THERMODYNAMIC ASPECTS OF PHOSPHORUS COMPOUNDS
WITH PARTICULAR REFERENCE TO THOSE CONTAINING
THE PHOSPHORUS-PHOSPHORUS BOND.

A thesis submitted by Abdul Hameed in candidature
for the degree of Doctor of Philosophy of the
University of London.


DEPARTMENT OF CHEMISTRY
ROYAL HOLLOWAY COLLEGE
ENGLEFIELD GREEN
SURREY, ENGLAND.
The enthalpies of sublimation for triiodophosphine and diphosphorus tetraiodide have been determined via an effusion manometric technique as $15.2 \pm 0.9 \text{ (63.6 } \pm 3.8 \text{ KJ. mole}^{-1})$ and $16.7 \pm 0.5 \text{ kcal mole}^{-1} (69.9 \pm 2.1 \text{ KJ. mole}^{-1})$ respectively. Incorporating these values in thermodynamic cycles along with ancillary literature data has resulted in a phosphorus-phosphorus bond energy in diphosphorus tetraiodide of 62 \text{ kcal mole}^{-1} (259 \text{ KJ. mole}^{-1}).

Mass spectrometric measurement of the appearance potentials for triiodophosphine and diphosphorus tetraiodide gave $11.9 \pm 0.15$ and $12.8 \pm 0.15$ eV respectively. These data in combination with known ionization potentials give $73 \pm 6 \text{ kcal mole}^{-1} (305 \pm 25 \text{ KJ. mole}^{-1})$ for the bond dissociation energy of the phosphorus-phosphorus bond in diphosphorus tetraiodide. Cracking patterns for some mononuclear adducts of the type $X_3PEX_3 (X = \text{Br} or \text{I})$ are reported.

Reproducible synthetic routes for pentaphenylcyclopentaphosphine and polymeric phenylphosphine have been established. Thermochemical investigations have been made for the pentameric and polymeric phosphobenzenes by reaction-solution calorimetry and thermal analysis techniques.

The standard heat of formation of tricyanophosphine (crystal) is derived via thermochemical measurements as $133.6 \pm 0.4 \text{ kcal mole}^{-1} (559.0 \pm 1.7 \text{ KJ. mole}^{-1})$ at $25^\circ \text{C}$.

The enthalpy of complexing of diphosphorus tetraiodide-boron tribromide (1:2) adduct from diphosphorus tetraiodide and boron tribromide in carbon disulphide has been measured as $-2.13 \pm 0.29 \text{ kcal mole}^{-1} (-8.91 \pm 1.21 \text{ KJ. mole}^{-1})$ and the standard heat of formation of this molecular adduct is derived as $-144.0 \pm 1.6 \text{ kcal mole}^{-1} (602.5 \pm 6.7 \text{ KJ. mole}^{-1})$. The enthalpy of hydrolysis
of pentabromophosphorane-boron tribromide is also recorded from which the standard heat of formation is found to be $-142.0 \pm 1.3$ kcal mole$^{-1}$ ($-594.1 \pm 5.4$ KJ. mole$^{-1}$).
V&A

Dedicated to the inspiration of
the late Hon. Lady Hanifa Bai
ACKNOWLEDGEMENTS

The author would like to thank Dr. Arthur Finch, Reader, University of London, and Dr. P.J. Gardner for their supervision and discussions on the subject of investigation. He also feels a deep sense of appreciation for their collaboration and encouragement shown throughout this work.

He would like to thank Professor E.J. Bourne, Head of the Chemistry Department and Dr. E. Marjorie Williamson, Principal of the College, for their good offices during this investigation. The award of the Post-Graduate Studentship by the Council of the Royal Holloway College is acknowledged with gratitude.

For many useful suggestions and co-operation he is pleased to acknowledge Professor T.G. Bonner, Dr. E.E. Percival, Dr. K.G. Singer, Dr. P.N. Gates, Dr. P. Powell, Dr. R.A. Hancock and all other members of the academic staff of the Chemistry Department.

The technical assistance of Mr. B.F. Smethurst was invaluable and that of his colleagues is much appreciated.

The grants made available by the Central Research Fund of the University of London and the Science Research Council for the purchase of a recorder and Quartz Crystal Thermometer respectively are acknowledged with gratitude.

Finally he is grateful for valuable discussions and for provision of financial aid, throughout the academic career, especially by late Hon. Lady Hanifa Bai, Bibi Bai (his mother) and Mr. Noormohammed Osman (his father) and his uncles Messrs. Haji Rehmtullah Adam and Habib Adam, Senior members, Karachi Stock Exchange Limited.
### CONTENTS

#### SECTION-I. INTRODUCTION

<table>
<thead>
<tr>
<th>Chapter One: Introduction</th>
<th>13-45</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) Classification and Nomenclature of Phosphorus Compounds</td>
<td>14-15</td>
</tr>
<tr>
<td>2) Some Aspects of Chemical Thermodynamics</td>
<td>16-19</td>
</tr>
<tr>
<td>3) Chemistry and Energetic Aspects of Phosphorus Compounds</td>
<td>20-45</td>
</tr>
<tr>
<td>(i) Phosphorus-Phosphorus Bonded Compounds (cyclic and acyclic)</td>
<td>20-33</td>
</tr>
<tr>
<td>(a) Phosphobenzenes</td>
<td>20-28</td>
</tr>
<tr>
<td>(b) Phosphorus Iodides</td>
<td>29-33</td>
</tr>
<tr>
<td>(ii) Phosphorus (III) Pseudohalides and Phosphorus (III) Compounds</td>
<td>34-41</td>
</tr>
<tr>
<td>Phosphorus (III) Pseudohalides</td>
<td>34-37</td>
</tr>
<tr>
<td>Phosphorus (III) Compounds</td>
<td>38-41</td>
</tr>
<tr>
<td>(iii) Phosphorus (V) Compounds</td>
<td>42-43</td>
</tr>
<tr>
<td>(iv) Molecular Adducts</td>
<td>43-45</td>
</tr>
</tbody>
</table>

#### SECTION-II. EXPERIMENTAL TECHNIQUES

<table>
<thead>
<tr>
<th>Chapter Two: Synthesis, Purification, Handling and Analysis</th>
<th>46-71</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYNTHESIS</td>
<td>47-58</td>
</tr>
<tr>
<td>(1) Phosphorus-Phosphorus Bonded Compounds</td>
<td>47-49</td>
</tr>
<tr>
<td>Pentaphenylcyclopentaphosphine</td>
<td>47</td>
</tr>
<tr>
<td>Hexaphenylcyclohexaphosphine</td>
<td>47-48</td>
</tr>
</tbody>
</table>
Polymeric Phenylphosphine 48-49
Diphosphorus Tetraiodide 49

(2) Phosphorus (III) Compounds 49-54
Phenylphosphine 49-50
Phenyltribromophosphine 50-51
Triphenylphosphine 51
Tricyanophosphine 51
Tri(isocyanato)phosphine 51-53

(3) Phosphorus (V) Compounds 54-55
Phenyltetrachlorophosphorane 54
Phenyltribromophosphorane 54-55

(4) Molecular Adducts 55-58
Diphosphorus Tetraiodide—Boron Tribromide (1:2) Adduct 55
Tribromophosphine—Boron Triiodide (1:1) Adduct 57
Triiodophosphine—Boron Tribromide (1:1) Adduct 57
Pentabromophosphorane—Boron Tribromide (1:1) Adduct 57-58

PURIFICATION 59-62

(1) Solvents 59-60
(2) Synthetic Materials 60-62

HANDLING 63-65

(1) Dry-Box Techniques 63
(2) Distillation Techniques 63
(3) Filtration Techniques 64
(4) Special Handling Techniques 64
(5) Storage 64
(1) Microanalysis
(2) Chemical Analysis
(3) Cryoscopic Measurements
(4) Vibrational Spectroscopy
(5) X-ray Crystallography

CHAPTER THREE: THERMOCHEMISTRY

(1) Solution Reaction Calorimetry
(2) Basic Principles and Construction
(3) Constructional Details
(4) Operating Procedure
   (i) Adiabatic Calorimeter
   (ii) Constant Temperature Environment (C.T.E.) Calorimeter
(5) Electronic Circuit for Adiabatic Control Unit

CHAPTER FOUR: (A) THERMAL ANALYSIS

(1) Thermal Analysis
(2) Thermogravimetric Analysis (TGA)
(3) Differential Thermal Analysis (DTA)
(4) Differential Scanning Calorimetry (DSC)
(5) Standard Test Materials

(B) MASS SPECTROMETRY

(1) Mass Spectrometry
(2) The Determination of Appearance Potentials from Ionization Efficiency Curves
CHAPTER FIVE: EFFUSION MANOMETRY

(1) Effusion Manometry
(2) Basic Principles
(3) Design and Construction
(4) Operating Procedure

SECTION-III. RESULTS

CHAPTER SIX: THERMOCHEMICAL RESULTS

Tris(hydroxymethyl)aminomethane (THAM) Results
Details of Typical C.T.E. Run
Details of Typical Adiabatic Run
Thermodynamic Cycle of Pentaphenylocyclopentaphosphine
Adiabatic Calorimetric Results for Polymeric Phenylphosphine
The Establishment of the Stoichiometry of the Bromination of (1) Pentaphenylocyclopentaphosphine
(2) Polymeric Phenylphosphine
Establishment of the Stoichiometry of the oxidation of Phenylphosphonic acid with Aqueous Bromine
C.T.E. Calorimetric Results for Tricyanophosphine (Hydrolysis)
C.T.E. Calorimetric Results for Tri(isocyanato)-phosphine (Hydrolysis)
C.T.E. Calorimetric Results for Phenyltetrabromo-phosphorane
Thermodynamic Cycle for Liposphorus Tetraiodide- Boron Tribromide (1:2) Adduct
C.T.E. Calorimetric Results of Pentabromophosphorane- Boron Tribromide (1:1) Adduct (Hydrolysis)
CHAPTER SEVEN: THERMAL ANALYSIS RESULTS

Thermal Analyzers and Programming 143-145
Differential Scanning Calorimetry Results for Indium 146-147
Differential Scanning Calorimetry Results for Pentaphenylcyclopentaphosphine 148-149
Differential Thermal Analysis Results for Pentaphenylcyclopentaphosphine 150-151
Differential Scanning Calorimetry Results for Hexaphenylcyclohexaphosphine 152-153
Differential Scanning Calorimetry Results for Polymeric Phenylphosphine 154-155
Thermogravimetric Analysis Results for Diphenophorus Tetraiodide 156-158
Differential Thermal Analysis Results for Diphenophorus Tetraiodide-Boron Tribromide (1:2) Adduct 159-160

CHAPTER EIGHT: MASS SPECTROMETRIC RESULTS

Probable Mode of Cracking 162-163
Mass Spectrum of Diphenophorus Tetraiodide and the Analysis of Major Significant Peaks 164-165
Mass Spectrum of Triiodophosphine and the Analysis of Major Significant Peaks 166
Mass Spectrum of Tribromophosphine and the Analysis of the Major Significant Peaks 167
Mass Spectrum of Boron Tribromide and the Analysis of the Major Significant Peaks 168-169
Mass Spectrum of Boron Tribromide and the Analysis of the Major Significant Peaks 170
Mass Spectrum of Tribromophosphine-Boron Tribromide (1:1) Adduct 171-172
Mass Spectrum of Triiodophosphine-Boron Tribromide (1:1) Adduct 173-174
Tricyanophosphine 221-222
Tri(isocyanato)phosphine 223-224

(2) Cryoscopic Results 225-228
Naphthalene (calibration) 226
Phenyldichlorophosphine 227
Tri(isocyanato)phosphine 228

(3) Vibrational Spectroscopic Results 229-235
Raman Spectra for Pentaphenylocyclopentaphosphine (Comparison) 229-232
Infra-Red Spectra for Pentaphenylocyclopentaphosphine (Comparison) 233

(4) X-ray Analysis Results 236-239
X-ray Crystallographic Results for Pentaphenylocyclopentaphosphine (Comparison) 236-237
X-ray Crystallographic Results for Polymeric Phenylphosphine (Comparison) 238-239

(5) Predicted Standard Heat of Formation for Diphosphorus Tetrabromide 240

(6) Classification of Phosphorus Compounds 241

SECTION-VI. REFERENCES

CHAPTER TWELVE: REFERENCES 242-267
Numerical 243-254
Alphabetical 255-267
SECTION-I. INTRODUCTION

CHAPTER ONE:
INTRODUCTION

(1) Classification and Nomenclature of Phosphorus Compounds

The type of phosphorus compounds synthesized or used in the present investigation may be classified as

(i) cyclic phosphorus-phosphorus bonded compounds
(ii) acyclic phosphorus-phosphorus bonded compounds
(iii) mononuclear phosphorus compounds
(iv) molecular adduct of phosphorus compounds
and (v) pseudohalides of phosphorus

The naming of the cyclic structures may be treated as an extension of the system followed by Cowley\(^1\) while that for the acyclic compounds, molecular adducts, and pseudohalides is due to the Chemical Society\(^2\) . Some examples of the nomenclature are as follows.

Phosphorus-Phosphorus Bonded Compounds

(cyclic and acyclic in which phosphorus atom is in trivalent state)

- Pentaphenylcyclopentaphosphine \((\text{C}_6\text{H}_5\text{P})_5\)
- Hexaphenylcyclohexaphosphine \((\text{C}_6\text{H}_5\text{P})_6\)
- Polymeric phenylphosphine \((\text{C}_6\text{H}_5\text{P})_n\)
- Diphenylphosphorus tetraiodide \(\text{P}_2\text{I}_4\)
### Phosphorus (III) Compounds and Phosphorus (III) Pseudohalides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylphosphine</td>
<td>C₆H₅PH₂</td>
</tr>
<tr>
<td>Phenyl dibromophosphine</td>
<td>C₆H₅PB₂</td>
</tr>
<tr>
<td>Tricyanophosphine</td>
<td>P(CN)₃</td>
</tr>
<tr>
<td>Tri(isocyanato)phosphine</td>
<td>P(NCO)₃</td>
</tr>
<tr>
<td>Tri(isocyanato)phosphine</td>
<td>P(NC)₃</td>
</tr>
<tr>
<td>Tri(thiocyanato)phosphine</td>
<td>P(SCN)₃</td>
</tr>
<tr>
<td>Tri(fulminato)phosphine</td>
<td>P(CNC)₃</td>
</tr>
</tbody>
</table>

### Phosphorus (V) Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyltetrachlorophosphorane</td>
<td>C₆H₅PCl₄</td>
</tr>
<tr>
<td>Phenyltetrabromophosphorane</td>
<td>C₆H₅PBr₄</td>
</tr>
<tr>
<td>Phosphoric oxide</td>
<td>P₄O₁₀</td>
</tr>
</tbody>
</table>

### Molecular Adducts of Phosphorus

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diphosphorus tetraiodide-</td>
<td>P₂I₂₂Br₃</td>
</tr>
<tr>
<td>Boron tribromide (1:2)</td>
<td></td>
</tr>
<tr>
<td>Triiodophosphine-</td>
<td>PBr₅BI</td>
</tr>
<tr>
<td>Boron triiodide (1:1)</td>
<td></td>
</tr>
<tr>
<td>Triiodophosphine-</td>
<td>PI₂BR₃</td>
</tr>
<tr>
<td>Boron tribromide (1:1)</td>
<td></td>
</tr>
<tr>
<td>Pentabromophosphorane-</td>
<td>PBr₅BB</td>
</tr>
<tr>
<td>Boron tribromide (1:1)</td>
<td></td>
</tr>
</tbody>
</table>

### Orsono-substituted Oxy-acids of Phosphorus

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenylphosphonous acid</td>
<td>C₆H₅PO₂H₂</td>
</tr>
<tr>
<td>Phenyl phosphonic acid</td>
<td>C₆H₅PO₂H₂</td>
</tr>
<tr>
<td>Phenylphosphinic acid</td>
<td>(C₆H₅PO₂H₂)</td>
</tr>
</tbody>
</table>

(See Appendix six for full details of the classification)
Some Aspects of Chemical Thermodynamics

A quantitative knowledge of energy changes is essential not only for a complete understanding of known reactions but also to make more predictions (see Appendix five p. 210) about still untried reactions. It is changes in the electronic energy in the ground state which commonly dominate the total energy change for a chemical reaction. The general term "bond energy" is a composite term. Logically, bond energy should be defined in a manner which must be understandable and experimentally derivable. In thermodynamics bond energy is defined at $0^\circ K$ in the absence of zero-point vibrational energy. Values derived at $298^\circ K$ include zero-point contribution in addition to rotational, translational and further vibrational components. However, for the majority of polyatomic molecules it is not possible to evaluate these contributions so it is conventional to express bond energies at $298^\circ K$.

Recently bond energies data for bonds in like atoms have been classified according to the position of the atoms in the periodic table. The values in such tables are derived either from a theoretical basis or are practically determined via thermochemical measurements or both. The present position of such tables indicates the necessity for ascertaining more experimental values and for revising those estimated previously. In the present investigation the bond energy for the phosphorus-phosphorus bond is determined via thermochemical measurements.

In practice many thermochemical values are obtained from combustion, reaction-solution calorimetry, equilibrium measurements etc. which are prerequisite for deriving thermodynamic data. The useful quantity most commonly derived is standard heat of formation ($\Delta H^\circ_f$) of the compound under standard conditions of temperature and pressure. Usually it is difficult to obtain heats of formation directly from the constituent elements. Thus the normal
procedure is to measure the enthalpy change of a reaction of the compound which yields products of known heat content. For any reaction to be studied thermodynamically it is essential that its stoichiometry be known exactly. The thermochemical values derived in the present work are obtained from constant temperature environment and adiabatic calorimetry operated at atmospheric pressure and at 25°C. The enthalpy change obtained for any general reaction may be expressed as

$$\Delta H = \sum \Delta H^0_{f\text{(products)}} - \sum \Delta H^0_{f\text{(reactant)}}$$

and when the products and reactants are in their standard states (the most stable form at 1 atm. and 25°C), then

$$\Delta H = \Delta H^0$$

For calculating the bond energy and average bond energy the most essential quantities needed are standard heat of formation, $\Delta H^0_f$; sublimation enthalpy, $\Delta H(c \rightarrow g)$; and enthalpy of atomisation, $\Delta H_{\text{atom}}$. The latent heat of sublimation mentioned above is often estimated in the absence of the experimental values. The sublimation enthalpy is always the most difficultly-accessible function for the determination of bond energies in compounds whose standard states are crystalline and which melt with decomposition. In this investigation, the sublimation enthalpy for triiodophosphine and diphosphorus tetraiodide have been determined via effusion manometry.

In common practice, therefore, the measurements of enthalpy change of reaction are achieved by direct or indirect methods. The direct method employs calorimetry (combustion or reaction-solution) while the indirect method make use of the slope of a graph of either $\log K$ vs. $T^{-1}$ or $\log p$ vs. $T^{-1}$ to obtain $\Delta H^0$ (as in effusion manometry).
\[
\frac{\delta (\ln p)}{\delta T} = \frac{\Delta H^0}{R T^2}
\]

where, \(\Delta H\) = enthalpy change, \(p\) = pressure, \(T\) = absolute temperature, \(R\) = gas constant.

Calorimetry as a direct method is regarded as superior to all indirect methods. Thermochemical investigations made by this technique cover a wide range of reactions. They include hydrolysis, aminolysis, complexing, partial oxidation and aqueous oxidation with bromine. Thermochemical data obtained from reaction-solution calorimetry usually compare favourably with the same data derived from combustion calorimetry. As an illustration Head obtained \(\Delta H^0_f (\text{H}_3\text{PO}_4, 4.0 \text{H}_2\text{O})\) from combustion calorimetry using a rotating bomb calorimeter as \(-309.34 \pm 0.4\) kcal mole\(^{-1}\) (by combustion of white phosphorus in a "wet" bomb to get a final thermodynamic state \(\text{H}_3\text{PO}_4, 4.0 \text{H}_2\text{O}\)). From reaction-solution calorimetry Birley and Skinner determined \(\Delta H^0_f (\text{H}_3\text{PO}_4, 100 \text{H}_2\text{O}) = -309.90 \pm 0.35\) kcal mole\(^{-1}\) using the following reaction.

\[
\text{PCl}_5(c) + (n+4) \text{H}_2\text{O}(1) = (\text{H}_3\text{PO}_4 + 5\text{HCl}) n\text{H}_2\text{O} \text{ (soln.)}
\]

The phosphorus compounds studied here, are from reaction-solution calorimetry which include some of the phosphorus-phosphorus bonded compounds, phosphorus (III) and phosphorus (V) compounds and the molecular adducts of type \(\text{PX}_2\text{BY}_2\) and \(\text{PX}_2\text{BY}_3\) (where \(X\) and \(Y\) are halogen). The reactions investigated were ring degradation with bromine, oxidative hydrolysis, aqueous oxidation with bromine and complexing.

Bond Dissociation Energy - One method by which this quantity may be determined is mass spectrometry. The essential requirement is the accurate measurement of appearance potentials and ionization potentials. In appearance potential measurements it is probable that some excess kinetic energy is
The investigations made here are concerned with appearance potential measurement for phosphorus iodides. Incorporation of the relevant literature ionization potentials has resulted in the calculations of the bond dissociation energies $D_3^P-I$ and $D_2^P-PI_2$. The probable cracking patterns were also investigated in some phosphorus (III) and boron (III) compounds and in molecular adducts of the type $X_3PBY_3$ (where $X, Y$ are halogen).

**Thermal Analysis** - This is one of the most rapid and useful techniques for investigating phase equilibria, decomposition analysis and for the determination of enthalpies of fusion, dissociation and association energies, purity, and percentage crystallinity. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) have been adapted to study diphenylphosphinoborane, triphenylphosphine, hexaphenylcyclohexaphosphate, polymeric phenylphosphine and diphenylphosphinoborane-boron tribromide (1:2 adduct). All of these compounds were manipulated in an inert atmosphere of nitrogen.

The aims of these investigations were:

(i) to ascertain if diphenylphosphinoborane decomposed prior to the melting point (TGA)

(ii) to determine the heat of fusion, precise melting point, and purity of triphenylphosphinoborane (DTA and DSC)

(iii) to investigate the inter-conversion of the phosphobenzenes pentaphenylcyclopentaphosphate, hexaphenylcyclohexaphosphate and polymeric phenylphosphine (DSC) and

(iv) to estimate quantitatively the relative dissociation energies in removing each of the boron tribromide molecules from diphenylphosphinoborane-boron tribromide (1:2 adduct) (TGA and DTA).
(3) Chemistry and Energetic Aspects of Phosphorus Compounds

Phosphorus Chemistry began three centuries ago with the discovery of the element, then called "light bearer", and since then the major interest in synthesis has been confined to mononuclear phosphorus compounds and their derivatives. Relatively new classes of compounds have emerged within the last two decades (see pp. 14, 214). This may be attributed to considerable interest in mechanistic, synthetic, structural, and energetic aspects of phosphorus-phosphorus bonded compounds in particular, phosphorus compounds and elemental phosphorus in general.

For convenience, the chemistry and energetic aspects of the compounds synthesised in this investigation will be described under the following headings (i) Phosphorus-Phosphorus Bonded Compounds (cyclic and acyclic) (ii) Phosphorus (III) Pseudohalides and Phosphorus (III) Compounds (iii) Phosphorus (V) Compounds (iv) Molecular Adducts

(i) Phosphorus-Phosphorus Bonded Compounds (cyclic and acyclic)

There is considerable current interest in compounds containing the phosphorus-phosphorus bond. It is obvious from recent publications and reviews on phosphorus-phosphorus bonded compounds that physical data for these compounds are scarce. Although most synthetic procedures are quite well-established, there seem to be unusual difficulties associated with the preparation of phosphobenzene, mainly due to interconversion in solution. This either results in pentaphenylocyclopentaphosphane, hexaphenylocyclohexaphosphane, or the so called polymeric phenylphosphane. There is no definite
reproducible route for synthesising hexaphenylocyclohexaphosphine or polymeric phenylphosphine. The pentaphenylocyclopentaphosphine may be readily prepared by the procedure of Fraizer et al., then reported as the tetramer. The compound is now well-characterised by Daly as pentamer and X-ray analysis data are compared in the present investigation (see Appendix four).

Phosphobenzene was first prepared by Köhler and Michaelis in the year 1817 from phenylphosphine and phenyldichlorophosphine. The resulting pale yellow crystalline mass (m.p.t. 149-150°C) was assigned a similar formula to azobenzene and called phosphobenzene C_{6}H_{5}P = PC_{6}H_{5}. On further investigation, the reactivities towards oxygen, chlorine, hydrogen chloride and water were established. Reaction of phosphobenzene with hydrochloric acid decomposed the material into phenylphosphine and phenyldichlorophosphine. Similarly, reaction with chlorine produced phenylchlorophosphine.

However, no peculiar emphasis was placed upon the isolation of phosphobenzene and this interesting field remained dormant for sixty-five years. In the year 1952, studies conducted by Erlenmeyer et al. revealed the complex nature of this compound. The preparation was essentially the same as Michaelis and Köhler but the resulting material obtained was quite different. This substance was a white crystalline solid with m.p.t. 193°C in a sealed tube (compared to 149-150°C). The empirical formula assigned to the new compound on the basis of microanalysis for carbon, hydrogen, and phosphorus, was C_{12}H_{10}P_{2}. The molecular weight by the camphor technique was 198, which corresponds approximately to (C_{6}H_{5})_{2}P. It was also suggested that the product made by Michaelis and Köhler was grossly impure. Reesor and Wright, in 1957, repeated exactly the work of Erlenmeyer et al. with the six-fold increase in the size of the experiment a different material was obtained. This material was also different from that of any of the other previous workers.
The melting point of this substance was 252-256°C, finally becoming clear at 278°C, then remelting at 148°C. It was also found that Erlenmeyer's compound (m.p. 193°C), remelted at 148°C. This was followed by the determination of the molecular weight of these compounds by the isopieatic method in carbon disulphide. The results obtained are as follows:

<table>
<thead>
<tr>
<th>M.pt. (°C)</th>
<th>Mol.wt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>154-156</td>
<td>206 (calc. 216)</td>
</tr>
<tr>
<td>193</td>
<td>402 (calc. 432)</td>
</tr>
<tr>
<td>252-256</td>
<td>Polymeric</td>
</tr>
</tbody>
</table>

The high melting point substance (m.p. 252°C) was also found to be insoluble in most of the solvents.

In 1957, Mahler and Burg postulated that phosphobenzene had a tetrameric structure. This was supported by Kuchen and Buchwald from the results of molecular weight studies. Accordingly the structure of the substance melting at 154-156°C was assigned the formula \((\text{C}_6\text{H}_5\text{P})_4\), i.e., tetraphenylcyclotetraphosphine. The chemistry of this compound was demonstrated in terms of oxidation, bromination and adduct formation etc. Some of the interesting reactions were:

1. \[(\text{C}_6\text{H}_5\text{P})_4 + 4\text{Br}_2 = 4\text{C}_6\text{H}_5\text{PBr}_2\]
2. \[(\text{C}_6\text{H}_5\text{P})_4 + 4\text{O}_2 + 4\text{H}_2\text{O} = 4\text{C}_6\text{H}_5\text{PO(OH)}_2\]
3. \[(\text{C}_6\text{H}_5\text{P})_4 + 4\text{Na} = 2\text{C}_6\text{H}_5\text{P} = \text{PO}_2\text{H} + 2\text{C}_6\text{H}_5\text{PNa}_2\]

The initial reaction in (iii) with sodium was shown to retain the
phosphorus-phosphorus bond. Further addition of sodium completely destroyed the P-P linkage. The resulting compound was a mononuclear phosphorus adduct. It may be recalled at this point that Reesor and Wright did not observe any monoadduct.

In 1963, Henderson et al. undertook a detailed survey of the cyclopolyporphosphines and proposed new approaches for synthesising and characterising these compounds. According to Henderson phospha benzene was treated as a group of compounds and classified as

<table>
<thead>
<tr>
<th>Form</th>
<th>M.p.t.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>148-152</td>
</tr>
<tr>
<td>(B)</td>
<td>195-199</td>
</tr>
<tr>
<td>(C)</td>
<td>270-283</td>
</tr>
<tr>
<td>(D)</td>
<td>260-285</td>
</tr>
</tbody>
</table>

The methods of synthesis for form (A) were based on (i) the reaction of phenylphosphine and phenyldichlorophosphine in ether (ii) reduction of phenyldichlorophosphine with magnesium in ether or tetrahydrofuran and (iii) reduction of phenyldichlorophosphine with lithium aluminium hydride. The synthesis for form (B) was via phenylphosphine and phenyldichlorophosphine in benzene and the same procedure was followed for form (C) and form (D) except that cyclohexane was used as solvent.

It can be seen that essentially the method for preparation of all three forms is more or less the same as the previous syntheses. Detailed investigations of physical properties of phospha benzene by various techniques have appeared in the literature. These include for form (A) and (D) (i) the determination of the molecular weight by isopiestic, cryoscopic and ebullioscopic methods in a variety of solvents (ii) mass spectrometric analyses with
heated inlet system at 200°C (iii) ultraviolet spectroscopy (iv) nuclear magnetic resonance for hydrogen and phosphorus and (v) infra-red (also for form (C) and (D)) and Raman spectroscopy (see for comparison of these with the present investigations in Appendix three). From these studies it has been concluded that both form (A) and (B) are tetraphenylcycloctetraphosphine, although both differ in structure in solution and solid phase.

At this time (1963), the problem of (i) explicit synthetic routes (ii) the mechanism of interconversion in solution and (iii) molecular structure, remained equivocal.

77 During 1964, Fraxier et al. developed a method of synthesis for tetraphenylcycloctetraphosphine m.p.t. 147-150°C (now adapted in the present investigation for pentaphenylcyclpentaphosphine, see chapter two: Synthesis) based on the reaction of phenyldichlorophosphine and tributylphosphine. The resulting compound was characterised by microanalysis and infra-red spectra and was identical with that of Kuchen and Buchwald. 84

In 1964 onwards, Daly produced X-ray crystallographic evidence on form (A) m.p.t. 143-150°C which was found to be monoclinic and existing as pentaphenylcyclpentaphosphine. In this form, the phosphorus atoms form an equilateral pentagon (see diagram for structures on pp. 25). The crystalline phosphobenzene form (B) m.p.t. 190°C (193°C) is polymorph. There are at least four crystal modifications known, consisting of monoclinic, triclinic, trigonal and hexagonal types, (see diagram for structure of trigonal modification on p. 26). All have the structure hexaphenylcyclohexasophosphate.

The crystalline phosphobenzene forms (C) and (D) (melting range 260-285°C, the so-called polymeric forms) give the same X-ray diffraction pattern. The structures of these are not yet known, nor their molecular weight. There also exists no reproducible synthetic route for these compounds.
Fig. Crystal Structure of Pentaphenyldicyclopentaphosphine
(after J.J. Daly)
Fig.: Crystal Structure of Hexaphenylocyclohexaphosphine (Trigonal)
(after J.J. Daly)
Fig. Molecular Stereochemistry (after L. Maier).  
(a) Pentaphenylcyclopentaphosphine.  
(b) Hexaphenylcyclohexaphosphine.
The problem in devising direct synthetic routes for all known forms of phosphobenzene was investigated by Meier in 1966. A new method of synthesis for pentaphenylcyclopentaphosphine (form (A)) was devised which was based on the following reaction:

$$5 \text{C}_6\text{H}_5\text{PH}_2 + 5 \text{C}_6\text{H}_5\text{P(\text{N(\text{CH}_3)_2})}_2 = 2(\text{C}_6\text{H}_5\text{P})_5 + 10 \text{HN(\text{CH}_3)_2}$$

In another attempt to find a reproducible route for the synthesis of hexaphenylcyclohexaphosphine (form (B)), Henderson's work was repeated in a modified way. Limited success was achieved when the reaction of phenylphosphine and phenylchlorophosphine was carried out in triethylamine. Inexplicably, however, on numerous occasions this reaction produced the common form (A). After detailed, but inconclusive studies, Maier suggested a probable interconversion scheme, which is as follows.

![Diagram showing interconversion of forms (B), (A), and (C)]

The exact conditions for these changes are not yet probably understood. These changes, in the solid phase, have been studied as part of this work, (see Chapter seven: Thermal Analysis Results). The X-ray powder pattern for each form has been studied by Meier and his results are compared with similar data in this work. Currently, there are no thermodynamic data for the phosphobenzene.

In conclusion, it appears that phosphobenzene is becoming a most useful precursor for the synthesis of phosphorus-phosphorus bonded compounds.
Phosphorus iodide (probably triiodide) was first synthesised via combination of the elements by Gay-Lussac in 1813. Diphosphorus tetraiodide was synthesised by Hoffmann (1857) via the reaction

$$6\text{PH}_3 + 5\text{I}_2 \rightarrow \text{P}_2\text{I}_4 + 6\text{PH}_4\text{I}$$

In 1900, Michaelis and Pitzer successfully prepared diphosphorus tetraiodide by reacting elemental phosphorus and iodine in the stoichiometric quantities in carbon disulphide

$$2\text{P}(s) + 2\text{I}_2 \rightarrow \text{P}_2\text{I}_4$$

This reaction demonstrated that partial retention of a P-P linkage was possible.

In 1925 and 1927, Traxler and German undertook a detailed investigation of these syntheses. It was ascertained that free sulphur in the carbon disulphide interfered in the main reaction to give $\text{P}_4\text{S}_3\text{I}_2$. A method of purification was suggested which was adopted with minor modifications in the present work (see Chapter two: purification).

According to Baudler and Fricke (1963) controlled oxidation of diphosphorus tetraiodide resulted in a polymer with the following composition.

$$7\text{P}_2\text{I}_4 + 6\text{O}_2 \rightarrow \frac{2}{n} (\text{P}_3\text{I}_2\text{O}_6)_n + 6\text{PI}_3$$

This study also indicated that dissolved oxygen in carbon disulphide could be a source of interference in the synthesis of iodides. Hence scrupulously dry and pure solvent is essential. Also handling should be carried out in a dry inert atmosphere, e.g. nitrogen.
The structural aspects of iodides, especially triiodophosphine and
diposphorus tetraiodide, have been studied by several techniques, such
as vibrational spectroscopy (infra-red, \(^{93,94}\) Raman, \(^{94}\)), by \(^{31}P\) NMR,\(^{57,93}\)
and by X-ray crystallography.\(^{95,96}\) Results for triiodophosphine indicate
that the molecule is pyramidal in shape. The interatomic distance\(^{96}\)
between P-I is 2.45 Å with a bonding angle I-P-I of 100° and symmetry \(C_3\).
The van der Waal radius for iodine is 2.15 Å. The diposphorus tetraiodide
molecule has the "trans" conformation\(^{93,94}\) in the solid and also in carbon
disulphide, dichloromethane or benzene (\(C_6H_6\)). The P-P distance\(^{95}\)
is 2.21 Å, the P-I bond length is 2.475 Å, the I-P-I bonding angle is 102°13', and I-P-P
is 93°58' and 93°56'.

A \(^{31}P\) NMR study, by Carroll and Carter\(^{57}\) in 1967, was conducted for
the formation of diposphorus tetraiodide from the reaction of elemental
phosphorus and iodine. The results indicate (i) all the phosphorus-phosphorus
bonds are broken when the reaction is performed in carbon disulphide or
carbon tetrachloride at 25°C. Evidence is presented that diposphorus
tetraiodide is formed via triiodophosphine

\[
\frac{1}{2} P_4 + 3I_2 \rightarrow 2P'I_3 \quad \text{(fast)}
\]
\[
2P'I_3 + \frac{1}{2} P_4 \rightarrow \frac{1}{2} P_2I_4 \quad \text{(slow)}
\]

(ii) that the phosphorus/iodine system is very labile and there exist
equilibria in solution of the type:

\[
\frac{3}{2} P_2I_4 \rightleftharpoons 2P'I_3 + \frac{1}{2} P_4
\]

The existence of this equilibrium is supported also by the fact that identical
U.V. spectra are obtained from solutions of triiodophosphine and diposphorus
tetraiodide in cyclohexane. Evidence is also presented for the existence of
the equilibria such as

$$P_2I_4 + I_2 \rightleftharpoons 2PI_3$$

This equilibrium lies very much on the side of triiodophosphine.

A possible disproportionation reaction suggested by Cowley and Cohen is

$$P_2I_4 \rightarrow PI_3 + \frac{1}{n} (PI)_n$$

This results in the formation of a phosphorus iodide polymer along with triiodophosphine. The structure, molecular weight and composition are unknown.

Very recently (1970) Kennedy and Sinclair have investigated the photochemical decomposition of cyclohexane and hexane solutions of triiodophosphine and diphosphorus tetraiodide. It has been suggested that disproportionation occurs with the formation of polymer along with triiodophosphine.

$$P_2I_4 \rightarrow 1.17 PI_3 + \frac{1}{6n} (P_2I_3)_n$$

This reaction indicates the stoichiometry of the polymer but the molecular weight is unknown. A simple linear structure of this polymer is proposed.

Recently (1967) Payne has reviewed the chemistry of phosphorus halides. It is clear that considerable interest is developed in the chemical properties of diphosphorus tetraiodide. The hydrolysis products have not yet been quantitatively evaluated due to the complex nature of reaction. According to Wiersman and Sandoval alkali hydrolysis of diphosphorus tetraiodide produces dipophosphate, phosphorus acid and hypophosphorus acid. Similar products are also formed by acid hydrolysis along with unknown mixture of oxyacids.
The hydrolysis of triiodophosphine in hydrochloric acid (2N) and in water is shown to yield quantitatively phosphorus acid and corresponding acid. The reaction is expressed as

\[ \text{PI}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HI} \]

The addition reaction of triiodophosphine with boron tribromide in carbon disulphide has been first reported by Tarible in 1901. The resulting adduct was assigned the formula \( \text{P}_2\text{I}_4\text{ZEBBr}_3 \) after elemental analysis. The modified syntheses by Cowley and Cohen has shown that the reaction of boron tribromide with (i) triiodophosphine proceeds according to the following equation in carbon disulphide as

\[ \text{PI}_3 + \text{EBr}_3 = \text{PI}_2\text{EBr}_3 \]

and (ii) with diphasorous tetraiodide as

\[ \text{P}_2\text{I}_4 + 2\text{EBr}_3 = \text{P}_2\text{I}_4\text{ZEBr}_3 \]

The crystalline structures of these adducts have been elucidated by X-ray diffraction pattern and compared with those of the parent iodides. The other physical techniques used for characterisation are \(^{11}\text{B n.m.r.}, \text{I.R.} \) and I.R. The same method of adduct synthesis is adopted in the present work.

The reaction of sulphur with triiodophosphine is additive:

\[ \text{PI}_3 + \text{S} = \text{SPI}_3 \]

Although the existence and stability of the compounds like \( \text{P}_2\text{I}_4 \) and \( \text{P}_4\text{I} \) have been claimed almost a century ago, there are no thermodynamic data to substantiate these claims. The first reported values for the phosphorus iodides was by Ogier in 1881. Accordingly \( \Delta H^0 \text{ of PI}_3 \) is
-10.9 kcal mol$^{-1}$, $\Delta H_{\text{sol}}$ for $\text{PI}_3$ is 3.3 kcal mol$^{-1}$ and $\Delta H_{\text{sol}}$ for $\text{P}_2\text{I}_4$ is -5.0 kcal mol (in solvent $\text{CS}_2$). The reaction used for the derivation of $\Delta H^\circ_f$ was the synthesis from the elements. Very recently (1969) detailed thermochemical studies on phosphorus iodides system have revealed considerable difference in $\Delta H^\circ_f$ and $\Delta H_{\text{sol}}$. The $\Delta H^\circ_f$ for $\text{PI}_3$ is -14.7 kcal mol$^{-1}$, and $\Delta H^\circ_f$ for $\text{P}_2\text{I}_4$ is -27.03 kcal mol$^{-1}$. The results have been derived from reaction-solution calorimetry, and the reactions utilized are well-characterized. These reactions are

$$\text{P}_2\text{I}_4 + \text{I}_2 = 2\text{PI}_3$$
$$\text{PI}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HI}$$

Attempts have also been made to estimate the average bond energy $E_{\text{P-I}}$ in triiodophosphine and the bond energy $E_{\text{I}_2\text{P-PI}_2}$ in the absence of experimental data for the heats of sublimation. According to Hartley et al. (assuming $E_{\text{P-I}} = E_{\text{I}_2\text{P-I}} = 44$ kcal mol$^{-1}$) a value of 67 kcal mol$^{-1}$ for phosphorus-phosphorus bond in diposphorus tetraiodide is derived, "using the questionable value for the heat of sublimation of $\text{P}_2\text{I}_4$ of 30 kcal/mole". This value was estimated by Rice in 1940; (for experimentally derived values of latent heat of sublimation for triiodophosphine and diposphorus tetraiodide, see Chapter nine: Effusion Monomeric Results). In conclusion, diposphorus tetraiodide is the only so far known crystalline diposphorus halide. Although little emphasized as a synthetic precursor until now, certainly it is the simple and most useful P-P bonded compound for the study of thermodynamic functions.
(ii) Phosphorus (III) pseudohalides and Phosphorus (III) Compounds

Phosphorus (III) pseudohalides

There is considerable interest in the synthetic, structural, and energetic aspects of pseudohalides of phosphorus, in particular tricyanophosphine and tri(isocyanato)phosphine. Although some physical data, for example vapour pressure measurements, Trouton's constant, etc., have been described in the literature, there are no thermochemical measurements for tricyanophosphine and tri(isocyanato)phosphine.

Pseudohalides (or halogenoids), as a well-defined class of compounds, were first reported by Browne et al. in 1923, although the first known pseudohalide (tricyanophosphine) was synthesised by Cendella in 1935. Gall and Schuppen, in 1930, described a method of preparation based on the following reaction.

$$ \text{POCl}_3 + 3\text{AgCN} = \text{P(CN)}_3 + 3\text{AgCl} $$

The resulting solid material sublimed at 190°C. A modification of the above procedure was suggested by Staat and Morgan, using solvents such as chloroform, carbon tetrachloride and benzene. In this method the trichlorophosphine was allowed to react with the suspension of silver cyanide. The reaction mixture was refluxed for a period of 18 to 20 hr. The excess solvent and trichlorophosphine were removed by vacuum distillation, followed by the sublimation of the residue. The sublimed material melted close to 200°C (a similar procedure was adopted in the present synthetic work).

Recently (1963) Maier devised a new synthetic route for tricyanophosphine. The reaction was based on the exchange reaction of tribromophosphine with silver cyanide in methylcyanide.

$$ \text{PBBr}_3 + 3\text{AgCN} = \text{P(CN)}_3 + 3\text{AgBr} $$
The resulting material turned orange at 180-200°C and decomposed without melting.

The solubility\textsuperscript{115} of tricyanophosphine has been shown to be low in solvents such as chloroform, carbon disulphide, trichlorophosphine and ether. The reactivity of this compound with moisture is described as being very high. The hydrolysis products are identified as hydrogen cyanide, phosphorous acid and yellow phosphorus-containing compounds. Recently (1963), Pollard\textsuperscript{99} et al. quantitatively estimated the hydrolysis products of pseudohalides and halides in sodium hydroxide (5N) and hydrochloric acid (2N). A chromatographic technique was used for this estimation (see Appendix one for a similar hydrolysis using a potentiometric technique). It was found that in 2N HCl, phosphorus pseudohalides hydrolyse quantitatively to phosphorus acid and the corresponding hydrogen pseudohalide. In a basic hydrolysing medium, a mixture of lower phosphorus acids with phosphorus acid was obtained.

A review\textsuperscript{67} on phosphorus isocyanates has recently appeared and describes synthetic, physical and chemical aspects of these compounds. An unusual feature is the reversible polymerization of tri(isocyanato)phosphine, which was the first isocyanate reported by Forbes and Anderson\textsuperscript{114} in 1940. The synthesis is based on the exchange reaction of silver isocyanate and trichlorophosphine in benzene (a similar procedure is adopted in the present work).

\[
\text{PCl}_3 + 3\text{AgNCO} \rightleftharpoons \text{P(NCO)}_3 + 3\text{AgCl}
\]

Structural aspects of the tri(isocyanato)phosphine have been investigated by infra-red and \textsuperscript{31}P n.m.r. techniques.

An interesting feature\textsuperscript{114} of the reversible polymerisation was demonstrated by supercooling, liquid tri(isocyanato)phosphine at -20°C. A white solid appeared which melted at -2°C (however a sample which had not been
cooled remained unchanged for fourteen days). The resulting liquid was held for three days at ambient temperature and deposited a white polymeric material which remelted at 80°C. The white solid was found to be insoluble in benzene, ether, chloroform and carbon tetrachloride.

In 1950, Anderson\(^\text{31}\) presented another synthetic route dealing with the exchange reaction between triiodophosphine and silver isocyanate in nitromethane.

\[ \text{PI}_3 + 3\text{AgNCO} = \text{P(NCO)}_3 + 3\text{AgI} \]

The same reaction when conducted in benzene did not proceed. This was the first time that a solvent effect on isocyanate synthesis was noticed. Anderson also investigated the following redistribution reaction

\[ 2\text{ClIP(NCO)}_2 = \text{Cl}_2\text{P(NCO)} + \text{P(NCO)}_3 \]

which was carried out upon distillation under normal pressure.

Thermal stability of substituted isocyanate follows the order

\[ \text{P(NCO)}_3 < \text{ClIP(NCO)}_2 < \text{Cl}_2\text{PNCO} \]

There are no thermodynamic data available to substantiate the thermal instability of these compounds. (See Chapter six for thermochemical measurements).

After detailed investigation of exchange reactions in various pseudo-halides an empirical generalization was put forward by Anderson\(^\text{31}\) for predicting the outcome of untried reactions. Accordingly, (i) exchange reactions are only possible when the atom to be replaced has a larger single-bond radius than the reactant atom (ii) molar volume is no criterion for exchange reaction and (iii) the strength of the corresponding isocyanic acid is also no criterion.
In 1959, Jenkins et al. successfully devised a synthetic route for the preparation of tri(isocyanato)phosphine. The reaction investigated was

$$3\text{LNCO} + \text{PCl}_3 = \text{P(NCO)}_3 + 3\text{LiCl}$$

This reaction was surprising, as the corresponding sodium and potassium isocyanates, after numerous attempts under various reaction conditions, did not react. The reaction conditions, involving potassium isocyanate and trichlorophosphine, included solvents such as benzene, toluene, xylene, carbon tetrachloride, nitromethane, liquid sulphur dioxide, liquid antimony trichloride and a mixture of solvents. In order to accelerate the reaction, catalysts were used, e.g. cuprous chloride. Also, reaction in the gas phase was tried. None of these produced any recoverable amount of tri(isocyanato)phosphine.

According to Jenkins et al., "The thermodynamic equation for the reaction of potassium isocyanate and phosphorus trichloride indicates that they should react more readily than silver isocyanate and phosphorus trichloride. Yet, this is not the case".

However, four years later (in 1963) Fielding successfully prepared tri(isocyanato)phosphine using the reactants sodium or potassium isocyanate and trichlorophosphine in polar organic solvents such as dry methyl cyanide or mixed solvent pairs such as benzene and petroleum ether, acetone and benzene, acetone and toluene, benzene and nitromethane. The equation for the reaction is as follows

$$\text{PCl}_3 + 3\text{LNCO} = \text{P(NCO)}_3 + 3\text{MCl} \quad (M = \text{K,Na})$$

The yield from the above reaction for tri(isocyanato)phosphine is claimed to be 62 to 95%.

The physical and chemical properties have been reviewed by Derkatsch.
Some of the interesting properties for tri(isocyanato)phosaphine include:

1. Violent reaction with water, aqueous sulphuric acid, aqueous silver nitrate, aqueous acetic acid and acetaldehyde. Reaction is mild with ether, ethyl alcohol, methyl alcohol, dimethyl ketone (warm), alkali metals and iodine. Tri(isocyanato)phosphine dissolves without reaction in dimethyl ketone (cold), benzene, chloroform, phenol, nitrobenzene, and propionic acid.

Recently Pollard et al. reported hydrolysis in 5N NaOH and 2N HCl. The hydrolysis products are quantitatively determined by chromatographic techniques. (See Appendix one for a similar hydrolysis where the products are evaluated by a potentiometric technique.) It was found that in 2N HCl the hydrolysis produced quantitatively phosphorous acid and isocyanic acid. These have been also reported earlier by Forbes and Anderson. In conclusion, synthesis of phosphorus-phosphorus bonded compounds (Noth and Derkatsch) using pseudohalides as precursors has been reported.

**Phosphorus (III) Compounds**

Numerous compounds of this type are now known which include mono-bi-tri and polynuclear derivatives. Reviews concerning synthetic structural and energetic aspects have appeared. The phosphorus (III) derivatives of interest to this work are phenyldibromophosphine, phenyldichlorophosphine and phenylphosphine. The syntheses of phenyldibromophosphine are based on the following reactions:

1. \[ 2C_6H_5PCl_2 + LiAlH_4 = 2C_6H_5PH_2 + LiCl + AlCl_3 \]
2. \[ C_6H_5PH_2 + Br_2 = C_6H_5PBr_2 + H_2 \]
(ii) $C_6H_5PCl_2 + 2HBr$ (anhyd.) $\rightarrow C_6H_5PBr_2 + 2HCl$

This reaction (ii) is conducted in tribromophosphine as solvent. (See Chapter two: Synthesis, for further details.)

(iii) $C_6H_5PCl_2 + PBr_3$ $\rightarrow C_6H_5PBr_2 + (PBr_{3-n}Cl_n)$

This reaction proceeds at 100-200°C and the compounds $PBr_{3-n}Cl_n$ are removed by continuous distillation. The resulting material, phenyldibromophosphine, has a b.p.t. 124 to 126°C/11 mm Hg.

Chemical and physical properties of phenyldibromophosphine of interest are:

(i) Hydrolysis: this yields quantitatively phenylphosphonous acid and hydrobromic acid.

$$C_6H_5PBr_2 + 2H_2O = C_6H_5PO_2H_2 + 2HBr$$

A thermochemical investigation based on this reaction gave an estimate of the standard heat of formation of liquid phenyldibromophosphine as Ca. -8 kcal mole$^{-1}$ and for crystalline phenylphosphonous acid as -130 kcal mole$^{-1}$

Precise thermodynamic data for phenylphosphonous acid are lacking.

(ii) The reaction with magnesium is reported (1963) to produce a cyclic compound, then called tetraphenylcyclotetraphosphine.

$$C_6H_5PBr_2 + Mg = \frac{1}{2} (C_6H_5P)_4 + MgBr_2$$

(iii) The reaction with pentaphenylcyclopentaphosphine causes partial degradation of the ring.

$$C_6H_5PBr_2 + \frac{1}{5} (C_6H_5P)_5 = (C_6H_5)_2P_2Br_2$$
Similar partial or complete degradation reactions may proceed by altering the stoichiometry, e.g.

\[
\frac{2}{5} (C_8H_5P) \cdot Br_2 = (C_6H_5)_{\frac{3}{5}} \cdot Br_2 \quad \text{(partial)}
\]

\[
\frac{1}{5} (C_8H_5P) \cdot Br_2 = C_6H_5 \cdot Br_2 \quad \text{(complete)}
\]

The latter reaction is quantitatively investigated in the present work by titrometry (see Chapter Six: Thermochemical Results).

(iv) With lithium, phenyl dibromophosphine reacts to produce a trinuclear phosphorus compound.

\[
3C_6H_5 \cdot Br_2 + 6LiH = (C_6H_5)_{\frac{3}{5}} \cdot H_2 + 6LiBr + 2H_2
\]

(v) Phenyl dibromophosphine reacts with mercury at 80°C under reflux, and the product in high yield is phosphobenzene.

\[
C_6H_5 \cdot Br_2 + 2nHg = (C_6H_5)_{\frac{n}{5}} + nHg_2 \cdot Br_2
\]

The phosphobenzene produced in this reaction has a m.p.t. of 151°C and therefore is presumably form (A).

Various methods of synthesising phenyl dichlorophosphine have been described in the literature. The synthesis reported in 1879 by Michaelis and Dittler is now usually employed in a modified form. According to Henderson et al., the modification is the slow and low-temperature (-50°C) transfer of primary phosphine onto carbonyl chloride dissolved in inert solvents such as methylene dichloride and carbon tetrachloride. On slow warming, reaction takes place.

\[
RPH_2 + 2CCl_2 = RFCl_2 + 2CO + 2HCl
\]

\( R = C_6H_5 \cdot C_6H_5 \cdot C_6H_5 \cdot C_6H_5 \)
Recently Maier (1963) proposed a probable mechanism for this reaction:

\[
4C_6H_5PH_2 + 4COC_1 \rightarrow (C_6H_5P)_4 + 4CO + 8HCl
\]

Phenyldichlorophosphine is of interest as a synthetic precursor for phosphorus-phosphorus bonded compounds:

(i) Reaction with primary phosphine produces a cyclic compound, e.g.

\[\text{RPCl}_2 + \text{RP}_2 = 2/n \text{(RP)}_n + 2\text{HCl} \]

\[(R = \text{alkyl, aryl (C}_6\text{H}_5)]\]

The reaction is carried in the absence of solvent or in the presence of benzene, ether, petroleum ether, toluene, cyclohexane etc.

(ii) Reaction with metals, such as lithium, sodium, magnesium, zinc in solvents like tetrahydrofuran, ether, benzene etc., produce cyclic phosphine.

\[\text{RPCl}_2 + 2M = 1/n \text{(RP)}_n + 2\text{MCl} \]

\[(R = \text{alkyl, aryl (C}_6\text{H}_5)]\]

Phenylphosphate is now most conveniently prepared by the method of Fluck and Binder. The preparation is carried out in ether as solvent.

\[2C_6H_5PCl_2 + \text{LiAlH}_4 = 2C_6H_5PH_2 + \text{LiCl} + \text{AlCl}_3\]

These investigators suggest that an intermediate complex, \(\text{Li(H}_3\text{AlPC}_6\text{H}_5(\text{Cl}))\), is formed prior to the hydrolysis (see Chapter two: Synthesis, for detailed procedure).
Phosphorus (V) Compounds

Many compounds of general formula \( \text{PX}_5 \), \( \text{PX}_5 \text{n} \text{Y}_5 \text{n} \) have been described in the literature which covers synthetic, structural, mechanistic and energetic aspects. The substituted compounds are usually alkyl or aryl. Of interest here are phenyltetrachlorophosphorane and phenyltetrabromophosphorane.

The methods of syntheses for phenyltetrachlorophosphorane are based on the addition reaction of chlorine to phenyldichlorophosphine. A convenient method is described by Herring and Douglas (see Chapter two: Synthesis; for experimental details).

\[
\text{C}_6\text{H}_5\text{PCl}_2 + \text{Cl}_2 = \text{C}_6\text{H}_5\text{PCl}_4
\]

Other solvents have been proposed for this reaction, while the method of Michalis uses no solvent at all.

Phenyltetrachlorophosphorane on heating decomposes into chlorine and phenyldichlorophosphine.

\[
\text{C}_6\text{H}_5\text{PCl}_4 \rightarrow \text{C}_6\text{H}_5\text{PCl}_2 + \text{Cl}_2
\]

On heating in a pressure tube at 180\(^\circ\)C trichlorophosphine and chlorobenzene are formed.

\[
\text{C}_6\text{H}_5\text{PCl}_4 = \text{C}_6\text{H}_5\text{Cl} + \text{PCl}_3
\]

Phenyltetrachlorophosphorane is hygroscopic and reacts vigorously with water forming phenylphosphonic acid.

\[
\text{C}_6\text{H}_5\text{PCl}_4 + 3\text{H}_2\text{O} = \text{C}_6\text{H}_5\text{PO}_{3}\text{H}_2 + 4\text{HCl}
\]
Phenyltetramethylphosphorane is synthesised by the addition reaction of bromine to phenyl dibromophosphine in the absence of solvent.

\[ C_6H_5PBr_2 + Br_2 = C_6H_5PBr_4 \]

A similar preparation in the presence of carbon tetrachloride was performed in this investigation (see Chapter two: Synthesis).

Phenyltetramethylphosphorane is hygroscopic and reacts with water to produce phenylphosphonic acid (see Chapter six: Thermochemical Results).

\[ C_6H_5PBr_4 + 3H_2O = C_6H_5PO_3H_2 + 4HBr \]

Currently there are no thermochemical measurements available for phenyltetraethylphosphorane and phenyltetramethylphosphorane.

(V) Molecular Adducts

The tendency of phosphorus halides to form molecular adduct, especially with boron halides, was noted by Terible seventy years ago. Since 1960 there has been considerable interest in such adducts. The literature includes synthetic, structural, and energetic aspects. The molecular adducts synthesised include mon-, bi- and polynuclear forms of general formula \( X_nPBX_n, X_nPBX_2, P_nX_nBY_n \), where \( R, X \), and \( Y \) may be halogen, alkyl, aryl, hydrogen etc. Of interest to this work is tribromophosphine - boron tribromide (1:1) adduct, triiodophosphine - boron tribromide (1:1) adduct, diphenylborane - boron tribromide (1:2) adduct, and pentabromophosphorane - boron tribromide (1:1) adduct.

According to Terible (1901) adduct formation was demonstrated by mixing and or heating phosphorus iodides \( (P_2I_4 \) or \( P_4I_6 \)) with boron tribromide.
in sealed tubes. The resulting crystalline materials were shown to be the same irrespective of whether triiodophosphine diphosphorus tetraiodide was used i.e. $P_2I_42Br_3$. It is now known with certainty that similar procedures produce two different adducts viz. diphosphorus tetraiodide - boron tribromide (1:2) adduct and triiodophosphine - boron tribromide (1:1) adduct with melting points dec. $130^\circ C$ and $159-160^\circ C$ respectively. Diphosphorus tetraiodide boron tribromide (1:2) adduct was soluble in boron tribromide, carbon disulphide, chloroform and insoluble in petroleum ether. The reactivity towards water was high, resulting in boric acid, phosphorus acid, hydrobromic acid and hydroiodic acid.

$$P_2I_42Br_3 + 11H_2O = 2H_3BO_3 + 2H_3PO_3 + 4HI + 6HBr$$

Cowley and Cohen (1965) undertook extensive studies of adduct formation of triiodophosphine and diphosphorus tetraiodide with boron tribromide and proposed a modification of Tarible's synthesis using carbon disulphide as solvent. The crystalline adduct diphosphorus tetraiodide - boron tribromide (1:2) adduct and triiodophosphine - boron tribromide were characterized by I.R. and X-ray techniques.

In the present investigation Cowley's method was used for the preparation of triiodophosphine - boron tribromide, while for diphosphorus tetraiodide - boron tribromide (1:2) adduct formation was conducted without solvent (see Chapter two: synthesis).

Complex formation has also been studied in detail by Armington et al. (1965). The suggested method for the tribromophosphine - boron tribromide (1:1) adduct is the reaction of tribromophosphine and boron triiodide in carbon disulphide.

The synthesis of pentabromophosphorane - boron tribromide was performed
by Terible by mixing pentabromophosphorane and boron tribromide in carbon
disulphide with cooling. The resulting substance was characterized by
elemental analysis. It sublimes from 105°C prior to the melting point 140°C
in a sealed tube. The adduct is soluble in hot carbon disulphide and is
hygroscopic. It reacts with water according to the following equation,

\[ \text{FBr}_5\text{BBr}_3 + 7\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + \text{H}_2\text{BO}_3 + 8\text{Br} \]

Recently (1966) the thermochemistry of some phosphorus halide-boron
halide complexes has been studied by Finch et al. The standard heats
of formation have been determined and the strengths of the donor-acceptor
bonds estimated. The investigation comprises of system \( X_3\text{PY}_3 \) where \( X, Y = \)
Br and I (i.e. four adducts). The bond strengths of these adducts are
reported as \( I_3\text{PBr}_6, 22\text{.} \), \( I_3\text{PBBR}_6, 65\text{.} \), \( \text{Br}_3\text{PBI}_6, \text{Br}_3\text{PBBR}_6, \text{7 Kcal}\)
mole\(^{-1}\). Similar thermochmmical results for pentavalent phosphorus compounds
have been reviewed by Webster. The reported data for adducts are between
pentachlorophosphorane (and mixed halides) with pyridine and pentfluoro-
phosphorane with ethers and organic sulphides. There are no thermochmmical
measurements for 1:2 complexes such as \( \text{P}_2\text{I}_2\text{BBR}_3 \) and data for molecular adducts
involving phosphorus e.g. \( \text{Br}_5\text{PBBR}_3 \) are scarce.
SECTION II. EXPERIMENTAL TECHNIQUES

CHAPTER TWO: SYNTHESIS

PURIFICATION

HANDLING

ANALYSIS
**SYNTHESIS**

(1) Phosphorus-Phosphorus Bonded Compounds

**Pentaphenylcyclopentaphosphine** - This was prepared according to the procedure of Fraxier et al. **\[77\]** Tri-\textit{n}-butylphosphine (99.1 g, 0.49 mol.) was added dropwise to phenylidichlorophosphine (87.7 g, 0.49 mol.) with stirring in an inert atmosphere of nitrogen. The reaction vessel was cooled externally by solid carbon dioxide as the reaction was exothermic. After complete addition of tri-\textit{n}-butylphosphine a rubber-like material appeared within ca. 20 min. (cf. crystalline material within a few seconds according to Fraxier et al.) This material was sublimed at 120°/1 mm. Hg for ca. 3 hr. The sublimate was found to contain mainly tributylidichlorophosphorane, identified by Reinecke's salt derivative, m.p. 121° dec. (lit.* m.p. 121-123° dec.). The residue (pentaphenylcyclopentaphosphine) was washed with absolute ethanol and dried under vacuum for ca. 48 hr. An X-ray diffraction pattern was compared with that of an authentic sample of Daly (see p. 25) and was found to be pentaphenylcyclopentaphosphine, m.p. 154° (closed capillary) lit.\[61,77,78\] m.p. 149-156° Yield 25.0 g., 47.2% based on phenylidichlorophosphine, lit.* m.p. 154° (closed capillary) \[61,77,78\] Yield, 30%. (Found: C, 66.68; H, 4.87; P, 28.4%). C\textsubscript{6}H\textsubscript{2}\textsubscript{15}P requires C, 66.68; H, 4.87; P, 28.4%.

**Attempted preparation of hexaphenylcyclohexaphosphine (Form B)** - The procedure of Henderson et al. was used but with no success probably due to interconversion to the more stable Form A. (see p. 28). A successful preparation was recently reported by Maier using a modification of the procedure of Henderson. An authentic sample was generously supplied by Maier and was used for the thermal analysis in the present work (see p. 152). Henderson's synthesis was based on the elimination of hydrogen chloride during the reaction of
Phenylphosphine with phenyldichlorophosphine. Phenylphosphine (3.1 g, 0.028 mol) was added, in one aliquot, to phenyldichlorophosphine (5.0 g, 0.028 mol) in dry benzene (15 ml) under dry nitrogen. The solution was warmed at ca. 40° until gas evolution ceased. The resulting white precipitate was filtered off under dry nitrogen, followed by vacuum drying at ca. 40°/0.05 mm Hg. On recrystallisation from acetonitrile, the solid (phospho-benzene) appeared as transparent long rod-shaped crystals. m.p. 130° (lit. for hexaphenyldicyclohexaphosphine (Form B), 195-199°, 190° (open capillary); lit. also described crystals of m.p. 130-155° as a clathrate in which one molecule of benzene for six phenylphosphine groups was present.). (Yield, 5.2 g, 86.6% based on C9H9Cl2).

Polymeric Phenylphosphine - This preparation was based on the disproportionation of phenyldifluorophosphine. Phenyldifluorophosphine was prepared by a modification of the procedure of Schmutzler. Phenyldichlorophosphine (14.2 g, 0.80 mol), freshly distilled at 80°/2 mm Hg, was added with stirring to a slurry of Analar sodium fluoride, (100.9 g, 1.20 mol.), dried at 400° for ca. 96 hr., in sulpholane (300 ml) under an inert atmosphere of nitrogen. The reaction vessel contents were maintained at ca. 100° using an oil bath. The resulting material was fractionally distilled at 100°/11-12 mm Hg. The fraction was collected under solid carbon dioxide. The colourless liquid changed to a white crystalline material on standing at room temperature for ca. 9 hr. (Cf. lit. report that the material was unstable at ordinary temperature, but solidified after 1 month standing at 0°). Which was removed under nitrogen and washed with dichloromethane. The material, probably polymeric, phenylphosphine was stable in air. An X-ray diffraction pattern was compared with that of an authentic sample of Maier (see p.238) which was found to be similar. The m.p. was 264-280° for Form C or D (cf. lit.61.
Phosphorus tetraiodide - This was prepared according to Germann and Traxler. The preparation was carried out under an inert atmosphere of nitrogen in a dry-box. Dried white phosphorus, under acetone, (2.0g, 0.016 mol. based on $P_4$) was scraped clean of its oxide coating and was dissolved in purified and freshly-distilled carbon disulphide (200 ml.). Analar iodine (16.38g, 0.064 mol. based on $I_2$) was added slowly with stirring and the reaction vessel was cooled externally by solid carbon dioxide, as the reaction was exothermic. On complete addition of iodine the solution appeared orange-yellow, and the reaction vessel was left for ½ hr. Partial crystallization of diphosphorus tetraiodide occurred. Further separation of crystals was achieved by removing some solvent under vacuum and finally filtering through a sintered funnel under vacuum. The crystals were washed with petroleum ether (b.p. 60-80°) and dried in a stream of dry nitrogen. Fine long orange-red needles of diphosphorus tetraiodide were collected, m.p. (closed capillary, 124.5°, lit. 124.5°, and preserved according to the technique given on p. 64 (Yield, 14.90g., 81.0% based on $P_4$, lit. $68-75%$) (conventional titrimetric analysis for iodine showed 98.3% purity for $P_2I_4$).

(2) Phosphorus (III) Compounds

Phenyldiphosphine - This was prepared according to Fluck and Binder and was based upon the reduction of phenyldichlorophosphine by lithium aluminium hydride. The reaction was carried out under an atmosphere of dry nitrogen. Freshly distilled phenyldichlorophosphine b.p. 80°/2 mm. Hg., lit. 90-100°/15 mm. Hg. (14.90g., 0.83 mol.) in dry ether (250 ml.) was
added dropwise to lithium aluminium hydride in dry ether (300 ml) in a three-necked flask equipped with stirrer. The flask was externally cooled with solid carbon dioxide. The complete transfer of phenyldichlorophosphine took 5 hrs. and then distilled water (100 ml) was added. The reaction mixture was refluxed for 4 hrs. till a white precipitate of aluminium hydroxide was visible. The liquid was filtered from the gelatinous residue. The filtrate was kept over calcium chloride for a period of 48 hrs. to remove any moisture. The supernatant liquid was decanted and distilled at atmospheric pressure to separate the ether and finally purified by redistillation at atmospheric pressure at 160°C (lit. 155, 157 b.p. 160°C) (yield, 70.0 g., 76.4% based on phenyldichlorophosphine, lit. 155 53.2%).

Phenyldibromophosphine - This was prepared according to the procedure of Koeller et al. which is based on the exchange reaction of hydrobromic acid with phenyldichlorophosphine in phosphorus tribromide. The reaction was carried out under an atmosphere of dry nitrogen. Anhydrous hydrogen bromide from a cylinder was bubbled for 20 hrs. through a mixture of phenyldichlorophosphine (250 g., 140 mol.) and phosphorus tribromide (176 ml.) in a three-necked flask fitted with a mercury seal stirrer. The mixture was maintained at refluxing temperature, ca. 173°C, for 20 hrs. After refluxing, the mixture was allowed to cool to room temperature. The resulting yellow-orange liquid was initially distilled to remove the solvent tribromophosphine at 54°C/11-12 mm. Hg., using oil-bath heating. This was followed by fractional distillation for phenyldibromophosphine using a 25 cm. Vigreux column insulated with cotton and asbestos packing. The fraction boiling at 84-86°C/1 mm. Hg. was collected (yellow liquid). (Cf. lit. b.p. 259-261°C, fractionally distilled at atmospheric pressure, lit. 159 b.p. 255-257°C). Yield, 230 g., 61.5% (lit. 158 60%) based on phenyldichlorophosphine, conventional titrimetric analysis for
bromide indicated 99.9% purity.

Tricyanophosphine - This preparation was based on the exchange reaction of trichlorophosphine with silver cyanide (Staats and Morgan). Initially, silver cyanide was prepared by mixing the solution of silver nitrate (127.4g, 0.75 mol.) in distilled water (1L) with potassium cyanide (48.8g, 0.75 mol.) in distilled water (1L) at ambient temperature. The resultant whitish precipitate of silver cyanide was filtered, washed with acetone, and dried in the dark under vacuum at 80/2 mm. Hg. m.p. (silver cyanide) 320° dec., lit 320° dec. (Yield, 89.6% based on silver nitrate). The same silver cyanide (50.0g, 0.37 mol.) in benzene (100 ml.) was mixed, under nitrogen, with excess trichlorophosphine (26.0g, 0.19 mol.) in benzene (50 ml.). The mixture was refluxed for ca. 24 hrs. at 80°. After refluxing, excess benzene along with excess trichlorophosphine was removed by distillation. The last traces of liquid from the white residue were removed under vacuum which was followed by sublimation, (see an apparatus on p. 52) at 110°/0.05 mm. Hg. The m.p. of thrice-sublimed material (tricyanophosphine) was 190°, lit 112° 200°, lit 190°. (Yield, 12.0g., 88.8% based on silver cyanide, lit 115° ca. 81%).

(Found: C, 32.77%, N, 36.21%, P, 28.15%. C₃N₅P requires C, 33.05, N, 33.54, P, 28.41%). As a further analytical check, a sample of the material was hydrolysed to phosphorous acid and hydrocyanic acid and the end-points due to these acids detected by a potentiometric titration pK₁ (H₂PO₃⁻) = 1.8, pK₂ (H₂PO₄⁻) = 6.15 and pK₃ (H-CN) = 9.14. Three end-points were detected (see graph on p. 222) and calculation, on the basis of the corresponding titres, indicated a purity of 99.02% for P(CN)₃.

Tri(isocyanato)phosphine - This was prepared by a modification of the procedure of Forbes and Anderson based on the replacement reaction between trichlorophosphine and silver isocyanate. Initially silver isocyanate was pre-
Fig. Sublimation Apparatus (x 0.50 natural size)
pared by the procedure of Neville and McGee. Equimolar solutions of silver nitrate (100.0g, 0.58 mol.) in distilled water (1L.) and potassium cyanate (47.7g, 0.58 mol.) in water (1L.) were mixed with stirring at ca. 0°. The resulting white precipitate of silver isocyanate (light-sensitive) was filtered off, washed with distilled water, then acetone, and finally dried under vacuum at 50°/1 mm. Hg. for 48 hrs. (Yield, 94.9% based on silver nitrate.) This silver isocyanate (83.5g, 0.56 mol.) in dry benzene (200 ml.) was added to trichlorophosphine (31.5g., 0.22 mol.) in one aliquot under a dry nitrogen atmosphere. The mixture was refluxed at 80° for 48 hrs. After refluxing, the solvent benzene, along with excess trichlorophosphine, were removed by distillation. The resulting yellowish-brown material was fractionally distilled through a 6 cm. Vigreux column at 40°/0.5 mm. Hg. (lit. b.p. 60.5-63.0/10 mm. Hg.) with oil-bath heating at 60°. The first distillate was a colourless liquid b.p. 169° (lit. 169.3°, 160°); Yield, 76%, based on silver isocyanate. The colourless liquid, after standing under nitrogen at room temperature for ca. 120 hrs., started solidifying into a whitish-yellow solid, but only two thirds of the liquid solidified over a period of 2 months. (Cf. ref. notes rapid polymerization at room temperature and ref. notes upon standing polymerizes to yellow-white solid.) The solid material (probably polymeric) was distilled into a colourless liquid at 40°/0.5 mm. Hg. indicating reversible depolymerisation. The freshly-distilled colourless liquid, (prior to any polymerisation), was, as a further analytical check, hydrolysed to phosphorous acid and isocyanic acid and the end-points due to these acids detected by potentiometric titration $pK_{160} (H_2PO_3^{-}) = 1.8$, $pK_{160} (HPO_3^{2-}) = 6.15$ and $pK_{117} (H-NCO) = 3.70$. Three end-points were detected (as described on p.221) and on the basis of the corresponding titres for the first and third end-points indicated a purity of 98.3% for $P(NCO)_3$. The
molecular weight was determined by precision cryoscopy (described on p. 228) (Found: C, 161; O, 0.84, P, 19.54; requires C, 161; O, 0.84, P, 19.54).  

(5) Phosphorus (V) Compounds  

Phenyltetraochlorophosphorane - This preparation was based on the addition reaction of chlorine to phenyl dichlorophosphine in carbon tetrachloride. According to a modification of the procedure of Michaelis, chlorine (ca. 29 g, 0.40 mol.) gas was bubbled into phenyl dichlorophosphine (70.0 g, 0.39 mol.) dissolved in dry carbon tetrachloride. The reaction mixture was maintained at ca. -70°. The mixture was allowed to come to room temperature, followed by refluxing for 3 hrs. After refluxing, carbon tetrachloride was removed by distillation under reduced pressure. The residue (crude, phenyltetraochlorophosphorane) turned into a viscous, creamy liquid at ambient temperature. Attempted sublimation of some of this crude material resulted in partial decomposition, presumably into phenyl dichlorophosphine and chlorine. Therefore crystallization from carbon tetrachloride was carried out and resulted in long transparent rods (measuring ca. 1 by 0.2 cm.), m.p. 75° (lit. 73, 75-76). Yield, 48.8 g, (50% based on phenyl dichlorophosphine) (conventional titrimetric analysis for chlorine showed 99.2% purity.)  

Phenyltetribromophosphorane - This preparation was based on the addition reaction of bromine with phenyl dibromophosphine in carbon tetrachloride. According to a modification of the procedure of Michaelis and Kohler, bromine (ca. 50 g, 0.31 mol.) was added slowly and with stirring to phenyl dibromophosphine (67.0 g, 0.25 mol.) dissolved in dry carbon tetrachloride (250 ml.) with moderate external cooling. After complete transference of
bromine, the reaction mixture was allowed to warm to room temperature, stirring continuously. After ca. 60 min. orange-yellow solid had deposited. The solid material (phenyltetrabromophosphorane) was removed under nitrogen using a sintered filter-funnel, washed with dry carbon tetrachloride, and finally vacuum-dried for ca. 8 hr. The dried powdery material was sublimed (see an apparatus on p.52) for further purification at 83°/2 mm. Hg. The purified material was in the form of long, yellow-reddish needles. m.p. (closed capillary) 207°, lit. 207° (conventional titrimetric analysis of bromine after hydrolysis indicated a purity of 98.7% for $C_6H_5PBr_4$).

(4) Molecular Adducts

Diphosphorus tetraiodide-boron tribromide (1:2) adduct - This preparation was based on the addition reaction boron tribromide to diphosphorus tetraiodide. According to a modification of the procedure of Ross and Tarble, freshly distilled boron tribromide (see p.61) (20.96 g, 0.083 mol.) was added to diphosphorus tetraiodide (8.65 g, 0.015 mol.) stored in a special distillation apparatus (see p.56) with occasional shaking until a golden yellow powdery material deposited (diphosphorus tetraiodide-boron tribromide adduct). After ca. 30 min. the excess boron tribromide was distilled off at ca. 25°/0.01 mm. Hg, for 2 hr., and trapped. By difference the weight of boron tribromide retained was found to be (16.2 g), i.e. 93% of theoretical 16.3 g. The m.p. of the adduct, (closed capillary) was 345°-350°. It partially decomposed between 129-138° (lit. describes decomposition with iodine vapour at 130° and lit. 134°-136° dec.) The decomposition was investigated by thermal analysis technique (see p.159). (Conventional titrimetric analysis for total halide followed by iodide gave I, 46.8; Br, 44.8; $P_2I_2Br_4$ requires I, 47.4%; Br, 44.8%)
Fig. Longitudinal Section through Mixing Vessel for Adduct Synthesis (x.3.75 natural size)
**Trilbromophosphine-boron triiodide (1:1) adduct** - This was prepared by the procedure of Armington et al. The reaction was performed under nitrogen in a dry box. Trilbromophosphine (6.95 g., 0.026 mol.) in carbon disulphide (125 ml.) was added dropwise with stirring to boron triiodide (10.0 g., 0.026 mol.) in freshly-distilled carbon disulphide (125 ml.), cooling the reaction mixture with solid carbon dioxide. After complete transference, carbon disulphide was removed under vacuum. The resulting brownish-orange solid (the impure adduct) was washed with carbon disulphide and dried under vacuum at ambient temperature. The m.p. of the adduct was 170°-182°, partially subliming at 65° (lit. sublimes at 65°). The mass spectrum of this material is given on p.172. Yield, 88.7% based on boron triiodide. (Conventional titrimetric analysis for total halide followed by iodide gave I, 56.66, Br, 55.79, P requires, I, 57.49, Br, 36.20, %).

**Triiodophosphine-boron tribromide (1:1) adduct** - This was prepared by the procedure of Cowley and Cohn. The reaction was performed under nitrogen in a dry box. Boron tribromide (6.6 g., 0.026 mol.) in freshly distilled carbon disulphide (solvent purification on p.59 ) (100 ml) was added dropwise with stirring to triiodophosphine (5.39 g., 0.013 mol.) in carbon disulphide (160 ml.) cooling with solid carbon dioxide. After complete transference, carbon disulphide was removed under reduced pressure at room temperature. The resulting reddish-yellow crystalline material (adduct) was finally dried in the dark for 10 hrs. under 0.1 mm. Hg. at room temperature. The m.p. of the adduct was 159-160° (lit. 159-160° dec. lit. 159-160° dec. near 50°) (Yield, 5.2 g., 60.4% based on triiodophosphine). The mass spectrum of this material is given on p.173. (Conventional titrimetric analysis for total halide followed by iodide gave I, 56.66, Br, 36.12, PBr requires, I, 57.49, Br, 36.20, %).

**Pentabromophosphorane-boron tribromide (1:1) adduct** - This preparation
was similar to that of Tarible\textsuperscript{101,72}, using methylene dichloride as solvent instead of carbon disulphide. The reaction was performed under dry nitrogen. Boron tribromide (13.10 g., 0.052 mol.) in dichloromethane (200 ml.) was added slowly with stirring to pentabromophosphorane (20.0 g., 0.046 mol.) in methylene dichloride (200 ml.), cooling with solid carbon dioxide. After complete transference the mixture was allowed to come to room temperature. The solvent was removed under vacuum. The resulting yellow powdery solid (the adduct) was dried under vacuum for ca. 15 hr. at ca. 25°/0.1 mm. Hg. The m.p. of the adduct was 150° (closed capillary) \textsuperscript{101} 140° (closed capillary), but partially sublimation occurred at 110°. Yield, 16.0 g., 50.5\% based on pentabromophosphorane. (Conventional titrimetric analysis for bromide showed 59.6\% purity. Also the bromine content was in agreement with a 1:1 adduct.) (Found: Br, 93.7\%, \text{Br}_2\text{Br}_3 requires, Br, 93.86\%).
Purification

1. Solvents

Carbon disulphide – The Analar carbon disulphide supplied by B.D.H. was further purified by a four-step procedure over a period of five to six days. Dissolved impurities e.g. sulphur, oxygen and moisture, have been proved to be the cause of a side reaction \(^{21,92}\) when impure solvent was used for phosphorus chemistry. Initially carbon disulphide was vigorously shaken with a saturated aqueous solution of potassium permanganate (solubility, \(6.48/100\) ml. cold water) for a period of 48-60 hr., followed by separation of the aqueous layer. The carbon disulphide was then dried over anhydrous calcium chloride for a period of 24 hr. The decanted solvent was treated with mercury metal for 48 hr. The tarnished mercury layer was occasionally removed and fresh mercury added. Finally the solvent was fractionally distilled under an atmosphere of dry nitrogen at \(46.5^\circ/760\) mm. Hg. Throughout this work, the carbon disulphide was distilled immediately prior to use.

Benzene – Analar grade (B.D.H.) benzene was distilled at \(80^\circ/760\) mm. Hg. (lit. \(70^\circ\)) and dried over sodium wire prior to use.

Ether – Reagent grade (May & Baker) was distilled at \(34.5^\circ/760\) mm. Hg. (lit. \(34.6^\circ\)) and dried over sodium wire.

Sulpholane – Pure grade (Koch Light Ltd.) was purified by distillation under vacuum at \(95-96^\circ/1\) mm. Hg. (lit. \(b.p. 283^\circ/760\) mm. Hg.) followed by drying over sodium wire.

Chloroform – Reagent grade (May & Baker) chloroform was purified by distillation at \(60-61^\circ/760\) mm. Hg. before use and dried over anhydrous calcium chloride.

Methylene Chloride – Reagent grade (May & Baker) was distilled at \(40^\circ/\)
760 mm. Hg. (lit. 40.1) and dried over anhydrous calcium chloride before use.

Petroleum Ether — Analar grade (B.D.H.) b.p. 60-80° was used directly.

Tetrahydrofuran — Reagent grade (B.D.H.) redistilled (to two-thirds of the initial volume) at 65°/760 mm. Hg. prior to use.

Pentamethylenimine (Piperidine) — Reagent grade (B.D.H.) was distilled at 106°/760 mm. Hg. (lit. b.p. 106°).

(2) Synthetic Materials

Diphosphorus tetraiodide — This was supplied by Koch-Light Laboratory Ltd. of 99% purity. (Also synthesised see p. 49).

Phosphorus (white) — The oxide film of material (B.D.H. 99.9%) was removed by scraping under water. Before use, the phosphorus was dried with acetone.

Hexaphenylcyclohexaphosphine — An authentic sample (m.p. 190° (open capillary)) was donated by Dr. L. Kaier (Konsato Research S.A., Switzerland).

Phenyl dichlorophosphine — This material (Aldrich Chemical Co.) was purified by fractional distillation up an insulated 50 cm. Vigreux column. The fraction boiling at 80°/2 mm. Hg. (colourless liquid) was collected (lit. 90-100°/15 mm. Hg.).

Phenyl dibromophosphine — Prior to use for synthetic purpose, phenyl dibromophosphine was distilled under reduced pressure. The fraction boiling at 84-86°/1 mm. Hg. (lit. b.p. 253-261°, lit. 255-257°) was collected (yellow liquid) (see p. 50 for synthesis).

n-Tributylphosphine — A grade supplied by Koch-Light Laboratory was used without further purification.

Trichlorophosphine — Reagent grade (B.D.H.) was distilled at 75.8°/
Triiodophosphine - Pure grade (Eastman organic, K. & K.) was supplied. In addition, a sample (m.p. 61°), prepared by Dr. I. H. Wood of this laboratory was used.

Phenyll phosphine - An authentic sample of b.p. 160°/760 mm. Hg. was donated by Dr. P. Powell of this laboratory (see p. 49 for synthesis).

Tribromophosphine - Pure grade (99%) colourless liquid b.p. 172°/760 mm. Hg. (lit. 172.9°) was supplied by (B.D.H.) and used directly.

Pentabromophosphorane - Reagent grade (B.D.H.) yellow crystals.

Phenylphosphonic acid - Impure phenylphosphinic acid, prepared by a procedure of Kosolapoff, was twice recrystallized in dry benzene, m.p. 86° (lit. 166 °/86°).

Boron tribromide - The reagent grade (B.D.H.) slightly pale yellow liquid was purified by a two-step procedure. Initially it was shaken with mercury to remove hydrobromic acid. This was followed by fractional distillation under dry nitrogen with the ground glass joints of the distillation unit connected by PTFE sleeves. The fraction boiling at 90°/760 mm. Hg. (lit. 90.1°/760 mm. Hg.)(colourless liquid) was collected.

Boron triiodide - 99.9% purity (Koch-Light Laboratory Ltd.) batch No: 31345 (colourless, transparent crystals) m.p. 43° (lit. 43°/m.p. 43°).

Bromine - AnalaR grade (B.D.H.) bromine of density (3.1 g./ml. at 20°) was used. The solubility was experimentally determined (titration) prior to a use for synthetic, conventional titrimetric analysis and solution reaction calorimetry.

Iodine - AnalaR grade (99.3%) (B.D.H.) was used.

Chlorine - High purity grade (99.2%) of Sp. vol. (5.4 cu. ft./lb.) was supplied by Cambrian Gases, Matheson and used directly.
Anhydrous hydrogen bromide - High purity grade, (99.3%) of Sp. vol. (4.8 cu. ft./lb.) supplied by Cambrian Gases, Matheson, was used directly.

Ferrocene - Ferrocene (B.D.H.) was twice recrystallized from absolute ethanol and sublimed in vacuo m.p. 175-176°C (lit. 167 m.p. 175.5-176°C). This sublimed material (yellow crystals) was used for effusion manometry (see p. 180).

Lithium aluminium hydride - Reagent grade white powder was supplied by Koch-Light Laboratory Ltd., batch No: 30091.

Ammonium Reineckate - Reagent grade (B.D.H.) reddish-brown crystals.

Sodium fluoride - Reagent grade (B.D.H.) powdered finely and dried in oven at 400°C for ca. 96 hr. prior to use.

Tris(hydroxymethyl)aminomethane - High grade purity material (not less than 99.3% of pure, Aristar) supplied by B.D.H., m.p. 171-172°C was used directly for calorimetric run.

Eosin Solution - A fresh sample, used as adsorption indicator, was prepared by dissolving Eosin (B.D.H., 0.1 g.) in ethanol (100 ml. of 70% aqueous).

Diiododimethylfluorescein Solution - This was prepared by dissolving 1.0 g. substance in ethanol (100 ml. of 70% aqueous) and used as an adsorption indicator.
(1) Dry-Box Techniques

Dry-Box - A dry-box was designed and constructed out of 2.0 mm. thick metal at this laboratory. The dimensions (cm.) of the main body were 90 x 45 x 60, the front window (perspex) was 60 x 18 x 0.5 and the entry-port was 21 x 20 x 23. Access was via flanged (reinforced) latex gloves (scientific supplies). Throughout this work, moisture and light-sensitive compounds were handled in this dry-box. The handling of the effusion manometer containing phosphorus iodides (see p. 108) was performed in a polyethylene glove bag, supplied by Instrument Research and Industry (U.S.A.) Model X-37x37. Drying in both cases was effected by trays of phosphoric oxide and calcium chloride (anhydrous). The dry atmosphere of nitrogen for the dry-box was maintained in a dynamic state using a fan driven by a 1/30 H.P. Paravalux motor. The humidity was monitored by a hair hygrometer (Fischer).

(2) Distillation Techniques

Many phosphorus compounds in the liquid state are easily hydrolysed or oxidised. Distillation of such compounds was performed under an atmosphere of dry nitrogen or dry nitrogen was flushed through distillation unit prior to the commencement. Grease of all grades was attacked by liquid phosphorus compounds and therefore PTFE sleeves (Fison Scientific) were used on all ground-glass joints. Throughout this work, unless otherwise mentioned, a two-stage rotary pump (2820 Speedivac, Edward High Vac. Ltd.) giving 0.01 mm. Hg. was used for vacuum distillation.
(3) Filtration Techniques

Vacuum and ordinary filtration were performed in a dry-box. A vacuum sintered filtration equipment which could be easily handled in a dry-box has been designed (see Fig. on p. 65). This could also be adapted for drying materials under nitrogen.

(4) Special Handling Techniques

Special care was taken with highly toxic compounds and those which were light and moisture sensitive, e.g. phenylphosphine, tricyanophosphine, tri(isocyanato)phosphine, phosphorus iodides, triiodophosphine-boron tribromide adduct.

(5) Storage

Where appropriate materials were preserved in sealed ampoules storage was at deep-freeze or at room temperatures. The following compounds were stored at -20°:

- Diposphorus tetraiodide
- Triiodophosphine
- Phenyltetraphosphorane

A report of the hazardous nature of tri(isocyanato)phosphine in the presence of moisture was noted.
Fig. Vacuum Filtration Equipment.
ANALYSIS

(1) Microanalysis

Elemental carbon, hydrogen, nitrogen, phosphorus, sulphur analyses were carried out by Alfred Bernhardt, Microanalytisches Laboratorium, 5251 Elbach Uber Engelkirchen, West Germany, and also at Microanalytical Laboratory, 164 Banbury Road, Oxford.

(2) Chemical Analysis

Halides and Halogen - Halide analyses were obtained by hydrolysis of the moisture-sensitive compounds followed by conventional argentimetric and iodometric titrations. The end-points were detected with eosin for total halide (e.g. bromide and iodide in $\text{P}_2\text{I}_4$, $\text{P}_2\text{Br}_5$, $\text{PBr}_5$, $\text{Br}_5\text{I}_5$), with diiodo-dimethyl fluorescein for iodide, and with tetrazine for chloride (e.g. in $\text{C}_6\text{H}_5\text{PCl}_4$). In the case of the pseudohalides (e.g. $\text{P}($CN$)_3$, $\text{P}($CO$)_3$), acidimetric analysis was performed on the hydrolysate. The end-points were detected potentiometrically (Pye Model 79 pH-meter). Usually three end-points were detected, two for phosphorus acid and one for the hydrogen pseudohalide, (see numerical results under synthesis p46 and titration graphs in appendix O HS p. 220).

(3) Cryoscopic Measurements

A precision cryoscope was designed in this laboratory by Finch et al. for molecular weight determination of moisture-sensitive compounds. This cryoscope (see fig. on p. 67) was operated under modified conditions for phenyl dichlorophosphate and tri(isocyanato)phosphine. Solid carbon dioxide in powder form was used as coolant and the air-jacket was not evacuated. All
B = Socket B_{24}  \quad S_L = Solenoid  \quad S = Stirrer
J = Jacket  \quad T = Thermistor

Fig.  Longitudinal Section of Cryoscopic Cell, Solenoid and Thermistor.
transfer operations were performed under an atmosphere of dry nitrogen. The depression of the freezing point was detected by a thermistor incorporated in a Wheatstone bridge circuit. The solution was kept in a dynamic state by a specially-designed stirrer actuated externally by a solenoid (see circuit diagram on p.69). Initially the cryoscope was calibrated with naphthalene in benzene. Finely ground naphthalene was injected via a wide-bore syringe (a precision-bore glass tube and rod). The amount of substance delivered by this syringe was determined by a weight-difference method. The mode of injection in the case of phenyl dichlorophosphate and tri(isocyanato)phosphine was via a weighing-pipette (Quickfit).

The molecular depression for a dilute ideal solution can be expressed as

\[ \Delta T_f = K_f \cdot \text{mol} \]

where

- \( \Delta T_f \) = molecular depression
- \( K_f \) = cryoscopic constant
- \( \text{mol} \) = molality of the solution

The approximate relationship for small changes in temperature and resistance for a thermistor is

\[ \Delta T \propto -\Delta R \]

Now

\[ \text{mol} = \frac{W}{M} \times \frac{1000}{\text{weight of solvent}} \]

where

- \( W \) = weight of solute
- \( M \) = molecular weight of solute
C = Cam  \quad T_R = \text{Transformer}  \quad S_m = \text{Synchronous motor}

P_L = \text{Pilot Lamp}  \quad M = \text{Mains}  \quad M_s = \text{Micro Switch}

S_1 \text{ and } S_2 = \text{Switches.}

Fig. Pulse Generating Circuit Diagram for Solenoid (Cryoscope).
So

\[- \Delta R = K \frac{W}{M} \]

or

\[- \Delta R = K \frac{W}{M} \text{ for constant quantity of solvent.} \]

In practice, a graph is plotted for the depression, \( \Delta R \) (in \( \Omega \)) Vs \( W \) (wt. of solute in a fixed amount (usually 20g.) of benzene). The gradient for naphthalene (n) is given by,

\[G_n = \left( \frac{W}{\Delta R} \right)_n\]

substituting in

\[- \Delta R = K \frac{W}{M} \]

we have

\[M_n = -K G_n\]

So for an unknown material (x),

\[M_x = -K G_x = \left( \frac{M_n}{G_n} \right) G_x\]

or

\[M_x = \left( \frac{M_n}{G_n} \right) G_x\]

The only unknown in this final equation is \( M_x \), the desired quantity. The detailed numerical results obtained for \( \text{C}_6\text{H}_5\text{PCl}_2 \) and \( \text{P(NO)}_3 \) are given in appendix two p. 225.

(4) Vibrational Spectroscopy

The structural analysis of phosphorus compounds in general
and phosphorus-phosphorus bond compounds in particular by infra-red and Raman spectroscopy is well-documented.

The following instruments were used in this work:

1. Infra-red grating spectrophotometer (Unicam instrument No: 21098,
s.p. 100), using KBr discs, in the range 1970 cm$^{-1}$ to 394 cm$^{-1}$.

(ii) Infra-red grating spectrophotometer, (Perkin Elmer 337), using 0.01 m.m. cells in the range 3300 cm$^{-1}$ to 685 cm$^{-1}$.

(iii) Raman scattering using He-Ne laser radiation (6328 A°) source in a Cary 81 instrument accuracy ± 1 cm$^{-1}$ in the range studied, 1531 cm$^{-1}$ to 155 cm$^{-1}$.

Details of the spectrum for pentaphenylocyclopentaphosphine are presented in appendix three p.229 along with the comparison of the so-called tetraphenyl-cycloptetraphosphine and tetraphenylcycloptetraphosphine forms A and B.

(5) X-ray crystallography

Structural analysis by this technique takes account of the geometrical arrangement of atoms in the lattice. This technique has been recently applied to phosphorus compounds containing the phosphorus-phosphorus bond to confirm the structures of phosphobenzene in the forms then known as (C$_6$H$_5$)$_4$P and (C$_6$H$_5$)$_4$P$_2$. According to Daly, phosphobenzene exists as

(1) Pentaphenylocyclopentaphosphine, (C$_6$H$_5$)$_5$P, m.p. 149-150°C

(11) Hexaphenylocyclohexaphosphine, (C$_6$H$_5$)$_6$P, m.p. 190°C

The crystal structures of these compounds are given on p.25 and the molecular stereochemistry is sketched on p.27. In the present work X-ray powder photographs were obtained to confirm the crystal structure of pentaphenylocyclopentaphosphine and polymeric phenylphosphine, prepared via different synthetic routes (see p.47,48 with that of the authentic samples of Daly and Maier respectively.

Numerical values of intensity and interplanar spacings for pentaphenylocyclopentaphosphine and so-called polymeric phenylphosphine are tabulated in appendix four on p.238.
SECTION II. EXPERIMENTAL TECHNIQUES

CHAPTER THREE: THERMOCHEMISTRY


THERMOCHEMISTRY

(1) Solution Reaction Calorimetry - The bulk of thermochemical information is derived from reaction and combustion calorimetry and equilibrium measurements. In this work thermochemical values are experimentally determined for some phosphorous compounds by reaction solution calorimetry and where appropriate, these values are used in thermodynamic cycles. (See p. 208 for the cycle of pentaphenylcyclopentaphosphine). Two types of calorimeter were used to determine the thermochemical values, depending upon the nature of the reaction. For slow reactions (10 min. onwards) an adiabatic calorimeter was used and for fast reactions (main period complete within 10 min.) a constant-temperature-environment calorimeter was used. All measurements were made at 25°C and at atmospheric pressure.

(2) Basic Principles and Construction - The basic principles of reaction solution calorimetry are well-known. A standard reference substance or electrical calibration is used for heat capacity measurements. The temperature differences and electrical energy input are determined very accurately. Thermal loss across the calorimeter boundary is commonly analysed using Newton's cooling Law. The calorimeter and its environment are treated as isothermal bodies and heat transfer between them is expressed as

\[ H_t = \frac{d(T_2-T_1)}{dt} \]

\[ H_t = k(T_2-T_1) \]

Where

\( H_t \) = heat transfer cal/sec.

\( T_1 \) and \( T_2 \) = low and high temperature respectively

\( k \) = constant for all conduction processes (radiation losses are neglected)
In practice the temperature gradient in the calorimeter and shield (in the case of adiabatic systems) cause a net heat exchange during the experiment. The calorimeter vessel used (for diagram see p.75,78) in both the adiabatic and constant-temperature-environment (abbreviated as C.T.E.) systems was similar to the original design of Finch and Gardner.

The temperature of the water jacket (adiabatic system) was automatically controlled (see circuit diagram p.87) so that the environment temperature was approximately equal to the internal calorimetric temperature at all times, thus minimizing thermal leakage. The accuracy and precision of this apparatus was checked using a standard reaction (see p.117 for adiabatic and C.T.E. results)."
H = Heater
T = Thermistor
S = Stirrer
A = Ampule
C = Cooling Well
J = Evacuated Jacket
F = Flange (1.5cm.)
R = Precision Glass Rod

Fig. Longitudinal Section through Calorimeter.
but \( \Delta H_0 \) is total input of electrical energy in terms of heat content, and

\[
\Delta H_0 = \frac{F \times P \times t}{J} \quad \text{where}
\]

\[
F = \text{lead factor}
\]

\[
P = \text{power}
\]

\[
t = \text{time}
\]

\[
J = 4.18 \text{ Joules cal}^{-1}
\]

For the adiabatic calorimeter \( F \) in the above expression is eliminated by precise measurement of input electrical energy in the heater windings (refer to details on p. 81).

Therefore the enthalpy change equation can be expressed as

\[
\Delta H_T = \frac{(F)Pt}{J} \times \frac{M}{W} \times \frac{\Delta T_r}{\Delta T_0} \quad (1)
\]

In actual practice the term \( \Delta T \) in equation (1) is expressed in terms of resistance change as the temperature sensing element is a thermistor

\[
\Delta T_T = T_2 - T_1 = \frac{B}{\ln R_2/A} - \frac{B}{\ln R_1/A}
\]

\[
= -B \ln R_2/A + B \ln R_1/A
\]

\[
\ln R_2/A \ln R_1/A
\]

Similarly \( \Delta T_C = T_4 - T_3 \).

Hence

\[
\frac{\Delta T_T}{\Delta T_0} = \frac{B \ln R_1/R_2}{B \ln R_3/R_4} \times \frac{\ln R_1/A \ln R_2/A}{\ln R_3/A \ln R_4/A}
\]

Now if \( R_3 \sim R_1 \) and \( R_2 \sim R_4 \), the second term in above equation becomes unity.

So

\[
\frac{\Delta T_T}{\Delta T_0} = \frac{\ln R_1/R_2}{\ln R_3/R_4}
\]
In the case of F 53 type of thermistor the following relationship was observed

\[ 0.1^\circ C (\Delta T) \approx 11-12 \alpha (\Delta E) \]

(3) Constructional Details

The Calorimeter - The calorimeter is made up of a pyrex Dewar vessel (see p. 75,78) with internal diameter 5 cm. and depth 17.5 cm. with a rounded base. The capacity of the calorimeter cylinder is 250 ml. water. Under normal working conditions 200 ml. of fluid is used. The space between Dewar walls measures 5 mm. and is evacuated to \(10^{-6}\) mm. Hg. for insulation. The multi-tubular lid of the calorimeter is fitted to a ground glass flanged collar. The joints are lightly greased to give a gas-tight seal. The multi-tubular lid contains six ground glass sockets usually two B\(_{14}\), four B\(_{10}\). The ground glass joints of B\(_{14}\) and B\(_{10}\) (or B\(_{7}\)) are mounted with P.T.F.E. sleeves (Fisons) to arrest the movement of the inserts during operation and to provide a gas-tight seal for operation under an inert atmosphere.

Stirrer - This is a precision glass rod the lower portion of which is converted into a double bladed propeller for downward motion of the calorimetric contents. The stirrer occupies the central position in the cylinder and is kept close to the rounded bottom of the cylinder for good circulation. The drive was effected by a 1/30 H.P. Paravalux motor (synchronous) at a constant speed of 1370 r.p.m. via a flexible cable.

Ampoule - The design of the ampoule was based on

(i) minimum glass content to be thrown in the calorimetric fluid on fracture, thereby minimizing the undesirable liberation of heat due to mechanical stirring.

(ii) rapid and complete liberation of the sample.
Fig. Longitudinal Section through Calorimeter Cylinder.
This was achieved by blowing onto a suitable glass tube two extremely small spherical bulbs at right angles to each other at ca. 2 cm. apart. The ampoule bulbs are fractured against the stirrer in rapid sequence for quick circulation of the calorimetric fluid.

Temperature Sensing - In the C.T.E. calorimeter a thermistor, F 53 (Standard Telephone and Cable Ltd.), was incorporated into a Wheatstone bridge powered by a 2 v. accumulator. Temperature changes were measured in terms of resistance change by a decade resistance box capable of reading to 0.1 ohm. The resistance change was recorded by a null-method, using either a 110 or 1400 ohm. Scalamp galvanometer. In the case of the adiabatic calorimeter three F 53 thermistors were inserted. One of them served exactly the same purpose as for the C.T.E. calorimeter. The remaining two thermistors inside the calorimeter were each coupled with a corresponding thermistor outside the water jacket (an evacuated large size Dewar vessel). One pair was connected to a Wheatstone bridge and used for recording temperature differential (see p. 80). The others were sensing thermistors for the adiabatic control unit (circuit on p. 87).

Calorimeter Heaters - Three heaters of resistances, 7.62, 15.631, 30.096, (for adiabatic calorimeter), 9.800 and 11.674 ohm. for C.T.E. calorimeter were made out of 42 S.W.G. constantan wire. The heater winding was specially designed to meet the requirement of complete transference of heat from wire to calorimetric fluid through the thin membrane of glass. Thin plates of mica were arranged in cross-sectional fashion with small grooves at regular intervals for equidistant winding. The ends of the constantan wire were soldered onto relatively thick copper wire (18 S.W.G.) which were in contact with the glass wall for efficient lateral flow of heat. The assembly was immersed in transformer oil, (see diagram p. 75).
Fig. Thermistor Bridges: (a) Temperature Differential.
(b) Temperature Detection.
Details of the circuit diagram are as follows:

(i) **Adiabatic calorimeter** - This specially designed circuit diagram is given in fig. on p. 82. It can be seen that the total current \( I \) flowing is given by

\[
I = I_1 + I_2 = \frac{V_s}{R_s}
\]

or

\[
I_1 + \frac{V_1}{10} = \frac{V_s}{R_s}
\]

or

\[
I_1 = \frac{V_s}{R_s} - \frac{V_1}{10}
\]

Where

\[ V_s = \text{potential across standard resistance} \]

\[ V_1 = \text{potential across resistance} \]

To measure the potential drop across the heater \( V_H \), it is necessary to exclude the voltage across the lead resistance. Hence measurement of potentials across \( P_1 \) and \( P_2 \) is made and the relationship that expresses voltage across heater element is

\[
V_H = 10V_1 + P_2 - P_1
\]

In actual practice \( P_1, P_2, V_1, V_s \) are measured on potentiometer (E. Tinsley & Co., No: 167943). The potentiometer is equipped with a 2V D.C. constant voltage source (Cropico), standardized with standard cell (Weston Normal cell No: L-409188).

(ii) **C.T.E. Calorimeter** - In this circuit (on p. 84) the potential drop across the heater (via a potential divider resistance) includes the potential across the heater leads. The power is reduced by a factor, \( F \), to take account of this fact. From circuit it could be seen that
I  Current  

R_{L1}  Lead Resistances  

R_{L2}  "  "  

R_H  Heater Resistance (15.930 kΩ)  

R_s  Standard Resistance (0.99820 kΩ)  

R_{100}  Resistance (100 kΩ)  

R_{10}  "  (10 Ω)  

V_I, V_s, P_1, P_2  Potential  

T  Timer (± 0.31 Sec.)  

C_V  Constant 6 Volt Source.  

Fig.  Heater and Timing Circuit Diagram for Adiabatic Calorimeter.
\[ R_{H} \text{ (calc.)} = 11 \frac{V_{1}}{V_{S} - V_{1}/10} \]
\[ P = R_{H} \text{ (actual)} / R_{H} \text{ (calc.)} \]

and \[ P = 11 \frac{V_{1}}{V_{S} - V_{1}/10} \]

\( V_{1}, V_{S} \) are measured by a potentiometer similar to that used for the adiabatic calorimeter (see above). \( R_{H} \text{ (actual)} \) is measured accurately during heater construction using probe leads across the windings only.

**TABLE** - Some typical potential readings obtained with different heaters are as follows

(1) **Adiabatic calorimeter**

<table>
<thead>
<tr>
<th>( R_{H} ) (ohm)</th>
<th>( V_{S} ) (volt.)</th>
<th>( V_{1} ) (volt.)</th>
<th>( P_{1} ) (volt.)</th>
<th>( P_{2} ) (volt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.672</td>
<td>0.3935</td>
<td>0.3926</td>
<td>0.0245</td>
<td>0.3533</td>
</tr>
<tr>
<td>15.601</td>
<td>0.3357</td>
<td>0.4202</td>
<td>0.0160</td>
<td>0.4023</td>
</tr>
<tr>
<td>30.006</td>
<td>0.2014</td>
<td>0.4336</td>
<td>0.0108</td>
<td>0.4221</td>
</tr>
</tbody>
</table>

\( R_{H} \) = Heater resistance \( (25^\circ) \), \( V_{S} \) = potential across standard resistance \( (0.9982) \), \( V_{1} \) = potential across 10 ohm. resistance, \( P_{1} \) = potential after lead resistance \( R_{L1} \), and \( P_{2} \) = potential before lead resistance \( R_{L2} \)

(2) **C.T.E. Calorimeter**

<table>
<thead>
<tr>
<th>( R_{H} ) (ohm.)</th>
<th>( V_{S} ) (volt.)</th>
<th>( V_{1} ) (volt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.800</td>
<td>0.5740</td>
<td>0.4800</td>
</tr>
<tr>
<td>11.674</td>
<td>0.5025</td>
<td>0.4883</td>
</tr>
</tbody>
</table>

\( R_{H} \) = Heater resistance \( (25^\circ) \), \( V_{S} \) = potential across standard resistance, \( V_{1} \) = potential across resistance \( (10 \text{ ohm.}) \)
I = Current
R_L1 = Lead Resistance
R_L2 = Lead Resistance
R_H = Heater Resistance
R_S = Standard Resistance (0.9990 ohms)
R_10 = Resistance (10 ohms)
R_100 = Resistance (100 ohms)
V_I and V_S = Potential across
T = Timer (± 0.01 Sec)
C_V = Constant Voltage Source

Fig. Heater and Timing Circuit Diagram for C.T.E. Calorimeter.
The Adiabatic Control Unit - Circuit diagram for this control unit is shown in Fig. on p. 87 and is responsible for detecting and maintaining a negligible temperature differential across the boundary wall of the calorimeter. The circuit is a modification of the design of Raymond et al. In this work 25 W. monitor heater and 250 W. booster heater with the latter coupled through a variac transformer was satisfactory.

(4) Operating Procedure

(i) Adiabatic Calorimeter - The loaded calorimeter (as on p. 75) was immersed and clamped in a vertical position inside the unsilvered pyrex Dewar (an adiabatic shield) containing 4 litres of stirred water. The temperature inside the calorimeter was maintained at ca. 25°. Fluctuations in temperature were adjusted by the adiabatic control unit. Care was taken to maintain a small heat transference value across the boundary of the calorimeter to compensate for the heat of stirring. Fore-run readings were taken on a Scalamp Galvanometer at \( \frac{1}{2} \) or 1 min. intervals after the calorimeter acquired the thermal equilibrium (in ca. 1 hr.). The fracture of the ampoule containing the sample initiated the reaction. An exothermic reaction gave a decrease in resistance and endothermic reaction an increase. Reading during this period following ampoule fracture was the after-run.

Graphical extrapolation of the fore-run reading to the start of the reaction gave \( R_1 \) and back extrapolation of the linear part of the after-run reading to the same time, gave \( R_2 \). Using the same procedure over a similar temperature range for the calibration gave \( R_3 \) and \( R_4 \).

(ii) O.T.E. Calorimeter - Operating procedure was similar to above. The loaded calorimeter was immersed in water tank whose temperature (± 0.01°) was automatically controlled by a relay system.
In both C.T.E. and adiabatic system value of $R_1$ and $R_2$, $R_3$ and $R_4$ were obtained from resistance vs. time graph (see p. 116) and from the equation, enthalpy of reaction was obtained.

\[
\frac{\text{Heat of reaction}}{\text{Heat of calibration}} = \frac{\log R_1/R_2}{\log R_3/R_4}
\]

$R_1 > R_2$, $R_3 > R_4$

A detailed procedure for a typical C.T.E. and adiabatic runs for the heat of neutralization is given in Chapter Six p. 109.

(5) **Electronic Circuit for Adiabatic Control Unit**

In the following figure and table details of the Adiabatic Control Circuit are given:
### Table: Electrical components of the Adiabatic control unit

<table>
<thead>
<tr>
<th>RESISTANCES</th>
<th>CAPACITORS</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYMBOL</td>
<td>VALUE (Ω)</td>
</tr>
<tr>
<td>R₁</td>
<td>2K</td>
</tr>
<tr>
<td>R₂</td>
<td>2K</td>
</tr>
<tr>
<td>R₃</td>
<td>150</td>
</tr>
<tr>
<td>R₄</td>
<td>500</td>
</tr>
<tr>
<td>R₅</td>
<td>15</td>
</tr>
<tr>
<td>R₆</td>
<td>100 (W)</td>
</tr>
<tr>
<td>R₇</td>
<td>10K</td>
</tr>
<tr>
<td>R₈</td>
<td>1M</td>
</tr>
<tr>
<td>R₉</td>
<td>1CM</td>
</tr>
<tr>
<td>R₁₀</td>
<td>220K</td>
</tr>
<tr>
<td>R₁₁</td>
<td>22K (4W)</td>
</tr>
<tr>
<td>R₁₂</td>
<td>1M</td>
</tr>
<tr>
<td>R₁₃</td>
<td>270</td>
</tr>
<tr>
<td>R₁₄</td>
<td>3.2K</td>
</tr>
<tr>
<td>R₁₅</td>
<td>4.7K</td>
</tr>
<tr>
<td>R₁₆</td>
<td>1M</td>
</tr>
<tr>
<td>R₁₇</td>
<td>1M</td>
</tr>
<tr>
<td>R₁₈</td>
<td>4.7K</td>
</tr>
<tr>
<td>R₁₉</td>
<td>4.7K (2W)</td>
</tr>
<tr>
<td>R₂₀</td>
<td>5K (5W)</td>
</tr>
<tr>
<td>R₂₁</td>
<td>5K (5W)</td>
</tr>
<tr>
<td>R₂₂</td>
<td>21 (5%)</td>
</tr>
</tbody>
</table>
V₁ Pentode valve, EF 86 Type, for signal voltage amplifier
V₂ Pentode valve, EF 91 Type, for signal voltage amplifier
V₃ Tetrode valve, 2D21 Type, for power amplifier
V₄ Tetrode valve, 2D21 Type, for power amplifier

A Relay post office 5000 Type to booster-heater 250W
B Relay post office 5000 Type to monitor-heater 25W

d₁ Diode OA81 Type
D₂ Diode OA81 Type

T₁ Thermistor F23 (Standard Telephones and Cables Ltd.)
T₂ incorporated to A.C. Wheatstone bridge circuit

a,a Connections for 3 V.A.C. bridge supply from transformer TR₂

TR₁ Step-up transformer from 250v. to 500v.
TR₂ Step-down transformer from 250v. to 6.3v.
TR₃ Step-down transformer from 6.3v. to 3v.

M Mains, 250 V.A.C. (50 c.p.s.)

I₁ Input 250v. to step-up transformer TR₁
I₂ Input 6.3v. to step-down transformer TR₂

① Output 250v. converted to D.C. voltage by built in E.R.T. for
  anodes of pentodes
② Output 250v. to relays
③ Output 6.3v. to negative bias device
④ Output 3v. to A.C. Wheatstone bridge
SECTION II. EXPERIMENTAL TECHNIQUES

CHAPTER FOUR: (A) THERMAL ANALYSIS

(B) MASS SPECTROMETRY
(A) THERMAL ANALYSIS

(1) Thermal Analysis - This technique makes use of the fact that the physical or chemical properties of the substances may change as a function of temperature. The theoretical and practical aspects of the subject are well-established. This has resulted in the commercial construction of various types of thermal analyzers, while the growing importance of this technique has resulted in a wide range of applications in the fields of physical, analytical, organic and inorganic chemistry. The recent publication of two new journals called "Thermochemica Acta" (Jan. 1970) and "Thermal Analysis" Quarterly (by Hungarian Academy of Science, in press) testifies to the scope of the subject. This technique has been used for the measurements of (i) transition energy involved at a phase change and (ii) relative dissociation energy in certain phosphorus compounds (see pp. 159, 161 under thermal analysis results).

Usually the results derived from thermal analyzers are based on the methods of Thermogravimetric analysis (TGA); Thermomechanical analysis (TMA); Electrical thermal analysis (ETA); Differential thermal analysis (DTA) and Differential Scanning calorimetry (DSC). Very often TGA is combined with DTA or DSC and has proved to be a most versatile combination. Most of these analyzers are designed to handle a milligram quantity of substance with a high degree of accuracy and precision. In the present work TGA (Netzsch and Du Pont), DTA (Du Pont) and DSC (Perkin Elmer) were used.

(2) Thermogravimetric analysis (TGA) - This method is based on weight loss (or gain) as a function of temperature or time. Hence in practice a thermogram of weight loss against temperature is recorded on a linear (or
time base X-Y) recorder. The pyrolysis curve is then analysed primarily for decomposition modes, followed by detailed investigations from the derivative graph (of weight per unit time vs. temperature).

Since this method is based on weight loss under the conditions of heating, a thermobalance of high precision is an essential requirement. A detailed discussion of thermobalances has been published. In practice these balances are classified as semi-micro, micro and macro, depending upon the quantity of sample that could be handled for analysis. The thermobalances used here are semi-micro and micro types.

(3) Differential Thermal Analysis (DTA) - This method produces a plot of the difference between the sample temperature and an inert reference temperature vs. the environmental temperature. In this type of analysis a micro quantity (mg) of sample is placed in small metallic pan and subjected to a controlled programming of temperature simultaneously with an inert reference sample (usually alumina). Both these specimens are heated simultaneously on the same platform. The difference in temperature between the two specimens is recorded as a thermovoltage by a thermocouple and fed via an amplifier to an X-Y recorder (see diagram on p. 93). When a phase transition occurs in the sample under study, AT becomes negative or positive. The area between the peak and the base line corresponds to the heat content requires for the transition to occur. In the present work, thermal analyses were performed on a Du Pont 900 thermal analyzer (basic unit) along with a DTA cell (850°C) using a nitrogen flow and a quartz cover for the DTA cell.

(4) Differential Scanning Calorimetry (DSC) - This method is based on a compensation principle whereby temperature differences produced by the
Fig. (a) Block diagram of Differential Thermal Analyzer measuring actual temperature change in a sample and records $\Delta T$ vs. $T$.

Fig. (b) Block diagram of Differential Scanning Calorimeter measuring power required to control a temperature change and records Calories set $\Delta T$ vs. Temperature.
sample undergoing a phase transition are compensated by suitably controlling the source of heat to the sample. In actual practice the equipment is so designed (see block diagram on P. 93) to measure the differential energy required to keep both sample and reference at the same temperature throughout the analysis, and records calories per second vs. temperature. The area under the peak gives a direct measure for the transition enthalpy. With suitable calibration this technique may be used to measure the heat capacities and the energies associated in endothermic and exothermic process. Heats of transition are measured with reference to standard substances (usually indium) whose specific heat is well known. Such a procedure is also adopted here to find the transition energy of the phosphorus-phosphorus bonded compounds and their molecular adducts. In practice the indium peak area \( (P_{\text{In}}) \) is expressed as

\[
P_{\text{In}} = \text{Weight of In} \times \text{Specific heat of In}
\]

and also

\[
P_{\text{Sample}} = \text{Weight of Sample} \times \text{Specific heat of Sample}
\]

Therefore with reference to indium the heat of transition (or heat of fusion, \( \Delta H_{\text{fus}} \)) of unknown sample could be expressed as

\[
\Delta H_{\text{Sample}} = \frac{P_{\text{Sample}}}{P_{\text{In}}} \times \frac{\text{Weight of In}}{\text{Weight of Sample}} \times \Delta H_{\text{fus}} \text{ In}
\]

\( P = \) peak area

\( \Delta H_{\text{fus}} \text{ In} = 6.79 \text{ cal.g}^{-1} \)

The type of thermal analyzer employed for this work was the DSC-1B (Perkin Elmer). Full details of the instrument and its operational principles and procedure are discussed in the commercial manual.
(5) **Standard Test Materials** - Recently a possible list of standard test materials covering a wide range of temperature and heat content measurement using DTA has been published by Gar. This list includes potassium nitrate, potassium sulphate, potassium chromate, potassium hydrogen sulphate, potassium persulphate, silver sulphate, silicon dioxide, barium carbonate and aluminium oxide. Indium is selected as the standard reference for DSC measurements for the following reasons (i) material of high grade purity is usually available (claimed to be 99.9999% pure), (ii) the specific heat is well-known, \((0.057 \text{ cal. g}^{-1} \text{ C}^{-1})\), (iii) the temperature reproducibility (i.e. \(156.5^\circ\), see P.147 for thermogram) at the melting point is excellent, (iv) on fusion, indium produces a sharp peak with a minimum transition temperature range. In the present work all the DSC results for transition energy calculations are measured against an indium standard.
(1) **Mass Spectrometry** - The use of a high-energy electron beam to split up molecules into fragment particles, and subsequent collection of these particles by means of an electric and magnetic field mutually at right angles, is the basis of mass spectrometry. The theoretical and practical background to the subject is now well-known and well documented. Thermodynamic data obtained from electron impact studies for phosphorus compounds, in general, and phosphorus-phosphorus bonded compounds in particular, are discussed in this thesis; electron impact studies are also extended to include the molecular adducts of phosphorus and certain phosphorus (III) compounds. e.g. triiodophosphine, diphenylphosphine, tribromophosphine-boron triiodide (1:1) adduct, triiodophosphine-boron tribromide (1:1) adduct, boron triiodide, tribromophosphine, and boron tribromide. Detailed results are presented in chapter 8 on P.161.

The basic quantitative equation for ion collection is

\[
\frac{m}{e} = \frac{H^2r^2}{2v}
\]

Thus it can be seen that the mass to charge ratio (m/e) is proportional to the square of the radius of motion (r) of the ion for constant field (H) and accelerating potential (v).

Molecular ions and atomic ions are formed whenever collision occurs with an electron having energy equal to, or greater than, the ionization energy of the molecule or atom (ionization energies range between 7 to 15 ev and bombarding potentials are commonly 70 ev). If the electron energy is below the ionization energy no ions are formed. Thus in actual operation it can be seen that the intensity of the ion current decreases steeply as the electron bom-
barding energy is lowered. In practice, ion current (usually positive or negative) is plotted against electron energy expressed in electron volt (ev). The shape of the curve obtained for positive ions is sigmoid, with tailing portion exponential in character, while for negative ions it is a sharp or broad peak followed by a sigmoid-like curve. The units for ion current are either expressed in microamperes or cross-section for ionization (i.e., units of $10^{-16}$ cm$^2$) or arbitrary units.

It is observed that increase in electron energy beyond 70 ev has little effect on the magnitude of ion-current and the curve obtained is relatively insensitive. Therefore an electron energy beam of 10 - 70 ev is commonly used for analytical purposes. In this work appearance potentials were obtained in order to derive bond dissociation energies in triiodophosphine and in diphenosphorus tetraiodide. Relevant results and the thermochemical cycles using these appearance and ionization potentials are given on pp.164-166. The cracking pattern in molecular adducts like I$_2^-$ - Br$_2^-$, Br$_2^-$ - BI$_3^-$ and those concerning phosphorus (III) compounds like PI$_3^-$, BI$_2^-$, PBr$_3^-$, BBr$_3^-$ are also discussed.

(2) The determination of appearance potential from Ionization Efficiency Curve (I.E.C.) Various treatments have been advanced, some empirical and others based on energy-compensating principles to derive accurate values of ionization and appearance potentials. In the present work the semi-logarithmic plot method of Lossing was used with argon as internal standard. The appearance potential measurements were performed using an AEI model MS2R mass spectrometer (in collaboration with Mr. M. Paul of the Explosives Research Development Establishment (E.R.D.E.)) with a direct inlet system for solid samples of PI$_3^-$ and P$_2$I$_4^-$.
Application of appearance potential (A.P.) and ionization potential (I.P.) data to thermodynamic problems 73, 74, 187, 190, 191, 213 Many thermodynamic functions are obtainable from appearance and ionization potential measurements e.g. electron affinity, proton affinity and bond dissociation energies (D or B.D.E.). A relationship for bond dissociation energy in terms of ionization and appearance potentials is

$$D(R - x) = A.P.(R^+)_{Rx} - I.P.(R) - KE - E_{\text{Excitation}} \ldots \ldots (1)$$

where

$$KE = \text{molecule (under consideration)}$$

$$KE = \text{kinetic energy of } R^+, < 0.2 \text{ ev}$$

$E_{\text{Excitation}} = 0$ as the reference states with respect to the neutral molecule and ion (parent or fragment(s)) are taken as ground states (i.e. lowest vibrational level of the nuclei of the molecule).

Thus it can be seen that by definition A.P. is the minimum electron energy required to produce an ion (or fragment ion) along with a neutral fragment, and I.P. by definition is the minimum energy required to remove an electron to produce a parent-ion from the neutral molecule.

Comparing ionization process with ionization from electron impact, a small difference in energy sometime occurs due to the kinetic energy imparted to the ion by accelerating voltage. If the kinetic energy imparted to the ion is ignored, then a relationship with thermochemical data can be derived for the appearance potential (A.P.) and bond dissociation energy (D).
SECTION II. EXPERIMENTAL TECHNIQUES

CHAPTER FIVE: EFFUSION VACUETRY
**Effusion Manometry**

(1) **Effusion Manometry** - This technique is based on an isothermal gas transportation mechanism at low applied pressure with negligible molecule-molecule collisions as compared with molecule-wall collisions at the orifice (or porous medium). The molecules in the effusing gas under such conditions possess no turbulent flow which is the essential condition for this mode of gas motion. Therefore a relationship for the conversion of the material loss to equilibrium vapour pressure can be derived on the basis of the kinetic theory of gases. In practice this relationship is well-established for the measurement of vapour pressure. Usually this technique is applied for substances having low vapour pressure at ambient temperature. In this work vapour pressure measurements are used to obtain the latent heats of sublimation for triiodophosphine and diphosphorus tetraiodide. These are then incorporated in the thermodynamic cycles (see p.200) for triiodophosphine and diphosphorus tetraiodide to obtain values for the average bond dissociation energy ($E_p-1$) and the bond energy ($E_{p-p}$) respectively.

(2) **Basic Principles** - On the basis of the kinetic theory of gases Knudsen proposed the following relationship between density ($\rho$), number of impacts ($n$) and the pressure ($p$) for an effusing gas

\[
\rho = Nm \quad \text{(I)}
\]

\[
n = \frac{1}{2}Nc \quad \text{(II)}
\]

\[
p = \frac{1}{2}Nmc^2 \quad \text{(III)}
\]

where

- $N$ = number of molecules $\text{cm}^{-3}$
- $m$ = mass of substance
- $c$ = mean velocity of molecules
- $c^2$ = mean square velocity of molecules
and for an equilibrium between a solid and its saturated vapour pressure
the expression is derived by combining equation (I) and (II) which gives

\[ \frac{W}{tA} = \frac{1}{4} \bar{\sigma} \left( \varrho - \varrho' \right) \quad ............ (IV) \]

where

\[ \varrho = \text{density of the material inside} \]
the effusion cell
\[ \varrho' = \text{density of the material outside} \]
the orifice of the cell (where
if condensed immediately \( \varrho = \varrho' \))
\[ W = \text{weight of material effused} \]
through area (A) in time (t)

While combining equations (I) and (III) with the ideal gas equation,
the mean thermal molecular velocity, \( \bar{\sigma} \), is obtained which is as follows

as \( p = \frac{1}{2} Nm \bar{\sigma}^2 \)

and \( Nm = \varrho = \frac{M}{V} = \frac{M}{RT/\rho} = \frac{M\varrho}{RT} \)

also \( \frac{1}{3} \bar{\sigma}^2 = \frac{\varrho}{\rho} (\bar{\sigma})^2 \) (Maxwellian law of distribution of velocities)

where
\[ (\bar{\sigma})^2 = \text{mean velocity square of the molecules} \]

therefore \( p = \frac{\varrho}{\rho} (\bar{\sigma})^2 \times \frac{M\varrho}{RT} \)

or \( (\bar{\sigma})^2 = \frac{8RT}{M \rho} \)

or \( \bar{\sigma} = \sqrt{\frac{8RT}{M \rho}} \quad ............ (V) \)

Also combining (IV) and (V) one arrives at
\frac{W}{tA} = \frac{1}{4} \sqrt{\frac{\text{CRT}}{\text{M}}} \frac{\text{Hp}}{\text{KT}}

or

p = \frac{W}{At} \sqrt{\frac{2\pi RT}{M}} \quad \cdots \cdots \cdots \ \text{(VI)}

where

\begin{align*}
\text{p} & \text{ = vapour pressure (mm. Hg.)} \\
\text{W} & \text{ = weight of substance (g)} \\
\text{A} & \text{ = area of the orifice (cm}^2\text{)} \\
\text{t} & \text{ = time (sec.)} \\
\text{R} & \text{ = gas constant (erg. deg}^{-1}\text{ mole}^{-1}\text{)} \\
\text{T} & \text{ = absolute temperature (}^\circ\text{K)} \\
\text{M} & \text{ = molecular weight of substance}
\end{align*}

Also, during the effusion process some of the molecules undergo diffuse reflection with the wall of the orifice. This can be expressed as

\[ C_o = \frac{(2 - f_o)}{f_o} \]

where

\[ f_o = \text{fraction of the molecules undergoing diffuse reflection, thus } f_o = 1 \]

Equation (VI) is valid under the ideal conditions of infinitely thin edges to the orifice and a large mean free path to orifice diameter ratio. In practice, neither of these conditions is exactly met and correction factors are introduced. The shape factor can be determined either by the Knudsen method (Kn) which gives

\[ \text{Kn} = 1 + \frac{8r}{2L} \]

or it can be obtained empirically from Clausing, who tabulated the ratio of \( \frac{1}{r} \) (where \( l \) = length of orifice, \( r \) = radius of the orifice) vs. the clausing constant (Kn).

Thus the equation (VI) can be written as
The values of \( p \) determined by equations (1) and (2) differ little. These equations are now extensively used in effusion manometry. Sometimes the average value of \( p \) from these equations is used.

Recent theoretical work by Hibi and Pahl has shown the importance of a correction factor \( (F) \) which takes account of the fact that, in practice, \( r/\lambda \) does not approach zero and hence for the transition region where \( r/\lambda \) is not zero a correction factor given by

\[
F = \left( \frac{1}{1 + K_2 \frac{r}{2\lambda}} \right) \quad \text{is applied.}
\]

where

\( r = \) radius of orifice

\( \lambda = \) mean free path

\( K_2 = \) shape constant \( = 0.48 \)

\( (r/2\lambda) \) is a pressure sensitive term

and hence the final equation is

\[
p = \frac{W}{tA} \sqrt{\frac{2 \pi RT}{M}} x \frac{1}{Kc} x \frac{1}{\delta_0} \quad \cdots \cdots \quad (3)
\]

The final equation (3) is in fact equal to equation (2) \( \times F \). In all these equations the value of \( \delta_0 \) is conventionally put to unity.
(3) Design and Construction - The effusion manometer is a vacuum holding assembly embodying (i) a sample cell fabricated in an inert material in good thermal contact with the heat sink, (ii) cold-zone devices to condense the material effused, and, (iii) a heat sink.

The effusion manometer designed and constructed for this work in this laboratory is shown on pp. 105, 107. This manometer is similar to that constructed by Edwards and Kington. Certain modifications were introduced because of (i) the corrosive nature of the phosphorus compounds (ii) the attack on greases of all kinds by such compounds (iii) quantitative removal of a thermally-conducting grease, around the outer body of the effusion cell, has been proved to be very difficult.

In view of the above limitations, the effusion cell body was made of stainless steel and the foil of gold. The foil was kept in position by a stainless steel locking ring. The drilling of the hole in the foil was performed using a No. 80 high-speed twist drill. The burring was removed by a fine abrasive paste. The radius of the orifice was measured by a travelling microscope and planimeter on a photomicrograph (linear magnification x 100). The thickness was deduced from a knowledge of weight, density and surface area of the foil. Thermal contact of the cell with the heat sink was established via precision threading (26 t.p.i. Whitworth) into the circular copper block. The circular copper block was silver-soldered to the Kovar-to-pyrex glass seal. Complete vacuum integrating was ensured by liberal use of Torr-Seal. The vacuum inside the effusion manometer \(10^{-5}\) mm. Hg was produced via a mercury diffusion pump backed by two-stage rotary pump. The pressure measurements were via a Pirani Gauge inserted just after the ball joint of the effusion manometer (i.e. before the liquid nitrogen trap) and also by a McLeod Gauge situated between two liquid nitrogen traps. The vapour pressure
Fig.  Longitudinal Section through Effusion Manometer.

(x 0.33 natural size)
studies were performed within two distinct temperature ranges. For the
temperature range of 20-26°C the thermal equilibrium of the heat sink was
achieved in the water-bath controlled by Tronac thermistor regulator
(FTC - 1000, Provo, Utah) leading to a bath control of \( \pm 0.001^\circ \text{C} \). The tem­
perature of the bath was monitored by a Quartz thermometer (2301A, Hewlett
Packard) with a resolution of \( \pm 0.0001^\circ \text{C} \) and also a mercury thermometer
(N.P.L., B.S. 791 type) of accuracy \( \pm 0.001^\circ \text{C} \). For the temperature range
50 - 80°C, the heat sink was immersed in a paraffin bath regulated by a
sunvio controller (type 102/4) coupled with a Callenkamp thermostat. The
temperature of this bath was recorded to \( \pm 0.02^\circ \text{C} \) using a mercury thermometer

The constructed effusion manometer was successfully operated up to a
maximum temperature limit of 100°C and with a vacuum of \( 10^{-5} \) mm. Hg, main­
tained over two to three days.

**Longitudinal Section through Effusion Manometer (x 0.33 natural size)**

\( (P = \text{part}) \)

- \( P_1 \) Copper block
- \( P_2 \) Stainless steel cell
- \( P_3 \) Kovar metal
- \( P_4 \) Lower pyrex section
- \( P_5 \) Central pyrex section (attached to vacuum line)
- \( P_6 \) Upper pyrex section (cold finger, FG 5 type, Quickfit)
- \( P_7 \) Flanges, 2.2 cm. (Quickfit)
- \( P_8 \) Tap \( H_{(10)} \) type (Jencons)
- \( P_9 \) Socket joint 625 type (Quickfit)
Longitudinal Section through Effusion Manometer (natural size)

and Effusion Cell (x 2 natural size)

A  Pyrex glass
B  Stainless steel
C  Gold foil
D  Duralumin yoke
E  Kovar metal
F  Silver solder
G  Copper block

(4) Operating procedure - The effusion manometer was initially operated with ferrocene as test compound. The ferrocene was twice re-crystallized using a modified purification procedure of Edwards et al. m.p.t. 175-176°C (found) (lit. m.p.t. 175.5-176°C). The cell was filled to two-thirds capacity with the powdered ferrocene. The cell was inserted into heat sink for effusion over a temperature range of 20-280°C for the period of ca. 24 hr. The effused material was immediately condensed above the effusion cell by a cold finger containing acetone and carbon dioxide mixture at ca. 80°C. At the end of each run, the weight loss of the ferrocene from the cell was determined by difference. Throughout the effusion manometric work weighings to ± 0.0001 g. were made using the same Stanton electrical balance (CL 41). The handling of the cell was via a special pair of clippers and thermally insulated gloves. In the case of phosphorus compounds, a similar procedure was followed in a dry-box filled with an inert atmosphere of nitrogen. Each run, in all of these experiments, was repeated at least three times over the same temperature range.
SECTION III. RESULTS

CHAPTER SIX: THERMOCHEMICAL RESULTS
The literature gives the following heats of solution of THAM in 0.1 M HCl at 25° for N (H₂O : THAM) = 500 to 2000. In this work the range 728-779 for the C.T.E. calorimeter and 964-1058 for adiabatic calorimeter was used.

<table>
<thead>
<tr>
<th>- ΔH (Kcal mole⁻¹)</th>
<th>- ΔH (KJ mole⁻¹)</th>
<th>Reference</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.107 ± 0.001</td>
<td>29.736</td>
<td>Gunn 207</td>
<td>1965</td>
</tr>
<tr>
<td>7.111 ± 0.001</td>
<td>29.752</td>
<td>Sunner and Wadsø 208</td>
<td>1966</td>
</tr>
<tr>
<td>7.112 ± 0.002</td>
<td>29.757</td>
<td>ØJeland 209 and Wadsø</td>
<td>1967</td>
</tr>
<tr>
<td>7.109 ± 0.001</td>
<td>29.744</td>
<td>Hill, ØJeland and Wadsø 177</td>
<td>1969</td>
</tr>
<tr>
<td>7.155 ± 0.002</td>
<td>29.936</td>
<td>This Work</td>
<td></td>
</tr>
</tbody>
</table>
TABLE  Heat of neutralization of THAM<sup>k</sup> in 0.1 M HCl

(150 ml.) at 25<sup>o</sup> using C.T.E. Calorimeter

$$(\text{HOCH}_2)_3\text{CCH}_2(\text{cryst}) + \text{HCl} \quad \text{H}_2\text{O} (\text{liq.}) = [(\text{HOCH}_2)_3\text{CCH}_2\text{Cl}^-\cdot n\text{H}_2\text{O}$$

<table>
<thead>
<tr>
<th>Wt. THAM (g)</th>
<th>N</th>
<th>$\Delta H_{obs}$ (KJ mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>$\Delta H_{obs}$ (Kcal mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3898</td>
<td>728</td>
<td>-29.99</td>
<td>-7.17</td>
</tr>
<tr>
<td>1.3000</td>
<td>777</td>
<td>-29.85</td>
<td>-7.13</td>
</tr>
<tr>
<td>1.3256</td>
<td>762</td>
<td>-31.00</td>
<td>-7.41</td>
</tr>
<tr>
<td>1.3836</td>
<td>730</td>
<td>-30.67</td>
<td>-7.33</td>
</tr>
<tr>
<td>1.5480</td>
<td>749</td>
<td>-29.75</td>
<td>-7.11</td>
</tr>
<tr>
<td>1.3791</td>
<td>732</td>
<td>-29.91</td>
<td>-7.15</td>
</tr>
<tr>
<td>1.5142</td>
<td>768</td>
<td>-30.42</td>
<td>-7.28</td>
</tr>
<tr>
<td>2.663</td>
<td>797</td>
<td>-29.50</td>
<td>-7.05</td>
</tr>
<tr>
<td>1.3243</td>
<td>762</td>
<td>-30.06</td>
<td>-7.19</td>
</tr>
<tr>
<td>1.3228</td>
<td>763</td>
<td>-29.75</td>
<td>-7.11</td>
</tr>
<tr>
<td>1.3778</td>
<td>768</td>
<td>-29.66</td>
<td>-7.09</td>
</tr>
<tr>
<td>1.3185</td>
<td>766</td>
<td>-30.20</td>
<td>-7.18</td>
</tr>
<tr>
<td>1.3175</td>
<td>766</td>
<td>-29.91</td>
<td>-7.15</td>
</tr>
<tr>
<td>1.3264</td>
<td>761</td>
<td>-29.66</td>
<td>-7.09</td>
</tr>
<tr>
<td>1.3506</td>
<td>747</td>
<td>-29.54</td>
<td>-7.06</td>
</tr>
<tr>
<td>1.3207</td>
<td>764</td>
<td>-29.75</td>
<td>-7.11</td>
</tr>
<tr>
<td>1.2949</td>
<td>750</td>
<td>-29.96</td>
<td>-7.16</td>
</tr>
<tr>
<td>1.3177</td>
<td>766</td>
<td>-29.83</td>
<td>-7.13</td>
</tr>
<tr>
<td>1.3188</td>
<td>765</td>
<td>-29.99</td>
<td>-7.17</td>
</tr>
<tr>
<td>1.3743</td>
<td>735</td>
<td>-29.87</td>
<td>-7.144</td>
</tr>
</tbody>
</table>

<sup>k</sup>Tris(hydroxymethyl)aminomethane

<sup>N</sup> is mole ratio of water to THAM

$25^oC = 298.15^oK$
### TABLE  Heat of neutralization of THAM<sup>x</sup> in 0.1 M HCl

(200 ml.) at 25° using Adiabatic Calorimeter

<table>
<thead>
<tr>
<th>Wt. THAM (g)</th>
<th>N&lt;sup&gt;x&lt;/sup&gt;</th>
<th>ΔHobs&lt;sup&gt;x&lt;/sup&gt; KJ mole&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>ΔHobs&lt;sup&gt;x&lt;/sup&gt; Kcal mole&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3900</td>
<td>963</td>
<td>29.83</td>
<td>-7.13</td>
</tr>
<tr>
<td>1.3954</td>
<td>965</td>
<td>29.87</td>
<td>-7.14</td>
</tr>
<tr>
<td>1.2721</td>
<td>1058</td>
<td>29.83</td>
<td>-7.13</td>
</tr>
<tr>
<td>1.3201</td>
<td>1020</td>
<td>29.91</td>
<td>-7.155</td>
</tr>
</tbody>
</table>

<sup>x</sup>Tris(hydroxymethyl)aminomethane

<sup>x</sup> is mole ratio of water to THAM
Details of a typical C.T.E. run:

(1) EXPERIMENT: $\Delta H_r \text{H}_2\text{NCO(CH}_2\text{CH)}_3\text{ (THAM)}$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Time (min)</th>
<th>Calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>4024.7</td>
<td>0</td>
<td>4034.1</td>
</tr>
<tr>
<td>4024.8</td>
<td>$\frac{1}{2}$</td>
<td>4034.0</td>
</tr>
<tr>
<td>4024.9</td>
<td>1</td>
<td>4034.0</td>
</tr>
<tr>
<td>4025.0</td>
<td>$\frac{1}{2}$</td>
<td>4033.9</td>
</tr>
<tr>
<td>4025.1</td>
<td>2</td>
<td>4033.8</td>
</tr>
<tr>
<td>4025.2</td>
<td>FORE-RUN</td>
<td>4033.8</td>
</tr>
<tr>
<td>4025.3</td>
<td>3</td>
<td>4033.7</td>
</tr>
<tr>
<td>4025.4</td>
<td>$\frac{3}{2}$</td>
<td>4033.6</td>
</tr>
<tr>
<td>4025.5</td>
<td>4</td>
<td>4033.5</td>
</tr>
<tr>
<td>4025.6</td>
<td>$\frac{4}{2}$</td>
<td>4033.4</td>
</tr>
<tr>
<td>4025.7</td>
<td>5</td>
<td>4033.3</td>
</tr>
<tr>
<td>3957.7</td>
<td>$\frac{5}{2}$</td>
<td>4023.2</td>
</tr>
<tr>
<td>3958.5</td>
<td>6</td>
<td>4007.2</td>
</tr>
<tr>
<td>3959.0</td>
<td>$\frac{6}{2}$</td>
<td>3991.2</td>
</tr>
<tr>
<td>3959.6</td>
<td>7</td>
<td>(160.10 sec.) 3975.3</td>
</tr>
<tr>
<td>3960.1</td>
<td>$\frac{7}{2}$</td>
<td>3960.3</td>
</tr>
<tr>
<td>3960.6</td>
<td>8</td>
<td>3950.0</td>
</tr>
<tr>
<td>3961.1</td>
<td>$\frac{8}{2}$</td>
<td>3949.1</td>
</tr>
<tr>
<td>3961.7</td>
<td>9</td>
<td>3949.5</td>
</tr>
<tr>
<td>3962.2</td>
<td>$\frac{9}{2}$</td>
<td>3950.0</td>
</tr>
<tr>
<td>3962.7</td>
<td>10</td>
<td>3950.6</td>
</tr>
<tr>
<td>3963.4</td>
<td>$10\frac{1}{2}$</td>
<td>3951.1</td>
</tr>
</tbody>
</table>

ampoule fracture at 5 min.
### Observations:

<table>
<thead>
<tr>
<th>Reaction Temp</th>
<th>Heater Time</th>
<th>Reactant</th>
<th>Reactant Temp</th>
<th>Solvent</th>
<th>Solvent Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.00 ± 0.01°C</td>
<td>160.10 sec.</td>
<td>THAM (trimethylethyl)</td>
<td>121.14 Mol. wt.</td>
<td>0.1 N HCl (150 ml.)</td>
<td>735 moles (solvent/reactant)</td>
</tr>
</tbody>
</table>

**Vol.**

N = moles (solvent/reactant) = 735
\( R_1 = 4025.8 \text{ ohms}, \log R_1 = 3.60485220 \)

\( R_2 = 3958.8 \text{ ohms}, \log R_2 = 3.59756356 \)

\[ \text{Difference} = 67.0 \text{-} \Delta T = 0.00720364 \]

\( R_3 = 4033.2 \text{ ohms}, \log R_3 = 3.60564976 \)

\( R_4 = 3947.5 \text{ ohms}, \log R_4 = 3.59632214 \)

\[ \text{Difference} = 85.7 \text{-} \Delta T = 0.00932762 \]

\[ V_s = 0.5740 \text{ Volts} \]

\[ V_I = 0.4800 \text{ Volts} \]

\[ P = 11V_s(V_s-V_I/10) = 2.7772 \text{ watts} \]

\[ R_H(\text{calo.)} = 11V_s/(V_s-V_I/10) = 10.038 \text{ ohms} \]

\[ f = \frac{R_H(\text{actual})}{R_H(\text{calo.)}} = \frac{9.600/10.038}{0.9762} \]

(III) **CALCULATIONS:**

\[ \Delta H = \frac{f \times P}{4164} \times \frac{M}{w} \times t \times \frac{\Delta T}{\Delta T_c} \]

(IV) **RESULT:** 7.14 kcal/mole

*This is not precisely the numerical temperature but rather a function directly proportional to it (see p. 76).*
$\Delta H_{\text{neu}} = 7.14 \text{ Kcal mole}^{-1}$

Fig. Typical Constant Temperature Environment Calorimeter Run for THAM.
Details of a typical adiabatic run:

(I) EXPERIMENT: $\Delta H_r \text{H}_2\text{NO(}\text{CH}_2\text{OH})_3\text{ (THAM)}$

<table>
<thead>
<tr>
<th>REACTION</th>
<th>TIME (MIN)</th>
<th>CALIBRATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>4610.0</td>
<td>0</td>
<td>4610.7</td>
</tr>
<tr>
<td>4610.4</td>
<td>1</td>
<td>4610.6</td>
</tr>
<tr>
<td>4610.3</td>
<td>2</td>
<td>4610.5</td>
</tr>
<tr>
<td>4610.2</td>
<td>3</td>
<td>4610.4</td>
</tr>
<tr>
<td>4610.2</td>
<td>4</td>
<td>4610.3</td>
</tr>
<tr>
<td>4610.1</td>
<td>5</td>
<td>4610.2</td>
</tr>
<tr>
<td>4610.1</td>
<td>6</td>
<td>4610.0</td>
</tr>
<tr>
<td>4609.9</td>
<td>7</td>
<td>4609.9</td>
</tr>
<tr>
<td>4609.9</td>
<td>8</td>
<td>4609.8</td>
</tr>
<tr>
<td>4609.9</td>
<td>9</td>
<td>4609.7</td>
</tr>
<tr>
<td>4609.9</td>
<td>10</td>
<td>4609.5</td>
</tr>
<tr>
<td>4609.8</td>
<td>11</td>
<td>4599.5</td>
</tr>
<tr>
<td>4550.8</td>
<td>12</td>
<td>4585.5</td>
</tr>
<tr>
<td>4550.8</td>
<td>13</td>
<td>4871.5</td>
</tr>
<tr>
<td>4550.9</td>
<td>14</td>
<td>4558.5</td>
</tr>
<tr>
<td>4550.9</td>
<td>15</td>
<td>4552.1</td>
</tr>
<tr>
<td>4550.9</td>
<td>16</td>
<td>4551.7</td>
</tr>
<tr>
<td>4550.9</td>
<td>17</td>
<td>4551.5</td>
</tr>
<tr>
<td>4550.9</td>
<td>18</td>
<td>4551.5</td>
</tr>
<tr>
<td>4550.8</td>
<td>19</td>
<td>4551.4</td>
</tr>
<tr>
<td>4550.7</td>
<td>20</td>
<td>4551.4</td>
</tr>
<tr>
<td>4550.6</td>
<td>21</td>
<td>4551.3</td>
</tr>
</tbody>
</table>

*ampoule fracture at 10 min.*
| 4550.5 | 22 | 4551.2 |
| 4550.5 | 23 | 4551.4 |
| 4550.4 | 24 | 4551.0 |
| 4550.3 | 25 | 4550.9 |
| 4550.2 | 26 | 4550.8 |
| 4550.1 | 27 | 4550.7 |
| 4550.0 | 28 | 4550.6 |
| 4549.9 | 29 | 4550.5 |
| 4549.8 | 30 | 4550.4 |
| 4549.7 | 31 | 4550.3 |
| 4549.5 | 32 | 4550.3 |
| 4549.5 | 33 | 4550.1 |
| 4549.4 | 34 | 4549.9 |
| 4549.2 | 35 | 4549.8 |
| 4549.1 | 36 | 4549.7 |
| 4548.8 | 37 | 4549.6 |
| 4548.6 | 38 | 4549.5 |
| 4548.4 | 39 | 4549.4 |
| 4548.1 | 40 | 4549.3 |

**II) OBSERVATIONS:**

| REACTION TEMP | = 25.00 ± 0.01°C |
| HEATER TIME | = 236.72 sec. |
| WT. REACTANT | = 1.3201 g. Tris(hydroxymethyl)aminomethane (THAM) |
| MOL. WT. REACTANT | = 121.14 |
| VOL. SOLVENT | = 0.1 N HCl (200 ml) |
| N = moles (solvent/reactant) | = 1020 |
\[ R_1 = 4609.9 \text{ ohms}, \log R_1 = 3.66369150 \]
\[ R_2 = 4551.6 \text{ ohms}, \log R_2 = 3.65816409 \]

\[ \text{Difference} \ 58.3 \ \Omega, \ \tau_T = 0.00552741 \]

\[ R_3 = 4609.5 \text{ ohms}, \log R_3 = 66355332 \]
\[ R_4 = 4552.4 \text{ ohms}, \log R_4 = 65824041 \]

\[ \text{Difference} \ 57.1 \ \Omega, \ \tau_T = 0.00541341 \]

\[ V_H = 10V_1 + P_2 - P_1 = 4.5894 \]
\[ V_1 = 0.4203 \text{ volts} \]
\[ V_2 = 0.3356 \text{ volts} \]
\[ P_1 = 0.0161 \text{ volts} \]
\[ P_2 = 0.4025 \text{ volts} \]

\[ I = \frac{V_s - V_1}{10} = 0.29417 \]
\[ R_s = 0.9982 \text{ ohm.} \]
\[ R_H = \frac{V_H}{I} = 15.601 \text{ ohm.} \]

\[ P = V_H \times I \]

(III) **Calculations:**

\[ \Delta H = \frac{-P}{4184} \times \frac{M}{w} \times t \times \frac{\Delta \tau_T}{\tau_T} \]

(IV) **Result:** 7.15 kcal/mole

^This is not precisely the numerical temperature but rather a function directly proportional to it (see p. 76).
\[ R(\text{ohm}) \]

Graph showing the relationship between calibration time and reaction time. The graph includes points and lines indicating data, with annotations such as:

- \[ R_1 = 4603.9 \, \Omega \]
- \[ R_2 = 4550 \, \Omega \]
- \[ R_3 = 4600.5 \, \Omega \]
- \[ R_4 = 4524 \, \Omega \]

Equation:

\[ \Delta H_{\text{rea}} = 7.15 \, \text{kcal mole}^{-1} \]

Legend:

- Typical Adiabatic Calorimeter Run for TiM.
Thermodynamic Cycle for Pentaphenylocyclopentaphosphine

Legend

A = \((\text{C}_6\text{H}_5\text{P})_5\) (cryst.) \hspace{1cm} (1) \hspace{1cm} = \text{Br}_2 \text{ (in } \text{C}_6\text{H}_6\text{)}

B = \text{C}_6\text{H}_5\text{FBr}_2 \text{ (in } \text{C}_6\text{H}_6\text{)} \hspace{1cm} (2) \hspace{1cm} = \text{C}_6\text{H}_6

C = \text{C}_6\text{H}_5\text{FBr}_2 \text{ (liq.)} \hspace{1cm} (3), (4) \hspace{1cm} = \text{H}_2\text{O}

D = \text{C}_6\text{H}_5\text{PO}_2\text{H}_2 \text{ (aq.)} \hspace{1cm} (5), (6), (7) \hspace{1cm} = \text{Br}_2 \text{ (aq.)}

E = \text{C}_6\text{H}_5\text{PO}_2\text{H}_2 \text{ (cryst.)}

F = \text{C}_6\text{H}_5\text{PO}_2\text{H}_2 \text{ (aq.)}
The following detailed reactions refer to the generalized thermodynamic cycle for pentaphenylocyclopentaphosphine. (All steps at $25^\circ C$). Heats of mixing of the products were ignored.

Step (1) The oxidation of pentaphenylocyclopentaphosphine with benzene solution of bromine

$$\frac{1}{5}(C_6H_5P)_5\text{ (cryst.)} + Br_2\text{ (in } C_6H_6) = C_6H_5PBr_2\text{ (in } C_6H_6) \quad \Delta H_1$$

$$\Delta H_1 = \Delta H_f^0\{C_6H_5PBr_2\text{ in } C_6H_6\} - \frac{1}{5}\Delta H_f^0\{(C_6H_5P)_5\text{, cryst.}\} - \Delta H_f^0\{Br_2\text{ in } C_6H_6\}$$

The stoichiometry of this bromination is described on p. 133

Step (2) The solution of phenyl dibromophosphine in benzene

$$C_6H_5PBr_2\text{ (liq.)} + C_6H_6\text{ (liq.)} = C_6H_5PBr_2\text{ (in } C_6H_6) \quad \Delta H_2$$

$$\Delta H_2 = \Delta H_f^0\{C_6H_5PBr_2\text{ in } C_6H_6\} - \Delta H_f^0\{C_6H_5PBr_2\text{, liq.}\}$$

Step (3) Hydrolysis of phenyl dibromophosphine

$$C_6H_5PBr_2\text{ (liq.)} + 2H_2O\text{ (liq.)} = (C_6H_5PO_2H_2 + 2HBr) \text{ aq.} \quad \Delta H_3$$

$$\Delta H_3 = \Delta H_f^0\{C_6H_5PO_2H_2, \text{ aq.}\} + 2\Delta H_f^0\{HBr, \text{ aq.}\} - 2\Delta H_f^0\{H_2O, \text{ liq.}\} - \Delta H_f^0\{C_6H_5PBr_2, \text{ liq.}\}$$

Step (4) The solution of phenyl phosphonic acid

$$C_6H_5PO_2H_2\text{ (cryst.)} + H_2O\text{ (liq.)} = (C_6H_5PO_2H_2) \text{ aq.} \quad \Delta H_4$$

$$\Delta H_4 = \Delta H_f^0\{C_6H_5PO_2H_2, \text{ aq.}\} - \Delta H_f^0\{C_6H_5PO_2H_2, \text{ cryst.}\}$$
Step (5) Oxidation of phenylphosphonous acid

\[
C_6H_5PO_2H_2 \text{ (cryst.)} + (Br_2 + H_2O) \text{aq.} = [C_6H_5PO_3H_2 + 2HBr] \text{aq.} \quad \Delta H_5
\]

\[
\Delta H_5 = \Delta H^0_f \{C_6H_5PO_3H_2, \text{aq.}\} + 2\Delta H^0_f \{\text{HBr, aq.}\} - \Delta H^0_f \{C_6H_5PO_2H_2, \text{cryst.}\}
\]

\[
- \Delta H^0_f \{\text{Br}_2, \text{aq.}\} - \Delta H^0_f \{\text{H}_2O, \text{liq.}\}
\]

Step (6) Oxidation of pentaphenylcyclopentaphosphine

\[
\frac{1}{5}(C_6H_5P)_5 \text{ (cryst.)} + (2\text{Br}_2 + 3\text{H}_2O) \text{aq.} = [C_6H_5PO_3H_2 + 4\text{HBr}] \text{aq.} \quad \Delta H_6
\]

\[
\Delta H_6 = \Delta H^0_f \{C_6H_5PO_3H_2, \text{aq.}\} + 4\Delta H^0_f \{\text{HBr, aq.}\} - \frac{4}{5}\Delta H^0_f \{(C_6H_5P)_5, \text{cryst.}\}
\]

\[
- 2\Delta H^0_f \{\text{Br}_2, \text{aq.}\} - 3\Delta H^0_f \{\text{H}_2O, \text{liq.}\}
\]

Summing up the equations for \(\Delta H_5\) to \(\Delta H_6\), one obtains,

\[
\Delta H_1 - \Delta H_6 = \Delta H^0_f \{\text{Br}_2, \text{aq.}\} - \Delta H^0_f \{\text{Br}_2 \text{ in } C_6H_6\}
\]

Step (7) Oxidation of phenyltribromophosphine

\[
C_6H_5PBr_2 \text{ (liq.)} + (\text{Br}_2 + 3\text{H}_2O) \text{aq.} = (C_6H_5PO_3H_2 + 4\text{HBr}) \text{aq.} \quad \Delta H_7
\]

\[
\Delta H_7 = \Delta H^0_f \{C_6H_5PO_3H_2, \text{aq.}\} + 4\Delta H^0_f \{\text{HBr, aq.}\} - \Delta H^0_f \{C_6H_5PBr_2, \text{liq.}\}
\]

\[
- \Delta H^0_f \{\text{Br}_2, \text{aq.}\} - 3\Delta H^0_f \{\text{H}_2O, \text{liq.}\}
\]

\[
\therefore \Delta H_7 = \Delta H_3 + \Delta H_4 + \Delta H_5
\]
Results for the cycle \( (\text{C}_6\text{H}_2\text{P})_2 \)

The experimental values at 23°C for individual steps in the cycle for pentaphenylocyclopentaphosphine are as follows:

<table>
<thead>
<tr>
<th>Step</th>
<th>( \Delta H_{\text{obs}} )</th>
<th>K cal mol(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(-28.64 \pm 0.35)</td>
<td>(This work)</td>
</tr>
<tr>
<td>2</td>
<td>(0.58 \pm 0.01)</td>
<td>(This work)</td>
</tr>
<tr>
<td>3</td>
<td>(-41.7 \pm 0.08)</td>
<td>(lit. and confirmed)</td>
</tr>
<tr>
<td>4</td>
<td>(-1.43 \pm 0.04)</td>
<td>(lit. and confirmed)</td>
</tr>
<tr>
<td>5</td>
<td>(-61.31 \pm 0.33)</td>
<td>(This work)</td>
</tr>
<tr>
<td>6</td>
<td>(-133.48 \pm 0.32)</td>
<td>(This work)</td>
</tr>
<tr>
<td>7</td>
<td>(-104.36 \pm 0.13)</td>
<td>(This work)</td>
</tr>
</tbody>
</table>

From the equations of the generalized thermodynamic cycle it can be seen that

\[
\Delta H_6 = \sum_{i=1}^{5} \Delta H_i = \Delta H^0_f [\text{Br}_2, \text{aq.}] - \Delta H^0_f [\text{Br}_2, \text{C}_6\text{H}_6]
\]

It can be seen from the measured data above, that the LHS of this equation equals to \(-0.98 \pm 0.53\) K cal. The heat of solution of \(\text{Br}_2\) in \(\text{C}_6\text{H}_6\) is reported on \(\text{Pu} 130\) as \(-1.44 \pm 0.02\) K cal and the corresponding value for \(\text{H}_2\text{O}\) is known as \(-0.62\) K cal. Thus the RHS equals \(0.82\) K cal.; hence the discrepancy is \(1.80\) K cal.

Also, comparison of the value obtained from \(\Delta H_7\) (i.e. \(-104.36 \pm 0.13\) K cal) with that of the sum of \(\Delta H_3 + \Delta H_4 + \Delta H_5\) (i.e. \(-104.44 \pm 0.34\) K cal), shows consistency in this section of the cycle. Therefore the discrepancy mentioned above of \(1.80\) K cal must be attributed to reactions 1, 2 or 6 (probably 6).
TABLE  C.T.E. Calorimetric Results for Step No: (1) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in benzene (125 ml.) at 25°C. N(Ph:Br₂) = 511-1075

\[
(\Phi P)_5 \text{ (cryst.)} + 5 \text{Br}_2 \text{ (in Ph)} = 5 \Phi \text{Br}_2 \text{ (in Ph)}
\]

\[\Phi = C_6H_5\]

<table>
<thead>
<tr>
<th>Wt. ((\Phi P)_5) (g)</th>
<th>Bromine required (g)</th>
<th>Bromine used (g)</th>
<th>% (Excess)</th>
<th>N(Ph: P)</th>
<th>(\Delta H_{obs.}^{\text{kJ mole}^{-1}})</th>
<th>(\Delta H_{obs.}^{\text{Kcal mole}^{-1}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3067</td>
<td>0.4543</td>
<td>0.4685</td>
<td>3.12</td>
<td>565</td>
<td>-127.57</td>
<td>-30.49</td>
</tr>
<tr>
<td>0.3077</td>
<td>0.4781</td>
<td>0.4982</td>
<td>4.20</td>
<td>563</td>
<td>-124.05</td>
<td>-29.65</td>
</tr>
<tr>
<td>0.3003</td>
<td>0.4448</td>
<td>0.4769</td>
<td>7.21</td>
<td>577</td>
<td>-117.95</td>
<td>-28.19</td>
</tr>
<tr>
<td>0.1504</td>
<td>0.2280</td>
<td>0.2385</td>
<td>4.60</td>
<td>1151</td>
<td>-117.28</td>
<td>-28.03</td>
</tr>
<tr>
<td>0.1573</td>
<td>0.2330</td>
<td>0.2385</td>
<td>2.36</td>
<td>1100</td>
<td>-124.18</td>
<td>-29.63</td>
</tr>
<tr>
<td>0.1483</td>
<td>0.2196</td>
<td>0.2385</td>
<td>8.60</td>
<td>1167</td>
<td>-111.38</td>
<td>-26.62</td>
</tr>
<tr>
<td>0.1480</td>
<td>0.2192</td>
<td>0.2385</td>
<td>8.80</td>
<td>1170</td>
<td>-116.02</td>
<td>-27.73</td>
</tr>
<tr>
<td>0.1513</td>
<td>0.2225</td>
<td>0.2385</td>
<td>7.19</td>
<td>1144</td>
<td>-120.04</td>
<td>-28.69</td>
</tr>
<tr>
<td>0.1512</td>
<td>0.2225</td>
<td>0.2385</td>
<td>7.19</td>
<td>1145</td>
<td>-119.95</td>
<td>-28.67</td>
</tr>
<tr>
<td>0.3000</td>
<td>0.4558</td>
<td>0.50138</td>
<td>10.00</td>
<td>577</td>
<td>-120.04</td>
<td>-28.69</td>
</tr>
</tbody>
</table>

\[\text{Av. } \Delta H_{obs} = -119.83 \pm 1.46 \text{ KJ mole}^{-1}\]

\[= -28.64 \pm 0.35 \text{ Kcal mole}^{-1}\]

(1) Complete thermodynamic cycle for pentaphenylcyclopentaphosphine is shown on P. 208

(2) The stoichiometry of the reaction under calorimetric conditions was established in various steps of the cycle.

\[25^\circ C = 298.15^\circ K, \text{ Av = Average, Obs = observed}\]
TABLE C.T.E. Calorimetric Results for Step No: (2) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in benzene (125 ml.) at 25°C

$$\Phi PBr_2 (\text{liq.}) + \Phi H (\text{liq.}) = \Phi PBr_2 (\text{in } \Phi H)$$

<table>
<thead>
<tr>
<th>Wt. $\Phi PBr_2$ (g)</th>
<th>(∆H$_{\Phi PBr_2}$)</th>
<th>$\Delta$Hobs at KJ mole$^{-1}$</th>
<th>$\Delta$Hobs at Kcal mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3644</td>
<td>1179</td>
<td>2.38</td>
<td>0.57</td>
</tr>
<tr>
<td>0.5400</td>
<td>795</td>
<td>2.43</td>
<td>0.58</td>
</tr>
<tr>
<td>0.5337</td>
<td>805</td>
<td>2.43</td>
<td>0.58</td>
</tr>
<tr>
<td>0.4892</td>
<td>878</td>
<td>2.30</td>
<td>0.55</td>
</tr>
<tr>
<td>0.7048</td>
<td>609</td>
<td>2.72</td>
<td>0.65</td>
</tr>
<tr>
<td>0.6628</td>
<td>648</td>
<td>2.22</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Av. $\Delta$Hobs. = 2.43 ± 0.04 KJ mole$^{-1}$

= 0.53 ± 0.01 Kcal mole$^{-1}$

Calorimetric values for step No: (3) and No: (4) stated in thermodynamic cycle for pentaphenylcyclopentaphosphine are from lit. which has been confirmed here.
TABLE: C.T.E. Calorimetric Results for step No: (5) in Thermodynamic cycle for Pentaphenylcyclopentaphosphine referring to the following reaction in aq. Bromine (125 mL) at 25°C, E(H₂O:Br₂) = 264.5

\[
\PhiPO₂H₂ (\text{cryst.}) + (2\text{Br}_2 + 3\text{H}_2\text{O}) (\text{aq.}) = (\PhiPO₃H₂ + 4\text{Br}) (\text{aq.})
\]

<table>
<thead>
<tr>
<th>Wt. (\PhiPO₂H₂) (g) x 2</th>
<th>Bromine required (g)</th>
<th>(\text{N(H}_2\text{O:}\PhiPO₂H₂)</th>
<th>% (Excess) Bromine used</th>
<th>(\Delta\text{Hobs}_{\text{KJ mole}})</th>
<th>(\Delta\text{Hobs. Kcal mole}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3552</td>
<td>0.3995</td>
<td>2776</td>
<td>5.13</td>
<td>-253.21</td>
<td>-60.52</td>
</tr>
<tr>
<td>0.3554</td>
<td>0.3997</td>
<td>2774</td>
<td>5.08</td>
<td>-258.78</td>
<td>-61.85</td>
</tr>
<tr>
<td>0.3550</td>
<td>0.3993</td>
<td>2777</td>
<td>5.18</td>
<td>-255.55</td>
<td>-61.08</td>
</tr>
<tr>
<td>0.3545</td>
<td>0.3987</td>
<td>2782</td>
<td>12.46</td>
<td>-250.16</td>
<td>-59.79</td>
</tr>
<tr>
<td>0.1758</td>
<td>0.1977</td>
<td>5609</td>
<td>6.22</td>
<td>-257.90</td>
<td>-61.64</td>
</tr>
<tr>
<td>0.2063</td>
<td>0.2320</td>
<td>4780</td>
<td>3.45</td>
<td>-259.53</td>
<td>-62.03</td>
</tr>
<tr>
<td>0.1761</td>
<td>0.1980</td>
<td>5599</td>
<td>6.06</td>
<td>-260.04</td>
<td>-62.23</td>
</tr>
</tbody>
</table>

Av. \(\Delta\text{Hobs} = -256.52 \pm 1.38 \text{ KJ mole}^{-1}\)

Av. \(\Delta\text{Hobs} = -61.31 \pm 0.33 \text{ Kcal mole}^{-1}\)
TABLE  Adiabatic calorimetric Results for Step No. (6) in Thermodynamic cycle for PentaPhenylCyclopentaphosphosphate referring to the following reaction in aq. Bromine (200 ml.) at 25° C \( \text{N(H}_2\text{O:Br}_2\text{)} = 2383 \)

\( \text{(C}_6\text{H}_5\text{P})_5 \text{(cryst.)} + \text{(2Br}_2 \text{+ 3H}_2\text{O) (aq.)} = \text{(C}_6\text{H}_5\text{PO}_2\text{H}_2 \text{+ 4HBr) aq.}} \)

<table>
<thead>
<tr>
<th>It. ( \text{(C}_6\text{H}_5\text{P})_5 ) (g)</th>
<th>Bromine ( \text{required (g)} )</th>
<th>( \text{N(H}_2\text{O:C}_6\text{H}_5\text{P)} )</th>
<th>% (Excess)</th>
<th>( \Delta\text{Hobs} ) KJ mole(^{-1} )</th>
<th>( \Delta\text{Hobs} ) Kcal mole(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2307</td>
<td>0.6322</td>
<td>5205</td>
<td>9.35</td>
<td>-559.82</td>
<td>-133.80</td>
</tr>
<tr>
<td>0.2304</td>
<td>0.6813</td>
<td>5212</td>
<td>9.49</td>
<td>-553.50</td>
<td>-132.29</td>
</tr>
<tr>
<td>0.2300</td>
<td>0.6802</td>
<td>5221</td>
<td>9.67</td>
<td>-561.11</td>
<td>-134.11</td>
</tr>
<tr>
<td>0.2302</td>
<td>0.6807</td>
<td>5216</td>
<td>9.59</td>
<td>-560.07</td>
<td>-133.86</td>
</tr>
<tr>
<td>0.2305</td>
<td>0.6816</td>
<td>5210</td>
<td>9.44</td>
<td>-557.94</td>
<td>-133.35</td>
</tr>
</tbody>
</table>

\( \text{Av. } \Delta\text{Hobs.} = -553.48 \pm 1.34 \text{ KJ mole}^{-1} \)

\( = -133.48 \pm 0.32 \text{ Kcal mole}^{-1} \)

(1) The length of the main period was ca. 30 min.

and readings were continued for further 120 min. The fore-run period was 10 min.
TABLE C.T.E. Calorimetric Results for step No: (7) in Thermodynamic cycle for Pentaphenylocyclopentaphosphine referring to the following reaction in aq. Bromine (125 ml.) at 25°C. N(H₂O:Br₂) = 3351-4171

\[ \text{C}_6\text{H}_5\text{PBr}_2 \text{(liq.)} + (\text{Br}_2 + 3\text{H}_2\text{O}) \text{(aq.)} = (\text{C}_6\text{H}_5\text{PO}_{3}\text{H}_2 + 4\text{HBr}) \text{(aq.)} \]

<table>
<thead>
<tr>
<th>Wt. C₆H₅PBr₂ (g)</th>
<th>Bromine required (g)</th>
<th>N(H₂O: C₆H₅PBr₂)</th>
<th>% (Excess) Bromine used</th>
<th>ΔHobs₁ KJ/mole</th>
<th>ΔHobs₁ Kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5200</td>
<td>0.3101</td>
<td>3579</td>
<td>6.90</td>
<td>-436.56</td>
<td>-104.36</td>
</tr>
<tr>
<td>0.4335</td>
<td>0.2586</td>
<td>4293</td>
<td>3.01</td>
<td>-435.18</td>
<td>-104.01</td>
</tr>
<tr>
<td>0.5118</td>
<td>0.3053</td>
<td>3636</td>
<td>8.58</td>
<td>-437.52</td>
<td>-104.57</td>
</tr>
<tr>
<td>0.4308</td>
<td>0.2570</td>
<td>4320</td>
<td>3.65</td>
<td>-437.35</td>
<td>-104.53</td>
</tr>
</tbody>
</table>

Av. ΔHobs = \(-436.64 \pm 0.54\) KJ/mole⁻¹

= \(-104.36 \pm 0.13\) Kcal/mole⁻¹
TABLE C.T.E. Calorimetric Results for the Heat of Solution of Bromine in Benzene (100 and 200 ml.)

<table>
<thead>
<tr>
<th>Wt. Bromine (g)</th>
<th>$\text{H}^{(\text{C}_6\text{H}_5\text{Br}_2)}$</th>
<th>$\Delta H_{\text{obs}}$ KJ mole$^{-1}$</th>
<th>$\Delta H_{\text{obs}}$ Kcal mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3789</td>
<td>541</td>
<td>-6.15</td>
<td>-1.47</td>
</tr>
<tr>
<td>0.7456</td>
<td>550</td>
<td>-5.90</td>
<td>-1.41</td>
</tr>
<tr>
<td>0.7674</td>
<td>535</td>
<td>-6.07</td>
<td>-1.45</td>
</tr>
<tr>
<td>0.7320</td>
<td>560</td>
<td>-6.02</td>
<td>-1.44</td>
</tr>
<tr>
<td>0.7513</td>
<td>546</td>
<td>-5.98</td>
<td>-1.43</td>
</tr>
</tbody>
</table>

Average $\Delta H_{\text{obs}} = -6.02 \pm 0.08$ KJ mole$^{-1}$

$= -1.44 \pm 0.02$ Kcal mole$^{-1}$
<table>
<thead>
<tr>
<th>Wt. THF (g)</th>
<th>(N(H_2O:THF))</th>
<th>(\Delta H_{obs,1}) KJ mole(^{-1})</th>
<th>(\Delta H_{obs,1}) Kcal mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0105</td>
<td>495</td>
<td>-16.44</td>
<td>-3.95</td>
</tr>
<tr>
<td>0.8544</td>
<td>585</td>
<td>-13.84</td>
<td>-3.30</td>
</tr>
<tr>
<td>0.8550</td>
<td>584</td>
<td>-14.06</td>
<td>-3.36</td>
</tr>
<tr>
<td>1.0100</td>
<td>495</td>
<td>-16.48</td>
<td>-3.94</td>
</tr>
<tr>
<td>0.9961</td>
<td>502</td>
<td>-15.15</td>
<td>-3.62</td>
</tr>
<tr>
<td>0.8777</td>
<td>570</td>
<td>-14.85</td>
<td>-3.55</td>
</tr>
</tbody>
</table>

\(\Delta H_{obs} = 15.15 \pm 0.46\) KJ mole\(^{-1}\)

\(= 3.62 \pm 0.11\) Kcal mole\(^{-1}\)

This heat of solution was the part of the four step procedure drawn for attempted concordant reaction for \((C_6H_5)\) to enhance the speed of reaction but with little success.
TABLE Adiabatic Calorimetric Results for Polymeric Phenylphosphine

(so called) referring to the following reaction in Benzene (200 ml.)

\[ \frac{1}{n} (C_6H_5P)_n \text{ (cryst.)} + 2Br_2 \text{ (in } C_6H_5H) = (C_6H_5PBr)_n \text{ (in } C_6H_5H) \]

\[ N(C_6H_5H) = 319 \]

\[
\begin{array}{cccccccc}
\text{Wt. } (C_6H_5)n & \text{Wt. Bromine required} & N(C_6H_5H) & \% \text{ (Excess)} & \Delta H_{obs} & \Delta H_{obs} & \text{Av. } \Delta H_{obs} \\
\text{(g)} & \text{(g)} & C_6H_5P & & \text{KJ mole}^{-1} & \text{Kcal mole}^{-1} & \text{KJ mole}^{-1} \\
0.1094 & 0.3235 & 2531 & 297.77 & -205.18 & -49.04 & -198.32 \\
0.1050 & 0.3105 & 2633 & 314.04 & -196.94 & -44.68 & -198.32 \\
0.1100 & 0.3253 & 2517 & 295.20 & -194.72 & -46.54 & -198.32 \\
0.1047 & 0.3096 & 2645 & 315.24 & -198.61 & -47.47 & -198.32 \\
0.1123 & 0.3321 & 2466 & 287.11 & -200.25 & -47.86 & -198.32 \\
0.1092 & 0.3229 & 2536 & 298.14 & -204.64 & -48.91 & -198.32 \\
0.1102 & 0.3252 & 2513 & 294.47 & -196.86 & -47.05 & -198.32 \\
0.1046 & 0.3093 & 2647 & 315.64 & -198.15 & -47.36 & -198.32 \\
0.1076 & 0.3182 & 2573 & 304.02 & -199.49 & -47.68 & -198.32 \\
\end{array}
\]

Av. \( \Delta H_{obs} = -198.32 \pm 1.80 \text{ KJ mole}^{-1} (C_6H_5P) \)

= -47.40 \pm 0.43 \text{ Kcal mole}^{-1} (C_6H_5P)

(1) This was slow reaction, fore-run 10 min., main reaction period of 35 min. and aft-run readings were recorded up to 180 min.

(2) Reaction based on \( C_6H_5PBr_2 \) was attempted with no success.

(3) Calorimetric reaction based on \( C_6H_5PBr_4 \) was further subjected for bromide content analysis by conventional titrimetry and gave the expected results \( C_6H_5PBr_4 + 3H_2O = C_6H_5P_3O_4 + 4HBr \).
The establishment of the stoichiometry of the bromination of

(i) pentaphenylocyclopentaphosphine and (ii) polymeric phenylphosphine

(i) Bromination of \((\mathcal{C}_6\mathcal{H}_5\mathcal{P})_5\) was based on the following reactions in benzene solution at room temperature:

\[
\frac{1}{5} \ (\mathcal{C}_6\mathcal{H}_5\mathcal{P})_5 + \mathcal{B}r_2 \quad = \quad \mathcal{C}_6\mathcal{H}_5\mathcal{P}\mathcal{B}r_2
\]

\[
\frac{1}{5} \ (\mathcal{C}_6\mathcal{H}_5\mathcal{P})_5 + 2\mathcal{B}r_2 \quad = \quad \mathcal{C}_6\mathcal{H}_5\mathcal{P}\mathcal{B}r_4
\]

Pentaphenylocyclopentaphosphine and bromine (5-10% excess, based on the formation of phenyldibromophosphine) were separately dissolved in benzene and the solutions mixed in a separating funnel. Initially a yellow precipitate appeared but on vigorous shaking it dissolved and a clear solution was obtained. On hydrolysis two distinct layers were obtained. The upper, (benzene), layer was separated and washed thrice, after which the washings were bromide-free. The aqueous fractions were collected and analysed for bromide by argentimetric titration. The bromide analysis indicated that quantitative formation of the phenyldibromophosphine occurred under these conditions.

This procedure was repeated using a slight excess of bromine (5-10%), based on the formation of phenyltetrabromophosphorane. In this case the bromide recovery indicated ca. 50% phenyltetrabromophosphorane formation up to the time of the extraction. Further washings gave another 10% of phenyltetrabromophosphorane. Leaving the reaction mixture at room temperature for 24 hr. gave quantitative conversion to phenyltetrabromophosphorane. Thus it appears that conversion to phenyltetrabromophosphorane is slow compared with phenyldibromophosphine. Therefore the calorimetric reaction was based on phenyldibromophosphine (see thermochemical results p. 125).
(ii) Bromination of \((C_5H_5P)_n\) was based on the following reactions in benzene:

\[
\frac{1}{n} (C_5H_5P)_n \text{ (suspension)} + Br_2 = C_5H_5PBr_2
\]

\[
\frac{1}{n} (C_5H_5P)_n \text{ (suspension)} + 2Br_2 = C_5H_5PBr_4
\]

A similar procedure for the determination of bromide content was adopted as mentioned above for pentaphenylcyclopentaphosphine.

The reaction based on phenyldibromophosphine using 5-7% excess bromine did not seem to proceed, even after repeated attempts. The reaction based on phenyltetram bromophosphine using ca. 200% excess bromine was relatively slow in excess of bromine but went to completion, as was evident from the quantitative recovery of bromide content, after several hours.

For calorimetry, an excess of ca. 300% bromine was used, when the reaction period was ca. 30 min. (see thermochemical results p. 132).

Establishment of the stoichiometry of the oxidation of phenylphosphonous acid with aqueous bromine

This was based on the following reaction.

\[
C_6H_5PO_2H_2 + Br_2 + H_2O = C_6H_5PO_2H_2 + 2Br
\]

It is possible that the above equilibrium lies appreciably to the left.

Phenylphosphonous acid was allowed to react with excess bromine (5-10%) and the resulting solution was analysed for bromine by an iodometric method. Bromine recovery indicated 100% reaction within 15 min. at room temperature.
TABLE C.T.E. Calorimetric Results for Tricyanophosphine referring to the following reaction in water (200 ml.) at 22°C.

\[
P(\text{CN})_3 \text{(cryst.)} + 3\text{H}_2\text{O (liq.))} + (\text{H}_3\text{PO}_3 + 3\text{HCN}) \text{(sol.)}
\]

<table>
<thead>
<tr>
<th>Wt. P(\text{CN})_3 (g)</th>
<th>N(H_2\text{O}+P(\text{CN})_3)</th>
<th>(\Delta H_{\text{obs}}) KJ mole(^{-1})</th>
<th>(\Delta H_{\text{obs}}) Kcal mole(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2491</td>
<td>4862</td>
<td>-207.86</td>
<td>-49.68</td>
</tr>
<tr>
<td>0.1898</td>
<td>6381</td>
<td>-207.15</td>
<td>-49.51</td>
</tr>
<tr>
<td>0.2055</td>
<td>5894</td>
<td>-207.15</td>
<td>-49.51</td>
</tr>
<tr>
<td>0.2599</td>
<td>4660</td>
<td>-206.02</td>
<td>-49.24</td>
</tr>
<tr>
<td>0.2444</td>
<td>4955</td>
<td>-209.73</td>
<td>-50.14</td>
</tr>
<tr>
<td>0.2500</td>
<td>4845</td>
<td>-206.69</td>
<td>-49.40</td>
</tr>
</tbody>
</table>

Average, \(\Delta H_{\text{obs}}\) = -207.44 ± 0.50 KJ mole\(^{-1}\) = -49.58 ± 0.12 Kcal mole\(^{-1}\)

(1) P(\text{CN})_3 thrice sublimed used for this purpose

(2) Purity checked by microanalysis and potentiometric titrations
TABLE C.T.E. Calorimetric Results for Tri(isocyanato)phosphine referring to the following reaction in water (200 ml.) at 25°C.

\[ \text{P(\text{NCO})}_3 (\text{liq.}) + 3\text{H}_2\text{O (liq.)} = (\text{MNCO} + \text{H}_3\text{PO}_3) (\text{sol.}) \]

| Wt. P(\text{NCO})_3 (g) | N(\text{H}_2\text{O}:P(\text{NCO})_3) | \(\Delta H_{\text{obs}^\ominus1}\) KJ mole | \(\Delta H_{\text{obs}^\ominus1}\) Kcal mole |  \\
|------------------------|-------------------------------|---------------------------------|---------------------------------|  \\
| 0.1747                | 9984                          | -333.63                        | -79.74                          |  \\
| 0.1950                | 8946                          | -334.47                        | -79.94                          |  \\
| 0.1737                | 10000                         | -333.33                        | -79.67                          |  \\
| 0.2140                | 8169                          | -331.92                        | -79.33                          |  \\
| 0.3580                | 4873                          | -331.96                        | -79.34                          |  \\
| 0.1883                | 9263                          | -334.26                        | -79.89                          |  \\
| 0.4266                | 4089                          | -334.93                        | -80.05                          |  \\
| 0.3562                | 4898                          | -336.73                        | -80.48                          |  \\

Av. \(\Delta H_{\text{obs}^\ominus1} = -333.92 \pm 1.30 \text{ KJ mole}^{-1} \)

\[= -79.81 \pm 0.31 \text{ Kcal mole}^{-1} \]

(1) P(\text{NCO})_3 freshly distilled was used for the calorimetric run.

The run was conducted within 1 hr. of distillation.
TABLE  C.T.E. Calorimetric Results for Phenyltetraiodophosphorane  
referring to the following reaction in water (125 ml.) at 25°C  

\[
C_6H_5Br_4 \text{(cryst.)} + 3H_2O \text{(liq.)} = (C_6H_5PO_3H_2 + 4HBr) \text{(sol.)}
\]

<table>
<thead>
<tr>
<th>Wt. C₆H₅Br₄</th>
<th>( n(H_2O:C_6H_5Br_4) )</th>
<th>( \Delta \text{Hobs.} ) KJ mole⁻¹</th>
<th>( \Delta \text{Hobs.} ) Kcal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1372</td>
<td>21667</td>
<td>-334.01</td>
<td>-79.83</td>
</tr>
<tr>
<td>0.2711</td>
<td>10965</td>
<td>-342.50</td>
<td>-81.86</td>
</tr>
<tr>
<td>0.2442</td>
<td>12171</td>
<td>-334.05</td>
<td>-79.84</td>
</tr>
<tr>
<td>0.2331</td>
<td>12751</td>
<td>-334.11</td>
<td>-80.81</td>
</tr>
<tr>
<td>0.2656</td>
<td>11190</td>
<td>-336.56</td>
<td>-80.44</td>
</tr>
</tbody>
</table>

\[\text{Av. } \Delta \text{Hobs.} = -337.06 \pm 0.58 \text{ KJ mole}^{-1}\]
\[= -80.56 \pm 0.14 \text{ Kcal mole}^{-1}\]
TABLE  Adiabatic Calorimetric Results of Step(I) in Thermodynamic Cycle
for Diphosphorus tetraiodide - boron tribromide (1:2) adduct
referring to the following reaction in carbon disulphide (200 ml.)
at 25°C.

\[ \text{P}_2\text{I}_4\text{ZBr}_3 \text{(solid)} + \text{CS}_2 \text{(liq.)} = (\text{P}_2\text{I}_4\text{ZBr}_3)(\text{CS}_2) \]

<table>
<thead>
<tr>
<th>Wt. P I ZBr  ( (g) )</th>
<th>( N(\text{CS}_2, \text{P}_2\text{I}_4\text{ZBr}_3) )</th>
<th>( \Delta \text{Hobs.} -1 ) ( \text{KJ mole}^{-1} )</th>
<th>( \Delta \text{Hobs.} -1 ) ( \text{Kcal mole}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0973</td>
<td>2564</td>
<td>-114.01</td>
<td>-27.25</td>
</tr>
<tr>
<td>1.0257</td>
<td>2743</td>
<td>-114.05</td>
<td>-27.26</td>
</tr>
<tr>
<td>1.0718</td>
<td>2625</td>
<td>-108.66</td>
<td>-25.97</td>
</tr>
<tr>
<td>1.0051</td>
<td>2799</td>
<td>-113.17</td>
<td>-27.05</td>
</tr>
</tbody>
</table>

\( \text{Av. } \Delta \text{Hobs.} = -111.92 \pm 1.13 \text{ KJ mole}^{-1} \)
\( = -26.75 \pm 0.27 \text{ Kcal mole}^{-1} \)

(1) All operations were performed under scrupulously dry conditions and under an inert atmosphere of nitrogen. Excess \( \text{BBr}_3 \) \((1.3214 = 0.5 \text{ ml.})\) added to test these conditions.

(2) This was slow reaction. The fore-run was of 10 min., main reaction period 30 min., and aft-period readings were taken up to 130 min.

(3) Equal area method was used to locate the position of \( R_1, R_2 \) and \( R_3, R_4 \) on graph. A weighted (precalibrated) planimeter was used to measure the area.
Adiabatic Calorimetric Results of Step (2) in Thermodynamic cycle for Diphosphorus tetraiodide-boron tribromide (1:2) adduct referring to the following reaction in carbon disulphide (200 ml.) at 25°C. \[ N(CS_2\cdot FBr_3) = 24.9. \]

\[ P_2I_4 \text{(cryst.)} + \(2EBr_3\text{(liq.)}) \ (CS_2) = (P_2I_4 + 2EBr_3) \ (CS_2) \]

<table>
<thead>
<tr>
<th>Wt. ( P_2I_4 ) (g)</th>
<th>( N(CS_2\cdot P_2I_4) )</th>
<th>( \Delta \text{Hobs.} ) KJ mole(^{-1} )</th>
<th>( \Delta \text{Hobs.} ) Kcal mole(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5250</td>
<td>2850</td>
<td>117.69</td>
<td>-28.13</td>
</tr>
<tr>
<td>0.5372</td>
<td>2786</td>
<td>118.45</td>
<td>-28.31</td>
</tr>
<tr>
<td>0.5314</td>
<td>2816</td>
<td>118.45</td>
<td>-28.31</td>
</tr>
<tr>
<td>0.5382</td>
<td>2780</td>
<td>120.25</td>
<td>-28.74</td>
</tr>
<tr>
<td>0.5420</td>
<td>2923</td>
<td>117.99</td>
<td>-28.20</td>
</tr>
</tbody>
</table>

\( \text{Av. Hobs.} = -118.57 \pm 0.46 \text{ KJ mole}^{-1} \)
\[ = -28.34 \pm 0.11 \text{ Kcal mole}^{-1} \]

(1) This was a slow reaction. The fore-run was 10 min., main reaction 30 min. and after-run readings were recorded up to 140 min.

(2) All operations under an inert atmosphere of nitrogen.

(3) Boron tribromide added 2.6424g (= 1 ml.)
### TABLE C.T.L. Calorimetric Results of Step (3) in Thermodynamic Cycle

For Phosphorus tetraiodide - boron tribromide (112) adduct

Referring to the following reaction in carbon disulphide (200 ml.) at 25°C

\[
\text{EBr}_3 \text{(liq.)} + \text{CS}_2 \text{(liq.)} = (\text{EBr}_3)(\text{CS}_2)
\]

<table>
<thead>
<tr>
<th>Wt. EBr₃ (g)</th>
<th>N(CS₂EBr₃)</th>
<th>ΔHobs KJ mole⁻¹</th>
<th>ΔHobs Kcal mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4194</td>
<td>464</td>
<td>1.09</td>
<td>0.26</td>
</tr>
<tr>
<td>1.3080</td>
<td>504</td>
<td>1.09</td>
<td>0.26</td>
</tr>
<tr>
<td>1.3593</td>
<td>484</td>
<td>1.13</td>
<td>0.27</td>
</tr>
<tr>
<td>1.3111</td>
<td>502</td>
<td>1.09</td>
<td>0.26</td>
</tr>
<tr>
<td>0.8111</td>
<td>812</td>
<td>1.13</td>
<td>0.27</td>
</tr>
<tr>
<td>0.8043</td>
<td>819</td>
<td>1.13</td>
<td>0.27</td>
</tr>
<tr>
<td>1.0227</td>
<td>644</td>
<td>1.13</td>
<td>0.27</td>
</tr>
<tr>
<td>0.9951</td>
<td>662</td>
<td>1.13</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Av. ΔHobs = 1.13 ± 0.004 KJ mole⁻¹ = 0.27 ± 0.001 Kcal mole⁻¹

(1) All operations were performed under scrupulously dry conditions.
TABELE C.T.E. Calorimetric Results of Pentabromophosphorane - Boron Tribromide (1:1) adduct referring to the following reaction
in water (150 ml.) at 25°C.

\[
PBr_5Br_3 \text{(solid)} + 7H_2O \text{(liq.)} \rightarrow (H_3PO_4 + H_3BO_3 + 8HBr) \text{(sol.)}
\]

<table>
<thead>
<tr>
<th>Wt. ( PBr_5Br_3 ) (g)</th>
<th>( n(H_2O:PBr_5Br_3) )</th>
<th>( \Delta Hobs. ) KJ mole(^{-1} )</th>
<th>( \Delta Hobs. ) Kcal mole(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2136</td>
<td>26614</td>
<td>-745.46</td>
<td>-178.17</td>
</tr>
<tr>
<td>0.2150</td>
<td>26433</td>
<td>-751.11</td>
<td>-179.52</td>
</tr>
<tr>
<td>0.2300</td>
<td>24709</td>
<td>-746.97</td>
<td>-178.53</td>
</tr>
<tr>
<td>0.2240</td>
<td>25371</td>
<td>-749.19</td>
<td>-179.06</td>
</tr>
<tr>
<td>0.2261</td>
<td>25135</td>
<td>-752.95</td>
<td>-179.96</td>
</tr>
<tr>
<td>0.2160</td>
<td>26311</td>
<td>-749.35</td>
<td>-179.10</td>
</tr>
</tbody>
</table>

Avg. \( \Delta Hobs. \) = \(-749.19 \pm 1.09\) KJ mole\(^{-1}\)

\(-179.06 \pm 0.26\) Kcal mole\(^{-1}\)
SECTION III. RESULTS

CHAPTER SEVEN: THERMAL ANALYSIS RESULTS
This chapter presents the results of the thermal analysis of phosphorus-phosphorus bonded compounds and certain molecular adducts. The aim of the study were: (i) Qualitative analysis to determine (a) melting points, (b) investigation of decomposition modes (especially in diphosphorus tetraiodide), (ii) quantitative analyses were performed to collect thermodynamic data (i.e. transition energy at fusion or phase change, as in pentaphenylcyclopentaphosphine and polymeric phenylphosphine). The heat of fusion of polymeric phenylphosphine; with respect to heat of fusion of polyethylene, are used to determine the percentage crystallinity. All operations were performed under nitrogen atmosphere. The reproducibility of the results presented here was checked at least thrice in each compound.

The types of thermal analyzers used in this work were:

(i) Differential Scanning Calorimeter model 1B (DSC-IB) Perkin Elmer.
(ii) Thermogravimetric Analyser (TGA) Netzsch model 404 fully automatic.
(iii) Differential Thermal Analyzer (DTA) Du Pont with 900 thermal analyzer (Basic Unit) and Standard D.T.A. cell (Quartz Cover).

Thermal Analyzers and Programming

(i) The D.S.C. 1B (Perkin Elmer) instrument was operated under the following conditions throughout this work unless otherwise mentioned

Sample Holder: volatile sample pan constructed from aluminium with cover
Reference Holder: Empty pan with cover (as above)
Wt. of Sample and Holder: Ca. 15 mg.

Range: 2 millicalories per sec. (m. cal. sec⁻¹)
full scale deflection (F.S.D.)

Scan: 8°C per minute

Chart: 60 inch per hour

Gas flow: 20 ml. per minute, nitrogen

Heater: Platinum wire

Temperature detector: Platinum resistance thermometer

Balance: "Cahn Gram" Electrobalance with accuracy 10⁻⁶ g.

(ii) D.T.A. Du Pont analyzer was operated under the following conditions throughout this work unless otherwise stated.

Sample Holder: Aluminium pan (6.6 m.m. internal diameter)
with cover weighing 3 mg.

Reference Holder: Aluminium pan with lid containing alumina

Sample size: Ca. 0.5 to 100 mg.

Sample thermocouple: Chromel-Alumel

Differential thermocouple: Chromel-constantan

Control thermocouple: Chromel-Alumel

Calorimetric sensitivity: 0.2 milli cal sec⁻¹ in⁻¹ (based on 40 milli volt recorder at ambient)

Calorimetric precision: ca. ± 1.0 %

Temperature repeatability: ± 1°C

Heater: 200 Watt. Nichrome Wound

Atmosphere: Nitrogen
(iii) Thermogravimetric Analyser (T.G.A.) fully automatic Netzsch model 404.

Sample Holder: Specially designed hexagonal and round cells (and cover constructed from) stainless steel in this laboratory weighing 4.890 g and 0.1 mm. hole in the cover.

Holder capacity (maximum): Ca. 2 g.

Gas flow: 125 c.c. min⁻¹ nitrogen

Chart Speed: 12 cm. hr⁻¹

Heating rate: 1°C min⁻¹
Table  Differential Scanning Calorimetry Results for Indium Standard

Mode of run:
Weight of Indium = 0.8465 mg.
Temperature range = 40 - 190°C

Analysis of Thermogram:

Transition temperature : 156.5°C (lit. 156.5°C)
Transition range : 155-157°C
Type of Peak : Endothermic, sharp (Height, 18.2 cm.)
Area under Peak : 0.043 planimeter unit (P.U.) cal. mole^{-1}
\( \Delta H_{\text{fusion}} \) : 779.6 cal. mole^{-1} (lit. 780 cal. mole^{-1})
Specific heat : 0.05 cal. g^{-1} °C^{-1} (lit. 0.05)

(1) Indium standard is used as calibrant for accurate measurements of temperature and heat content. (see graph on P.

(2) The calculations for heat of transition of an unknown sample with reference to Indium (In) are performed as follows:

\[
\text{Peak area (In)} = \text{Wt. (In)} \times \text{Specific heat (In)}
\]

\[
\text{Peak area (Sample)} = \text{Wt. (Sample)} \times \text{Specific heat (Sample)}
\]

Therefore the heat of transition is given by

\[
\Delta H_{\text{Sample}} = \Delta H_{\text{In}} \times \frac{\text{Wt. (In)}}{\text{Wt. (Sample)}} \times \frac{\text{Peak area (Sample)}}{\text{Peak area (In)}}
\]

where Wt. is in mg., and \( \Delta H_{\text{In}} \) (fusion) = 6.79 milli cal. mg^{-1} (or 6.79 cal. g^{-1})
Thermograph for the fusion of Indium: Fusion temperature, 156.5°C and 
\[ \Delta H_{\text{fus.}} = 779.6 \text{ cal. mole}^{-1} \]
Table: Differential Scanning Calorimetry Results
for Penta-phenylcyclcopentaphosphine

1st mode of run:

Weight of \((C_6H_5P)_5\) : 1.242 mg.

Temperature range : 40 - 350°C (Heating)

Analysis of Thermogram:

1st Transition temperature : 86°C (Cf. the transition in piperidine)
Transition range : 65 - 105°C
Type of peak : Exothermic, sharp, (Height, 6 cm.)
Area under peak : 0.1190 P.U.
Transition energy : 12.77 cal. g\(^{-1}\) (6.89 kcal per \((C_6H_5P)_5\))

2nd Transition temperature : 154°C (lit. m.p. 149-156°C)
Transition range : 138 - 157°C
Type of peak : Endothermic, melting, sharp, (Height, 7 cm.)
Area under peak : 0.1207 P.U.
Transition energy (\(\Delta H_{\text{fusion}}\)) : 12.95 cal. g\(^{-1}\) (6.99 kcal per \((C_6H_5P)_5\))

2nd mode of run : 350 - 50°C (cooling) and
3rd mode of run : 40 - 350°C (heating)

(1) Actual graph showing transition peak and the area measured by planimeter is shown on P. 149.

(2) Additional run on the same sample weighing 5 mg. and range 4 m. cal. sec\(^{-1}\) produced no significant change on the part of the thermogram.

(3) The Exothermic transition peak at 86°C (Cf. with D.T.A. same temperature transition, see graph on P. 151) is indicative of a probable phase change occurring in solution (i.e. piperidine) at about the same temperature (Ca. 80°C). It is possible that these two facts are connected. In this work three attempts were made with little success to convert \((C_6H_5P)_5\) to \((C_6H_5P)_n\). Hence a direct synthetic route was investigated (see P. 48 under synthesis).
DSC (Perkin Elmer) THERMOGRAM OF (ΦP)\textsubscript{5}

**Fig.** Thermograph for pentaphenylcyclopentaphosphine (form A) showing exothermic peak at 86°C and melting and endothermic peak at 154°C.
<table>
<thead>
<tr>
<th>Table</th>
<th>Differential Thermal Analysis Results for Pentaphenylcyclopentaphosphine</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mode of run:</strong></td>
<td></td>
</tr>
<tr>
<td>Weight of ((\text{C}_6\text{H}_5\text{P})_5)</td>
<td>7 mg.</td>
</tr>
<tr>
<td>Temperature range</td>
<td>30 - 200°C</td>
</tr>
<tr>
<td>Rate of heating</td>
<td>10°C min(^{-1})</td>
</tr>
<tr>
<td>(\Delta T)</td>
<td>0.5°C inch(^{-1})</td>
</tr>
<tr>
<td>Temperature scale</td>
<td>20°C inch(^{-1})</td>
</tr>
</tbody>
</table>

**Analysis of Thermogram**

1st Transition temperature: 86°C (Cf. the transition in piperidine)

- **Transition range**: 70 - 90°C
- **Type of peak**: Exothermic, sharp flattening (Height, 5.7 cm.)

2nd Transition temperature: 154°C

- **Transition temperature**: 152 - 162°C
- **Type of peak**: Endothermic, melting, sharp (Height 7.3 cm.)

(1) Characteristic melting peak of monoclinic type of crystal was identified for pentaphenylcyclopentaphosphine (Also private communication with Dr. I. C. Wylie Du Pont Company (U.K.) Ltd., their Ref. ICW:SO dated 1st August, 1963.)

(2) Exothermic peak at 86°C before melting point of \((\text{C}_6\text{H}_5\text{P})_5\) shows that most probably phase change is taking place.

(3) Exothermic peak at 86°C is also evident on the D.Sc. thermogram. (See graph on P. 151.)
Fig. Thermograph of pentaphenylnyclopentaphosphine (form A) showing exothermic peak at Ca. 86 °C and the melting endotherm at 154 °C.
Table Differential scanning calorimetry Results for Hexaphenylcyclotetraphosphine

<table>
<thead>
<tr>
<th>1st Mode of run:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of ((C_6H_5P)_6)</td>
<td>0.915 mg. (single crystal)</td>
</tr>
<tr>
<td>Range</td>
<td>4 m cal. sec⁻¹</td>
</tr>
<tr>
<td>Temperature range</td>
<td>40 - 210°C</td>
</tr>
</tbody>
</table>

Analysis of Thermogram

<table>
<thead>
<tr>
<th>1st Transition temperature</th>
<th>76°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition range</td>
<td>70 - 80°C</td>
</tr>
<tr>
<td>Type of peak</td>
<td>Endothermic, broad softening type, (Height 0.5 cm)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd Transition temperature</th>
<th>130°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition range</td>
<td>110 - 131°C</td>
</tr>
<tr>
<td>Type of peak</td>
<td>Twin exothermic, broad followed by sharp.</td>
</tr>
<tr>
<td>(Height: broad 1.5 cm, sharp, 2 cm.)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3rd Transition temperature</th>
<th>190°C (lit. 190°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition range</td>
<td>172 - 195</td>
</tr>
<tr>
<td>Type of peak</td>
<td>Exothermic melting, broad softening peak (Height, 1 cm.)</td>
</tr>
</tbody>
</table>

(1) Transition at 76°C shows softening effect of crystal followed by, probably, a phase change at 130°C, and finally melts at 190°C.

(2) Lit. also refers to (i) 130-155°C for the clathrate compound of composition one molecule of benzene to six \(C_6H_5P\) groups (ii) thermal change produces \((C_6H_5P)_5\) from \((C_6H_5P)_6\) (iii) solvents like \(C_6H_6\) and HCl also bring about the conversion of \((C_6H_5P)_6\) to \((C_6H_5P)_5\).

*This sample was donated by Dr. L. Maier*
2nd Mode of run:

<table>
<thead>
<tr>
<th>Weight of (C₆H₅P)₆</th>
<th>3.130 mg. (four crystals)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature range</td>
<td>40 - 300°C (heating)</td>
</tr>
</tbody>
</table>

Analysis of Thermogram

<table>
<thead>
<tr>
<th>Transition temperature</th>
<th>Type of peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>76°C</td>
<td>Endothermic, broad softening type to sharp</td>
</tr>
<tr>
<td>130°C</td>
<td>Twin exothermic, broad followed by sharp</td>
</tr>
<tr>
<td>190°C</td>
<td>Endothermic melting, broad softening peak</td>
</tr>
</tbody>
</table>

(1) Exothermic transition at 130°C suggests possible phase change. The literature refers to a phase change with no definite temperature and phase change occurring in solution phase (i.e. C₆H₅ and HCl). It is possible that these facts are connected.
Table Differential Scanning Calorimetry Results for polymeric phenylphosphine referring to transition energy and percentage crystallinity

1st Mode of run:

Weight of \((C_6H_5)_n\) : 2.085 mg.
Temperature range: 40 - 350°C (Heating)

Analysis of Thermogram

1st transition temperature: 86°C
Transition range: 75 - 105°C
Type of peak: Twin exothermic, sharp followed by broad
(Height: sharp 3.3 cm., broad 1 cm.)
Area under peak: 0.1127 P.U.
Transition energy: 7.22 cal. gm⁻¹ (0.73 kcal mole⁻¹ \((C_6H_5)\))

2nd transition temperature: 285°C (liq. 252 - 305)
Transition range: 190 - 325°C
Type of peak: Endothermic melting, broad (Height, 3 cm.)
Transition energy: 41.56 cal. g⁻¹ (4.49 kcal mole⁻¹ \((C_6H_5)\))

3rd Mode of run:

2nd Mode of run:

3rd Mode of run: 350 - 50°C (Cooling)
40 - 350°C (Reheating)

(1) No significant peak appeared in 2nd and 3rd runs. Also two other such type of thermograms were run on different quantities of the same sample. Thermograms of similar types were produced.
(2) Exothermic transition peak at 86°C is indicative of phase change. Literature\textsuperscript{85} refers to phase change \((\text{C}_6\text{H}_5\text{P})_n\) to \((\text{C}_6\text{H}_5\text{P})_5\) at no definite temperature and also occurring in solution phase (i.e. diphenyl ether). It is possible these facts are connected.

(3) 2nd and 3rd mode of runs suggest that direct heat treatment to crystalline polymeric phenylphosphine produces partial phase change.

(4) The percentage crystallinity of polymeric phenylphosphine is measured in this work via heat of fusion and is expressed as

\[
\% \text{ crystallinity } (\text{C}_6\text{H}_5\text{P})_n = \frac{\Delta H_{\text{fusion}} (\text{C}_6\text{H}_5\text{P})_n}{\Delta H_{\text{fusion}} \text{ Polyethylene}} \times 100
\]

where

\[
\Delta H_{\text{fusion}} (\text{C}_6\text{H}_5\text{P})_n = 41.56 \text{ cal. g}^{-1}
\]

\[
\Delta H_{\text{fusion}} \text{ Polyethylene} = 68.4 \text{ cal. g}^{-1}
\]

\[
\% \text{ crystallinity } (\text{C}_6\text{H}_5\text{P})_n = \frac{41.56}{68.4} \times 100 = 74.5
\]

(5) The presence of 74.5\% crystallinity suggests heterogeneity and the substance does not possess sharp melting point (literature\textsuperscript{61} give m.p.t. 252-285°C)
Table  Thermogravimetric Analysis Results for
Diphosphorus tetraiodide referring to decompositions

Mode of run:

Weight of $P_2I_4$: 184.2 mg
Temperature range: 20 - 285°C
Range (Full scale deflection): 200 mg

Heating rate: $1^\circ C$ min$^{-1}$
Chart speed: 2 mm. min$^{-1}$

Detailed Analysis of Thermogram

$\Delta W =$ weight change (mg)
$\Delta t =$ time in minutes

<table>
<thead>
<tr>
<th>NORMAL THERMOGRAM</th>
<th>DERIVATIVE OF THERMOGRAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight Loss (mg)</td>
<td>Temperature (°C)</td>
</tr>
<tr>
<td>0.00</td>
<td>20</td>
</tr>
<tr>
<td>0.00</td>
<td>65</td>
</tr>
<tr>
<td>0.80</td>
<td>70</td>
</tr>
<tr>
<td>1.20</td>
<td>75</td>
</tr>
<tr>
<td>1.60</td>
<td>80</td>
</tr>
<tr>
<td>2.40</td>
<td>85</td>
</tr>
<tr>
<td>3.20</td>
<td>90</td>
</tr>
<tr>
<td>3.20</td>
<td>95</td>
</tr>
<tr>
<td>4.00</td>
<td>100</td>
</tr>
<tr>
<td>4.40</td>
<td>105</td>
</tr>
<tr>
<td>4.80</td>
<td>110</td>
</tr>
<tr>
<td>5.20</td>
<td>115</td>
</tr>
<tr>
<td>5.60</td>
<td>120</td>
</tr>
<tr>
<td>6.00</td>
<td>125</td>
</tr>
<tr>
<td>6.08</td>
<td>130</td>
</tr>
<tr>
<td>6.58</td>
<td>135</td>
</tr>
<tr>
<td>7.12</td>
<td>140</td>
</tr>
<tr>
<td>7.20</td>
<td>145</td>
</tr>
<tr>
<td>7.20</td>
<td>150</td>
</tr>
<tr>
<td>7.28</td>
<td>155</td>
</tr>
<tr>
<td>7.60</td>
<td>160</td>
</tr>
<tr>
<td>7.76</td>
<td>165</td>
</tr>
<tr>
<td>8.00</td>
<td>170</td>
</tr>
<tr>
<td>8.40</td>
<td>175</td>
</tr>
<tr>
<td>9.60</td>
<td>180</td>
</tr>
<tr>
<td>10.40</td>
<td>185</td>
</tr>
<tr>
<td>11.20</td>
<td>190</td>
</tr>
<tr>
<td>12.00</td>
<td>195</td>
</tr>
<tr>
<td>13.20</td>
<td>200</td>
</tr>
<tr>
<td>14.40</td>
<td>205</td>
</tr>
<tr>
<td>16.40</td>
<td>208</td>
</tr>
<tr>
<td>17.60</td>
<td>210</td>
</tr>
<tr>
<td>18.40</td>
<td>213</td>
</tr>
<tr>
<td>22.40</td>
<td>215</td>
</tr>
<tr>
<td>24.80</td>
<td>220</td>
</tr>
<tr>
<td>28.56</td>
<td>225</td>
</tr>
<tr>
<td>32.80</td>
<td>230</td>
</tr>
<tr>
<td>37.60</td>
<td>235</td>
</tr>
</tbody>
</table>
(1) Another run on the same sample, weighing 430.1 mg., with a heating rate of 5°C min⁻¹ and with nitrogen flow 150 cc. min⁻¹ was performed. A similar type of thermogram was obtained (as above), with no sign of decomposition before melting.

(2) That, there is negligible weight loss before melting point, hence the possibility of decomposition prior to m.pt. is very remote.

(3) A derivative graph plot of ΔW/Δt vs. temperature showed no sign of decomposition before melting.

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>142.40</td>
<td>240</td>
<td>4.80</td>
<td>5</td>
<td>96</td>
</tr>
<tr>
<td>42.40</td>
<td>245</td>
<td>6.00</td>
<td>5</td>
<td>120</td>
</tr>
<tr>
<td>55.40</td>
<td>250</td>
<td>7.00</td>
<td>5</td>
<td>140</td>
</tr>
<tr>
<td>64.40</td>
<td>255</td>
<td>9.00</td>
<td>5</td>
<td>180</td>
</tr>
<tr>
<td>74.40</td>
<td>260</td>
<td>10.00</td>
<td>5</td>
<td>200</td>
</tr>
<tr>
<td>86.40</td>
<td>265</td>
<td>12.00</td>
<td>5</td>
<td>240</td>
</tr>
<tr>
<td>100.00</td>
<td>270</td>
<td>14.00</td>
<td>5</td>
<td>280</td>
</tr>
<tr>
<td>115.00</td>
<td>275</td>
<td>16.00</td>
<td>5</td>
<td>320</td>
</tr>
<tr>
<td>134.40</td>
<td>280</td>
<td>18.40</td>
<td>5</td>
<td>368</td>
</tr>
<tr>
<td>154.40</td>
<td>285</td>
<td>20.40</td>
<td>5</td>
<td>408</td>
</tr>
<tr>
<td>173.40</td>
<td>290</td>
<td>16.00</td>
<td>5</td>
<td>320</td>
</tr>
</tbody>
</table>
TABLE - Differential Thermal Analysis Results for Diposphorus tetraiodide-Boron tribromide (1:2) Adduct

Mode of Run:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of ( \text{P}_2\text{I}_4\text{Br}_3 )</td>
<td>15 mg</td>
</tr>
<tr>
<td>Temperature range</td>
<td>25-300°C</td>
</tr>
<tr>
<td>Temperature scale</td>
<td>20°C inch(^{-1})</td>
</tr>
<tr>
<td>Rate of heating</td>
<td>10°C min(^{-1})</td>
</tr>
<tr>
<td>( \Delta T )</td>
<td>0.5°C inch(^{-1})</td>
</tr>
</tbody>
</table>

Analysis of Thermogram

1st transition temperature: 100°C

<table>
<thead>
<tr>
<th>Transition range</th>
<th>82-110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of peak</td>
<td>Endothermic, broad</td>
</tr>
<tr>
<td></td>
<td>sharp (Height 1.7 cm.)</td>
</tr>
<tr>
<td>Peak area</td>
<td>0.50 sq. in.</td>
</tr>
</tbody>
</table>

2nd transition temperature: 122°C

<table>
<thead>
<tr>
<th>Transition range</th>
<th>110-131°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of peak</td>
<td>Endothermic, broad</td>
</tr>
<tr>
<td></td>
<td>sharp (Height 2 cm.)</td>
</tr>
<tr>
<td>Peak area</td>
<td>0.66 sq. in.</td>
</tr>
</tbody>
</table>

(1) The transition peaks area was measured by extrapolation, by cutting and weighing and also by using a weighted planimeter.

(2) It is possible that the first endotherm corresponds to the loss of two molecules of boron tribromide (cf. normal b.pt. \( \text{BBr}_3 \) = 91°C).

(3) It is equally likely that the second endotherm corresponds to the melting of diposphorus tetraiodide (cf. m.pt. \( \text{P}_2\text{I}_4 \) = 124.5°C).
(4) TGA runs on a model 404 Netzsch indicates no appreciable weight loss until 130°C. Thereafter regular weight loss occurred (ca. 0.7 mg. deg⁻¹) until an inflexion at ca. 250°C.

Similar studies on Du Pont T.G.A. 950 equipment indicated steady weight loss from 20 to 100°C (ca. 20%) followed by a more rapid loss to 200°C (a further 50%) followed by a 5% loss over another 350°C. No suitable conclusion as to the mode of decomposition can be derived from these results.
SECTION-III. RESULTS

CHAPTER EIGHT: IAS: SPECTROSCOPIC RESULTS
Probable mode of cracking obtained by electron impacts for the compound containing phosphorus-phosphorus bond, Phosphorus (III), Boron (II) and molecular adducts of phosphorus (III).

\[ \text{P}_2\text{I}_4 \rightarrow \text{P}_2\text{I}_4^0 \rightarrow \text{P}_2\text{I}_4^+ \rightarrow \text{P}_2\text{I}_2^{+} + \text{PI}^+ \]
(\text{m/e 570}) (\text{m/e 285})

\[ \text{PI}^+ \rightarrow \text{I}^+ \]
(\text{m/e 158}) (\text{m/e 127})

\[ \text{P}_3\text{I}_3 \rightarrow \text{P}_3\text{I}_3^0 \rightarrow \text{P}_3\text{I}_3^+ \rightarrow \text{P}_2\text{I}_2^{+} + \text{I}^+ \]
(\text{m/e 412}) (\text{m/e 285})

\[ \text{PI}^+ \rightarrow \text{I}^+ \]
(\text{m/e 127})

\[ \text{PBr}_3 \rightarrow \text{PBr}_3^0 \rightarrow \text{PBr}_3^+ \rightarrow \text{PBr}_2^{+} + \text{Br}^+ \]
(\text{m/e 265-274}) (\text{m/e 189-193})

\[ \text{PBr}^+ \rightarrow \text{Br}^+ \]
(\text{m/e 110,112}) (\text{m/e 79,81})

\[ \text{BI}_3 \rightarrow \text{BI}_3^0 \rightarrow \text{BI}_3^+ \rightarrow \text{BI}_2^{+} + \text{I}^+ \]
(\text{m/e 391,392}) (\text{m/e 264,265})

\[ \text{BI}^+ \rightarrow \text{I}^+ \]
(\text{m/e 137,138}) (\text{m/e 127})

\[ \text{BBr}_3 \rightarrow \text{BBr}_3^0 \rightarrow \text{BBr}_3^+ \rightarrow \text{BBr}_2^{+} + \text{Br}^+ \]
(\text{m/e 247-254}) (\text{m/e 168-173})

\[ \text{BBr}^+ \rightarrow \text{Br}^+ \]
(\text{m/e 89,92}) (\text{m/e 79,81})
$\text{Br}_3P\text{EBI}_3 \rightarrow \text{Br}_3\text{P}^0 + \text{BrI}_3^0$  
$\text{Br}_3\text{P}^+ \quad (m/e \ 266-274)$  
$\text{Br}_3\text{I}^+ \quad (m/e \ 391, 392)$  
$\text{PBr}_2^+ \quad (m/e \ 189-193)$  
$\text{Br}^+ \quad (m/e \ 79-81)$  
$\text{IBr}_2^+ \quad (m/e \ 264, 265)$  
$I^+ \quad (m/e \ 127)$

$\text{I}_3P\text{EBR}_3 \rightarrow \text{PI}_3^0 + \text{EBR}_3^0$  
$\text{PI}_3^+ \quad (m/e \ 412)$  
$\text{PI}_2^+ \quad (m/e \ 235)$  
$I^+ \quad (m/e \ 127)$  
$\text{EBR}_2^+ \quad (m/e \ 163-173)$  
$\text{EBR}^+ \quad (m/e \ 89, 92)$  
$\text{Br}^+ \quad (m/e \ 79, 81)$

$^o$ = shows neutral molecule in gaseous state  
$^* =$ unobserved species  
$^- =$ a range of m/e data due to isotope splitting  
$^+$ = unpaired electron
Table: Mass Spectrum of Diphenylphosphorus tetraisodide and the analysis of major significant peaks (M.S.P.)

Spectrometer: AEI model MS902 (double focusing)
Insertion mode: Direct inlet system
Source temperature: 235°C
Electron Energy (input): 70 ev

<table>
<thead>
<tr>
<th>m/e</th>
<th>31</th>
<th>62</th>
<th>63-64</th>
<th>124</th>
<th>127</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>17.0</td>
<td>35.7</td>
<td>8.5</td>
<td>51.0</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>128</th>
<th>158</th>
<th>254</th>
<th>285</th>
<th>570</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>40.8</td>
<td>44.2</td>
<td>51.0</td>
<td>68.0</td>
<td>85.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M.S.P. (m/e)</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>P⁺</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>P₂⁺</td>
<td></td>
</tr>
<tr>
<td>63 - 64</td>
<td>I⁺/II⁺</td>
<td>Possibly arising from elemental phosphorus in sample.</td>
</tr>
<tr>
<td>124</td>
<td>P₄⁺</td>
<td>Base peak, 60 mm, 100%</td>
</tr>
<tr>
<td>127</td>
<td>I⁺</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>HI⁺</td>
<td></td>
</tr>
<tr>
<td>158</td>
<td>PI⁺</td>
<td></td>
</tr>
<tr>
<td>254</td>
<td>I₂⁺</td>
<td>Possibly from elemental iodine</td>
</tr>
<tr>
<td>285</td>
<td>PI₂⁺</td>
<td></td>
</tr>
<tr>
<td>443</td>
<td>P₂I⁺</td>
<td></td>
</tr>
<tr>
<td>570</td>
<td>P₂I₄⁺</td>
<td></td>
</tr>
</tbody>
</table>
(1) Peak heights less than 2% are not accounted for.

(2) Mass Spectrometry at School of Pharmacy their Ref. No: 63/327 (iv) dated 14.3.63.

(3) Under similar conditions except source temperature 190°C, probe at 150°C three more spectra were run on the same sample at EREZ, Waltham Abbey, using AZI model MS2H mass spectrometer, their Ref. No: 166. No significant change in the location of peaks or percentage abundance was noticed. The appearance potential (A.P.) by the method of Lossing et al for one of the runs for the following process gave the value of \((\text{AP}^*)^\text{P}_2\text{I}_4 = 12.8 \text{ ev} \pm 0.15 \text{ ev.}\)

\[
P_2\text{I}_4 + e \rightarrow \text{PI}_2^+ + \text{PI}_2 + 2e. \quad \text{AP}^*(\text{PI}_2^+) = 12.8 \text{ ev} \pm 0.15 \text{ ev.}
\]
Table: Mass Spectrum of Triiodophosphine and the analysis of major significant peaks

Spectrometer: AEI model MS 902 (double focusing)
Insertion mode: Direct inlet system
Source temperature: 155°C
Electron energy (input): 70 ev

<table>
<thead>
<tr>
<th>m/e</th>
<th>126</th>
<th>127</th>
<th>128</th>
<th>165</th>
<th>195</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>40.0</td>
<td>100.0</td>
<td>42.0</td>
<td>36.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>285</th>
<th>412</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>72.2</td>
<td>84.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M.S.P. (m/e)</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>127</td>
<td>$I^+$</td>
<td>Peak peak, 25 mm., 100%</td>
</tr>
<tr>
<td>285</td>
<td>$PI_2^+$</td>
<td></td>
</tr>
<tr>
<td>412</td>
<td>$PI_3^+$</td>
<td></td>
</tr>
</tbody>
</table>

(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry at School of Pharmacy their Ref. No: 68/533 dated 6.5.63.

(3) Under similar conditions another three spectra were run on the same sample, at ERDE, Waltham Abbey, using AEI model MS2H mass spectrometer. No significant change in the location of peaks or percentage abundance was noticed. The appearance potential measurements (A.P.) by the method of Lossing et al, for one of the runs for the following process gave the value of $^{194}(PI_2^+PI_3 = 11.9 \text{ ev} \pm 0.15$

$PI_3 + e^{-} \rightarrow PI_2^+ + I + 2e$. A.P. $(PI_2^+PI_3$
Table. Mass Spectrum of Tribromophosphine and the analysis of the major significant peaks

Spectrometer: AEI MS 902 (double focusing)
Insertion mode: Direct
Source temperature: 250°C (Probe at 30°C)

Electron energy (input) = 70 ev.

<table>
<thead>
<tr>
<th>m/e</th>
<th>79</th>
<th>80</th>
<th>81</th>
<th>82</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>90</td>
<td>100</td>
<td>80</td>
<td>80</td>
<td>23.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>111</th>
<th>189</th>
<th>191</th>
<th>270</th>
<th>271</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>22.0</td>
<td>40.0</td>
<td>80.5</td>
<td>26.2</td>
<td>25.0</td>
</tr>
</tbody>
</table>

M.S.P. (m/e) | Probable Species | Remarks
---|---|---
79 | Br⁺ | Base peak (10 mm, 100%)
80 | \[\text{HB}\text{r}⁺\]
81 | \[\text{HB}\text{r}⁺\]
82 | \[\text{PB}\text{r}⁺\]
110 | \[\text{PB}\text{r}⁺\]
111 | \[\text{PB}\text{r}⁺\]
189 | \[\text{PB}\text{r}⁺\]
191 | \[\text{PB}\text{r}⁺\]
270 | \[\text{PB}\text{r}⁺\]
271 | \[\text{PB}\text{r}⁺\]

(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry performed at School of Pharmacy their Ref. No: 70/849 dated 23.7.69.
Table  Mass Spectrum of Boron Triiodide and the analysis of the  
  major significant peaks

Spectrometer : AEI MS 902 (double focusing)
Insertion mode : Direct
Source Temperature : 150°C

Electron energy (input) = 70 ev.

<table>
<thead>
<tr>
<th>m/e</th>
<th>28</th>
<th>36</th>
<th>43</th>
<th>49</th>
<th>62</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>9.2</td>
<td>2.1</td>
<td>2.5</td>
<td>2.5</td>
<td>9.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>64</th>
<th>127</th>
<th>128</th>
<th>137</th>
<th>138</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>8.3</td>
<td>95.9</td>
<td>71.3</td>
<td>4.2</td>
<td>16.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>142</th>
<th>173</th>
<th>254</th>
<th>264</th>
<th>265</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>7.5</td>
<td>4.2</td>
<td>37.5</td>
<td>25.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>300</th>
<th>391</th>
<th>392</th>
<th>396</th>
<th>414</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.5</td>
<td>16.6</td>
<td>70.8</td>
<td>2.0</td>
<td>20.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>426</th>
<th>464</th>
<th>502</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>12.5</td>
<td>16.6</td>
<td>29.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M.S.P. (m/e)</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>127</td>
<td>I⁺</td>
<td></td>
</tr>
<tr>
<td>137</td>
<td>Br⁺ (BI)</td>
<td></td>
</tr>
<tr>
<td>138</td>
<td></td>
<td></td>
</tr>
<tr>
<td>264</td>
<td>Br⁺₂</td>
<td>Base peak, 24 mm, 100%</td>
</tr>
<tr>
<td>265</td>
<td></td>
<td></td>
</tr>
<tr>
<td>391</td>
<td>Br⁺₃</td>
<td></td>
</tr>
<tr>
<td>392</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(1) Peak heights less than 2% are not accounted for.

(2) Mass spectrometry at School of Pharmacy
    their Ref. No: D 1370/0 dated 15.4.70.
    Ref. No: 69/1231 dated 9.10.69.

(3) Exact mass number at 364 and 392 were determined by introducing
    perfluorobutylamine (mol. wt. 671) as reference inert compound.
    (Ref. No: D 1370/0 dated 15.4.70.)
Table. Mass Spectrum of Boron tribromide and the analysis of the major significant peaks

Spectrometer: AEI MS 902 (double focusing)
Insertion mode: Cold
Source Temperature: 250°C
Electron energy (input) = 70 ev

<table>
<thead>
<tr>
<th>m/e</th>
<th>18</th>
<th>28</th>
<th>35</th>
<th>36</th>
<th>38</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.2</td>
<td>2.2</td>
<td>3.9</td>
<td>4.0</td>
<td>13.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>40</th>
<th>41</th>
<th>44</th>
<th>79</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>2.6</td>
<td>2.6</td>
<td>2.6</td>
<td>39.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>81</th>
<th>82</th>
<th>125</th>
<th>127</th>
<th>168</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>33.3</td>
<td>94.4</td>
<td>7.2</td>
<td>10.4</td>
<td>12.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/e</th>
<th>170</th>
<th>171</th>
<th>173</th>
<th>250</th>
<th>252</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>4.4</td>
<td>25.0</td>
<td>12.2</td>
<td>6.9</td>
<td>6.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>M.S.P. (m/e)</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>Br⁺</td>
<td>Base peak (16 mm, 100%)</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>HBr⁺</td>
<td></td>
</tr>
<tr>
<td>168</td>
<td>EBr⁺</td>
<td></td>
</tr>
<tr>
<td>173</td>
<td>EBr₂⁺</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>EBr₃⁺</td>
<td></td>
</tr>
<tr>
<td>252</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Peak heights less than 2% are not accounted for.
(2) Mass Spectrometry performed at School of Pharmacy their Ref. No: 70/450 dated 10.4.70.
Table. Mass spectrum of tribromophosphine-boron triiodide (1:1) adduct

Spectrometer: AEI MS 902 (double focusing)
Insertion mode: Direct
Source Temperature: 260°C
Electron energy (input) = 70 ev

<table>
<thead>
<tr>
<th>m/e</th>
<th>31</th>
<th>34</th>
<th>35</th>
<th>36</th>
<th>37</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>4.0</td>
<td>9.0</td>
<td>27.0</td>
<td>4.0</td>
<td>12.5</td>
</tr>
<tr>
<td>m/e</td>
<td>38</td>
<td>39</td>
<td>41</td>
<td>43</td>
<td>44</td>
</tr>
<tr>
<td>%</td>
<td>4.0</td>
<td>2.5</td>
<td>5.3</td>
<td>5.0</td>
<td>2.5</td>
</tr>
<tr>
<td>m/e</td>
<td>55</td>
<td>57</td>
<td>62</td>
<td>62-63</td>
<td>64</td>
</tr>
<tr>
<td>%</td>
<td>2.5</td>
<td>3.0</td>
<td>8.0</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td>m/e</td>
<td>65</td>
<td>69</td>
<td>79</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>%</td>
<td>3.4</td>
<td>2.3</td>
<td>4.2</td>
<td>100.0</td>
<td>46.0</td>
</tr>
<tr>
<td>m/e</td>
<td>82</td>
<td>91</td>
<td>110</td>
<td>112</td>
<td>124</td>
</tr>
<tr>
<td>%</td>
<td>96.1</td>
<td>11.5</td>
<td>3.8</td>
<td>3.8</td>
<td>11.5</td>
</tr>
<tr>
<td>m/e</td>
<td>127</td>
<td>128</td>
<td>142</td>
<td>145</td>
<td>147</td>
</tr>
<tr>
<td>%</td>
<td>42.3</td>
<td>54.0</td>
<td>13.0</td>
<td>3.8</td>
<td>4.0</td>
</tr>
<tr>
<td>m/e</td>
<td>156</td>
<td>158</td>
<td>188-189</td>
<td>190</td>
<td>192</td>
</tr>
<tr>
<td>%</td>
<td>3.8</td>
<td>5.7</td>
<td>7.9</td>
<td>7.9</td>
<td>15.4</td>
</tr>
<tr>
<td>m/e</td>
<td>236</td>
<td>238</td>
<td>254</td>
<td>270</td>
<td>272</td>
</tr>
<tr>
<td>%</td>
<td>8.4</td>
<td>7.9</td>
<td>3.9</td>
<td>4.6</td>
<td>5.0</td>
</tr>
<tr>
<td>m/e</td>
<td>284</td>
<td>315</td>
<td>317</td>
<td>319</td>
<td>364</td>
</tr>
<tr>
<td>%</td>
<td>5.0</td>
<td>3.0</td>
<td>6.5</td>
<td>3.9</td>
<td>5.3</td>
</tr>
<tr>
<td>m/e</td>
<td>365</td>
<td>407</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>%</td>
<td>5.3</td>
<td>5.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(1) Base peak at m/e 80 (26 mm, 100%)
(2) Peak heights less than 2% are not accounted for.
(3) Mass spectrometry at School of Pharmacy their Ref. No: 69/693 dated 14.5.69.
(4) No significant peak observed between 407-663 (mol. wt. of compound)
**Table**  
**Mass Spectrum analysis of tribromophosphine-boron triiodide**  

*(1:1) adduct referring to major significant peaks*

<table>
<thead>
<tr>
<th>Major peaks m/e</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>P⁺</td>
<td></td>
</tr>
<tr>
<td>62</td>
<td>P₂⁺</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>Br⁺</td>
<td>Base peak (26 mm, 100%)</td>
</tr>
<tr>
<td>81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82</td>
<td>HBr⁺</td>
<td>HBr probably formed due to reaction with wall of mass spectrometer</td>
</tr>
<tr>
<td>124</td>
<td>P₄⁺</td>
<td>Fossibly arising from elemental phosphorus in sample as phosphorus in vapour phase is tetrahedral P₄ molecules.</td>
</tr>
<tr>
<td>127</td>
<td>T⁺</td>
<td></td>
</tr>
<tr>
<td>128</td>
<td>H⁺</td>
<td></td>
</tr>
<tr>
<td>142</td>
<td>P₂Br⁺</td>
<td></td>
</tr>
<tr>
<td>153</td>
<td>PI⁺</td>
<td></td>
</tr>
<tr>
<td>188-189</td>
<td>P₂T⁺</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>Br₂P⁺</td>
<td></td>
</tr>
<tr>
<td>192</td>
<td></td>
<td></td>
</tr>
<tr>
<td>233</td>
<td>PBrI⁺</td>
<td></td>
</tr>
<tr>
<td>254</td>
<td>T₂⁺</td>
<td></td>
</tr>
<tr>
<td>270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>272</td>
<td>P⁺Br₃</td>
<td></td>
</tr>
<tr>
<td>294</td>
<td>PI⁺</td>
<td></td>
</tr>
<tr>
<td>317</td>
<td></td>
<td></td>
</tr>
<tr>
<td>319</td>
<td>Br₂PI⁺</td>
<td></td>
</tr>
<tr>
<td>364</td>
<td></td>
<td></td>
</tr>
<tr>
<td>365</td>
<td>PI₂Br⁺</td>
<td></td>
</tr>
</tbody>
</table>
Table: Mass Spectrum of triiodophosphine-boron tribromide (1:1) adduct

Spectrometer: AEI MS 902 (double focusing)
Insertion mode: Direct
Source Temperature: 260°C

Electron energy (input) = 64.0 eV

<table>
<thead>
<tr>
<th>m/e</th>
<th>11</th>
<th>15</th>
<th>28</th>
<th>32</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>6.0</td>
<td>3.6</td>
<td>15.1</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>m/e</td>
<td>61</td>
<td>76</td>
<td>79</td>
<td>80</td>
<td>81</td>
</tr>
<tr>
<td>%</td>
<td>3.0</td>
<td>5.1</td>
<td>21.2</td>
<td>30.3</td>
<td>21.2</td>
</tr>
<tr>
<td>m/e</td>
<td>82</td>
<td>89</td>
<td>90</td>
<td>91</td>
<td>92</td>
</tr>
<tr>
<td>%</td>
<td>30.3</td>
<td>2.7</td>
<td>13.3</td>
<td>2.4</td>
<td>10.3</td>
</tr>
<tr>
<td>m/e</td>
<td>124</td>
<td>125</td>
<td>127</td>
<td>128</td>
<td>142</td>
</tr>
<tr>
<td>%</td>
<td>9.1</td>
<td>3.6</td>
<td>18.2</td>
<td>15.1</td>
<td>3.3</td>
</tr>
<tr>
<td>m/e</td>
<td>153</td>
<td>167</td>
<td>168</td>
<td>169</td>
<td>170</td>
</tr>
<tr>
<td>%</td>
<td>5.1</td>
<td>15.1</td>
<td>51.5</td>
<td>27.3</td>
<td>100.0</td>
</tr>
<tr>
<td>m/e</td>
<td>171</td>
<td>172</td>
<td>188</td>
<td>190</td>
<td>192</td>
</tr>
<tr>
<td>%</td>
<td>14.8</td>
<td>48.5</td>
<td>3.0</td>
<td>5.4</td>
<td>2.7</td>
</tr>
<tr>
<td>m/e</td>
<td>236</td>
<td>238</td>
<td>246</td>
<td>247</td>
<td>248</td>
</tr>
<tr>
<td>%</td>
<td>6.1</td>
<td>6.1</td>
<td>3.0</td>
<td>11.2</td>
<td>8.8</td>
</tr>
<tr>
<td>m/e</td>
<td>249</td>
<td>250</td>
<td>251</td>
<td>252</td>
<td>253</td>
</tr>
<tr>
<td>%</td>
<td>30.3</td>
<td>7.9</td>
<td>27.3</td>
<td>2.7</td>
<td>24.2</td>
</tr>
<tr>
<td>m/e</td>
<td>285</td>
<td>317-318</td>
<td>364</td>
<td>365-366</td>
<td>412</td>
</tr>
<tr>
<td>%</td>
<td>6.1</td>
<td>2.4</td>
<td>4.5</td>
<td>4.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>

(1) Base peak at m/e 170 (33 mm, 100%)
(2) Peak heights less than 2% are not accounted for.
(3) Mass spectrometry at School of Pharmacy (University of London)
      Intercolligate Research Service their Ref. No: 69/644 dated 7.5.69.
(4) No significant peak observed between 413-663 (mol. wt. of compound).
Table  Mass Spectrum analysis of triiodophosphine-boron tribromide (1:1) adduct referring to major significant peaks

<table>
<thead>
<tr>
<th>M.S.P. (m/e)</th>
<th>Probable Species</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>Br⁺/iBr</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>81</td>
<td></td>
<td></td>
</tr>
<tr>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>89</td>
<td>EBr⁺(EBr)</td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>124</td>
<td>P⁴⁺</td>
<td></td>
</tr>
<tr>
<td>127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>168</td>
<td></td>
<td></td>
</tr>
<tr>
<td>169</td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>EBr₂⁺</td>
<td>Base peak at m/e 170, 33 mm, 100%</td>
</tr>
<tr>
<td>171</td>
<td></td>
<td></td>
</tr>
<tr>
<td>172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>247</td>
<td></td>
<td></td>
</tr>
<tr>
<td>248</td>
<td></td>
<td></td>
</tr>
<tr>
<td>249</td>
<td>EBr³⁺</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>251</td>
<td></td>
<td></td>
</tr>
<tr>
<td>253</td>
<td></td>
<td></td>
</tr>
<tr>
<td>285</td>
<td>PI²⁺</td>
<td></td>
</tr>
<tr>
<td>412</td>
<td>PI³⁺</td>
<td></td>
</tr>
</tbody>
</table>
SECTION-III. RESULTS

CHAPTER I.E: EFUSION NANOETRIC RESULTS
Effusion Manometric Results

This chapter presents the results for the latent heat of sublimation determined via experimental measurements of vapour pressure as a function of temperature of:

(i) Ferrocene (as test compound)
(ii) Triiodophosphine
(iii) Diphosphorus tetraiodide

These data were obtained from an effusion manometer constructed in this laboratory. The basic equations for deriving vapour pressure data are as follows:

\[ p = \frac{W}{tA} \sqrt{\frac{2 \pi RT}{M}} \times \frac{1}{K_0} \times \frac{1}{c_0} \]  \hspace{1cm} (1)

\[ p = \frac{W}{tA} \sqrt{\frac{2 \pi RT}{M}} \times K_n \times \frac{1}{c_0} \]  \hspace{1cm} (2)

\[ p = \frac{W}{tA} \sqrt{\frac{2 \pi RT}{M}} \times \left( \frac{3L + 8r}{8r} \right) \left( \frac{1}{1 + K_2 + r/2\gamma} \right) \times \frac{1}{c_0} \]  \hspace{1cm} (3)

where:

- \( p \) = pressure (mm. Hg.)
- \( W \) = weight loss (g.)
- \( t \) = time (sec.)
- \( A \) = area of the orifice (cm²)
- \( R \) = gas constant, \( 8.3143 \times 10^7 \) erg, deg⁻¹, mole⁻¹
- \( T \) = absolute temperature \( (t(°) + 273.15) °K \)
- \( M \) = molecular weight Ferrocene = 186.041
- \( \text{F}_{13} \) = 411.6870
- \( \text{P}_{2L4} \) = 569.5652
\[ \xi_0 = 1 \]
\[ \frac{1}{K_e} = 1.07158 \]
\[ K_n = 1.05415 \]
\[ r = 1.349 \times 10^{-2} \text{ cm.} \]
\[ \lambda = \frac{kT}{\sqrt{2 \pi \sigma^2 p}} \quad \left( = \frac{1}{\sqrt{2 \pi N \rho^2}} \right) \]

where
- \( \lambda \) = mean free path (cm.)
- \( k \) = Boltzmann's Constant, \( 1.3805 \times 10^{-16} \text{ erg} \cdot \text{K}^{-1} \)
- \( \sigma \) or \( d \) = effective collision diameter (\( \text{Å} \))
- \( N \) = number density (or number of molecules per unit volume)

(for further details see ch. 5 p. 99)

The vapour pressure data derived from equation (1) and (2) are presented in this chapter as average values. While the data obtained from equation (3) are given as such. The relevant graphs are presented with and without the Hiby and Pahl correction factors to illustrate their magnitude. The corrected vapour pressure data are used to determine the latent heat of sublimation via the Clausius Clapeyron equation,

\[ \log_{10} p = \frac{-\Delta H_{\text{sub}}}{2.3026 \cdot 3026 \cdot RT} + C \quad \text{where} \, C = \text{constant} \]

The uncertainty interval for the slope of the \( \log_{10} p \) vs \( 1/T \) plot was determined from the following expression

\[ \frac{1}{n} \left[ \frac{x_1^2}{(n-2)} \left( \frac{\sum x_1^2}{n} - n \bar{x}^2 \right) \right]^{\frac{1}{2}} \]

where \( r \) = residual
- \( n \) = no. of sets
- \( x = T^{-1} \)
TABLE. Comparison of the available literature data for the vapour pressure ($P_{298}$) and latent heat of sublimation ($\Delta H (c \rightarrow g)$) for ferrocene.

<table>
<thead>
<tr>
<th>LITERATURE</th>
<th>$\Delta H (c \rightarrow g)_{298}$</th>
<th>$P_{298}$ (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kcal mole$^{-1}$</td>
<td>KJ mole$^{-1}$</td>
</tr>
<tr>
<td>Edwards &amp; Kington (1962)</td>
<td>17.53 $\pm$ 0.10</td>
<td>73.34 $\pm$ 0.42</td>
</tr>
<tr>
<td>Andrews &amp; Westrum (1969)</td>
<td>17.33 $\pm$ 0.13</td>
<td>72.72 $\pm$ 0.54</td>
</tr>
<tr>
<td>This work</td>
<td>17.84 $\pm$ 0.96</td>
<td>74.64 $\pm$ 4.02</td>
</tr>
</tbody>
</table>
### Table: Synopsis of Effusion Manometric Data

<table>
<thead>
<tr>
<th>DATUM</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of empty stainless steel cell (complete)</td>
<td>25.8161 g.</td>
</tr>
<tr>
<td>Weight of Ferrocene (2/3 cell capacity)</td>
<td>1.7719 g.</td>
</tr>
<tr>
<td>Weight of PI₃ (2/3 cell capacity)</td>
<td>5.9657 g.</td>
</tr>
<tr>
<td>Weight of P₂I₄ (2/3 cell capacity)</td>
<td>6.1244 g.</td>
</tr>
<tr>
<td>Area of the orifice (A)</td>
<td>1.0740 x 10⁻³ cm²</td>
</tr>
<tr>
<td>Thickness of the gold foil (t)</td>
<td>2.6702 x 10⁻³ cm.</td>
</tr>
<tr>
<td>Radius of the orifice (r)</td>
<td>1.849 x 10⁻² cm.</td>
</tr>
<tr>
<td>Radius of the foil (R)</td>
<td>8.729 x 10⁻¹ cm.</td>
</tr>
<tr>
<td>Ratio of thickness to radius</td>
<td>1.444 x 10⁻¹ cm.</td>
</tr>
<tr>
<td>Mean free path λ₉Ferrocene ca. 25°C</td>
<td>1.335 x 10⁻¹ cm.</td>
</tr>
<tr>
<td>Mean free path λ₉PI₃ ca. 25°C</td>
<td>2.447 x 10⁻¹ cm.</td>
</tr>
<tr>
<td>Mean free path λ₉P₂I₄ ca. 55°C</td>
<td>4.809 x 10⁻¹ cm.</td>
</tr>
<tr>
<td>Effective collision diameter including Vander Waals Radii d (or σ)</td>
<td></td>
</tr>
<tr>
<td>d Ferrocene</td>
<td>7.36⁰Å</td>
</tr>
<tr>
<td>d PI₃</td>
<td>8.56⁰Å</td>
</tr>
<tr>
<td>d P₂I₄</td>
<td>9.85⁰Å</td>
</tr>
<tr>
<td>ΔH (Ferrocene, C → g) 298</td>
<td>74.64 ± 4.02 KJ mole⁻¹</td>
</tr>
<tr>
<td>(17.84 ± 0.96 Kcal mole⁻¹)</td>
<td>63.64 ± 3.60 KJ mole⁻¹</td>
</tr>
<tr>
<td>ΔH (PI₃, C → g) 298</td>
<td>69.87 ± 2.09 KJ mole⁻¹</td>
</tr>
<tr>
<td>(16.70 ± 0.50 Kcal mole⁻¹)</td>
<td>63.64 ± 3.60 KJ mole⁻¹</td>
</tr>
</tbody>
</table>
(1) Ferrocene : m. pt. 175 - 176°C (purified by a modification of the procedure of Edwards et al.\textsuperscript{167}) was used in powdered form.

(2) Triiodophosphine : m. pt. 61°C, the samples of Dr. I. H. Wood of this laboratory and K. & K. laboratory Inc., California, (batch No: 17819) were used in powdered form.

(3) Diphosphorus tetraiodide : m. pt. 124.5°C prepared according to the method of German and Traxler\textsuperscript{91} (see, synthesis on p. 49) and also a Koch-Light sample were used in powdered form.

(*) Weight of cell after each experiment was checked and remained the same.)
TABLE  Photomicrographic measurements on gold foil (linear magnification x 100) from effusion manometric cell

<table>
<thead>
<tr>
<th>(i) Radius of Orifice (r)</th>
<th>(a) By Travelling Microscope : $1.8480 \times 10^{-2}$ cm.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b) By Weighted Planimeter : $1.8498 \times 10^{-2}$ cm.</td>
</tr>
<tr>
<td></td>
<td>Radius of Orifice (r) : $1.849 \times 10^{-2}$ cm.</td>
</tr>
<tr>
<td>(ii) Thickness of foil (l)</td>
<td>$2.670 \times 10^{-3}$ cm.</td>
</tr>
<tr>
<td>(iii) Radius of foil (R)</td>
<td>$8.729 \times 10^{-4}$ cm.</td>
</tr>
</tbody>
</table>

$$x = \frac{m}{Q\left(R^2 - r^2\right)} \times \frac{1}{\kappa}$$

Where

- $m = \text{mass of foil} = 0.1233$ g.
- $Q = \text{density of foil (Au)} = 19.3$ g. ml$^{-1}$
<table>
<thead>
<tr>
<th>S  (°C)</th>
<th>tu  uncorrected (°C)</th>
<th>E.S.H. (°C)</th>
<th>E.S.C. (°C)</th>
<th>t  corrected (°C)</th>
<th>Q  corrected (°C)</th>
<th>Δn (Q-t)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.09</td>
<td>21.471</td>
<td>3.186</td>
<td>0.0007</td>
<td>21.4717</td>
<td>21.459</td>
<td>-0.0127</td>
</tr>
<tr>
<td>20.11</td>
<td>22.460</td>
<td>4.195</td>
<td>0.0015</td>
<td>22.4515</td>
<td>22.467</td>
<td>-0.0145</td>
</tr>
<tr>
<td>20.12</td>
<td>23.520</td>
<td>5.235</td>
<td>0.0028</td>
<td>23.5228</td>
<td>23.505</td>
<td>-0.0178</td>
</tr>
<tr>
<td>20.15</td>
<td>24.478</td>
<td>6.193</td>
<td>0.0042</td>
<td>24.4822</td>
<td>24.469</td>
<td>-0.0132</td>
</tr>
<tr>
<td>20.16</td>
<td>25.460</td>
<td>7.175</td>
<td>0.0060</td>
<td>25.4660</td>
<td>25.452</td>
<td>-0.0140</td>
</tr>
<tr>
<td>20.10</td>
<td>26.013</td>
<td>7.730</td>
<td>0.0073</td>
<td>26.0203</td>
<td>26.006</td>
<td>-0.0143</td>
</tr>
<tr>
<td>20.20</td>
<td>27.018</td>
<td>8.763</td>
<td>0.0096</td>
<td>27.0576</td>
<td>27.045</td>
<td>-0.0126</td>
</tr>
</tbody>
</table>

*resolution to 0.0001°C
s = average surrounding temperature over a period of 1 hr.
tu = Mercury thermometer (N.F.L.B.S. 791 type)
t = Mercury thermometer (N.F.L.B.S. 791 type) corrected. (Exposed stem correction, E.S.C.)
E.S.C. = 1.6 × 10^{-4} × H (tu - s)
H = exposed mercury stem height (ESH, in °C)
Q = Z - 0.01, corrected Quartz temperature (°C)
Z = Uncorrected Quartz temperature (°C)
n = difference in temperatures (°C)
CALIBRATION OF MERCURY THERMOMETER AGAINST QUARTZ THERMOMETER (2801A, HEWLETT PACKARD)

Fig. Absolute temperature error (Δm) of Mercury in glass thermometer vs. apparent temperature.
### TABLE: Comparison of Vapour Pressure Data for Ferrocene (See graph on P.185)

<table>
<thead>
<tr>
<th></th>
<th>EDWARDS and KINTON 196</th>
<th>ANDREWS and WESTRUM 200</th>
<th>THIS WORK 76</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°K)</td>
<td>10^3/T (°K)</td>
<td>10^3 P (mm Hg.)</td>
</tr>
<tr>
<td>295.039</td>
<td>3.389</td>
<td>5.129</td>
<td>0.7101</td>
</tr>
<tr>
<td>295.082</td>
<td>3.389</td>
<td>5.165</td>
<td>0.7131</td>
</tr>
<tr>
<td>298.004</td>
<td>3.356</td>
<td>6.908</td>
<td>0.8393</td>
</tr>
<tr>
<td>298.007</td>
<td>3.356</td>
<td>6.894</td>
<td>0.8385</td>
</tr>
<tr>
<td>290.007</td>
<td>3.356</td>
<td>6.897</td>
<td>0.8386</td>
</tr>
<tr>
<td>300.345</td>
<td>3.329</td>
<td>8.730</td>
<td>0.9410</td>
</tr>
<tr>
<td>300.314</td>
<td>3.330</td>
<td>8.694</td>
<td>0.9392</td>
</tr>
<tr>
<td>303.056</td>
<td>3.299</td>
<td>11.174</td>
<td>1.0482</td>
</tr>
<tr>
<td>303.073</td>
<td>3.299</td>
<td>11.226</td>
<td>1.0500</td>
</tr>
</tbody>
</table>

- The table lists data points for temperature (T), inverse temperature (1/T), vapour pressure (P), and logarithm of vapour pressure (log_{10}P) for three different sets of data: Edwards and Kinton (196), Andrews and Westrum (200), and this work (76).
Comparison of Vapour Pressure Data for Ferrocene.
TABLE  Effusion Manometric Results for Ferrocene \((C_5H_5)_2Fe\)

\(\lambda = \text{free-mean path} = \left(\frac{1}{2} \pi \frac{N a^2}{N}\right)^{-1}\), \(N = \text{number density}, \quad \bar{F} = \frac{1}{2}(P_1 + P_2)\) [See pp. 100-3 for the expressions.]

\(d = \text{effective collision diameter with van der Waals radii (7.36A)}\)

\(P = P_3 = P_2 \times F\) (\(F = \text{Hiby and Fahl correction factor}\))

<table>
<thead>
<tr>
<th>(\bar{v}/t^{-1}) (cm/sec)</th>
<th>(T) (°K)</th>
<th>(10^3\bar{v}/(°K))</th>
<th>(10^3\bar{F}) (mmHg.)</th>
<th>(10\lambda) (cm.)</th>
<th>(F)</th>
<th>(10^3 P) (mmHg.)</th>
<th>(3 + \log_{10} P)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0168/72000</td>
<td>294.137</td>
<td>3.399</td>
<td>4.998</td>
<td>2.542</td>
<td>0.9628</td>
<td>4.672</td>
<td>0.6877</td>
</tr>
<tr>
<td>0.0178/72000</td>
<td>295.134</td>
<td>3.388</td>
<td>5.304</td>
<td>2.404</td>
<td>0.9619</td>
<td>5.165</td>
<td>0.7131</td>
</tr>
<tr>
<td>0.0201/72000</td>
<td>296.132</td>
<td>3.377</td>
<td>5.999</td>
<td>2.132</td>
<td>0.9796</td>
<td>5.829</td>
<td>0.7656</td>
</tr>
<tr>
<td>0.0226/72000</td>
<td>297.134</td>
<td>3.365</td>
<td>6.757</td>
<td>1.899</td>
<td>0.9771</td>
<td>6.549</td>
<td>0.8161</td>
</tr>
<tr>
<td>0.0246/75600</td>
<td>298.136</td>
<td>3.354</td>
<td>7.017</td>
<td>1.835</td>
<td>0.9784</td>
<td>6.795</td>
<td>0.8322</td>
</tr>
<tr>
<td>0.0274/72000</td>
<td>299.136</td>
<td>3.343</td>
<td>8.220</td>
<td>1.572</td>
<td>0.9725</td>
<td>7.929</td>
<td>0.8992</td>
</tr>
<tr>
<td>0.0309/72000</td>
<td>300.137</td>
<td>3.332</td>
<td>9.285</td>
<td>1.396</td>
<td>0.9692</td>
<td>8.926</td>
<td>0.9506</td>
</tr>
</tbody>
</table>
Fig. Vapour Pressure vs. Absolute Temperature for Ferrocene.
Fig. Logarithm of Vapour Pressure vs. Reciprocal Absolute Temperature for Ferrocene.
TABLE   Effusion Yanometric Results for HF

\( \lambda \) = Free-mean path = \( \left( \frac{1}{2} \pi N d^2 \right)^{-1} \), \( N \) = number density, \( F = \frac{1}{2}(P(1) + P(2)) \) (See pp. 100-3 for the expressions)
\( d \) = effective collision diameter with Vander Waals radii (8.56 Å), \( P = P(3) = P(2) \times F \) (F = Hibi and Pahl correction factor)

<table>
<thead>
<tr>
<th>( \frac{w}{t} ) (cm. Sec)</th>
<th>( T ) (°K)</th>
<th>( 10^3 \frac{\lambda}{T} ) (cm)</th>
<th>( 10^3 \frac{F}{(mmHg)} )</th>
<th>( 10^3 \frac{P}{(mmHg)} )</th>
<th>( F )</th>
<th>( 3 + \log_{10} P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0135/72000</td>
<td>294.137</td>
<td>3.399</td>
<td>2.690</td>
<td>3.492</td>
<td>0.9874</td>
<td>2.634</td>
</tr>
<tr>
<td>0.0135/72000</td>
<td>294.137</td>
<td>3.399</td>
<td>2.690</td>
<td>3.492</td>
<td>0.9874</td>
<td>2.634</td>
</tr>
<tr>
<td>0.0143/72000</td>
<td>295.1345</td>
<td>3.388</td>
<td>2.854</td>
<td>3.303</td>
<td>0.9867</td>
<td>2.793</td>
</tr>
<tr>
<td>0.0152/72000</td>
<td>295.1345</td>
<td>3.388</td>
<td>3.034</td>
<td>3.107</td>
<td>0.9859</td>
<td>2.966</td>
</tr>
<tr>
<td>0.0166/72000</td>
<td>296.132</td>
<td>3.377</td>
<td>3.319</td>
<td>2.850</td>
<td>0.9847</td>
<td>3.241</td>
</tr>
<tr>
<td>0.0166/72000</td>
<td>296.132</td>
<td>3.377</td>
<td>3.318</td>
<td>2.850</td>
<td>0.9847</td>
<td>3.241</td>
</tr>
<tr>
<td>0.0171/72000</td>
<td>297.134</td>
<td>3.365</td>
<td>3.424</td>
<td>2.771</td>
<td>0.9842</td>
<td>3.343</td>
</tr>
<tr>
<td>0.0174/72000</td>
<td>297.134</td>
<td>3.365</td>
<td>3.424</td>
<td>2.771</td>
<td>0.9842</td>
<td>3.343</td>
</tr>
<tr>
<td>0.0206/72000</td>
<td>298.136</td>
<td>3.354</td>
<td>4.132</td>
<td>2.304</td>
<td>0.9611</td>
<td>4.021</td>
</tr>
<tr>
<td>0.0194/72000</td>
<td>298.136</td>
<td>3.354</td>
<td>3.891</td>
<td>2.447</td>
<td>0.9822</td>
<td>3.791</td>
</tr>
<tr>
<td>0.0204/72000</td>
<td>299.136</td>
<td>3.343</td>
<td>4.099</td>
<td>2.331</td>
<td>0.9813</td>
<td>3.989</td>
</tr>
<tr>
<td>0.0225/72000</td>
<td>300.137</td>
<td>3.332</td>
<td>4.528</td>
<td>2.117</td>
<td>0.9795</td>
<td>4.399</td>
</tr>
</tbody>
</table>
Fig. Vapour Pressure vs. Absolute Temperature for Trithiophosphine.
Fig.
Logarithm of Vapor Pressure vs. Reciprocal Absolute Temperature for Trifluorophosphine.
<table>
<thead>
<tr>
<th>( W_b^{-1} ) (sec⁻¹)</th>
<th>( d )</th>
<th>( \lambda )</th>
<th>( (\text{cm}^3/\text{mole}) )</th>
<th>( (\text{cm}^3/\text{mole}) )</th>
<th>( \text{P} )</th>
<th>( \text{P} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0145/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
<tr>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
<td>0.0149/86.00</td>
</tr>
</tbody>
</table>
Fig. Vapour Pressure vs. Absolute Temperature for Phosphorus Tetraiodide.
Logarithm of Vapour Pressure vs. Reciprocal Absolute Temperature for Diphenylphosphorus Pentadiode.
SECTION IV. DISCUSSION

CHAPTER TEN:
DISCUSSION

The Phosphorus-Phosphorus Bond Strength in Diphosphorus Tetraiodide

Bond energies and bond dissociation energies are usually derived from\textsuperscript{12,25,29,32,35,36,213} thermochromal and mass-spectrometric \textsuperscript{25,41,187,190,213} measurements respectively. These procedures are adopted in the present investigation for the determination of the bond energy, $E_{P-P}$, and the bond dissociation energy, $D_{P-P}$, in diphosphorus tetraiodide. The ancillary data required for the determination of $E_{P-P}$ can be seen from the following thermodynamic equations.

\[
P_2I_4(g) = 2P(g) + 4I(g)
\]

\[
E_{P-P} + 4E_{P-I} = 2\Delta H^\circ_I(P, g) + 4\Delta H^\circ_I(I, g) - \Delta H^\circ_I(P_2I_4, g)
\]

There is no direct method for the determination of the phosphorus-iodine bond in diphosphorus tetraiodide, hence the assumption is made that $E_{P-I}$ in diphosphorus tetraiodide equals $E_{P-I}$ in triiodophosphine. This also presumes a knowledge of the standard heat of formation of triiodophosphine (gas). Data for the standard heat of formation of diphosphorus tetraiodide (crystal) and triiodophosphine (crystal) are now available in the literature\textsuperscript{104} but no experimental data for the latent heats of sublimation of triiodophosphine or diphosphorus tetraiodide were available in the literature. Therefore these have been determined via an effusion manometric technique. A full description of this technique appears in Chapter five. Previously estimates for these functions have been made. For example, the latent heat of sublimation of diphosphorus tetraiodide was estimated as 30 Kcal mole\textsuperscript{-1} in 1940. Doubts have been expressed as to the magnitude of this estimate. This investigation now shows that the sublimation enthalpy is $16.70 \pm 0.5$ Kcal mole\textsuperscript{-1}, much lower than the estimate.
(See Chapter nine: Effusion Manometric Results, for further details). Sublimation enthalpies are always the most difficultly-accessible functions in the determination of bond energies in compounds whose standard states are crystalline and which melt with decomposition. Therefore the thermal stability of diposphorus tetraiodide has been investigated by a thermal analysis technique (see Chapter four: (A)). Results obtained from thermogravimetric analysis (TGA) show a negligibly small (ca. 0.5%) weight-loss prior to the melting point, which is presumably due to sublimed material escaping from volatile sample cell. (See Chapter seven: Thermal Analysis Results for design of cell and full details of TGA). For substances having low vapour pressures, less than 0.05 mm. Hg. at ambient temperature, effusion manometry is a suitable technique for vapour pressure determination. An effusion manometer similar to the design of Edwards and Kington has been constructed for this work (see Chapter five: Effusion Manometry, for design and description of the manometer). A minor modification in the material of the effusion cell was introduced due to the corrosive nature of the phosphorus iodides. The effusion cell is fabricated in stainless steel and the foil in gold. Initially the effusion manometer was tested with a carefully purified sample of ferrocene. The purification procedure of Edwards et al. was used (see Chapter two: Purification). The fundamental quantity measured by an effusion manometer is vapour pressure. There are two sets of reliable data in the literature for ferrocene, using a similar manometer and temperature range. The present results for the vapour pressure of ferrocene are in excellent agreement with Edwards and Kington. (See Chapter nine: Effusion Manometric Results, for numerical data and graphs).
### Table - Comparison of Effusion Nanometric Data for Ferrocene

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>MATERIAL</th>
<th>VAPOUR PRESSURE</th>
<th>$\Delta H^{\circ} (\text{cell})$</th>
<th>$\Delta H^{\circ} (\text{foil})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$298 \text{ K}$ (mm Hg.)</td>
<td>(Kcal mole$^{-1}$)</td>
<td>(KJ mole$^{-1}$)</td>
</tr>
<tr>
<td>Edwards and Kington</td>
<td>Aluminium</td>
<td>0.00684</td>
<td>17.53 ± 0.10</td>
<td>73.34 ± 0.42</td>
</tr>
<tr>
<td>Andrews and Westrum</td>
<td>Copper</td>
<td>0.00714</td>
<td>17.38 ± 0.13</td>
<td>72.72 ± 0.54</td>
</tr>
<tr>
<td>This Work</td>
<td>Stainless Steel</td>
<td>0.00680</td>
<td>17.64 ± 0.96</td>
<td>74.64 ± 4.02</td>
</tr>
</tbody>
</table>

The value of the enthalpy of sublimation of ferrocene, listed in the above table, is derived from the Clausius-Clapeyron equation. There is nearly an order of magnitude difference in precision of the present data compared with that of Edwards and Kington or Andrews and Westrum. This may be attributed to the necessity of fabricating the effusion cell in stainless steel, a relatively poor thermal conductor compared with copper or aluminium (Cu, 3.85; Al, 2.38; stainless steel, 0.245 Joule cm$^{-2}$ sec$^{-1}$ deg$^{-1}$ at 0°C). Using this apparatus, the vapour pressure of triiodophosphine and diphosphorus tetraiodide were determined. These compounds are oxygen- and moisture-sensitive, so appropriate precautions were taken in their handling. Triiodophosphine was studied over the temperature range 20-28°C and diphosphorus tetraiodide over a higher range, 50-80°C. This is because preliminary experiments for this compound gave irreproducibly small weight losses. Each run over the same temperature range was repeated thrice in ascending and descending order of temperature. The sublimate of triiodophosphine and diphosphorus tetraiodide in isolated runs was analysed. In both cases the theoretical I:P ratio was confirmed. Also the absolute weight loss in isolated runs was confirmed by analysis of the sublimate. The correction to be applied for conversion of the diphosphorus tetraiodide data (observed at 340 K) to 298.15 K is assumed to be within the experimental limits.
of error. Least-squares analysis gave (see Chapter nine: Diffusion Nanometric Results, for complete numerical and graph details).

\[ \Delta H \left( \text{PH}_3, \text{c-g} \right) 298 = 15.21 \pm 0.36 \text{ Kcal mole}^{-1} \]

\[ \Delta H \left( \text{P}_2\text{I}_4, \text{c-g} \right) 298 = 16.70 \pm 0.50 \text{ Kcal mole}^{-1} \]

Incorporating the first figure in a thermodynamic cycle for triiodophosphine along with ancillary data (as shown on p. 200), the average bond dissociation energy, \( E_{\text{P-I}} \) is obtained as 50 Kcal mole\(^{-1}\). This figure, assumed equal to \( E_{\text{P-I}} \) in diposphorus tetraiodide, is inserted into a similar cycle for diposphorus tetraiodide and a value of 62 Kcal has resulted for bond energy \( E_{\text{P-P}} \).

Most phosphorus-phosphorus bonded compounds (acyclic and cyclic) have a nearly constant P-P bond length of ca. 2.21 Å. Some of these are listed below with exceptions.

Table - Phosphorus-Phosphorus Bond Lengths

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>PHASE STUDIED</th>
<th>METHOD</th>
<th>P-P BOND LENGTH (Å)</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{P}_2\text{I}_4 )</td>
<td>Solid</td>
<td>X-ray</td>
<td>2.21 ± 0.06</td>
<td>95</td>
</tr>
<tr>
<td>( \text{P}_2(\text{CH}_3)_4 )</td>
<td>Gas</td>
<td>Electron Diffraction</td>
<td>2.190 ± 0.009</td>
<td>216</td>
</tr>
<tr>
<td>( \text{P}_4 )</td>
<td>Gas</td>
<td>Electron Diffraction</td>
<td>2.21 ± 0.02</td>
<td>217</td>
</tr>
<tr>
<td>( (\text{CF}_3\text{P})_4 )</td>
<td>Solid</td>
<td>X-ray</td>
<td>2.210 ± 0.005</td>
<td>218</td>
</tr>
<tr>
<td>( (\text{C}_6\text{H}_2\text{P})_5 )</td>
<td>Solid</td>
<td>X-ray</td>
<td>2.210 ± 0.006</td>
<td>78</td>
</tr>
<tr>
<td>( (\text{C}_6\text{H}_2\text{P})_6 )</td>
<td>Solid</td>
<td>X-ray</td>
<td>2.230 ± 0.005</td>
<td>79</td>
</tr>
</tbody>
</table>

In contrast, the data concerning phosphorus-phosphorus bond energy \( E_{\text{P-P}} \) and bond dissociation energy \( D_{\text{P-P}} \) are divergent. These appear in the following table.
Fig. Thermodynamic cycles, for average bond dissociation energy of phosphorus iodide bonds in triiodophosphate and for bond energy of phosphorus-phosphorus bond in diphosphorus tetraiodide using Thermochemical and Effusion manometric Data.
The extent of the participation of the 3s, 3p and 3d orbitals in the P-P bond remains unsettled. Hence energetic calculations based on the electronic character of the bond are not yet meaningful.

From comparison of the relative percentage abundances in the mass spectra of diphosphorus tetrafluoride and dinitrogen tetrafluoride, it has been suggested that the P-P bond strength is greater than N-N bond strength. Appearance potential measurements for the phosphorus-chloride system (P4Cl2 and P2Cl4) have shown that D_{P-P} in diphosphorus tetrachloride is ca. 53 kcal mole\(^{-1}\). In this work, the phosphorus-iodide system has been investigated by a similar technique to obtain D_{P-P} in diphosphorus tetraiodide. (See Chapter four: (B) for Mass Spectrometric technique and Chapter eight: Mass Spectrometric Results for complete details of the mass spectra). The determination of D_{P-P} in diphosphorus tetraiodide requires a knowledge of the ionization potential I.P.\,(P2I2) in P2I4 and the appearance potential A.P.\,(P2I2\,\,+) for P2I4 species. Both these values are not available in the literature. Therefore A.P.\,(P2I2\,\,+) for P2I4 was experimentally measured in this work using an AEI model MS2H mass spectrometer with a direct inlet system for solid samples. The method of Lossing et al. was
\[ \text{D(B.DE)} = \text{BOND DISSOCIATION ENERGY} \]

\[ \text{A.P.} = \text{APPEARANCE POTENTIAL} \]

\[ \text{I.P.} = \text{IONIZATION POTENTIAL} \]

\[ [\text{eV}] \]

(1) \[ \text{A.P.} (\text{PI}_3^+ \text{PI}_3) = 11.9 \pm 0.15 \] (This work)

(2) \[ \text{A.P.} (\text{I}^+_3 \text{PI}_3) = 12.7 \pm 0.15 \] [Assumed, \( = E_{\text{I.P}} + \text{I.P} (\text{I}) \)]

(3) \[ \text{I.P.} (\text{I}) = 10.45 \] (Lit.)^223

(4) \[ \text{D}_{\text{P.I}} = 2.25 \] (Calc.)

(5) \[ \text{I.P.} (\text{PI}_2) = 9.65 \] (Calc.)

(6) \[ \text{A.P.} (\text{PI}_2^+ \text{PI}_4) = 12.9 \pm 0.15 \] (This work)

(7) \[ \text{I.P.} (\text{PI}_4) = 9.65 \] [Calc. as in (5)]

(8) \[ \text{D}_{\text{P.I}} = 3.15 \pm 0.26 \] (Calc.)

Fig. Thermodynamic cycles for bond dissociation energies of phosphorus iodide bond in triiodophosphine and of phosphorus-phosphorus bond in diphosphorus tetraiodide using Mass Spectrometric Data.
employed to determine the appearance potential using argon as internal standard.

\[ \text{P}_2\text{I}_4 + e \rightarrow \text{P}^+ + \text{P}_2\text{I}_2 + 2e \quad A.P.(\text{P}^+)_{\text{P}_2\text{I}_4} = 12.8 \pm 0.15 \text{eV} \]

Since there are no data available in the literature for I.P.(P\text{I}_2) from P\text{I}_4, an indirect method can be used by equating this function via I.P.(P\text{I}_2) from P\text{I}_3.

I.P.(I) = 10.45 eV\textsuperscript{223}, but A.P.(P\text{I}_2\text{I}_2)\text{P}_3, A.P.(I^+)\text{P}_3, and I\text{P}_2-I are unknown.

The experimental measurement of A.P.(P\text{I}_2\text{I}_2) for P\text{I}_3 in the present work was performed using the same instrument and adopting similar procedure as for P\text{I}_4.

The process investigated under electron impacts was

\[ \text{P}_2\text{I}_3 + e \rightarrow \text{P}^+ + \text{I} + 2e \quad A.P.(\text{P}^+)_{\text{P}_2\text{I}_3} = 11.9 \pm 0.15 \text{eV} \]

The further assumption is made that D\text{P}_2-I = D\text{P}_2-I in triiodophosphine, and hence, inserting the relevant values, it follows that D\text{P}_2-P in diposphorus tetraiodide is 72.60 \pm 6 \text{Kcal mole}^{-1}. This must be considered as an upper limit in view of the kinetic energy imparted to the fragment-ion by the accelerating voltage.
Phosphobenzene

The tendency towards catenation rather than to multiple bonding in phosphorus compounds is demonstrated in the synthesis of mono-, bi-, tri, and polycyclic compounds (see Appendix six: Classification, for illustrations). This fact, as with other members of the second period may be attributed to increased inner shell repulsion and reluctance to form π bonds. The term phosphobenzene comprises groups of compounds which readily interconvert in solution. Some forms, identified as stable crystals under atmospheric conditions, are homocyclic, e.g. pentaphenylocyclopentaphosphine, hexaphenylocyclohexaphosphine and the so-called polymeric phenylphosphine. There seem to be unusual difficulties associated with the methods of synthesis in the above compounds, and as a result, no reproducible routes are available. Hexameric phosphobenzene is known to exist in four different allotropic modifications i.e. monoclinic, triclinic, trigonal and hexagonal (see Chapter one, for hexameric trigonal structure). In the present work synthetic methods for these compounds have been investigated. For the pentamer, a method based on the following reaction has proved to be the most reliable and reproducible.

\[ 5C_6H_5PCl_2 + 5(C_4H_9)_2P = (C_6H_5P)_5 + 5(C_4H_9)_3PCl_2 \]

The reaction takes approximately 20 min. to complete, rather than a few seconds as reported in literature. Further, this reference quotes the product as tetrameric. This material has now been identified as the pentamer by comparison of the interplanar spacings obtained via X-ray analysis with that of an authentic sample of pentaphenylocyclopentaphosphine. The numerical data and intensity estimation are presented in Appendix four. The melting-point and the purity of the material has been established via DSC and DTA methods (see Chapter four (A)). The results indicate that pentaphenylocyclopentaphosphine is pure from the
characteristic sharp melting point peak at 154°C (see Chapter seven: Thermal Analysis Results). Confirmation of purity of this material was also obtained by microanalysis. It can be seen that the material is 99.0% pure based on C₆H₅P. The L.K. and Raman spectra show some different features compared to the then-called tetramer ⁷⁷ (See Appendix three).

Repeated attempts to synthesise hexaphenylcyclohexaphosphine by literature methods have failed in the present investigation. It appears that interconversion in this form of phosphobenzene is very facile. Also low thermal stability within the allotrope modifications is manifested. For example, a change in crystal habit of an authentic sample of hexamer was observed (also noted by Maier;). This was the conversion of transparent trigonal to milky triclinic. The possibility of atmospheric oxidation was excluded as the crystals were stored in dry nitrogen. The exact conditions for interconversion are not yet completely understood. (See Chapter one; for interconversion scheme;). A method suggested for the synthesis of polymeric phenylphosphine via warming the pentamer in piperidine at 80°C did not produce satisfactory results after repeated attempts. Hence a direct synthetic route for the polymeric substance was investigated. This is based on the disproportionation reaction of phenyldifluorophosphine. The same reaction has been reported to yield form A (m.p. 151-154°C), this was confirmed by X-ray analysis. The proposed disproportionation reaction was

\[
10\text{C}_6\text{H}_5\text{PF}_2 \longrightarrow 5\text{C}_6\text{H}_5\text{PF}_4 + (\text{C}_6\text{H}_5\text{P})_5
\]

In the present work, however, the polymeric phenylphosphine was produced. The initial reaction shown below proceeds in sulpholane at 100°C, followed by disproportionation of phenyldifluorophosphine at room temperature after nine hours standing.
The resulting material had a m.p. range 264-280°C (sealed tube) compared with the literature m.p. for C and D of 252-285°C. Confirmation was obtained by comparison of the X-ray diffraction pattern with that of an authentic sample (from Kailer). The comparison showed minor differences in both intensities and interplanar spacings but eliminated the possibility of form A. The disproportionation of phenylidifluorophosphine in the presence of phenylidichlorophosphine under nitrogen also gives polymeric phenylphosphine.

There are no thermodynamic data for phosphobenzene at present in the literature. The thermochemical results obtained in this investigation were achieved by reaction-solution calorimetry (see Chapter three and Chapter six) and thermal analysis (see Chapter four (A) and Chapter seven). In order that any reaction be studied thermodynamically it is essential that its stoichiometry be known exactly. Stoichiometric reactions of pentamer and polymeric phosphobenzene to phenyl dibromophosphine and phenyl tetrabromophosphorane have been established (see Chapter six: Thermochemical Results) by bromine oxidation in non-aqueous solvents.

\[
\begin{align*}
(C_6H_5P)_2(\text{cryst.}) + 2\text{Br}_2(\text{in } C_6H_6) &= 5C_6H_5\text{PBr}_2(\text{in } C_6H_6) \\
\frac{1}{n}(C_6H_5P)_n(\text{cryst.}) + 2\text{Br}_2(\text{in } C_6H_6) &= C_6H_5\text{PBr}_4(\text{in } C_6H_6)
\end{align*}
\]

The fundamental quantity usually measurable by reaction-solution calorimetry is the heat of reaction, and the thermodynamically significant quantity derivable is the standard heat of formation, \( \Delta H^\circ_f \). For phosphobenzene (pentamer and polymer), heats of reaction are measured in this work which would be useful in deriving standard heat of formation of the pentamer when auxiliary thermodynamic
Data are available (see Chapter six). These are the standard heat of formation for phenylphosphonic and phenylphosphonic acids. The reactions studied calorimetrically for pentaphenylcyclopentaphosphine are shown in the thermodynamic cycle on p. 208. Details of the thermodynamic equations and the corresponding enthalpies are shown in Chapter six. The discrepancy of 1.80 kcal has appeared in the present cycle for pentaphenylcyclopentaphosphine. This error probably occurs in the slow reaction (step (6)) in the first half of the cycle. That the second half of the cycle is self-consistent is shown by the excellent agreement between steps (3), (4) and (5), and step (7).

Phase change studies in solids are most conveniently conducted by DSC or DTA methods. Qualitative analysis of the thermograms (DSC and DTA) obtained for phosphobenzene indicate the following phase changes (recorded on a temperature-increasing programme).

<table>
<thead>
<tr>
<th>PHOSPHOBENZENE</th>
<th>TRANSITION TEMPERATURE (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PHASE CHANGE (exothermic)</td>
</tr>
<tr>
<td>((C_6H_5P)_5)</td>
<td>86</td>
</tr>
<tr>
<td>((C_6H_5P)_6)</td>
<td>76 and 130</td>
</tr>
<tr>
<td>((C_6H_5P)_n)</td>
<td>86</td>
</tr>
</tbody>
</table>

Calibration with an indium standard indicates these temperatures are accurate to ± 0.5°C. No phase changes are noted on recycling any of these samples. Presumably, therefore, solidification on cooling to ambient temperature under calorimetric conditions did not occur. Quantitative measurements for the enthalpy change at fusion have been made for the pentamer and the polymeric form (with reference to an indium standard). The thermogram (DSC) for the polymeric form was analysed to determine the crystallinity of the sample,
\[ \Delta H_{\text{obs.}} \]

\begin{align*}
(1) & \quad -28.64 \pm 0.35 \\
(2) & \quad +0.58 \pm 0.01 \\
(3) & \quad -41.7 \pm 0.08 \\
(4) & \quad -1.43 \pm 0.04 \\
(5) & \quad -61.31 \pm 0.33 \\
(6) & \quad -133.48 \pm 0.32 \\
(7) & \quad -104.36 \pm 0.13 \\
\end{align*}

\[ \Delta H (6) = \sum_{i=1}^{5} \Delta H = \Delta H_f^0 [\text{Br}_2, \text{aq}] - \Delta H_f^0 [\text{Br}_2, \Phi H] \]

**Fig.** Thermodynamic cycle for pentaphenylcyclopentaphosphine
compared to a polyethylene reference. The result shows ca. 73\% crystallinity in polymeric phenylphosphine and suggests heterogeneity (see Chapter seven: Thermal Analysis for details). The literature records only one crystalline form for the pentamer, so the transition at 86° may not be classified. Four crystalline modifications are reported for the hexamer, and the transitions recorded here may involve these allotropes. Henderson et al. mentioned two polymeric forms (C and D) with distinct melting ranges. The partial crystallinity of present polymeric sample could account for this fact.
Pseudohalides

Members of the pseudohalides, especially those having the isocyanato-group, have been shown to be energy-rich molecules \( \text{126} \), but experimentally derived energetic data are very scarce. In this work, thermochemical measurements for tricyanophosphine and tri(isocyanato)phosphine via reaction-solution calorimetry are presented (see Chapter six: Thermochemical Results). The synthetic procedures for pseudohalides of phosphorus usually involve exchange reactions, e.g.

\[
PCL_3 + 3AgN = P(CN) + 3AgCl
\]

and

\[
PCL_3 + 3AgNO = P(NO) + 3AgCl
\]

An interesting feature of tri(isocyanato)phosphine is its reversible polymerisation. It is reported \( \text{114} \) that a liquid sample of tri(isocyanato)-phosphine (m.p.t. = -2 ± 0.5°C, b.p.t. = 169.3 ± 0.5°C) remains unchanged upon two weeks standing. However, on supercooling to -20°C, a solid material separates which melts at -2°C. Further, this liquid, on standing for three days, solidifies into a white insoluble material with a m.p.t. of ca. 80°C. This solid was distillable to yield the original compound, b.p.t. 169.3°C. Another report describes \( \text{99} \) that tri(isocyanato)phosphine "upon standing polymerises to a yellow-white solid". In the present investigation a colourless liquid b.p.t. 169°C (lit. 169.5°C) was collected after the completion of the reaction between trichlorophosphine and silver isocyanate. (See Chapter two: Synthesis: for further details). This liquid, on standing for ca. 120 hr. under nitrogen at room temperature, started solidifying into a whitish-yellow material. Two-thirds of the liquid solidified over a period of two months. The solid material (probably polymeric) was distilled to yield a colourless liquid boiling at 40°C/0.5 mm.Hg. Subsequently this liquid was confirmed to
be monomeric tri(isocyanato)phosphine, indicating reversible depolymerisation on distillation.

Recently Pollard et al. reported the hydrolysis products of the phosphorus pseudohalides, i.e. tricyanophosphine and tri(isocyanato)phosphine in aqueous sodium hydroxide (\(\text{NaOH}\)) and hydrochloric acid (\(\text{HCl}\)). A chromatographic technique was used for the detection of the hydrolysis products. It was found that in hydrochloric acid (\(\text{HCl}\)), phosphorus pseudohalides hydrolyse quantitatively to phosphorus acid and presumably to corresponding hydrogen pseudohalides. In a basic hydrolysing medium, a mixture of lower phosphorus acids with phosphorus acid was obtained. In this investigation samples of tricyanophosphine and tri(isocyanato)phosphine were hydrolysed and the products were quantitatively estimated by a potentiometric technique, e.g.

\[
P(\text{CN})_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{HCN}
\]

For tricyanophosphine three end-points were detected, corresponding to\(pk(\text{H}-\text{H}_2\text{PO}_3) = 1.8\), \(pk(\text{H}-\text{HPO}_2\text{O}) = 6.15\), and \(pk(\text{H}-\text{CN}) = 9.14\). The purity of the sample, based on the corresponding titres, indicated a purity of 99.02\% for tricyanophosphine. A similar hydrolysis of freshly-distilled tri(isocyanato)phosphine produced three end-points (see Appendix one: Potentiometric Results) \(pk(\text{H}_2\text{PO}_3) = 1.8\), \(pk(\text{H}-\text{HPO}_2\text{O}) = 6.15\) and \(pk(\text{H}-\text{HCO}) = 3.70\). On the basis of the corresponding titres for the first and third end-points (i.e. phosphorus acid end points) a purity of 98.33\% was found for tri(isocyanato)phosphine. Calculations based on the isocyanic acid end-point gave a purity of ca. 74\%. It is known with certainty that isocyanic acid decomposes rapidly in acid solution

\[
\text{H}_2\text{NCO} + \text{H}_3\text{O}^+ \rightarrow \text{CO}_2 + \text{NH}_4^+
\]

This fact accounts for the anomalous isocyanic acid end-point.
Owing to the reversible polymerisation of tri(isocyanato)phosphine, it is essential that the molecular weight be known exactly at the time of hydrolysis in the calorimeter. A sample was shown to be monomeric by molecular weight determination (see Appendix two: Cryoscopic Results). This molecular weight determination was performed on a freshly-distilled sample of tri(isocyanato)phosphine which was stored under dry nitrogen for 12 hr. Due to the hygroscopic nature of this compound all operations were performed under an inert atmosphere of nitrogen. A cryoscopic method was used using naphthalene for calibration and testing with phenyldichlorophosphine. The result for the molecular weight determination of phenyldichlorophosphine is in excellent agreement with calculated.

For both tricyanophosphine and tri(isocyanato)phosphine, the reaction selected for the thermochemical study was the hydrolysis.

\[
P(CN)_3(c) + 3H_2O(l) = (H_3PO_3 + 3HCN)(sol.) \quad H_{obs.} = -49.58 \pm 0.12 \text{ kcal mole}^{-1}
\]

The enthalpies of reaction were determined via constant-temperature-environment (C.T.E.) calorimetry as the reactions were fast (main period for reaction was less than 2 min.). The \( \Delta H_{obs.} \) recorded for tri(isocyanato)phosphine was \(-79.81 \pm 0.31 \text{ kcal mole}^{-1} \). Using the following ancillary data in the thermodynamic equation above, it can be seen that the standard heat of formation of tricyanophosphine is \(133.63 \pm 0.4 \text{ kcal mole}^{-1} \). The literature data for \( \Delta H^\circ_{f} (H_3PO_3, aq.) = -228.9 \pm 0.3 \text{ kcal mole}^{-1} \), \( \Delta H^\circ_{f} (HCN, aq.) = 36.0 \pm 0.1 \text{ kcal mole}^{-1} \), \( \Delta H^\circ_{f} (H_2O, liq.) = -68.3 \text{ kcal mole}^{-1} \), and \( \Delta H^\circ_{f} (H_2O, liq.) = -68.3 \text{ kcal mole}^{-1} \).

A similar evaluation of the standard heat of formation for tri(isocyanato)phosphine is complicated by the fact that one of the reaction products (i.e. isocyanic acid) decomposes at a significant rate in acid solution. Lister has studied the kinetics of this decomposition under a variety of conditions.
Accordingly, in acid solution at 0°C, the rate constant $K_2$ is equal to 0.86 mole, $\text{min}^{-1}$, and the activation energy, $E_a$, equals to 14.5 kcal. From these data, the half-life of the reaction at 25°C is deduced to be between 3 and 7 min. As this time is comparable with the length of the main period for the hydrolysis (1-2 min.), no accurate derived data can be obtained.
Phosphorus (III) and Phosphorus (V) Compounds

Although numerous compounds of these classes are reported in the literature, energetic data are mainly limited to symmetric derivatives e.g. \((\text{FX}_3\), \(x = \text{halogen, alkyl, or aryl}\). The preparation of phenyltetrabromophosphorane and phenyltetrahydrochlorophosphorane is based on the following reactions in carbon tetrachloride.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{PBr}_2 + \text{Br}_2 &= \text{C}_6\text{H}_5\text{PBr}_4 \\
\text{C}_6\text{H}_5\text{PCl}_2 + \text{Cl}_2 &= \text{C}_6\text{H}_5\text{PCl}_4
\end{align*}
\]

In the present investigation phenyl dichlorophosphine has been utilized as a synthetic precursor for the phosphobenzene. Both phenyl dibromophosphine and phenyltetra dibromophosphorane were degradation products from the thermochemical reaction of phosphobenzene (i.e. \((\text{C}_6\text{H}_5\text{P})_5\) and \((\text{C}_6\text{H}_5\text{P})_n\). Hence a knowledge of their thermochemistry is important. The hydrolysis products of phenyl dibromophosphine and phenyltetra dibromophosphorane were quantitatively evaluated prior to calorimetry (see Chapter six: Thermochemical Results). Hydrolysis was shown to be quantitative according to the following equations.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{PBr}_2 + 2\text{H}_2\text{O} &= \text{C}_6\text{H}_5\text{PO}_2\text{H}_2 + 2\text{HBr} \\
\text{C}_6\text{H}_5\text{PBr}_4 + 3\text{H}_2\text{O} &= \text{C}_6\text{H}_5\text{PO}_3\text{H}_2 + 4\text{HBr} \\
\text{C}_6\text{H}_5\text{PBr}_2 + \text{Br}_2 + 3\text{H}_2\text{O} &= \text{C}_6\text{H}_5\text{PO}_3\text{H}_2 + 4\text{HBr}
\end{align*}
\]

The thermochemical reaction for phenyltetra dibromophosphorane hydrolysis was

\[
\text{C}_6\text{H}_5\text{PBr}_4(\text{cryst.}) + 3\text{H}_2\text{O}(\text{l}) = (\text{C}_6\text{H}_5\text{PO}_3\text{H}_2 + 4\text{HBr})(\text{sol.}) \quad \Delta H_{\text{obs.}} = -80.56 \pm 0.14 \text{ kcal.}
\]

and the \(\Delta H^\circ\) for \(\text{C}_6\text{H}_5\text{PBr}_4\) can be derived if the relevant ancillary data are
available. In the absence of reliable data for phenylphosphonic acid the derivable data are

\[ \Delta H_f^0 (\text{C}_6\text{H}_5\text{PBr}_4(c)) - \Delta H_f^0 (\text{C}_6\text{H}_5\text{PO}_3\text{H}_2(aq)) = 169.31 \pm 0.5 \text{ kcal mole}^{-1} \]

Similarly

\[ \text{C}_6\text{H}_5\text{PBr}_2(l) + \text{ZnCl}_2(l) = (\text{C}_6\text{H}_5\text{PO}_2\text{H}_2 + 2\text{HBr})(\text{sol.}) \Delta H_{\text{obs.}} = -41.7 \pm 0.08 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{C}_6\text{H}_5\text{PBr}_2(l)) - \Delta H_f^0 (\text{C}_6\text{H}_5\text{PO}_2\text{H}_2(aq)) = 120.2 \pm 0.2 \text{ kcal mole}^{-1} \]

Also

\[ \text{C}_6\text{H}_5\text{PBr}_2(l) + \text{Br}_2 \text{aq.} + \text{3H}_2\text{O}(l) = (\text{C}_6\text{H}_5\text{PO}_2\text{H}_2 + 4\text{HBr}) \text{aq.} \quad H_{\text{obs.}} = -104.36 \pm 0.13 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{C}_6\text{H}_5\text{PBr}_2(l)) - \Delta H_f^0 (\text{C}_6\text{H}_5\text{PO}_2\text{H}_2(\text{aq.})) = 193.7 \pm 0.4 \text{ kcal mole}^{-1} \]

Using ancillary data for \( \Delta H_f^0 \text{HBr aq.} = -29.05 \pm 0.09 \text{ kcal mole}^{-1} \), \( \Delta H_f^0 \text{H}_2\text{O} = -68.317 \), \( \Delta H_f^0 \text{Br}_2 \text{aq.} = -0.62 \text{ kcal mole}^{-1} \). Heats of mixing of the products were ignored.
Molecular Adducts

There are numerous complexes of phosphorus (III) and phosphorus (V) compounds with the trihalides of the main group three elements (see Appendix six: Classification for illustration). A recent publication and a review reveal the importance of thermochemical measurements for understanding the nature of complexing. The present work is concerned with the thermochemistry of diphosphorus tetraiodide-boron tribromide (1:2) adduct and pentabromophosphorane-boron tribromide, and mass-spectrometric studies for tribromophosphine-boron triiodide and triiodophosphine-boron tribromide. Using a thermal analysis technique it was attempted to determine relative bond strengths for each boron tribromide in the diphosphorus tetraiodide-boron tribromide (1:2) adduct. The syntheses of the molecular adducts were carried out by allowing the two components to react in the presence of dichloromethane and or carbon disulphide. Some syntheses (e.g., P$_2$I$_4$ZBr$_3$) proceed more smoothly in the absence of solvent. The results from the thermochemical investigation for the diphosphorus tetraiodide-boron tribromide (1:2) adduct are presented in the thermodynamic cycle shown on p217. It can be seen that the enthalpy of complexing (P$_2$I$_4$ZBr$_3$) for the components in their standard states is $-2.13 \pm 0.29$ kcal mole$^{-1}$. This evaluation assumes that the equilibrium in carbon disulphide is rapidly attained. Constant temperature environment calorimetry was used for step (3) and adiabatic calorimetry for step (1) and (2) (see Chapter three: for calorimetric technique). The standard heat of formation for diphosphorus tetraiodide-boron tribromide (1:2) adduct is derived from

$$
P_{2}I_{4}ZBr_{3}(c) = P_{2}I_{4}(c) + 2BB_{r_{3}}(l), \Delta H = +2.13 \pm 0.29 \text{ kcal mole}^{-1}
$$

$$
\Delta H^\circ_f (P_{2}I_{4}ZBr_{3}(c)) = -144.0 \pm 1.6 \text{ kcal mole}^{-1}.
$$
\[
\begin{align*}
\text{P}_2\text{I}_4\text{2BBR}_3(\text{sol}) & \iff \text{P}_2\text{I}_4(\text{sol}) + 2\text{BBR}_3(\text{sol}) \\
\text{AH}(1) & = \Delta H(2) = -28.34 \pm 0.11 \\
\text{AH}(3) & = 0.54 \pm 0.001 \\
\therefore \Delta H(4) & = \Delta H(3) + \Delta H(2) - \Delta H(1) \\
\Delta H(4) & = -2.13 \pm 0.29 \text{ Kcal mole}^{-1}
\end{align*}
\]

*Fig.* Thermodynamic cycle for diphosphorus tetraiodide-boron tribromide (1:2) adduct.
using the literature ancillary data for

\[ \Delta H_f^0 (P_2I_4(c)) = -27.03 \pm 1.19 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{BER}_3(l)) = -57.4 \pm 0.5 \text{ kcal mole}^{-1} \]

Since the (1:1) molecular adduct of diphosphorus tetraiodide with boron tribromide is not known, it would be of interest to examine the relative bond strengths for the boron tribromide groups. This has been attempted here via a thermal analysis technique. The results obtained by differential thermal analysis (as shown in Chapter seven) indicate two endotherms over the temperature ranges 82-110°C and 110-131°C, with the corresponding areas of the peaks being 0.50 sq.in. and 0.66 sq.in. It is probable that the first endotherm corresponds to the loss of two molecules of boron tribromide (normal b.p.t. of boron tribromide is 91°C). It is equally likely that the second endotherm corresponds to the melting of diphosphorus tetraiodide (m.pt. \( P_2I_4 = 124.5°C \)). Hence the 1:1 adduct cannot be detected by thermal analysis.

The complex pentabromophosphorane-boron tribromide (probably \( \text{FER}_4^+ \text{BBr}_4^- \)) was studied thermochemically via its hydrolysis in a CTE calorimeter

\[ \text{FER}_2\text{BBr}_3(c) + 7\text{H}_2\text{O}(l) = (\text{H}_3\text{PO}_4 + \text{H}_2\text{BO}_3 + \text{8HBr})\text{sol.}, \quad \Delta H_{\text{obs}} = -179.06 \pm 0.26 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{FER}_2\text{BBr}_3(c)) = -142.0 \pm 1.3 \text{ kcal mole}^{-1} \]

The ancillary data are: \( \Delta H_f^0 (\text{H}_2\text{O}(l)) = -68.317 \pm 0.1 \text{ kcal mole}^{-1} \)

\[ \Delta H_f^0 (\text{H}_3\text{PO}_4(\text{aq.})) = -310.5 \pm 1.0 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{H}_2\text{BO}_3(\text{aq.})) = -256.35 \pm 0.2 \text{ kcal mole}^{-1} \]

\[ \Delta H_f^0 (\text{BER}_3(\text{aq.})) = -29.05 \pm 0.09 \text{ kcal mole}^{-1} \]
SECTION V. APPENDIX

CHAPTER ELEVEN: POTENTIOMETRIC TITRATION RESULTS

CRYOSCOPIC RESULTS

VIBRATIONAL SPECTROSCOPIC RESULTS

X-RAY ANALYSIS RESULTS
APPENDIX ONE

Potentiometric Titration Results

This appendix contains the potentiometric titration graphs for the analyses of tricyanophosphine and tri(isocyanato)phosphine.

Two graphs are presented for each compound (i) pH Vs V and (ii) $\Delta$pH/$\Delta$V Vs V. For tricyanophosphine, hydrolysis proceeded according to

$$\text{P(GN)}_3^+ + 3\text{H}_2\text{O} = \text{H}_2\text{PO}_3^- + \text{HNCO}$$

Three end-points were detected corresponding to $\text{pK(H-\text{HPO}_3)} = 6.15$, $\text{pK(H-\text{PO}_3)} = 6.15$ and $\text{pK(H-CN)} = 9.14$.

For tri(isocyanato)phosphine, hydrolysis proceeded according to

$$\text{P(NCO)}_3^+ + 3\text{H}_2\text{O} = 3\text{HNCO} + \text{H}_2\text{PO}_3^-$$

Three end-points were detected, corresponding to $\text{pK(H-\text{HPO}_3)} = 1.8$, $\text{pK(H-\text{PO}_3)} = 6.15$, and $\text{pK(H-NCO)} = 3.70$.

For tricyanophosphine, the titres indicate a purity of 99.0%. For tri(isocyanato)phosphine, the first and third end-points (these for $\text{H}_2\text{PO}_3^-$) indicate a purity of 98.5%. The end-point for isocyanic acid gives anomalous results due to the decomposition of HNCO in acid solution (see Chapter ten: Discussion).

Details of the experimental equipment used are given in Chapter two.
Potentialometric Titration Graph of the Hydrolysate of Tricyanophosphine.
Fig. Derivative Graph for the Potentiometric Titrations of Tricyanophosphine.
Fig. Potentiometric Titration Graph of the Hydrolysate of Tri(isocyanato)phosphine.
Derivative Graph for the Potentiometric Titration of Tw(isonitrato)phosphine.
APPENDIX TWO

Cryoscopic Results

This appendix contains detailed results of molecular weight determinations via cryoscopy. Details of the apparatus and method are on p.66.

The results are presented in the form of graphs of weight of dissolved solute per 20 ml. benzene (solvent) vs. the freezing point (in °C). The graphs are given in the following order.

(i) Naphthalene (calibration) Mol. wt. (calc.), 128.16.
(ii) C₇H₅Cl₂ (Test compound) Mol. wt. (calc.), 178.99; Found, 179.
(iii) P(NO₃)₃, distilled and stored at ambient under nitrogen for 11.5 hr. Mol. wt. (calc.), 157.02; Found, 161.
### Concentration of Naphthalene in Benzene vs. Freezing Point (in ohms) of Solution

**NAPHTHALENE (mol.wt) 128.16**

**GRADIENT (G Δ) 1.533 x 10^{-3}**

<table>
<thead>
<tr>
<th>R (ohms)</th>
<th>$10^2W(g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.660</td>
<td>2.00</td>
</tr>
<tr>
<td>2.672</td>
<td>4.02</td>
</tr>
<tr>
<td>2.685</td>
<td>5.58</td>
</tr>
<tr>
<td>2.690</td>
<td>6.90</td>
</tr>
<tr>
<td>2.701</td>
<td>9.42</td>
</tr>
<tr>
<td>2.715</td>
<td>10.60</td>
</tr>
<tr>
<td>2.725</td>
<td>12.15</td>
</tr>
<tr>
<td>2.730</td>
<td>14.42</td>
</tr>
<tr>
<td>2.745</td>
<td>15.50</td>
</tr>
</tbody>
</table>
Fig. Concentration of Phenyl Dichlorophosphine in Benzene vs. Freezing Point (in Chr.) of Solution.
Fig. Concentration of Tri(isocyanato)phosphine in Benzene vs. Freezing Point (in ohms) of Solution.
### APPENDIX THREE

**TABLE - Comparison of Raman Spectra**

<table>
<thead>
<tr>
<th>R.L. ABSTER, W.A. HENDERSON and N.B. COLTHUP</th>
<th>THIS WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(C_{6}H_{5})<em>{4}P</em>{4}(A)$</td>
<td>$(C_{6}H_{5})<em>{4}P</em>{4}(B)$</td>
</tr>
<tr>
<td>$\bar{V}$ (cm$^{-1}$)</td>
<td>RELATIVE INTENSITY</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3192</td>
<td>0.5</td>
</tr>
<tr>
<td>3141</td>
<td>0.5</td>
</tr>
<tr>
<td>3047</td>
<td>1</td>
</tr>
<tr>
<td>1479</td>
<td>1</td>
</tr>
<tr>
<td>1480</td>
<td>1</td>
</tr>
<tr>
<td>1431</td>
<td>0.5</td>
</tr>
<tr>
<td>-</td>
<td>1380</td>
</tr>
<tr>
<td>-</td>
<td>1330</td>
</tr>
<tr>
<td>-</td>
<td>1316</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>1266</td>
</tr>
<tr>
<td>1261</td>
<td>0.5</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1190</td>
<td>1</td>
</tr>
<tr>
<td>-</td>
<td>1184</td>
</tr>
<tr>
<td>C-H in-plane bend (a)</td>
<td>1158 1.9</td>
</tr>
<tr>
<td>-----------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>X-sensitive (g)</td>
<td>1088 4.7</td>
</tr>
<tr>
<td>C-H in-plane bend (d)</td>
<td>1073 5</td>
</tr>
<tr>
<td>C-H in-plane bend (b)</td>
<td>1024 2.4</td>
</tr>
<tr>
<td>Ring (p)</td>
<td>997 9.5</td>
</tr>
<tr>
<td>C-H out-of-plane bend (j)</td>
<td></td>
</tr>
<tr>
<td>C-H out-of-plane bend (h)</td>
<td></td>
</tr>
<tr>
<td>C-H out-of-plane bend (i)</td>
<td></td>
</tr>
<tr>
<td>C-H out-of-plane bend (g)</td>
<td>804 0.5</td>
</tr>
<tr>
<td>C-H out-of-plane bend (f)</td>
<td>744 0.1</td>
</tr>
<tr>
<td>X-sensitive (v)</td>
<td>687 1</td>
</tr>
</tbody>
</table>

- shoulder 1160 1
- 1095 5
- 1081 5
- shoulder 1027 5
- 1004 10
- 988 0.5
- 936 0.5
- 915 0.5
- 867 0.5
- 745 1
- 693 1
- 687 1
<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Intensity (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>620</td>
<td>1</td>
</tr>
<tr>
<td>512</td>
<td>shoulder</td>
</tr>
<tr>
<td>501</td>
<td>6</td>
</tr>
<tr>
<td>440</td>
<td>6</td>
</tr>
<tr>
<td>427</td>
<td>5</td>
</tr>
<tr>
<td>398</td>
<td>2</td>
</tr>
<tr>
<td>370</td>
<td>1</td>
</tr>
<tr>
<td>366</td>
<td>0.5</td>
</tr>
<tr>
<td>329</td>
<td>0.5</td>
</tr>
<tr>
<td>304</td>
<td>1</td>
</tr>
<tr>
<td>289</td>
<td>1</td>
</tr>
</tbody>
</table>

C-C-C bend(s)

Asymmetric P-P stretch

Symmetric P-P stretch + t-y phenyl vibrations

F₈ ring + C₅H₅-P deformations + substituent sensitive phenyl vibrations

---

Note: The values in the table represent vibrational frequencies and intensities. The wavenumbers are given in cm⁻¹, and the intensities are in arbitrary units (a.u.).
<table>
<thead>
<tr>
<th>277</th>
<th>1</th>
<th></th>
<th></th>
<th></th>
<th>263</th>
<th>1.3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>236</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>222</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>210</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>178</td>
<td>1.8</td>
</tr>
<tr>
<td>178</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>155</td>
<td>2.5</td>
</tr>
</tbody>
</table>
### TABLE - Comparison of Infra-red Spectra

<table>
<thead>
<tr>
<th></th>
<th>KUCHEN AND BUCHAMAL</th>
<th>THIS WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_6H_5P)_4</td>
<td>(C_6H_5P)_5</td>
<td></td>
</tr>
<tr>
<td>Range: 4000-667 cm(^{-1})</td>
<td>Range: 3070-394 cm(^{-1})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(\bar{\nu} (cm^{-1}))</th>
<th>Relative Intensity</th>
<th>In KBr disc.</th>
<th>(\bar{\nu} (cm^{-1}))</th>
<th>Relative Intensity</th>
<th>In CS(_2) solution</th>
<th>(\bar{\nu} (cm^{-1}))</th>
<th>Relative Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3050</td>
<td>m</td>
<td></td>
<td>3070</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1970</td>
<td></td>
<td></td>
<td>1970</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1952</td>
<td></td>
<td></td>
<td>1952</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1889</td>
<td></td>
<td></td>
<td>1889</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1873</td>
<td>w</td>
<td></td>
<td>1873</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1810</td>
<td></td>
<td></td>
<td>1810</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1746</td>
<td></td>
<td></td>
<td>1746</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1647</td>
<td></td>
<td></td>
<td>1647</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1619</td>
<td></td>
<td></td>
<td>1619</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1581</td>
<td>vs</td>
<td></td>
<td>1581</td>
<td>vs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1570</td>
<td>vs</td>
<td></td>
<td>1570</td>
<td>vs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1482</td>
<td>vs</td>
<td></td>
<td>1482</td>
<td>vs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1475</td>
<td>m</td>
<td></td>
<td>1475</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1425</td>
<td>m</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1405</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1320</td>
<td>w</td>
<td>1320</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1300</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1295</td>
<td>w sh</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1271</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1191</td>
<td>m s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1180</td>
<td>w</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1160</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1150</td>
<td>w sh</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1090</td>
<td>m s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1083</td>
<td>s h</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1080</td>
<td>w sh</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1071</td>
<td>v s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1027</td>
<td>v s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1050</td>
<td>m</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1027</td>
<td>v s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1020</td>
<td>m</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1015</td>
<td>v w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>1001</td>
<td>v s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>997</td>
<td>m</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>988</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>980</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>968</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>w</td>
<td>908</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>848</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>841</td>
<td>w</td>
<td>641</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>833</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>746</td>
<td>w sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>740</td>
<td>vs</td>
<td>740</td>
<td>ws</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>733</td>
<td>ws</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>692</td>
<td>vs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-</td>
<td></td>
<td>685</td>
<td>sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>680</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>618</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>514</td>
<td>w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>496</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>486</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>475</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>463</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>449</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>427</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>416</td>
<td>s</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>405</td>
<td>sh</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>400</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>394</td>
<td>m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Legend: s = strong, m = medium, w = weak, sh = shoulder, v = very

## APPENDIX FOUR

### TABLE - Comparison of X-ray crystallographic results for pentaphenylcyclopentaphosphine

<table>
<thead>
<tr>
<th>Pentaphenylcyclopentaphosphine</th>
<th>J. J. Daly</th>
<th>This Work</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interplanar Spacing $d(\AA)$</td>
<td>Interplanar Spacing $d(\AA)$</td>
<td>Intensity $I$</td>
</tr>
<tr>
<td>13.73</td>
<td>13.80</td>
<td>s</td>
</tr>
<tr>
<td>9.18</td>
<td>9.47</td>
<td>s</td>
</tr>
<tr>
<td>8.15</td>
<td>8.15</td>
<td>m</td>
</tr>
<tr>
<td>6.89</td>
<td>6.88</td>
<td>m</td>
</tr>
<tr>
<td>6.80</td>
<td>6.19</td>
<td>vwd</td>
</tr>
<tr>
<td>5.57</td>
<td>5.59</td>
<td>m</td>
</tr>
<tr>
<td>4.87</td>
<td>4.90</td>
<td>md</td>
</tr>
<tr>
<td>4.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.59</td>
<td>4.61</td>
<td>m</td>
</tr>
<tr>
<td>4.44</td>
<td>4.46</td>
<td>w</td>
</tr>
<tr>
<td>4.33</td>
<td>4.34</td>
<td>sd</td>
</tr>
<tr>
<td>4.18</td>
<td>4.20</td>
<td>ww</td>
</tr>
<tr>
<td>4.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.97</td>
<td>3.96</td>
<td>w</td>
</tr>
<tr>
<td>3.87</td>
<td>3.85</td>
<td>m</td>
</tr>
<tr>
<td>3.70</td>
<td>3.76</td>
<td>w</td>
</tr>
<tr>
<td>3.64</td>
<td>3.67</td>
<td>s</td>
</tr>
<tr>
<td>3.52</td>
<td>3.42</td>
<td>3.45</td>
</tr>
<tr>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>3.33</td>
<td>3.36</td>
<td>3.36</td>
</tr>
</tbody>
</table>

Legend: I = Intensity estimated visually
s = strong, m = medium, w = weak, v = very,
d = diffuse

Camera: Phillips-Straumanis, Diameter: 11.46 mm.
Radiation: CuKα, operating condition: 36 Kv, 25 mA.

These spacings were synthesised by Miss R. S. Osborn (ICULRS) using a computer programme from Daly's single crystal reflections.
TABLE - Comparison of X-ray crystallographic results for polymeric phenylphosphine

<table>
<thead>
<tr>
<th>Polymeric Phenylphosphine</th>
<th>L. MAIER (Form D)</th>
<th>THIS WORK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Interplanar Spacing $d$(Å)</td>
<td>Intensity</td>
</tr>
<tr>
<td></td>
<td>8.79</td>
<td>vsd</td>
</tr>
<tr>
<td></td>
<td>7.51</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>5.31</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>4.50</td>
<td>vsd</td>
</tr>
<tr>
<td></td>
<td>4.03</td>
<td>w</td>
</tr>
<tr>
<td></td>
<td>3.74</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>3.50</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>3.23</td>
<td>s</td>
</tr>
<tr>
<td></td>
<td>3.11</td>
<td>w</td>
</tr>
<tr>
<td></td>
<td>3.03</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>2.92</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>2.76</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>2.64</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td>2.52</td>
<td>m</td>
</tr>
</tbody>
</table>
Legend: \( I \) = Intensity estimated visually

\( s \) = strong, \( m \) = medium, \( w \) = weak,

\( v \) = very, \( d \) = diffuse

Camera: Phillips-Straumanis, Diameter: 11.46 mm.

Radiation: CuK\(_\alpha\), operating condition: 36 Kv, 25 mA.

These spacings were synthesised by Miss R. S. Osborn (ICULIR)\(^+\).

\(^+\)This was prepared by disproportionation of \( C_6H_5PF_2 \) (see p.48 under synthesis).
Of the phosphorus sub-halides ($P_2X_4$), only $P_2Br_4$ has not yet been synthesized nor characterised energetically.

$$\begin{align*}
P_2F_4, \text{ m.pt.} &= -86.5 \pm 0.5^\circ\text{C}^{221} & \Delta H^\circ_f (P_2F_4(g)) &= -290^{25} \\
P_2Cl_4, \text{ m.pt.} &= -34^\circ\text{C}, 65,232,233 & \Delta H^\circ_f (P_2Cl_4(l)) &= -106^{74} \\
P_2I_4, \text{ m.pt.} &= 124.5^\circ\text{C}, 157 & \Delta H^\circ_f (P_2I_4(c)) &= -27^{104}
\end{align*}$$

It is interesting to estimate the standard heat of formation of diphosphorus tetraiodide using the following expressions.

$$E_{P-P} + 4E(P-Br) = 2 \Delta H^\circ_f (P,(g)) + 4 \Delta H^\circ_f (Br,(g)) - \Delta H^\circ_f (P_2Br_4(o)) - \Delta H(P_2Br_4(c \rightarrow g))$$

Taking $E_{P-P}$ as in diphosphorus tetraiodide $^{76}$ and $E(P-Br)$ as in tribromo-phosphine $^{25}$ (i.e. 62 and 64 kcal respectively), $\Delta H^\circ_f (P,(g)) = 75.5$ kcal,

$\Delta H^\circ_f (Br,(g)) = 27$ kcal and estimating $H(P_2Br_4(c \rightarrow g)) = 10 \pm 5$ kcal mole$^{-1}$

we have

$$\Delta H^\circ_f (P_2Br_4(o)) \simeq -69 \pm 5 \text{ kcal mole}^{-1}$$
Numerical References

39 Szware, K., Quart. Rev., 1951, 5, 22.
43 Gray, A.P., and Casey, K., J. Polymer Sci., 1964, 2, 381.
60 Wiberg, E., Chemen, M.V., and Muller-Schiedmayer, G., Angew.Chem.
5, 103.
1963, 52, 2462.
65 Payne, D. S., "Topics in Phosphorus Chemistry", Ed., Grayson, M., and
6433.
75 Stephenson, C. C., Potter, R. L., Maple, T. C., and Marrow, J. C., J.Chem.
Thermodynamics, 1969, 1, 59.
2869.
89 Ogier, Compt. rend., 1881, 22, 83.
101 Tarible, M., Comp. rend. a) 1904, 132, 204, b) 1993, 116, 1523 c) 1904, 132, 83.
111 Both, H., and Vetter, I.J., Ber., 1963, 96, 1109.
126 Pauling, L., Chem. in Britain, 1970, 6, 468.
129 Cenedella, J., Pharm., 1835, 21, 633.
146 Michaelis, A., Ber., 1873, 6, 816.
147 Beilstein Organische Chemie, 1933, 16, 804.


"Netzsch" bulletins, Geratebau, G.MBH Selb/BAY, Werkstrasse, 19, Germany


ALPHABETICAL REFERENCES

112 Anderson, H.H., I.U.P.A.C. Colloquium, Munster Westfalen, Verlag
Chemie, 1954, 235


Chem.Soc., 1923, 45, 2541


147 Beilstein Organdische Chem., 1933, 16, 804

& Co., 1966, 311


Cenedella, J. Pharm. 1835, 24, 683.


144 Michaelis, A., and Dittler, F., Ber., 1879, 12, 338.
159 Michaelis, A., and Kohler, H., Ber., 1876, 2, 519.


Ogier, Compt.rend., 1881, 22, 83.


"Periodic Table of Elements", Sargent Scientific Laboratory, Birmingham, Cat. No: S-18806, 1964.


Tarible, M., Compt rend., a) 1901, 132, 204, b) 1899, 116, 1523, c) 1901, 132, 83.


THE PHOSPHORUS-PHOSPHORUS BOND 
ENERGY IN DIPHOSPHORUS 
TETRA-IODIDE

A. FINCH, P. J. GARDNER and ABDUL HAMEED
Department of Chemistry, Royal Holloway College, Englefield Green, Surrey, England

(Received 25 January 1970)

Abstract—The enthalpies of sublimation at 298.15 K of phosphorus tri-iodide and diphosphorus tetra-iodide (15.2 ± 0.9 and 16.7 ± 0.5 kcal. mole⁻¹ respectively) have been determined using an effusion manometer. Combination of these enthalpies with literature thermodynamic data gives an estimate of 62 kcal for the phosphorus-phosphorus bond energy in P₂I₄.

INTRODUCTION

There is considerable current interest in compounds containing the phosphorus-phosphorus bond [1]. A feature of such compounds is the nearly constant phosphorus-phosphorus bond length (2.21 Å), a possible exception being the sulphide, P₄S₇. In contrast, estimates of the phosphorus-phosphorus bond energy, $E(P-P)$, or of the bond dissociation energy, $D(P-P)$, are divergent (vide infra). The former derive from thermochemical investigations while the latter stem from appearance potential data obtained from electron-impact studies.

Recently, the standard enthalpy of formation of P₂I₄ has been reported [2] in conjunction with a revised corresponding figure for PI₃. Combination of these data with the enthalpies of sublimation for these iodides, the determination of which is described in this paper, yields $E(P-P)$ in P₂I₄. The sublimation enthalpy is always the most difficultly accessible function for the determination of bond energies in compounds whose standard state are crystalline and which melt with decomposition.

EXPERIMENTAL

The manometer

An effusion manometer was constructed to a design similar to that of Kington and Edwards [3]. In view of the corrosive nature of the phosphorus iodides the effusion cell was fabricated in stainless steel (B) and the foil (C) in gold (Fig. 1b). The foil was retained in position by a stainless-steel locking ring. Kington and Edwards used a film of Apiezon N lubricant on the walls and the base of the cell to ensure good contact between the cell and block. This film must be quantitatively removed prior to weighing at the end of each run. This has proved difficult [4] and hence the cell in this apparatus was screwed into the block via a precision thread (26 t.p.i., Whitworth) (see Fig. 1). The foil was drilled using a No. 80 high speed twist drill, and burrs removed with a fine abrasive paste. The radius was determined by photomicrography (linear magnification × 100) followed by planimetry. The thickness was deduced from a knowledge of the weight, density and surface area of the foil. A mercury diffusion pump backed by a two-stage rotary pump gave a pressure of 10⁻⁵ mm of Hg at the man-

Individual runs were ca. 24 hr in duration and condensation was achieved using an acetone/solid CO$_2$ mixture. The temperatures were determined as follows: (i) over the range 21-27°C, a mercury-in-glass thermometer reading to ±0.002°C and calibrated against a Quartz Crystal Ther-
mometer (Hewlett-Packard) was used, and (ii) over the range 54–80°C, an NPL-calibrated mercury-in-glass thermometer accurate to ±0.02°C was used. For the lower temperature range the block was thermostatted to ±0.001°C in a water bath, and over the higher range, to ±0.02°C in an oil bath.

RESULTS

Testing the manometer

There are two independent reliable determinations of the vapour pressure of ferrocene over the range 20–28°C via effusion manometry [3, 5]. Kington and Edwards (KE), who review the earlier work, obtain systematically higher vapour pressures than Andrews and Westrum (AW) but the enthalpies of sublimation are concordant. The ferrocene (BDH) used in this work was twice crystallised from absolute ethanol and sublimed in vacuo, m.p. 175–176°C, lit.[6] m.p. 175.5–176°C. This is a modification of the purification procedure of Edwards et al.[6].

The equation to convert material loss from the cell to equilibrium vapour pressure is

\[
p = \frac{w}{tA} \left[ \frac{2\pi RT}{M} \right]^{1/2} \left[ \frac{8r + 3l}{8r} \right] \left[ \frac{1}{1 + 0.48 r/2\lambda} \right]
\]

where \( p \) = pressure (dynes cm\(^{-2}\)), \( \lambda \) = mean free path \( = \sqrt{kT/2\pi r^2 p} \) (cm), \( r \) = radius of effusion orifice (cm), \( l \) = length of orifice (cm), \( R \) = gas constant (ergs deg\(^{-1}\) mole\(^{-1}\)), \( M \) = molecular wt., \( T \) = absolute temp. (K), \( w \) = weight loss (g), \( t \) = time (sec) and \( A \) = orifice area (cm\(^2\)). The second term in brackets corrects the ideal Langmuir expression for finite orifice length, and the third term takes account of the fact that the ratio of the mean free path to orifice diameter is significant (in this work, \( 5 < \lambda/d < 20 \)). This expression is fully discussed by Kington and Edwards [3] and Carman [7].

<table>
<thead>
<tr>
<th>( \Delta H (c \rightarrow g) \text{298} ) (kcal. mole(^{-1}))</th>
<th>( p \text{298} ) (mm of Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KE 17.53 ± 0.10</td>
<td>0.00684</td>
</tr>
<tr>
<td>AW 17.38 ± 0.13</td>
<td>0.00714</td>
</tr>
<tr>
<td>This work 17.84 ± 0.96</td>
<td>0.00680</td>
</tr>
</tbody>
</table>

The results were obtained by a least squares analysis and the uncertainty interval was \( \pm \left[ \sum r_i^2/(n-2)(\sum x_i^2-n\bar{x}^2) \right]^{1/2} \) where \( r_i \) = residual, \( x = T^{-1} \) and \( n = n_o \) of sets. Also, throughout this paper 1 cal = 4.1840 Joule, 1 mm Hg = 0.133322 kNm\(^{-2}\) and 1 Å = 0.1 nm.

Vapour pressures of the phosphorus iodides

Orifice area \( (A) = 1.074 \times 10^{-3} \text{ cm}^2 \) \((r = 1.849 \times 10^{-2} \text{ cm})\)

Orifice length \( (l) = 2.670 \times 10^{-3} \text{ cm} \).

Table 2. Phosphorus tri-iodide

<table>
<thead>
<tr>
<th>( T ) (°K)</th>
<th>( 10^6 w/t ) (g. sec(^{-1}))</th>
<th>( 10^3 p ) (mm of Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>294.137</td>
<td>1.8750</td>
<td>2.634</td>
</tr>
<tr>
<td>294.137</td>
<td>1.8750</td>
<td>2.634</td>
</tr>
<tr>
<td>295.134</td>
<td>2.1111</td>
<td>2.966</td>
</tr>
<tr>
<td>296.132</td>
<td>2.3055</td>
<td>3.241</td>
</tr>
<tr>
<td>296.132</td>
<td>2.3055</td>
<td>3.241</td>
</tr>
<tr>
<td>297.134</td>
<td>2.3750</td>
<td>3.343</td>
</tr>
<tr>
<td>297.134</td>
<td>2.4166</td>
<td>3.400</td>
</tr>
<tr>
<td>298.136</td>
<td>2.6944</td>
<td>3.791</td>
</tr>
<tr>
<td>298.136</td>
<td>2.8611</td>
<td>4.021</td>
</tr>
<tr>
<td>299.136</td>
<td>2.8333</td>
<td>3.989</td>
</tr>
<tr>
<td>300.137</td>
<td>3.1250</td>
<td>4.399</td>
</tr>
</tbody>
</table>

Experiments with \( \text{P}_2\text{I}_4 \) over a range including 25°C yielded irreproducibly small material loss.

Table 3. Diphosphorus tetra-iodide

<table>
<thead>
<tr>
<th>( T ) (°K)</th>
<th>( 10^6 w/t ) (g. sec(^{-1}))</th>
<th>( 10^3 p ) (mm of Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>328.09</td>
<td>1.3079</td>
<td>1.661</td>
</tr>
<tr>
<td>328.09</td>
<td>1.2847</td>
<td>1.632</td>
</tr>
<tr>
<td>328.09</td>
<td>1.2731</td>
<td>1.617</td>
</tr>
<tr>
<td>330.09</td>
<td>1.4930</td>
<td>1.899</td>
</tr>
<tr>
<td>331.09</td>
<td>1.4930</td>
<td>1.902</td>
</tr>
<tr>
<td>333.08</td>
<td>1.7361</td>
<td>2.215</td>
</tr>
<tr>
<td>333.08</td>
<td>1.7130</td>
<td>2.186</td>
</tr>
<tr>
<td>333.08</td>
<td>1.7245</td>
<td>2.200</td>
</tr>
<tr>
<td>333.08</td>
<td>1.7130</td>
<td>2.186</td>
</tr>
<tr>
<td>338.06</td>
<td>2.6157</td>
<td>3.341</td>
</tr>
<tr>
<td>338.06</td>
<td>2.5926</td>
<td>3.312</td>
</tr>
<tr>
<td>343.04</td>
<td>3.6885</td>
<td>4.702</td>
</tr>
<tr>
<td>343.04</td>
<td>3.5069</td>
<td>4.485</td>
</tr>
<tr>
<td>343.04</td>
<td>3.5185</td>
<td>4.500</td>
</tr>
<tr>
<td>343.04</td>
<td>3.4954</td>
<td>4.471</td>
</tr>
<tr>
<td>343.04</td>
<td>3.4722</td>
<td>4.442</td>
</tr>
<tr>
<td>348.02</td>
<td>4.9768</td>
<td>6.349</td>
</tr>
<tr>
<td>353.00</td>
<td>9.2361</td>
<td>11.34</td>
</tr>
</tbody>
</table>

The collision diameter \((8.56 \text{ Å})\) for \( \text{PI}_3 \) was evaluated from the diameter of the minimum circumscribing sphere including the van der Waals' radii of the iodine atoms. For \( \text{P}_2\text{I}_4 \), the I–I internuclear distance via the inversion centre plus twice
the van der Waals' radii was set equal to the collision diameter (9.85 Å). Crystallographic data were used for bond lengths[8, 9]. These are rather crude estimates of collision diameter but the approximation is unlikely to affect markedly the sublimation enthalpies as the sensitivity of the correction is ca. —0.05 kcal. mole⁻¹ Å⁻¹.

Analysis of the sublimate in isolated runs for both series revealed the theoretical quantity of easily-hydrolysable iodide and the theoretical I : P ratio. Hence, the possibility of thermal decomposition was excluded. For P₂I₄, confirmation of this point was obtained from thermogravimetric experiments when no decomposition below the melting point was observed. The correction for the conversion of the P₂I₄ data from the reference temperature of 340 to 298.15 K was assumed to be within the experimental limits of error. Least squares analysis gave

\[
\Delta H [\text{P}₁₃, c → g]_{298} = 15.21 ± 0.86 \text{ kcal.mole}⁻¹
\]

\[
\Delta H [\text{P}₂I₄, c → g]_{298} = 16.70 ± 0.50 \text{ kcal.mole}⁻¹
\]

The precision of these data are nearly an order of magnitude less than that obtained by Kington and Edwards or Andrews and Westrum using similar equipment. This is possibly due to the necessity of fabricating the cell in stainless steel, a relatively poor thermal conductor.

**DISCUSSION**

The functional dependence of material loss from an effusion cell and equilibrium vapour pressure, under ideal conditions of infinitely thin edges to the orifice and a large mean free path to orifice diameter ratio (\(\lambda/d\)), was first derived by Langmuir[10]. In the present work an equation containing correction factors for an orifice of finite length (Knudsen)[11] and a non-ideal \(\lambda/d\) ratio (Hiby and Pahl)[12] is used. Notwithstanding these corrections, vapour pressures via Knudsen effusion techniques are often found to be dependent on orifice size[13]. However, the slope of the \(\ln p \text{ vs. } T⁻¹\) line (and hence \(\Delta H [c → g]\)) is independent of this factor[14]. No attempt was made in this work to study the effect of orifice diameter and hence the quoted pressures are less significant than the derived sublimation enthalpies.

The bond energies in the phosphorus iodides are derived as follows, all thermochemical data being quoted at 298-15 K. Head has recently reported a definitive value for \(\Delta H^\circ[\text{H}_₃\text{PO}_₄ \cdot 4\text{H}_₂\text{O}] \approx 309.39 ± 0.24 \text{ kcal.mole}⁻¹\)[15]. Thus,

using enthalpies of dilution from Ref. [16], $\Delta H^\circ_r\left[H_3PO_4, 3000H_2O\right] = -310.18 \pm 0.24 \text{ kcal.mole}^{-1}$. Combination of this figure with the results of a thermochemical study of phosphorous acid oxidation[17] gives $\Delta H^\circ_r\left[H_3PO_4, \text{cryst.}\right] = -228.81 \pm 0.3 \text{ kcal.mole}^{-1}$ and with dilution data[16], $\Delta H^\circ_r\left[H_3PO_4aq.\right] = -228.9 \pm 0.3 \text{ kcal.mole}^{-1}$. Combination of this latter datum with the results of a thermochemical investigation of $\text{PI}_3$ and $\text{P}_2\text{I}_4[2,18]$ gives $\Delta H^\circ_r\left[\text{PI}_3, c\right] = -13.9 \pm 0.4 \text{ kcal.mole}^{-1}$ and $\Delta H^\circ_r\left[\text{P}_2\text{I}_4, c\right] = -26.5 \pm 0.8 \text{ kcal.mole}^{-1}$. Using the sublimation enthalpies derived earlier, we have $\Delta H^\circ_r\left[\text{PI}_3, g\right] = +1.3 \pm 0.9 \text{ kcal.mole}^{-1}$ and $\Delta H^\circ_r\left[\text{P}_2\text{I}_4, g\right] = -9.8 \pm 0.9 \text{ kcal.mole}^{-1}$. Taking $\Delta H^\circ_r\left[P, g\right] = 75.20$ [16], and $\Delta H^\circ_r\left[1, g\right] = 25.535$ [16] kcal.g.atom$^{-1}$ we may readily derive the mean bond dissociation energy in $\text{PI}_3(D(P-I) = 50.2 \text{ kcal})$ and assuming that $D$ in $\text{PI}_3$ may be set equal to the phosphorus–iodine bond energy ($E(P-I)$) in $\text{P}_2\text{I}_4$, a value of 61.7 kcal for $E(P–P)$ follows. The overall uncertainty in these bond strengths is ca. 2 kcal. This value may be compared to other determinations of $E(P–P)$; 51 [19], 47 (in $\text{P}_2\text{H}_4$)[20], 67 (in $\text{P}_2\text{I}_4$)[21] and corresponding determinations of $D(P–P)$; 58 (in $\text{P}_2\text{Cl}_4$)[22], 65 (in $\text{P}_2\text{I}_4$)[23], 86 (in $(\text{C}_2\text{H}_5)_4\text{P}_2$)[24], and 74 (in $\text{P}_2\text{H}_4$)[25] kcal.mole$^{-1}$.

Acknowledgements—We are indebted to Messrs. T. Crowdy and S. Ashdown for assistance in constructing the manometer and to the Central Research Fund of the University of London and the Science Research Council for grants to purchase a recorder and a Quartz Crystal Thermometer respectively.

The Phosphorus-Phosphorus Bond: some Electron Impact Studies

By Arthur Finch, A. Hammed, and P. J. Gardner,
(Williams Laboratory, Royal Holloway College, University of London, Englefield Green, Surrey)
and N. Paul
(Explosives Research and Development Establishment, Waltham Abbey, Essex)

Reprinted from

Chemical Communications 1969

The Chemical Society, Burlington House, London W1V OBN
The Phosphorus–Phosphorus Bond: some Electron Impact Studies

By Arthur Finch, A. Hameed, and P. J. Gardner,
(Williams Laboratory, Royal Holloway College, University of London, Englefield Green, Surrey) and N. Paul
(Explosives Research and Development Establishment, Waltham Abbey, Essex)

Physical data concerning the P–P bond, even in very simple systems, are scarce. From some detailed mass spectroscopic studies of both phosphorus tri-iodide and diphosphorus tetraiodide, an estimate of the strength of the P–P bond may be made. Relevant results are shown in the cycles:

\[
P_1\xrightarrow{A} P_1^+ + I_2^+ \quad P_1^+ \xrightarrow{A'} P_1^2 + P_2^+ \quad P_2^+ \xrightarrow{B} P_1^2 + P_2^+
\]

The appearance potentials for processes A and A', are 11.9 ± 0.15 and 12.8 ± 0.15 ev respectively. If the literature value for the energy of the dissociation process C, 184.1 kJ mole\(^{-1}\) (44 kcal. mole\(^{-1}\)), is adopted, then the bond dissociation energy \(D(P_1^2-I_2^+)\) (process C) is 271.0 kJ mole\(^{-1}\) (64.8 kcal. mole\(^{-1}\)). This is in excellent agreement with a previous estimate, i.e. 289.9 kJ mole\(^{-1}\) (69.9 kcal. mole\(^{-1}\)) and also with two values, 283.6 and 217.6 kJ mole\(^{-1}\) (66.3 and 52 kcal. mole\(^{-1}\)) derived from a mass spectroscopic study of PCl\(_4\) and PIF\(_4\) for \(D\) (PCl\(_4\)–FCl\(_4\)). Cracking patterns for the chloride and iodide systems differ considerably and in the former the appearance potential of PCl\(_4^+\) from PCl\(_3\) exceeds that of the appearance potential of FCl\(_4^+\) from PCl\(_4\). In contrast to the above results (processes A, A'),

In both chloride and iodide systems the value corresponding to process C was estimated as one third of the heat of formation of PX\(_4\) with respect to the gaseous elements i.e. with the implicit assumption that \(D(PX_4-X) = \bar{D}(P-X)\). This is known to be invalid for other Group V molecules, e.g. NF\(_3\), NH\(_3\); hence a third experimental result of this investigation, a value of 12.7 ± 0.15 ev for the appearance potential of I\(^+\) from PI\(_3\) is relevant. On the assumption that this results from the process

\[
PI_3 + e \rightarrow PI_4 + I^+ + 2e,
\]

use of the value of 10.45 ev for the ionisation potential of iodine, gives \(D(PI_3-I) = 217 kJ.mole^{-1}\) (52 kcal.mole\(^{-1}\)) and \(D(PI_3-PI_2) = 309 kJ.mole^{-1}\) (73 kcal.mole\(^{-1}\)).

Since all values for the phosphorus–iodine bond strengths have previously relied on assumed values of \(\Delta H^\circ_{\text{vap}}\) PI\(_3\) or PI\(_4\), the latter values are entirely reasonable. Hence they may now be used to estimate the heats of sublimation.

Direct determination of these is extremely difficult, owing to the very low vapour pressures at ambient temperatures and thermal instability at elevated temperatures. However, experimental studies, with Knudsen-type and thermal conductivity gauges are in progress.

Appearance potential measurements were performed by use of an AEI model MS2H mass spectrometer with a direct inlet system for solid samples of PI\(_3\) and PI\(_4\); the method of Lossing et al.\(^{1}\) was used, with argon as internal standard.

\(\text{Received, February 13th, 1969; Com. 198.}\)

1 A. Finch, A. Hameed, P. J. Gardner, and N. Paul, to be published.
The Disproportionation of Phenyldifluorophosphine

By Arthur Finch, P. J. Gardner, Abdul Hameed, and K. K. Sen Gupta

[Moore Laboratory, Royal Holloway College, (University of London), Englefield Green, Surrey]

Reprinted from

Chemical Communications 1969

The Chemical Society, Burlington House, London WIV OBN
The Disproportionation of Phenyldifluorophosphine

By Arthur Finch, P. J. Gardner, Abdul Hameed, and K. K. Sen Gupta

[Moore Laboratory, Royal Holloway College, University of London, Englefield Green, Surrey]

Summary Polymeric phenylphosphines are formed on spontaneous disproportionation of phenyldifluorophosphine under nitrogen at room temperature.

Ang and Schmutzler recently reported the spontaneous disproportionation of phenyldifluorophosphine to pentaphenylpentaphospholan and phenyltetrafluorophosphorane:

\[ 10\text{PhPF}_3 \rightarrow 5\text{PhPF}_4 + (\text{PhP})_n \]

While the constitution of all forms of the phenylphosphines, \((\text{PhP})_n\), is not established, it is agreed that at least three species exist: Form A \((n = 5, \text{ m.p. } 149-150^\circ)\), Form B \((n = 6, \text{ m.p. } 190^\circ)\), and at least one (presumed polymeric) form of unknown molecularity which melts within the range 232-285\(^\circ\), and is insoluble in organic solvents. Henderson et al. have distinguished two high melting forms, C and D, melting within the ranges 270-283\(^\circ\) and 260-285\(^\circ\), respectively.

On the basis of observed melting point (151-154\(^\circ\)), and comparison of the X-ray diffraction pattern with that of an authentic sample, Ang and Schmutzler report that the disproportionation product is the pentamer, Form A. However, this disproportionation was observed in these laboratories some years ago, and has been re-checked recently. Both phenyldifluorophosphine, and an equimolar mixture of phenyldifluorophosphine and phenyl dichlorophosphine, allowed to stand at room temperature under nitrogen, deposit a white powder, insoluble in organic solvents, which melts near 280\(^\circ\). This clearly indicates the production of a polymeric form, probably D:

\[ 2\text{PhPF}_3 \rightarrow \frac{1}{n}(\text{PhP})_n + \text{PhPF}_4 \]

and not A, as found by Ang and Schmutzler. Samples of our product re-melted at 150\(^\circ\), and were then soluble in organic solvents, as previously noted elsewhere for D.

An X-ray diffraction pattern for our product further confirmed that it was not Form A, but was markedly similar to the corresponding (identical) patterns obtained for authentic samples of Forms C and D, although minor differences in both intensities and line sequence were noted.

There is at present no reproducible synthetic route to the polymeric phenylphosphines. Although interconversion from Form A, (which is readily prepared) to Form C via warming in piperidine at 80\(^\circ\) has been reported, we have had little success with this procedure. Hence direct formation of a polymeric form from the above disproportionation represents a simple synthesis from readily available precursors.

Identical samples of polymeric phenylphosphine were obtained from disproportionation experiments of very different time-span (2 days and some months). It is therefore difficult to reconcile the difference in product obtained in these experiments and those reported earlier. However, it seems clear that the polymeric form(s) is thermally unstable with respect to the pentamer, and lack of synthetic reproducibility is apparently a feature of these systems.

We thank Miss R. Osborn and Professor D. Rogers for provision and discussion of the X-ray data, and Messrs. Albright and Wilson (Mfg.) Ltd. for partial financial support (to K.K.S.G.).

Received, June 6th, 1969; Com. 800.)

7. L. Maier, personal communication.