393.51] - [-957.53]$$

$$= \underline{\underline{-1077.61\pm1.95 \text{ kJ mol}^{-1}}}$$

Tribasic lead styphnate

$$\text{Ii, } C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 4PbO_{,s}+1\tfrac{1}{2}N_{2,g}+3\tfrac{1}{2}H_2O_{,g}$$

$$+3\tfrac{1}{4}CO_{2,g}+2.3/4C_{,s}$$

$$\Delta_r H^\theta = 4[-218.99] + 3\tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-1972.4]$$

$$= \underline{\underline{-1028.82\pm5.33 \text{ kJ mol}^{-1}}}$$

$$\text{IIi, } C_6H(NO_2)_3(OPbOH)_2 2PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 4Pb_{,s}+1\tfrac{1}{2}N_{2,g}+3\tfrac{1}{2}H_2O_{,g}$$

$$+5\tfrac{1}{4}CO_{2,g}+3/4C_{,s}$$

$$\Delta_r H^\theta = 3\tfrac{1}{2}[-241.814] + 5\tfrac{1}{4}[-393.51] - [-1972.4]$$

$$= \underline{\underline{-939.88\pm3.57 \text{ kJ mol}^{-1}}}$$

Pentabasic lead styphnate

$$\text{Ij, } C_6H(NO_2)_3(OPbOH)_2 4PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 6PbO_{,s}+3\tfrac{1}{2}H_2O_{,g}+3\tfrac{1}{4}CO_{2,g}$$

$$+1\tfrac{1}{2}N_{2,g}+2.3/4C_{,s}$$

$$\Delta_r H^\theta = 6[-218.99] + 3\tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-2464.3]$$

$$= \underline{\underline{-974.90\pm7.95 \text{ kJ mol}^{-1}}}$$

$$\text{IIj, } C_6H(NO_2)_3(OPbOH)_2 4PbO.2H_2O_{,s} \xrightarrow{\Delta_r H^\theta} 6Pb_{,s} + 3\tfrac{1}{2}H_2O_{,g} + 6CO_{2,g}$$

$$+ 1\tfrac{1}{2}N_{2,g} + \tfrac{1}{4}O_{2,g}$$

$$\Delta_r H^\theta = 3\tfrac{1}{2}[-241.814] + 6[-393.51] - [-2464.3]$$

$$= \underline{\underline{-743.11 \pm 5.26 \text{ kJ mol}^{-1}}}$$

For metal salts other than those containing lead,

Ancillary data used

$\Delta_f H^\theta[BaO_{,s}] = -553.5\ 0.6 \text{ kJ mol}^{-1}$[16]

Barium styphnate

$$\text{Ik, } C_6H(NO_2)_3O_2Ba.H_2O_{,s} \xrightarrow{\Delta_r H^\theta} BaO_{,s} + 1\tfrac{1}{2}H_2O_{,g} + 1\tfrac{1}{2}N_{2,g} + 3\tfrac{1}{4}CO_{2,g}$$

$$+ 2.3/4C_{,s}$$

$$\Delta_r H^\theta = [-553.5] + 1\tfrac{1}{2}[-241.814] + 3\tfrac{1}{4}[-393.51] - [-1285.31]$$

$$= \underline{\underline{-909.82 \pm 1.31 \text{ kJ mol}^{-1}}}$$

$$\text{IIk, } C_6H(NO_2)_3O_2Ba.H_2O_{,s} \xrightarrow{\Delta_r H^\theta} Ba_{,s} + 1\tfrac{1}{2}H_2O_{,g} + 1\tfrac{1}{2}N_{2,g} + 3.3/4CO_{2,g}$$

$$+ 2\tfrac{1}{4}C_{,s}$$

$$\Delta_r H^\theta = 1\tfrac{1}{2}[-241.814] + 3\ 3/4[-393.51] - [-1285.31]$$

$$= \underline{\underline{-553.07 \pm 1.19 \text{ kJ mol}^{-1}}}$$

Silver styphnate

IIl, $C_6H(NO_2)_3(OAg)_{2,s} \xrightarrow{\Delta_rH^\theta} 2Ag_{,s}+\frac{1}{2}H_2O_{,g}+3\ 3/4CO_{2,g}+3/2N_{2,g}$

$+2\frac{1}{4}C_{,s}$

$$\Delta_rH^\theta = 3\ 3/4[-393.51] + \tfrac{1}{2}[-241.814] - [-251.56]$$

$$= \underline{\underline{-1345.01 \pm 2.12 \text{ kJ mol}^{-1}}}$$

Thallous styphnate

IIm, $C_6H(NO_2)_3(OTl)_{2,s} \xrightarrow{\Delta_rH^\theta} 2Tl_{,s}+\frac{1}{2}H_2O_{,g}+1\frac{1}{2}N_{2,g}+3\ 3/4CO_{2,g}$

$+2\frac{1}{4}C_{,s}$

$$\Delta_rH^\theta = \tfrac{1}{2}[-241.814] + 3\ 3/4[-393.51] - [-503.99]$$

$$= \underline{\underline{-1092.58 \pm 1.14 \text{ kJ mol}^{-1}}}$$

Thallous styphnate (½ Acid)

IIn, $C_6H(NO_2)_3OTlOH_{,s} \xrightarrow{\Delta_rH^\theta} Tl_{,s}+H_2O_{,g}+1\frac{1}{2}N_{2,g}+3\frac{1}{2}CO_{2,g}+2\frac{1}{2}C_{,s}$

$$\Delta_rH^\theta = [-241.814] + 3\tfrac{1}{2}[-393.51] - [-468.48]$$

$$= \underline{\underline{-1150.62 \pm 0.97 \text{ kJ mol}^{-1}}}$$

From analysis of these enthalpies of decomposition, some comparison can be seen to exist between the enthalpy and their energetic nature. For example, the enthalpy of decomposition of silver styphnate is substantially greater than that of barium styphnate. This is also comparable to their explosive nature, as silver styphnate detonates much more violently than barium styphnate. Similarly comparison is also observable in the different series of lead salts. When silver styphnate is compared with monobasic lead styphnate, the reverse is true.

Several decomposition product mixtures have been considered here. To speculate on an explosive or otherwise decomposition mechanism is far more difficult as the probability of carbon monoxide also being formed has to be great, and the decomposition would not be limited by the availability of internal oxygen.

Table IV-27

Summary of Results for the various metallo styphnates

	Nitric Acid concn (N)	$\Delta_r H^\theta$/kJ mol^{-1}	$\Delta_f H^\theta$/kJ mol^{-1}
Normal Lead Styphnate Monohydrate	0.1	-17.29±0.18	-714.70±1.17
Monobasic Lead Styphnate	0.1	-61.92±0.20	-957.53±1.87
Tribasic Lead Styphnate Dihydrate	1.0	-196.37±0.19	-1972.42±3.48
Pentabasic Lead Styphnate Dihydrate	1.0	-281.12±0.79	-2464.27±5.19
Silver Styphnate	1.0	+14.17±0.54	-251.16±2.06
Thallous Styphnate	0.1	+26.80±0.17	-468.48±0.86
Thallous Styphnate	0.1	+64.56±0.24	-503.99±1.03
Barium Styphnate	0.1	+17.12±0.62	-1285.31±1.24

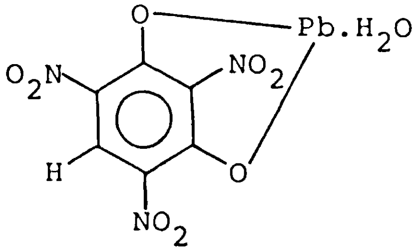
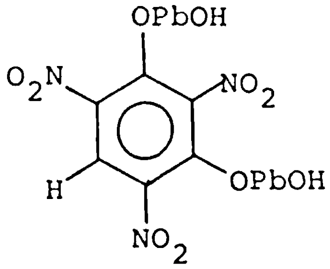
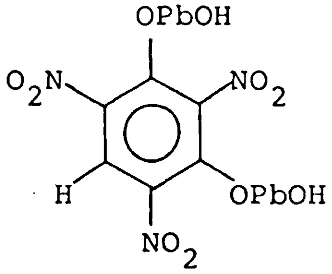
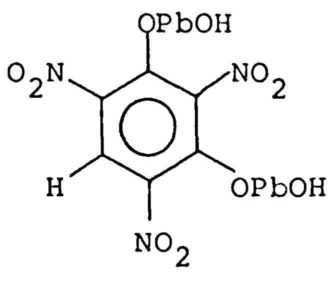
Table IV-28

Summary of Results for the various metallo dinitroresorcinates

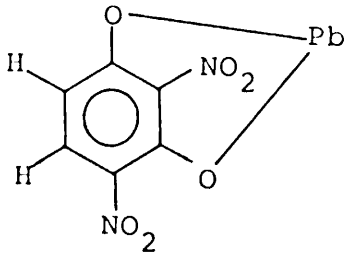
	Nitric Acid conc^n (N)	$\Delta_r H^\theta$/kJ mol^{-1}	$\Delta_f H^\theta$/kJ mol^{-1}
Monobasic Lead 4,6-DNR	1.0	-96.62±0.14	-912.87±1.87
Dibasic Lead 4,6-DNR	1.0	-175.88±0.45	-1118.08±2.69
Tribasic Lead 4,6-DNR	1.0	-162.47±0.53	-1419.96±3.50
Normal Lead 2,4-DNR	1.0	-29.36±0.17	-381.17±1.17
Monobasic Lead 2,4-DNR	1.0	-85.34±0.53	-613.62±1.94
Tribasic Lead 2,4-DNR	1.0	-179.12±0.42	-1382.53±3.50
Quadrabasic Lead 2,4-DNR	1.0	-227.37±0.92	-1622.71±4.45

Table IV-29

Lead Salt structures and their related Enthalpies of Formation, $-\Delta_f H^\theta$/kJ mol^{-1}

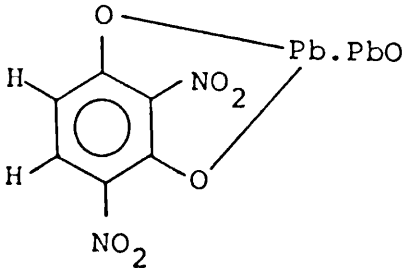
1/		714.70±1.17
2/		957.53±1.87
3/	 $2PbO.2H_2O$	1972.4±3.5
4/	 $4PbO.2H_2O$	2464.3±5.2

5/



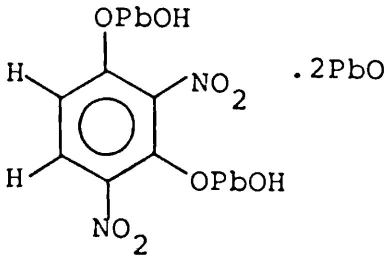
381.17±1.17

6/



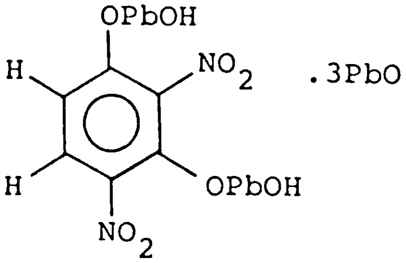
613.62±1.94

7/



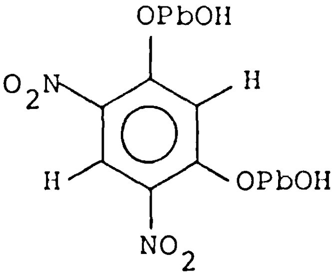
1382.5±2.1

8/



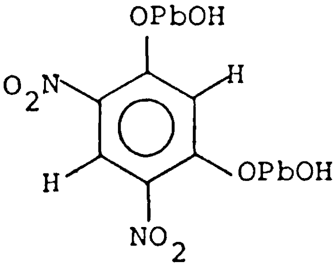
1622.7±4.5

9/



912.87±1.87

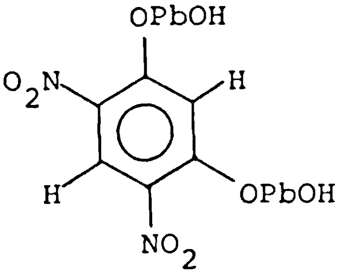
10/



.PbO

1118.08±2.69

11/



.2PbO

1419.96±3.5

Table IV-30

Estimated Enthalpies of Formation, $-\Delta_f H^\theta/\text{kJ mol}^{-1}$

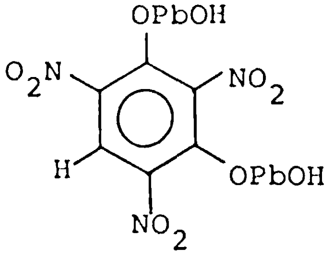
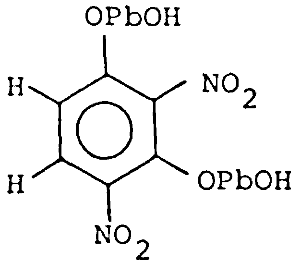
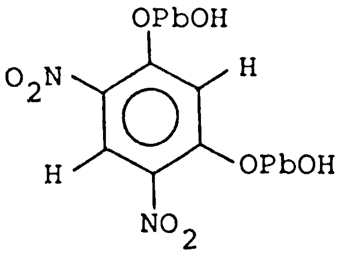
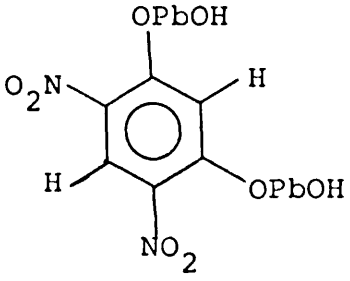
A.		.PbO	1162.1
B.		.4PbO	1871.0
C.		.3PbO	1643.3
D.		.4PbO	1891.6

Table IV-31

Calculated Enthalpies of Decomposition, $-\Delta_r H^\theta$/kJ mol^{-1}

	MO_2	MO	M
Normal lead 2,4-DNR	728.31±1.43	718.65±1.56	844.42±1.22
Monobasic lead 2,4-DNR	576.50±2.52	853.19±2.80	808.72±1.98
Tribasic lead 2,4-DNR	604.24±3.83	764.11±4.53	675.17±2.17
Quadrabasic lead 2,4-DNR	———	742.90±6.73	631.72±4.54
Monobasic lead 4,6-DNR	519.07±2.47	795.76±2.75	751.29±1.91
Dibasic lead 4,6-DNR	394.50±3.61	809.54±4.04	742.83±2.73
Tribasic lead 4,6-DNR	566.77±4.74	726.65±5.32	637.71±3.54
Normal lead styphnate	1007.57±1.46	1145.92±1.60	1123.68±1.27
Monobasic lead styphnate	845.39±2.48	1122.08±2.77	1077.61±1.95
Tribasic lead styphnate	475.44±4.75	1028.82±5.33	939.88±3.57
Pentabasic lead styphnate	144.82±7.08	974.90±7.95	743.11±5.26
Barium styphnate	793.86±1.34	909.82±1.31	553.07±1.19

	M_2O	MO	M
Thallous styphnate (½ Acid)	1141.57±0.99	———	1150.62±0.97
Thallous styphnate	1074.48±1.22	———	1092.58±1.14
Silver styphnate	1179.30±2.33	———	345.01±2.12

M is the metal ion.

IV-EI: References

1. WADSÖ,I.,Science Tools,The LKB Instrument Journal, 13,33,(1966).
2. DICKINSON,H.C.,Bull.Natl.Bur.Stand.(U.S.),11,189,(1914).
3. COOPS,J.,JESSUP,R.S.and VAN NES,K.,'Experimental Thermochemistry',1,Interscience,(1956).
4. GUNN,S.R.,J. Chem.Therm.,3,19,(1971).
5. PEAKE,S.J.,PhD. Thesis,Univ. of Lon.,(1976).
6. PRITCHARD,H.O.,and SKINNER,H.A.,J.Chem.Soc.,272,(1950).
7. FAULKER,E.A.,and McGLASHAN,M.L.,J.Chem.Soc.,510,2837,(1965).
8. EILBECK,W.J.,HOLMES,F.,and THOMAS,T.W.,J.Chem.Soc.(A), 2062,(1970).
9. FOSSUM,J.H.,MARKUNAS,P.C.,and RIDDICK,J.A.,Anal.Chem., 23,491,(1951).
10. IRVING,R.J.and WADSÖ,I.,Acta Chem.Scand.,18,195,(1964).
11. VANDERZEE,C.E.,WAUGH,D.H.,and HAAS,N.C.,J.Chem. Thermodynamics,13,1,(1981).
12. PROSEN,E.J.,and KILDAY,M.V.,J.Res.Nat.Bur.Stand.,77A, 581,(1973).
13. HILL,J.O.,ÖJELUND,G.,and WADSÖ,I.,J.Chem.Thermodyn., 1,111,(1969).
14. CODATA,Recommended Key Values for Thermodynamics, J.Chem.Thermodyn.,8,603,(1976).
15. STEELE,W.N.,CARSON,A.S.,LAYE,P.G.,and SPENCER,J.A., J.Chem.Thermodyn.,5,477,(1973).
16. WAGMAN,D.D.,EVANS,W.H.,PARKER,V.B.,SCHUMM,R.M.,MALOW,I., BAKEY,S.M.,CHURNEY,K.L.,and NUTTALL,R.L.,J.Phys.Chem. Ref.Data,National Bureau of Standards,11,2,(1982).
17. KURZ,E.,and KOBER,G.,Zeistchrift fur Analylische Chemie, 254,2,127,(1971).
18. VOGEL,A.,Textbook of Quantitative Inorganic Analysis, 3rd Edn.,P275,Longman,London,(1961).

19. VOGEL,A.,Textbook of Quantitative Inorganic Analysis, 4th Edn.,Longman,London,(1978).

20. ABRAHAM,M.H.,Themochemistry and its Applications to Chemical and Biochemical Systems,392-409,Riedel,N.Y., (1984).

21. SHAW,R.,J.Phys.Chem,75,26,4047,(1971).

22. TOMPKINS,F.C.,and YOUNG,D.A.,Trans.Faraday Soc.,1245, (1956).

23. TOMPKINS,F.C.,and YOUNG,D.A.,J.Chem.Soc.,3331,(1956).

24. FLANAGAN,T.B.,Trans.Faraday Soc.,57.1,797,(1961).

25. FEDOROFF,B.T.,Pic.Ars.Tech.Rep.,2700,5,(1972).

26. COOK,M.A.,The Science of High Explosives,P405,Reinhold, N.Y.,(1959).

27. MEYER,R.,Explosives,2nd Edn.,Verlag Chemie,P211,(1981).

28. TANG,T.,Thermochimica Acta,61,341,(1983).

29. WAGMAN,D.D.,EVANS,W.H.,HALOW,I.,PARKER,V.B.,BAILEY,S.M., and SCHUMM,R.H.,Nat.Bur.Std.Tech.Note 270-2,(1966).

30. TYLER,F.,Heat & Thermodynamics,Arnold,London,P38,(1965).

Chapter V

SOLUBILITY AND ENTHALPY OF SOLUTION BY THE DYNAMIC PRECIPITATION METHOD

V-A: Solubility and Enthalpy of Solution

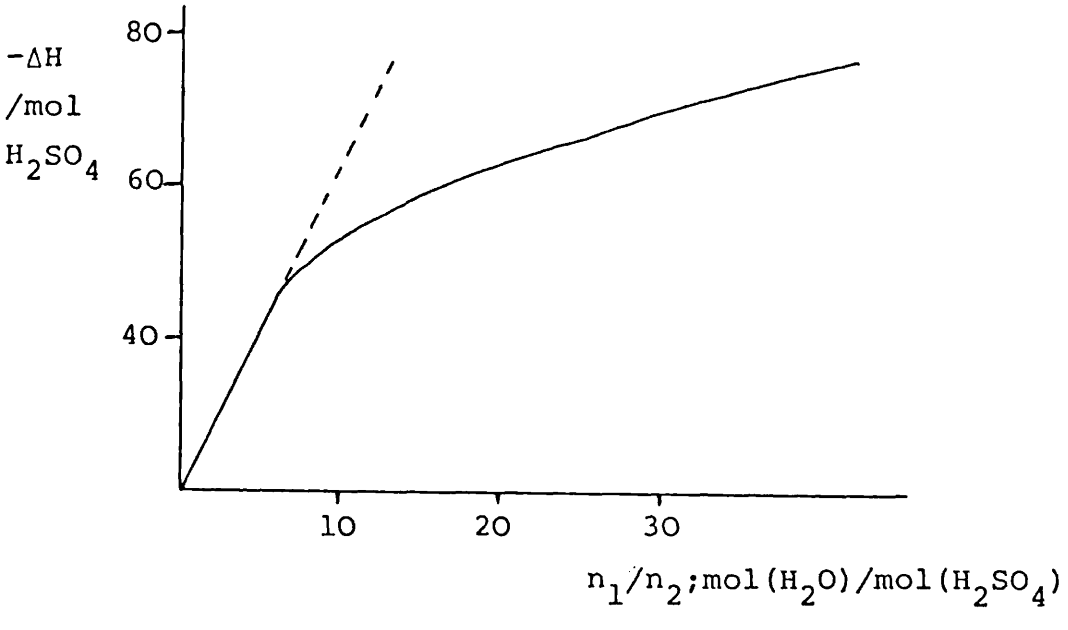
Solubility may be defined as the extent to which a solute will dissolve in a solvent. When calorimetric studies are undertaken it is important to determine if a differential or integral thermal quantity is being considered. As it is possible to derive a differential from an integral enthalpy change, the most common data recorded are those of integral or total heats of solution and dilution.

V-B: Integral (Total) Heat of Solution

By considering the reaction of 1 mole of liquid sulphuric acid into n_1 moles of water,

$$H_2SO_{4,\ell} + n_1H_2O_{,\ell} \longrightarrow H_2SO_4(n_1H_2O)$$

the associated enthalpy change per mole of H_2SO_4 is the integral heat of solution. If this reaction was performed experimentally, it would be noted, that with constant stirring, and constant addition of sulphuric acid, the solution would become steadily hotter, but the rate of heating decreased towards the end[1].



From this graph the effect of dilution of the sulphuric acid can also be seen, as at infinite dilution n_2 (number moles H_2SO_4) will tend to zero, and the ΔH value obtained will be the integral heat of solution to infinite dilution.

V-C: Heats of Dilution

From the differents between the ΔH values obtained from two separate integral heats of solution, the integral heat of dilution is obtained.

V-D: Differential (Partial) Heat of Solution

If n_1 moles of a solute are dissolved in a solvent containing n_2 moles of water and n_3 moles of solvated solute, a differential heat of solution is obtained.

V-E: Calorimetry

So far, the calorimetric processes studied in this investigation have only been concerned with integral enthalpy changes. The dynamic precipitation technique is concerned with enthalpies of solution. By consideration of the enthalpies of solution of lead nitrate in water, a comparative study was made between value obtained from this technique, and those from solution calorimetry.

V-F: Ions in Solution

When any metal salt is dissolved in an aqueous solution, several equilibria are possible, e.g., ion pairing, polymerisation, cluster formation and hydrolysis. All of these are dependent on the degree of dissociation of the ions, and thus to ionic concentration of the solution. The thermodynamic equilibrium constant is related to the standard free energy by the reaction isotherm, equation VA

$$\Delta G^{\theta} = -RT\ell nK \qquad \text{(VA)}$$

where K is the equilibrium constant, and ΔG^{θ} is the Gibbs free energy of the solvated anion and cation pairs.

Applying this equation to a sparingly soluble salt (MX) system that contains crystalline salt and a saturated solution, it can be shown that equation VB can be written where S is the solubility of a completely ionized two ion system.

$$\Delta_{sol}G^{\theta} = -2RT\ell nS \qquad \text{(VB)}$$

Combining equation VB with the Gibbs-Helmholtz equation (in the form of equation VC), the van't Hoff isochore is derived; equation VD

$$\frac{d}{dT}\left(\frac{\Delta_{sol}G^{\theta}}{T}\right) = -\frac{\Delta_{sol}H^{\theta}}{T^2} \qquad \text{(VC)}$$

$$\frac{d\ell nS}{dT} = \frac{\Delta_{sol}H^{\theta}}{2RT^2} \qquad \text{(VD)}$$

For a given equilibrium, two equilibrium constants at different temperatures are found, allowing the differential equation VD to be solved.

Equation VE is the integrated form of equation VD. Equation VE is applied to the dynamic precipitation technique.

$$\ell nS = -\frac{\Delta_{sol}H^{\theta}}{2RT} + \text{cont.} \qquad \text{(VE)}$$

When high ion concentrations are being considered for the calculation of $\Delta_{sol}H^{\theta}$, consideration is needed to the standard state of the reactants and resultants. It is hence necessary to use ionic activity coefficients, γ, at the concentrations of the saturated solution to calculate the Gibbs free energy of solution.

where γ = mean ionic activity coefficient[6].

n = stoichiometric number of ions produced per mole of electrolyte.

$\underline{m}$ = molality of the saturated solution.

$$-\Delta_{sol}G^{\theta} = nRT\ell n(\underline{m}\gamma)_{sat} \qquad \text{(VF)}$$

$$-\Delta_{sol}H^{\theta} = nRT^{2}\left(\frac{d\ell n(\underline{m}\gamma)}{dT}\right)_{sat} \qquad \text{(VG)}$$

and

$$\Delta_{sol}H^{\theta} = nRT^{2}(d\underline{m}/dT)_{sat}[(\partial\ell n\gamma/\partial\underline{m})_{T} + (1/\underline{m})_{sat}] \qquad \text{(VH)}$$

Equation VG only applied to ideal solutions; however equation VH has been derived by Williamson[3] for non-ideal systems of anhydrous electrolytes.

V-G: Solubility and Enthalpy of Solution of Lead Nitrate

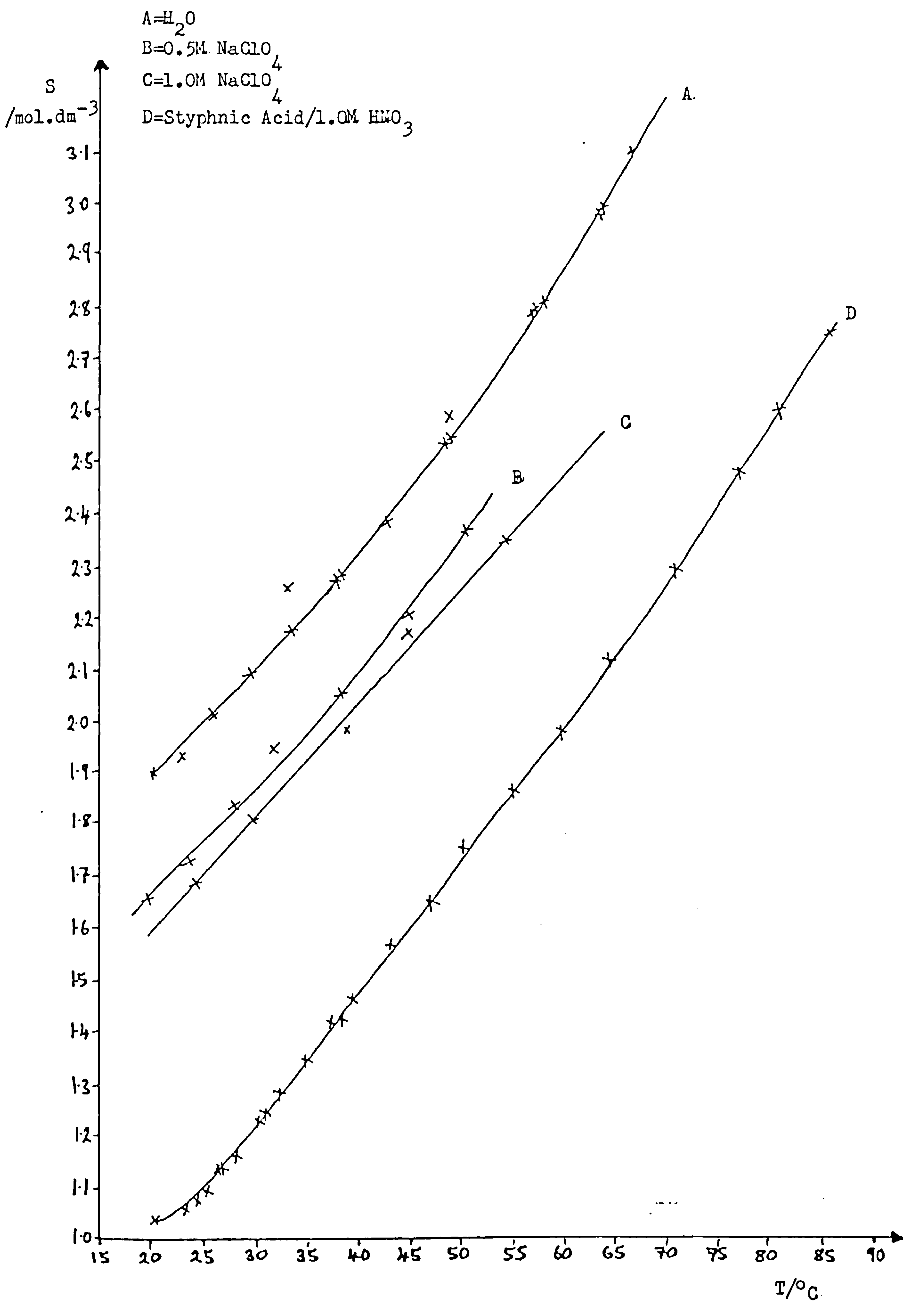
The method of dynamic precipitation[4], was used to determine the solubility of lead nitrate in water and in a nitric acid/styphnic acid mixture, and in aqueous solutions of varying ionic strength. Temperature readings were repeated until three successive readings within ± 0.2° were obtained, using a calibrated 0.1° thermometer.

The results obtained are collated in Table I-1; V-2; V-3; V-4, and illustrated in Figures V-A and B. Using Figure V-B and an application[2] of the van't Hoff isochore differential enthalpies of solution have been estimated; Table V-5.

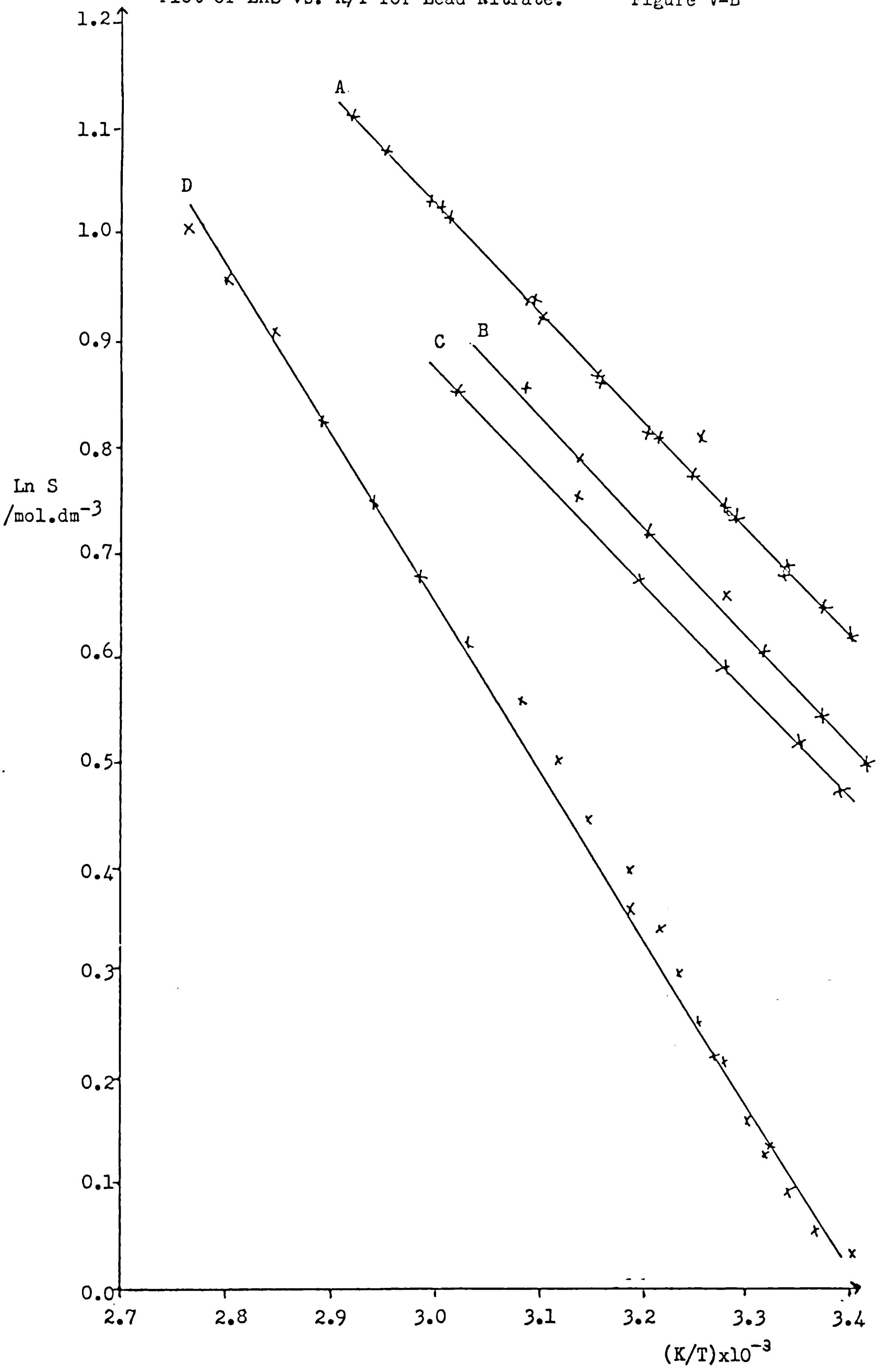
$$\ell nS = -\frac{\Delta_{sol}H^{\theta}}{nRT} + \frac{\Delta_{sol}S^{\ominus}}{R} \qquad \text{(VI)}$$

As a plot of ℓnS versus $1/T$ will give a straight line of gradient $\Delta_{sol}H^{\theta}/nR$, and a Y-axis intercept of $\Delta_{sol}S^{\ominus}/R$.

Solubility plot of Lead Nitrate in various solutions. Figure V-A



Plot of LnS vs. K/T for Lead Nitrate. Figure V-B



Comparison of the $\Delta_{sol}H^{\theta}$ values from the dynamic precipitation, and the calorimetric methods showed a difference of approximately 8 kJ. This difference was far greater than any experimental error; it was thus necessary to consider the nature of the experiment for an explanation.

As previously mentioned, the dynamic precipitation method gives a differential enthalpy of solution. As this solute is an electrolyte, then the activities of the individual ionic species in solution needs consideration.

V-H: Activity Correction

As no experimental method exists for the determination of the activity coefficient of a single ionic species, an expression of the mean ionic activity coefficient has been determined on the theoretical concepts of Debye and Hückel[5].

$$\gamma_{\pm}^{\nu} = \gamma_{+}^{\nu+}\gamma_{-}^{\nu-} \qquad \text{(VJ)}$$

where $\nu = \nu_{+} + \nu_{-}$, the total number of ions produced per molecule of electrolyte.

Taking the logarithms of equation VJ gives,

$$\ell n\ \gamma_{\pm} = \frac{\nu_{+}\ \ell n\ \gamma_{+} + \nu_{-}\ \ell n\ \gamma_{-}}{\nu_{+} + \nu_{-}} \qquad \text{(VK)}$$

Various substitutions in this equation gives rise to the Debye-Hückel limiting law, VL[9]

$$-\ell n\ \gamma_{\pm} = \alpha \left| Z_{+}\ Z_{-} \right| I^{\frac{1}{2}} \qquad \text{(VL)}$$

where α = 0.5115 for aqueous solutions at 25°C.
Z_{+} and Z_{-} = numerical valencies.
I = ionic strength.

$$I = \tfrac{1}{2} \sum_i m_i z_i^2 \qquad \text{(VM)}$$

The problem of calculating an enthalpy of solution can now be seen to be dependent on the calculation of a suitable set of values for the mean activity coefficient, e.g. from Debye and Hückel theory. The problem here is that Debye and Hückel theory only applies to electrolytes in solution at very low concentrations ($m \leqslant 2\times10^{-3}$ mol Kg^{-1}). Many attempts have been made to apply Debye-Hückel theory to higher concentration solutions, these new theories usually fail when applied to systems other to those they were originally postulated for. The possibility of extrapolation of values of γ from lower to high concentrations is unsatisfactory since unpredictable deviations from the Debye-Hückel theory occur. The approach that was finally used was based on some work recently performed by Sandall[7].

In recent work by Mordecai[8], the study of aqueous lead nitrate solutions had been undertaken using nuclear magnetic resonance (N.M.R.) spectroscopy. In this work the postulation of a $PbNO_3^+$ (aqueous) ion existing in acidic solutions has been made. A single ^{207}Pb resonance signal was observed for each solution of lead nitrate, and was thought to be due to the rapid exchange between Pb^{2+} (aqueous) and $PbNO_3^+$ (aqueous). From shifts in the position of signal with acidity, the equilibrium constant for

$$Pb^{2+}_{,aq} + NO^{-}_{3,aq} \rightleftarrows PbNO^{+}_{3,aq}$$

was calculated. Sandall applied the Debye-Hückel approximation in the form,

$$\ell n\gamma_{\pm} = -4A\left[\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}}\right] + CI \qquad \text{(VN)}$$

where I = ionic strength, calculated by using equation VM.
$A = 0.5115$ for water.

$$I = \tfrac{1}{2}\Sigma_i m_i Z_i^2 \qquad \text{(VM)}$$

where Z_i = ionic charge or valency.
m_i = molality of ion i in solution.

Combining equations VN and VM, a range of C values were produced at given temperatures. The values of C were then plotted against temperature, Figure V-C, and using statistical analysis, Appendix V, and value for C at 298.15K was obtained. This value was then substituted back into equation VN and the mean activity coefficients calculated over the range of concentrations used experimentally. Once the values of $-\ell n\ \gamma\pm$ had been calculated, they could then be used in conjunction with the experimental data from the dynamic precipitation method to determine $(d\ell n\ \gamma\pm/dm)_{sat}$. This was then substituted into the Williamson equation with other ancillary data to produce an activity-corrected enthalpy of solution. From Figure V-C, a linear regression equation of the form $y=mx+c'$ was calculated.
$y = 3.5\times10^{-3}x - 0.861$

Correlation coefficient, $r^2 = 0.88$

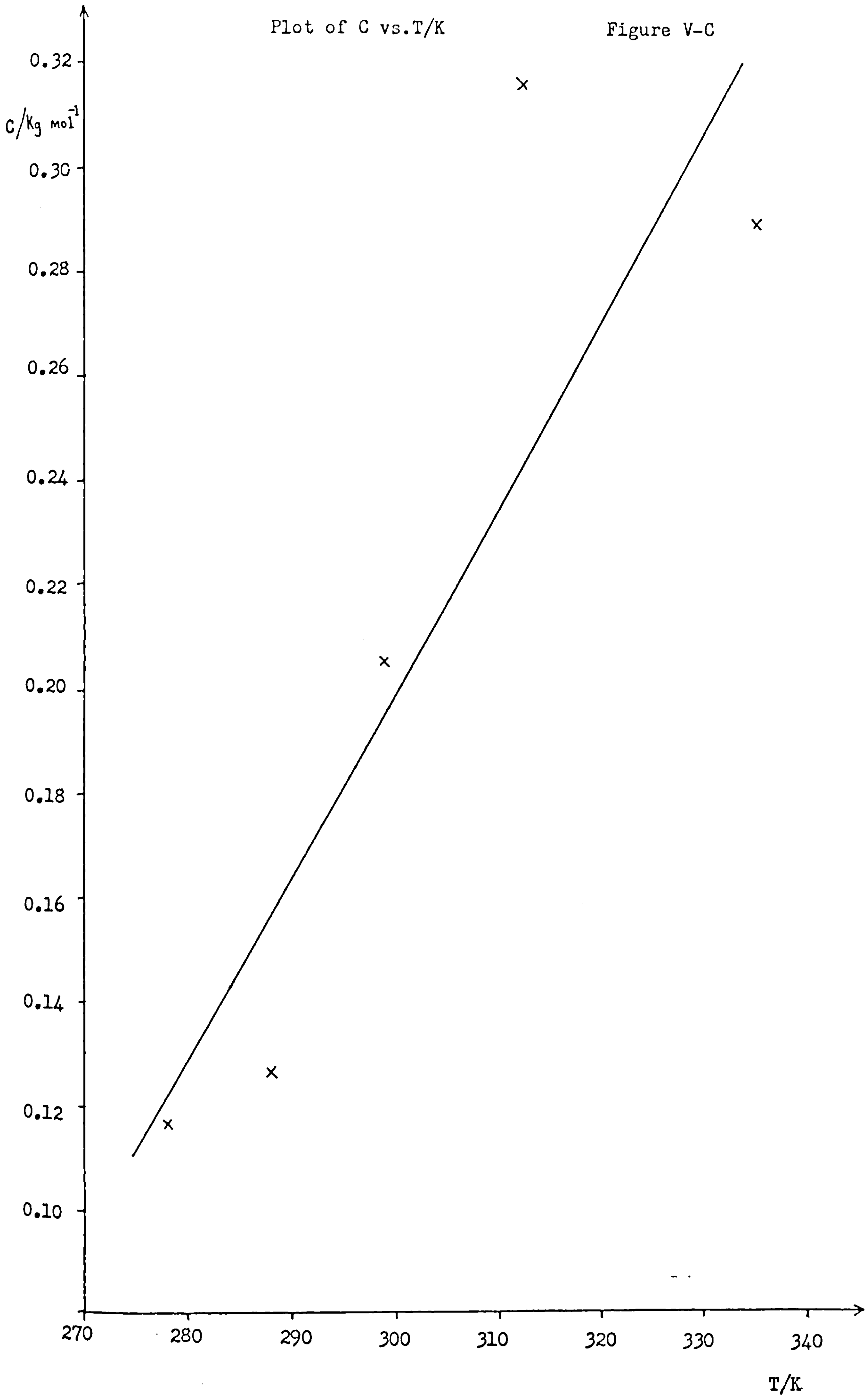
Giving $C = 0.1938$ at 298.15K.

Using this C value, the values of $-\ell n\ \gamma\pm$ were calculated, Table V-6.

From data, the following were calculated.

$$\left(\frac{d\ell n\gamma}{dm}\right)_{sat} = -0.3948$$

$$\left(\frac{dm}{dT}\right)_{sat} = 0.02513$$


Plot of C vs.T/K
Figure V-C
C/Kg mol^{-1}
0.32
0.30
0.28
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
270
280
290
300
310
320
330
340
T/K

Substituting in equation VH with the ancillary data below, an enthalphy of solution was calculated.

Ancillary data.

$\left(\frac{1}{m}\right)_{sat} = 0.224 \text{ mol}^{-1} \text{ 1000g } H_2O$[9].

It can be seen, Table V-7, that this method of correction has proved most successful. The enthalpy of solution was calculated with the assumption of there only being three moles of ions producted in solution, Pb^{2+} and $2NO_3^-$.

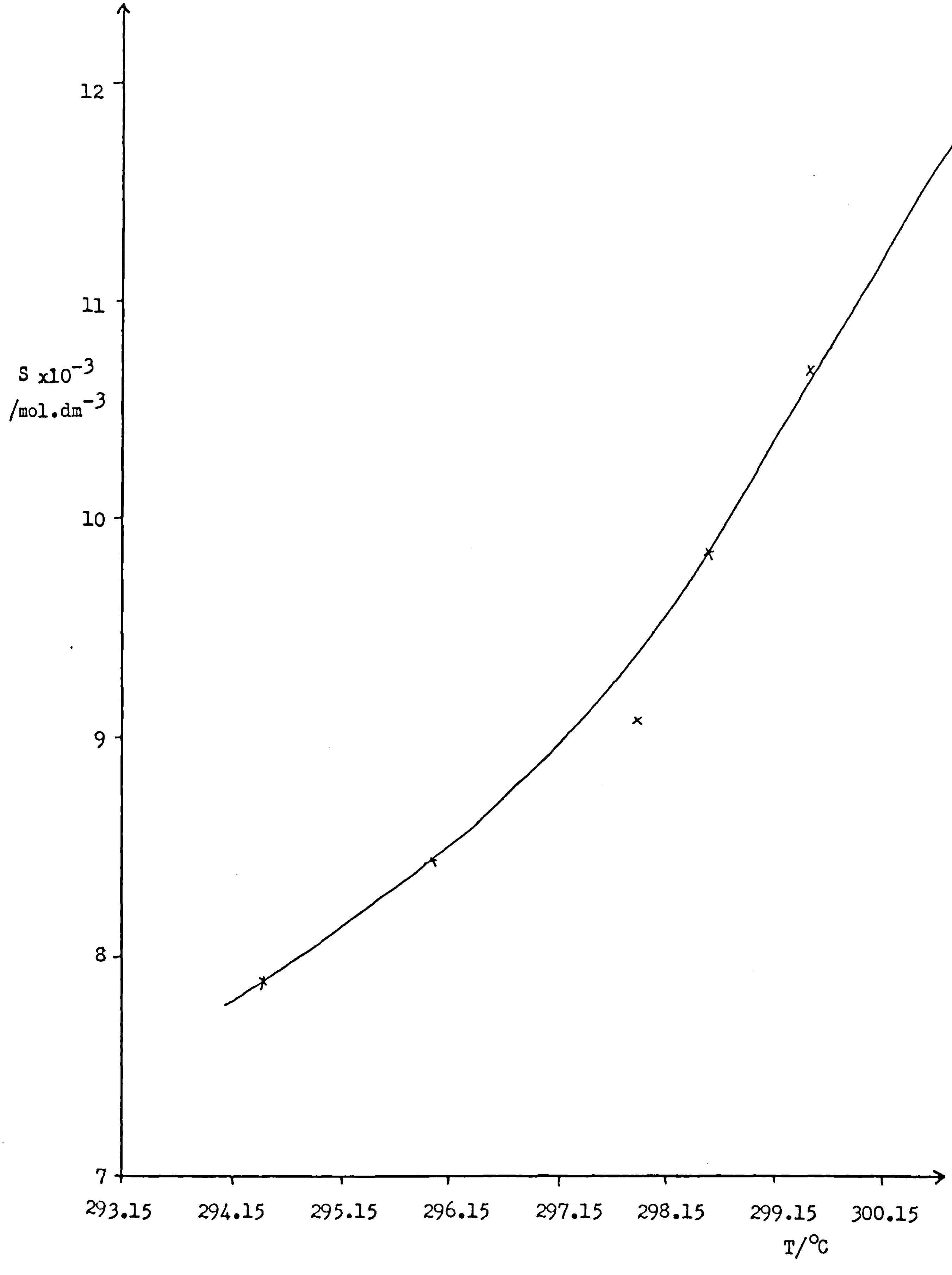
V-I: Solubility of Styphnic Acid in Hydrochloric Acid

The method of dynamic precipitation was used to determine the solubility of styphnic acid in hydrochloric acid (B.D.H. 0.1M). Hydrochloric acid was added to a sample (0.0304g) of purified styphnic acid. By the method previously described, temperature readings were taken repeatedly until three successive readings within ±0.2° were obtained using a calibrated 0.1° thermometer. One cubic centimetre of hydrochloric acid was then pipetted into the mixture and the process repeated. The results obtained are tabulated in Table V-8.

The van't Hoff isochore, in conjunction with a plot of ℓnS vs 1/T, Figure V-E, and the VEGA program, Appendix I, was used to calculate the enthalpy of solution. The results are shown in Table V-9.

Solubility plot of Styphnic Acid in Hydrochloric Acid.

Figure V-D



Plot of Ln S vs. 1/T for Styphnic Acid. Figure V-E

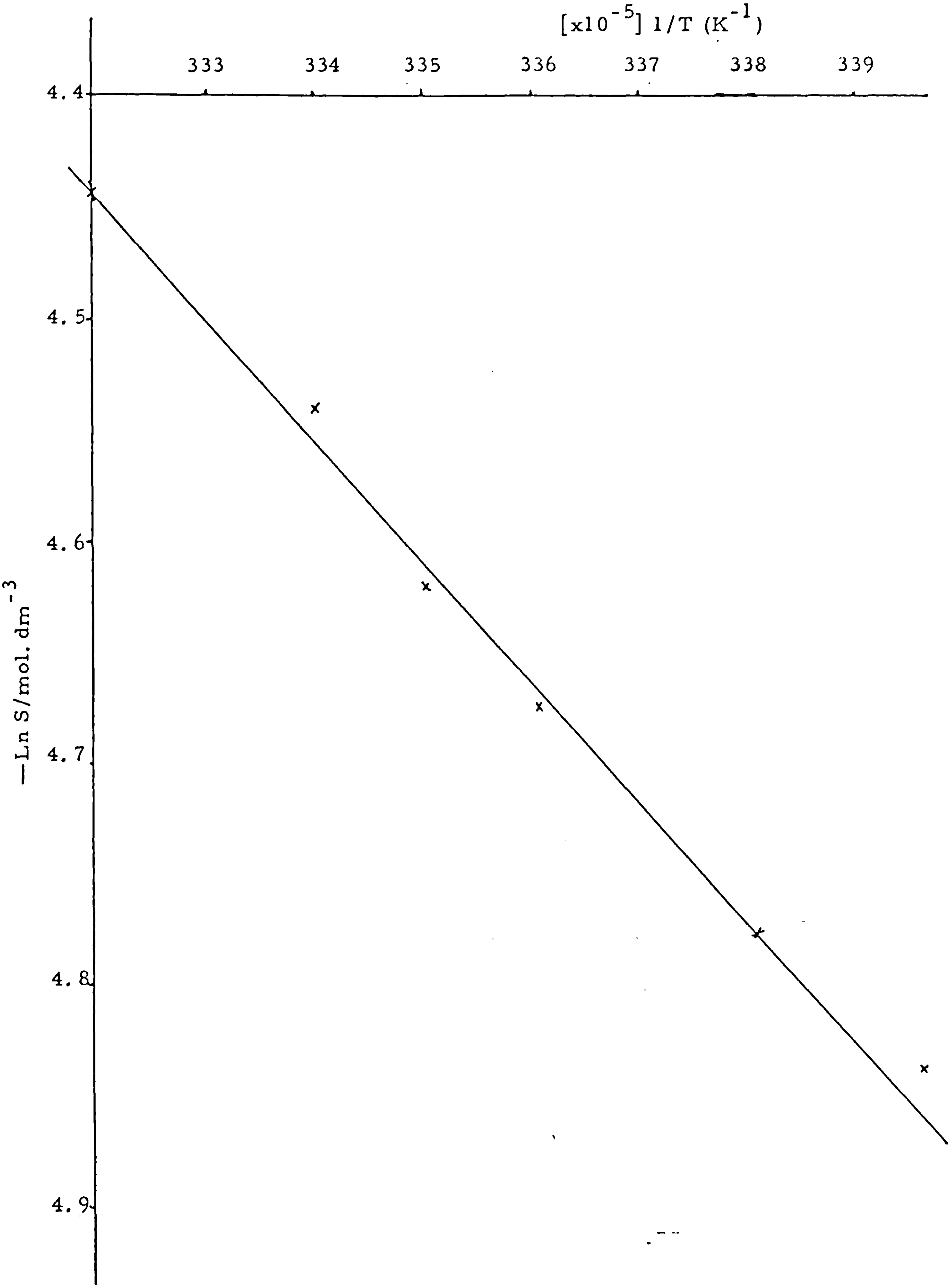


Table V-1

Solubility of Lead Nitrate in Styphnic Acid/Nitric Acid

W/g	Vol. of Sty. Acid/ Nitric Acid; cm^3	S/ mol dm^{-3}	ℓn S	T/K	10^3K/T
3.3080	6.0	1.665	0.5096	318.05	3.14
	7.0	1.427	0.3555	312.75	3.20
	8.0	1.248	0.2219	304.95	3.28
	8.5	1.175	0.1613	302.25	3.31
	8.8	1.135	0.1266	301.35	3.32
	9.1	1.098	0.0931	299.15	3.34
	9.4	1.063	0.0607	296.95	3.37
	9.7	1.030	0.0293	293.65	3.40
4.9293	5.4	2.756	1.0138	360.75	2.77
	5.7	2.611	0.9598	355.65	2.81
	6.0	2.480	0.9085	351.25	2.85
	6.5	2.289	0.8284	345.35	2.90
	7.0	2.126	0.7543	338.55	2.95
	7.5	1.984	0.6853	334.35	2.99
	8.0	1.860	0.6208	329.05	3.04
	8.5	1.751	0.5602	323.95	3.09
	9.0	1.654	0.5030	320.45	3.12
	9.5	1.567	0.4489	317.05	3.15
	10.0	1.488	0.3976	313.15	3.19
	10.5	1.417	0.3488	310.95	3.22
	11.0	1.353	0.3023	308.65	3.24
	11.5	1.294	0.2579	306.35	3.26
	12.0	1.240	0.2153	304.45	3.28
	13.0	1.145	0.1353	300.35	3.33

Table V-2

Solubility of Lead Nitrate in Aqueous solution of 1.0M Sodium Perchlorate

W/g	Vol. of 1.0M $NaClO_4/cm^3$	S/ mol dm^{-3}	ℓn S	T/K	$10^3K/T$
3.9143	5.0	2.364	0.8602	328.95	3.04
	5.5	2.149	0.7649	318.47	3.14
	6.0	1.970	0.6779	312.59	3.20
	6.5	1.818	0.5978	304.87	3.28
	7.0	1.688	0.5237	248.51	3.35
	7.3	1.619	0.4818	294.98	3.39

Table V-3

Solubility of Lead Nitrate in Aqueous solution of 0.5M Sodium Perchlorate

W/g	Vol. of 0.5M $NaClO_4/cm^3$	S/ mol dm^{-3}	ℓn S	T/K	$10^3K/T$
5.4886	7.0	2.367	0.8618	323.55	3.09
	7.5	2.209	0.7928	318.55	3.14
	8.0	2.071	0.7283	312.25	3.20
	8.5	1.950	0.6676	304.95	3.28
	9.0	1.841	0.6105	301.20	3.32
	9.5	1.744	0.5564	297.18	3.36
	10.0	1.657	0.5051	292.83	3.42

Table V-4

Solubility of Lead Nitrate in Water

W/g	Vol. of Water/cm^3	S/ mol dm^{-3}	ℓn S	T/K	10^3K/T
3.5626	3.9	2.818	1.036	332.35	3.01
	4.2	2.573	0.945	323.95	3.09
	4.5	2.399	0.875	315.85	3.17
	4.8	2.259	0.815	311.75	3.21
	5.1	2.120	0.752	304.95	3.28
	5.4	1.986	0.686	299.65	3.34
2.9947	4.0	2.260	0.816	306.75	3.26
3.3574	4.0	2.534	0.930	321.54	3.11
3.6938	4.0	2.788	1.025	331.13	3.02
3.9383	4.0	2.973	1.089	337.84	2.96
3.7417	4.0	2.824	1.038	333.33	3.00
5.1154	5.0	3.089	1.128	341.05	2.93
	6.0	2.574	0.946	322.75	3.10
	6.5	2.376	0.866	316.15	3.16
	6.8	2.271	0.820	311.85	3.21
	7.1	2.175	0.777	307.35	3.25
	7.4	2.087	0.736	303.25	3.30
	7.7	2.006	0.696	299.65	3.34
	8.0	1.931	0.658	296.65	3.37
	8.2	1.884	0.633	293.65	3.40

Table V-5

Aqueous solubility data

	0.0M $NaClO_4$	0.5M $NaClO_4$	1.0M $NaClO_4$	Styphnic Acid/HNO_3 (M)
Solubility of lead nitrate at 25^{o}C g mol dm^{-3}	1.97	1.77	1.68	1.11
$\Delta_{sol}H^{\theta}$; kJ mol^{-1}	25.83	26.74	27.29	40.06
n	20	7	6	24
m	-1.036	-1.072	-1.094	-1.606
c	4.152	4.168	4.188	5.492
r	0.997	0.997	0.998	0.997
$\Delta_{sol}S^{\theta}$; J mol^{-1}K^{-1}	34.52	34.65	34.82	45.66

n = No. of Readings
m = Slope ($\Delta_{sol}H^{\theta}/R$)
c = Intercept with ℓn S axis ($\Delta_{sol}S^{\theta}/R$)
r = Correlation Coefficient

Table V-6

m/mol. kg^{-1}	T(k)	I/mol Kg^{-1}	CI	$-4A\left[\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}}\right]$	$-\ell n\ \gamma\pm$
2.826	332.35	7.065	1.3692	1.4867	0.1175
2.581	323.95	6.453	1.2506	1.4681	0.2175
2.406	315.85	6.015	1.1657	1.4534	0.2877
2.266	311.75	5.665	1.0978	1.4407	0.3429
2.126	304.95	5.315	1.0300	1.4270	0.3970
1.992	299.65	4.980	0.9651	1.4128	0.4477
2.267	306.75	5.667	1.0983	1.4408	0.3425
2.541	321.54	6.353	1.2312	1.5255	0.2943
2.796	331.13	6.990	1.3547	1.4845	0.1298
2.982	337.84	7.455	1.4448	1.4975	0.0527
2.832	333.33	7.08	1.3721	1.4871	0.1150
3.098	341.05	7.74	1.5000	1.5050	0.0050
2.582	322.75	6.455	1.2509	1.4681	0.2172
2.383	316.15	5.957	1.1545	1.4513	0.2968
2.278	311.85	5.695	1.1037	1.4418	0.3381
2.181	307.35	5.453	1.0568	1.4325	0.3757
2.093	303.25	5.232	1.0139	1.4236	0.4097
2.012	299.65	5.03	0.9748	1.4150	0.4402
1.937	296.65	4.84	0.9379	1.4066	0.4687
1.889	293.65	4.722	0.9151	1.4012	0.4861

I = ionic strength
A = 0.5115, universal constant for water
C = 0.1938 at 298.15K

Table V-7

Enthalpy of Solution of Lead Nitrate and method of measurement

		$/\mathrm{kJ\ mol^{-1}}$	n
Calorimetric value	$\Delta_{sol}H^{\theta}$ (measured)	= 33.76±0.13	-
Dynamic pptn.	$\Delta_{sol}H^{\theta}$ (uncorrected)	= 25.83	3
Dynamic pptn.	$\Delta_{sol}H^{\theta}$ (activity corrected)	= 34.48	3
Literature value[10]	$\Delta_{sol}H^{\theta}$ [10000 H_2O]	= 33.47±0.7	-

n = stoichiometric number of ions produced per mole of electrolyte.

TABLE V-8

Solubility of Styphnic Acid in 0.1M Hydrochloric Acid

0.1M $HCl_{,aq}/cm^3$	Conc$^{n.}$ of Styphnic Acid/mol dm^{-3},*S*.	-ln S	Mean temperature for precipitation/k	$1000/_T$
10.0	0.0118	4.44	299.81	3.335
11.0	0.0107	4.53	299.51	3.339
12.0	0.00985	4.62	298.55	3.350
13.0	0.00909	4.70	297.92	3.357
14.0	0.00845	4.77	295.92	3.379
15.0	0.00788	4.84	294.45	3.396

TABLE V-9

Solubility data

Solubility of styphnic acid at 25°C = 9.8×10^{-3} g mol dm^{-3}

Regression Equation:

$$\ln S = -6.036\times\frac{1000}{T} + 15.625$$

$\Delta_{sol}H^{\ominus} = 100.18$ kJ mol^{-1}

$\Delta_{sol}S^{\ominus} = 129.91$ J mol^{-1} K^{-1}

Correlation Coefficient = 0.96

V-J: References

1. MOORE,W.J.,Physical Chemistry,P64,Longman,London,(1972).
2. IVES,D.J.G.,Chemical Thermodynamics,P129,MacDonald,London,(1971).
3. WILLIAMSON,A.T.,Trans. Fara. Soc.,40,421,(1944).
4. SMITH,A.N.,PhD.Thesis,London,(Jan. 1983).
5. DEBYE,P.,and HÜCKEL,E.,Phys.Z.,24,185,(1923);25,97,(1924).
6. LEWIS,G.N.and RANDALL,M.,Thermodynamics,P242,2nd Ed^{n},McGraw-Hill,London,(1961).
7. SANDALL,J.P.B.,Private Commun.
8. MORDECAI,K.J.,PhD.Thesis,London,(Nov. 1982).
9. STEPHEN,H.,and STEPHEN,T.,Solubility of Inorg. and Org. Compounds,1,321,Pergamon Press,Oxford,(1963).
10. WAGMAN,D.D.,EVANS,W.H.,HALOW,I.,PARKER,V.B.,BAILEY,S.M.,and SCHUMM,R.H.,Selected Values of Chemical Thermodynamic Properties,National Bureau of Standards Technical Note 270-2,U.S. Government Printing Office,Washington D.C.,(1966).

Chapter VI

DIFFERENTIAL SCANNING CALORIMETRY

VI-A: Differential Scanning Calorimetry

VI-AI: Historical background

In the 1960's, development[4] of the differential thermal analysis (DTA) apparatus[1,2,3], Figure VI-1, produced the differential scanning calorimeter (DSC) Figure VI-2. The DSC is designed to measure the differential heat flow required to maintain a sample of the compound and the inert reference pan at the same temperature. The electronics are needed to monitor and adjust the temperature of sample and reference pans, as for example during a phase change from solid to gas, the transition from one crystalline form to another, or a chemical change. The temperature equilibrium between the two pans is maintained by the adjustment of the current to the heaters.

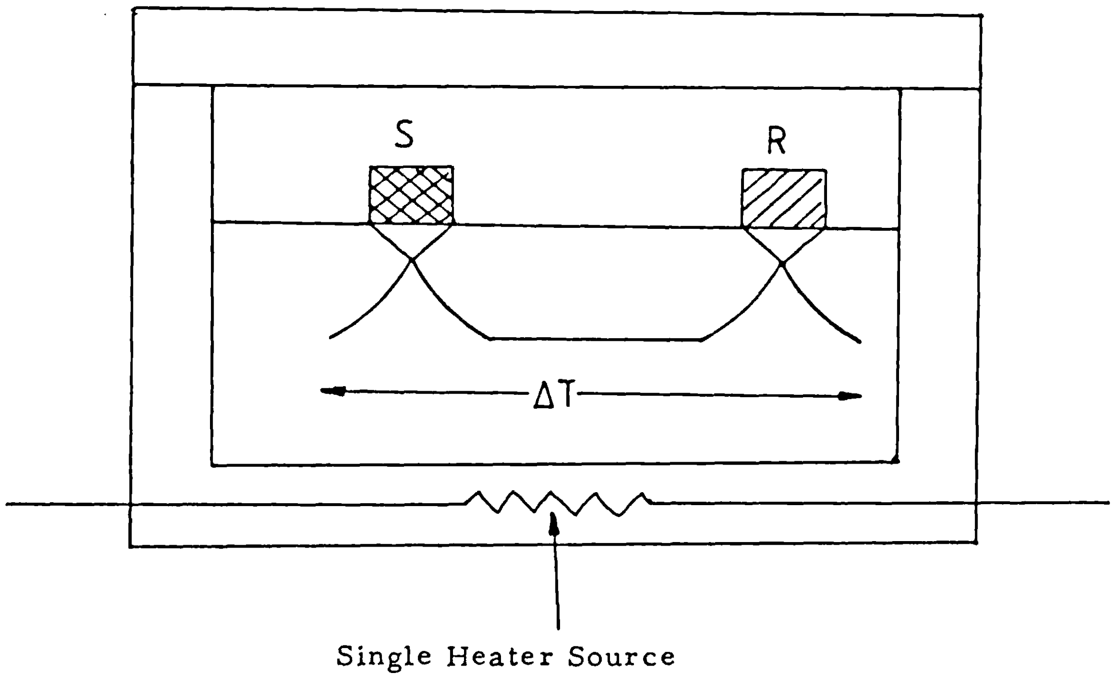
This is called the null-balance principle. The output of the DSC is usually a signal that is the sum of the average temperature of the sample and reference, with the signal proportional to the difference between the heat input to the sample and that to the reference, dH/dt.

In the DTA apparatus, a plot is made of the temperature difference between the sample, T_s, and reference T_r, against time,

$$\Delta T = T_s - T_r \qquad \text{(VIA)}$$

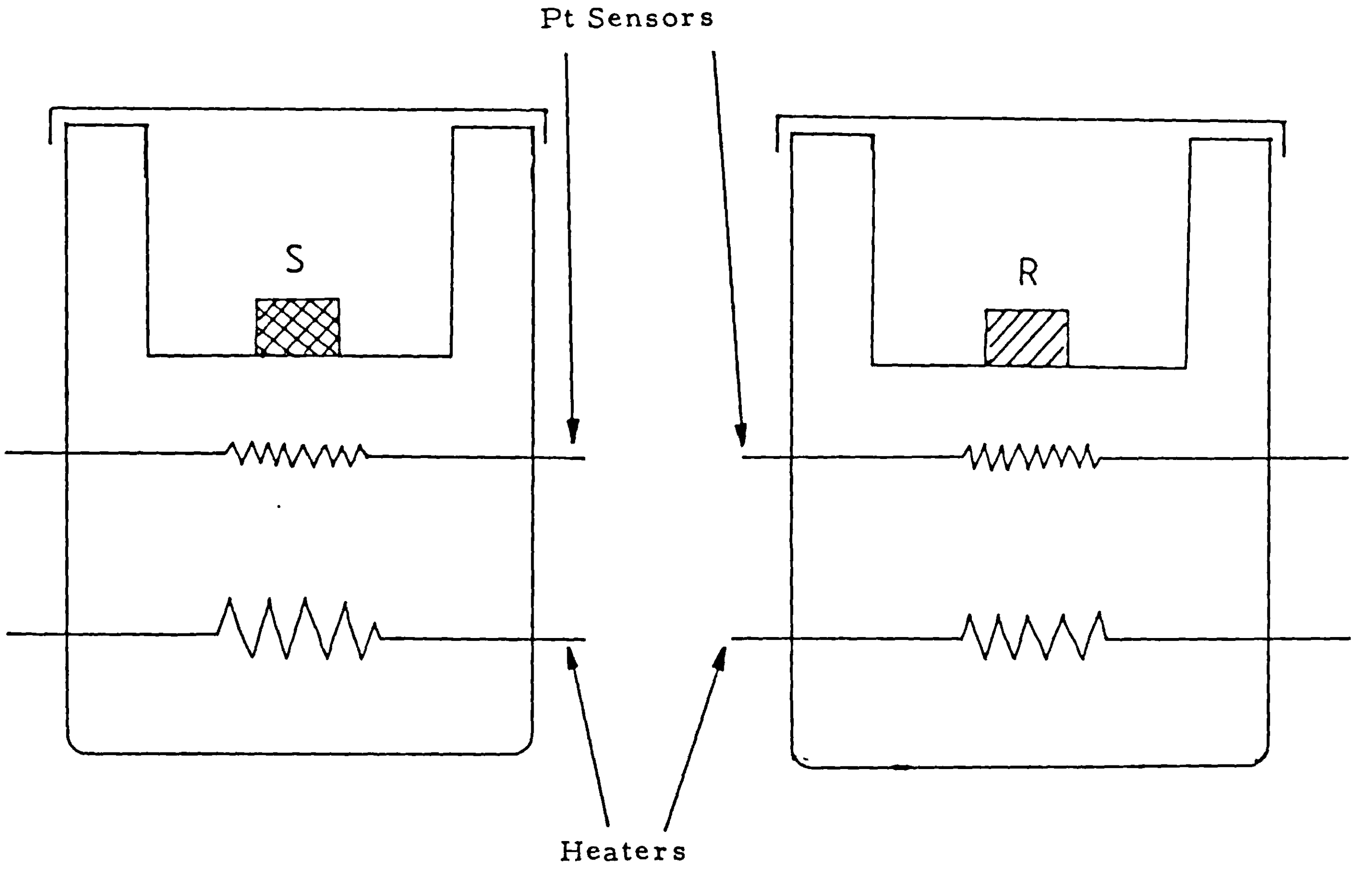
Scanning calorimetry was developed to overcome difficulties experienced in converting peak height[4] from a plot of ΔT against time, into energy units.

Figure VI-1



DTA

Figure VI-2



DSC

VI-B: Experimental

A Perkin-Elmer differential scanning calorimeter (DSC-2) was used in these experiments. Operation and calibration of the instrument was performed according to the instruction manual supplied with the calorimeter. All samples were weighed (to $\pm 10^{-3}$g, Cahn electrobalance) into aluminium pans which were hermetically sealed.

VI-C: Purity determinations by calorimetric measurements

The determination of the purity of an organic compound by DSC is principally based on the fact that for the melting of a compound at a characteristic temperature, T_o, involves a first-order transition. Theoretically the melting transition for a perfectly crystalline, absolutely pure compound should be infinitely sharp.

It is a well-known fact that the presence of even minute amounts of impurity in a material broadens its melting range and lowers the final melting point of the material from T_o to a lesser temperature, T_m; Figure VI-3.

The accuracy of temperature measurement and the amount of energy absorbed or emitted by a sample is measureable per unit time, using the DSC. The thermal energy measured per unit time can therefore be expressed.

$$\frac{dq}{dt} = \frac{dT_s}{dt} \times \frac{dq}{dT_s} \qquad \text{(VIB)}$$

where

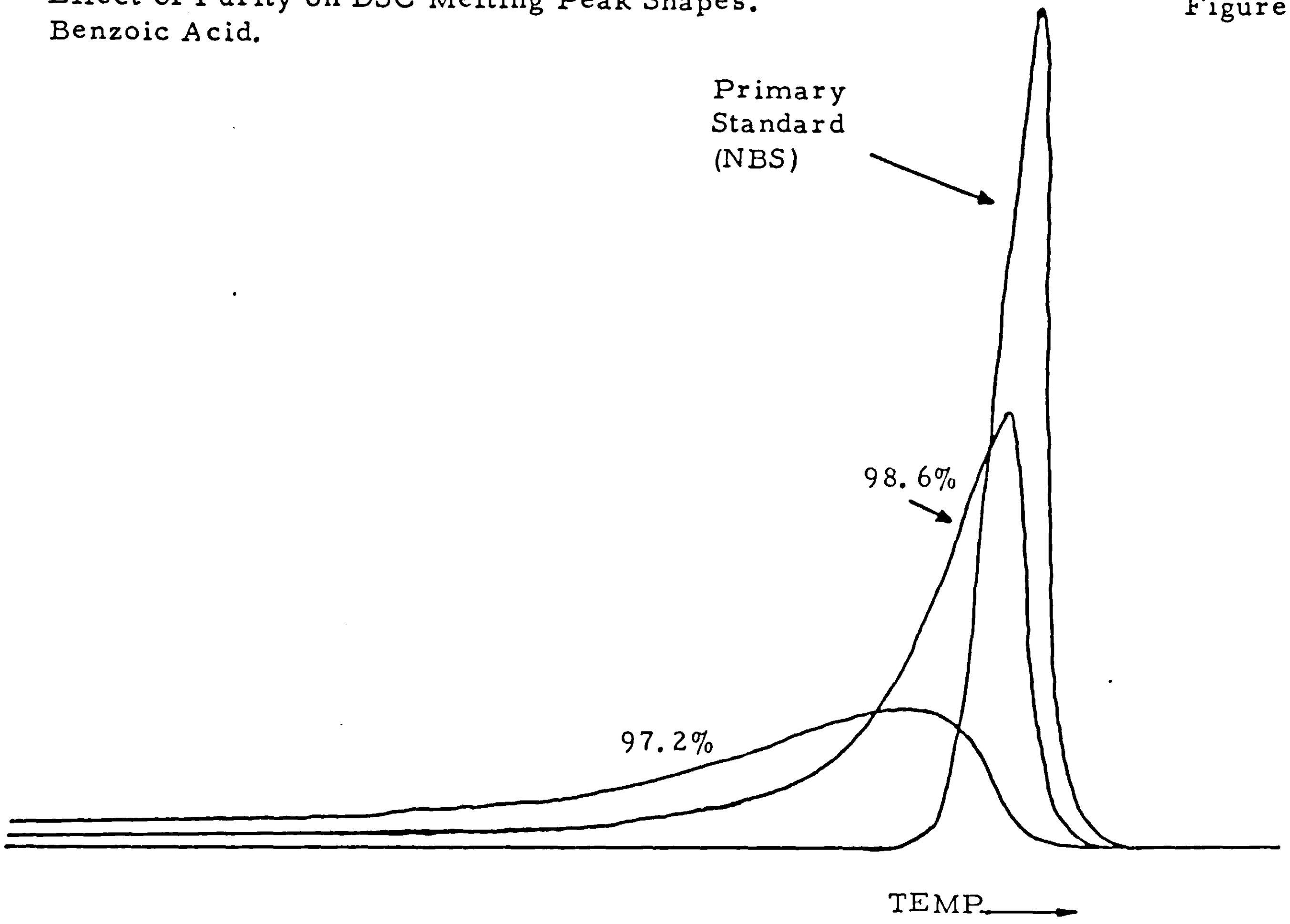
dq/dT_s = heat capacity of the sample or the energy required to accomplish a transition/ J K^{-1}, and

dT_s/dt = scanning rate/ K min^{-1}[5,6].

From the van't Hoff equation, the relationship describing the heat flow to or from a sample and the melting point

Figure VI-3

Effect of Purity on DSC Melting Peak Shapes.
Benzoic Acid.



depression of a sample due to the presence of an impurity is obtainable.

$$\frac{dq}{dT_s} = \frac{\Delta q(T_o - T_m)}{(T_o - T_s)^2} \qquad \text{(VIC)}$$

where
Δq = total heat of fusion of the sample/joules;
T_o = melting point of a 100% pure material/K;
T_m = melting point of sample/K;
(T_o-T_m) = melting point depression due to impurity/K;
T_s = sample temperature/K.

where the melting point depression due to impurity is expressed as

$$(T_o - T_m) = \frac{RT_o^2 \chi_2}{\Delta_f H^\theta} \qquad \text{(VID)}$$

where
R = molar gas constant, 8.314 J $\mathrm{mol^{-1}K^{-1}}$;
χ_2 = mole fraction of the impurity; and
$\Delta_f H^\theta$ = molar heat of fusion of sample/J $\mathrm{mol^{-1}}$.

To apply the basic van't Hoff relationship to the DSC, Equation VIC is integrated to describe the fraction of material melted at any sample temperature on the melting curve.

$$F = \frac{T_o - T_m}{T_o - T_s} \qquad \text{(VIE)}$$

Rearranging the equation.

$$T_s = T_o - \frac{(T_o - T_m)}{F} \qquad \text{(VIF)}$$

where
F = fraction melted.

Substituting Equation VID, which defines the melting point depression due to an impurity, into Equation VIF, a linear equation is obtained

$$T_s = T_o - \frac{RT_o^2 \chi_2}{\Delta_f H^\theta} \cdot \frac{1}{F} \qquad \text{(VIG)}$$

Plotting sample temperature (T_s) versus the reciprocal of the fraction of material melted at that temperature (1/F) should give a straight line with a slope equal to the melting point depression $RT_o^2 \chi_2/\Delta_f H^\theta$, and a Y intercept of T_o.

An example of this linear plot (van't Hoff plot) is given in Figure VI-4. The fraction of material melted at any sample temperature is proportional to the peak area under the curve up to that temperature. By generating this van't Hoff plot from a series of sample temperatures and fraction melted results in the range from approximately 5 to 60% melted, it is a relatively simple procedure to obtain values for T_o, the slope of the line, and finally the direct determination of the mole fraction of impurity from Equation VIG.

Heat capacity contributions of the sample pan and sample have to be included in the calculations. In Figure VI-5, the specific heat contributions are illustrated graphically. For point A the temperature is read off at D and the peak area is measured up to line AB. The area EBCD is also

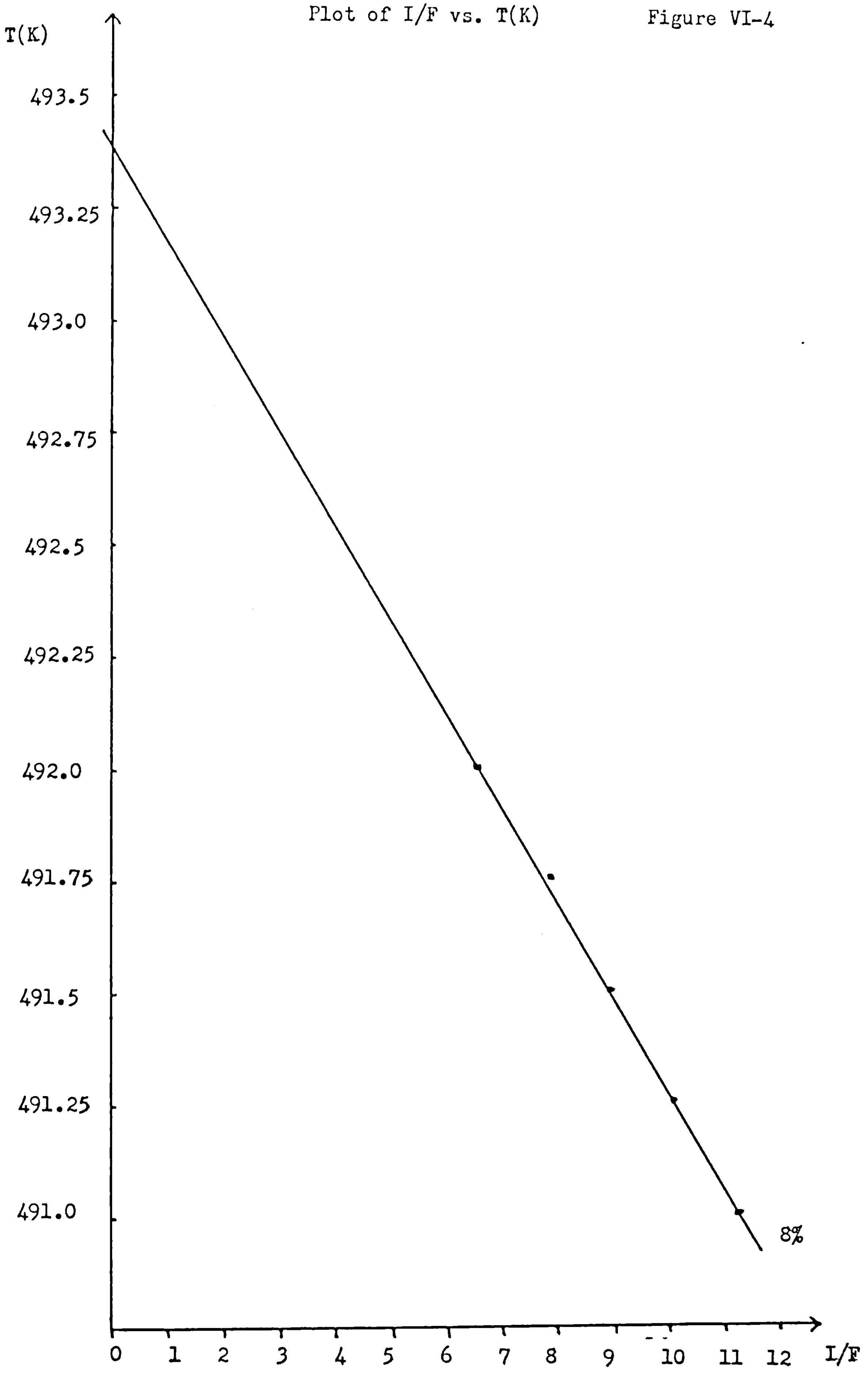
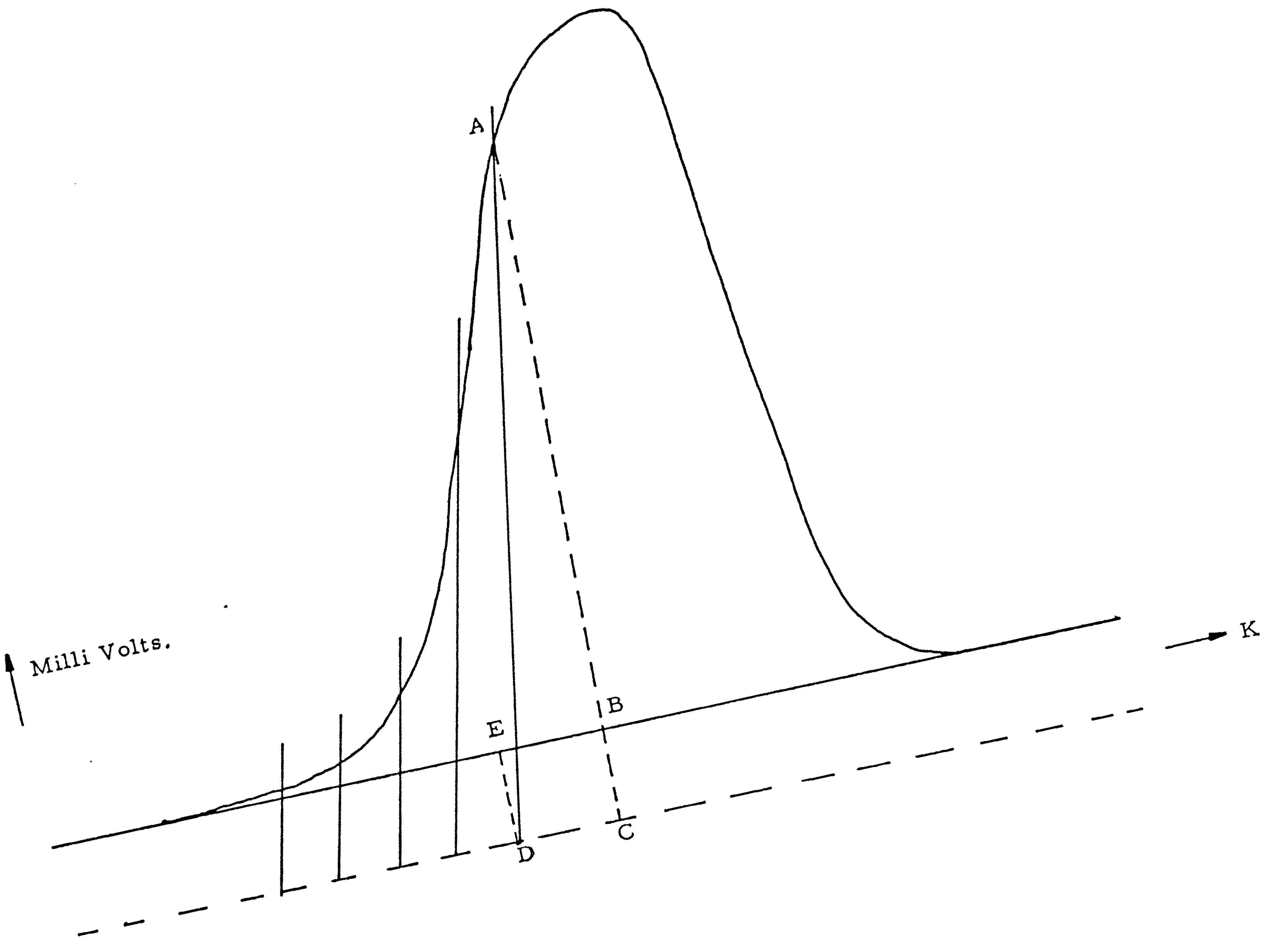

Plot of I/F vs. T(K)
Figure VI-4
T(K)
493.5
493.25
493.0
492.75
492.5
492.25
492.0
491.75
491.5
491.25
491.0
8%
0
1
2
3
4
5
6
7
8
9
10
11
12
I/F

Figure VI-5



included in the calculations as this area is equivalent to heat of fusion.

The heat capacity energy provided before sample melting is no longer required during melting, making the area left equivalent to heat of fusion energy. The distance BC is equal to $C_o dT_s/dt$, where C_o is the heat capacity of the sample pan plus sample; dT_s/dt is the heating rate in K sec^{-1}.

For samples of higher impurity level, a marked degree of departure from linearity in the van't Hoff plot is often observed, Figure VI-6. The departure has been attributed to in particular the formation of solid solutions.

To be able to apply Equation VIG, to the plot, Figure VI-6, a small correction factor x is applied as a percentage of the total area,[8] until a linear plot is obtained. The heat of fusion of the sample has to be also corrected by the same percentage for Equation VIG.

VI-D: Crystal Transitions in 2,6-Dinitrotoluene

It has been observed[10] that 2,6-DNT does exhibit very unusual crystal behaviour in so far as its melting point. The melting point of purified 2,6-DNT (section II-AVII) was found to be 56°C. After cooling and re-heating, the literature value[11] of 66°C was found. This latter value was reproducible. Hence at least one crystal transition is taking place as follows,

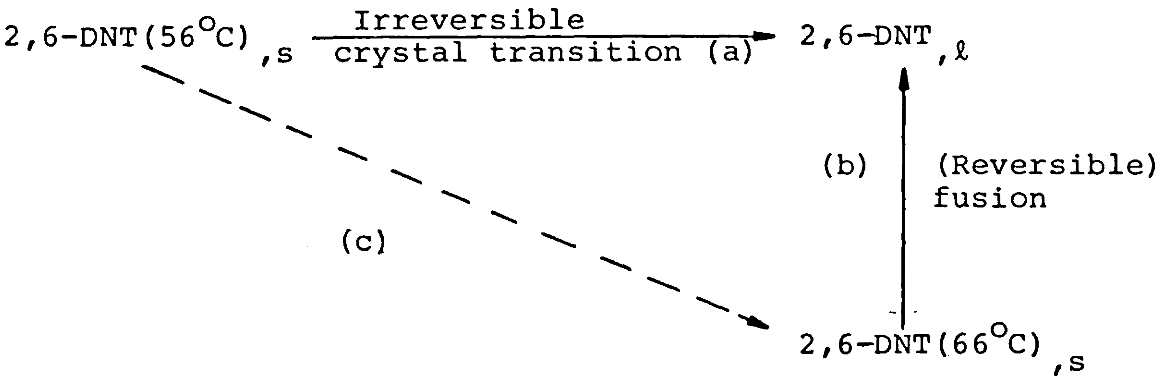
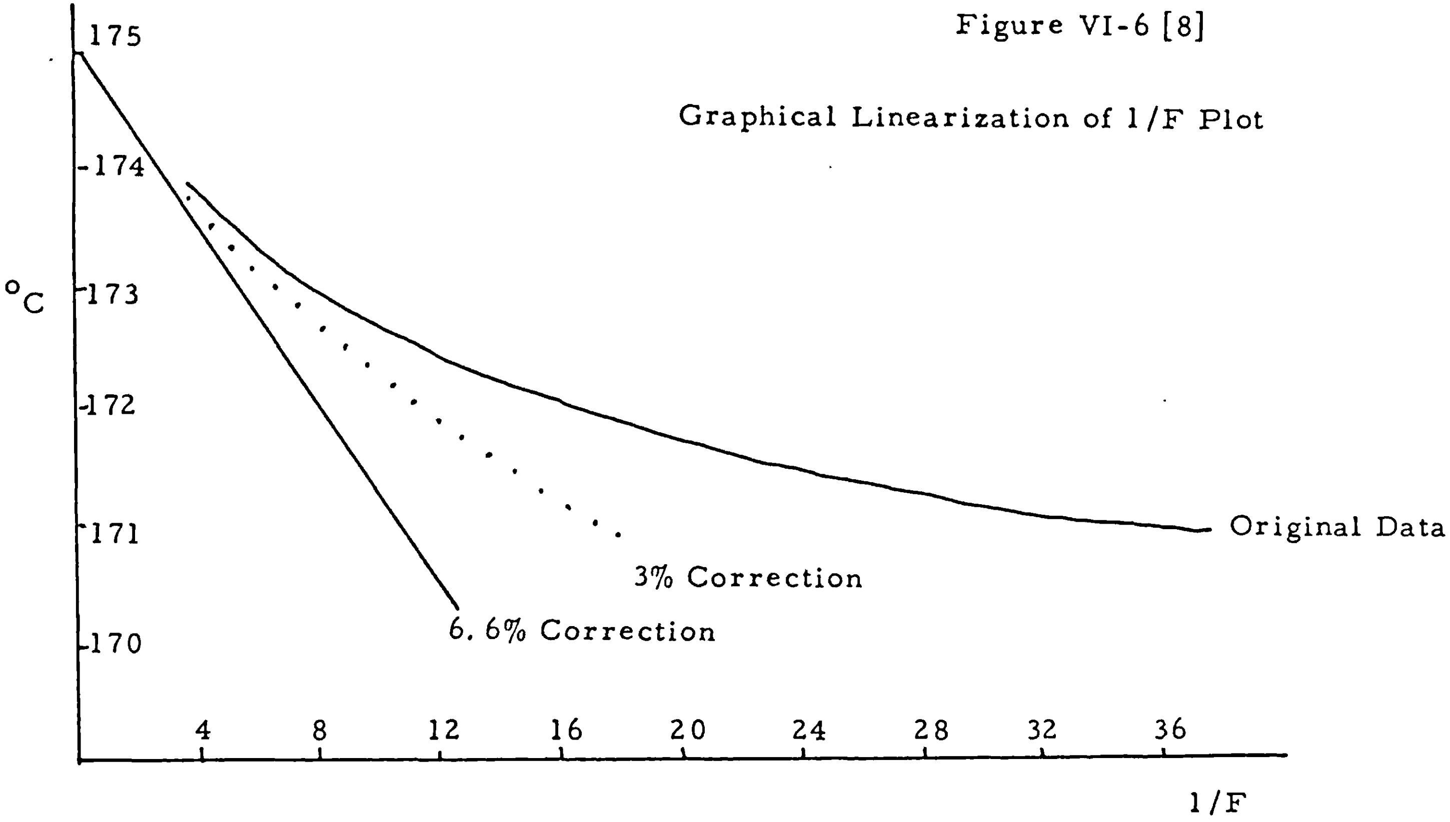


Figure VI-6 [8]

Graphical Linearization of 1/F Plot



Parentheses designate the temperature of melting of the relevant crystal, viz. 2,6-DNT(56°)[Form A] and 2,6-DNT (66°)[Form B].

Steps (a) and (b) were followed quantitatively using differential scanning calorimetry. Six runs on each of the two forms were then made using the combustion calorimetric system, Section III-D.

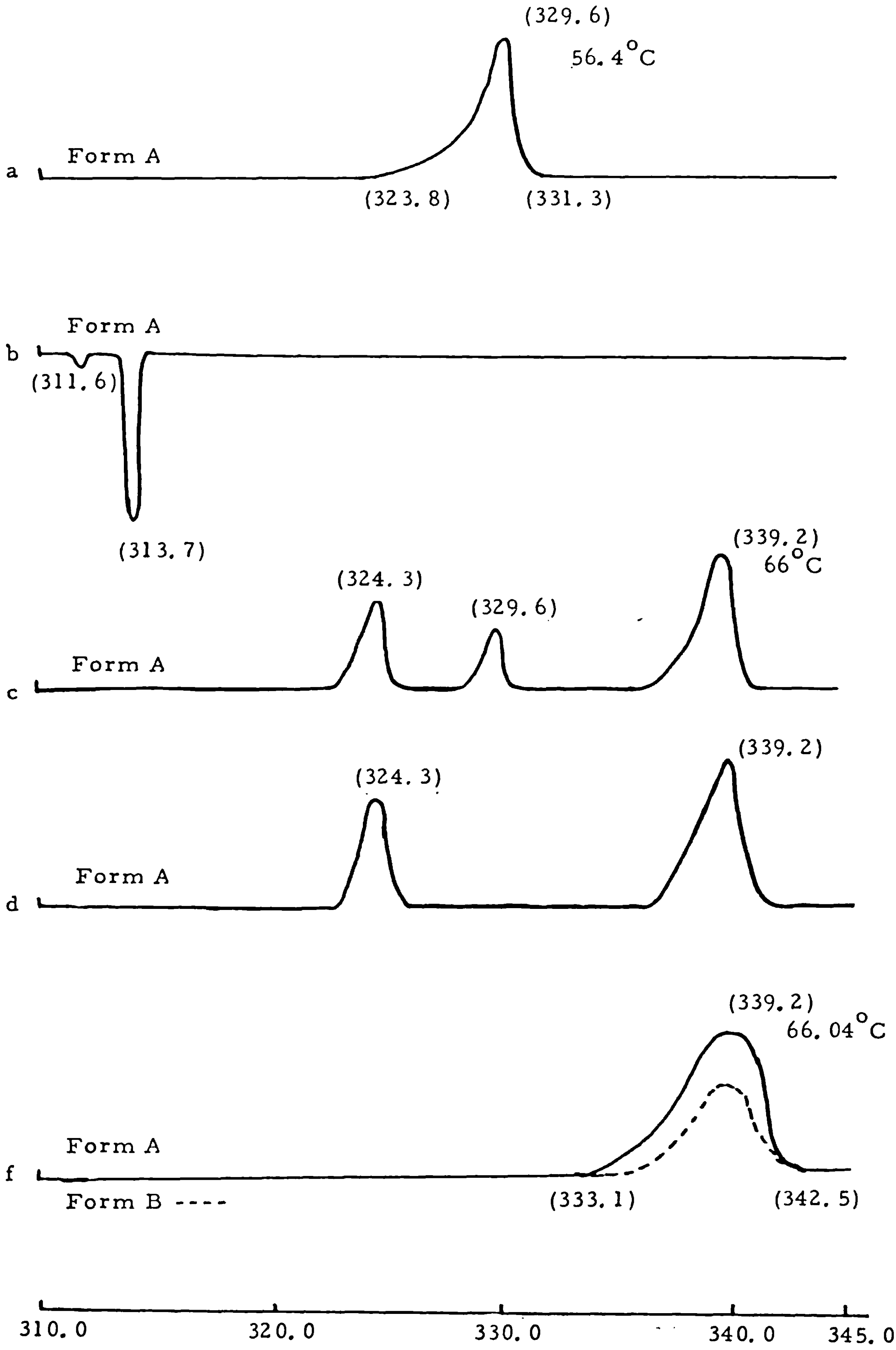
VI-E: Differential Scanning Measurements of 2,6-Dinitrotoluene

A sample of 2,6-DNT[Form A]$_{,s}$ was weighed (3.98 mg) and hermetically sealed in an aluminium pan. The sample was placed in the DSC2 and scanned from 310.0K to 345.0K (scan speed 5° min^{-1}, chart speed 80 mm min^{-1}). The result is shown in Figure VI-7a. The sample was held at the maximum temperature of the scan for ca 10 min. before being scanned down (scan speed -5° min^{-1}) to 310.0K, Figure VI-7b. Two exotherms were noted at 313.75K and 311.62K respectively. The sample was then scanned from 310.0K to 345.0K, Figure VI-7c. Only an endotherm was expected at 339.15K, but the observed thermogram revealed three endothermic peaks at 324.25, 329.59 and 339.19K respectively. The sample was cooled back down to 310.0K prior to scanning up again to 345.0K. This time the thermogram only revealed peaks at 324.25 and 339.19K, Figure VI-7d. The cooling and heating process was then repeated to produce scan e and f, Figure VI-7f. Scan e revealed again only two peaks but the first endotherm at 324.25K was significantly reduced in size. The final scan, Figure VI-7f, produced a single peak of similar shape to that obtained from a sample of Form B.

VI-F: Enthalpies of Transition

The enthalpies of transition, $\Delta_t H^\theta$, were obtained for the following.

Figure VI-7
Sequential Study of the Crystal Transitions of 2,6-DNT.



$$2,6\text{-DNT[A]}_{,s} \xrightarrow[(a)]{} 2,6\text{-DNT[A]}_{,\ell} \quad \text{(Fig. VI-7a).}$$

$$2,6\text{-DNT[A]}_{,s} \xrightarrow[(b)]{} 2,6\text{-DNT[A]}_{,\ell} \quad \text{(Fig. VI-7f).}$$

$$2,6\text{-DNT[B]}_{,s} \underset{(d)}{\overset{(c)}{\rightleftharpoons}} 2,6\text{-DNT[B]}_{,\ell}$$

Table VI-1

Enthalpies of Transition

Step	$\Delta_t H^\theta$/kJ mol^{-1}
(a)	19.28
(b)	16.07
(c)	16.09
(d)	-16.00

Although the difference between combustion values from the two crystal modifications (viz, 56° and 66°) are not statistically significant, it is encouraging to note that the difference in (mean) value of $\Delta_f H^\theta$ is 3.67 kJ mol^{-1} (section III-E), which is in reasonable agreement with that of the independent differential scanning calorimetry studies; viz 4.04 kJ mol^{-1}. In an attempt to try and account for the unusually slow crystal transition from form A to form B, the heat capacity of both compounds in their solid and liquid states was measured (section VI-G). A structure determination for the crystal forms of both A and B was also attempted (Chapter VII).

VI-G: Heat Capacities by Differential Scanning Calorimetry

The molar heat capacity of a system is by definition the heat absorbed per mole per degree rise in temperature. As the heat absorbed per mole can be either under condition of constant pressure or volume, two heat capacities are definable.

$$C_p = \lim_{\Delta T \to o} \left(\frac{\Delta H}{\Delta T}\right)_p \qquad \text{(VIH)}$$

and

$$C_v = \lim_{\Delta T \to 0} \left(\frac{\Delta E}{\Delta T} \right)_v \qquad \text{(VII)}$$

where

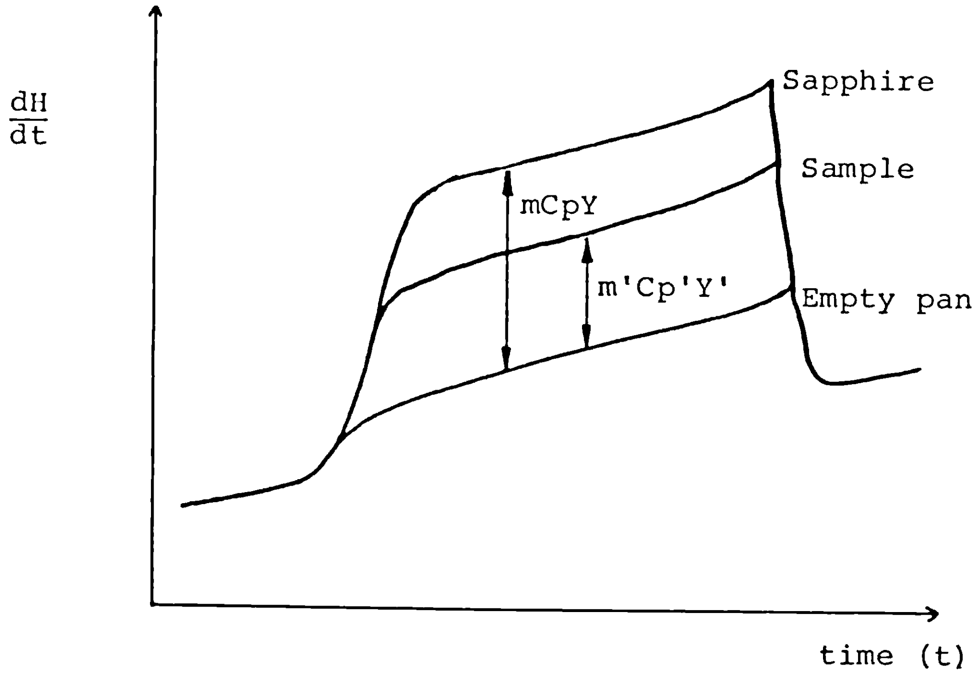
E = internal energy.
C_p = heat capacity at constant pressure/J K^{-1} mol^{-1}.
C_v = heat capacity at constant volume/J K^{-1} mol^{-1}.

C_p is used exclusively in this investigation and should not be confused with Specific Heat found in older texts (heat capacity per g). C_p is a thermodynamic property that is directly related to atomic or molecular structure as heat is used mostly to initiate translational, rotational and vibrational motion within a material. Another heat capacity that is important to calorimetry is the operational heat capacity or energy equivalent ε (Equation IIIC). This term includes the heat capacity of the calorimeter itself, i.e. stirrer, ampoule. etc. as well as C_p of the reaction material.

When a material is subjected to a linear temperature increase, the instantaneous specific heat is proportional to the heat flowing into the material.

$$\frac{dH}{dt} = mC_p . \frac{dT}{dt} \qquad \text{(VIJ)}$$

By regarding the rate of heat flow as a function of temperature, and comparing it with a standard material under the same conditions, the C_p can be obtained as a function of temperature.



$$\frac{C'_p}{C_p} = \frac{Y'}{Y} \cdot \frac{m}{m'}$$

VI-H: Experimental

The same instrument (DSC2) and calibration procedures were followed as previously mentioned (Section VI-B).

Aluminium pans and lids were placed both in the sample and reference holders, and the base line recorded over the desired working temperature. The procedure was repeated with the pre-weighed sapphire standard added. Finally the procedure was again repeated, but this time with the sample material hermetically sealed in the sample pan.

For the heat capacity of 2,6-DNT, the above process was repeated in triplicate for each compound with a chart speed of 80 mm min^{-1}; range setting 5, and temperature scan rate = 5^{o} min^{-1}.

The following compound weights were used,

Sample no.	1	2	3	4	5	6	7	8
Mass/mg	5.09	4.97	6.66	3.53	5.51	4.77	5.21	7.78

The heat capacities obtained are tabulated in Tables VI-3 to 6. To test that the instrument was functioning satisfactorily, a sample of sodium chloride (B.D.H.,A.R.) was put in the DSC2 under the same conditions as the DNT. The results obtained are given in Table VI-2. A plot of C_p^θ against temperature is shown in Figure VI-8. A statistical analysis (Appendix VI) of the data was performed to check if any significant difference existed between the heat capacities of both liquids and solids, Table VI-7; confidence limits are indicated by shaded areas on Figure VI-8.

TABLE VI-2

Heat Capacity of Sodium Chloride

T(K)	Cp^{θ} (kJ $mol^{-1}K^{-1}$)		Δ%
	Sample	Ref[12]	
315	0.0513	0.0508	0.97
320	0.0513	0.0509	0.78
325	0.03135	0.05099	0.70
330	0.05136	0.05108	0.55
335	0.05137	0.0511	0.53
340	0.05138	0.0512	0.35
345	0.05139	0.0514	-0.02
350	0.05141	0.05145	-0.08
355	0.05142	0.0515	-0.16
360	0.05143	0.0516	-0.33

TABLE VI-3

Heat Capacity of 2,6-DNT (56^{o}) solid [form A]

T(K)	Cp^{θ} (kJ $mol^{-1}K^{-1}$) Sample 1	 Sample 2	 Sample 3	 Sample 4	Mean
305.0	0.2160	0.2180	0.2163	0.2174	0.2169±0.0029
307.5	0.2215	0.2207	0.2205	0.2211	0.2210±0.0013
310.0	0.2229	0.2235	0.2232	0.2230	0.2332±0.0009
312.5	0.2311	0.2307	0.2309	0.2307	0.2309±0.0006
315.0	0.2323	0.2286	0.2239	0.2289	0.2284±0.0111
317.5	0.2309	0.2304	0.2302	0.2311	0.2307±0.0013
320.0	0.2379	0.2303	0.2398	0.2349	0.2357±0.0130

TABLE VI-4

Heat Capacity of 2,6-DNT (56°) liquid [form B]

T(K)	Cp^{θ} (kJ mol^{-1}K^{-1}) Sample 1	Sample 2	Sample 3	Sample 4	Mean
335.0	0.2600	0.2606	0.2546	0.2598	0.2588±0.0089
337.5	0.2614	0.2609	0.2639	0.2611	0.2618±0.0045
340.0	0.2779	0.2682	0.2642	0.2701	0.2701±0.0183
342.5	0.2647	0.2688	0.2645	0.2673	0.2663±0.0066
345.0	0.2698	0.2708	0.2677	0.2701	0.2696±0.0042
347.5	0.2731	0.2710	0.2719	0.2722	0.2721±0.0028
350.0	0.2755	0.2752	0.2742	0.2750	0.2750±0.0018
352.5	0.2761	0.2757	0.2788	0.2772	0.2770±0.0044
355.0	0.2779	0.2774	0.2833	0.2783	0.2792±0.0087
357.5	0.2738	0.2778	0.2819	0.2782	0.2779±0.0105
360.0	0.2847	0.2801	0.2827	0.2831	0.2827±0.0061
362.5	0.2807	0.2811	0.2832	0.2843	0.2823±0.0055
365.0	0.2823	0.2823	0.2841	0.2821	0.2827±0.0030

TABLE VI-5

Heat Capacity of 2,6-DNT (66^{o}) solid [form C]

T(K)	Cp^{θ} (kJ $mol^{-1}K^{-1}$) Sample 5	Sample 6	Sample 7	Sample 8	Mean
305.0	0.2230	0.2242	0.2235	0.2240	0.2237±0.0016
307.5	0.2250	0.2264	0.2252	0.2251	0.2254±0.0021
310.0	0.2287	0.2252	0.2263	0.2271	0.2268±0.0047
312.5	0.2237	0.2274	0.2267	0.2289	0.2267±0.0070
315.0	0.2311	0.2366	0.2302	0.2309	0.2322±0.0094
317.5	0.2356	0.2355	0.2322	0.2348	0.2345±0.0051
320.0	0.2333	0.2353	0.2408	0.2397	0.2373±0.0113
322.5	0.2414	0.2401	0.2463	0.2485	0.2441±0.0127
325.0	0.2404	0.2444	0.2498	0.2499	0.2461±0.0146
327.5	0.2513	0.2515	0.2581	0.2508	0.2529±0.0110
330.0	0.2675	0.2684	0.2666	0.2654	0.2670±0.0041

TABLE VI-6

Heat Capacity of 2,6-DNT (66^{o}) liquid [form D]

T(K)	Cp^{θ}(kJ mol^{-1}K^{-1})				Mean
	Sample 5	Sample 6	Sample 7	Sample 8	
345.0	0.2601	0.2607	0.2574	0.2600	0.2596±0.0047
347.5	0.2609	0.2620	0.2584	0.2606	0.2605±0.0048
350.0	0.2618	0.2624	0.2641	0.2618	0.2625±0.0035
352.5	0.2637	0.2618	0.2649	0.2621	0.2631±0.0046
355.0	0.2645	0.2685	0.2653	0.2630	0.2653±0.0074
357.5	0.2659	0.2651	0.2666	0.2636	0.2653±0.0041
360.0	0.2663	0.2646	0.2677	0.2643	0.2657±0.0050
362.5	0.2675	0.2644	0.2683	0.2659	0.2665±0.0055
365.0	0.2688	0.2696	0.2692	0.2680	0.2689±0.0022

TABLE VI-7

Statistical Analysis

58^o solid (A)

Linear Regression; $Cp^\theta = 0.00116T - 0.135$
Standard deviation of 0.00116 is 0.00012, and 0.135 is 0.0316
Correlation Coefficient; $r^2 = 83.5\%$

66^o solid (B)

Linear Regression; $Cp^\theta = 0.00078T + 0.0001$
Standard deviation of 0.00078 is 0.000044, and 0.0001 is 0.015
Correlation Coefficient; $r^2 = 86.2\%$

Covariance between A & B
Fisher F = 81.929
Probability of being the same = 00.00%

58^o liquid (C)

Linear Regression; $Cp^\theta = 0.00154T - 0.252$
Standard deviation of 0.00154 is 0.000094 and 0.252 is 0.0297
Correlation Coefficient; $r^2 = 86.6\%$

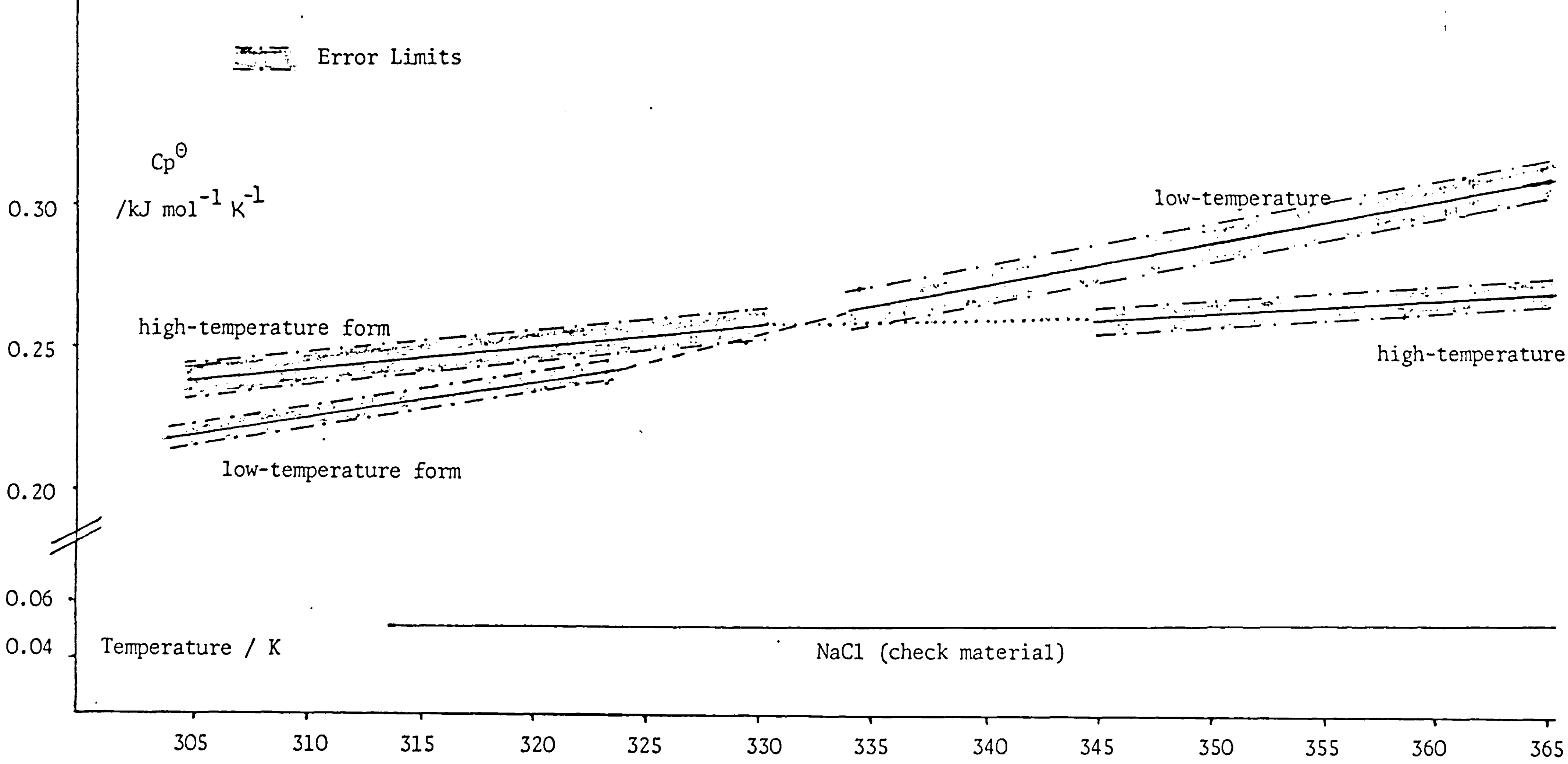
66^o liquid (D)

Linear Regression; $Cp^\theta = 0.00043T + 0.112$
Standard deviation of 0.00043 is 0.000038 and 0.112 is 0.0136
Correlation Coefficient; $r^2 = 78.5\%$

Covariance between C & D
Fisher F = 25.169
Probability of being the same = 00.00%

Heat Capacity (Cp^{Θ}) as a function of temperature for 2,6-dinitrotoluene

Figure VI-8



VI-I: References

1. KURNAKOV,N.S.,Z.Anorg.Chem.,42,184,(1904).
2. SALADIN,E.,Iron and Steel Metallurgy Metallography, 7,237,(1904).
3. LE CHATELIER,H.,Rev.Met.,1,134,(1904).
4. WATSON,E.S.,O'NEILL,M.J.,JUSTIN,J.,and BRENNER,N., Anal.Cham.,36,1233,(1963).
5. NAVARD,P.,and HAUDIN,J.M.,J. Therm Anal.,29,405, (1984).
6. "Thermal Analysis Newsletter No. 5",Perkin-Elmer Corporation,Norwalk,Conn.
7. "Thermal Analysis Newsletter No. 6",Perkin-Elmer Corporation,Norwalk,Conn.
8. BRENNAN,W.P.,DiVITO,M.P.,FYANS,R.L.,and GRAY,A.P., Purity Determinations by Thermal Methods,ASTM STP 838, American Society for Testing and Materials,(1984).
9. RICE,O.K.,"Statistical Mechanics,Thermodynamics and Kinetics",Freeman,London,(1967).
10. ANDREEN,J.H.,and McCRONE,W.C.,Anal.Chem.,26,12, 1997,(1954).
11. BADOCHE,M.M.,Bull.Soc.Chim.,6,570,(1939).
12. BARRON,T.H.K.,LEADBETTER,A.J.,and MORRISON,J.A., Proc.Roy.Soc.(Lond.),A279,1376,62,(1964).

Chapter VII

X-RAY CRYSTALLOGRAPHY

VII-A: X-Ray Crystallography

In an attempt to account for the different melting points of 2,6-DNT reported in section VI-D. A powder X-ray study of the 56° and the 66° modifications of 2,6-DNT was attempted. The X-ray analysis was performed in the physics department by Dr. A.M. Moore using the Debye-Scherrer method. The sample being contained in a thin-walled glass capillary. From the Bragg relationship

$$n\lambda = 2d \, \mathrm{Sin}\theta \qquad \text{(VIIA)}$$

reflections from each set of planes can be understood. These relections are recorded on photographic film using a Debye-Scherrer camera, Figure VII-1. As the photographic film covers a scattering angle of 360° of the camera with radius r. A simple relationship can be written.

$$\frac{x}{2\pi r} = \frac{2\theta}{360} \qquad \text{(VIIB)}$$

where x is the distance each line from central spot. In Table VII-1, d values are calculated, and quantitative intensities noted. An incident X-ray beam of wavelength, $\lambda = 1.5406\text{Å}$ was employed. Calculated d values (d') derived from parameters listed in reference[1] were computed using the relationship,

$$d'_{hkl} = \frac{abc}{\sqrt{(h^2b^2c^2+k^2c^2a^2+l^2a^2b^2)}} \qquad \text{(VIIC)}$$

where $a = 7.82\text{Å}$; $b = 13.70\text{Å}$ and $c = 97.39\text{Å}$. and are listed for comparison in Table VII-1. All lines represented in the referenced determination[1] can be assigned as originating from either 56° or the 66°C form. A possible assumption is hence that the 2,6-DNT used in reference[1] is neither 56°, or pure 66°, but a mixture. However, this assumes that no line of intensity less than 4 in our results is significant.

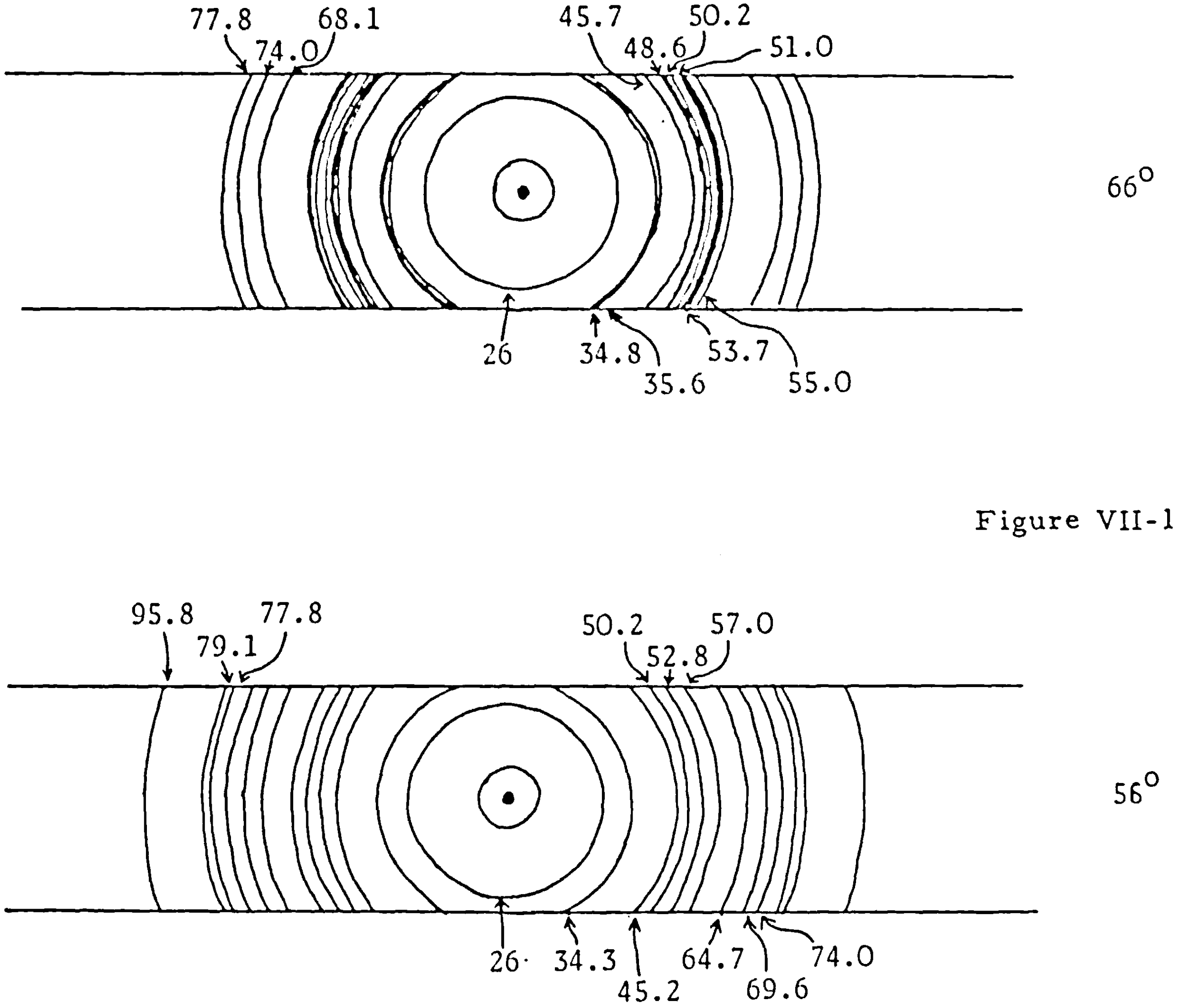

77.8
74.0
68.1
45.7
48.6
50.2
51.0
26
34.8
35.6
53.7
55.0
66°
95.8
79.1
77.8
50.2
52.8
57.0
26
34.3
45.2
64.7
69.6
74.0
56°

Figure VII-1

Table VII-1

Powder X-Ray Crystallographic Data

No.	hkl	d′	d(INTENSITY)[1]	d(56°)(I)	d(66°)(I)
1.	010	13.7			
2.	100	7.82			
3.	001	7.39			
4.	020	6.85	6.86(10)		
5.	110	6.79		6.80(V.S)	6.80(V.S)
6.	011	6.50			
7.	101	5.37			
8.	120	5.15	5.18(4)	5.17(S)	5.09(W)
9.	021	5.02			
10.	111	5.00	4.98(6)		4.98(W)
11.	030	4.57			
12.	121	4.23	4.21(3)		
13.	130	3.94		3.93(W)	
14.	200	3.91	3.90(5)		
15.	031	3.88			3.89(S)
16.	210	3.76			
17.	002	3.69	3.67(6)		3.66(W)
18.	012	3.57	3.56(9)	3.54_5(S)	3.54(S)
19.	131	3.48	3.48(5)		3.49(W)
20.	201	3.46			
21.	040	3.43			
22.	220	3.39		3.37(S)	
23.	211	3.35	3.35(8)		
24.	102	3.34			3.32(W)
25.	022	3.25	3.24(5)		3.24(S)
26.	112	3.25			
27.	140	3.14	3.14(4)	3.13(W)	
28.	041	3.11	3.10(3)		
29.	221	3.08			
30.	122	3.00	3.00(2)		
31.	230	2.97			
32.	141	2.89	2.89(2)		
33.	032	2.87			
34.	231	2.76	2.76(4)	2.76(W)	
35.	132	2.69	2.70(4)		
36.	202	2.69			
37.	212	2.64	2.64(5)		2.63(W)
38.	300	2.61			
39.	240	2.57	2.58(5)	2.57_6(S)	
40.	310	2.56			
41.	042	2.51	2.51(3)		
42.	222	2.50			
43.	003	2.46			
44.	301	2.46			
45.	320	2.44	2.44(6)		

No.	hkl	d′	d(INTENSITY)[1]	d(56°)(I)	d(66°)(I)
46.	241	2.43		2.43(S)	2.43(W)
47.	311	2.42			
48.	013	2.42			
49.	142	2.39			
50.	103	2.35			
51.	023	2.32	2.32(4)	2.31(W)	2.31(W)
52.	113	2.32			
53.	232	2.31	2.29(3)	2.28(W)	
54.	321	2.31			
55.	123	2.22	2.21(<1)		
56.	033	2.17	2.17(4)		
57.	331	2.16			
58.	302	2.13			
59.	242	2.11	2.11(2)		
60.	312	2.10			
61.	133	2.09			
62.	203	2.08	2.08(1)		
63.	340	2.07			
64.	213	2.06			
65.	322	2.03			
66.	043	2.00			
67.	400	1.96			
68.	223	1.99	1.996(2)		
69.	341	1.99			
70.	410	1.94	1.94(4)		
71.	143	1.94			
72.	332	1.93			
73.	223	1.89	1.90(4)	1.898(W)	
74.	401	1.88			
75.	420	1.88			
76.	411	1.87			

I, Intensity recorded by visual observation only.
V.S = very strong (intense)
S = strong
W = weak

VII-B: References

1. ANDREEN,J.H.,and McCRONE,W.C.,Anal.Chem.,26,12,1997, (1954).

Chapter VIII

FURTHER WORK

VIII-A: Further Work

For a group of compounds that have such industrial importance, thermochemical data on the metal polynitroresorcinols is very lacking. This investigation has been mainly based on the lead salts, as they constitute by far the most industrially important, followed closely by those of barium, thallium and silver. It has been noted that compounds with cations which have high ionization potentials and which are not excessively hydrated are far more explosive than those, (e.g. sodium, lithium, etc.), that have low ionization potentials. If a reaction for the decomposition is highly exothermic, then self-heating may lead to an explosive regimè. To be able to note any significant correlations in the thermochemical data already obtained, a further series of compound[1] would need to be investigated as before (Chapter IV), e.g.
Potassium 2,4-dinitroresorcinate, $KC_6H_3N_2O_6$
Barium 4,6-dinitroresorcinate, $Ba(C_6H_3N_2O_3)_2$
and $BaC_6H_2N_2O_6$
Potassium styphnate, $KC_6H_2N_3O_8.H_2O$
Dipotassium styphnate, $K_2C_6HN_3O_8.H_2O$
Sodium styphnate, $NaC_6H_2N_3O_8.3H_2O$

The styphnate salts of copper, mercury, cadmium, gold and tin are also of interest. A major problem is the preparation of such compounds in a highly pure state. With the enthalpies of formation of such compounds and those found in this investigation, it may be possible to draw some distinction between an unstable and explosive compound.

The elucidation of a decomposition mechanism is of paramount importance, as to estimate the relative stability of an explosive compound, consideration not just the enthalpy, but also the entropy and the Gibbs' free energy associated with a particular thermal decomposition, a working knowledge of the kinetics of the decomposition reaction would also be needed. The slowest part of an explosive decomposition is with the activation phase, (slowness with which molecules get activated). The net rate of reaction may become very fast when the activation energy can be provided very rapidly, and this is the case for an explosive material.

To study a fast reaction (>1 sec) is by no means a simple task. Three possible techniques are those of flash photolysis, stopped-flow, and relaxation. The latter two techniques cannot be considered as the decomposition does not occur in the solution phase, and that the reaction is not one of an equilibrium. Flash photolysis[4] would appear most likely to yield results if the compounds respond to the required stimuli. Two other possible experimental methods were considered, that of differential scanning calorimetry[3] in conjunction with the Kissinger-Ozawa method[2] and micro mass spectroscopy[5]. The former was not attempted as the experiment would have proved hazardous and the latter was known to be hazardous as styphnates could possibly be catalysed by the wall of the ionization chamber into other possibly explosive compounds that would be retained in the instrument.

With sufficient thermodynamic and kinetic data, a study would then need to be made between this data and the crystal structure of the compounds. It should then be possible to deduce accurately what is needed to constitute an explosive compound. A stability analysis of the long term storage would also be of interest as a decomposition mechanism here would probably be different to that obtained in an explosive environment.

VIII-B: References

1. FEDOROFF,B.T.,and SHEFFIELD,O.E.,Pic. Arsenal.Tech. Rep.,2700,5,(1972).

2. PATEL,R.G.,and CHAUDHRI,M.M.,4th Symposium on Chemical Problems connected with the Stability of Explosives, (May-June 2,1976).

3. KRIEN,G.,Jahrestag.,Inst.Chem.Treib-Explosivstoffe Fraunhofer-Ges.,p25-39,(1972).

4. NORRISH,R.G.W.,and THRUSH,B.S.,Quarterly Reviews-Chem.Soc.,10,149-169,(1956).

5. TANG,T.B.,Thermochimica Acta,61,341-356,(1983).

Appendix I

COMPUTER PROGRAMS

Appendix I

AI-A: DSC2/Purity Program

It was first necessary to build an interface to link the Perkin-Elmer DSC-2 to the micro-computer. The micro used was an ACT Sirius, which has a 16 bit 8088/8086 microprocessor. The standard unit comes with a 128 kilobyte random access memory (RAM). This was later expanded to 256 kilobytes because of problems of program storage. The operating system used was originally that of CP/M-86 (Ver. 1.1/2.4 Serial C86-336-23436, Digital Research Inc.) which is a 16-bit version of the more common CP/M. The programming languages used were BASIC-86 (Microsoft), and GW-BASIC (Microsoft). The operating system was later changed, and all programs re-written except for the bomb calorimetry calculation program. The system finally used for most programs was the MS-DOS Ver. 1.25a/2.6, Serial 23774, Microsoft), and the language generally used was GW-BASIC. Unfortunately this language only became available much later, after most of the initial programming had been done. The Sirius is supplied with two single-sided disk drive units, and a high resolution graphics facility. It was also interfaced with an Epsom FX-80 printer for hard copies.

AI-B: The Interface

This was designed and built by Mr P. Willmore. The original system was designed with a variable clock on the front of the interface box, which allowed for the sample rate to be varied. Unfortunately problems were experienced, e.g. the port reading program became repeatedly out of phase with the signals from the interface. Hence the system was changed to have the interface running 'flat-out', so that the data collect programs would flag the port when ready and accept whatever signal was at the port at any particular time. A brief description of the interface follows; see also Figure AI-1.

The use of opto isolators was found necessary because of a noise problem on the temperature scale. The versatile interface adaptor (V.I.A.) within the Sirius is used. This is an 8-bit port input, so any number has to be segmented in the interface and then the correct segments recombined in a data collection routine.

AI-C: The Data Collection Program

Data storage is a problem with such a type program as that for the DSC. It is very easy to go 'out of memory' even with the expanded RAM. This is the reason for writing a separate program for the collection and sorting of data, and then storing this modified data on disk for use in the DSC program. Having a separate data collection program was found to have several advantages. Namely that the collection program was short in comparison to a program containing the calculations needed for the DSC problems and data collection as an integral part. Thus allowing an initially greater part of the RAM available for raw data. These programs were written in BASIC-86 for three reasons.
1/ The BASIC-86 interpreter is significantly smaller than that of the GW-BASIC, and thus taking up less of the RAM.
2/ The BASIC-86 interpreter works at least ten-times faster than that of GW-BASIC.
3/ GW-BASIC seems to have a very unusual method of stacking in the RAM. As when the PEEK and POKE statements are used, the data PEEKed in will differ to that POKEed out at the same location. This problem does not occur using BASIC-86, and as it is critical to PEEK and POKE the RAM and data bus locations, GW-BASIC could not be used.

Three data collecting programs were written; LOADS (LOAD-PUR); LOAD, and LOAD-CP. LOADS is the program in its simplest

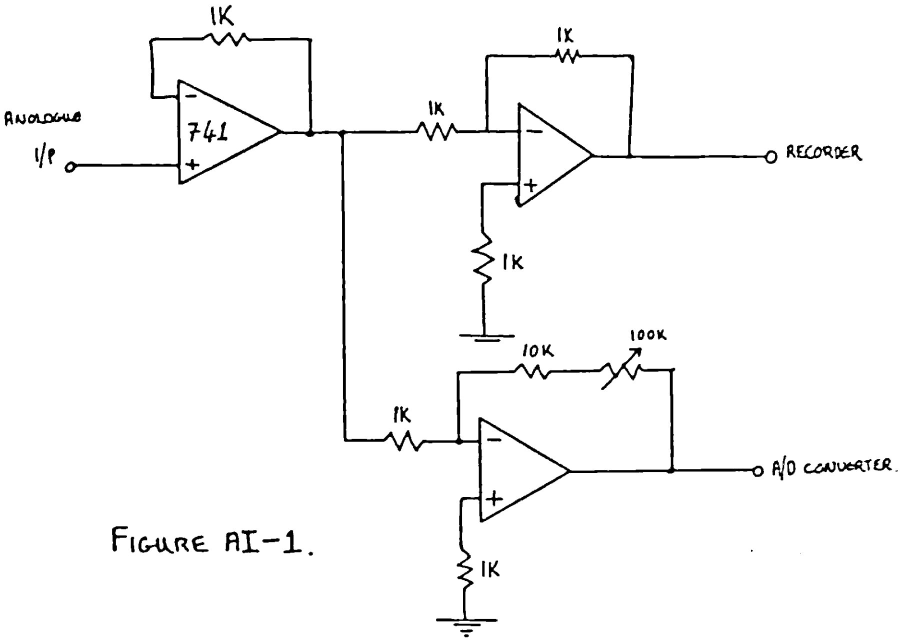
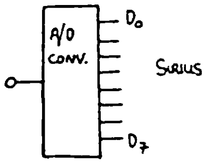
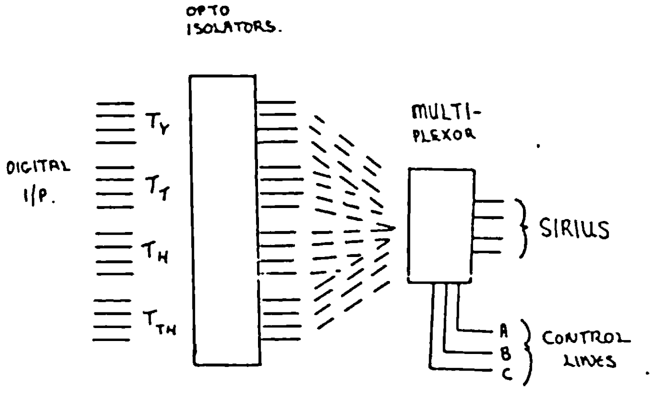

1K
ANALOGUE
I/P
741
1K
1K
RECORDER
1K
100K
10K
1K
A/D CONVERTER.
1K

Figure AI-1.


A/D
CONV.
D0
SIRIUS
D7


OPTO
ISOLATORS.
DIGITAL
I/P.
TY
TT
TH
TTH
MULTI-
PLEXOR
SIRIUS
A
B
C
CONTROL
LINES

form. A listing of the program is given in Table AI-1. Lines 20-30, are put in to stop the computer going 'out of memory'. Line 30 calculates the number of data points collectable. The limitation here being the efficiency of the ACT Sirius/DSC-2 interface. Lines 90-390 are dedicated to the collection of data by poking the relevant pins of the V.I.A. Lines 500-600 are for the storage of the total amount of data collected on a separate disk (disk drive B). The operator inputs his own file name (line 530) and this name (string) is cattenated to the file specifier (.DAT) and the directive to dump onto disk drive B (B:), Line 550 lines up the read/write heads of the disk drive with the next randomly accessable disk segment, and to create a map of this disk file with the specified file name given it. The first data segment is always the number of data points to be stored. The program has been written in this way so that when reading up from disk,

1/ The minimum amount of RAM will be taken up for data.

2/ No extra data points will be read from other files.

Line 600 closes the data file and returns to the higher program level for the next command. This program stores all the data collected and thus uses large segments of disk per file.

To reduce this disk space and help the main programs (DSC/purity; heat capacity, etc.) to run fast, the other two programs contain sorting routines.

<u>AI-CI: LOAD</u> This program, Table AI-2, has a routine written in that will average every data point. That is for example if temperature was scanned over a ten degree range, one-hundred data points might be read, (10 data points per degree). This routine (line 480-660) will take the average data point per degree, and it is these averaged points that are stored with their respective temperatures (lines 670-770). (N.B. The temperature readings are real numbers, when per degree is referred to above, it is to

LOADS TABLE AI-1

```
10 PRINT"DSC2 DATA READ PROGRAM"
20 INPUT "MAX TIME OF ANY SCAN(MINS.)";TM
30 TD=INT(TM*315)
35 DIM Y(TD),S(TD)
36 DEFDBL B-G.R.K,L
37 DEFINT J.P
40 PRINT "HIT ANY KEY TO START DATA COLLECTION(NOT N OR Q)"
45 J=0
50 PRINT "HIT Q TO ABORT PROG."
60 PRINT "HIT N TO ABORT DATA COLLECTION"
70 A$=INKEY$:IF A$="" THEN 70
80 IF A$="Q" OR A$="q" THEN GOTO 620
90 DEF SEG=&HE808
91 POKE 3.0
92 POKE 2,15
100 PRINT CHR$(27)+"E"
110 IF INKEY$="N" THEN GOTO 490
140 POKE 0,8
150 FOR A=1 TO 0
160 NEXT A
170 POKE 0,0
180 FOR A=1 TO 0
190 NEXT A
240 POKE 0,7
250 B=PEEK(15)
260 POKE 0,6
270 C=PEEK(15)
280 POKE 0,5
290 D= PEEK(15)
300 E=256*B+16*C+D
310 PRINT E
320 POKE 0,4
330 F=PEEK(15)
340 POKE 0,3
350 G=PEEK(15)
360 POKE 0.2
370 R=PEEK(15)
380 POKE 0,1
390 K=PEEK(15)
400 L=(K+10*R+100*G+1000*F)/10
410 PRINT L
420 Y(J)=E
430 S(J)=L
440 J=J+1
450 IF J=INT(TD+1) THEN GOTO 480
460 GOTO 100
480 PRINT "AUTOMATIC DATA ABORT"
490 J=J-1
500 PRINT "DO YOU WANT DATA STORED"
510 A$=INKEY$:IF A$="" THEN 510
520 IF A$="N" THEN GOTO 40
530 INPUT "NAME OF FILE";H$
540 H$="B:"+H$+".DAT"
550 OPEN"O".£1.H$
560 WRITE£1,J
570 FOR P=0 TO J
580 WRITE£1.Y(P),S(P)
590 NEXT P
600 CLOSE£1
610 GOTO 40
620 END
```

LOAD

TABLE AI-2

```
10 PRINT"DSC2 DATA READ PROGRAM"
20 INPUT "MAX TIME OF ANY SCAN(MINS.)";TM
30 TD=INT(TM*315)
40 DIM Y(TD),X(TD),Q(TD),V(TD)
50 DEFDBL B-G,R,K,L
60 DEFINT J,P,I,N
70 PRINT "HIT ANY KEY TO START DATA COLLECTION(NOT N OR Q)"
80 J=0
90 PRINT "HIT Q TO ABORT PROG."
100 PRINT "HIT N TO ABORT DATA COLLECTION"
110 A$=INKEY$:IF A$="" THEN 110
120 IF A$="Q" OR A$="q" THEN GOTO 790
130 DEF SEG=&HE800
140 POKE 3,0
150 POKE 2,15
160 PRINT CHR$(27)+"E"
170 IF INKEY$="N" THEN GOTO 400
180 POKE 0.8
190 FOR A=1 TO 0
200 NEXT A
210 POKE 0.0
220 FOR A=1 TO 0
230 NEXT A
240 POKE 0.7
250 B=PEEK(15)
260 POKE 0.6
270 C=PEEK(15)
280 POKE 0.5
290 D= PEEK(15)
300 E=256*B+16*C+D
310 PRINT E
320 POKE 0.4
330 F=PEEK(15)
340 POKE 0.3
350 G=PEEK(15)
360 POKE 0.2
370 R=PEEK(15)
380 POKE 0.1
390 K=PEEK(15)
400 L=(K+10*R+100*G+1000*F)/10
410 PRINT L
420 Y(J)=E
430 X(J)=L
440 J=J+1
450 IF J=INT(TD+1) THEN GOTO 470
460 GOTO 160
470 PRINT "AUTOMATIC DATA ABORT"
480 N=1
490 IS=0
500 J=J-1
510 I=1
520 LS=Y(I)
530 IF X(I)<X(I+1) THEN GOTO 590
540 N=N+1
550 I=I+1
560 LS=LS+Y(I)
570 IF I=J+1 THEN GOTO 590
580 GOTO 530
590 Q(IS)=LS/N
600 V(IS)=X(I-1)
610 LS=Y(I)
620 IS=IS+1
630 N=1
640 IF I=J+1 THEN GOTO 660
645 I=I+1
650 GOTO 530
660 IS=IS-1
670 PRINT "DO YOU WANT DATA STORED"
680 A$=INKEY$:IF A$="" THEN 680
690 IF A$="N" THEN GOTO 70
700 INPUT "NAME OF FILE";H$
710 H$="B:"+H$+".DAT"
720 OPEN"O",£1,H$
730 WRITE£1,IS
740 FOR P=0 TO IS
750 WRITE£1,Q(P),V(P)
760 NEXT P
770 CLOSE£1
780 GOTO 70
790 END
```

the first decimal place).

AI-CII: LOAD-CP This program is written specifically for use in collecting heat capacity data. The program has a routine built into it (line 515-780) that will find an average displacement reading per degree (integer) by averaging readings from -0.5° to $+0.5^{\circ}$, and taking this averaged reading as the integer temperature value ($X.0^{\circ}$), and storing it with the respective averaged displacement reading (line 790-900).

AI-CIII: The Program Two versions of the DSC/purity program have been written, namely DSGW16.BAS and DSGW18.BAS. The greatest problem experienced with this type program was being able to distinguish when a peak began and ended. The original version DSGW16 uses a routine (line 550-1030) that first finds the peak zenith, and then goes about finding where the peak begins and ends. This is done by taking twenty points at the beginning of the data collection and twenty near the end, and calculating the least squares linear regression equation with them. The value of every point is then analysed either side of the peak maximum to see if they differ significantly from the generated least squares value. If the values are very similar, then that point is taken to be the peak start or end. The variable CX can be altered to decrease or increase the sensitivity as required. The program than executes a least squares calculation on all the data outside the range of the peak to gain a more accurate baseline.

At this point a least squares polynomial was considered, but with the baseline noise experienced it was found that an ordinary least squares linear regression was good enough. To reduce baseline noise, a cubic spline routine was considered, but this was thought to be too elaborate for such a program.

LOAD-CP

TABLE AI-3

```
10 PRINT"DSC2 DATA READ PROGRAM"
20 INPUT "MAX TIME OF ANY SCAN(MINS.)";TM
30 TD=INT(TM*315)
40 DIM Y(TD),X(TD),Q(TD),S(TD)
50 DEFDBL B-G,R,K,L
60 DEFINT J,P,I,N
70 PRINT "HIT ANY KEY TO START DATA COLLECTION(NOT N OR Q)"
80 J=0
90 PRINT "HIT Q TO ABORT PROG."
100 PRINT "HIT N TO ABORT DATA COLLECTION"
110 A$=INKEY$:IF A$="" THEN 110
120 IF A$="Q" OR A$="q" THEN GOTO 890
130 DEF SEG=&HC000
140 POKE 3.0
150 POKE 2,15
160 PRINT CHR$(27)+"E"
170 IF INKEY$="N" THEN GOTO 480
180 POKE 0.8
190 FOR A=1 TO 0
200 NEXT A
210 POKE 0,0
220 FOR A=1 TO 0
230 NEXT A
240 POKE 0.7
250 B=PEEK(15)
260 POKE 0,6
270 C=PEEK(15)
280 POKE 0,5
290 D= PEEK(15)
300 E=256*B+16*C+D
310 PRINT E
320 POKE 0,4
330 F=PEEK(15)
340 POKE 0,3
350 G=PEEK(15)
360 POKE 0,2
370 R=PEEK(15)
380 POKE 0,1
390 K=PEEK(15)
400 L=(K+10*R+100*G+1000*F)/10
410 PRINT L
420 Y(J)=E
430 X(J)=L
440 J=J+1
450 IF J=INT(TD+1) THEN GOTO 470
460 GOTO 160
470 PRINT "AUTOMATIC DATA ABORT"
480 J=J-1
490 PRINT "DO YOU WANT DATA STORED"
500 A$=INKEY$:IF A$="" THEN 500
510 IF A$="N" THEN GOTO 70
515 LS=0
516 PX=0
520 N=0
530 IX=FIX(X(0))
540 FOR I=0 TO J
550 IF FIX(X(I))>IX THEN GOTO 575
560 NEXT I
570 GOTO 790
575 IF PX=0 THEN GOTO 900
580 IS=I
590 IE=I
600 IM=I
610 IF X(IS)<(FIX(X(I))-.5) THEN 650
620 IS=IS-1
630 IF IS=0 THEN GOTO 650
640 GOTO 610
650 IF X(IE)>(FIX(X(I))+.5) THEN GOTO 690
660 IE=IE+1
670 IF IE=J THEN GOTO 690
680 GOTO 650
690 IM=IE-IS
700 FOR ID=IS TO IE
720 LS=LS+Y(ID)
730 NEXT ID
740 S(N)=X(I)
750 Q(N)=LS/IM
760 N=N+1
770 IX=FIX(X(I))
775 LS=0
780 GOTO 560
790 INPUT "NAME OF FILE";H$
800 J=N
810 H$="B:"+H$+".DAT"
820 OPEN"O",£1,H$
830 WRITE£1,J
840 FOR P=0 TO J
850 WRITE£1,Q(P),S(P)
860 NEXT P
870 CLOSE£1
880 GOTO 70
890 END
900 PX=PX+1
910 GOTO 560
```

The second program (DSGW18) was written identical to DSGW16 except for the above routine. This version was written as it was hoped to improve the accuracy of the baseline deviation stop/start. In this version lines 570-1225 are dedicated to the peak stop/start analysis. The first ten points are taken and their mean and standard deviation are calculated. The next ten points are then sampled and compared to see if they differ by more than two standard deviation of the mean of the first sample. If they do not, then the counter was incremented by five and the whole process repeated from the beginning so a new mean and standard deviation is calculated. It also means that there is always a five point overlap. The deviation of greater than two standard deviations of the mean must occur on fifty percent or more of the ten samples taken before a decision that a peak has started is taken. This was done to try and reduce the possibility of taking 'noise' as peak start. The program then finds the peak maximum as in DSGW16. Both programs from line 1039 and 1225 respectively are almost identical. Thus to briefly describe the working of DSGW16 will cover that of DSGW18 also.

Lines 20-230 set up the printer configuration (i.e. creates a triangle for delta sign); prints header and declares all variables used as either integers or double-precision numbers. Lines 240-460 are all challenge commands for directing the program. Lines 230-1039 have been delt with above as the peak location routines. Lines 1070-1470, are for calculating the baseline using a least squares regression. Lines 1530-1770, here the program finds the area under the total peak by calculating the baseline location at every point and subtracting it from the peak displacement value. Simpson's rule is then used to calculate the peak area. Line 1780 then asks if the peak is a reference (i.e. Indium, etc.) then a least squares line is calculated through the forward slope of the peak. The program step is then returned to

DSGW16

TABLE AI-4

```
10 LPRINT CHR$(27):":":CHR$(0);CHR$(0):CHR$(0);
20 LPRINT CHR$(27);"&":CHR$(0);"^^";CHR$(139);
30 LPRINT CHR$(14);CHR$(16);CHR$(34);CHR$(64);
40 LPRINT CHR$(130);CHR$(64);CHR$(34);CHR$(16);
50 LPRINT CHR$(14);CHR$(0);CHR$(0);
60 LPRINT CHR$(27);"%";CHR$(1);CHR$(0)
70 LPRINT CHR$(27);"!";CHR$(30);
80 LPRINT CHR$(27);"W";CHR$(1);
90 LPRINT "DSC2 ENTHALPY OF FUSION & PURITY PROGRAM+GRAPHICS [Mk.I]."
100 DEFINT A,J,Q,G,I,H,P
110 DEFDBL B-F,K-M,O,R-Y
120 LPRINT CHR$(27);"W";CHR$(0);
125 LPRINT CHR$(27);"!";CHR$(0);
130 LPRINT "by ";
135 LPRINT CHR$(27);"!";CHR$(30);
140 LPRINT CHR$(27);"4";
150 LPRINT "J.R.Payne."
160 LPRINT CHR$(27);"5";
165 LPRINT CHR$(27);"!";CHR$(0);
170 LPRINT CHR$(27);"M";
180 LPRINT "Royal Holloway College April 83 [Rev.Ver.Nov.84]"
190 LPRINT CHR$(27);"!";CHR$(0);
200 AD=0
210 KEY OFF
220 SUM=0
230 CLS
240 PRINT "PURITY ANALYSIS(type Y/N)"
250 A$=INKEY$:IF A$="" THEN 250
260 IF A$="Y" OR A$="y" THEN AD=1
270 GOTO 390
280 CLS
290 PRINT CHR$(7);
300 PRINT "IS THIS DATA REQUIRED (type Y/N)"
310 A$=INKEY$:IF A$=""THEN 310
320 IF A$="N" OR A$="n"THEN 220
330 CLS
340 PRINT CHR$(7);
350 PRINT "DO YOU REQUIRE THE DATA STORED(typeY/N)"
360 A$=INKEY$:IF A$=""THEN 360
370 IF A$="Y" OR A$="y"THEN 4040
380 GOTO 450
390 CLS
400 PRINT CHR$(7);
410 PRINT "DO YOU REQUIRE A STORED FILE(typeY/N)"
420 A$=INKEY$:IF A$=""THEN 420
430 IF A$="Y" OR A$="y"THEN 4140
440 IF A$="N" OR A$="n"THEN 4030
450 AM=0
460 FB=0
470 CLS
480 LPRINT CHR$(15):"Number of Data Points Collected=";J
490 LPRINT CHR$(18);
550 MAX=Y(1)
560 FOR I=2 TO J
570 IF MAX < Y(I) THEN GOTO 600
580 NEXT I
590 GOTO 630
600 MAX=Y(I)
610 AM=I
620 GOTO 580
630 IF AM=0 THEN GOTO 800   -
640 TMAX=S(AM)
650 RB1=0
660 MR1=0
670 N=0
680 FOR I=10 TO 30
690 X(N)=S(I)
700 Z(N)=Y(I)
710 N=N+1
720 NEXT I
730 N=N-1
740 FOR I=(J-30) TO (J-10)
750 X(N)=S(I)
760 Z(N)=Y(I)
770 N=N+1
780 NEXT I
790 GOTO 1220
800 LPRINT "NO PEAK FOUND"
810 GOTO 220
820 REM*FORWARD INTERCEPT*
830 REM*CX IS SENSITIVITY Hi(lo sens.).Lo(hi sens.)*
840 CX=6
850 PKIS=AM-1
860 GOTO 880
870 PKIS=PKIS-1
880 IF B$="-"THEN B=ABS(B)*(-1)
890 YF=S(PKIS)*M+B
900 IF PKIS=0 THEN GOTO 220
910 IF (YF+CX)> Y(PKIS) THEN GOTO 930
920 GOTO 870
930 REM*BACK INTERCEPT*
940 PKIE=AM+1
950 GOTO 970
960 PKIE=PKIE+1
970 IF B$="-"THEN B=ABS(B)*(-1)
```

```
980 YB=M*S(PKIE)+B
990 IF (YB+CX) > Y(PKIE) THEN GOTO 1010
1000 GOTO 950
1010 LPRINT CHR$(27);"M"
1020 TS=S(PKIS)
1030 TX=S(PKIE)
1035 PRINT CHR$(7);
1036 PRINT "DO YOU REQUIRE A GRAPHICS PLOT(typeY/N)"
1037 A$=INKEY$:IF A$="" THEN 1037
1038 IF A$="Y" OR A$="y"THEN 4290
1039 CLS
1040 LPRINT "PEAK STARTS AT TEMP.";CSNG(TS);"DEGREES K"
1050 LPRINT "PEAK MAXIMUM AT TEMP.";CSNG(TMAX);"DEGREES K"
1060 LPRINT "PEAK ENDS AT TEMP.";CSNG(TX);"DEGREES K"
1070 FOR I=0 TO J-1
1080 X(I)=0
1090 Z(I)=0
1100 NEXT I
1110 FOR I=0 TO PKIS-1
1120 X(I)=S(I)
1130 Z(I)=Y(I)
1140 NEXT I
1150 N=I+1
1160 FB=1
1170 FOR I=PKIE+1 TO J-1
1180 X(N)=S(I)
1190 Z(N)=Y(I)
1200 N=N+1
1210 NEXT I
1220 N=N-1
1230 B$="-"
1240 X1=0
1250 Y1=0
1260 XY=0
1270 X2=0
1280 FOR I=0 TO N
1290 X1=X1+X(I)
1300 Y1=Y1+Z(I)
1310 XY=XY+X(I)*Z(I)
1320 X2=X2+X(I)*X(I)
1330 NEXT I
1340 REM *X(?)=E,Z(?)=L*
1350 WT=(N*X2)-(X1*X1)
1360 IF WT<>0 THEN 1390
1370 LPRINT "NO SOLUTION TO LEAST SQUARES BASELINE FOUND"
1380 GOTO 220
1390 M=(N*XY-X1*Y1)/WT
1400 M=INT(1000*M+.5)/1000
1410 B=(Y1*X2-X1*XY)/WT
1420 IF ABS(B)=B THEN B$="+"
1430 B=INT(1000*B+.5)/1000
1440 IF FB=0 THEN GOTO 820
1450 MR1=M
1460 RB1=B
1470 D$=B$
1480 LPRINT "--------------------------------------------------------------"
1490 LPRINT "LINEAR BASELINE EQUATION IS:"
1500 LPRINT "Y=";M;"X";B$;ABS(B)
1510 LPRINT "NO. OF DATA POINTS=";N
1520 LPRINT "------------------------------------------------------------ "
1530 REM *FIND AREA UNDER TOTAL PEAK*
1540 B5=S(PKIS)
1550 RF=0
1560 B6=B5
1570 G=PKIS
1580 FOR H=PKIS TO PKIE
1590 TE(H)=Y(H)-(ABS(MR1*S(H)+RB1))
1600 NEXT H
1610 I=1
1620 IF B5>=(B6+.1) THEN GOTO 1660
1630 B5=S(PKIS+I)
1640 I=I+1
1650 GOTO 1620
1660 I=I-1
1670 RF=RF+(.05*(TE(PKIS+I)+TE(G)))
1680 B6=S(PKIS+I)
1690 IF G>=PKIE THEN GOTO 1720
1700 G=PKIS+I
1710 GOTO 1620
1720 U=RF
1730 PRINT CHR$(7);
1740 LPRINT CHR$(27);"G";
1750 LPRINT "AREA OF PEAK=";CSNG(U)
1760 LPRINT CHR$(27);"H";
1770 LPRINT CHR$(27);"!";CHR$(0);
1780 PRINT "IS THIS THE REFERENCE PEAK(type Y/N)"
1790 A$=INKEY$: IF A$=""THEN 1790
1800 IF A$="N" OR A$="n"THEN 2290
1810 REM *PEAK REFERENCE ANALYSIS*
1820 IF AQ=0 THEN UR=U
1830 IF AQ=0 THEN GOTO 390
1940 REM *FIND FRONT SLOPE OF REFERENCE*
1850 LPRINT
1860 LPRINT CHR$(27);"M";
1070 LPRINT CHR$(27);"-";CHR$(1);
1880 LPRINT "REFERENCE CALCULATIONS"
```

```
1890 LPRINT CHR$(27);"-";CHR$(0);
1900 CLS
1910 N=0
1920 X1=0
1930 Y1=0
1940 XY=0
1950 X2=0
1960 B$="-"
1970 FOR I=(PKIS+1) TO (AM-1)
1980 P(N)=S(I)
1990 Q(N)=Y(I)
2000 N=N+1
2010 NEXT I
2020 N=N-1
2030 FOR I=0 TO N
2040 X1=X1+P(I)
2050 Y1=Y1+Q(I)
2060 XY=XY+P(I)*Q(I)
2070 X2=X2+P(I)*P(I)
2080 NEXT I
2090 WN=N*X2-X1*X1
2100 IF WN<>0 THEN 2130
2110 LPRINT "NO SOLUTION TO LEAST SQUARES SLOPE FOUND"
2120 GOTO 390
2130 M=(N*XY-X1*Y1)/WN
2140 M=INT(1000*M+.5)/1000
2150 B=(Y1*X2-X1*XY)/WN
2160 IF ABS(B)=B THEN B$="+"
2170 B=INT(1000*B+.5)/1000
2180 LPRINT "-----------------------------------------------------------"
2190 LPRINT "FORWARD LINE EQUATION IS:"
2200 LPRINT "Y=";M;"X";B$;ABS(B)
2210 LPRINT "No. OF DATA POINTS=";N
2220 LPRINT "----------------------------------------------------"
2230 MR=M
2240 R$=B$
2250 RB=B
2260 UR=U
2270 LPRINT CHR$(27);"!";CHR$(0)
2280 GOTO 390
2290 REM *CALCULATIONS WITH SAMPLE PEAK*
2300 REM *FIND MAX HEIGHT ABOVE BASELINE*
2310 LPRINT
2320 IF AQ=0 THEN GOTO 3730
2330 LPRINT CHR$(27);"M";
2340 LPRINT CHR$(27);"-";CHR$(1);
2350 LPRINT "SAMPLE CALCULATIONS"
2360 LPRINT CHR$(27);"-";CHR$(0);
2370 CLS
2380 MAM=AM-PKIS
2390 MM=INT(MAM*2/3)+PKIS
2400 REM *MM IS 2/3 OF MAX PEAK HEIGHT*
2410 MN=INT((MAM*5)/8)+PKIS
2420 MP=INT(MAM/2)+PKIS
2430 MO=INT(MAM/4)+PKIS
2440 Q=0
2450 PX=1
2460 MAM=MM
2470 X6=(MR-MR1)
2480 B1=Y(MM)-(S(MM)*MR)
2490 B2=Y(MN)-(S(MN)*MR)
2500 B3=Y(MP)-(S(MP)*MR)
2510 B4=Y(MO)-(S(MO)*MR)
2520 G=PKIS
2530 RS=0
2540 B5=S(PKIS)
2550 B6=B5
2560 I=1
2570 IF B5>=(B6+.1) THEN GOTO 2610
2580 B5=S(PKIS+I)
2590 I=I+1
2600 GOTO 2570
2610 I=I-1
2620 RS=RS+(.05*(TE(PKIS+I)+TE(G)))
2630 B6=S(PKIS+I)
2640 IF G>=MAM THEN GOTO 2670
2650 G=PKIS+I
2660 GOTO 2570
2670 IF Q>0 THEN GOTO 2750
2680 Q=Q+1
2690 MAM=MN
2700 X5=ABS(RB1-B1)/X6
2710 V1=RS-(ABS((S(MM)-X5)/2)*TE(MM))
2720 LPRINT "FRACTIONAL AREA=";CSNG(V1)
2730 TW1=X5
2740 GOTO 2520
2750 IF Q>1 THEN GOTO 2830
2760 Q=Q+1
2770 MAM=MP
2780 X5=ABS(RB1-B2)/X6
2790 V2=RS-(ABS((S(MN)-X5)/2)*TE(MN))
2800 LPRINT "FRACTIONAL AREA=";CSNG(V2)
2810 TW2=X5
2820 GOTO 2520
2830 IF Q>2 THEN GOTO 2910
2840 Q=Q+1
```

```
2850 MAM=MO
2860 X5=ABS(RB1-B3)/X6
2870 V3=RS-(ABS((S(MP)-X5)/2)*TE(MP))
2880 LPRINT "FRACTIONAL AREA=":CSNG(V3)
2890 TW3=X5
2900 GOTO 2520
2910 X5=ABS(RB1-B4)/X6
2920 V4=RS-(ABS((S(MQ)-X5)/2)*TE(MQ))
2930 LPRINT "FRACTIONAL AREA=":CSNG(V4)
2940 UC=(U/100)*.5
2950 F(1)=U/V1
2960 F(2)=U/V2
2970 F(3)=U/V3
2980 F(4)=U/V4
2990 REM *FIND CORRELATION COEFFICIENT*
3000 U1=F(1)+F(2)+F(3)+F(4)
3010 U2=TW1+TW2+TW3+TW4
3020 U3=(TW1*F(1))+(TW2*F(2))+(TW3*F(3))+(TW4*F(4))
3030 U5=(F(1)*F(1))+(F(2)*F(2))+(F(3)*F(3))+(F(4)*F(4))
3040 U6=(TW1*TW1)+(TW2*TW2)+(TW3*TW3)+(TW4*TW4)
3050 U7=(U3*4)-(U2*U1)
3060 U8=SQR((U5*4)-(U1*U1))
3070 U9=SQR((U6*4)-(U2*U2))
3080 U10=U7/(U8*U9)
3090 CLS
3100 REM *IF r (U10)>0.98 THEN ALRIGHT*
3110 IF ABS(U10)>=.98 THEN GOTO 3360
3120 VC=UC*PX
3130 PX=PX+1
3140 IF U10=-1*(ABS(U10)) THEN GOTO 3160
3150 GOTO 3240
3160 REM *0.5% CORRECTION PER LOOP*
3170 UV=U+VC
3180 U1=V1+VC
3190 U2=V2+VC
3200 U3=V3+VC
3210 U4=V4+VC
3220 UJ=U+VC
3230 GOTO 3310
3240 REM *CORRECTION LOOP FOR NEGATIVE r*
3250 UV=U-VC
3260 U1=V1-VC
3270 U2=V2-VC
3280 U3=V3-VC
3290 U4=V4-VC
3300 UJ=U-VC
3310 F(1)=UV/U1
3320 F(2)=UV/U2
3330 F(3)=UV/U3
3340 F(4)=UV/U4
3350 GOTO 2990
3360 CR=.5*(PX-1)
3370 LPRINT "CORRECTION FACTOR=":CR:"%"
3380 LPRINT"r=":CSNG(U10)
3385 IF CR=0 THEN UJ=U
3390 REM *LEAST SQUARES REGRESSION FOR ^T & To *
3400 X1=0
3410 Y1=0
3420 XY=0
3430 X2=0
3440 B$="-"
3450 C(1)=TW1
3460 C(2)=TW2
3470 C(3)=TW3
3480 C(4)=TW4
3490 FOR I=1 TO 4
3500 X1=X1+F(I)
3510 Y1=Y1+C(I)
3520 XY=XY+C(I)*F(I)
3530 X2=X2+F(I)*F(I)
3540 NEXT I
3550 OX=4*X2-X1*X1
3560 IF OX<>0 THEN GOTO 3590
3570 LPRINT "NO SOLUTION FOUND TO 1/F GRAPH"
3580 GOTO 390
3590 M=(4*XY-X1*Y1)/OX
3600 M=ABS(INT(1000*M+.5)/1000)
3610 B=(Y1*X2-X1*XY)/OX
3620 IF ABS(B)=B THEN B$="+"
3630 B=INT(1000*B+.5)/1000
3640 D2=0
3650 FOR I=1 TO 4
3660 D2=D2+(C(I)-M*F(I)-B)^2
3670 D2=INT(1000*D2+.5)/1000
3680 NEXT I
3690 LPRINT "------------------------------------------------------------"
3700 LPRINT "1/F GRAPH VARIANCE=":CSNG(D2)
3710 LPRINT "^H(fusion) INDIUM=0.00679 cal/mg"
3720 LPRINT "------------------------------------------------------------"
3725 PRINT CHR$(7);
3730 INPUT "WEIGHT (in air) OF INDIUM USED(mg)=";RN
3735 CLS
3736 PRINT CHR$(7);
3740 INPUT "WEIGHT(in air) OF SAMPLE(mg)=";SA
3745 CLS
```

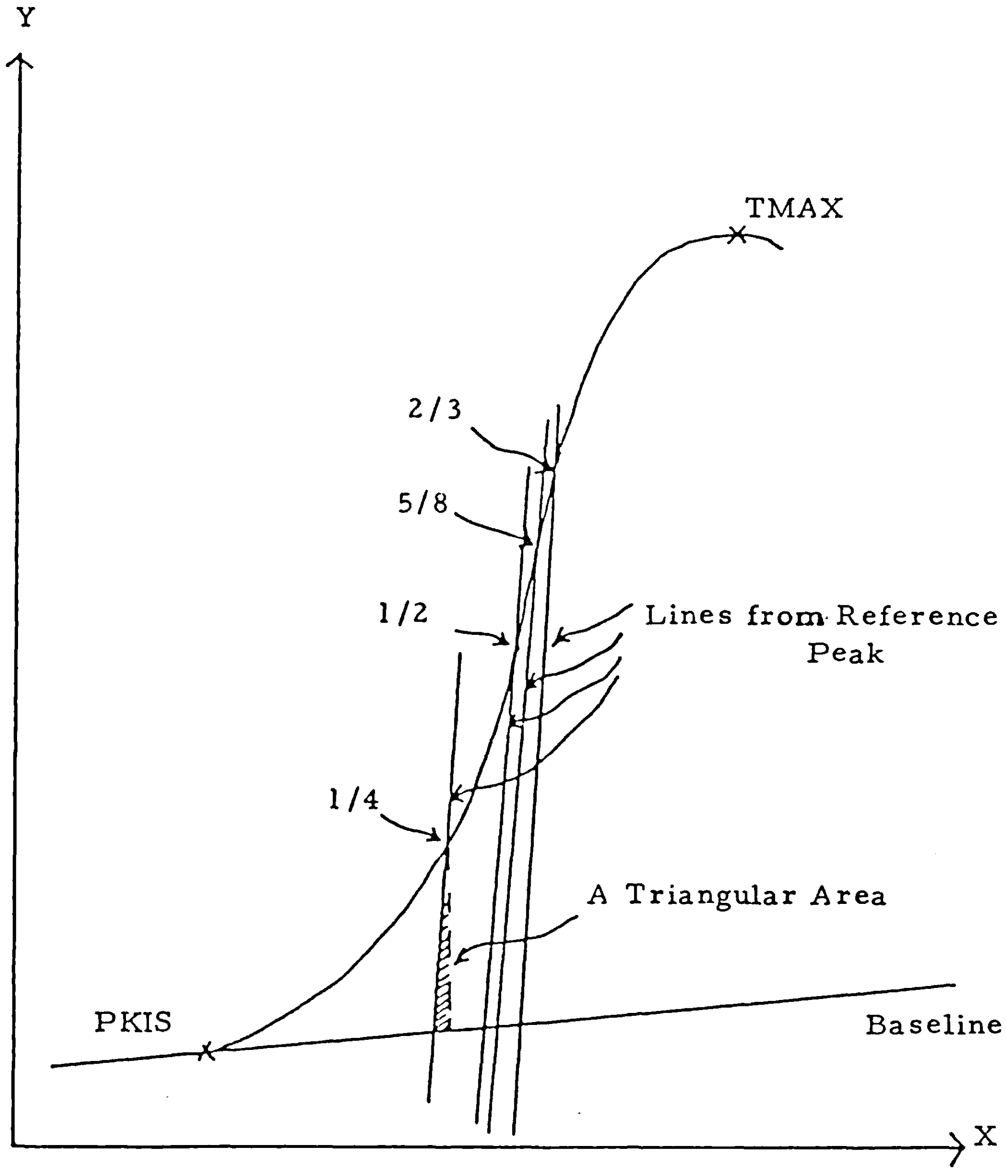
```
3746 PRINT CHR$(7);
3750 INPUT "No. OF C ATOMS IN COMPOUND":CS
3760 INPUT "No. OF H ATOMS IN COMPOUND":S2
3770 INPUT "No. OF O ATOMS IN COMPOUND":OS
3780 INPUT "No. OF N ATOMS IN COMPOUND":FS
3785 CLS
3790 MS=12.01115*CS+1.00797*S2+15.9994*OS+14.0067*FS
3000 LPRINT "Molecular Weight=":CSNG(MS)
3810 IF AO=0 THEN GOTO 4710
3820 FH=.00679*(HN/SA)*(UJ/UR)*1000
3830 FI=((FH*MS)*4.184)/1000
3840 S3=(FH*MS*M)/(B*B*1.9872)
3850 LPRINT "HEAT OF FUSION FOR SAMPLE=":CSNG(FI);"J/MOL."
3860 LPRINT CHR$(27);"'":CHR$(30);
3070 LPRINT CHR$(27):"-";CHR$(1);
3080 LPRINT "IMPURITY=";S3;"%"
3890 LPRINT CHR$(27):"-";CHR$(0);
3900 LPRINT CHR$(27);"4";
3910 S4=100-S3
3920 LPRINT "[Compound is ";S4;"% Pure]"
3930 LPRINT CHR$(27);"5";
3940 LPRINT CHR$(27); '";CHR$(0);
3950 PRINT CHR$(7);
3960 LPRINT CHR$(7);
3970 FOR H=1 TO 2000:NEXT H
3980 LPRINT CHR$(7);
3990 PRINT "DO YOU WISH TO STOP (type Y/N)"
4000 A$=INKEY$:IF A$=""THEN 4000
4010 IF A$="N" OR A$="n"THEN GOTO 390
4020 LPRINT CHR$(27);"%":CHR$(0);CHR$(0)
4030 END
4040 REM *DATA STORAGE*
4050 INPUT "NAME OF FILE":H$
4060 H$="B:"+H$+".DAT"
4070 OPEN"O",£1,H$
4080 WRITE£1,J
4090 FOR I=0 TO J-1
4100 WRITE£1,Y(I),S(I)
4110 NEXT I
4120 CLOSE£1
4130 GOTO 450
4140 REM *DATA READ*
4150 IF SUM>0 THEN 4570
4160 INPUT "NAME OF FILE":H$
4170 H$="B:"+H$+".DAT"
4180 OPEN "I",£1,H$
4190 J=0
4200 INPUT£1,J
4210 DIM Y(J),X(J),Z(J),TE(J),C(4),F(4),S(J),Q(J),P(J)
4220 SUM=SUM+1
4230 FOR I=0 TO J-1
4240 INPUT£1,Y(I),S(I)
4250 NEXT I
4260 CLOSE£1
4270 JJ=J
4280 GOTO 280
4290 REM*GRAPHICS*
4300 PRINT "HARD COPY,HIT C AT END"
4310 FOR A5=0 TO 2000:NEXT A5
4320 CLS
4330 SCREEN 2
4340 PSET (100,350)
4350 LINE(100,350)-(800,350),1
4360 LINE(100,350)-(100,0),1
4370 PSET(100,300)
4380 TG=300/MAX
4390 TT=700/JJ
4400 TV1=300-(Y(0)+TG)
4410 TH1=100+TT
4420 FOR I=0 TO JJ-1
4430 TV=300-(Y(I)*TG)
4440 TH=100+(I*TT)
4450 LINE(TH1,TV1)-(TH,TV),1
4460 TV1=TV
4470 TH1=TH
4480 NEXT I
4490 PRINT "HIT ANY KEY TO CONTINUE (EXCEPT C)"
4500 A$=INKEY$: IF A$="" THEN 4500
4510 IF A$="C" OR A$="c" THEN GOTO 4540
4520 SCREEN 0
4530 GOTO 1039
4540 REM*HARD COPY*
4550 LCOPY
4560 GOTO 4520
4570 INPUT "NAME OF FILE":H$
4580 H$="B:"+H$+".DAT"
4590 OPEN"I",£1,H$
4600 JJ=J
4610 JB=0
4620 INPUT£1,JB
4630 IF JB>J THEN JT=J
4640 IF JB<=J THEN JT=JB
4650 FOR I=0 TO JT-1
4660 INPUT£1,Y(I),S(I)
4670 JJ=JT
4675 J=JJ
4680 NEXT I
4690 CLOSE£1
```

```
4700 GOTO 280
4710 REM *ENTHALPY OF TRANSITION*
4720 F7=(.00679*(RN/SA)*(MS/114.82)*4.184*(U/UR))/1000
4730 LPRINT "^Ht=";CSNG(F7);"kJ/mol."
4740 GOTO 4020
```

line 380, keeping the slope and intercept data for later sample calculations. Setting the program up in this form allows the analysis of a reference peak many times. If the peak is selected to be a sample, then the program jumps to line 2290. Line 2290-2930 are concerned with calculating the fractional areas only. The intercepts of the forward slope with the peak are taken at 2/3rds; 5/8ths; 1/2, and 1/4 of the maximum height of the peak above the baseline, Figure AI-2 is relevant. The calculating of these fractional areas proved to be more difficult than first thought as firstly the two least squares regression lines had to be solved to find the intercept between the forward slope and the baseline slope. Secondly, using Simpson's rule, the area up to the point where the forward slope intercepted the peak could be calculated. The problem here is that using Simpson's rule meant that a line at a right-angle to the baseline through the peak/forward intercept was being used. Thus the area of a right-angle triangle upto the intercept of the forward slope with the baseline had to be calculated by Simpson's rule to give the true fractional area. This process was repeated for all fractional areas. The fraction being found by comparison with the total area calculated before. Once the fractional areas have been calculated, the reciprocals of the fraction of the total area is calculated; lines 2950-2980, and the correlation coefficient is found, lines 2990-3090. The correlation is performed on a comparison of the reciprocal fractions with their respective intercept temperatures. If needed, then a positive or negative correction loop of 0.5% is started, lines 3160-3350. This is continued until a correction within a 99.5% confidence interval is obtained. The least squares regression of this line is then calculated; lines 3390-3670, to allow the calculation of slope (ΔT), and intercept (T_o).

The program then asks for the weight of indium in air, and the weight of sample in air; lines 3730-3740, the program

Figure AI-2


Y
TMAX
2/3
5/8
1/2
Lines from Reference Peak
1/4
A Triangular Area
PKIS
Baseline
X

```
10 LPRINT CHR$(27);":";CHR$(0);CHR$(0);CHR$(0);
20 LPRINT CHR$(27);"&";CHR$(0);"^^";CHR$(139);
30 LPRINT CHR$(14);CHR$(16);CHR$(34);CHR$(64);
40 LPRINT CHR$(130);CHR$(64);CHR$(34);CHR$(16);
50 LPRINT CHR$(14);CHR$(0);CHR$(0);
60 LPRINT CHR$(27);"%";CHR$(1);CHR$(0)
70 LPRINT CHR$(27);"!";CHR$(30)
80 LPRINT CHR$(27);"W";CHR$(1);
90 LPRINT "DSC2 ENTHALPY OF FUSION & PURITY PROGRAM+GRAPHICS [Mk.II]."
100 DEFINT A,J,Q,G,I,H,P
110 DEFDBL B-F,K-M,O,R-Y
120 LPRINT CHR$(27);"W";CHR$(0);
125 LPRINT CHR$(27);"!";CHR$(0);
130 LPRINT "by ";
135 LPRINT CHR$(27);"!";CHR$(30);
140 LPRINT CHR$(27);"4";
150 LPRINT "J.R.Payne."
160 LPRINT CHR$(27);"5";
165 LPRINT CHR$(27);"!";CHR$(0);
170 LPRINT CHR$(27);"M";
180 LPRINT "Royal Holloway College Nov.84"
190 LPRINT CHR$(27);"!";CHR$(0);
200 AO=0
210 KEY OFF
220 SUM=0
230 CLS
240 PRINT "PURITY ANALYSIS(type Y/N)"
250 A$=INKEY$:IF A$="" THEN 250
260 IF A$="Y" OR A$="y" THEN AO=1
270 CLS
280 GOTO 400
290 PRINT CHR$(7);
300 CLS
310 PRINT "IS THIS DATA REQUIRED (type Y/N)"
320 A$=INKEY$:IF A$=""THEN 320
330 IF A$="N" OR A$="n"THEN 400
340 CLS
350 PRINT CHR$(7);
360 PRINT "DO YOU REQUIRE THE DATA STORED(typeY/N)"
370 A$=INKEY$:IF A$=""THEN 370
380 IF A$="Y" OR A$="y"THEN 4260
390 GOTO 460
400 CLS
410 PRINT CHR$(7);
420 PRINT "DO YOU REQUIRE A STORED FILE(typeY/N)"
430 A$=INKEY$:IF A$=""THEN 430
440 IF A$="Y" OR A$="y"THEN 4360
450 IF A$="N" OR A$="n"THEN 4240
460 AM=0
470 FD=0
480 CLS
490 LPRINT CHR$(15);"Number of Data Points Collected=";J
500 LPRINT CHR$(18);
560 REM*PEAK START*
570 I=0
580 INPUT "no.to start baseline dev.anal";I
590 CLS
600 O0=0
610 FOR IQ=I TO (I+9)
620 O0=O0+Y(IQ)
630 NEXT IQ
640 O3=O0/10
650 O0=0
660 FOR IQ=I TO (I+9)
670 O4=(O3-Y(IQ))*(O3-Y(IQ))
680 O0=O0+O4
690 NEXT IQ
700 O5=2*SQR(O0/90)
710 IN=0
720 FOR IQ=(I+5) TO (I+15)
730 R(IQ)=Y(IQ)-O3
740 IF R(IQ)>ABS(O5) THEN IN=IN+1
750 NEXT IQ
760 IF IN>5 THEN GOTO 820
770 I=I+5
780 IF I>=J1 THEN GOTO 800
790 GOTO 600
800 LPRINT "NO PEAK FOUND"
810 GOTO 400
820 FOR IQ=I+15 TO (I+5) STEP -1
830 IF R(IQ)>ABS(O5) THEN IN=IQ
840 NEXT IQ
850 TS=S(IN)
860 PKIS=IN
870 REM *PEAK END*
880 I=J1
890 O0=0
900 FOR IQ=(I-9) TO I
910 O0=O0+Y(IQ)
920 NEXT IQ
930 O3=O0/10
940 O0=0
950 FOR IQ=(I-9) TO I
960 O4=(O3-Y(IQ))*(O3-Y(IQ))
970 O0=O0+O4
980 NEXT IQ
```

```
990 O5=2*SQR(U0/70)
1000 IN=0
1010 FOR IO=(I-15) TO (I-5)
1020 R(IO)=Y(IO)-O7
1030 IF R(IO) ABS(O5) THEN IN=IN+1
1040 NEXT IO
1050 IF IN>5 THEN GOTO 1080
1060 I=I-5
1070 GOTO 890
1080 FOR IO=(I-15) TO (I-5) STEP 1
1090 IF R(IO)<ABS(O5) THEN IN=IO
1100 NEXT IO
1110 PKIE=IN
1120 TX=S(IN)
1130 REM*PEAK MAX*
1140 MAX=Y(PKIS)
1150 FOR I=PKIS TO PKIE
1160 IF MAX<Y(I) THEN GOTO 1190
1170 NEXT I
1180 GOTO 1220
1190 MAX=Y(I)
1200 AM=I
1210 GOTO 1170
1220 TMAX=S(AM)
1221 LPRINT CHR$(7);
1222 PRINT "DO YOU REQUIRE A GRAPHICS PLOT (type/N)"
1223 A$=INKEY$: IF A$=""THEN 1223
1224 IF A$="Y" OR A$="y"THEN 4510
1225 CLS
1230 LPRINT CHR$(27);"M"
1240 LPRINT "PEAK STARTS AT TEMP.";CSNG(TS);"DEGREES K"
1250 LPRINT "PEAK MAXIMUM AT TEMP.";CSNG(TMAX);"DEGREES K"
1260 LPRINT "PEAK ENDS AT TEMP.";CSNG(TX);"DEGREES K"
1270 FOR I=0 TO J-1
1280 X(I)=0
1290 Z(I)=0
1300 NEXT I
1310 FOR I=0 TO PKIS-1
1320 X(I)=S(I)
1330 Z(I)=Y(I)
1340 NEXT I
1350 QI=I+1
1360 FB=1
1370 FOR I=PKIE+1 TO J-1
1380 X(QI)=S(I)
1390 Z(QI)=Y(I)
1400 QI=QI+1
1410 NEXT I
1420 QI=QI-1
1430 B$="-"
1440 X1=0
1450 Y1=0
1460 XY=0
1470 X2=0
1480 FOR I=0 TO QI-1
1490 X1=X1+X(I)
1500 Y1=Y1+Z(I)
1510 XY=XY+X(I)*Z(I)
1520 X2=X2+X(I)*X(I)
1530 NEXT I
1540 REM *X(?)=E,Z(?)=L*
1550 WT=(QI*X2)-(X1*X1)
1560 IF WT<>0 THEN 1590
1570 LPRINT "NO SOLUTION TO LEAST SQUARES BASELINE FOUND"
1580 GOTO 420
1590 M=(QI*XY-X1*Y1)/WT
1600 M=INT(1000*M+.5)/1000
1610 B=(Y1*X2-X1*XY)/WT
1620 IF ABS(B)=B THEN B$="+"
1630 B=INT(1000*B+.5)/1000
1640 IF FB=0 THEN GOTO 1110
1650 MR1=M
1660 RB1=B
1670 D$=B$
1680 BS=0
1690 IF B$="+"THEN BS=ABS(B) ELSE BS=-1*ABS(B)
1700 LPRINT "--------------------------------------------------------------"
1710 LPRINT "LINEAR BASELINE EQUATION IS:"
1720 LPRINT "Y=";M;"X";B$;ABS(B)
1730 LPRINT "NO. OF DATA POINTS=";QI
1740 LPRINT "--------------------------------------------------------------"
1750 REM *FIND AREA UNDER TOTAL PEAK*
1760 B5=S(PKIS)
1770 RF=0
1780 B6=B5
1790 G=PKIS
1800 FOR H=PKIS TO PKIE
1810 TE(H)=Y(H)-(ABS(MR1*S(H)+RB1))
1820 NEXT H
1830 I=1
1840 IF B5>=(B6+.1) THEN GOTO 1880
1850 B5=S(PKIS+I)
1860 I=I+1
1870 GOTO 1840
1880 I=I-1
1890 RF=RF+(.05*(TE(PKIS+1)+TE(G)))
1900 B6=S(PKIS+1)
1910 IF G>=PKIE THEN GOTO 1940
```

```
1920 G=PKIS+I
1930 GOTO 1840
1940 U=RF
1950 PRINT CHR$(7);
1960 LPRINT CHR$(27);"G";
1970 LPRINT "AREA OF PEAK=";CSNG(U)
1980 LPRINT CHR$(27);"H";
1990 LPRINT CHR$(27);"!";CHR$(0);
2000 PRINT "IS THIS THE REFERENCE PEAK(type Y/N)"
2010 A$=INKEY$: IF A$=""THEN 2010
2020 IF A$="N" OR A$="n"THEN 2510
2030 REM *PEAK REFERENCE ANALYSIS*
2040 IF AQ=0 THEN UR=U
2050 IF AQ=0 THEN GOTO 400
2060 REM *FIND FRONT SLOPE OF REFERENCE*
2070 LPRINT
2080 LPRINT CHR$(27);"M";
2090 LPRINT CHR$(27);"-";CHR$(1);
2100 LPRINT "REFERENCE CALCULATIONS"
2110 LPRINT CHR$(27);"-";CHR$(0);
2120 CLS
2130 QI=0
2140 X1=0
2150 Y1=0
2160 XY=0
2170 X2=0
2180 B$="-"
2190 FOR I=(PKIS+1) TO (AM-1)
2200 P(QI)=S(I)
2210 Q(QI)=Y(I)
2220 QI=QI+1
2230 NEXT I
2240 QI=QI-1
2250 FOR I=0 TO QI-1
2260 X1=X1+P(I)
2270 Y1=Y1+Q(I)
2280 XY=XY+P(I)*Q(I)
2290 X2=X2+P(I)*P(I)
2300 NEXT I
2310 WN=QI*X2-X1*X1
2320 IF WN<>0 THEN 2350
2330 LPRINT "NO SOLUTION TO LEAST SQUARES SLOPE FOUND"
2340 GOTO 400
2350 M=(QI*XY-X1*Y1)/WN
2360 M=INT(1000*M+.5)/1000
2370 B=(Y1*X2-X1*XY)/WN
2380 IF ABS(B)=B THEN B$="+"
2390 B=INT(1000*B+.5)/1000
2400 LPRINT "--------------------------------------------------------------"
2410 LPRINT "FORWARD LINE EQUATION IS:"
2420 LPRINT "Y=";M;"X";B$;ABS(B)
2430 LPRINT "No. OF DATA POINTS=";QI
2440 LPRINT "--------------------------------------------------------------"
2450 MR=M
2460 R$=B$
2470 RB=B
2480 UR=U
2490 LPRINT CHR$(27);"!";CHR$(0)
2500 GOTO 400
2510 REM *CALCULATIONS WITH SAMPLE PEAK*
2520 LPRINT
2530 IF AQ=0 THEN GOTO 3950
2540 LPRINT CHR$(27);"M";
2550 LPRINT CHR$(27);"-";CHR$(1);
2560 LPRINT "SAMPLE CALCULATIONS"
2570 LPRINT CHR$(27);"-";CHR$(0);
2580 CLS
2590 MAM=AM-PKIS
2600 MM=INT(MAM*2/3)+PKIS
2610 REM *MM IS 2/3 OF MAX PEAK HEIGHT*
2620 MN=INT((MAM*5)/8)+PKIS
2630 MP=INT(MAM/2)+PKIS
2640 MQ=INT(MAM/4)+PKIS
2650 Q=0
2660 PX=1
2670 MAM=MM
2680 X6=(MR-MR1)
2690 B1=Y(MM)-(S(MM)*MR)
2700 B2=Y(MN)-(S(MN)*MR)
2710 B3=Y(MP)-(S(MP)*MR)
2720 B4=Y(MQ)-(S(MQ)*MR)
2730 G=PKIS
2740 RS=0
2750 B5=S(PKIS)
2760 B6=B5
2770 I=1
2780 IF B5>=(B6+.1) THEN GOTO 2820
2790 B5=S(PKIS+I)
2800 I=I+1
2810 GOTO 2780
2820 I=I-1
2830 RS=RS+(.05*(TE(PKIS+I)+TE(G)))
2840 B6=S(PKIS+I)
2850 IF G>=MAM THEN GOTO 2880
2860 G=PKIS+I
2870 GOTO 2780
```

```
2880 IF Q>0 THEN GOTO 2960
2890 Q=Q+1
2900 MAM=MN
2910 X5=ABS(RB1-B1)/X6
2920 V1=RS-(ABS((S(MM)-X5)/2)*TE(MM))
2930 LPRINT "FRACTIONAL AREA=";CSNG(V1)
2940 TW1=X5
2950 GOTO 2730
2960 IF Q>1 THEN GOTO 3040
2970 Q=Q+1
2980 MAM=MP
2990 X5=ABS(RB1-B2)/X6
3000 V2=RS-(ABS((S(MN)-X5)/2)*TE(MN))
3010 LPRINT "FRACTIONAL AREA=";CSNG(V2)
3020 TW2=X5
3030 GOTO 2730
3040 IF Q>2 THEN 3120
3050 Q=Q+1
3060 MAM=MQ
3070 X5=ABS(RB1-B3)/X6
3080 V3=RS-(ABS((S(MP)-X5)/2)*TE(MP))
3090 LPRINT "FRACTIONAL AREA=";CSNG(V3)
3100 TW3=X5
3110 GOTO 2730
3120 X5=ABS(RB1-B4)/X6
3130 V4=RS-(ABS((S(MQ)-X5)/2)*TE(MQ))
3140 LPRINT "FRACTIONAL AREA=";CSNG(V4)
3150 TW4=X5
3160 UC=(U/100)*.5
3170 REM **1/F FRACTIONS*
3180 F(1)=U/V1
3190 F(2)=U/V2
3200 F(3)=U/V3
3210 F(4)=U/V4
3220 REM *FIND CORRELATION COEFFICIENT*
3230 U1=F(1)+F(2)+F(3)+F(4)
3240 U2=TW1+TW2+TW3+TW4
3250 U3=(TW1*F(1))+(TW2*F(2))+(TW3*F(3))+(TW4*F(4))
3260 U5=(F(1)*F(1))+(F(2)*F(2))+(F(3)*F(3))+(F(4)*F(4))
3270 U6=(TW1*TW1)+(TW2*TW2)+(TW3*TW3)+(TW4*TW4)
3280 U7=(4*U3)-(U1*U2)
3290 U8=SQR((U5*4)-(U1*U1))
3300 U9=SQR((U6*4)-(U2*U2))
3310 U10=U7/(U8*U9)
3320 REM *IF r (U10)>0.98 THEN ALRIGHT*
3330 IF ABS(U10)>=.98 THEN GOTO 3580
3340 VC=UC*PX
3350 PX=PX+1
3360 IF U10=-1*(ABS(U10)) THEN GOTO 3380
3370 GOTO 3460
3380 REM *0.5% CORRECTION PER LOOP*
3390 UV=U+VC
3400 U1=V1+VC
3410 U2=V2+VC
3420 U3=V3+VC
3430 U4=V4+VC
3440 UJ=U+VC
3450 GOTO 3530
3460 REM *CORRECTION LOOP FOR NEGATIVE r*
3470 UV=U-VC
3480 U1=V1-VC
3490 U2=V2-VC
3500 U3=V3-VC
3510 U4=V4-VC
3520 UJ=U-VC
3530 F(1)=UV/U1
3540 F(2)=UV/U2
3550 F(3)=UV/U3
3560 F(4)=UV/U4
3570 GOTO 3220
3580 CR=.5*(PX-1)
3590 LPRINT "CORRECTION FACTOR=";CR;"%"
3600 LPRINT "r=";CSNG(U10)
3605 IF CR=0 THEN UJ=U
3610 REM *LEAST SQUARES REGRESSION FOR ^T & To *
3620 X1=0
3630 Y1=0
3640 XY=0
3650 X2=0
3660 B$="-"
3670 C(1)=TW1
3680 C(2)=TW2
3690 C(3)=TW3
3700 C(4)=TW4
3710 FOR I=1 TO 4
3720 X1=X1+F(I)
3730 Y1=Y1+C(I)
3740 XY=XY+C(I)*F(I)
3750 X2=X2+F(I)*F(I)
3760 NEXT I
3770 OX=4*X2-X1*X1
3780 IF OX<>0 THEN GOTO 3810
3790 LPRINT "NO SOLUTION FOUND TO 1/F GRAPH"
3800 GOTO 400
3810 M=(4*XY-X1*Y1)/OX
3820 M=ABS(INT(1000*M+.5)/1000)
```

```
3830 B=(Y1*X2-X1*XY)/DX
3840 IF ABS(B)=B THEN B$="+"
3850 B=INT(1000*B+.5)/1000
3860 D2=0
3870 FOR I=1 TO 4
3880 D2=D2+(C(I)-M*F(I)-B)^2
3890 D2=INT(1000*D2+.5)/1000
3900 NEXT I
3910 LPRINT "---------------------------------------------------------------"
3920 LPRINT "1/F GRAPH VARIANCE=";CSNG(D2)
3930 LPRINT "^H(fusion) INDIUM=0.00679 cal/mg"
3940 LPRINT "---------------------------------------------------------------"
3945 PRINT CHR$(7);
3950 INPUT "WEIGHT (in air) OF INDIUM USED(mg)=";RN
3955 CLS
3956 PRINT CHR$(7);
3960 INPUT "WEIGHT(in air) OF SAMPLE(mg)=";SA
3965 CLS
3967 PRINT CHR$(7);
3970 INPUT "No. OF C ATOMS IN COMPOUND";CS
3980 INPUT "No. OF H ATOMS IN COMPOUND";S2
3990 INPUT "No. OF O ATOMS IN COMPOUND";OS
4000 INPUT "No. OF N ATOMS IN COMPOUND";FS
4005 CLS
4010 MS=12.01115*CS+1.00797*S2+15.9994*OS+14.0067*FS
4020 LPRINT "Molecular Weight=";CSNG(MS)
4030 IF AO=0 THEN GOTO 4930
4040 FH=.00679*(RN/SA)*(UJ/UR)*1000
4050 FI=((FH*MS)*4.184)/1000
4060 S3=(FH*MS*M)/(B*B*1.9872)
4070 LPRINT "HEAT OF FUSION FOR SAMPLE=";CSNG(FI);"kJ/mol."
4080 LPRINT CHR$(27);"!";CHR$(30);
4090 LPRINT CHR$(27);"-";CHR$(1);
4100 LPRINT "IMPURITY=";CSNG(S3);"%"
4110 LPRINT CHR$(27);"-";CHR$(0);
4120 LPRINT CHR$(27);"4";
4130 S4=100-S3
4140 LPRINT "[Compound is ";S4;"% Pure]"
4150 LPRINT CHR$(27);"5";
4160 LPRINT CHR$(27);"'";CHR$(0);
4170 PRINT CHR$(7);
4180 LPRINT CHR$(7);
4190 FOR H=1 TO 2000:NEXT H
4200 LPRINT CHR$(7);
4210 PRINT "DO YOU WISH TO STOP (type Y/N)"
4220 A$=INKEY$:IF A$=""THEN 4220
4230 IF A$="N" OR A$="n"THEN GOTO 400
4240 LPRINT CHR$(27);"%";CHR$(0);CHR$(0)
4250 END
4260 REM *DATA STORAGE*
4270 INPUT "NAME OF FILE";H$
4280 H$="B:"+H$+".DAT"
4290 OPEN"O",£1,H$
4300 WRITE£1,J
4310 FOR I=0 TO J-1
4320 WRITE£1,Y(I),S(I)
4330 NEXT I
4340 CLOSE£1
4350 GOTO 790
4360 REM *DATA READ*
4370 IF SUM>0 THEN 4790
4380 INPUT "NAME OF FILE";H$
4390 H$="B:"+H$+".DAT"
4400 OPEN "I",£1,H$
4410 J=0
4420 INPUT£1,J
4425 IF J>900 THEN J=900
4430 DIM Y(J),X(J),Z(J),TE(J),C(4),F(4),S(J),Q(J),P(J),R(J),V(J)
4440 SUM=SUM+1
4450 FOR I=0 TO J-1
4460 INPUT£1,Y(I),S(I)
4470 NEXT I
4480 CLOSE£1
4490 JJ=J
4500 GOTO 390
4510 REM*GRAPHICS*
4520 PRINT"HARD COPY.HIT C AT END"
4530 FOR A5=0 TO 2000:NEXT A5
4540 CLS
4550 SCREEN 2
4560 PSET (100,350)
4570 LINE(100,350)-(800,350),1
4580 LINE(100,350)-(100,0),1
4590 PSET(100,300)
4600 TG=300/MAX
4610 TT=700/JJ
4620 TV1=300-(Y(0)*TG)
4630 TH1=100+TT
4640 FOR I=1 TO JJ
4650 TV=300-(Y(I)*TG)
4660 TH=100+(I*TT)
4670 LINE(TH1,TV1)-(TH,TV),1
4680 TV1=TV
4690 TH1=TH
4700 NEXT I
4710 PRINT"HIT ANY KEY TO CONTINUE(EXCEPT C)"
```

```
4720 A$=INKEY$:IF A$="" THEN 4720
4730 IF A$="C" OR A$="c" THEN GOTO 4760
4740 SCREEN 0
4750 GOTO 1225
4760 REM*HARD COPY*
4770 LCOPY
4780 GOTO 4740
4790 INPUT "NAME OF FILE";H$
4800 H$="B:"+H$+".DAT"
4810 OPEN"I",£1,H$
4820 JJ=J
4830 JB=0
4840 INPUT£1,JB
4850 IF JB>J THEN JT=J
4860 IF JB<=J THEN JT=JB
4870 FOR I=0 TO JT-1
4880 INPUT£1,Y(I),S(1)
4890 NEXT I
4900 JJ=JT
4905 J=JJ
4910 CLOSE£1
4920 GOTO 290
4930 REM *ENTHALPY OF TRANSITION*
4940 F7=(.00679*(RN/SA)*(MS/114.82)*4.184*(U/UR))/1000
4950 LPRINT "^Ht=":CSNG(F7);"kJ/mol."
4960 GOTO 4240
```

calculates the buoyancy corrected mass. It then asks for the number of C,H,N and O atoms in the compound; lines 3750-3800, and calculates the molecular weight. The program then goes on to calculate the heat of fusion with any relevant correction, and then the purity of the sample according to the method described in Plato and Glasgow[1].

Lines 4040-4280 are the data read and dump routines for reading from disk files already created by the load programs (described before). To cut RAM usage to a minimum the size of the storage arrays are here created to be the exact size of the stored data files.

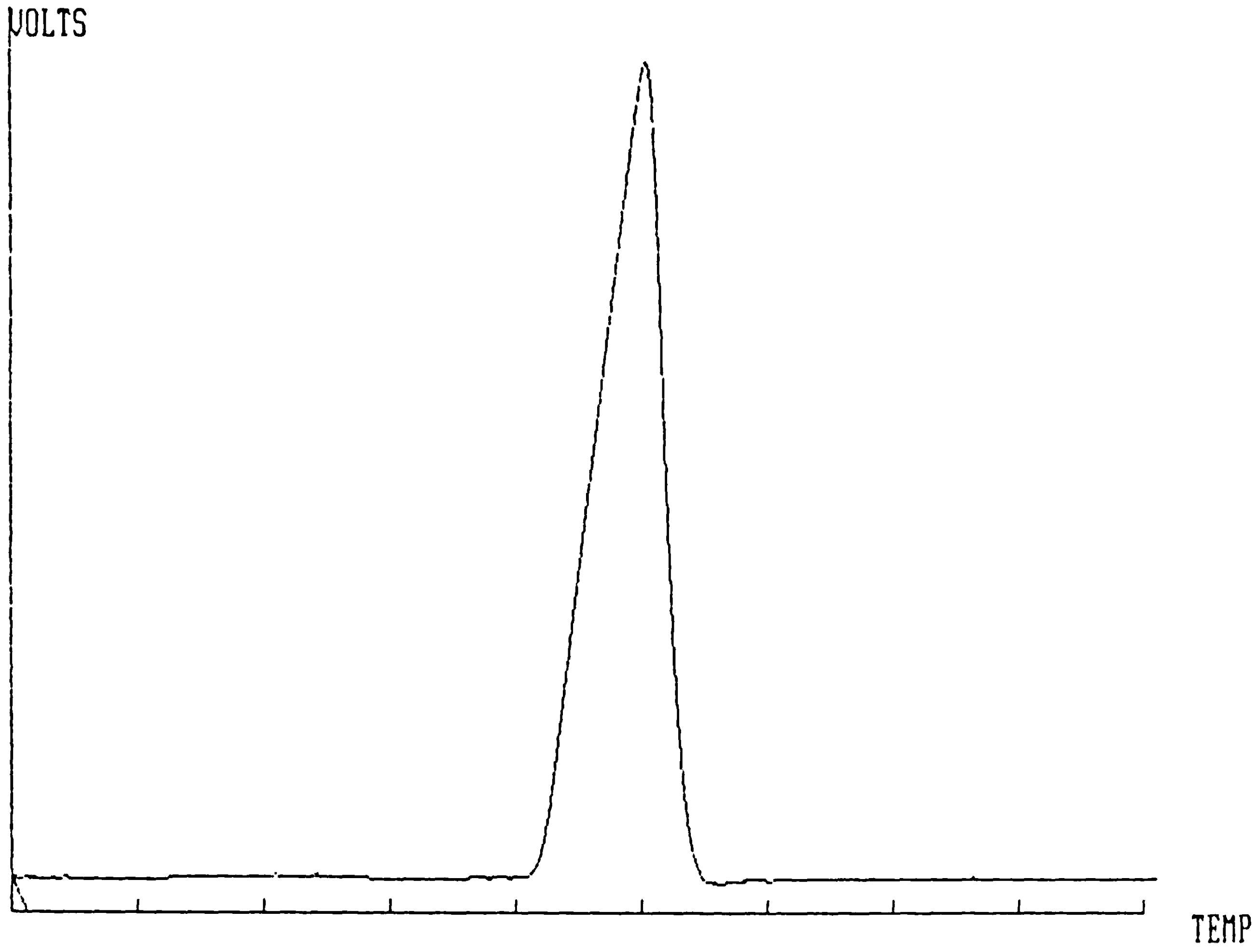
Lines 4290-4530 is a small graphics routine that prints the peak on the screen and lines 4540-4560 allow a hard copy to be made, Figure AI-3.

Lines 4710-4740 allow the enthalpy of transition to be calculated only, if the purity of the sample is not required. This routine is directed from an assignment in line 260.

AI-D: Heat Capacity Program

This program, CPGW1, like the purity programs can be run at any time as the LOAD-CP program is used to collect and store on disk the required data. A brief summary of the listing should give an idea of how the program works. Lines 10-130 sets up print headings, etc. and defines the double precision and integer variables. Lines 180-340 are the program directives. Line 350-560 are all part of the advanced stages of the data read from the disk files. It is important to first know if the data is the baseline, sample or reference. Secondly to have all the data files the same length (i.e. the same number of data points). Thus the smallest file is the maximum size. Thirdly, that all the readings are perfectly ordered (i.e. data point temperature T is the same array location in every file

Figure AI-3



```
10 LPRINT CHR$(27);"'";CHR$(30);
20 LPRINT CHR$(27);"W";CHR$(1);
30 LPRINT "DSC2 HEAT CAPACITY PROGRAM+GRAPHICS"
40 DEFINT I,J,H,Q,G
50 DEFDBL R,S,C,M,X,Y,B,D,U
60 LPRINT CHR$(27);"W";CHR$(0);
65 LPRINT CHR$(27);"!";CHR$(0);
70 LPRINT "by ";
80 LPRINT CHR$(27);"4";
85 LPRINT CHR$(27);"!";CHR$(30);
90 LPRINT "J.R.Payne."
95 LPRINT CHR$(27);"!";CHR$(0);
100 LPRINT CHR$(27);"5";
110 LPRINT CHR$(27);"M";
120 LPRINT "Royal Holloway College Feb.85"
130 LPRINT CHR$(27);"'";CHR$(0);
140 AD=0
150 KEY OFF
160 SUM=0
170 CLS
180 PRINT CHR$(7);
190 PRINT "DO YOU REQUIRE A STORED FILE(typeY/N)"
200 A$=INKEY$:IF A$=""THEN 200
210 IF A$="Y" OR A$="y"THEN 2620
220 IF A$="N" OR A$="n"THEN 2480
230 REM *DSC CALCULATION*
240 PRINT "IS THIS DATA REQUIRED (type Y/N)"
250 A$=INKEY$:IF A$=""THEN 250
260 IF A$="N" OR A$="n"THEN 170
270 REM *ANALYSIS OF DATA*
280 CLS
290 PRINT CHR$(7);
300 PRINT "DO YOU REQUIRE THE DATA STORED(typeY/N)"
310 A$=INKEY$:IF A$=""THEN 310
320 IF A$="Y" OR A$="y"THEN 2500
330 CLS
340 PRINT CHR$(7);
350 PRINT"is this"
360 PRINT "1.Baseline"
370 PRINT"2.Sapphire Reference."
380 PRINT "3.Sample."
390 A$=INKEY$:IF A$="" THEN GOTO 390
400 IF A$="1" THEN GOTO 430
410 IF A$="2" THEN GOTO 500
420 GOTO 560
430 DIM P(JJ),Q(JJ)
440 SUM=1
450 FOR I=0 TO (JJ-1)
460 P(I)=Y(I)
470 Q(I)=X(I)
480 NEXT I
490 GOTO 170
500 DIM K(JJ),L(JJ)
510 FOR I=0 TO (JJ-1)
520 K(I)=Y(I)
530 L(I)=X(I)
540 NEXT I
550 GOTO 170
560 DIM T(JJ),V(JJ),W(JJ),A(26),Z(26)
570 LPRINT CHR$(15);"Number of Data Points Collected=";(JJ-1)
580 LPRINT CHR$(18);
590 CLS
600 REM*DATA MEASUREMENTS*
610 FOR I=0 TO (JJ-1)
620 T(I)=FIX(Q(I))
630 V(I)=FIX(L(I))
640 W(I)=FIX(X(I))
650 NEXT I
660 I=0
670 IF T(I)=V(I) THEN GOTO 900
680 IF T(I)=V(I) THEN I=I+1 ELSE GOTO 710
690 IF I=JX THEN GOTO 900
700 GOTO 680
710 IX=I
720 IF T(I)>V(IX) THEN IX=IX+1 ELSE GOTO 740
730 GOTO 720
740 IF T(I)<V(IX) THEN I=I+1 ELSE GOTO 760
750 GOTO 740
760 IY=ABS(I-IX)
770 JJ=JJ-IY
780 IF IY<0 THEN GOTO 850
790 REM*+ve loop*
800 FOR I=0 TO (JJ-1)
810 P(I)=P(I+IY)
820 Q(I)=Q(I+IY)
830 NEXT I
840 GOTO 900
850 REM *-ve loop*
860 FOR I=0 TO (JJ-1)
870 K(I)=K(I+IY)
880 L(I)=L(I+IY)
890 NEXT I
900 JK=JJ
910 I=0
```

```
920 IF T(I)=W(I) THEN GOTO 1170
930 IF T(I)=W(I) THEN I=I+1 ELSE GOTO 960
940 IF I=JK THEN GOTO 1170
950 GOTO 930
960 IX=I
970 IF T(I)>W(IX) THEN IX=IX+1 ELSE GOTO 990
980 GOTO 970
990 IF T(I)<W(IX) THEN I=I+1 ELSE GOTO 1010
1000 GOTO 970
1010 IY=ABS(I-IX)
1020 JJ=JJ-IY
1030 IF IY<0 THEN GOTO 1120
1040 REM*+VE LOOP*
1050 FOR I=0 TO (JJ-1)
1060 P(I)=P(I+IY)
1070 Q(I)=Q(I+IY)
1080 K(I)=K(I+IY)
1090 L(I)=L(I+IY)
1100 NEXT I
1110 GOTO 1170
1120 REM*-VE LOOP*
1130 FOR I=0 TO JJ-1
1140 Y(I)=Y(I+IY)
1150 X(I)=X(I+IY)
1160 NEXT I
1170 JK=JJ
1180 FOR I=0 TO JK-1
1190 K(I)=K(I)-P(I)
1200 Y(I)=Y(I)-P(I)
1210 NEXT I
1220 CLS
1230 INPUT"WEIGHT(in air) OF SAPPHIRE(mg)=";R3
1240 INPUT "WEIGHT(in air) OF SAMPLE(mg)=";S3
1250 CLS
1260 REM*LOAD UP STD. Cp DATA*
1270 FOR I=0 TO 25
1280 READ A(I)
1290 READ Z(I)
1300 NEXT I
1310 I=0
1320 IF FIX(X(0))>=A(I) THEN I=I+1 ELSE GOTO 1340
1330 GOTO 1320
1340 IZ=I
1350 I=0
1360 IF A(IZ)=FIX(X(I)) THEN GOTO 1390
1370 I=I+1
1380 GOTO 1360
1390 IY=I
1400 IF IY=0 THEN GOTO 1450
1410 RD=(A(IZ)-FIX(X(0)))/10
1420 RE=(Z(IZ)-Z(IZ-1))*RD
1430 RF=Z(IZ)-RE
1440 GOTO 1570
1450 I=0
1460 IF FIX(X(I))>A(IZ+1) THEN GOTO 1500
1470 IF I=JJ THEN GOTO 1540
1480 I=I+1
1490 GOTO 1460
1500 RD=(A(IZ+1)-FIX(X(0))/I
1510 RE=(Z(IZ+1)-Z(IZ))*RD
1520 RF=Z(IZ)
1530 GOTO 1570
1540 RD=(FIX(X(JJ))-A(IZ))/10
1550 RE=(Z(IZ+1)-Z(IZ))*RD
1560 RF=Z(IZ)
1570 INPUT"MOLECULAR WEIGHT OF SAMPLE(grm)";SM
1580 CLS
1590 FOR I=0 TO JJ-1
1600 P(I)=0
1610 NEXT I
1620 P(0)=(4.184*RF*R3*Y(0))/(K(0)*S3)
1630 FOR I=1 TO JX-1
1640 P(I)=((4.184*(RF+(I*RE))*R3*Y(I))/(K(I)*S3))*SM/1000
1650 NEXT I
1660 LPRINT"TEMP[K]" TAB(10) "Cp[kJ/mol/K]" TAB(25) "TEMP[K]" TAB(35) "Cp[kJ/mol
/K]
1670 FOR I=1 TO (JX-1) STEP 2
1680 LPRINT X(I);TAB(10) CSNG(P(I));TAB(25) X(I+1);TAB(35) CSNG(P(I+1))
1690 NEXT I
1700 U1=0
1710 U2=0
1720 U3=0
1730 U4=0
1740 U5=0
1750 FOR I=1 TO (JX-1)
1760 U1=U1+X(I)
1770 U2=U2+P(I)
1780 U3=U3+(P(I)*X(I))
1790 U4=U4+(X(I)*X(I))
1800 U5=U5+(P(I)*P(I))
1810 NEXT I
1820 U6=(JX*U3)-(U1*U2)
1830 U7=SQR((JX*U4)-(U1*U1))
1840 U8=SQR((JX*U5)-(U2*U2))
1850 U9=U6/(U7*U8)
1860 LPRINT
```

```
1860 LPRINT
1870 LPRINT "CORRELATION COEF.r=":CSNG(U9)
1871 X1=0
1872 Y1=0
1873 XY=0
1874 X2=0
1875 B$="-"
1876 FOR I=1 TO JX-1
1877 X1=X1+X(I)
1878 Y1=Y1+P(I)
1879 XY=XY+X(I)*P(I)
1880 X2=X2+X(I)*X(I)
1881 NEXT I
1882 RT=(JX*X2)-(X1*X1)
1883 IF RT<>0 THEN 1886
1884 LPRINT "NO SOLUTION TO LEAST SQUARES"
1885 GOTO 170
1886 M=(JX*XY-X1*Y1)/RT
1887 M=INT(1000*M+.5)/1000
1888 B=(Y1*X2-X1*XY)/RT
1889 IF ABS(B)=B THEN B$="+"
1890 B=INT(1000*B+.5)/1000
1891 D2=0
1892 FOR I=0 TO JX-1
1893 D2=D2+(P(I)-M*X(I)-B)^2
1894 D2=INT(1000*D2+.5)/1000
1895 NEXT I
1910 LPRINT "--------------------------------------------------------"
1920 LPRINT "LINEAR BASELINE EQUATION IS:"
1930 LPRINT "Y=";M;"X";B$;ABS(B)
1940 LPRINT "VARIANCE=";D2
1950 LPRINT "--------------------------------------------------------"
1960 REM*GRAPHICS*
1970 CLS
1980 SCREEN 2
1990 PSET(100,350)
2000 LINE(100,350)-(800,350),1
2010 LINE(100,350)-(100,0),1
2020 PSET(100,300)
2030 TG=300/(P(JX-1)-P(0))
2040 D3=700/JX
2050 TH1=100
2060 TV1=300
2070 TH=100+D3
2080 TV=300-(TG*P(1))
2090 LINE(TH1,TV1)-(TH.TV),1
2100 FOR I=2 TO (JX-1)
2110 TH1=TH
2120 TV1=TV
2130 TH=100+(D3*I)
2140 TV=300-(TG*P(I))
2150 LINE(TH1.TV1)-(TH.TV),1
2160 NEXT I
2440 PRINT"HIT ANY KEY TO CONTINUE (EXCEPT C)"
2450 A$=INKEY$: IF A$="" THEN 2450
2460 IF A$="C" OR A$="c" THEN GOTO 2830
2470 SCREEN 0
2480 END
2490 LPRINT CHR$(7);
2500 REM*DATA STORAGE*
2510 INPUT"NAME OF FILE":H$
2520 CLS
2530 H$="B:"+H$+".DAT"
2540 OPEN"O".£1.H$
2550 WRITE£1.JX
2560 FOR I=0 TO JX-1
2570 WRITE£1.Y(I),X(I)
2580 NEXT I
2590 CLOSE£1
2600 JJ=JX
2610 GOTO 240
2620 REM*DATA READ*
2630 INPUT"NAME OF FILE":H$
2640 CLS
2650 H$="B:"+H$+".DAT"
2660 OPEN"I".£1,H$
2670 JX=0
2680 INPUT£1.JX
2690 IF SUM>0 THEN GOTO 2710
2700 DIM Y(JX),X(JX)
2710 FOR I=0 TO (JX-1)
2720 INPUT£1,Y(I),X(I)
2730 NEXT I
2740 CLOSE£1
2750 JJ=JX
2760 GOTO 240
2770 DATA 250,0.15708,260,0.16350,270,0.16962,280,0.17543,290,0.18094
2780 DATA 300,0.18615.310,0.19109,320,0.19574,330,0.20017,340,0.20834
2790 DATA 350,0.20834,360,0.21219,370,0.21580,380,0.21920.390,0.22241
2800 DATA 400,0.22543,410,0.22832,420,0.23102,430,0.23357,440,0.23603
2810 DATA 450,0.23835,460,0.24061,470,0.24271,480,0.24477,490,0.24672
2820 DATA 500,0.24860
2830 REM*HARD COPY*
2840 LCOPY
2850 GOTO 160
```

for all three files). These problems are all solved in lines 590-1210 where various positive and negative array movement loops are used. If an array has to be drastically re-alined then this can sometimes decrease the overall number of data points available for heat capacity calculations. Lines 1250-1300 loads up the standard heat capacities, (lines 2770-2820[2]). This data is then lined up according to the sample temperature range in lines 1310-1380, and the standard heat capacities of the fractional temperatures are calculated in lines 1390-1560. The relevant subtractions or additions to the sample displacements are made to give the displacement required for the heat capacity calculations, and these calculations are expedited in lines 1590-1650. The results are then printed by lines 1660-1690. The degree of correlation in the heat capacities; least squares regression and variance of the data is then calculated and output; lines 1700-1950. Lines 1960-2470 is a graphics routine. Lines 2490-2760 are the disk reader routines and array definition statements. Lines 2830-2850 are to produce hard copies in conjunction with the specified directive lines.

AI-E: Lattice Energy Program

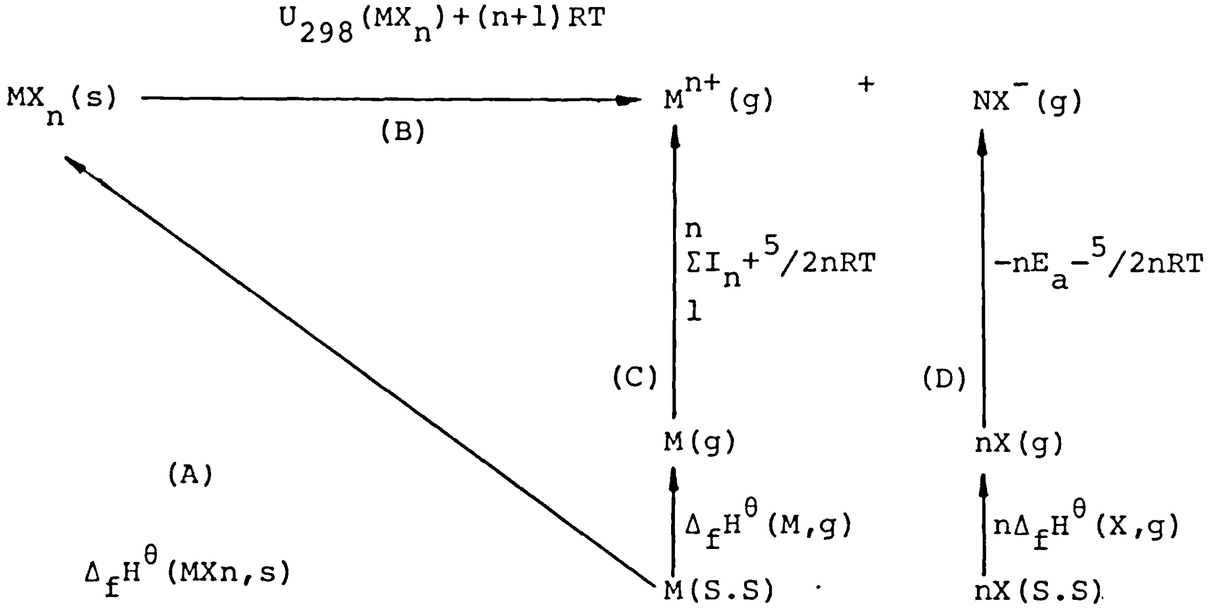
For the calculations of theoretical enthalpies of formation for metallo nitroresorcinols, a semi-empirical method has been devised[3,4,5]. For the calculations, a set of experimental data is needed for two anhydrous metallo salts; viz the cationic radius; enthalpy of formation of gaseous cation, and the enthalpy of formation of the crystalline solid. The calculations give the lattice energies and the anionic thermochemical radius. By using these results a re-calculation can be performed to give the enthalpies of formation of other metallo salts. The only ancillary data then needed are the ionic radius of the new cation and its enthalpy of formation in the gaseous phase.

KAPUT7 TABLE AI-7

```
10 LPRINT CHR$(27);":";CHR$(0);CHR$(0);CHR$(0);
20 LPRINT CHR$(27);"&";CHR$(0);"  ";CHR$(139);
30 LPRINT CHR$(14);CHR$(16);CHR$(34);CHR$(64);
40 LPRINT CHR$(130);CHR$(64);CHR$(34);CHR$(16);
50 LPRINT CHR$(14);CHR$(0);CHR$(0);
60 LPRINT CHR$(27);"%";CHR$(1);CHR$(0)
70 LPRINT CHR$(27);"!";CHR$(30);
80 LPRINT CHR$(27);"W";CHR$(1);
90 LPRINT"KAPUSTINSKII-YATSIMIRSKII PROGRAM"
100 LPRINT CHR$(27);"W";CHR$(0);
105 LPRINT CHR$(27);"!";CHR$(0);
110 LPRINT"by";
115 LPRINT CHR$(27);"!";CHR$(30);
120 LPRINT CHR$(27);"4";
130 LPRINT " J.R.Payne."
140 LPRINT CHR$(27);"5";
145 LPRINT CHR$(27);"!";CHR$(0);
150 LPRINT CHR$(27);"M";
160 LPRINT"Royal Holloway College May 84"
170 LPRINT CHR$(27);"!";CHR$(0);
180 LPRINT CHR$(7);
190 DEFDBL A-E.U
200 HF1=0
210 HF2=0
220 INPUT "DO YOU WISH TO INPUT IONIC RADIUS OF. 1 (CATION),2 (ANION)";RC
230 IF RC=1 THEN GOTO 290
240 INPUT "rm1-,(nm)";M1
250 INPUT "rm2-,(nm)";M2
260 INPUT "^Hf[M1-,g](kJ/mol)";H1
270 INPUT "^Hf[M2-,g](kJ/mol)";H2
280 GOTO 330
290 INPUT "rm1+,(nm)";M1
300 INPUT "rm2+,(nm)";M2
310 INPUT "^Hf[M1+,g](kJ/mol)";H1
320 INPUT "^Hf[M2+,g](kJ/mol)";H2
330 INPUT "^Hf[M1X,c](kJ/mol)";X1
340 INPUT "^Hf[M2X,c](kJ/mol)";X2
350 PRINT CHR$(27);"E";
360 U=H1-H2+X2-X1
370 E=242.8/U
380 A=M1+M2
390 B=(M1^2)+(M2^2)+(4*M1*M2)+(E*(M1-M2))
400 C=(2*(M1^2)*M2)+(2*M1*(M2^2))+(E*((M1^2)-(M2^2)))-(.069*E*(M1-M2))
410 D=((M1^2)*(M2^2))+E*(((M1^2)*M2)-((M2^2)*M1))+.0345*E*((M2^2)-(M1^2))
420 PRINT A ,B ,C .D
430 K=1
440 R=.5
450 GOTO 480
460 K=1
470 R=1
480 Y1=(R^4)+(2*A*(R^3))+(B*R^2)+(C*R)+D
490 Y2=4*R^3+6*A*R^2+2*B*R+C
500 J=R-(ABS(Y1/Y2))
510 IF R-J<.000001 THEN GOTO 550
520 K=K+1
530 R=J
540 GOTO 480
550 IF J<0 THEN 460
560 LPRINT CHR$(27);CHR$(15);
570 CLE1=(242.8/(J+M1))*(1-(.0345/(J+M1)))
580 CLE2=(242.8/(J+M2))*(1-(.0345/(J+M2)))
590 IF RC=1 THEN GOTO 650
600 LPRINT "rm1-";M1;"nm"
610 LPRINT "rm2-";M2;"nm"
620 LPRINT "^Hf[M1-,g]";H1;"kJ/mol"
630 LPRINT "^Hf[M2-,g]";H2;"kJ/mol"
640 GOTO 690
650 LPRINT"rm1+";M1;"nm"
660 LPRINT"rm2+";M2;"nm"
670 LPRINT"^Hf[M1+,g]";H1;"kJ/mol"
680 LPRINT "^Hf[M2+,g]";H2;"kJ/mol"
690 LPRINT "^Hf[M1X,c]";X1;"kJ/mol"
700 LPRINT "^Hf[M2X,c]";X2;"kJ/mol"
710 LPRINT CHR$(27);"E";
720 LPRINT "THERMOCHEMICAL RADIUS is";J;"nm"
730 LPRINT CHR$(27);"F";
740 LPRINT "VALUE OF Y1(ROOT) IS ";Y1
750 LPRINT "NUMBER OF APPROXIMATIONS TO ROOT ";K
760 LPRINT CHR$(27);"E";
770 IG1=(X1+CLE1)-H1
780 IG2=(X2+CLE2)-H2
790 LPRINT "CRYSTAL LATTICE ENERGY Uo OF M1X IS ";
800 LPRINT USING "££££.££££";CLE1;
810 LPRINT " kJ/mol"
820 LPRINT "CRYSTAL LATTICE ENERGY Uo OF M2X IS ";
830 LPRINT USING "££££.££££";CLE2;
840 LPRINT " kJ/mol"
850 IF RC=1 THEN GOTO 910
860 LPRINT "^Hf[M+,g]";IG1;"kJ/mol"
870 INPUT "new rX1-,(nm)";NM1
880 IF NM1=0 THEN GOTO 1000
890 INPUT "new ^Hf[X1-,g](kJ/mol)";NH1
900 GOTO 950
```

```
910 LPRINT "^Hf[X-,g]";IG1;"kJ/mol"
920 INPUT "new rm1+,(nm)";NM1
930 IF NM1=0 THEN GOTO 1000
940 INPUT "new ^Hf[M1+,g](kJ/mol)";NH1
950 NCLE1=(242.8/(J+NM1))*(1-(.0345/(J+NM1)))
960 LPRINT "NEW CRYSTAL LATTICE ENERGY is";
970 LPRINT USING "££££.££££";NCLE1;
980 LPRINT "kJ/mol."
990 HF1=(IG1+NH1)-NCLE1
1000 IF RC=1 THEN GOTO 1050
1010 INPUT  "new rx2-,(nm)";NM2
1020 IF NM2=0 THEN GOTO 1130
1030 INPUT "new ^Hf[X2-,g](kJ/mol)";NH2
1040 GOTO 1080
1050 INPUT "new rm2+,(nm)";NM2
1060 IF NM2=0 THEN GOTO 1130
1070 INPUT "new ^Hf[M2+,g](kJ/mol)";NH2
1080 NCLE2=(242.8/(J+NM2))*(1-(.0345/(J+NM2)))
1090 LPRINT "NEW CRYSTAL LATTICE ENERGY[2]";
1100 LPRINT USING "££££.££££";NCLE2;
1110 LPRINT "kJ/mol."
1120 HF2=(IG2+NH2)-NCLE2
1130 LPRINT "^Hf[nM1X,c]";HF1;"kJ/mol"
1140 LPRINT "^Hf[nM2X,c]";HF2;"kJ/mol"
1150 LPRINT CHR$(27);"F";
1160 LPRINT CHR$(18);
1170 LPRINT CHR$(27);"%";CHR$(0);CHR$(0)
1180 END
```

The lattice energy at 298K, U_{298} is related to other thermodynamic quantities by the Born-Haber cycle:



$\Sigma_1^n I_n$ is the sum of the first n ionisation potentials of M, and E_a is the electron affinity of the radical X. These values are corrected to 298K by the addition of the ${}^5/2nRT$ term. No interactions need be considered between the ions $M^{n+}(g)$ and $X(\bar{g})$ as they are in the hypothetical ideal gas state.

From the above cycle, the initial calculations thus produce (D) as a thermochemical radii. Upon introduction of a new cation with known (C), (A) can be deduced.

At an early stage it was hoped to be able to perform these sort of calculations for the metallo-nitroresorcinols. Thus the computer program KAPUT7.BAS was written in GWBMK1 basic for use in the Sirius computer. Unfortunately two criteria are needed for the calculations.

a/ The compounds are anhydrous.

b/ The compounds have identical molecular structure.

AI-F: Confidence Limits Program[7]

The program used to calculate the confidence limits is listed on Table AI-8. It is written in Fortran 77 and is run on the Royal Holloway College DEC VAX 11/780 computer.

AI-G: Dynamic Precipitation Program

From the dynamic precipitation experiment crystallisation temperatures are found for various solution concentrations. A new apparatus of a digital calibrated thermocouple was developed called the Andromeda. It was initially hoped to link Andromeda to Sirius using an interface program, and thus allowing for the calculations with the Sirius. Two separate programs were written, one for data collection by the Sirius from the Andromeda, and the second for the van't Hoff calculations for the van't Hoff enthalpy of solution. The data collection program is listed in Table AI-9, and the van't Hoff program [Vega program] is listed in Table AI-10 In Table AI-10, lines 10-210 are for setting up the program banner, delta sign; etc. and lines 230-250 are setting up the array dimensions and declarations of integers and double-precision identifiers. (All other non-declared locations are defaulted to single-precision numbers). Line 270 gives the option of working in molalities or molarities. Line 340 is activated only if molality is asked for. Line 380 asks for mass of the compound. Line 410, the number of ions in solution. Line 430, molecular weight of compound. Line 470, the volume of solvent, and finally Line 530, the crystallisation temperature. Lines 590-620, do some initial calculations and lines 630-660 store the data in arrays. If more data is needed to be input, program returns to line 460 and the program continues execution from there. Lines 710-910 are for the least squares regression equation calculations. Lines 920-940 calculate ΔH^{θ},ΔG^{θ} and ΔS^{θ}; the latter two from the Gibbs equation.

Table AI-8 [7]

```
TY C.
      PROGRAM LIM95
      REAL*8 X(1:20),T(1:19),MEAN,SUM,N
      INTEGER I,J
      DATA T/12.706,4.303,3.182,2.776,2.571,2.447,2.365,2.306,2.262,
     +2.228,2.201,2.179,2.160,2.145,2.131,2.120,2.110,2.101,2.903/
100   WRITE(6,600)
600   FORMAT(' Enter number of results (up to 20)')
      READ(5,*)J
      IF(J.LT.1.OR.J.GT.20)THEN
        GO TO 100
      ENDIF
      N=DFLOTJ(J)
      SUM=0.0
      DO 1,I=1,J,1
        WRITE(6,601)I
601     FORMAT(' Enter result ',I2)
        READ(5,*)X(I)
        SUM=SUM+X(I)
    1 CONTINUE
      MEAN=SUM/N
      SUM=0.0
      DO 2,I=1,J,1
        SUM=SUM+(X(I)-MEAN)**2
    2 CONTINUE
      N=DSQRT(SUM/(N*(N-1)))
      WRITE(6,603)MEAN,T(J-1)*N,N
603   FORMAT(' Result is ',E12.5,'+/-',E12.5/
     +       ' Standard error is ',E12.5)
      STOP
      END
$
```

VEGAINT

TABLE AI-9

```
10 REM *VEGA/SIRIUS-ANDROMEDA INTERFACE PROGRAM*
20 DEFDBL B.D
30 DEFINT J.P,N
40 DIM Y(300)
50 J=0
60 PRINT "PRESS ANY KEY TO START DATA COLLECTION(NOT N OR Q)"
70 PRINT "HIT Q TO ABORT PROGRAM"
80 PRINT"HIT N TO ABORT DATA COLLECTION"
90 A$=INKEY$:IF A$="" THEN 90
100 IF A$="Q" OR A$="q" THEN GOTO 490
110 PRINT CHR$(27)+"E"
120 DEF SEG=&HE808
130 POKE 3,0
140 POKE 2,255
150 POKE 0,129
160 FOR A=1 TO 200
170 IF INKEY$="N" THEN GOTO 360
180 NEXT A
190 POKE 0,0
200 FOR A=1 TO 200
210 NEXT A
220 POKE 0.129
230 FOR A=1 TO 200
240 NEXT A
250 B=PEEK(1)
260 B=CSNG(B/2.55)
270 C=INT(B)
280 D=B-C
290 IF D>.5 THEN C=C+.5
300 J=J+1
310 IF J>300 THEN GOTO 350
320 PRINT C
330 Y(J)=C
340 GOTO 150
350 PRINT "AUTO DATA ABORT"
360 PRINT "DO YOU WANT TO STORE DATA(Y/N)"
370 B$=INKEY$:IF B$="" THEN 370
380 IF B$="N" OR B$="n" THEN GOTO 50
390 INPUT "NAME OF FILE";H$
400 J=N
410 H$="B:"+H$+".DAT"
420 OPEN "O",£1.H$
430 WRITE£1,J
440 FOR P=1 TO J
450 WRITE£1,Y(P)
460 NEXT P
470 CLOSE£1
480 GOTO 50
490 END
```

VEGA TABLE AI-10

```
10 LPRINT CHR$(27);":";CHR$(0);CHR$(0);CHR$(0);
20 LPRINT CHR$(27);"&";CHR$(0);"^^^";CHR$(139);
30 LPRINT CHR$(14);CHR$(16);CHR$(34);CHR$(64);
40 LPRINT CHR$(130);CHR$(64);CHR$(34);CHR$(16);
50 LPRINT CHR$(14);CHR$(0);CHR$(0);
60 LPRINT CHR$(27);"%";CHR$(1);CHR$(0)
70 LPRINT CHR$(27);"!";CHR$(30)
80 LPRINT CHR$(27);"W";CHR$(1);
90 LPRINT "van't Hoff Program [VEGA]."
100 LPRINT CHR$(27);"W";CHR$(0);
110 LPRINT CHR$(27);"!";CHR$(0);
120 LPRINT "by";
130 LPRINT CHR$(27);"!";CHR$(30);
140 LPRINT CHR$(27);"4";
150 LPRINT " J.R.Payne."
160 LPRINT CHR$(27);"5";
170 LPRINT CHR$(27);"!";CHR$(0);
180 LPRINT CHR$(27);"M";
190 LPRINT "Royal Holloway College Sept 85"
200 LPRINT CHR$(27);"!";CHR$(0)
210 LPRINT CHR$(7);
220 KEY OFF
230 DIM D(100),E(100),F(100),G(100)
240 DEFDBL B,J-N,O,S-Z
250 DEFINT P,C,I
260 CLS
270 PRINT "Do you wish to work in MOLARITY (R) or MOLALITY (L) (type R or L)"
280 A$=INKEY$:IF A$="" THEN 280
290 CLS
300 IF A$="R" OR A$="r" THEN GOTO 370
310 IF A$="L" OR A$="l" THEN GOTO 330
320 GOTO 270
330 C=C+1
340 INPUT "Density of solvent (grams/1000cm3)";A
350 CLS
360 GOTO 380
370 C=0
380 INPUT "Mass of compound (in grams)";M
390 CLS
400 P=0
410 INPUT "Stoichiometric number of ions (n)";N
420 CLS
430 INPUT "Molecular weight of compound (in grams)";J
440 CLS
450 K=(M/J)*1000
460 V=0
470 INPUT "Volume of solvent (in cm3)";V
480 CLS
490 IF C=0 THEN GOTO 520
500 L=K/(V*A)
510 GOTO 530
520 L=K/V
530 INPUT "Crystallisation temperature (degrees C)=";T
540 CLS
550 PRINT "Is this data correct (type y or n)."
560 A$=INKEY$:IF A$="" THEN 560
570 CLS
580 IF A$="N" OR A$="n" THEN GOTO 460
590 P=P+1
600 T=T+273.15
610 U=1000/T
620 S=LOG(L)
630 D(P)=L
640 E(P)=S
650 F(P)=T
660 G(P)=U
670 PRINT "Do you wish to enter another reading (type y or n)"
680 A$=INKEY$: IF A$="" THEN 680
690 CLS
700 IF A$="Y" OR A$="y" THEN GOTO 460
710 X1=0
720 Y1=0
730 XY=0
740 X2=0
750 B$="-"
760 FOR I=1 TO P
770 X1=X1+G(I)
780 Y1=Y1+E(I)
790 XY=XY+(G(I)*E(I))
800 X2=X2+(G(I)*G(I))
810 NEXT I
820 WN=(P*X2)-(X1*X1)
830 IF WN<>0 THEN 860
840 LPRINT "NO SOLUTION TO LEAST SQUARES SLOPE FOUND"
850 GOTO 270
860 Q=((P*XY)-(X1*Y1))/WN
870 Q=INT(1000*Q+.5)/1000
880 B=((Y1*X2)-(X1*XY))/WN
890 IF ABS(B)=B THEN B$="+"
900 B=INT(1000*B+.5)/1000
910 IF B$="+" THEN BS=ABS(B) ELSE BS=-1*ABS(B)
920 SD=BS*8.314
```

```
925 LPRINT "Y=";Q;"X";B$;ABS(B)
930 H=-1*Q*8.314*N
940 SG=H-(298.15*SD)
950 LPRINT "^H=";H;"kJ/mol"
960 LPRINT "^S=";CSNG(SD);" J/mol/K"
970 LPRINT "^G=";CSNG(SG);"kJ/mol"
980 IF C=0 THEN GOTO 1010
990 LPRINT"T/C" TAB(10) "T/K" TAB(20) "1000/T" TAB(30) "Conc/mol 1000g-1";TAB(45
) "LN S"
1000 GOTO 1020
1010 LPRINT"T/C" TAB(10) "T/K" TAB(20) "1000/T" TAB(30) "Conc/mol dm-3";TAB(45)
"Ln S"
1020 FOR I=1 TO P
1030 R=CSNG(F(I)-273.15)
1040 LPRINT R; TAB(8) CSNG(F(I)); TAB(20) CSNG(G(I)); TAB(30) CSNG(D(I)); TAB(40
) CSNG(E(I))
1050 NEXT I
1060 PRINT "Do you wish to stop (type y or n)"
1070 A$=INKEY$:IF A$="" THEN 1070
1080 CLS
1090 IF A$="N" OR A$="n" THEN 270
1100 LPRINT CHR$(27);"%";CHR$(0);CHR$(0)
1110 KEY ON
1120 END
```

$$\Delta G^{\theta} = \Delta H^{\theta} - T\Delta S^{\theta}$$

Lines 950-1050 print the relevant data, and lines 1060-1120, gives the option to stop and defaults the delta sign setting.

AI-H: Bomb Calorimetry Program

Several versions of this program were initially written in BASIC-86 (CP/M-86); BASIC-86 (MS-DOS), and finally GW-BASIC (MS-DOS). The final version is listed in Table AI-11. Lines 10-180 are for setting up delta sign; banner, etc. Lines 190-300 set up an array, calculates the molecular weight, etc. Lines 320-350, are some constants used in the calculations that are specific for the R.H.C. bomb calorimeter. Lines 360-370 calculates the number of moles gained or lost during the combustion. Lines 400-560, ask for several parameters needed for the calculations. Lines 590-940 contain the calculation for the Washburn correction, etc. Lines 940-1140, output all the corrections calculated and $\Delta_c U^{\theta}$ for that experiment. Lines 1150-1450 are for calculation of the mean value of all the runs and the two times the standard deviation of the mean. From the calculated mean $\Delta_c U^{\theta}$ value the program calculated $\Delta_c H^{\theta}$ and $\Delta_f H^{\theta}$ for the compound and prints out the results with lines 1420-1440.

AI-I: Least Squares Regression Program

This program was written to perform the least squares regression calculation using the regression equations,[6].

$$M = \frac{n\Sigma xy - \Sigma x\Sigma y}{n\Sigma x^2 - (\Sigma x)^2}$$

BOMB

TABLE AI-11

```
10 LPRINT CHR$(27);":"CHR$(0);CHR$(0);CHR$(0);
20 LPRINT CHR$(27);"&";CHR$(0);"^^";CHR$(139);
30 LPRINT CHR$(14);CHR$(16);CHR$(34);CHR$(64);
40 LPRINT CHR$(130);CHR$(64);CHR$(34);CHR$(16);
50 LPRINT CHR$(14);CHR$(0);CHR$(0);
60 LPRINT CHR$(27);"%";CHR$(1);CHR$(0)
70 LPRINT CHR$(27);"!";CHR$(30)
80 LPRINT CHR$(27);"W";CHR$(1);
90 LPRINT "BOMB CALORIMETRY PROGRAM"
100 LPRINT CHR$(27);"W";CHR$(0);
110 LPRINT "by";
120 LPRINT CHR$(27);"4";
130 LPRINT " J.R.Payne."
140 LPRINT CHR$(27);"5";
150 LPRINT CHR$(27);"M";
160 LPRINT "Royal Holloway College October 84"
170 LPRINT CHR$(27);"!";CHR$(0)
180 LPRINT CHR$(7);
190 INPUT"TYPE NUMBER OF SAMPLES";N0
200 NX=N0+1
210 DIM E2(NX)
220 INPUT"NUMBER OF C ATOMS IN COMPOUND";X0
230 INPUT"NUMBER OF H ATOMS IN COMPOUND ";Y0
240 INPUT"NUMBER OF O ATOMS IN COMPOUND";Z0
250 INPUT"NUMBER OF N ATOMS IN COMPOUND";W0
260 M0=12.01115*X0+1.00797*Y0+15.9994*Z0+14.0067*W0
270 D1=44.01*.655*X0/M0+18.0153*4.18*Y0/(2*M0)+28.0134*.743*W0/(2*M0)
280 D1=D1-31.9988*.655*(X0+.25*Y0-.5*Z0)/M0
290 INPUT"DENSITY OF COMPOUND[g/ml]";D0
300 INPUT"ENERGY EQUIVALENT OF SYSTEM[kJ/K]";E3
310 JN=((X0*2)+(Y0/2)-Z0)/2
320 V0=.36
330 T0=298.15
340 P1=30
350 R0=.082065
360 BX=X0+(W0/2)-JN
370 LPRINT " n =";BX
380 FX=X0
390 GX=Y0/2
400 LPRINT"DENSITY[g/ml]=";D0
410 LPRINT"ENERGY EQUIV. OF SYSYEM[kJ/K]=";E3
420 LPRINT"F.Wt.[g]=";M0
430 N=0
440 N=N+1
450 PRINT CHR$(27);"E"
460 PRINT "RUN No.=";N
470 INPUT "SAMPLE WEIGHT IN AIR";MX
480 INPUT"FUSE WEIGHT";F
490 INPUT"Pt WIRE WEIGHT";P
500 INPUT"CRUCIBLE WEIGHT";C
510 INPUT"H2O";W
520 INPUT"No. ml OF (0.1M) NaOH ";JP
530 INPUT"(C)";C7
540 Q9=C7*33
550 INPUT"^T/K";T
560 PRINT "IS THIS DATA CORRECT(type Y/N)"
570 E$=INKEY$: IF E$="" THEN 570
580 IF E$="N" OR E$="n" THEN 470
590 Q5=.00183+(17.49*F)
600 Q6=.005972*JP
610 JF=(1/D0)-(1/7.8)
620 M=MX*(1+.0012*JF)
630 N1=M/M0
640 M1=W/18.015
650 MZ=.0001*(6.74-.0218*P1)
660 V1=V0-.018*M1-M/(1000*D0)
670 R1=P1*V1/(R0*T0*(1-MZ*P1))
680 IF W0=0 THEN 690 ELSE 710
690 R2=R1-N1*(X0+.25*Y0-.5*Z0)-1.75*(Q6/59.72)
700 GOTO 720
710 R2=R1-N1*(X0+.25*Y0-.5*Z0)-1.25*(Q6/59.72)
720 M2=M1+Y0*N1/2
730 V2=V0-.018*M2
740 S2=N1*W0/2-.5*Q6/59.72
750 X=X0*N1/(R2+S2+X0*N1)
760 MA=MZ*(1+3.21*X*(1+1.33*X))
770 P2=(R2+S2+X0*N1)*R0*T0*(1-MA*P1)/V2
780 M3=(13.04+.04125*P1)*.0001*V1
790 M4=(13.04+(.04125+.216*X)*P2)*.0001*V2
800 Q2=.003553*M2*P2*X
810 Q3=X0*N1-Q2
820 P3=(R2+S2+Q3)*R0*T0*(1-MA*P2)/V2
830 A0=R2+S2+Q3
840 RZ=R2/A0
850 SZ=S2/A0
860 QZ=Q3/A0
870 U1=-6.59*P1*R1
880 U2=(6.57*RZ+6.04*SZ+28.9*QZ-11.15*QZ*(RZ+SZ))*P3*A0
890 U3=-41530!*(M4-M3)
900 U4=17100*Q2
910 Q8=.001*(U1+U2+U3+U4)
920 E1=.001*(20.96*.449395+4.18*W+D1*M+.136*P+.76*C)
930 E2(N)=((E3+E1)*T-Q5-Q6+Q9-Q8)/M
940 LPRINT TAB(15);"RUN No";N
950 LPRINT"--------------------------------------------------------------"
960 LPRINT"M(SAMPLE)[in air]                    =";MX
```

```
970 LPRINT"M(SAMPLE)[in vacuo]                    =":M
980 LPRINT"M(FUSE)                                =";F
990 LPRINT"M(Pt WIRE)                             =";P
1000 LPRINT"M(CRUCIBLE)                            =";C
1010 LPRINT"M(SOOT)                               =";U/
1020 LPRINT"M(H2O)                                =";W
1030 LPRINT"q(ign)                                =";U5
1040 LPRINT"q(HNO3)                               =";U6
1050 LPRINT"q(C)                                  =";U7
1060 LPRINT"q(W)                                  =";U8
1070 LPRINT"^T/K                                   =";T
1080 A$="Ecf(kJ/K)        ="
1090 B$="-^u(kJ/g)        ="
1100 LPRINT A$;
1110 LPRINT E1
1120 LPRINT B$;
1130 LPRINT E2(N)
1140 LPRINT"------------------------------------------------------------------"
1150 IF N=N0 THEN 1170
1160 GOTO 440
1170 S0=0
1180 FOR N=1 TO N0
1190 S0=S0+E2(N)
1200 NEXT N
1210 S1=S0/N0
1220 C$="(-^u)/298.15K ="
1230 D$="2sdm          ="
1240 S0=0
1250 FOR N=1 TO N0
1260 S2=(S1-E2(N))*(S1-E2(N))
1270 S0=S0+S2
1280 NEXT N
1290 S3=2*SQR(S0/(N0*(N0-1)))
1300 LPRINT C$;
1310 LPRINT S1
1320 LPRINT D$;
1330 LPRINT S3
1340 E2(NX)=-1*S1
1350 GOSUB 1390
1360 LPRINT"------------------------------------------------------------------"
1370 LPRINT CHR$(27);"%";CHR$(0);CHR$(0)
1380 END
1390 CX=M0*E2(N)*-1
1400 DX=(.0083143*298.15*BX)+CX
1410 EX=(393.51*FX)+(285.83*GX)-DX
1420 LPRINT "-^Uc(kJ/mol)                 =";CX
1430 LPRINT "-^Hc(kJ/mol)                 =";DX
1440 LPRINT "-^Hf(kJ/mol)                 =";EX
1450 RETURN
```

and

$$c = \frac{\Sigma x^2 \Sigma y - \Sigma x \Sigma xy}{n\Sigma x^2 - (\Sigma x)^2}$$

where n = number of points (x,y)

Giving the parameters to the equation Y=MX+C. The program also calculates a correlation coefficient r^2 according to the equation,

$$r^2 = \frac{n\Sigma xy - \Sigma x \Sigma y}{\sqrt{[n\Sigma x^2 - (\Sigma x)^2][n\Sigma y^2 - (\Sigma y)^2]}}$$

In the listing of the program REGRESS, lines 10-190 are for setting up the printer and program parameters. All undeclared parameters are single precision (16 bit) real numbers by default of the INTEL processor unit. Lines 230-320 sets all addition locations for the FOR loop calculations to zero. Lines 340 and 350 are the input lines for x and y data points. Lines 360-450 hold all the multiplication and addition calculations. The program has been written in such a way as to avoid the use of an array. (N.B. If this program is to be used on a main-frame computer, serious consideration should be given to the amount of central processing unit (C.P.U.) time the program will use). As this program has been written specifically for use on a micro computer where storage is limited and C.P.U. time unlimited. Lines 500-590 are dedicated to the least squares calculation, and lines 600-640 for the correlation calculations. The KEYOFF and KEYON statements seen in several of the authors programs are to toggle the screen buffer that displays the functions available on the softy keys, namely; RUN<; CONT<; LCOPY<; SAVE"; LOAD"; FILES<; LIST.

REGRESS

TABLE AI-12

```
10 LPRINT CHR$(27);"!";CHR$(30)
20 LPRINT CHR$(27);"W";CHR$(1);
30 LPRINT "LEAST SQUARES REGRESSION PROGRAM"
40 LPRINT CHR$(27);"W";CHR$(0);
50 LPRINT CHR$(27);"!";CHR$(0);
60 LPRINT "by";
70 LPRINT CHR$(27);"!";CHR$(30);
80 LPRINT CHR$(27);"4";
90 LPRINT "J.R.Payne."
100 LPRINT CHR$(27);"5";
110 LPRINT CHR$(27);"!";CHR$(0);
120 LPRINT CHR$(27);"M";
130 LPRINT "Royal Holloway College Oct.85"
140 LPRINT CHR$(27);"!";CHR$(0)
150 LPRINT CHR$(7);
160 DEFINT N,I
170 CLS
180 N=0
190 KEY OFF
200 INPUT "No.OF POINTS";N
210 LPRINT "NUMBER OF DATA POINTS=";N
220 CLS
230 X1=0
240 U1=0
250 U2=0
260 U3=0
270 U5=0
280 U6=0
290 XY=0
300 Y1=0
310 X2=0
320 B$="-"
330 FOR I=1 TO N
340 INPUT "X-POINT";J
350 INPUT "Y-POINT";K
360 CLS
370 X1=X1+J
380 Y1=Y1+K
390 XY=XY+(J*K)
400 X2=X2+(J*J)
410 U1=U1+K
420 U2=U2+J
430 U3=U3+(J*K)
440 U5=U5+(K*K)
450 U6=U6+(J*J)
460 LPRINT "X=";J;"Y=";K
470 J=0
480 K=0
490 NEXT I
500 W=(N*X2)-(X1*X1)
510 IF W<>0 THEN 540
520 LPRINT "NO SOLUTION TO LEAST SQUARES"
530 GOTO 650
540 M=((N*XY)-(X1*Y1))/W
550 M=INT(1000*M+.5)/1000
560 B=((Y1*X2)-(X1*XY))/W
570 IF ABS(B)=B THEN B$="+"
580 B=INT(1000*B+.5)/1000
590 LPRINT "Y=";M;"X";B$;ABS(B)
600 U7=(U3*N)-(U2*U1)
610 U8=SQR((U5*N)-(U1*U1))
620 U9=SQR((U6*N)-(U2*U2))
630 U10=U7/(U8*U9)
640 LPRINT "Correlation Coefficient r=";U10
650 KEY ON
660 END
```

AI-J: References

1. PLATO,C.,and GLASGOW,A.R.,Anal.Chem.,41.1,330-336,(1969).
2. GINNINGS,D.C.,and FURUKAWA,G.T.,J.Am.Chem.Soc.,75,522,(1953).
3. YATSIMIRSKII,Y.B.,Inzvest.Akad.Nauk.SSSR Otdel.Khim.Nauk,453,(1947).
4. KAPUSTINSKII,A.F.,Z.Phys.Chem,22B,257,(1933).
5. KAPUSTINSKII,A.F.,Quart.Rev.,10,283,(1956).
6. MODE,E.B.,Elements of Statistics,3rd Edtn.,P223,Prentice-Hall Inc.,(1961).
7. ALLOTT,P.H.,Private Commun.

Appendix II

BUOYANCY CORRECTION

Appendix II

AII-A: Buoyancy Correction:[1]

For all calorimetry where very accurate weighings are required, buoyancy corrections are needed. It is self-evident that the weight of an object in vacuo is equal to the weight of air plus the weight of the air displaced by the object, minus the weight of air displaced by the balance weights.

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

where

W_v = weight in vacuo/g.

W_a = apparent weight in air/g.

d_a = density of air/g cm^{-3}.

d_w = density of weight/g cm^{-3}.

d_b = density of body/g cm^{-3}.

The density of air is usually taken as 0.0012 g cm^{-3}. As the difference between W_v and W_a does not normally exceed 1-2 parts per thousand.

Therefore

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

$$= W_a + (kW_a/1000)$$

where

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

d_w = 8.0 g cm^{-3}, density of stainless-steel balance weights.

AII-B: References

1. VOGEL,A.I.,'Textbook of Quantative Inorganic Analysis', Longman,London,4th Ed.,P70,(1978).

Appendix III

LEAD ANALYSIS

Appendix III

AIII-A: Analysis for Lead

For the analysis of lead in the lead polynitroresorcinates, several methods are available[1,2,3,4,5]. The analysis adopted for this investigation is a titrimetric method developed by Kurz[3], as follows.

The lead polynitroresorcinates (∿200 mg, 0.5×10^{-3} mol) was added to ethanol (20 cm^3) containing nitric acid (5 cm^3, 0.1 mol). The mixture was swirled to dissolve all the lead compound. To this mixture, EDTA (25.0 cm^3, 0.02 mol), water (250 cm^3) and xylenol orange solution (10-15 drops, 0.2%) were added, and then sodium hydroxide (1N) was carefully added to neutralize to the first reddish tinge. A further amount of nitric acid (1-2 drops, 0.1N) was then added until the colour changed to bright yellow. Acetic acid (100 cm^3, 1M) was added to sodium acetate (1 dm^3, 1M) and 5 cm^3 of this buffer solution was added to the nitroresorcinate mixture. The excess EDTA was then back-titrated with lead nitrate (0.02M) solution to the first reddish tinge. The analysis was performed also with a blank.

Typical result:

Wt. of sample = 0.04199g
Titre of sample with 0.02M $Pb(NO_3)_{2,aq}$ = 18.4 cm^3.
Titre of reference with 0.02M $Pb(NO_3)_{2,aq}$ = 24.9 cm^3.

$$\left[\frac{(24.9 - 18.4) \times 207.2 \times 0.02}{1000 \times 0.04199}\right] \times 100 = \underline{\underline{64.15\%}}$$

Theoretical lead content = (207.2x2)/646.512 = 64.1%

The analysis would be performed in duplicate.

AIII-B: References

1. COLLINS,P.,Private Commun.
2. KURZ,E.,Zeit.fur Anal.Chemie,246,386,(1969).
3. KURZ,E.,and KOBER,G.,Zeit.fur Anal.Chemie,254,2, 127,(1971).
4. "Analytical Methods for Powders and Explosives",Bofors, Nobelkrut,Sweden,(1974).
5. VŘEŠTÁL,J.,Chem.Průnyst,6,50,(1956).
6. KURZ,E.,and KOBER,G.,Analyst,92,391,(1967).
7. KŎRBL,J.,and PŘIBIL,R.,Chemist-Analyst,45,102,(1956).

Appendix IV

DENSITY MEASUREMENTS

Appendix IV

AIV-A: Density measurements of 2,4- and 4,6-DNR

For the buoyancy correction and Washburn calculation in combustion calorimetry the density of the test material is required. The method used was that of volumetric displacement using a pycnometer[1].

For this determination a liquid had to be found in which the compounds were insoluble. A very simple quantitative analysis experiment was devised to test for solubility.

Five watch glasses (∿ 10 cm diam.) were heated in an oven (105°C) for 2 h, then cooled in a desiccator and then weighed.

This procedure was repeated until constant weights were obtained. A sample of each compound (1.0g) was weighed into conical flasks, and the test liquid added (20.0 cm^3). The mixtures were then agitated and warmed on a hot plate. After allowing to settle and cool to room temperature, samples of the liquid (5.0 cm^3) were taken and added to the pre-weighed watch-glasses. The liquid was then allowed to evaporate off before the watch-glasses were subjected to the same heating/cooling cycle to constant weight. All the analysis was done in duplicate and with blanks. The liquid finally selected was petroleum ether (60°-80°C).

For the calculations four weights are needed.

(1) Pycnometer filled with liquid only: $W_1 = W_2 + W_L$

(2) Empty pycnometer: W_2

(3) Pycnometer partly filled with solid: $W_3 = W_2 + W_S$

(4) Pycnometer containing the solid (3) and enough added liquid to fill the vessel: $W_4 = W_2 + W_S + W_L$.

W_L and W_S are respectively the weights of the liquid and solid.

Thus approximate density, d_s' is obtained using the expression,

$$\frac{(W_3 - W_2)}{(W_1 - W_2) - (W_4 - W_3)} \times d_L \qquad \text{(AIV-A)}$$

from the fundamental equation

$$d_s = W_S/V_{DL} \qquad \text{(AIV-B)}$$

V_{DL} is the amount of liquid (W_{DL} g, of density d_L) that would be displaced if W_s g of solid were added to a completely liquid-filled vessel.

To find the absolute density d_s it is necessary to correct for air buoyancy effects using the following equations.

$$d_s = d_s' + D(1 - d_s' /d_L) \qquad \text{(AIV-C)}$$

where D = density of air and is determined by

$$D = 0.001293\ (P - k)/(1 + 0.00367t)\ 760 \qquad \text{(AIV-D)}$$

The determination of D was most conveniently accomplished by measuring the balance room temperature, $t^oC.$, the barometric pressure, P mm. of mercury; k is the corrected humidity.

The weights measured and densities calculated are shown in Table AIV-1.

Table AIV-1

Determination of the Density of DNR's Data

Determination 1

{all weights in g}

Pressure = 745.47 mm Hg; t = 22.61°C

d_L Petroleum Ether = 0.67 g cm^{-3} at 20°C

	2,4-DNR	4,6-DNR
W_2	13.4322	24.4763
W_1	20.0871	57.9534
W_3	13.5648	25.2750
W_4	20.1707	58.4627
d_L =	1.81	1.846 g cm^{-3} at 25°C

Determination 2

{all weights in g}

Pressure = 763.20 mm Hg: t = 24.72°C

	2,4-DNR	4,6-DNR
W_2	25.2682	24.4778
W_1	58.7623	57.8558
W_3	25.5665	25.5713
W_4	58.9503	58.5543
d_L =	1.809	1.85 g cm^{-3} at 25°C

Mean result = 1.81 & 1.85 g cm^{-3} at 25°C

AIV-B: References

1. WEISSBERGER,A.,Physical Methods of Organic Chemistry, 3rd Ed.,1,Interscience,New York,(1959).

Appendix V

STATISTICAL ANALYSIS

Appendix V

Statistical Analysis

AV-A: Regression

Sir Francis Galton (1822-1911) first introduced the word regression[1] when studying heredity, and found that "the sons of fathers who deviate x inches from the mean height of all fathers, themselves deviate from the mean height of all sons by less than x inches". Galton called this "regression to mediocrity". Today the word finds a much wider use i.e. regression curves; regression lines, etc. For all data analysis in this investigation where a regression line is required, the calculation were performed as follows.

To calculate an equation of the form,

$$y = a + bx \qquad \text{(AV-A)}$$

From a set of values of x and y, with means $\bar{x}$ and $\bar{y}$ respectively.

$$b = \frac{\sum_i [(x-\bar{x})(y-\bar{y})]}{\sum_i (x-\bar{x})^2} = \frac{n\Sigma x_i y_i - \Sigma x_i \Sigma y_i}{n\Sigma x_i^2 - (\Sigma x_i)^2} \qquad \text{(AV-B)}$$

$$a = \frac{\Sigma x_i^2 \Sigma y_i}{n\Sigma x_i^2} - \frac{-\Sigma x_i \Sigma x_i y_i}{-(\Sigma x_i)^2} = \bar{y} + b\bar{x} \qquad \text{(AV-C)}$$

where n = number of points (x_i, y_i).

All calculations were performed manually, and checked using a program available on the Royal Holloway College DEC VAX 11/780 computer. For a more detailed description of regression, refer to Snedecor and Cochran[2].

AV-B: Correlation

Correlation may be defined as "the amount of similarity, in direction and degree, of variations in corresponding pairs of observations of two variables." The principle of correlation was first introduced in a study by Pearson and Lee[3] on the height of brother and sisters.

The resultant was an equation of the form[4],

$$r^2 = \left[\underset{i}{\Sigma} XY - \left(\underset{i}{\Sigma}\, X\underset{i}{\Sigma} Y/N\right)\right] \Big/ \left[\underset{i}{}(\Sigma X^2-(\Sigma X)^2/N)(\Sigma Y^2-(\Sigma Y)^2/N)\right]^{\frac{1}{2}} \qquad \text{(AV-D)}$$

The equation used for the calculations in this investigation is a variation of equation(AV-D) in a form that is easier to use

$$r^2 = \frac{\underset{i}{\Sigma}(X-\overline{X})(Y-\overline{Y})}{\sqrt{\Sigma(X-\overline{X})^2\underset{i}{\Sigma}(Y-\overline{Y})^2}} \qquad \text{(AV-E)}$$

where $\Sigma(X-\overline{X})(Y-\overline{Y})$ = sum-of-products of X and Y, simplified to Σxy.

$\overline{X}$ and $\overline{Y}$ are the sample means.

Equation(AV-E) sometimes written as,

$$r^2 = \frac{\Sigma xy}{\sqrt{(\Sigma x^2 \Sigma y^2)}} \qquad \text{(AV-F)}$$

AV-C: Confidence Limits using "Student's" t-distribution

The "Student's" t-distribution was first discovered by Gosset in 1908[5] and perfected by Fisher in 1926[6], and it has since then been adapted to processes using Chi-square analysis. In the simple form used in this investigation the population mean μ and sample standard deviation, $\hat{s}$ is calculated.

$$\hat{s} = \sqrt{\frac{\Sigma_i (X-\bar{X})^2}{n-1}} = \sqrt{\frac{\Sigma x^2}{n-1}} \qquad \text{(AV-G)}$$

where $\bar{X}$ = sample mean, and Σx^2 = sum of squares.

The quantity t is given by the equation

$$t = \frac{\bar{X}-\mu}{\hat{s}/\sqrt{n}} \qquad \text{(AV-H)}$$

Thus by re-arrangement, the 95% confidence limit can be found,

$$\bar{X} - t_{0.05}\hat{s}/\sqrt{n} \leqslant \mu \leqslant \bar{X} + t_{0.05}\hat{s}/\sqrt{n}$$

where a suitable value for t can be found in tables e.g.[7]. The results were all checked using a program written for use on Royal Holloway College DEC VAX 11/780 (refer to Appendix I for listing).

AV-D: Covariance

For a full explanation of covariance, reference[2] should be consulted. Very briefly, a one-way classification was

$$Y_{ij} = \mu_i + \beta(X_{ij} - \bar{X}..) + \varepsilon_{ji} \qquad \text{(AV-I)}$$

μ_i = population means of the classes
ε_{ij} = population residuals of the means (Total- Replications- Treatments).
& β = the regression coefficient of Y on X.

Thus the observed mean for the i^{th} treatment will be

$$\bar{Y}_i = \mu_i + \beta(\bar{X}_i-\bar{X}..) + \bar{\varepsilon}_i \qquad \text{(AV-J)}$$

From section 1 of this Appendix it can be seen that
$b = \Sigma xy/\Sigma x^2$.
β is estimated from the Error line in the analysis of variance.
Therefore $b = Exy/Exx$

Exx = Error quantity in the sum of squares of X in variance analysis.
Exy = Error sum of products of X and Y.

It is these error sums of products that are used in the F-test of the adjusted means, the adjusted mean being given by

$$\hat{\mu}_i = \overline{Y}_i - \beta(\overline{X}_{i}. - \overline{X}..) \qquad \text{(AV-K)}$$

For the actual calculation of the experiment results in this investigation it was found to be a too complicated and tedious technique to perform manually. A program was found to be available on the Royal Holloway College DEC VAX 11/780 computer.

AV-E: References

1. GALTON,F.,Natural Inheritance,MacMillan,London,(1889).
2. SNEDECOR,G.W.and COCHRAN,W.G.,"Statistical Methods", Iowa State University Press,Ames,IOWA,U.S.A.,6th Ed., (1974).
3. PEARSON,K.,and LEE,A.,Biometrika,2,357,(1902).
4. PARKER,R.E.,"Introductory Statistics for Biology", 2nd Ed.,(Edward),Arnold,(1983).
5. "STUDENT",Biometrika,6,1,(1908).
6. FISHER,R.A.,Metron,5,90,(1926).
7. FISHER,R.A.,"Statistical Methods for Research Workers", Oliver and Boyd,Edinburgh,(1925).