THERMOCHEMISTRY OF SOME PLATINUM AND PALLADIUM COMPOUNDS

by

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Abstract

Enthalpies of reaction, at 298 K in the liquid phase have been measured using isoperibol reaction calorimetry, and some enthalpies of isomerisation have been measured using differential scanning calorimetry.

The enthalpy of formation of crystalline ammonium tetrachloropalladite has been obtained from measurement of its enthalpy of decomposition by ethylene in water.

The value $\Delta H_f^o[(NH_4)_2PdCl_4](c) = -(841.0 \pm 1.7)$ kJ mol^{-1} has been used as a datum in determining the enthalpies of formation,

$$\Delta H_f^o[(SEt_2)_2PdCl_2](c) = -(563.1 \pm 2.1) \text{ kJ mol}^{-1}$$
$$\Delta H_f^o[(SeEt_2)_2PdCl_2](c) = -(528.9 \pm 3.8) \text{ kJ mol}^{-1}$$
$$\Delta H_f^o[(TeEt_2)_2PdCl_2](c) = -(587.6 \pm 20.5) \text{ kJ mol}^{-1}$$

from which relative mean bond dissociation energies have been established as follows:

$$\langle D(Pd\text{-}Se)\rangle - \langle D(Pd\text{-}S)\rangle = (9 \pm 9) \text{ kJ mol}^{-1}$$
$$\langle D(Pd\text{-}Te)\rangle - \langle D(Pd\text{-}Se)\rangle = (28 \pm 13) \text{ kJ mol}^{-1}$$

The enthalpies of reaction of the complex bis(triphenylphosphine)-(ethylene)platinum(0) with tetracyanoethylene and with diphenylacetylene have also been studied:

$$(PPh_3)_2Pt(C_2H_4)(c) + (CN)_2C{=}C(CN)_2(c) \rightarrow (PPh_3)_2Pt\{(CN)_2C{=}C(CN)_2\}(c) + C_2H_4(g)$$

$$(PPh_3)_2Pt(C_2H_4)(c) + PhC{\equiv}CPh(c) \rightarrow (PPh_3)_2Pt(PhC{\equiv}CPh)(c) + C_2H_4(g)$$

the values obtained lend support to a bonding model in complexes of this type.

The enthalpy of reaction of bis(triphenylphosphine)(diphenylacetylene)platinum(0) with hydrogen chloride has been measured:

$(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + HCl(g) \rightarrow (PPh_3)_2Pt(Cl)(PhC{=}CHPh)(c)$

$(PPh_3)_2Pt(Cl)(PhC{=}CHPh)(c) + HCl(g) \rightarrow (PPh_3)_2PtCl_2(c) +$ trans-$PhHC{=}CHPh(c)$

The results have been used to estimate the values,

D(Pt-diphenylacetylene) = 398 ± 23 kJ mol^{-1}

D(Pt-vinylstyrene) = 215 ± 23 kJ mol^{-1}

The two complexes, bis(triphenylphosphine)(tetrachloroethylene)platinum(0) and bis(triphenylphosphine)(vinylstyrene)platinum(0), have been subjected to differential scanning calorimetry, and enthalpies of isomerisation reactions have been measured.

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Chapter 1 Introduction

For a reaction such as

$$A + B \rightarrow C + D$$

measurement of the enthalpy change for the reaction yields the enthalpy of formation of one of the participants of the reaction, relative to the enthalpies of formation of the other participants. If values for the enthalpies of formation are known of three of the compounds, then Hess's law can be used to calculate the value for the fourth species since

$$\Delta H \text{ reaction} = \Sigma\Delta H^o_f(\text{products}) - \Sigma\Delta H^o_f(\text{reactants}).$$

If the measured enthalpy refers to a reaction in which one or more of the reactants or products is in solution, then enthalpies of solution will be required in order to calculate the enthalpies of formation of the participants in their standard states.

The complex tetrahalopalladite ions $[PdX_4]^{2-}$ will react with a wide variety of ligands, A, to give compounds of the type A_2PdCl_2, where $A = RCN, NR_3, PR_3, AsR_3, SR_2, SeR_2, TeR_2, OSR_2$. Enthalpies of formation of the compounds, A_2PdCl_2, can be obtained by measuring the enthalpies of the following reactions:

$$(NH_4)_2PdCl_4 + 2A \rightarrow A_2PdCl_2 + 2NH_4Cl$$

provided that there is a reliable value for the enthalpy of formation of $(NH_4)_2PdCl_4$. The enthalpy of formation of NH_4Cl is established, and values are also available for many of the listed ligands.

The value for $\Delta H^o_f\{(NH_4)_2PdCl_4,c\}$ is a key datum in this area of thermochemistry. To provide this datum, the enthalpy of the reaction:

$$\begin{aligned}(NH_4)_2PdCl_4(c) + C_2H_4(g) + H_2O(\ell) \rightarrow \\ Pd(s) + 2NH_4Cl(c) + \{CH_3CHO \text{ in } 1000\ H_2O\}(\ell) + \\ 2\{HCl + 111\ H_2O\}(\ell)\end{aligned}$$

has been determined.

Thermochemical data for the compounds A_2PdCl_2 may be used to provide information about factors which influence the strength of bonds involving palladium. Such information is relevant to an understanding of certain biological processes.

Thus, several platinum complexes, especially *cis*-$Pt(NH_3)_2Cl_2$, have anti-cancer properties,$^{(1)}$ whereas the corresponding palladium complexes are inactive. It has been suggested$^{(2)}$ that the therapeutic action depends on reaction with methionine, in which a Pt-S bond forms. Clearly, information about the strengths of Pt-S and Pd-S bonds is needed.

As an introduction to this study, enthalpies of the following reactions have been determined:

$$(NH_4)_2PdCl_2(c) + 2(E\mathrm{Et}_2)_2(\ell) \rightarrow (E\mathrm{Et}_2)_2PdCl_2(c) + 2NH_4Cl(c)$$

where E = S, Se or Te.

Enthalpies of formation of the complexes $(E\mathrm{Et}_2)_2PdCl_2(c)$ may then be calculated from our values of $\Delta H_f^o\{(NH_4)_2PdCl_2,c\}$ and the enthalpies of formation of SEt_2, $SeEt_2$, $TeEt_2$. Values of $\Delta H_f^o(SEt_2)(\ell)$ and $\Delta H_f^o(SeEt_2)(\ell)$ have been obtained previously by the use of combustion calorimetry, although for $(TeEt_2)(\ell)$ no value is yet available, and an estimated value must be used.

Mean bond dissociation energy, <D>, is defined as the enthalpy of the gas-phase reaction

$$AB_2(g) \rightarrow A(g) + 2B(g)$$

in which a molecule, AB_2, dissociates into the fragments A and B. Thus, the mean bond dissociation energy is given by the relationship

$$2\langle D(A-B)\rangle = \Delta H_f^o(A,g) + 2\Delta H_f^o(B;g) - \Delta H_f^o(AB_2,g)$$

From these thermochemical data it has been possible to calculate relative values for the mean bond dissociation energies, $\langle(Pd-E)\rangle$.

It has been suggested that palladium is a "soft"(3,4) acceptor, preferring more polarisable ligands. This would imply that the order of increasing bond dissociation energy should be D(Pd-S), D(Pd-Se), D(Pd-Te). To test this the study of this series of compounds was undertaken.

For the bond dissociation energies, for the palladium complexes, $(E\mathrm{Et}_2)\mathrm{PdCl}_2$, we may write,

$$2\langle D(\mathrm{Pd}\text{-}E)\rangle = \Delta H^{o}_{f}(\mathrm{PdCl}_2,\mathrm{g}) + 2\Delta H^{o}_{f}(E\mathrm{Et}_2,\mathrm{g}) - \Delta H^{o}_{f}\{(E\mathrm{Et}_2)_2\mathrm{PdCl}_2,\mathrm{g}\}$$

Recently, there has been a surge of interest in the chemistry of zerovalent platinum compounds, for example, those of the type $(\mathrm{PR}_3)_2\mathrm{PtX}$, where X is an olefin, acetylene or "unsaturated" ligand such as CS_2.(5) Such compounds are potential catalysts for organic synthesis, such as hydrogenation of alkenes, polymerisation, etc.

To provide more insight into the role of these compounds in such processes, it is desirable to have values for the enthalpies of formation of a wide range of zerovalent platinum complexes.

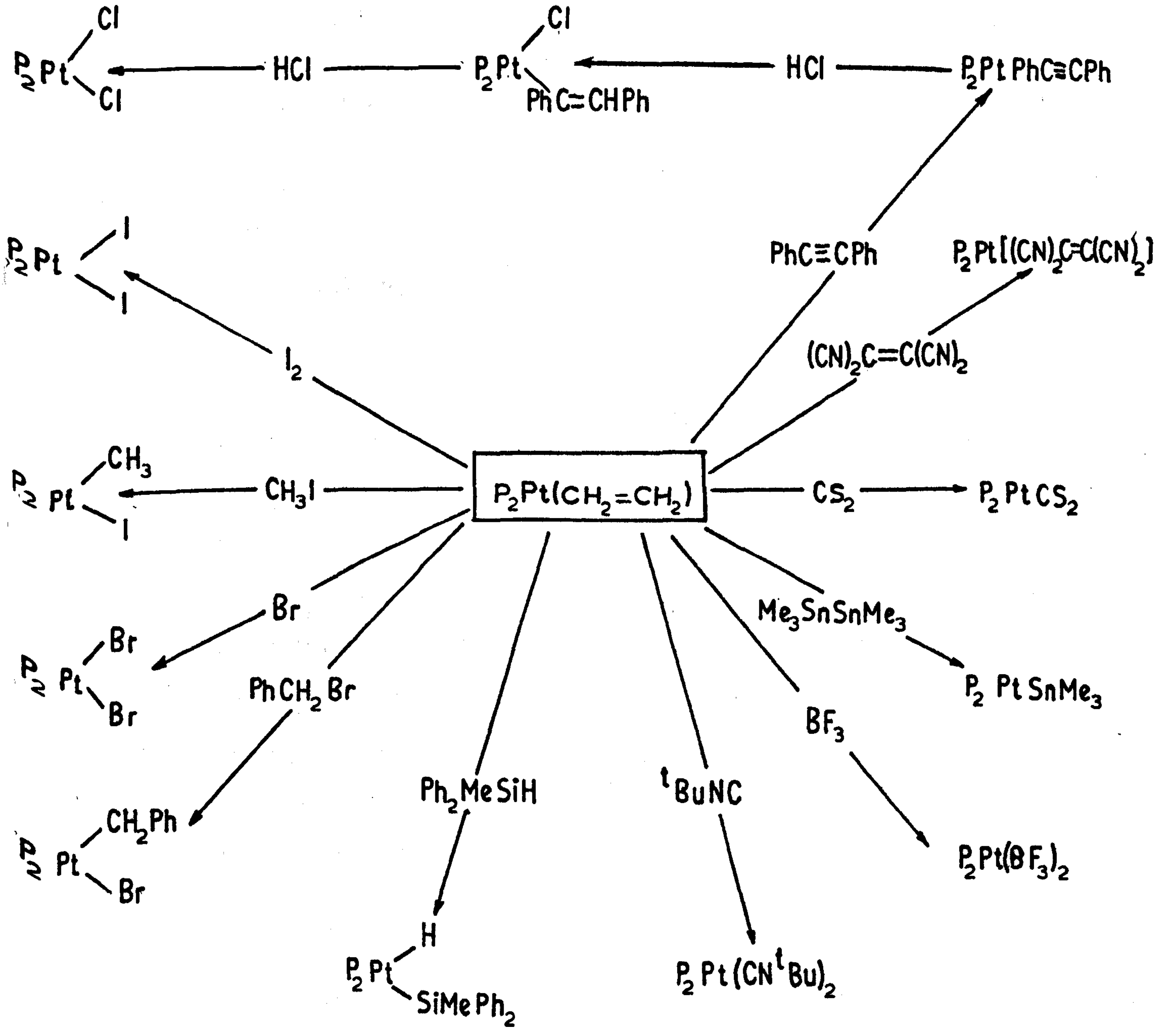
A variety of calorimetric methods (which are reviewed in the next section) might be used to determine these enthalpies of formation. However, the method designed to measure the enthalpies of reaction in solution, appears to be the most suitable.

The compound, $(\mathrm{PPh}_3)_2\mathrm{Pt}$(ethylene), is particularly useful as a starting point, since it reacts at room temperature, both rapidly and quantitatively, with a wide variety of unsaturated ligands in replacement reactions, where the platinum remains zerovalent, for example, the two reactions:

$$(\mathrm{PPh}_3)_2\mathrm{Pt}(\mathrm{CH}_2{=}\mathrm{CH}_2) + \mathrm{C(CN)}_2 = \mathrm{C(CN)}_2 \rightarrow (\mathrm{PPh}_3)_2\mathrm{Pt}\{\mathrm{C(CN)}_2 = \mathrm{C(CN)}_2\} + \mathrm{CH}_2{=}\mathrm{CH}_2 \quad \text{and}$$

$$(\mathrm{PPh}_3)_2\mathrm{Pt}(\mathrm{CH}_2{=}\mathrm{CH}_2) + \mathrm{CPh{\equiv}CPh} \rightarrow (\mathrm{PPh}_3)_2\mathrm{Pt}(\mathrm{CPh{\equiv}CPh}) + \mathrm{CH}_2{=}\mathrm{CH}_2$$

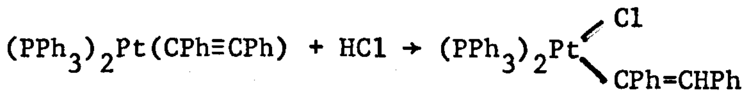
FIG. 1



$P_2 = (PPh_3)_2$

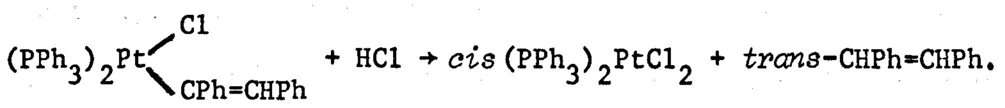
Typical reactions of $(ph_3p)_2Pt(CH_2{=}CH_2)$.

The product of the second reaction, the tolan adduct $(PPh_3)_2Pt(CPh{\equiv}CPh)$, undergoes a two stage oxidative-addition reaction with hydrogen chloride,



$$(PPh_3)_2Pt(CPh{\equiv}CPh) + HCl \rightarrow (PPh_3)_2Pt\begin{matrix} Cl \\ CPh{=}CHPh \end{matrix}$$

, and



$$(PPh_3)_2Pt\begin{matrix} Cl \\ CPh{=}CHPh \end{matrix} + HCl \rightarrow cis\,(PPh_3)_2PtCl_2 + trans\text{-}CHPh{=}CHPh.$$

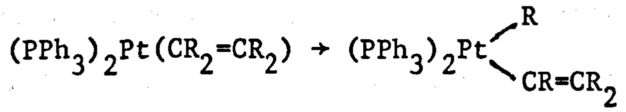
The parent compound, $(PPh_3)_2Pt(CH_2{=}CH_2)$, also undergoes oxidative-addition reactions quite readily, e.g.:

$$(PPh_3)_2Pt(CH_2{=}CH_2) + CH_3I \rightarrow (PPh_3)_2Pt(CH_3)I + CH_2{=}CH_2.$$

Figure 1 shows the diversity of reactions of these two types.

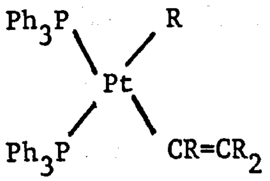
The disadvantage of this approach is that it provides enthalpy of formation data which are relative to that of the starting material, $(PPh_3)_2Pt(CH_2{=}CH_2)$. It is important that, at some future time, the absolute value for the enthalpy of formation of the ethylene adduct (or any one of the reaction products) be established. Nevertheless, it is possible, in the meantime, to use the measured enthalpies of reaction to provide information about the relative strength, with which the different ligands are bonded to platinum.

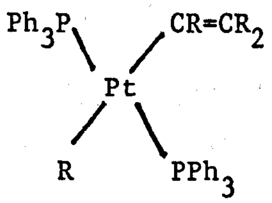
The compounds, $(PPh_3)_2Pt(CR_2{=}CR_2)$, may undergo an isomerisation reaction in which a σ-bond between platinum and carbon (vinyl) forms:



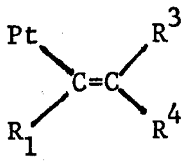
$$(PPh_3)_2Pt(CR_2{=}CR_2) \rightarrow (PPh_3)_2Pt\begin{matrix} R \\ CR{=}CR_2 \end{matrix}$$

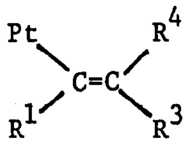
In this case the product may exist in either the cis or trans forms, viz.,



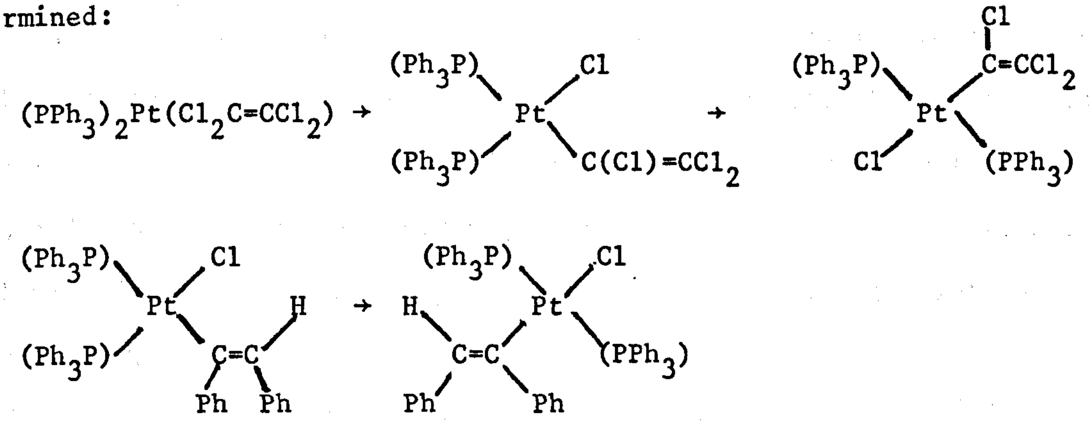


Where the substituent R groups differ, as in the olefin, $CR^1R^2{=}CR^3R^4$, isomerisation about the olefinic bond may also occur,





Differential scanning calorimetry is suitable for the measurement of the enthalpies of such reactions, in some suitable cases. Using this method, enthalpies of isomerisation of the following reactions have been determined:



Determination of the thermochemical measurements on some palladium and platinum compounds, which are reported in this thesis, has involved the use of a "reaction calorimeter" and a "differential scanning calorimeter". In the next section a brief resumé of these two calorimetric methods is given, together with a short description of the widely used technique of "combustion calorimetry". This method has been used to determine the enthalpies of formation of a number of the other reactants and products, to which reference will be made in the interpretation of our reported thermochemical data. Thus, for example, flame calorimetry has been used to determine the enthalpies of formation of H_2O and C_2H_4; static-bomb combustion calorimetry has been used for the determination of enthalpies of formation of diphenylacetylene ($CPh\equiv CPh$), *cis* and *trans* stilbene ($CHPh=CHPh$), and tetracyanoethylene ($C(CN)_2=(CN)_2$); rotating-bomb combustion calorimetry has been used to determine the enthalpy of formation of diethylsulphide (Et_2S).

1.1. Reaction calorimetry

The term reaction calorimetry is used to enclose the part of calorimetry not covered by the combustion method. It includes such reactions as hydrogenation, hydrolysis, polymerisation, and halogenation carried out in solution.

The types of calorimeter used for these reactions, fall into two classes, isothermal and non-isothermal. In the former, the temperature of the reaction system is constant and any heat generated by reaction is transferred from the system. Non-isothermal calorimeters, on the other hand, rely on a measured temperature change to estimate the heat effect in the reaction. The latter type includes the majority of reaction calorimeters.

Both classes of calorimeter have been thoroughly reviewed(6) and will only be outlined here.

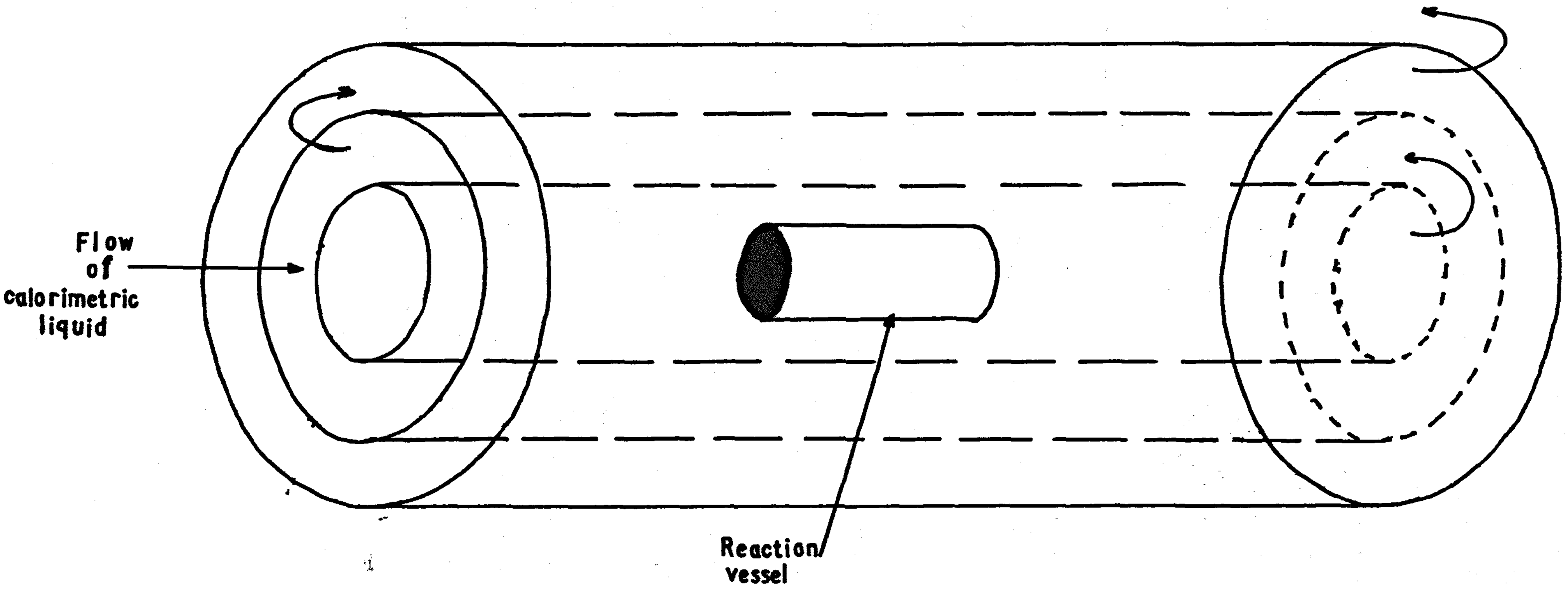
1.2. Isothermal calorimetry

1.2.(1) Phase change

In this type of calorimeter the reaction vessel is surrounded by a mantle of solid at its melting temperature. Heat generated in the vessel causes some of the solid mantle to melt. The resulting volume change is observed as the movement of a mercury thread in a capillary tube. Calibration is achieved by observing the traverse of the thread corresponding to the dissipation of a known amount of electrical energy in the reaction vessel. The advantages are high precision and the suitability for the studies of slow reactions.

The most familiar is the Bunsen Calorimeter, which uses ice as the solid mantle, but other substances have been used successfully e.g. naphthalene (m.p. 353.70 K)(7), diphenylmethane (m.p. 297.4 K)(8) and diphenylether (m.p. 300.02 K)(9). For work at lower temperatures a

FIG 2.



Labyrinth flow calorimeter (schematic)

liquid mantle has been used. Here it is the volume change, which accompanies vaporisation, which is observed. Both liquid ammonia (b.p. 239.8 K)(10) and liquid nitrogen (b.p. 77.4 K)(11) have been used.

There are, however, disadvantages associated with the use of this type of calorimeter, chiefly (i) the establishment of a stable thermodynamic equilibrium and (ii) the formation of a satisfactory solid mantle, around the calorimeter, is difficult and tedious. The liquid/vapour type are also especially sensitive to small pressure changes.

1.2.(2) Labyrinth flow

The labyrinth flow calorimeter is described as isothermal, although it is more accurately described as "very nearly" isothermal in operation.

The reaction vessel is situated at the centre of a series of concentric tubes, Fig.2. The liquid passes through the innermost tube, cooling the reaction vessel, and then through the labyrinth of successive concentric tubes. Any heat exchange between tubes will simply serve to increase the effectiveness of the overall heat transfer.

The enthalpy of reaction is obtained from measurement of the flow rate, the specific heat of the flowing liquid, and the relative temperature difference between inlet and outlet of the calorimeter. Junkers(12) built and used such a construction to measure the enthalpy of combustion of gases, and Swietoslawski(13) used an improved version of the apparatus.

1.3. Non-isothermal calorimetry

1.3.(1) Constant temperature environment (isoperibol)

The principles of this type of system have been reviewed frequently.(14) Briefly, the measurement depends on establishing a thermal head between a jacket, at constant temperature, and the reaction vessel at a different temperature. Providing no convection takes place, then the heat exchange will follow Newton's Law:

$$\frac{dT}{dt} = K(T_J - T)$$

K = heat leakage constant, T_J = jacket temperature, T = reaction-vessel temperature, and t = time.

Convection does not follow this law and therefore must be reduced to a minimum; ideally by evacuating the space between the reaction vessel and jacket.

In a number of isoperibol calorimeter systems the reaction vessel is immersed in a liquid contained in a second vessel. Heat transfer occurs from the reaction vessel to the liquid, and it is the temperature rise of this liquid which is used to measure the reaction heat.

Evaporation of this liquid (which is an endothermic process) must also be minimised, by sealing the vessel in which it is contained. This is often impractical, but the thermal discrepancies, caused by evaporation, can be reduced by arranging that the temperature of this liquid is always below that of the jacket.

A second important additional heat effect is that of stirring. Adequate stirring of liquid surround the reaction vessel is essential, and stirring of the contents of the reaction vessel is often desirable. Such stirring causes heat generation and this effect must be constant.

1.3.(2) Adiabatic

By making the temperature difference between the reaction vessel and jacket as small as possible, most of the heat exchange (thermal head) is eliminated. This condition is very difficult to realize in practice, especially for fast reactions. For slow reactions, however, such conditions may be obtainable and indeed advantages (15) can be found. These are as follows.

(a) Errors in the assumption of a constant heat leakage constant are minimized, as the thermal head is small; this also reduces convection.

(b) Evaporation is less serious.

(c) Applied corrections are smaller, the heat loss term being only a small fraction of the total energy term.

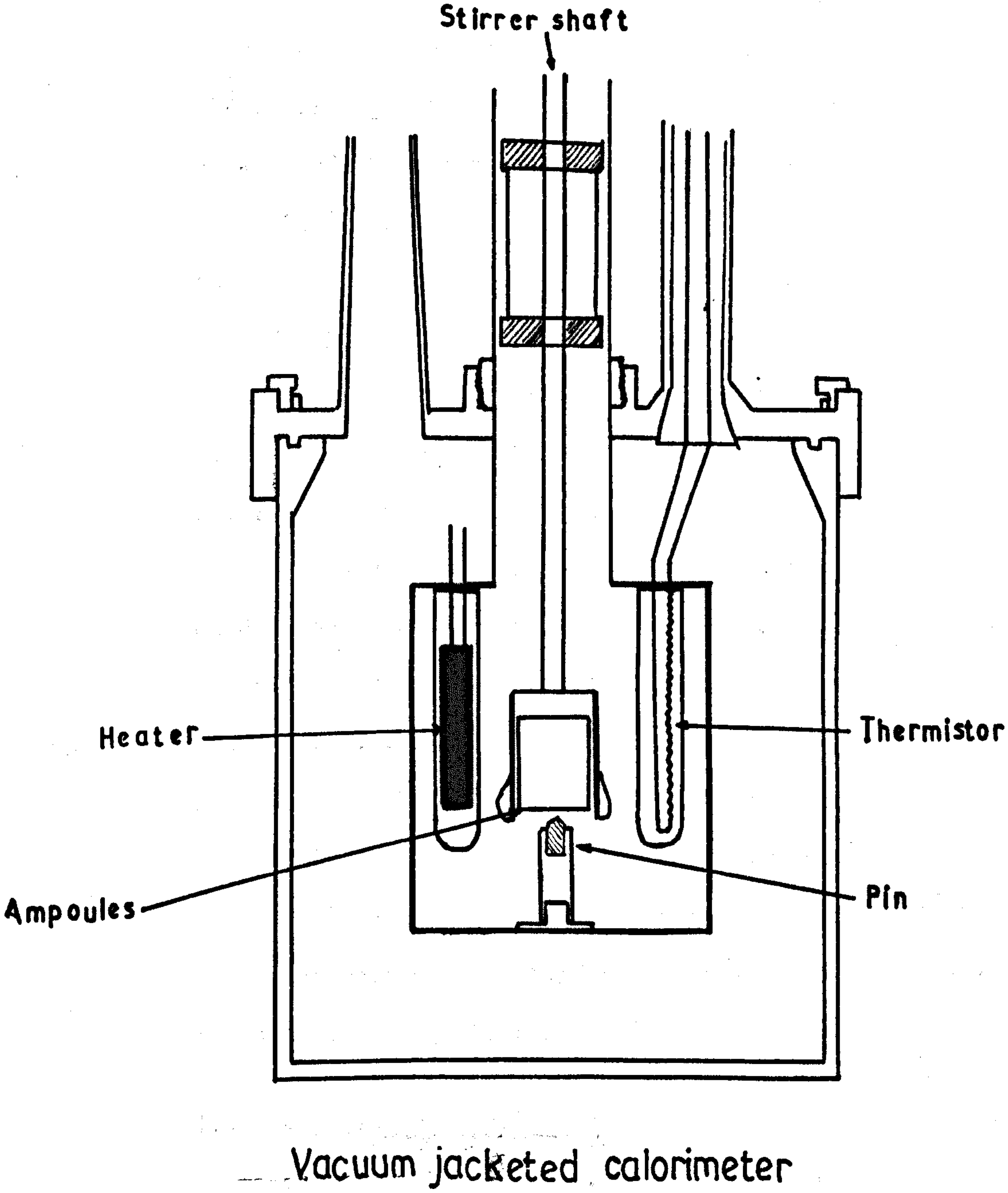
1.3.(3) Twin calorimeters

Here, two calorimeters, which are as similar as possible, are used in identical conditions, one being used as a reference. In practice this means that the system involves two reaction vessels, surrounded by the same jacket. Temperature differences can be measured between the reaction vessels, so that much of the error associated with heat leakage is eliminated. There are, however, some small corrections, to be applied, such as different stirring rates in the two ~~reactions~~ reaction vessels. The major advantage is the precision with which very small heat outputs can be measured.

1.3.(4) Vacuum jacketed calorimeters

Sunner and Wadsö (16) designed and tested a variety of these calorimeters, which are suitable for the measurement of enthalpies of reaction in the liquid phase, and which take place rapidly at room temperature. One of the most efficient (Fig.3) has a chrome-plated, thin-walled brass can as the reaction vessel. This was equipped with

FIG. 3



Vacuum jacketed calorimeter

a thermistor, heater and a central pin for breaking glass ampoules, which contained one of the reactants. A Teflon coated steel stirrer, also acted as an ampoule holder. The other reactants, in the liquid phase, were contained in the can. A glass suspension tube connected the calorimeter to the outer jacket and the interspace between this jacket and the reaction vessel was evacuated.

Equilibration of the system was quick, less than two minutes, and reaction enthalpies could be obtained to within an uncertainty interval of ± 0.1 per cent.

The slightly modified design has been produced commercially, a glass reaction vessel being used. This system, the L.K.B. "precision calorimeter system", is discussed in greater detail, later in this work.

Glass dewar vessels have also been frequently used as reaction calorimeters, chiefly because they are inexpensive and readily replaced. Their construction is very simple, consisting of a glass dewar equipped with heater, thermistor, stirrer and an ampoule breaking device, usually spikes, onto which glass ampoules are crushed.

This arrangement can give results which are reasonably accurate. More sensitive systems use twin type calormeters.(17)

The main disadvantage of glass dewar calorimeters is the long time taken to reach equilibrium.(16)

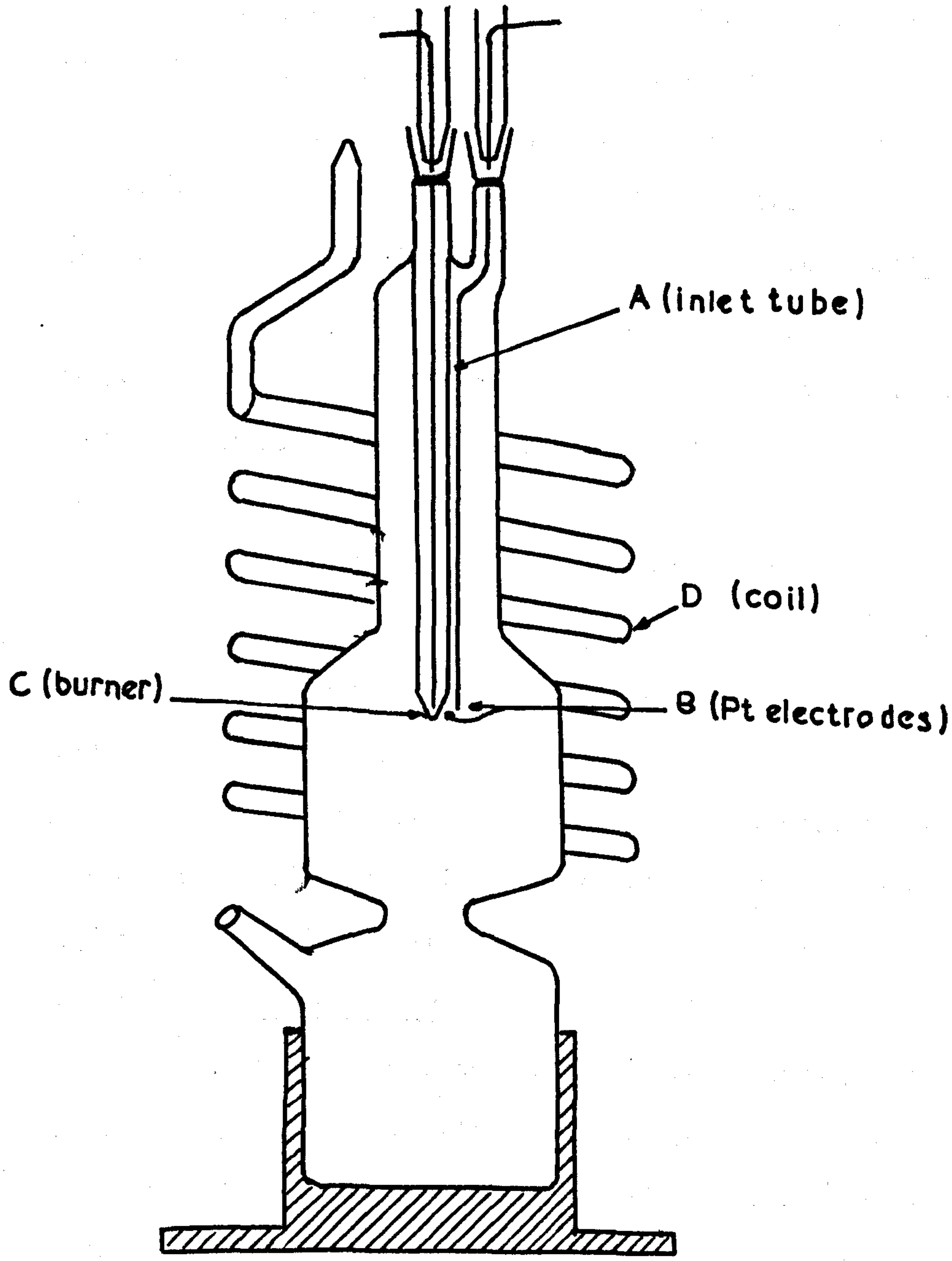
1.4. Combustion calorimetry

Combustion calorimetry falls conveniently into two types:

(1) flame calorimetry:- where volatile samples react at atmospheric pressure with a powerful gaseous oxidant; and

(2) bomb calorimetry:- where a sample, usually a solid, is subjected to high pressures of gaseous oxidant in a sealed vessel.

FIG. 4



Reaction vessel for flame calorimetry.

1.4.(1) Flame calorimetry

The calorimeter is generally of the isoperibol type. The oxidant is normally oxygen.

Such a system is shown in Fig.4. The sample, a gas or volatile liquid, and oxygen are led into the glass combustion chamber via tubes, A.

The gaseous mixture is ignited by a spark between two platinum electrodes, B, and combustion takes place at the burner C. Waste gases are led away through the coil, D. The vessel is usually immersed in water, contained in a can which is surrounded by a constant-temperature jacket. Calibration is either by the electrical substitution method, or by combustion of hydrogen, for which standard enthalpy values have been obtained.(18)

A flame calorimeter, developed by Rossini, was used for the first(18) accurate determination of the enthalpy of formation of water. The method has also been used for measurement of the enthalpy of formation of ethylene(19) and other hydrocarbons.(20)

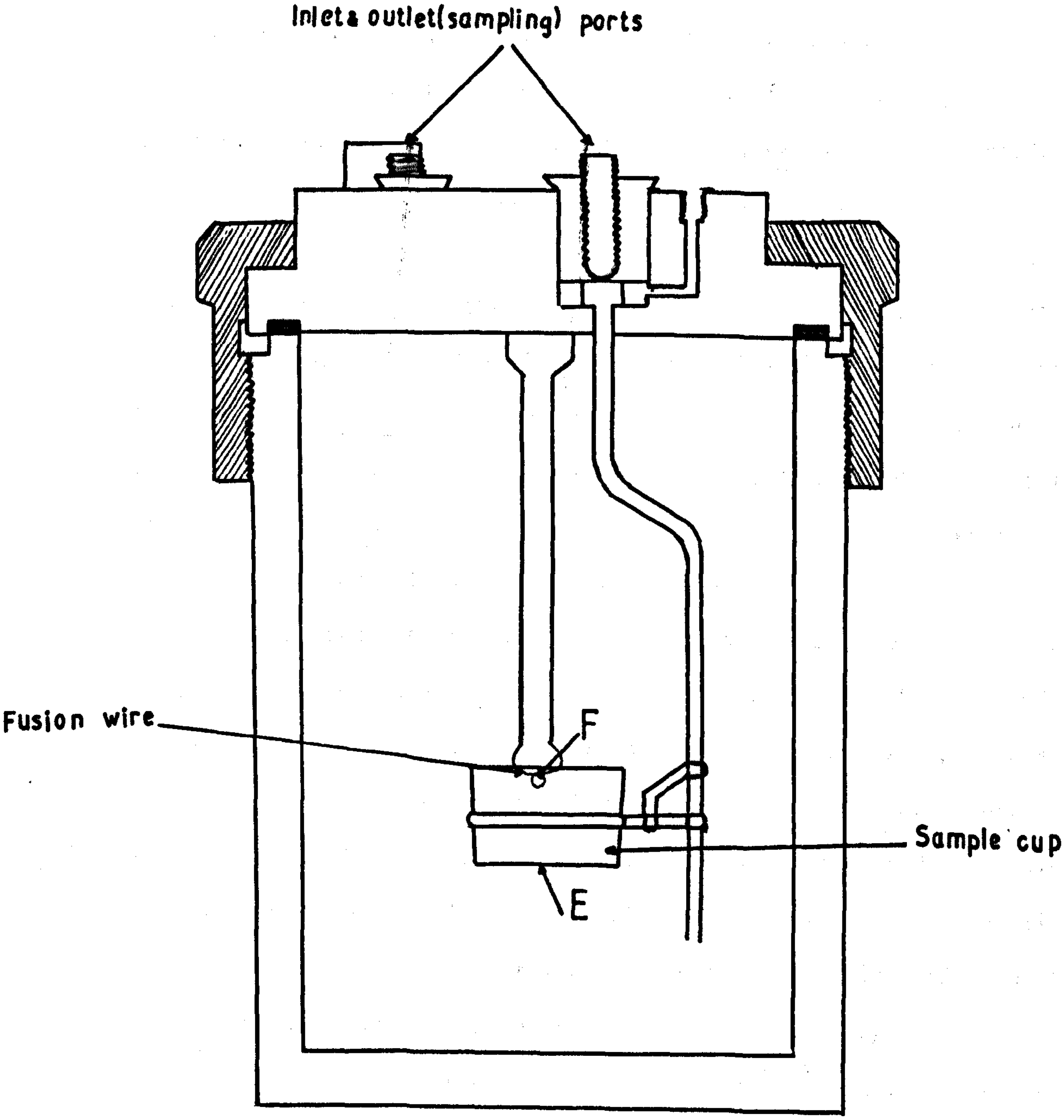
Although oxygen is the common oxidant, fluorine has also been used,(21) and since fluorine often ignites spontaneously with many materials, spark ignition is rarely required.

1.4.(2) Bomb calorimetry

Here, combustion of the sample is under high pressure of gaseous oxidant, usually oxygen, although other gases have been used. The combustion bomb is immersed in a can of water, the temperature change of which is measured when combustion occurs. The system is operated either adiabatically or isoperibolly.

A typical bomb, used in a "static bomb" calorimeter, is shown in Fig.5. It consists of a thick-walled vessel of some corrosion resistant metal. The sample is placed in a cup, E, which is usually

FIG. 5.



Combustion calorimetry bomb.

of platinum. After pressurising the vessel (ca. 30 atmospheres) and allowing equilibration to be attained, within the calorimeter system, a small current is passed through a platinum wire, F, to initiate combustion of the sample. Provision is also made for analysis of gaseous bomb products, to test for completion of reaction.

Calibration of the bomb is electrical, either directly or indirectly using a standardised intermediate, usually benzoic acid, the enthalpy of combustion of which is accurately known.(22)

Enthalpies of formation of a large number of organic compounds have been determined by the use of a bomb combustion calorimeter.(23) The derived ΔH_f^o values depend upon the enthalpies of formation of the "key" compounds CO_2 and H_2O, which are the products of combustion. The enthalpies of formation of both trans-stilbene, (CHPh=CHPh), and tolane, (CPh≡CPh), which are used in thermochemical calculations later in this thesis, have been determined by this method.

Such a static system is suitable for the combustion of compounds which contain only the elements C, H, O and N. Where the compound contains other elements, the final state of the combustion products is often ill-defined thermodynamically. Thus, combustion of an organosulphur compound yields sulphuric acid, which is deposited as droplets of different concentration on the walls of the bomb. Organometallic compounds often produce several oxides, which may be in differing states of hydration. Many of these problems were overcome by the development of the "rotating bomb" combustion calorimeter.(24) A mechanism is provided which allows the bomb to rotate about both its vertical and horizontal axes after the combustion has taken place. By charging the bomb, prior to combustion, with a suitable solvent, the combustion products can be taken into solution, to produce a homogeneous final state. This device is, effectively, a static bomb combustion calorimeter, and a solution reaction calorimeter, combined into one apparatus. A much greater range of organic compounds could thus be studied, together with a variety of organometallic compounds.

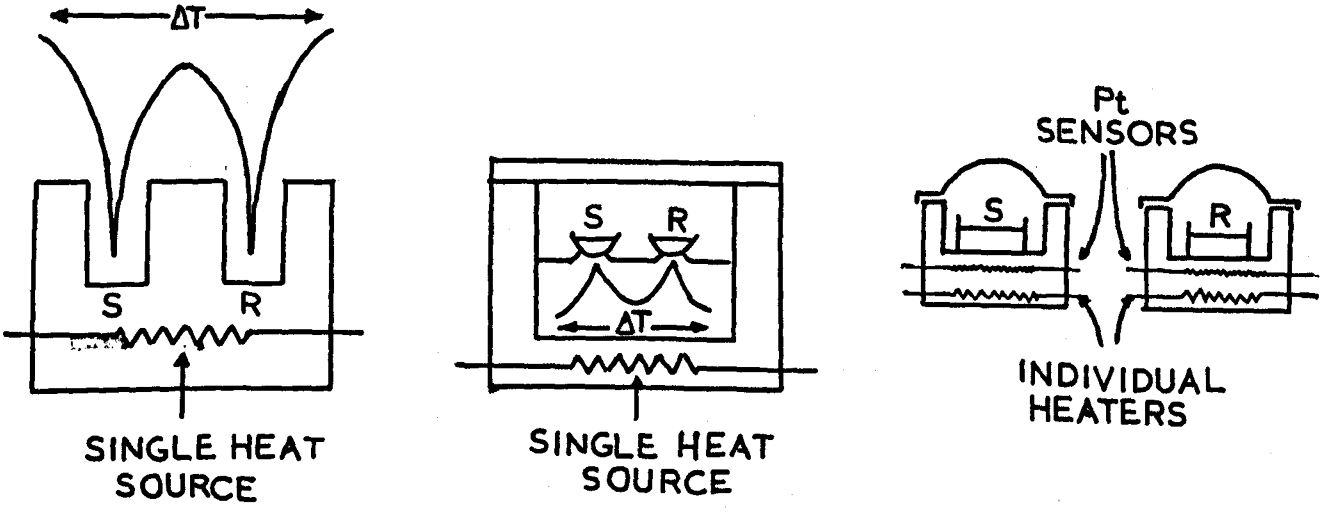
The enthalpy of formation of diethyl sulphide (SEt_2), a datum which is used in calculations later in this thesis, has been determined by the use of rotating-bomb calorimetry. This method is clearly appropriate for measurements of the enthalpies of combustion of diethylselenide, ($SeEt_2$), and diethyltelluride, ($TeEt_2$), (for which ΔH_f^o values are used subsequently) although for diethylselenide only a static bomb has been used for measurements so far, and for diethyltelluride no datum is yet available.

Further study has also been carried out using a variety of oxidants. Fluorine, chlorine, nitrogen dioxide, and even nitrogen (for the determination of the enthalpies of formation of metal nitrides) have been used. The versatility and usefulness of combustion in a bomb has thus been markedly increased.

More recently, "aneroid rotating bomb' calorimeters(25) have been developed. In this case, the bomb is placed inside a large block of metal (in place of the water in which the bomb is normally immersed). This is said to reduce errors, due to vaporisation of the surrounding water, and variations in heat capacity. However, large metal blocks suffer from slow temperature equilibration, which introduces other errors. To try and reduce these, a further innovation,(26) has been tried, using sealed hemispheres, containing carbon tetrachloride, to replace the metal blocks.

Irrespective of the type of bomb employed, the results must be subjected to the Washburn Corrections.(27) These are included to refer the measured change in internal energy, under the conditions which prevail

FIG. 6



(a) CLASSICAL DTA

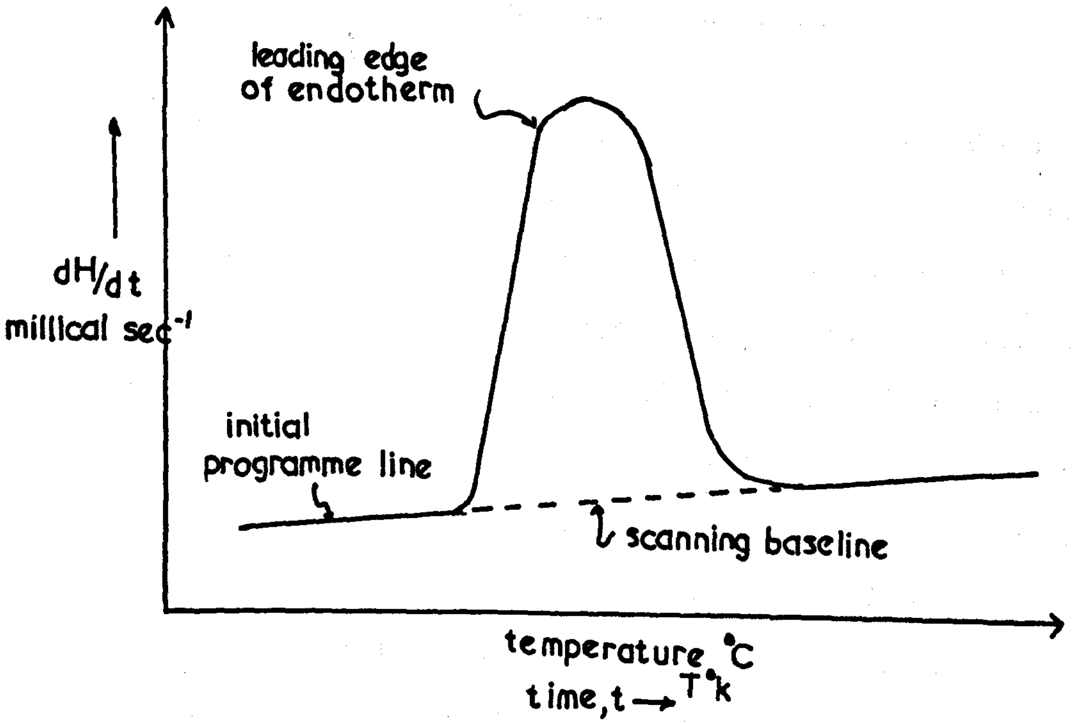
(b) "BOERSMA" DTA

(c) DSC

Schematic representation of the three principal thermal analysis systems.

Courtesy of the Perkin-Elmer Corporation.

FIG. 7



Idealised DSC thermogram.

in the bomb, to those under standard conditions and thence obtain the standard enthalpy of reaction. Such corrections are not necessary for flame calorimetry, where reactants can be arranged to be in standard conditions.

In the reaction calorimeters described, in the first part of this Chapter, the reactions are generally carried out at room temperature. In combustion calorimetry, although measurements refer to room temperature, the reaction actually takes place at quite high temperatures, and is initiated by the use of a hot-zone (the fusion of a platinum wire). In the technique of differential scanning calorimetry, which is now described, reaction are generally carried out at temperatures higher than room temperature, and the measured enthalpies refer to these higher temperatures.

1.5. Differential Thermal Analysis (D.T.A.) and Differential Scanning Calorimetry (D.S.C.)

1.5.(1) D.T.A.

These systems are twin calorimeters, in which two identical reaction vessels, which are small pans, are embedded in the same block of metal. A sample and a reference, contained in the two pans, are both heated by a single heat source. Temperatures are measured by sensors, either in both sample and reference materials (classical), or in the pans (Boersma) (Fig.6). The temperature differences, $\Delta T = Ts - Tr$, which accompanies any change, physical or chemical, in the sample, is a measure of the difference in the enthalpy change between sample and reference, when both are heated. A plotted output of ΔT against time, on a recorder, is usually made and from this enthalpy measurements are indirectly established. The lack of direct conversion to energy units is an extreme disadvantage, particularly, as functions, such as heat capacity and variation of thermal resistance, which need to be known, are often difficult to establish.

1.5.(2) D.S.C.

The differential scanning calorimeter employs individual heaters and sensors, for both sample and reference. A principal of null balance is used, whereby a control loop compensates for temperature differences between sample and reference, as exothermic or endothermic reactions arise in the sample. A second control loop increases or decreases the average temperature at a predetermined rate. A recorder displays a signal proportional to the differential heat input between sample and reference. An idealised thermogram of dH/dt against time or temperature is shown in Fig.7. Details of the theory and design of differential scanning calorimeters have been given by Watson(28) and O'Neill.(29)

The usefulness of such a system is that enthalpies can be measured directly (see Chapters 5 and 6), and can be adapted to the study of many chemical and physical processes. A more detailed review has been recently published.(30)

Using some of the aforementioned techniques, information has been obtained about several metal/ligand interactions. This work is reported in this thesis.

1.6. Symbols and units

In the subsequent chapters, equations and tables are numbered consecutively for the individual chapters.

Heat quantities are given in terms of joules and the value 1 cal = 4.184 absolute joules has been used to recalculate certain figures. The atomic weights used are those recommended by the International Union of 1961.(31) Weights used were calibrated against N.P.L. standards.

In the work reported in this thesis, the standard deviation, $\overline{S}$, of n results about a mean value, $\overline{x}$ is given by the expression

$$\overline{S} = \pm\sqrt{\frac{\Sigma(\overline{x}-x)^2}{n(n-1)}}$$

where x refers to an individual result. The uncertainty interval is defined at ± $2\overline{S}$, and refers to a 95% chance that other values will be within. Where an "overall" standard deviation, $\overline{S}_0$, was required, for the combination of different enthalpies, the value was obtained from the sum of the square of the individual standard deviations

$$\overline{S}_0^2 = (\overline{S}_1^2 + \overline{S}_2^2 + \overline{S}_n^2)$$

where $\overline{S}_n^2$ represents individual standard deviations. Errors quoted, with results, are the ~~uncertainty intervals.~~ standard deviations

The symbol, M/g, refers to the weight of sample in vacuo and the symbol, 1Torr refers to a pressure, (101, 325)kPa.

Chapter 2 Experimental

The LKB 8700 has been used for measurement of the majority of enthalpies of reaction reported in this thesis. For measurement of the enthalpies of two thermally induced isomerisation reactions, the Perkin Elmer D.S.C.1B has been used.

Both instruments are commercially available, and are adaptable to a wide range of thermochemical problems.

The LKB 8700 is of a constant-temperature environment (isoperibol) type, in which there is a heat exchange between the calorimeter and its environment. To enable enthalpies of reaction to be determined, corrections for this heat flow must be applied.

The Perkin Elmer Differential Scanning Calorimeter (D.S.C.) type 1B, is of the type described in the previous section, in which enthalpies are obtained from measurement of the differential heat flow between a sample and a reference.

2.1. The LKB 8700 Calorimeter

There are two main parts of the instrument, the (1) calorimeter assembly and the (2) electronic assembly.

2.1.(1) Calorimeter assembly

This consists of (i) the thermostatic bath and (ii) the calorimeter unit.

(i) The thermostatic bath is a large-volume cylindrical tank, filled with water, and stirred by a magnetically driven impellor. The temperature sensor is a thermistor, which allows sensitive control of the bath temperature.

Although the temperature of the bath can be varied between 293 K and 313 K, for the work reported here the range was limited between 293.18 K and 293.21 K. Stability of such a temperature is maintained

L.K.B. CALORIMETER VESSEL

FIG. 1

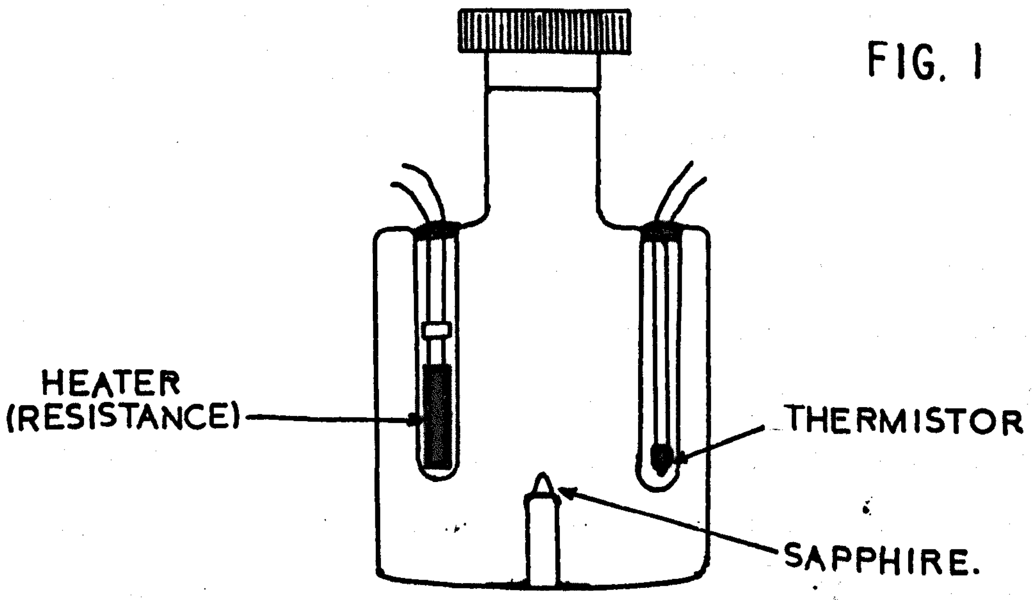
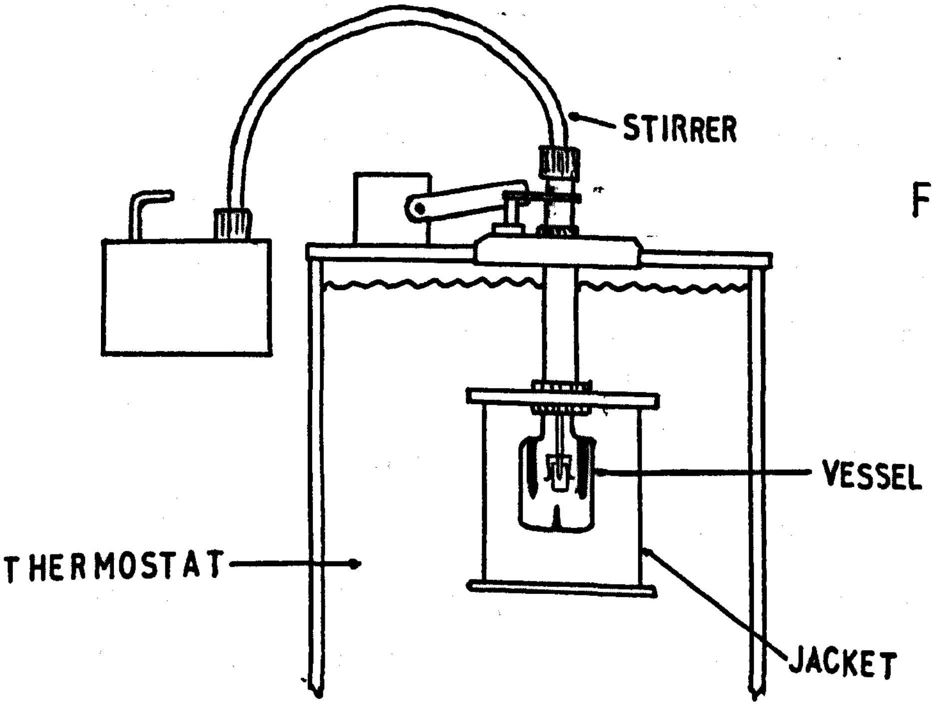


FIG. 2



THERMOSTAT & VESSEL.

by allowing the heater to work continuously against cooling, provided by a water flow through a coil surrounding the tank.

(ii) The calorimeter unit is based around the Pyrex reaction vessel (Fig.1) of which there are two options, 25 ml capacity and 100 ml capacity; they are similar in construction and were used in an identical manner.

The vessel contains a 50 ohm coil, which is used as a calibration heater, and a 2000 ohm thermistor, both held in glass pockets. Leads from the heater and thermistor are connected by a pin and socket (gold) to wires which pass through the calorimeter lid. The glass pockets contain liquid paraffin for thermal connection with the calorimeter contents. At the base of the vessel there is a short glass rod, tipped with a sapphire crystal, enabling the glass ampoules, which contain one of the reactants, to be broken and thereby initiate the reaction.

The reaction vessel is attached to the outer can by a screwed collar sealed on to the top of the vessel.

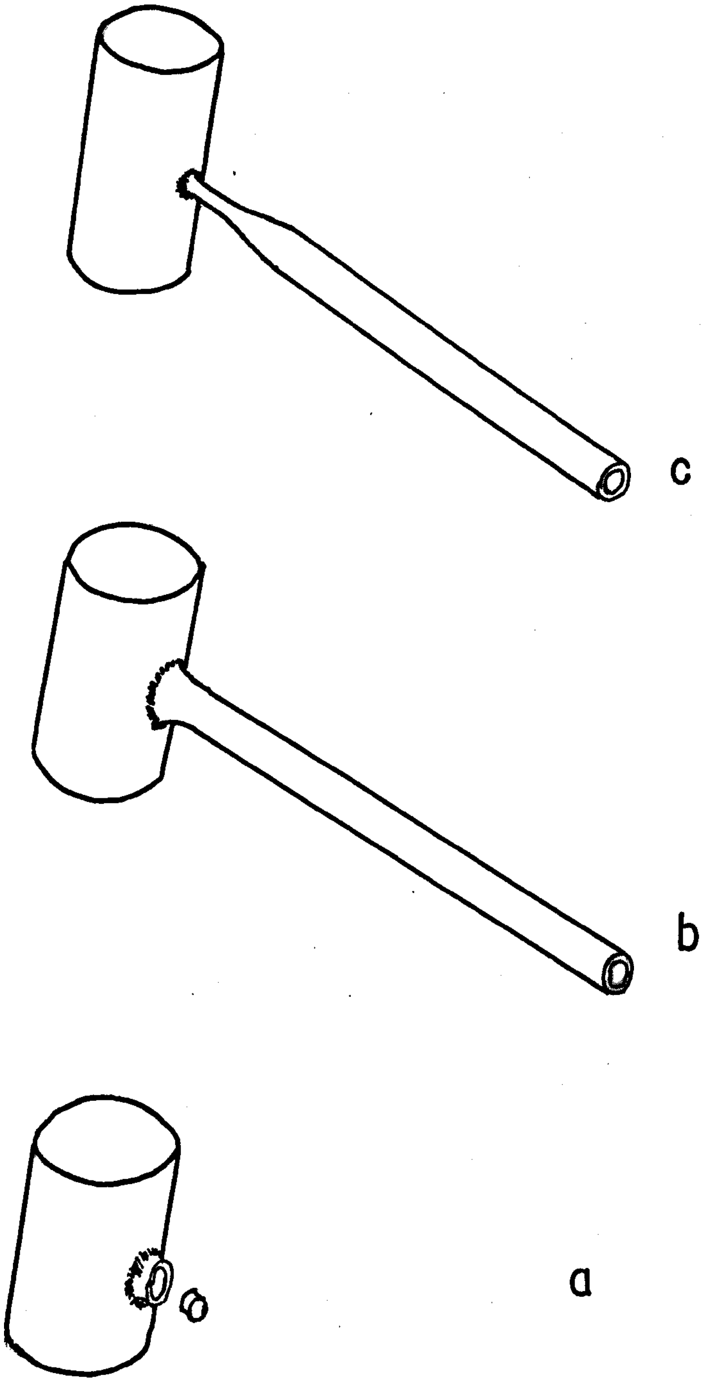
The reaction vessel is suspended inside a chromium-plated outer can, and the whole assembly can be immersed in the thermostat, as shown in Fig.2.

For the reactions investigated, encapsulation of the reactant was in thin-walled glass ampoules, of which there are three types available (shown in Fig.3): (a) for solids in aqueous solution, sealing is by a silicon rubber stopper and microwax; (b) and (c) for solids and liquids respectively, sealing is achieved by drawing off the glass side arm, by use of twin microburners on a purpose-built sealing device.

The ampoules are located into a stirrer by means of four prongs. The stirrer itself is fitted to a shaft which is connected to a three-speed stirrer motor via a flexible drive, ampoule breaking being

FIG. 3

L.K.B. AMPOULES



facilitated by vertical movement of the stirrer shaft, by an electronic device operated from the control unit (Fig.2).

2.1.(2) Electronic assembly

This consists of a Wheatstone Bridge, potentiometer, galvanometer, power supply and timer (Fig.4).

Wheatstone Bridge (11)

This balances the varying resistance of the thermistor. A range of 0-6000 ohm is available in six decades, i.e. down to 0.01 ohm which approximates to 1×10^{-4} °C temperature change.

Potentiometer (12)

This is used, in conjunction with a standard cell [inside reference unit (14)] to measure the current passing through, and the potential across, the heater used to calibrate the calorimeter.

Galvanometer (10)

A Hewlett Packard, type 419A galvanometer, is included in the electronic assembly. This galvanometer has a centre zero and variable sensitivity setting. A null detector operating from the scale zero can be used to (i) operate an external event timer (a stop watch) and also, either (ii) activate the ampoule breaker, or (iii) cause current to pass through the calibration heater.

Power supply (9)

This provides power for the calorimeter heater and other ancillary instruments.

Electronic timer (13)

This controls the time during which current is dissipated through the heater during a calibration. It can be preset for periods in the range 1 to 99 seconds, or 10 to 990 seconds.

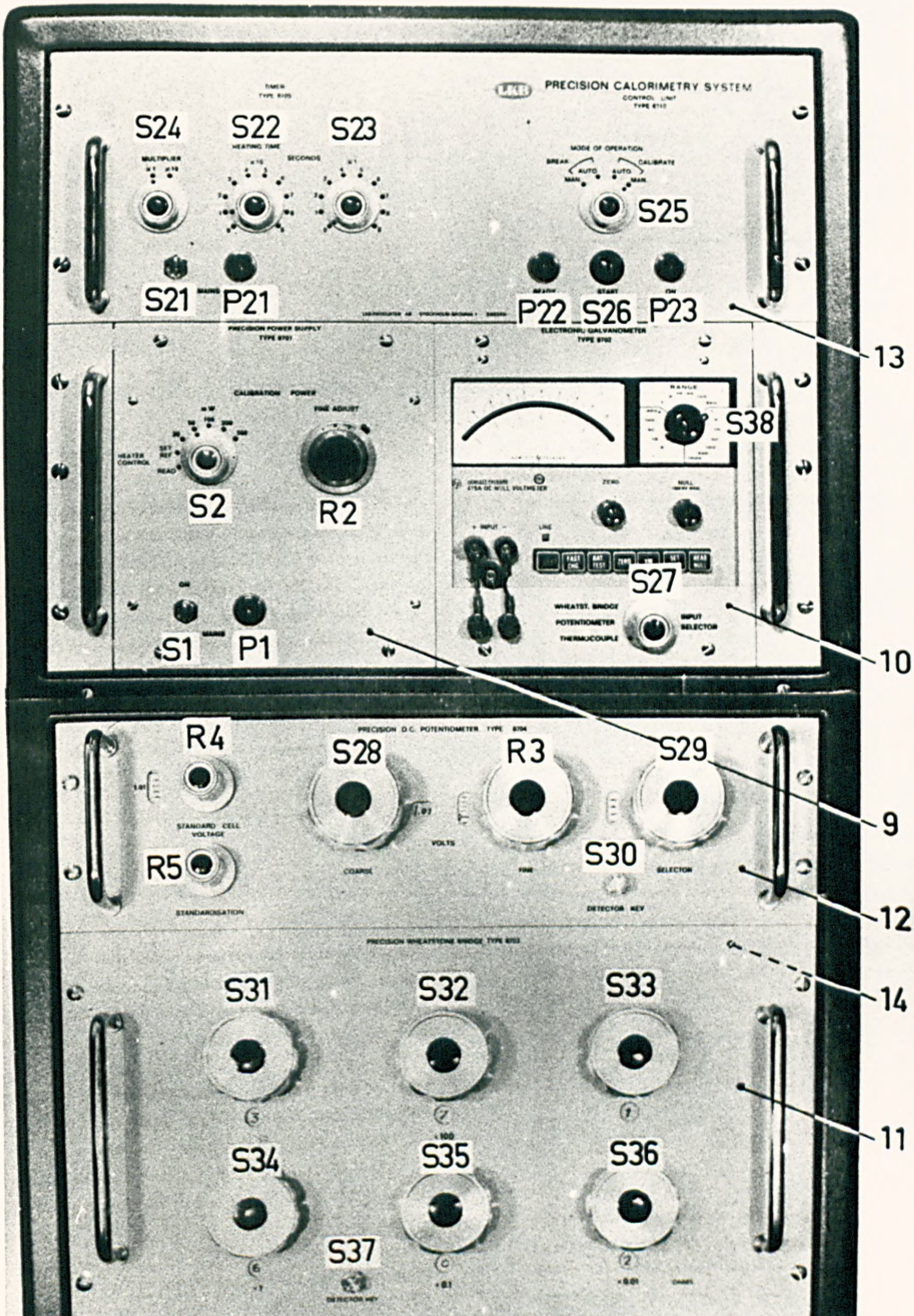

PRECISION CALORIMETRY SYSTEM
CONTROL UNIT
TIMER
MULTIPLIER
HEATING TIME
SECONDS
MODE OF OPERATION
BREAK
CALIBRATE
AUTO
MAN.
READY
START
ON
MAINS
PRECISION POWER SUPPLY
CALIBRATION POWER
FINE ADJUST
HEATER CONTROL
SET
REF
READ
ON
ELECTRONIC GALVANOMETER
RANGE
ZERO
NULL
INPUT
LINE
FAST CHG
BAT TEST
ZERO
SET
WHEATST. BRIDGE
POTENTIOMETER
THERMOCOUPLE
INPUT SELECTOR
PRECISION D.C. POTENTIOMETER
STANDARD CELL VOLTAGE
STANDARDISATION
COARSE
VOLTS
FINE
SELECTOR
DETECTOR KEY
PRECISION WHEATSTONE BRIDGE
DETECTOR KEY
OHMS
S24
S22
S23
S25
S21
P21
P22
S26
P23
13
S38
S2
R2
S27
S1
P1
10
R4
S28
R3
S29
9
R5
S30
12
14
S31
S32
S33
11
S34
S35
S36
S37

FIG 4

2.2. Procedure

The reaction vessel was charged with the necessary volume, 100 ml or 25 ml, of suitable liquid, and an ampoule fixed in ampoule holder/stirrer. The vessel was placed in the can and the whole unit was immersed in the thermostat.

Thermal equilibration of calorimeter and contents was allowed to occur (about five minutes) and, if necessary, further heating applied to bring the temperature near to the final equilibrium temperature (bath temperature). The bath temperature being set at slightly above standard temperature (at 298.55 K). The final equilibration temperature was established by leaving the calorimeter in the thermostat overnight. The actual temperature at which the experiment was started, was deduced from a knowledge of the final equilibrium temperature and the temperature change for the reaction, which was established by preliminary experimentation. The temperature measurements were made in terms of the resistance of the thermistor.

Initiation of either calibration heating or chemical reaction was always below, or at, 298.15 K. For endothermic reactions, the reactions were initiated at 298.13 K. For exothermic reactions, and calibrations, the starting temperature was chosen to be below 298.13 K, such that the final temperature, after reaction or calibration, was 298.13 K.

2.2.(1) Calibration procedure

Calibration constants were established for each run, and calculated from (i) the amount of power supplied and (ii) the corrected resistance change.

The exact process of calibration involved: (i) establishment of a time-resistance graph; and (ii) calibration of heater.

Some initial adjustments are also required to set the power supply, to give an exact current supply, involving:-

(a) standardisation of the potentiometer against the standard cell;

(b) adjusting the calibration current, i, to the required setting i.e. 0.4, 1.0, 2.0, 4.0 or 10.0×10^{-3} amps;

(c) adjusting the power supply to give 1.00000 volt across the respective resistance (in (b) above), for the calibration current setting; and

(d) setting the timer to the desired heating time.

Time-resistance readings were then taken for a five minute fore period, such that approximately 0.3 minute time intervals occurred between consecutive resistance readings. The Wheatstone bridge was then set to a resistance, which was slightly different from that of the thermistor at the starting temperature. The off-balance current resulted in a small deflection of the galvanometer. As the temperature changed the deflection decreased to zero. This actuated the null-point detector which was programmed to stop the slave hand of a stopwatch (calibrated in units of 0.01 minute). The time corresponding to the particular setting of the resistance was therefore recorded. This process was repeated. After this the Wheatstone bridge resistance was reset and the null-point detector was programmed to "automatic". In this mode of operation, when the galvanometer deflection next became zero, current was automatically switched to flow through the calibration heater, for a prearranged time, t. During this heating period and subsequently, during an after period, further time/resistance readings were recorded in a like manner to the fore period.

The heater itself was then calibrated, firstly, by adjusting the potentiometer to supply a voltage of 1.00000 volts across a 50 ohm standard resistance (in the "Set Ref." position on the power supply); secondly, the voltage drop across the heater was measured (in the "Read" position on the power supply). This gives the potential drop between the gold pins, in the calorimeter lid, to which the heater is connected by short leads. The resistance of the heater and leads is then calculated from the values of current and potential. The correction for resistance of the leads can be estimated from a knowledge of the resistance per unit length, and the length of the leads. This yields a value for the resistance, R_c, of the calibration heater.

The energy dissipated in the heater, Q(calib), can be calculated from the relationship:

$$Q(\text{calib}) = i^2 R_c t \text{ joules}$$

The corrected resistance change was then found, as indicated in the subsequent section, and a calibration constant, ε, calculated from:

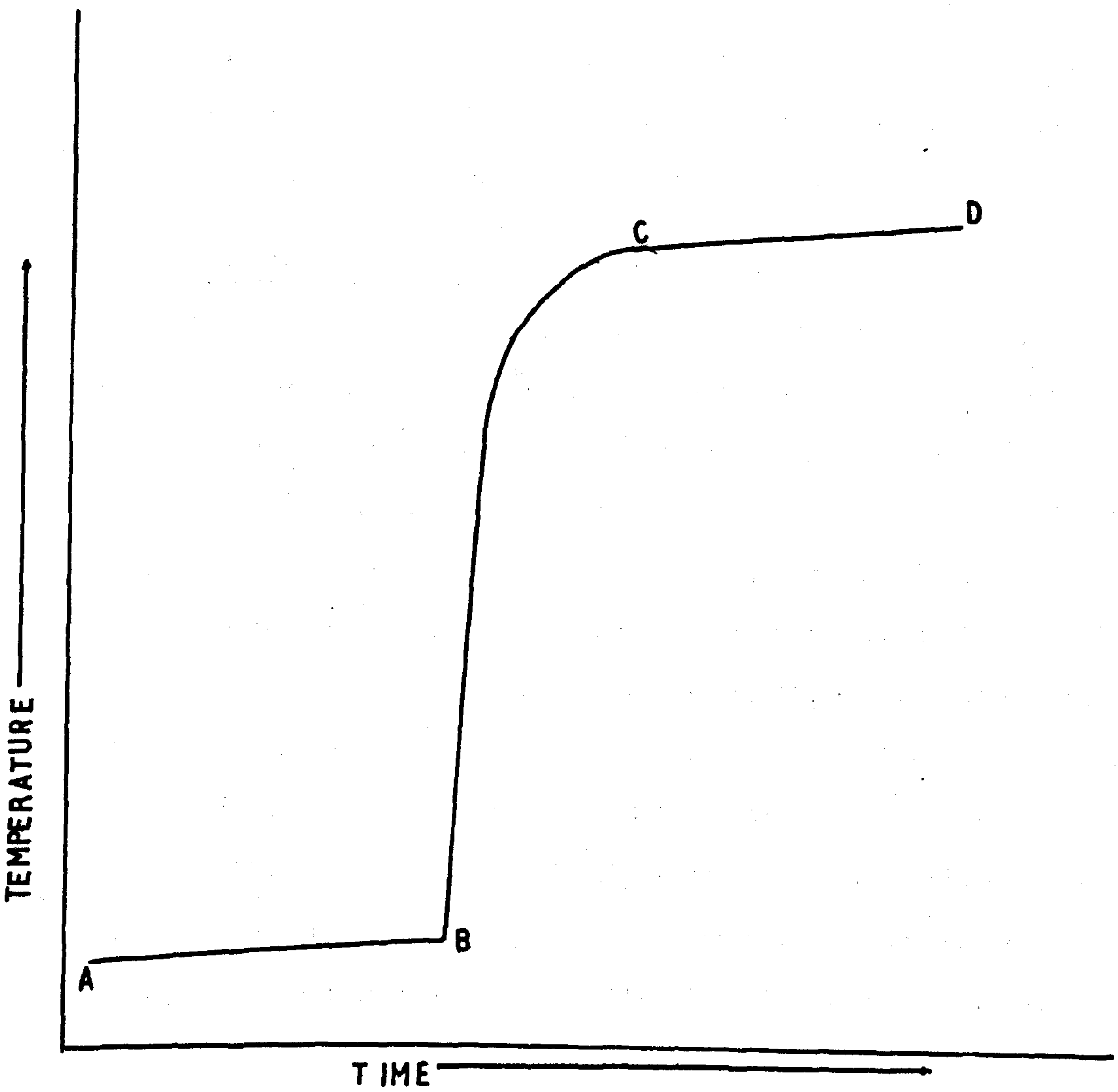
$$\varepsilon = \frac{Q(\text{calib})}{\text{corrected resistance change}}$$

2.2.(2) Reaction procedure

The procedure adopted was similar to that used for calibration. A five minute fore-period was followed by a reaction period, during which time/resistance readings were taken as often as possible. Finally, after-period measurements were taken for five minutes when the time interval, for constant resistance changes, itself became constant. The technique for reaction initiation was either automatic, using the 'mode of operation' control, set to 'break automatic', or alternatively, and always when the 25 ml vessel was used, to depress the stirrer by hand until both faces of the ampoule were heard to break. The difference in technique in the latter case was to avoid removal of reactant following excessive depression of the stirrer. The actual time at which initiation occurred was estimated by extrapolation of the fore period to the time noted for breaking of the first face of ampoule.

The energy change [Q(react)] for the particular reaction is given by (in joules)

FIG. 5



TIME - TEMPERATURE RELATIONSHIP
DURING A REACTION.

$$Q(\text{react}) = \varepsilon \times (\text{corrected resistance change for reaction})$$

where ε = calibration constant (see previous section).

The enthalpy change, ΔH per mole, could then be calculated from the relationship:

$$\Delta H = \frac{Q(\text{react})}{n} \times 10^{-3}\ \text{kJ mol}^{-1}$$

where n is the number of moles of reactant.

The use of Q(react) is not strictly correct as a few small corrections need to be added (see later sections).

2.3. Calculation of corrected resistance change

The observed resistance, or temperature change accompanying a reaction in an isoperibol calorimeter includes the effects due to stirring and heat transfer between the reaction vessel and its surroundings. To correct the heat transference various method have been described: two of which have been used throughout this thesis, are explained.

The temperature change during a reaction is shown diagrammatically in Fig.5. This shows a linear fore period, AB, where heating, caused by the thermal head, takes place at a constant rate. The second section, BC, is the main period, which refers to heating caused by (a) the thermal head and (b) some heat source in the vessel itself. This heat source being either from a reacting system, or from electrical power supplied to a heater, within the vessel. The final linear section, CD, is the after period caused once again by the thermal head.

The observed temperature change, ΔT, equivalent to C-B, is made up of the corrected temperature change, Θ, and a correction term, ΔT_{corrn}.

$$\Delta T = \Theta + \Delta T_{\text{corrn}}.$$

From Newton's law of cooling, the equation is given:

$$\frac{dT}{dt} = U + \ (T_i - T)$$

where U is the heat generated within the calorimeter, K is the thermal leakage constant, and T_i is the jacket temperature.

It is assumed that this law is obeyed in the operation of the LKB 8700, which is of a constant temperature environment type.

Now, when $T = T_\infty$ $\frac{dT}{dt} = 0$

$$\frac{dT}{dt} = k(T_\infty - T) = g, \qquad (1)$$

which is the slope of the linear fore-period, or after-period.

Integration of this between the extremities of the main period leads to

$$\Delta T_{corrn} = k(T_\infty - T_m)\Delta t \qquad (2)$$

where Tm is the mean temperature during the main period and Δt the time of the entire main period (B-C). Now, from equation (1)

$$GB = k(T_\infty - T_B) \qquad (3)$$

where GB is the value of G at point B, i.e. the point at which the reaction starts. However, for convenience the slope G, of the initial period is usually taken:

$$Gi = k(T_\infty - T_i) \qquad (3a)$$

Combination of (2) and (3a) leads to:

$$\Delta T_{corrn} = [G_i - k(T_m - T_i)]\Delta t$$

and similarly, $\Delta T_{corrn} = [G_f - k(T_m - T_f)]\Delta t$,

the subscripts i and f referring to the initial (fore) period and final (after) period, respectively.

The corrected temperature rise is therefore given by:

$$\Theta = \Delta T - [G_{(i\ or\ f)} - k(T_m - T_{(i\ or\ f)})]\Delta t$$

The value of k can be estimated from the values of G and the mean temperatures of the two linear periods:

$$k = (G_i - G_f)/(T_f - T_i)$$

END POINT ESTIMATION OF A REACTION

FIG. 6

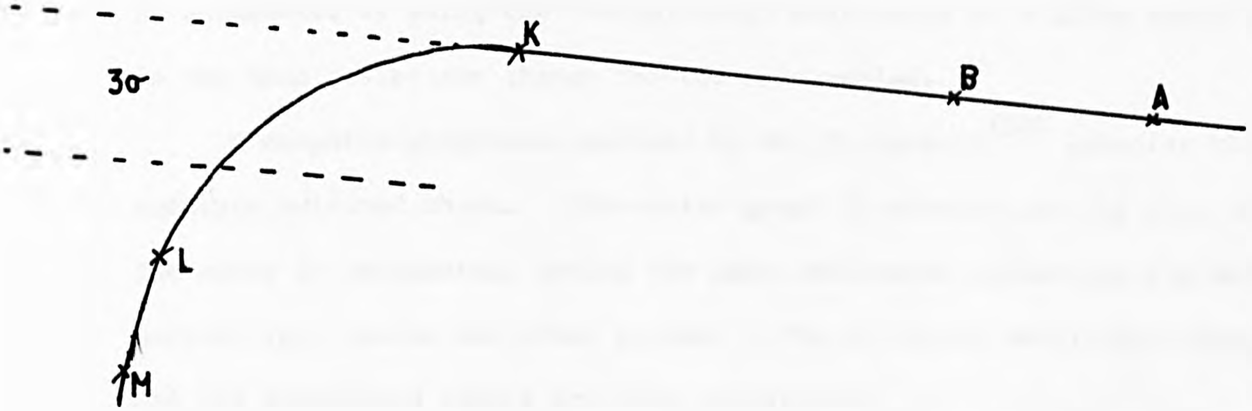
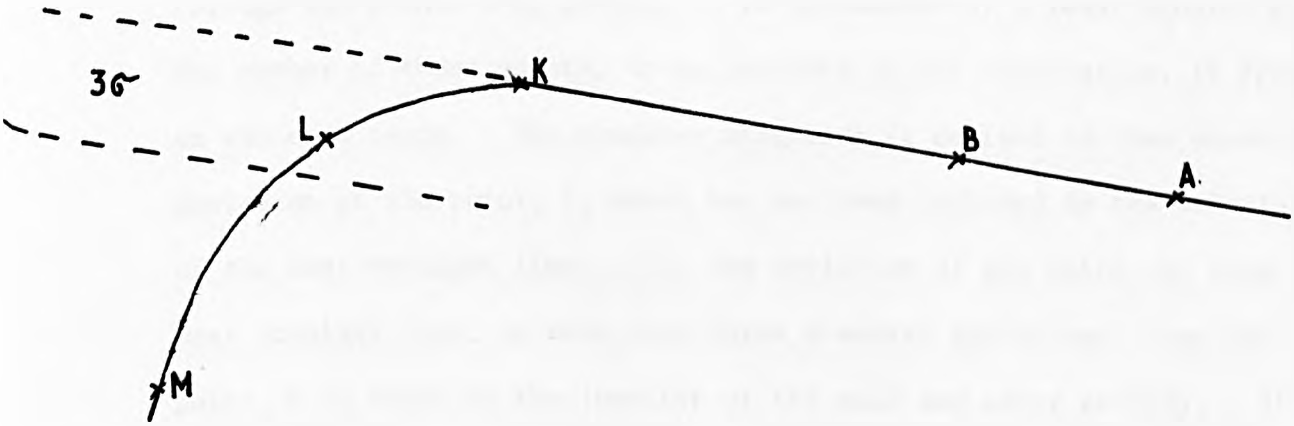


FIG. 7



The above equations are also applicable to resistance, however, corrected values obtained are not strictly comparable, as the resistance of a thermistor is not a linear function of temperature. The problem is surmounted by using the "normalising" expression $\Delta T \approx \Delta R/Rm$ where Rm is the mean resistance change for the main period.

A computer programme, devised by Dr. P. Borrell(32) embodies the concepts outlined above. The entire graph is plotted and the area under the curve is integrated, giving the mean resistance values for the main period, fore period and after period. The corrected resistance change and the normalised values are then calculated.

The process employed is to build the plot from time/resistance readings fed into the computer on cards, together with various parameters needed for the plotting and calculation processes.

A best straight line, correspondong to the fore period, is determined by a least squares plot, using the number of points specified by the data cards. A mean resistance (R_i) is then calculated.

The after period is plotted similarly. The best straight line through the points A-K, of Fig.6., is calculated by a least squares plot. The number of these points, to be included in the calculation, is specified on the data cards. The computer programme is devised to then examine the deviation of the point, L, which has not been included in the calculation of the best straight line. If, the deviation of the point, L, from the best straight line, is more than three standard deviations, then the point, K is taken as the junction of the main and after periods. If the deviation of the point, L, is less than three standard deviations (Fig.7.) then a best straight line is recalculated to include the point L, i.e. through the points A-L. If, now, the deviation of the point M is more than three standard deviations of the recalculated straight line, then the point L is taken as the junction of the main and after periods.

If necessary the process is repeated until the point of departure is established. Having established the number of points in the main period and after period, the mean resistance (R_f) for the after period is established.

The main period is then fitted, and thence plotted, to a curve using a cubic spline routine, in which sequential pairs of points are fitted to a cubic equation. This produces a continuous curve (not a smoothed one) passing through all the points. The mean resistance R_m, is then calculated from the coefficients of the cubic equation by integration.

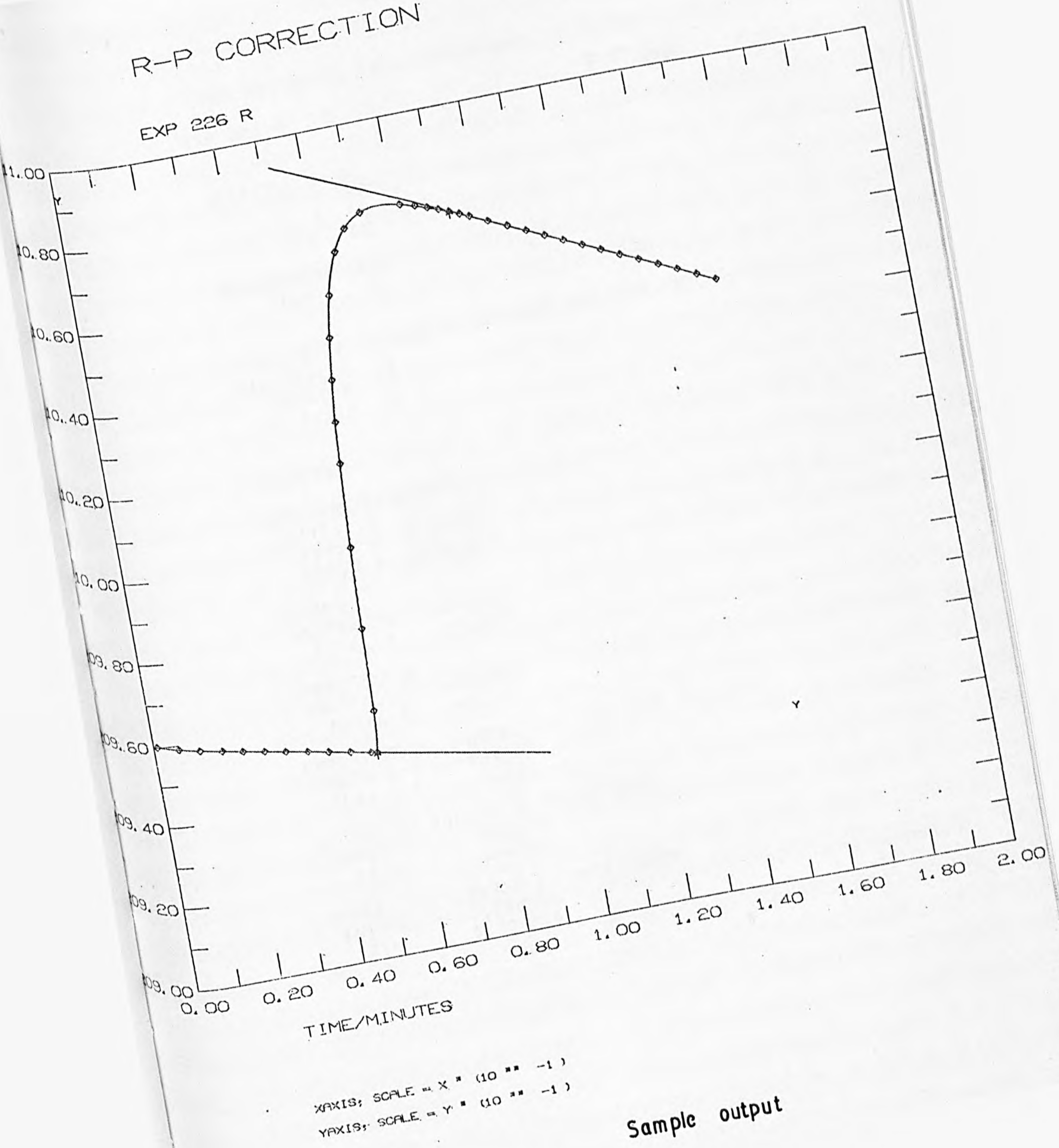
The values of mean resistances (R_i, R_m, R_f) observed resistance change, ΔR, and time length of main period, Δt, are evaluated from the data. Other values, for the constant k and the fore and after period slopes, G_i and G_f, are also calculated from the data and all are substituted into the Regnault-Pfaundler equations:

$$\Theta = \Delta R - [G_{(i \text{ or } f)} - k\{R_m - R_{(i \text{ or } f)}\}]\Delta t$$

All the above data, input and calculated values, together with a graph of time/resistance readings, joined by appropriate calculated lines, are printed out by the computer. The graph immediately displays the sensibility of the plot, as errors can occur, other than by mispunching cards. Occasionally "overshooting" takes place, when the gradient change, between the point on the end of the main period and the point on the beginning of the after period, is very rapid. The result is a "loop" between these two points connecting the two periods. Correction is simply a matter of interpolating points, usually only one is necessary, between the junction of the two periods.

A typical output is shown in Fig.8(a), Fig.8(b) and Fig.8(c).

FIG 8a



Sample output

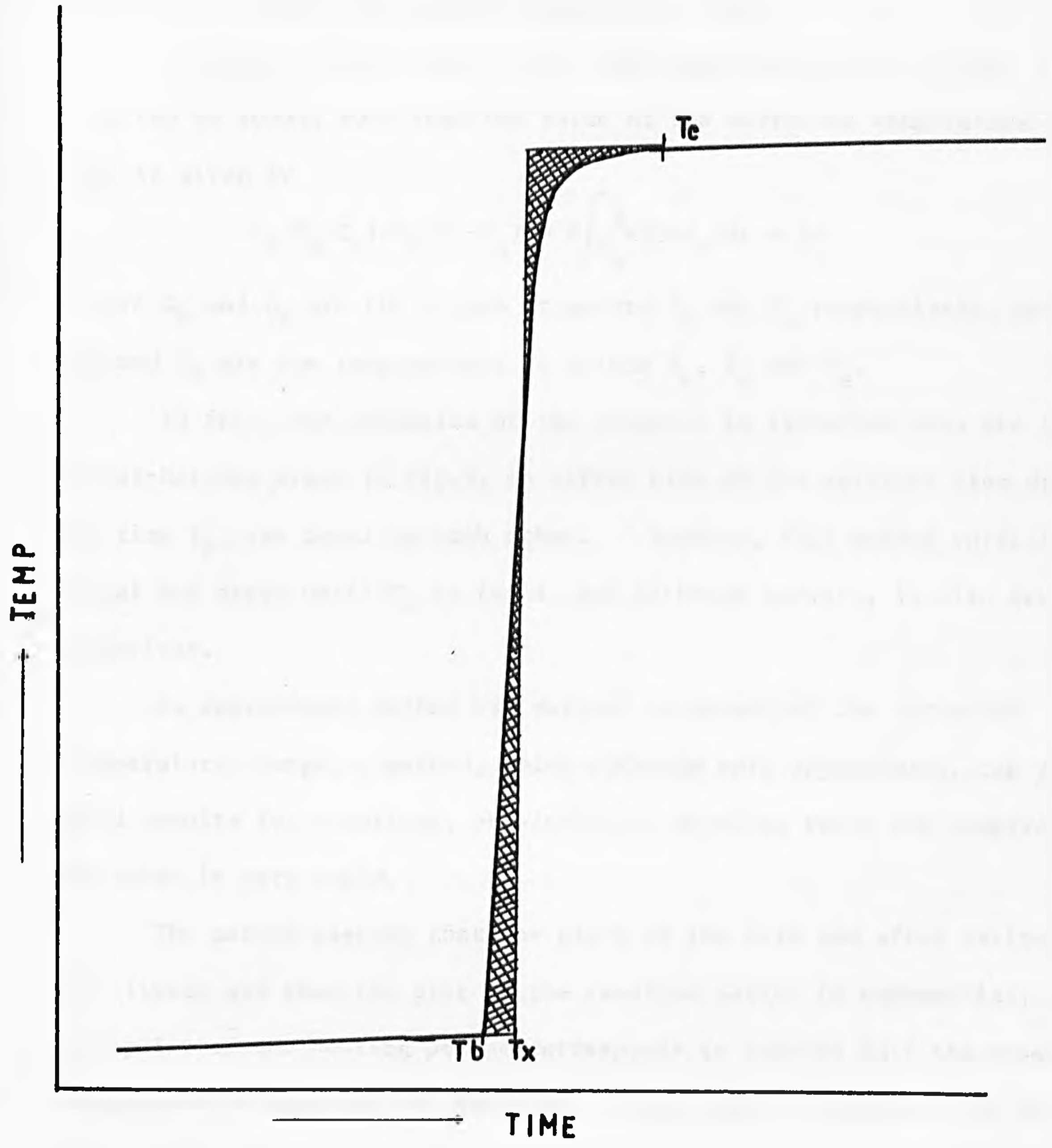
FIG 8b

```
  CORRECTION BY REGNAULT-PFAUNDLER METHOD

EXP 226 R


 ORIGINAL DATA
        N =  43
       NI =  12
       NF=   12

 PARAMETERS USED
     KDEV =   3


 NUMBERS OF POINTS DETERMINED (=N+2)
 MINITIAL =  12
   NCURVE =  17
   NFINAL =  16


 RESULTS

 MEAN RESISTANCES
  INITIAL =  2095,487
    FINAL =  2106,002
    CURVE =  2106,270

 SLOPES
  INITIAL =     -0,201
    FINAL =     -0,465

 CORRECTIONS
  INITIAL =     -1,926
    FINAL =     -1,926

 EXPERIMENTAL RESISTANCE AND TIME CHANGES
  DELTA R =     12,430
  DELTA T =      4,080

 CORRECTED VALUES OF RESISTANCE
  INITIAL =     14,356
    FINAL =     14,356

 NORMALISED CHANGE IN RESISTANCE
  INITIAL =  0,006816
    FINAL =  0,006816
```

FIG 8c

```
                DATA USED

                  TIME        R(EXPER)   R(CALC)     DIFF
 INITIAL PERIOD
                   0,090     2096,000   2096,001    -0,001
                   0,600     2095,900   2095,899     0,001
                   1,080     2095,800   2095,802    -0,002
                   1,600     2095,700   2095,697     0,003
                   2,080     2095,600   2095,601    -0,001
                   2,580     2095,500   2095,500     0,000
                   3,070     2095,400   2095,401    -0,001
                   3,580     2095,300   2095,299     0,001
                   4,070     2095,200   2095,200     0,000
                   4,580     2095,100   2095,097     0,003
                   5,060     2095,000   2095,001    -0,001
                   5,200     2094,970   2094,972    -0,002
REACTION PERIOD
                   5,200     2094,970   2094,970     0,000
                   5,310     2096,000   2096,000     0,000
                   5,390     2098,000   2098,000     0,000
                   5,480     2100,000   2100,000     0,000
                   5,600     2102,000   2102,000     0,000
                   5,670     2103,000   2103,000     0,000
                   5,770     2104,000   2104,000     0,000
                   5,900     2105,000   2105,000     0,000
                   6,080     2106,000   2106,000     0,000
                   6,400     2107,000   2107,000     0,000
                   6,720     2107,500   2107,500     0,000
                   7,150     2107,800   2107,800     0,000
                   8,140     2107,800   2107,800     0,000
                   8,490     2107,700   2107,700     0,000
                   8,780     2107,600   2107,600     0,000
                   9,040     2107,500   2107,500     0,000
                   9,280     2107,400   2107,400     0,000
   FINAL PERIOD
                   9,280     2107,400   2107,412    -0,012
                   9,520     2107,300   2107,300    -0,000
                   9,750     2107,200   2107,193     0,007
                  10,170     2107,000   2106,998     0,002
                  10,610     2106,800   2106,793     0,007
                  11,040     2106,600   2106,593     0,007
                  11,460     2106,400   2106,397     0,003
                  11,880     2106,200   2106,202    -0,002
                  12,310     2106,000   2106,002    -0,002
                  12,730     2105,800   2105,806    -0,006
                  13,160     2105,600   2105,606    -0,006
                  13,590     2105,400   2105,406    -0,006
                  14,030     2105,200   2105,202    -0,002
                  14,460     2105,000   2105,001    -0,001
                  14,900     2104,800   2104,797     0,003
                  15,340     2104,600   2104,592     0,008
```

FIG 9



HYPOTHETICAL DETERMINATION OF END POINT.

A second method, Dickenson's extrapolation(33) was also employed, for the calculation of corrected resistance changes. This is suitable for reactions which are completed in a short time, or for short heating periods, of about five minutes duration or less.

Dickenson showed that on the time/temperature plot (Fig.9), a time, tx, can be found, such that the value of the corrected temperature change $\Delta\Theta$, is given by

$$-G_b(T_x-T_b)-G_e(T_e-T_x) = K\int_{T_b}^{T_e}(\Theta-\Theta_\infty)dt = \Delta\Theta$$

where G_b and G_e are the slopes at points T_b and T_e respectively, and T_b, T_x and T_e are the temperatures at points T_b, T_x and T_e.

In fact, the condition of the equation is satisfied when the two cross-hatched areas in Fig.9, on either side of the vertical line drawn at time T_x, are equal to each other. However, this method entails trial and error until T_x is found, and although correct, is also very laborious.

An approximate method was devised to establish the corrected temperature change, a method, which although only approximate, can yield good results for reactions, or electrical heating, where the temperature increase is very rapid.

The method assumes that the plots of the fore and after periods are linear and that the plot of the reaction period is exponential. The mid-point of the heating period corresponds to exactly half the observed temperature change for the reaction. The former is derived from the 'half-life' equation for the exponential

$$(1-\frac{1}{e}) = 0.63 \approx 0.6$$

The entire procedure can be done graphically, by drawing linear fore and after periods, and connecting the two lines with a linear main period. The 'mid-point' for the main period is estimated, and values for the fore and after periods are found from extrapolation of the linear lines for the two periods.

Both this method and the computer method outlined previously have been used in this thesis and are mentioned within the appropriate text.

2.4. Corrections

The term Q(react), in the relationship $\Delta H = \frac{Q(\text{react})}{n}$, cannot be equated to the enthalpy of the reaction, since several other small heating effects usually occur during reaction initiation.

When the contents of an ampoule are ejected into solution, heat effects other than reaction occur.

(i) Air bubbling through solution, from a partially filled ampoule, causes evaporation of solvent, to saturate the gas passing through.

(ii) Evaporation of ampoule contents to saturate the gaseous phase above the liquid in the unbroken ampoule.

(iii) Dissolution of a solute will cause a change of vapour pressure of the solvent and therefore have a heat effect.

(iv) The temperature change of the reaction or calibration causes a further heat effect by changing the vapour pressure of the solvent. Hence the need for similarity between the temperature change of the reaction and calibration.

(v) Evaporation of volatile reactant or product, in the reaction vessel, into the vapour space above the solvent, can also have a heat effect, depending on volatility and quantity present.

(vi) Gas evolution, as a result of reaction, has a similar effect to (i), the gas produced becoming saturated with solvent.

(vii) Other effects include heat of breaking glass ampoules; heat effect caused by changing of stirring after ampoule breakage, and also spurious effects from using tightly packed ampoule contents, solidified melts, etc.

Of the above effects only (i) and (ii) were corrected for, the remainder were assumed to be too small to need the inclusion of correction terms. The corrections for effect (i) were based upon direct data for breaking empty ampoules into the relevant solvent or solutions, an "average" solution being used if product and reaction solution were similar. Effect (ii) was estimated from vapour pressure and enthalpy of vaporisation data.

2.5. Calibration of calorimeter

Measurement of the enthalpy of solution of tris(hydroxymethyl)-aminomethane), (T.H.A.M.), into 0.1N HCl to give a final solution of 5 g ℓ^{-1} is recommended,(34) as a test substance in calorimetry. The calorimeter was tested by use of this standard. The results for the two reaction vessels, used in this work are shown in Table 1.

Table 1

	ΔH(100 ml vessel)	ΔH(25 ml vessel)
	-29.783 kJ mol^{-1}	-29.798 kJ mol^{-1}
	-29.920 kJ mol^{-1}	-29.941 kJ mol^{-1}
	-29.764 kJ mol^{-1}	-29.868 kJ mol^{-1}
	-29.839 kJ mol^{-1}	-29.919 kJ mol^{-1}
		-29.798 kJ mol^{-1}
		-29.360 kJ mol^{-1}
mean	-29.827 ± 0.070 kJ mol^{-1}	-29.781 ± 0.175 kJ mol^{-1}

The sample of T.H.A.M. used was proved by Dr.I. Wadsö, University of Lund, and the 0.1N HCl by B.D.H., Concentrated Volumetric Solutions (C.V.S.). The results can be compared to the recommended value of -29.744 kJ mol.(35) at 298.15 K.

2.6. Differential scanning calorimetry

A small section of the work, described in this thesis, utilised the Perkin Elmer differential scanning calorimeter, D.S.C. 1B.

Briefly, the system consists of three parts, control unit, recorder and analyser, (Fig.10).

(i) The control unit contains the operating controls and indicators consisting of the following.

(a) Slope control, to correct baseline slope.

(b) Range control, this is calibrated in millicalories per second, and gives the value of sensitivity for full scale deflection.

(c) Scan speed control, this is calibrated in degrees per minute and gives the rate of temperature increase.

(d) Temperature control, this is a mechanical counter indicating the temperatures in degrees K.

(ii) Pen recorder, a Texas Instruments Inc. 5Ma. recorder is used. This has a variable chart speed and two pens, one to follow the output from the analyser and the second to follow the temperature rise in individual degrees.

(iii) Analyser, this contains controls for temperature calibration and the sample head.

2.6.(1) Technique

Samples weighing five to ten milligrams were encapsulated in aluminium pans closed by domed lids. A Cahn Gram Electrobalance was used to weigh samples and pans and indium (99.999% purity, Koch Light Ltd.) was used for calibration of the instrument. All thermograms were recorded with nitrogen flowing over the sample at a rate of $\sim 20\ \text{ml min}^{-1}$.

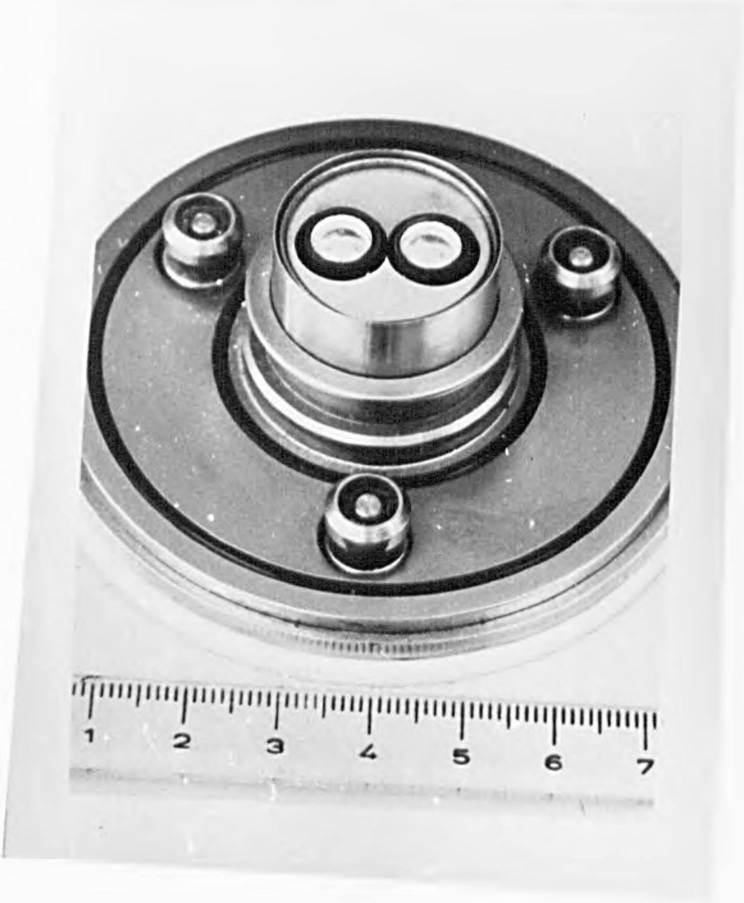


FIG 10

2.6.(2) Measurement of Enthalpies

The temperature and enthalpy of fusion of indium (429.55 K and + 3.26 kJ mol^{-1}) were checked on the calorimeter, before the recording of each series of thermograms. Results obtained are shown in Table 2.

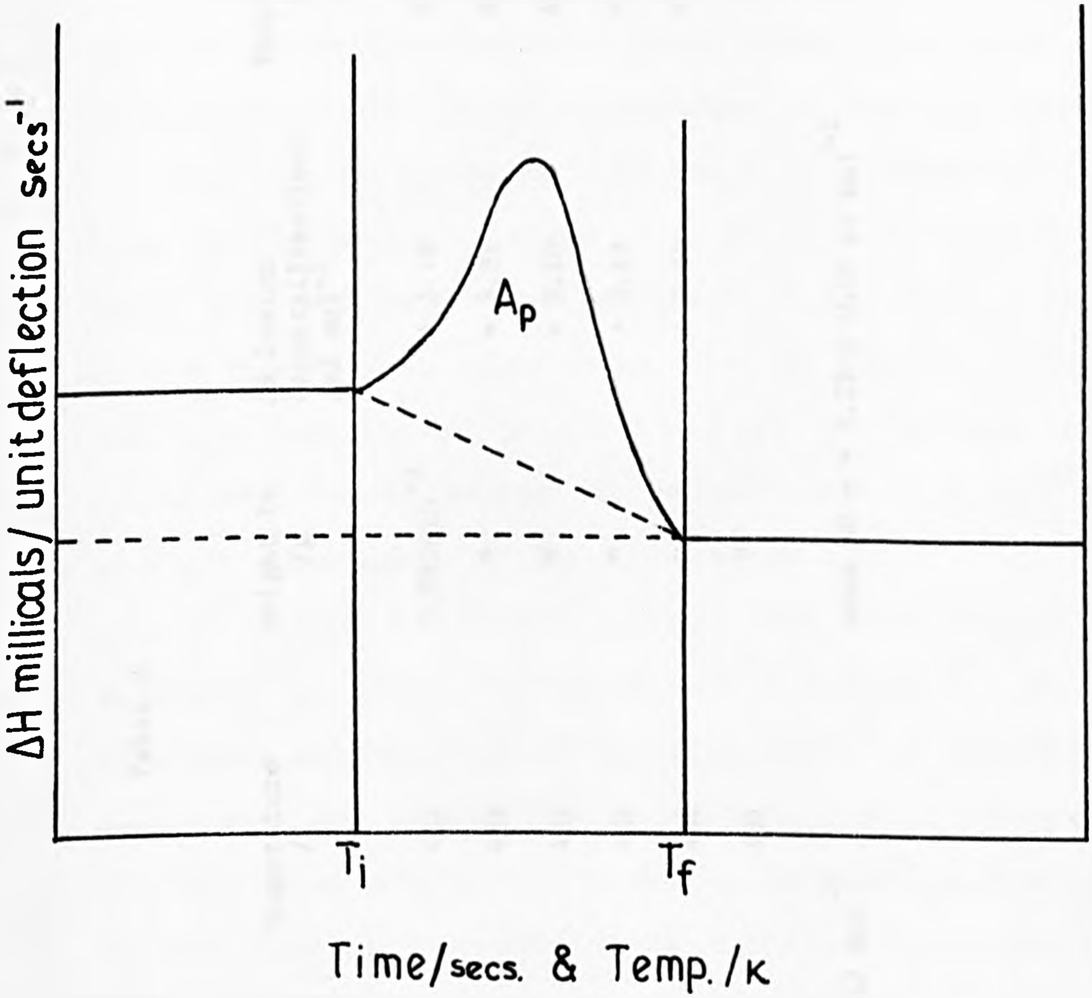
Thermograms were recorded for about six samples of any one compound and enthalpies of reaction were calculated from the formula

$$\Delta H = \frac{A_p \times R}{A_r \times 1000 \times \text{No of moles}} \times 60 \times 4.184 \ \text{kJ mol}^{-1}$$

where A_p is the area of transition: the area of the thermogram bounded by the peak and an interpolated scanning baseline (see Fig.11); A_r is the area of a rectangle, an area of half the chart paper width, traversed in 1 minute at the particular chart speed chosen; and R is the range setting of the instrument.

Areas were determined using a planimeter (Allbritt).

FIG 11



Determination of enthalpy of D.S.C. plot

Table 2

Weight In /g	ΔH Fusion (melting) /kJ mol^{-1}	Temperature /K	Weight In /g	ΔH Fusion (crystallisation) /kJ mol^{-1}	Temperature /K
6.607×10^{-3}	+ 3.09	431	5.993×10^{-3}	+ 3.18	424
"	+ 3.34	431	"	+ 3.31	424
"	+ 3.35	431	"	+ 3.10	424
"	+ 3.19	431	"	+ 3.19	424
"	+ 3.10	431	"	+ 3.34	424
"	+ 3.09	431	"		

mean ΔH = + 3.17 ± 0.06 kJ mol^{-1}

mean ΔH = + 3.22 ± 0.04 kJ mol^{-1}

Chapter 3

Enthalpy of formation of ammonium chloropalladite $(NH_4)_2PdCl_4$

There is no value available for the enthalpy of formation of ammonium tetrachloropalladite, although enthalpies of formation of the tetrachloropalladite ion and the ammonium ion, have been determined.

Goldberg and Hepler, in their review,(36) recommended a best value for the enthalpy of formation of the tetrachloropalladite ion, $PdCl_4^{2-}$, at infinite dilution, of -523.0 ± 2.1 kJ mol^{-1}. Recalculation of this figure, using a more recent value for $\Delta H_f^o(Cl^-)$, given in the C.A.T.C.H. tables gives -522.0 ± 2.1 kJ mol^{-1}. The value of -523.0 ± 2.1 kJ mol^{-1} was derived from the work of Templeton et al.(37) based on e.m.f. measurements for the cell reaction

$$Pd(c) + 4Cl^-(aq) + 2H^+(aq) \rightarrow PdCl_4^{2-}(aq) + H_2(g)$$

An older value, calculated from the work of Thomsen,(38) was rejected by Goldberg and Hepler, as the entropies of $Pd^{2+}(aq)$ and $Pd(OH)_2(c)$ appear to be less reasonable when calculated from this value.

A further value of -473 kJ mol^{-1}, established by Izatt et.al.(39) was also rejected, the stoichiometry of the reaction studied being somewhat uncertain.

$$Pd^{2+}(aq) + 3I^-(aq) \rightarrow Pd(s) + I_3^-(aq)$$

The purpose of this investigation was to obtain a value for the enthalpy of formation of crystalline ammonium tetrachloropalladite.

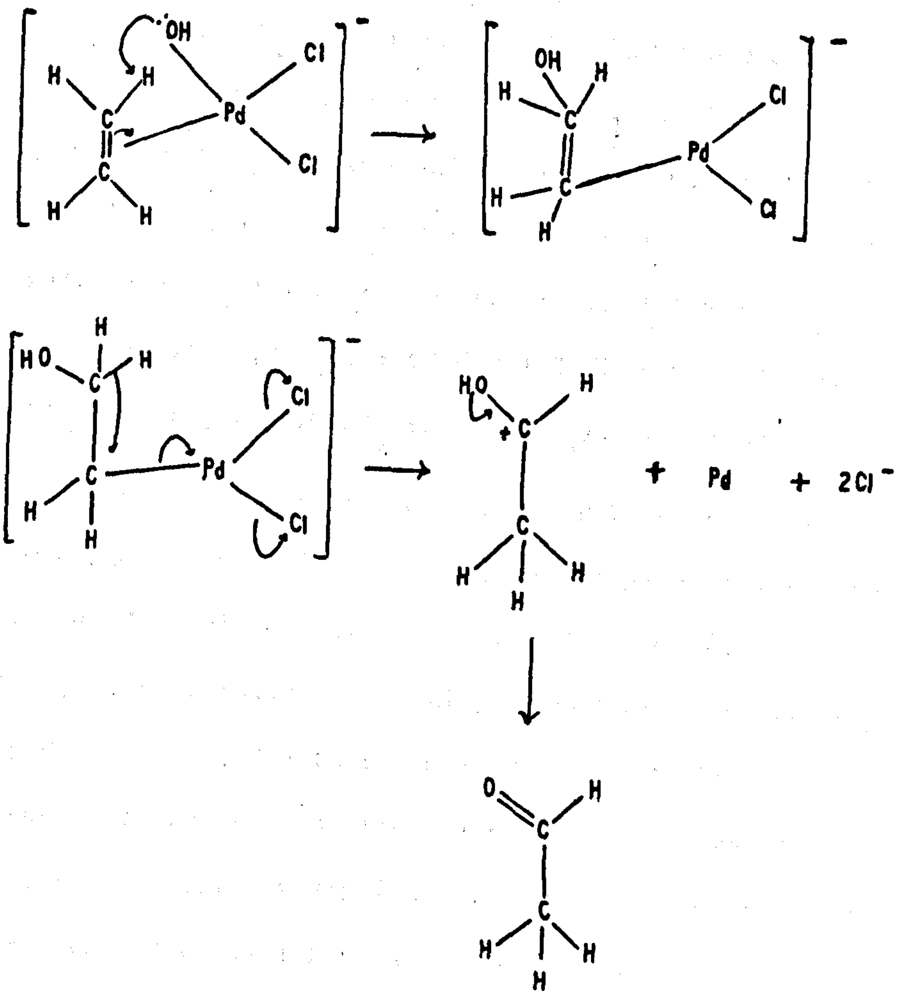
This salt has the advantage of being less hygroscopic than the alkali metal salts, allowing for easier handling. Conversely, it has a disadvantage in being less soluble in organic solvents.

Ammonium tetrachloropalladite is rapidly and quantitatively reduced(40) by ethylene, in the presence of water, to metallic palladium and acetaldehyde. This forms the central part of the so-called Wacker process.(41) A stepwise mechanism has been proposed for the reaction.(42)

$$PdCl_4^{2-} + CH_2{=}CH_2 \rightleftarrows [Pd(CH_2CH_2)Cl_3]^- + Cl^-$$

$$[Pd(CH_2CH_2)Cl_3]^- + H_2O \rightleftarrows [Pd(CH_2CH_2)(H_2O)Cl_2] + Cl^-$$

$$[Pd(CH_2CH_2)(H_2O)Cl_2] + H_2O \rightleftarrows [Pd(CH_2CH_2)(OH)Cl_2]^- + H_3O^+$$



The use of gaseous ethylene as the reductant introduces certain experimental difficulties,as the LKB 8700 calorimeter is not designed for the introduction of a gaseous reactant. Preliminary experiments were carried out with other liquid olefins, but the reactions were too slow to be studied satisfactorily in the calorimeter. These trials were abandoned in favour of using ethylene in a slightly modified calorimeter (see later).

The following reaction scheme was devised.

$$(NH_4)_2PdCl_4(c) + C_2H_4(g) + [8201H_2O + x\,C_2H_4](\ell) \rightarrow$$
$$Pd(s) + [2NH_4Cl + CH_3CHO + 2HCl + 8200H_2O + x\,C_2H_4](\ell), \quad (1)$$
$$[HCl + 111H_2O](\ell) + [3489H_2O + 0.5\,x\,C_2H_4](\ell) \rightarrow$$
$$[HCl + 3600H_2O + 0.5\,x\,C_2H_4](\ell) \quad (2)$$
$$[CH_3CHO + 1000H_2O](\ell) + 2[HCl + 3600H_2O + 0.5\,x\,C_2H_4](\ell) \rightarrow$$
$$[CH_3CHO + 2HCl + 8200H_2O + x\,C_2H_4](\ell) \quad (3)$$
$$(NH_4Cl) + [0.5\,CH_3CHO + HCl + 4100H_2O + 0.5\,x\,C_2H_4](\ell) \rightarrow$$
$$[NH_4Cl + 0.5\,CH_3CHO + HCl + 4100H_2O + 0.5\,x\,C_2H_4](\ell) \quad (4)$$
$$Pd(s) + [2NH_4Cl + CH_3CHO + 2HCl + 8200H_2O + x\,C_2H_4](\ell) \rightarrow$$
$$Pd(s) + [2NH_4Cl + CH_3CHO + 2HCl + 8200H_2O + x\,C_2H_4](\ell) \quad (5)$$
$$(NH_4)_2PdCl_4(c) + 1850H_2O(\ell) \rightarrow [(NH_4)_2PdCl_4 + 1850H_2O](\ell) \quad (6)$$

The quantity $x\,C_2H_4$ represents the unknown mole fraction of ethylene dissolved in the solutions by virtue of the constant stream of gaseous ethylene through the system. Reaction (5) refers to the wetting of finely-divided palladium metal produced in reaction (1).

Unfortunately, due to the need to use enthalpies of formation of reactants and products in standard reference states, the reactions given above were not strictly applicable. Modified reactions were needed to utilize literature data for various compounds.

The following arguments indicate why these particular concentrations were adopted.

$(NH_4)_2PdCl_4(c)$ The weight chosen (∿ 0.05g, 1.7×10^{-4} mol) was a compromise between the need to maximise the temperature rise and yet restrain the reaction time to an acceptable period of not more than five minutes. This weight of ammonium tetrachloropalladite and the volume of water (25 ml, 1.3g mol), dictated by the use of the selected reaction vessel, lead to the final concentrations of reaction (1).

$[HCl + 111\ H_2O](\ell)$ The ratio of volumes of ampoule (∿ 1 ml) and reaction vessel (25 ml) made it convenient to choose the concentration $[HCl + 111\ H_2O]$, for measurements of the enthalpy of solution, reaction (2). The enthalpy of formation of $[HCl + 111\ H_2O]$ is well established.(43)

$[CH_3CHO + 1000\ H_2O](\ell)$ Values for the enthalpies of formation of acetaldehyde in the gaseous and liquid states(44) and in the state, $[CH_3CHO + 1000\ H_2O](\ell)$, are available in the literature. In view of the experimental difficulties in handling a liquid with a high vapour pressure (b.p.293 K) it was decided to use the state $[CH_3CHO + 1000\ H_2O](\ell)$ as the reference. However, with a maximum ampoule capacity of 1 ml and a reaction vessel volume of 25 ml, the most concentrated final solution which could be achieved in a single stage dilution was that indicated in reaction (3a).

$$[CH_3CHO + 1000H_2O](\ell) + [2HCl + 22{,}000H_2O + x\ C_2H_4](\ell) \rightarrow [CH_3CHO + 2HCl + 23{,}000H_2O + x\ C_2H_4](\ell) \qquad (3a)$$

$$[CH_3CHO + 1000H_2O](\ell) + [CH_3CHO + 2HCl + 23{,}000H_2O + x\ C_2H_4](\ell) \rightarrow 2[CH_3CHO + HCl + 12{,}000H_2O + 0.5\ x\ C_2H_4](\ell) \qquad (3b)$$

$$[CH_3CHO + HCl + 12{,}000H_2O + 0.5\ x\ (C_2H_4)](\ell) + [HCl + 11{,}000H_2O + 0.5\,x\,C_2H_4](\ell) \rightarrow [CH_3CHO + 2HCl + 23{,}000H_2O + x\ C_2H_4](\ell) \qquad (3c)$$

The enthalpy of this reaction (3a) was measured as $\Delta H(3a) = -(1.56 \pm 0.24)\ kJ\ mol^{-1}$. The enthalpy of the dilution, reaction (3b), was also measured as $\Delta H(3b) = -(1.45 \pm 0.15)\ kJ\ mol^{-1}$, so that the enthalpy of the dilution reaction (3c) is $\frac{1}{2}\{(1.56 \pm 0.24) + (1.45 \pm 0.15)\} = -(0.05 \pm 0.14)\ kJ\ mol^{-1}$. The enthalpy of dilution from the state $[CH_3CHO + 2HCl + 8200H_2O](\ell)$ to $[CH_3CHO + 2HCl + 12{,}000H_2O](\ell)$ is assumed to be of similar magnitude, $-0.05\ kJ\ mol^{-1}$, so that we estimate the enthalpy of reaction (3) as $-(1.46 \pm 0.24)\ kJ\ mol^{-1}$.

The enthalpy of solution of $(NH_4)_2PdCl_4(c)$ in water, reaction 6, was also measured.

3.1. Experimental

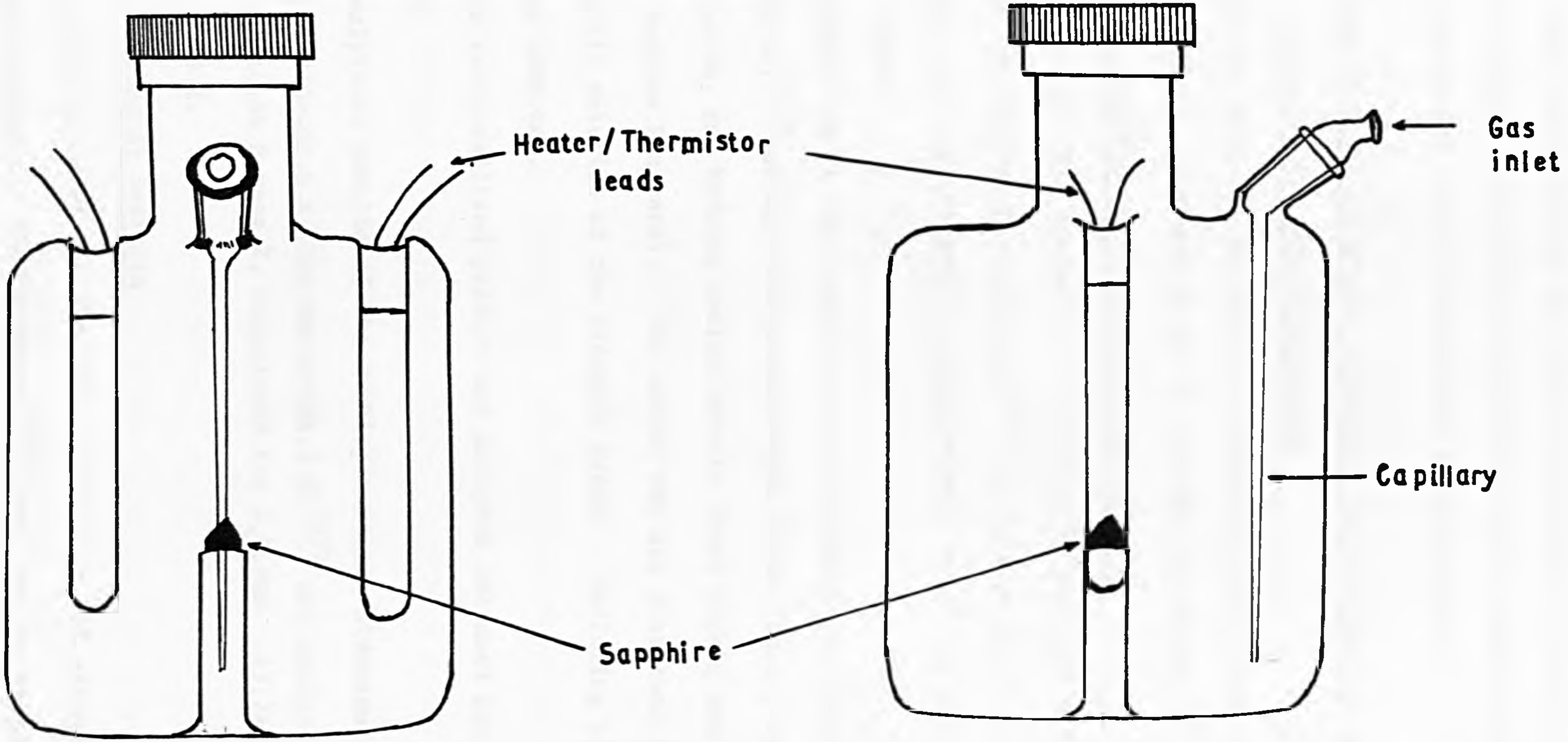
A glass calorimeter of 25 ml capacity was produced, similar to the conventional design, except for the provision of a B5 socket and a B5 tail-cone. To the tail of this cone, was sealed a capillary of sufficient length to almost reach the calorimeter bottom (see Fig.1.). The vessel was also provided with a sapphire tipped pin and two pockets to receive a thermistor and a calibration heater.

Before entering the reaction vessel, via the capillary tube, the ethylene gas passed through a spiral, made from ⅛" internal diameter copper tube, which was suspended inside the calorimeter can. This assured that the temperature of the ethylene and that of the contents of the reaction vessel were the same. In order to minimize the thermal effects of evaporation, caused by a stream of dry gas through the liquid in the reaction vessel, the gaseous ethylene was saturated with water vapour. This saturator consisted simply of a two-necked flask immersed in the thermostat. The outlet of the flask was connected to the copper spiral and the inlet to the gas supply. This inlet tube entered the calorimeter system through a hole, in the calorimeter lid, which is normally used for ingress of a cooling gas, or to evacuate the system. The pressure of the ethylene gas was set to approximately 7 psi, giving a flow rate of 10 ml/min, which was checked before and after each experiment.

To ascertain the effect of any slight variations of flow rate on the performance of the calorimeter system, electrical calibrations were made: (a) with a constant flow rate of 10 ml/min and (b) with a flow rate which was allowed to vary during the calibration between the limits 5-25 ml/min. For constant flow rate the calibration constant was 2980 ± 6j. ohm^{-1} whilst for a variable flow rate the constant was 2980 ± 12j. ohm^{-1}.

FIG. 1

MODIFIED L.K.B. CALORIMETER VESSEL



It was concluded that any small variations in the flow rate of the ethylene gas would have an effect which was acceptably negligible on the reproducibility of the measured reaction heats.

3.2. Preparation of analytical compounds and analysis of reaction products

3.2.(1) Analysis with dimethylglyoxime

This was used for one series of analyses only, that of ammonium chloropalladite. The method was by standard procedure.(45)

3.2.(2) Preparation of 2-thiophenetrans-aldoxime

The use of this reagent is thought to be preferable to most other analytical procedures for palladium(46) on account of stability, ease of filtration, and low tendency to supersaturation of the palladium complex of this ligand.

Preparation of the reagent was by the method of Tandon and Bhattacharya,(47) using 2-thiophenaldehyde (Koch Light), hydroxylamine hydrochloride, and hydrous sodium acetate (both Hopkin and Williams, General Purpose Reagents). The latter two are dissolved in water, and an ethanolic solution of the aldehyde added. Refluxing produces the necessary compound.

The recrystallised product was analysed and used for all subsequent analyses.

Analytical results of the 2-thiophenetrans-aldoxime gave melting point of 402.0-403.0 K (lit 406.0-406.5 K)(47) and analysis of: 47.33 C; 4.01 H and 10.94 N mass %, calculated for C_5H_5NOS 47.74 C; 3.96 H; 11.02 N mass %.

3.2.(3) Method of analysis

A 2% solution of the aldoxime was made in 95% ethanol, to give the complexing reagent. The technique(46) used, was to extract the palladium from the complex by boiling with aqua regia, and following conversion to the hexachloropalladite, by use of concentrated hydrochloric acid, the solution was diluted and the aldoxime added. After standing overnight the complex was filtered.

3.2.(4) Analysis of reaction products

The quantitative yield of the reaction was checked as follows.

A weighed sample of ammonium chloropalladite was dissolved in water and ethylene bubbled through the resultant solution for 5 min., when palladium was precipitated. After filtration through a sinter, the precipitate was dissolved in aqua regia, treated with conc. HCl, and the palladium reprecipitated as the aldoxime complex.

The result of two experiments indicated palladium yields of 100.9 mass % and 100.1 mass % respectively.

3.3. Compounds

Ammonium chloropalladite (Johnson Matthey) was analysed for palladium content by precipitation as the dimethylglyoxime complex; found 37.41 mass % Pd; calculated for $(NH_4)_2PdCl_4$, 37.43 mass % Pd.

A 0.5M solution of HCl was made by dilution of a 1M HCl standard (C.V.S. B.D.H. Ltd). The molarity of the prepared solution was standardised against borax, $Na_2BO_4 \cdot 10H_2O$ (Analar), using methyl-red as indicator.

The average of six titrations gave a value of 0.5022M ± 0.0003. Acetaldehyde (B.D.H. Laboratory Reagent), distilled at 295 K and 756 mm Hg, was used to make a solution in water. An Agla Micrometer (Wellcome Reagents Ltd.) was used to measure the required volume of acetaldehyde (0.3042 ml) into a 100 ml of water. At 289 K, the temperature at which this dilution was carried out, these volumes yield a solution of concentration (CH_3CHO + 1000 H_2O).

Palladium metal was prepared by precipitation with ethylene from ammonium chloropalladite. The product was dried in an oven for several days and stored over phosphorus pentoxide.

Ammonium chloride (Hopkin and William, Technical Grade) was dried at 378 K and stored over calcium chloride.

Ethylene (B.D.H. Laboratory Reagent) was used.

3.4. Procedures

A series of seven ampoules for each product and reactant were made, containing the following:

reaction (1)	$(NH_4)_2PdCl_4$, 0.05g, $1.7\text{x}10^{-4}$ mol.
reaction (2)	HCl, 0.685 ml of a 0.5022M solution, $3.4\text{x}10^{-4}$ mol HCl
reaction (3a)/(3b)	CH_3CHO, 1 ml of the solution ($1CH_3CHO{:}1000H_2O$), $0.6\text{x}10^{-4}$ mol CH_3CHO
reaction (4)	NH_4Cl, 0.018g, $3.4\text{x}10^{-4}$ mol.
reaction (5)	Pd metal, 0.018g, $1.7\text{x}10^{-4}$ mol.
reaction (6)	$(NH_4)_2PdCl_4$, 0.235g, $2.2\text{x}10^{-3}$ mol.

The number of moles required, for reactions (2) and (3), were estimated from the weight of solution in the ampoules, and densities, drawn from available data.(48, 49)

For reactions, (1), (4), (5) and (6), the calorimeter was charged with 25 ml. of water, plus the relevant solutes. The procedure for reactions (2) and (3) was similar, except that after filling, 2.7 ml of water were extracted, so that after addition of the acid or acetaldehyde solutions, the total volume of solution would be 25 ml.

The relevant ampoule was fitted to the stirrer and the calorimeter assembled to the gas supply system (with the exception of reaction (6), where no ethylene was bubbled through the water).

Reactions were initiated at 298.15 K for the endothermic reactions (4) and (6), and at a temperature, such that the final temperature was 298.15 K, for the exothermic reactions (1), (2), (3) and (5).

In the reactions (1), (4), (5) and (6) the glass ampoules were only partially filled with solid and the remaining space was occupied by air. A correction must be made for the thermal effect of releasing this volume of air into the aqueous solutions. In order to estimate this correction, a series of five air-filled ampoules were also broken into the final solution of reaction (6), and the heat effect was measured. A correction was then applied to the measured heat changes of reactions (1), (4), (5) and (6).

The computer programme was used to estimate the heat change for reaction (1), and Dickenson's extrapolation was used for the remaining reactions which were completed in a shorter time.

The results are shown in Tables 1 and 2.

3.5. Discussion

The enthalpy change, $\Delta H(7)$, of reaction (7)

$$(NH_4)_2PdCl_4(c) + CH_2CH_2(g) + H_2O(\ell) \rightarrow$$
$$Pd(s) + 2NH_4Cl(aq.) + CH_3CHO(aq.) + 2HCl(aq.) \qquad (7)$$

may be calculated from the relationship

$$\Delta H(7) = \Delta H(1) - 2\Delta H(2) - \Delta H(3) - 2\Delta H(4) - \Delta H(5)$$

as $\Delta H(7) = -(96.71 \pm 1.05)\ \text{kJ mol}^{-1}$

The enthalpy of formation of crystalline ammonium tetrachloropalladite can be obtained from the relationship

$$\Delta H_f^o[(NH_4)_2PdCl_4,c] = -\Delta H(7) + 2\Delta H_f^o(NH_4Cl,c) + 2\Delta H_f^o(HCl\ \text{in}\ 111H_2O,\ell)$$
$$+ \Delta H_f^o(CH_3CHO\ \text{in}\ 1000H_2O,\ \ell) - \Delta H_f^o(H_2O,\ \ell) - \Delta H_f^o(CH_2CH_2,\ g)$$

Using the values

$\Delta H_f^o(NH_4Cl,C) = -314.43\ \text{kJ mol}^{-1}$ 50

$\Delta H_f^o(HCl\ \text{in}\ 111H_2O,\ell) = -210.66\ \text{kJ mol}^{-1}$ 43

$\Delta H_f^o(CH_3CHO\ \text{in}\ 1000H_2O,\ell) = -165.893\ \text{kJ mol}^{-1}$ 44

$\Delta H_f^o(H_2O,\ell) = -285.830\ \text{kJ mol}^{-1}$ 51

$\Delta H_f^o(CH_2CH_2,g) = -52.26\ \text{kJ mol}^{-1}$ 52

Table 1

Enthalpies of solution of $(NH_4)_2PdCl_4$(c) in $[8201H_2O + xC_2H_4]$(ℓ) reaction (1)

$M(NH_4)_2PdCl_4$/g	0.046575	0.048499	0.042716	0.046758	0.052006
$\Delta H(1)$/kJ mol^{-1}	-71.546	-70.925	-71.518	-71.374	-68.814

$\langle\Delta H(1)\rangle = -(70.84 \pm 0.99)$ kJ mol^{-1}

Enthalpies of solution of HCl in 0.5022N solution in $[3489H_2O + xC_2H_4]$(ℓ), reaction (2)

M HCl /g	0.013732	0.013648	0.013692	0.013772	0.013948
$\Delta H(2)$/kJ mol^{-1}	-1.025	-1.001	-1.018	-0.994	-1.051

$\langle\Delta H(2)\rangle = -(1.02 \pm 0.02)$ kJ mol^{-1}

Enthalpies of solution of $CH_3CHO(1:1000H_2O)$(ℓ) in $[2HCl + 22{,}000H_2O + xC_2H_4]$(ℓ), reaction (3a)

M CH_3CHO/g	0.002383	0.002590	0.002562	0.002482	0.002594
$\Delta H(3a)$/kJ mol^{-1}	-1.67	-1.64	-1.87	-1.15	-1.46

$\langle\Delta H(3a)\rangle = -(1.56 \pm 0.24)$ kJ mol^{-1}

Enthalpies of solution of $CH_3CHO(1:1000H_2O)$(ℓ) in $[2HCl + CH_3CHO + 23{,}000H_2O + xC_2H_4]$(ℓ), reaction (3b)

MCH_3CHO/g	0.002624	0.002621	0.002617	0.002612	0.002651
$\Delta H(3b)$/kJ mol^{-1}	-1.48	-1.70	-1.31	-1.30	-1.48

$\langle\Delta H(3B)\rangle = -(1.45 \pm 0.15)$ kJ mol^{-1}

Enthalpies of solution of NH_4Cl(c) in $[2HCl + 0.5CH_3CHO + 4{,}100H_2O + xC_2H_4]$(ℓ), reaction (4)

M NH_4Cl /g	0.019136	0.016690	0.022535	0.018319	0.021132
$\Delta H(4)$/kJ mol^{-1}	+14.790	+14.800	+14.831	+14.920	+14.820

$\langle\Delta H(4)\rangle = +(14.83 \pm 0.\overset{05}{\cancel{21}})$ kJ mol^{-1}

Table 2

Enthalpies of solution of

Pd(s) in $[2NH_4Cl + 2HCl + 0.5CH_3CHO + 8200H_2O + xC_2H_4](\ell)$ reaction (5)

MPd/g	0.018628	0.017957	0.017927	0.019294	0.018212
$\Delta H(5)/kJ\ mol^{-1}$	-0.498	-0.189	-0.223	-0.343	-0.191

$\langle\Delta H(5)\rangle = -(0.29 \pm 0.12)\ kJ\ mol^{-1}$

Enthalpy of solution of $(NH_4)_2PdCl_4(c) + [1850H_2O](\ell)$, reaction (6)

$M(NH_4)_2PdCl_4/g$	0.235507	0.230958	0.236719	0.234770	0.242206
$\Delta H(6)/kJ\ mol^{-1}$	+48.64	+48.37	+48.47	+48.01	+49.21

$\langle\Delta H(6)\rangle = +(48.54 \pm 0.34)\ kJ\ mol^{-1}$

leads to the value

$$\Delta H_f^o[(NH_4)_2PdCl_4,c] = -(841 \pm 1.7)\ kJ\ mol^{-1}$$

Incorporating the value $\Delta H(6) = +(48.54 \pm 0.34)\ kJ\ mol^{-1}$ for the enthalpy of solution of $(NH_4)_2PdCl_4(c)$ leads to the value

$$\Delta H_f^o[(NH_4)_2PdCl_4\ in\ 1850H_2O] = -(792.5 \pm 2.0)\ kJ\ mol^{-1}$$

It was not possible to measure the enthalpy of solution of $(NH_4)_2PdCl_4$ at dilutions greater than this, and so extrapolate to a value at infinite solution, because at greater dilution the tetrachloropalladite ion dissociates.

We assume that the enthalpy of dilution for the state $[(NH_4)_2PdCl_4\ in\ 1850\ H_2O]$ to $[(NH_4)_2PdCl_4\ in\ \infty\ H_2O]$ is negligible and therefore propose the value

$$\Delta H_f^o[(NH_4)_2PdCl_4,aq] = -(792.5 \pm 2.0)\ kJ\ mol^{-1}.$$

If the enthalpy of formation of the *ammonium* ion,(53) $\Delta H_f^o(NH_4^+,aq) = -(133.13 \pm 0.19)\ kJ\ mol^{-1}$, is incorporated into the above value, the enthalpy of formation of the tetrachloropalladite ion itself, is derived as

$$\Delta H_f^o(PdCl_4^{2-},aq) = -(526.3 \pm 2.2)\ kJ\ mol^{-1}$$

This value is in agreement with that established as $-(522.0 \pm 2.1)\ kJ\ mol^{-1}$, derived from the value selected by Goldberg and Hepler which was referred to earlier. Their recommendation would appear to be well founded.

Chapter 4

Enthalpies of formation of the complexes trans-Pd(EEt$_2$)$_2$Cl$_2$ where E is S, Se or Te.

According to the classification of Chatt,(54) the palladium(II) ion fits into a class "b"(54) or soft acid(55) category, therefore preferring "soft" or more polarizable bases, i.e. elements of higher atomic number in any particular group. Consequently, ligands containing sulphur, selenium and tellurium atoms should form more stable complexes than those containing oxygen; the exact order of stability depending upon the nature of other ligands on the metal.

No ether complexes have been reported but an extensive series of complexes, formed by dialkyl and diaryl sulphides, selenides and tellurides, is known. The series for the telluride has, however, been less well studied. Unlike platinum analogues, the palladium complexes are formed in only one isomeric form, the lability being sufficient to yield only the more stable isomer,(56) in this case the trans.

The purpose of this part of the investigation was to gain information about the palladium-sulphur, selenium and tellurium bonds.

Enthalpy changes were measured for the reactions (1) to (5), where E = S, Se or Te, and the values obtained, used to estimate the enthalpies of formation for the various complexes, and thence the dissociation energies for the Pd-S, Pd-Se, and Pd-Te bonds.

$$[(NH_4)_2PdCl_4 + 760\ CH_3COCH_3 + 820\ H_2O](\ell) + (2+x)EEt_2(\ell) \rightarrow$$
$$[2NH_4Cl + trans(EEt_2)_2Pd_2Cl_2 + xEEt_2 + 760\ CH_3COCH_3 + 820H_2O](\ell) \quad (1)$$

$$xEEt_2(\ell) + [2NH_4Cl + trans(EEt_2)_2PdCl_2 + 760\ CH_3COCH_3 + 820H_2O](\ell) \rightarrow$$
$$[2NH_4Cl + trans(EEt_2)_2PdCl_2 + xEEt_2 + 760\ CH_3COCH_3 + 820H_2O](\ell) \quad (2)$$

$$\text{trans-}(E\text{Et}_2)_2\text{PdCl}_2(\text{c}) + [2\text{NH}_4\text{Cl} + 760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}](\ell) \rightarrow$$
$$[2\text{NH}_4\text{Cl} + \text{trans-}(E\text{Et}_2)_2\text{PdCl}_2 + 760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}](\ell) \qquad (3)$$

$$2\text{NH}_4\text{Cl}(\text{c}) + [760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}](\ell) \rightarrow$$
$$[2\text{NH}_4\text{Cl} + 760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}](\ell) \qquad (4)$$

$$(\text{NH}_4)_2\text{PdCl}_4(\text{c}) + [760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}[(\ell) \rightarrow$$
$$[(\text{NH}_4)_2\text{PdCl}_4 + 760\ \text{CH}_3\text{COCH}_3 + 820\text{H}_2\text{O}](\ell) \qquad (5)$$

4.1. Experimental

The complexes trans-$(E\text{Et}_2)_2\text{PdCl}_2$ were prepared by the addition of three moles of the required ligand to one mole of sodium or ammonium tetrachloropalladite, well stirred in water, as described previously.(57) The compounds were recrystallised from acetone/petroleum ether for E = S,(58) and methyl alcohol for E = Se(57) and E = Te.(59)

Analytical results are given in Table 1, palladium content was determined by 2-thiophene trans-aldoxime and carbon and hydrogen by use of a Perkin-Elmer micro analyser.

Table 1

	M.P./K		FOUND			CALCULATED		
COMPOUND	FOUND	LIT.	C %	H %	Pd %	C %	H %	Pd %
$(\text{SEt}_2)_2\text{PdCl}_2$	353	353(58)	26.7	5.51	29.75	26.9	5.64	29.75
$(\text{SeEt}_2)_2\text{PdCl}_2$	318	318(57)	21.5	4.37	23.55	21.3	4.46	23.57
$(\text{TeEt}_2)_2\text{PdCl}_2$	371	372(59)	17.7	3.53	19.41	17.5	3.67	19.39

Ammonium chloropalladite (Johnson Matthey) was used throughout the thermochemical reactions (see chapter 3 for analysis). Diethyl sulphide (Koch Light), diethylselenide and diethyltelluride (both Strem Chemicals) were used for the respective preparations and reactions, after purification by distillation through a six-inch fenske column. Boiling points are given in Table 2.

Table 2

B.P./K

COMPOUND	FOUND	LIT.	pressure/torr
SEt_2	362-363	365.3 (76)	729
$SeEt_2$	381.7	382 (60)	742
$TeEt_2$	409-410	410-411 (60)	745

A small quantity of diethylselenide, b.p. 378 K, was prepared from selenium, in sodium/liquid ammonia, using diethylsulphate as the alkylating agent.(60)

Due to the oxygen sensitivity of the diethyl telluride, the distillation was carried out under a nitrogen atmosphere, and the sample stored in sealed ampoules until used.

The solvent used in the reactions was an acetone-water (3:1) by volume mixture. Acetone (B.D.H. Laboratory Reagents) was used for the work concerned with the diethylsulphide, diethyl selenide complexes. In work connected with the diethyl telluride complexes, commercial grade acetone (Hopkin and Williams) was purified by use of potassium permanganate,(61) before use.

The enthalpies of the reactions (1) to (3) were measured by use of the 100 ml vessel, except that for measurement of the enthalpy of solution, of $(TeEt_2)_2PdCl_2$, the 25 ml vessel was used. This was necessitated by there being available only a small quantity of this complex.

The corrected resistance changes were calculated by Dickenson's method, except for reaction (5), and also reactions (1) and (3) for the diethyl telluride complex; these latter three being estimated by the computer method, mentioned previously.

The results obtained are shown in Tables 3, 4, and 5.

4.2. Discussion

The enthalpy change, $\Delta H(6)$, of reaction (6)

$$(NH_4)_2PdCl_4(c) + 2EEt_2(\ell) \rightarrow$$
$$\text{trans-}(EEt_2)_2PdCl_2(c) + 2NH_4Cl(c) \qquad (6)$$

may be calculated from the relationship

$$\Delta H(6) = [\Delta H(1) - x\Delta H(2) - \Delta H(3) - 2\Delta H(4) + \Delta H(5)]$$

as $<\Delta H(6)> = -(112.78 \pm 0.26)$ kJ mol^{-1}, where E = S

$<\Delta H(6)> = -(124.38 \pm 0.70)$ kJ mol^{-1}, where E = Se

$<$ H(6)$> = -(175.49 \pm 4.12)$ kJ mol^{-1}, where E = Te

The enthalpy of formation of trans-$(EEt_2)_2PdCl_2(c)$ can be calculated from the relationship

$$\Delta H^o_f[(EEt_2)_2PdCl_2,c] = \Delta H(6) - 2\Delta H^o_f(NH_4Cl,c) +$$
$$\Delta H^o_f[(NH_4)_2PdCl_4,c] + 2\Delta H^o_f[(EEt_2)_2\ell].$$

The values

$\Delta H^o_f(NH_4Cl,c) = -(314.43 \pm 0.05)$ kJ mol^{-1} 62

$\Delta H^o_f[(NH_4)_2PdCl_4,c) = -(841.0 \pm 1.7)$ kJ mol^{-1} 63

$\Delta H^o_f(SEt_2,\ell) = -(119.07 \pm 0.79)$ kJ mol^{-1} 64

$\Delta H^o_f(SeEt_2,\ell) = -(96.2 \pm 3.3)$ kJ mol^{-1} 65

are available, but no value for $\Delta H^o_f(TeEt_2,\ell)$ has been reported. An estimated value of -100 ± 20 kJ mol^{-1} is adopted.

Using these values, yields the following values for the enthalpies of formation of the complexes

$$\Delta H^o_f[(SEt_2)_2PdCl_2,c] = -(563.1 \pm 2.1) \text{ kJ mol}^{-1}$$
$$\Delta H^o_f[(SeEt_2)_2PdCl_2,c] = -(528.9 \pm 3.8) \text{ kJ mol}^{-1}$$
$$\Delta H^o_f[(TeEt_2)_2PdCl_2,c] = -(587.6 \pm 20.5) \text{ kJ mol}^{-1}$$

The enthalpy changes, $\Delta H(7)$, $\Delta H(8)$ and $\Delta H(9)$, for the reactions (7), (8) and (9)

$$\text{trans-}(SEt_2)_2PdCl_2(c) = PdCl_2(c) + 2SEt_2(g) \qquad (7)$$

Table 3

Enthalpies of solution of $SEt_2(\ell)$, $SeEt_2(\ell)$ and $TeEt_2(\ell)$ in $[(NH_4)_2PdCl_4 + 760CH_3COCH_3 + 820H_2O](\ell)$, reaction (1)

$M(NH_4)_2PdCl_4$/g	0.484524	0.464506	0.511634	0.485411	0.470065	0.470231
$MSEt_2$/g	0.371562	0.320333	0.373536	0.352702	0.325879	0.309285
$\Delta H(1)$/kJ mol^{-1}	68.41	69.25	69.20	69.14	69.82	69.53
$[\Delta H(1)-x\Delta H(2)]$/kJ mol^{-1}	-70.36	-70.12	-70.62	-70.53	-70.75	-69.97

$\langle[\Delta H(1)-x\Delta H(2)]\rangle = -(70.39 \pm 0.22)$ kJ mol^{-1}

$M(NH_4)_2PdCl_4$/g	0.500111	0.494457	0.499559	0.495430	0.492883	0.483007
$MSeEt_2$/g	0.654358	0.650303	0.666296	0.627548	0.698910	0.671694
$\Delta H(1)$/ kJ mol^{-1}	73.12	70.85	72.05	72.09	70.78	71.24
$[\Delta H(1)-x\Delta H(2)]$/kJ mol^{-1}	-78.79	-76.54	-78.02	-77.01	-78.08	-78.12

$\langle[\Delta H(1)-x\Delta H(2)]\rangle = -(77.58 \pm 0.68)$ kJ mol^{-1}

$M(NH_4)_2PdCl_4$/g	0.501194	0.498917	0.498825	0.499172	0.499048
$MTeEt_2$/g	0.879059	0.876264	0.849430	0.854059	0.837899
$\Delta H(1)$/kJ mol^{-1}	118.16	117.37	115.56	108.19	111.47
$[\Delta H(1)-x\Delta H(2)]$/kJ mol^{-1}	-124.41	-123.64	-121.07	-113.82	-116.66

$\langle[\Delta H(1)-x\Delta H(2)]\rangle = -(119.92 \pm 4.08)$ kJ mol^{-1}

Table 4

Enthalpies of solution of $SEt_2(\ell)$, $SeEt_2(\ell)$ and $TeEt_2(\ell)$ in $[2NH_4Cl + trans\text{-}(EEt_2)_2PdCl_2 + 760CH_3COCH_3 + 820H_2O](\ell)$, reaction (2)

$MSEt_2$ /g	0.146795	0.139666	0.137377	0.142466	0.139810	0.135445
ΔH/kJ mol^{-1}	+4.32	+4.13	+4.27	+4.20	+4.20	+4.27

$\langle \Delta H(2) \rangle = +(4.23 \pm 0.06)$ kJ mol^{-1}

$MSeEt_2$ /g	0.212226	0.202427	0.203206	0.230689	0.245041	0.309000
ΔH/kJ mol^{-1}	+7.60	+7.22	+7.63	+7.55	+7.78	+8.05

$\langle \Delta H(2) \rangle = +(7.64 \pm 0.70)$ kJ mol^{-1}

$MTeEt_2$ /g	0.339169	0.345692	0.301514	0.340388	0.315893
ΔH/kJ mol^{-1}	+9.58	+10.29	+9.64	+9.67	+8.07

$\langle \Delta H(2) \rangle = +(9.45 \pm 0.74)$ kJ mol^{-1}

Enthalpies of solution of $trans\text{-}(SEt_2)_2PdCl_2(c)$, or $trans\text{-}(SeEt_2)_2PdCl_2(c)$, or $trans\text{-}(TeEt_2)_2PdCl_2(c)$ + $[2NH_4Cl + 760CH_3COCH_3 + 820H_2O](\ell)$, reaction (3)

$Mt(SEt_2)_2PdCl_2$ /g	0.607677	0.631612	0.625816	0.628654	0.602551	0.643871
ΔH/kJ mol^{-1}	+37.05	+37.02	+36.94	+37.08	+37.23	+37.27

$\langle \Delta H(3) \rangle = +(37.10 \pm 0.10)$ kJ mol^{-1}

$Mt(SeEt_2)_2PdCl_2$ /g	0.774368	0.793101	0.776157	0.780734	0.773862	0.777925
ΔH/kJ mol^{-1}	+41.25	+41.40	+41.50	+41.52	+41.45	+41.62

$\langle \Delta H(3) \rangle = +(41.46 \pm 0.11)$ kJ mol^{-1}

$Mt(TeEt_2)_2PdCl_2$ /g	0.148790	0.151149	0.149010	0.152756	0.149774
ΔH/kJ mol^{-1}	+49.95	+49.88	+50.78	+51.07	+49.73

$\langle \Delta H(3) \rangle = +(50.28 \pm 0.54)$ kJ mol^{-1}

Table 5

Enthalpy of solution of $NH_4Cl(c)$ in $[760CH_3COCH_3 + 820H_2O](\ell)$, reaction 4

MNH_4Cl /g	0.193644	0.186484	0.183424	0.188751	0.169574	0.195568
ΔH/kJ mol^{-1}	+9.10	+8.96	+9.00	+8.96	+8.96	+8.94

$<\Delta H(4)> = +(8.99 \pm 0.05)$ kJ mol^{-1}

Enthalpy of solution of $(NH_4)_2PdCl_4(c)$ in $[760CH_3COCH_3 + 820H_2O](\ell)$, reaction (5)

$M(NH_4)_2PdCl_4$ /g	0.506433	0.533160	0.503761	0.499655	0.506279	0.501778
ΔH/kJ mol^{-1}	+13.77	+12.80	+12.45	+12.81	+12.66	+12.73

$<\Delta H(5)> = +(12.69 \pm 0.06)$ kJ mol^{-1}

$$\text{trans-}(SeEt_2)_2PdCl_2(c) = PdCl_2(c) + 2SeEt_2(g) \qquad (8)$$

$$\text{trans-}(TeEt_2)_2PdCl_2(c) = PdCl_2(c) + 2TeEt_2(g) \qquad (9)$$

may be calculated as

$$\Delta H(7) = (233 \pm 10)\ \text{kJ mol}^{-1}$$

$$\text{and } \Delta H(8) = (251 \pm 12)\ \text{kJ mol}^{-1}$$

by incorporation of the enthalpies of vaporisation

$$\Delta H\ \text{vap}\ (SEt_2) = (35.86 \pm 0.04)\ \text{kJ mol}^{-1} \qquad (66)$$

$$\Delta H\ \text{vap}\ (SeEt_2) = (38.9 \pm 4.0)\ \text{kJ mol}^{-1} \qquad (67)$$

and the enthalpy of formation

$$\Delta H_f^o(PdCl_2)(c) = -(163.2 \pm 10)\ \text{kJ mol}^{-1} \qquad (36)$$

Similarly, by incorporation of an estimated value of (41 ± 8) kJ mol^{-1} for the enthalpy of vaporisation of $TeEt_2$, we obtain the value

$$\Delta H(9) = (306 \pm 31)\ \text{kJ mol}^{-1}$$

Calculation of the enthalpy changes, ΔH(10), ΔH(11) and ΔH(12), of the gas-phase dissociation reactions (10), (11) and (12)

$$\text{trans-}(SEt_2)_2PdCl_2,g) = PdCl_2(g) + 2SEt_2(g) \qquad (10)$$

$$\text{trans-}(SeEt_2)_2PdCl_2,g) = PdCl_2(g) + 2SeEt_2(g) \qquad (11)$$

$$\text{trans-}(TeEt_2)_2PdCl_2,g) = PdCl_2(g) + 2TeEt_2(g) \qquad (12)$$

requires knowledge of the enthalpies of sublimation of $PdCl_2$ and the three complexes, none of which is known.

However, for the two complexes $(SEt_2)_2PdCl_2$ and $(SeEt_2)_2PdCl_2$ using the term

$$x = \Delta H\ \text{sub}\ [(SEt_2)_2PdCl_2] - \Delta H\ \text{sub}[(SeEt_2)_2PdCl_2]$$

then

$$\begin{aligned} \langle D\rangle\ (Pd\text{-}S) - \langle D\rangle\ (Pd\text{-}Se) &= \tfrac{1}{2}[\Delta H(10) - \Delta H(11)] \\ &= \tfrac{1}{2}[\Delta H(7) - \Delta H(8) - x] \\ &= -(9 \pm 5)\ \text{kJ mol}^{-1} - x/2 \end{aligned}$$

where <D> refers to the mean bond dissociation energy. It seems likely that the magnitude of x will be small since the structures of the two complexes are presumably similar,(68) consisting of discrete monomeric molecules. The larger molar mass of the selenoether, compared to that of the thioether will give a higher sublimation enthalpy but enhanced hydrogen bonding, in the thioether complex, will increase the sublimation enthalpy in this complex. If x is in the range ± 8 kJ mol^{-1} then

$$\langle D\rangle\,(Pd\text{-}Se) - \langle D\rangle\,(Pd\text{-}S) = (9 \pm 9)\ kJ\ mol^{-1}$$

However, this assumption of counterbalancing of effects to give a small value of x may not be valid, since there is evidence(69) that in the square planar Pd(II) complexes, there is sometimes a weak axial interaction between Pd and S in neighbouring molecules. If this was present in these complexes, x could become quite large.

Applying similar arguments to reactions (11) and (12) leads to

$$\langle D\rangle\,(Pd\text{-}Se) - \langle D\rangle\,(Pd\text{-}Te) = \tfrac{1}{2}[\Delta H(9) - \Delta H(10) - x]$$
$$= -\tfrac{1}{2}\ (55 \pm 18)\ kJ\ mol^{-1} - x/2$$

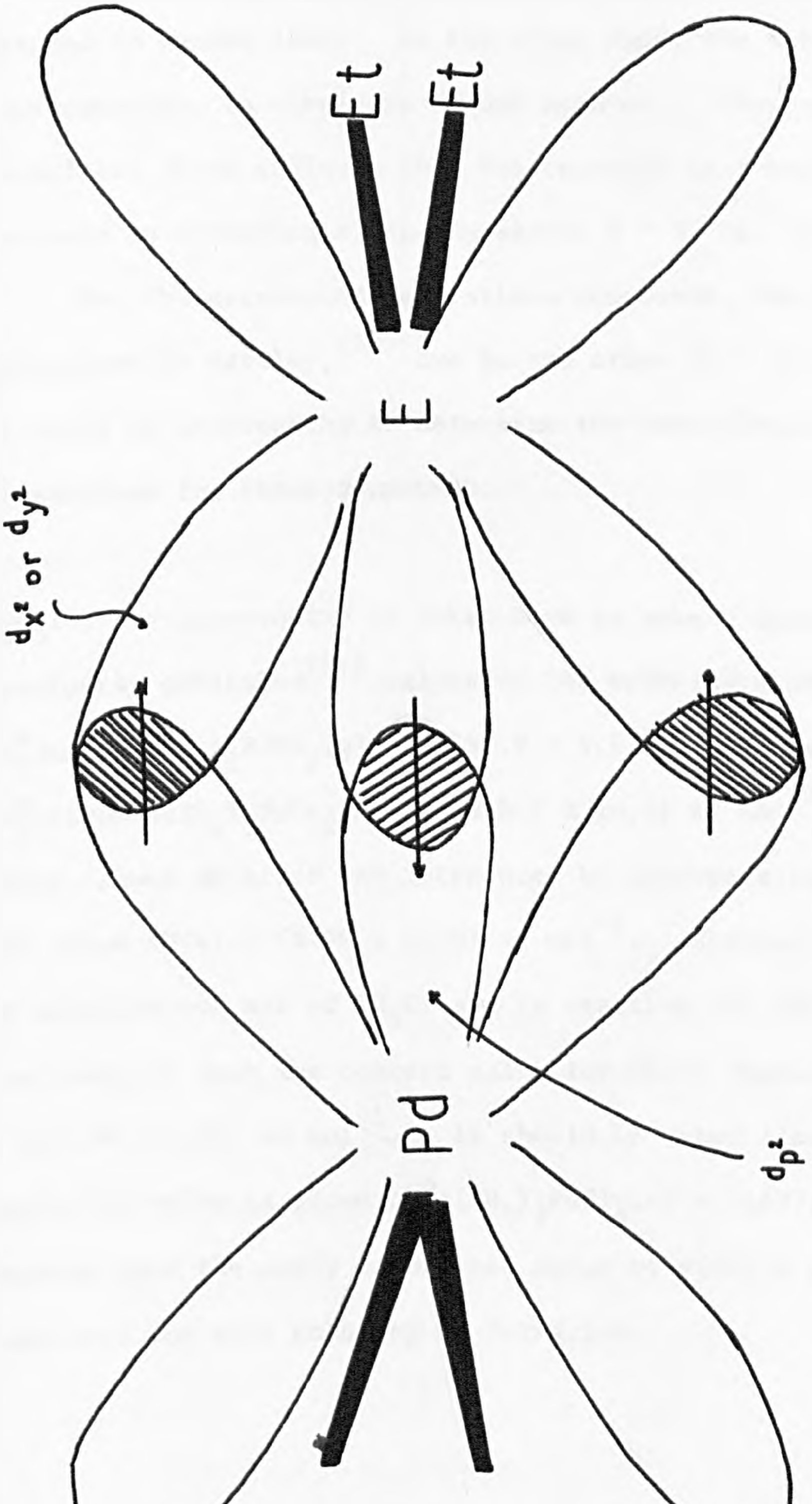
It seems more probable that in this case x could well be in the range ± 8, since axial interactions would be expected to be less. Therefore the difference is obtained

$$\langle D\rangle\,(Pd\text{-}Te) - \langle D\rangle\,(Pd\text{-}Se) = (28 \pm 13)\ kJ\ mol^{-1}$$

The indications of these data are that the palladium-sulphur and palladium-selenium bond dissociation energies are similar but weaker than the palladium-tellurium bond dissociation energy.

The bonding in compounds of the type $[(EEt_2)_2PdCl_2]$ has been explained in terms of a synergic combination of σ and π bonding. The σ bond results from donation of a lone pair of electrons of the atom E (S, Se or Te) into a dp^2 hybrid of the Pd atom, formed from a combination of d_{xy}, p_x and p_y orbitals. The π component of the bond results from overlap of a filled orbital, the d_{xz}, of the Pd atom with an empty d_{xz}

FIG. 1



BONDING IN $(EEt_2)_2PdCl_2$

or d_{yz} orbital of the *E* atom. This back donation of electrons in the series Pd→*E* reduces the charge difference caused by the σ-donor bond *E*→Pd. This bonding model is illustrated in Fig.1.

As the size of the atom, *E*, increases, the σ-bond contribution is assumed to become less. On the other hand, the π-bond interaction, or back-donation, is likely to become greater. The bond dissociation energies calculated above indicate that the increase in π-bond effect outweighs the decrease in σ-bonding along the series *E* = S, Se, Te.

For the corresponding platinum compounds, the force constants, determined by Hartley,(70) are in the order Pt - S > Pt - Se ∿ Pt - Te, it would be interesting to determine the bond dissociation energy differences for these compounds.

Note: The opportunity is taken here to make a correction to the previously published(71) values of the enthalpies of formation $\Delta H_f^o[\text{trans}(SEt_2)_2PdCl_2,c] = -(550.9 \pm 4.9)$ kJ mol^{-1} and $\Delta H_f^o[\text{trans}(SeEt_2)_2PdCl_2,c] = -(516.7 \pm 10.4)$ kJ mol^{-1}. In calculating these values an error was introduced by incorporating into the calculation, the value $\Delta H(4) = (8.99 \pm 0.05)$ kJ mol^{-1}. However this is the enthalpy of solution per mol of NH_4Cl and in reaction (4) *two* mol of NH_4Cl are involved, so that the correct value for ΔH(4) should be 2x(8.99 ± 0.05) = (17.98 ± 0.10) kJ mol^{-1}. It should be noted also that in the published paper the value is given $\Delta H_f^o[(NH_4)_2PdCl_4,c] = -(837.8 \pm 2.8)$ kJ mol^{-1}, whereas here the newly determined value of $-(841.0 \pm 1.7)$ kJ mol^{-1} has been used for this enthalpy of formation.

Chapter 5

Enthalpies of substitution of bis-(triphenylphosphine)platinum(0) olefin complexes

In this section of the thesis, details are reported of measurement of enthalpies of the following reactions:

$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + (CN)_2C{=}C(CN)_2(c) \rightarrow$$
$$(PPh_3)_2Pt[(CN)_2C{=}C(CN)_2](c) + CH_2{=}CH_2(g) \qquad (1)$$

$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + PhC{\equiv}CPh(c) \rightarrow$$
$$(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + CH_2{=}CH_2(g) \qquad (2)$$

In order to determine the enthalpies of these reactions the following reaction scheme was devised, where THF is tetrahydrofuran and TOL is toluene.

$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + [100(CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \rightarrow$$
$$[(PPh_3)_2Pt[(CN)_2C{=}C(CN)_2] + 99(CN)_2C{=}C(CN)_2 + CH_2{=}CH_2 +$$
$$10{,}000THF](\ell) \qquad (3)$$

$$(CN)_2C{=}C(CN)_2(c) + [99(CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \rightarrow$$
$$[100(CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \qquad (4)$$

$$CH_2{=}CH_2(g) + [99(CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \rightarrow$$
$$[CH_2{=}CH_2 + 99(CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \qquad (5)$$

$$(PPh_3)_2Pt[(CN)_2C{=}C(CN)_2](c) + [CH_2{=}CH_2 + (CN)_2C{=}C(CN)_2 + 10{,}000THF](\ell) \rightarrow$$
$$[(PPh_3)_2Pt[(CH)_2C{=}C(CN)_2] + CH_2{=}CH_2 + 99(CN)_2C{=}C(CN)_2 +$$
$$10{,}000THF](\ell) \qquad (6)$$

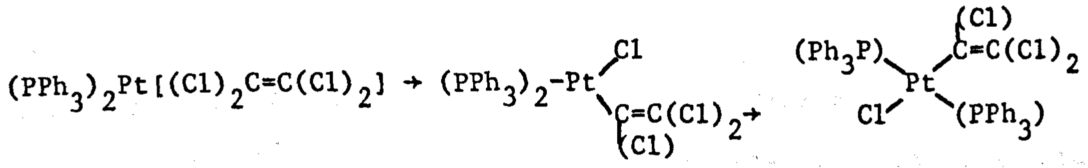
$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + [22PhC{\equiv}CPh + 2000TOL](\ell) \rightarrow$$
$$[(PPh_3)_2Pt(PhC{\equiv}CPh) + 21PhC\ CPh + CH_2{=}CH_2 + 2000TOL](\ell) \qquad (7)$$

$$PhC{\equiv}CPh(c) + [21PhC{\equiv}CPh + 2000TOL](\ell) \rightarrow$$
$$[22PhC{\equiv}CPh + 2000TOL](\ell) \qquad (8)$$

$$CH_2{=}CH_2(g) + [21PhC{\equiv}CPh + 2000TOL](\ell) \rightarrow [CH_2{=}CH_2 + 21PhC{\equiv}CPh + 2000TOL](\ell) \qquad (9)$$

$$(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + [CH_2{=}CH_2 + 21PhC{\equiv}CPh + 2000TOL](\ell) \rightarrow [(PPh_3)_2Pt(PhC{\equiv}CPh) + CH_2{=}CH_2 + 21PhC{\equiv}CPh + 2000TOL](\ell) \qquad (10)$$

In addition, details are also reported in this section of the determination of the isomerisation reaction



(11)

A B

The ethylene complex, $(PPh_3)_2Pt(CH_2{=}CH_2)$, was prepared according to the method of Cook and Jauhal,(72) in a one-stage process, from bis(triphenylphosphine)platinum dichloride, by reduction with sodium borohydride in ethanol solution, via the complex bis(triphenylphosphine)(dioxygen)platinum(0).

The tetracyanoethylene complex was made according to the method of Baddley and Venanzi(73) from bis(triphenylphosphine)(phenylacetylene) platinum(0), $(PPh_3)Pt(PhC{\equiv}CH)$, and tetracyanoethylene in benzene. The product was recrystallised from a solution of methylene chloride and ethanol.

The tetrachloroethylene complex was made according to the method of Bland and Kemmitt.(74) The complex bis(triphenylphosphine)(diphenylacetylene)platinum(0) was made by replacement of the ethylene in $(PPh_3)_2Pt(CH_2{=}CH_2)$ by diphenylacetylene. The product was recrystallised from dichloromethane/methanol.

A small sample of bis(triphenylphosphine)(dioxygen)platinum(0) was also isolated from a preparation made according to the method of Cook and

Jauhal,(72) in a one-stage process, from bis(triphenylphosphine)platinum dichloride, by reduction with sodium borohydride in ethanol solution, via the complex bis(triphenylphosphine)(dioxygen)platinum(0).

The tetracyanoethylene complex was made according to the method of Baddley and Venanzi(73) from bis(triphenylphosphine)(phenylacetylene) platinum(0), $(PPh_3)Pt(PhC{\equiv}CH)$, and tetracyanoethylene in benzene. The product was recrystallised from a solution of methylene chloride and ethanol.

The tetrachloroethylene complex was made according to the method of Bland and Kemmitt.(74) The complex bis(triphenylphosphine)(diphenylacetylene)platinum(0) was made by replacement of the ethylene in $(PPh_3)_2Pt(CH_2{=}CH_2)$ by diphenylacetylene. The product was recrystallised from dichloromethane/methanol.

A small sample of bis(triphenylphosphine)(dioxygen)platinum(0) was also isolated from a preparation made according to the method of Cook and Jauhal.(72) Samples of the compounds $(PPh_3)_2Pt(CH_2{=}CH_2)$, $(PPh_3)_2[(Cl)_2C{=}C(Cl)_2]$ and $(PPh_3)_2Pt[(CN)_2C{=}C(CN)_2]$ were kindly supplied by Dr. R.J. Puddephatt.

The infra-red spectrum of one sample of the reaction products, of each series of reactions, was recorded. These were checked against the spectrum of the dioxygen complex, since this has a characteristic frequency at 818 cm^{-1}. This peak was never observed in the products of any of the reactions, indicating that the precautions taken to exclude oxygen from the system had been adequate.

Table 1 shows the analyses for the complexes studied.

Table 1 (analyses)

COMPOUND	all with decomposition FOUND	LIT.	FOUND C%	H%	CALCULATED C%	H%
$(PPh_3)_2Pt(CH_2CH_2)$	396	395-7(72)	60.7	4.8	61.0	4.58
$(PPh_3)_2Pt[C_2(CN)_4]$	550	549(73)			59.5	3.57
$(PPh_3)_2Pt[C_2Ph_2]$	433	434-443(75)	66.8	4.50	66.9	4.46
$(PPh_3)_2(C_2Cl_4)$	468[a]	463(74)	52.9	3.42	51.6	3.40

[a] see section 5.3 for further details

The sources of other compounds used were as follows: Tetracyanoethylene (R.N. Emanuel), tetrahydrofuran (Koch Light), ethylene (Air Products), diphenylacetylene (Koch Light), toluene (Hopkin and Williams).

The tetracyanoethylene was resublimed prior to use. Diphenylacetylene was recrystallised twice from ethanol m.p. 334.7 K, lit.(76) 335.7 K.

The two solvents tetrahydrofuran and toluene were dried over molecular sieve and sodium respectively. The tetrahydrofuran was subjected to g.l.c. and showed one major peak, together with a small amount [(<<) 0.5%] of impurity. Both solvents were saturated with nitrogen prior to being used, to fill the reaction vessel of the calorimeter.

The ethylene was used directly from the cylinder.

5.1. Experimental

The 25 ml vessel was used throughout the series of reactions.

All of the solid samples were sealed into the wide long-necked ampoules (see chapter 2 Fig.3b). However, in the determination of the enthalpy of solution of ethylene, the thin necked ampoules were chosen, to reduce the area for gas effusion. Since the ethylene never completely filled the ampoule the following technique was used.

The volume of the ampoules were estimated using water as a calibrant. After drying, the ampoules were filled with ethylene, by displacement of air using a fine capillary, and then sealed in the usual manner. The ampoule was placed in the holder and its length was measured by use of a cathetometer. Only the lower face of the ampoule was broken during measurement of the enthalpy of solution, so that the solvent rose inside the ampoule, partially filling it. The cathetometer was again used to determine the length of the ampoule filled and so calculate the volume of solvent occupying the ampoule. It was assumed that a linear volume/length relationship applied.

The ampoule never filled completely with solvent. The reasons for this incomplete filling were not investigated, but two possibilities are fairly apparent.

(1) The ethylene diffused through the neck of the ampoule, in the time between removing the ethylene source and sealing.

(2) Pyrolysis of the ethylene would produce a fairly large volume of hydrogen, plus small amounts of carbon oxides. This also produced a secondary problem, in that carbon deposits often prevented complete sealing of the neck.

Reactions were initiated in the usual manner and the calibration procedure was that previously described. Reactions (4), (6), (8) and (10) were endothermic, the remaining reactions were exothermic.

Corrected resistance changes were all calculated by Dickenson's extrapolation except for reaction (3). This was the only reaction of longer than five minutes duration.

The results are shown in Tables 2 and 3.

Finally, the effect of temperature on bis(triphenylphosphine)(tetrachloroethylene)platinum was studied using a differential scanning

Table 2

Enthalpies of solution of

$(PPh_3)_2Pt(C_2H_4)$(c) in $[100[(CN)_2C{=}C(CN)_2] + 10{,}000THF](\ell)$, reaction (1)

$M(PPh_3)_2PtC_2H_4$/g	0.025926	0.019776	0.023179	0.027598	0.020010
ΔH(1)/ kJ mol^{-1}	-88.7	-82.1	-89.7	-86.2	-77.8

<ΔH(1) = -(84.9 ± 1.8) kJ mol^{-1}

Enthalpies of solution of

$[(CN)_2C{=}C(CN)_2]$(c) in $[99[(CN)_2C{=}C(CN)_2] + 10{,}000THF](\ell)$, reaction (2)

$M(CN)_2C{=}C(CN)_2$/g	0.005554	0.003713	0.003371	0.005067	0.005829
ΔH(2)/kJ mol^{-1}	+1.5	+2.7	+1.6	+2.0	+2.3

<ΔH(2)> = +(2.0 ± 0.4) kJ mol^{-1}

Enthalpies of solution of

C_2H_4 (g) in $[99[(CN)_2C{=}C(CN)_2] + 10{,}000THF](\ell)$, reaction (3)

$M(C_2H_4$/g	0.000406	0.000765	0.000486	0.000586	0.000641
ΔH(3)/kJ mol^{-1}	-13.8	-15.0	-13.5	-13.7	-12.3

<ΔH(3)> = -(13.7 ± 0.8) kJ mol^{-1}

Enthalpies of solution of

$(PPh_3)_2Pt\{(CN)_2C{=}C(CN)_2\}$(c) in $[C_2H_4 + 99[(CN)_2C{=}C(CN)_2] + 10{,}000THF](\ell)$ reaction (4)

$M(PPh_3)_2Pt(CN)_2C{=}C(CN)_2$/g	0.02372	0.026258	0.029967	0.027140	0.023560
ΔH(4)/kJ mol^{-1}	+5.9	+5.2	+5.2	+4.6	+6.0

<ΔH(4)> = +(5.4 ± 0.6) kJ mol^{-1}

Table 3

Enthalpies of solution of $(PPh_3)_2Pt(C_2H_4)(c)$ in $[22(PhC{\equiv}CPh) + 2000TOL](\ell)$, reaction (5)

$M(PPh_3)_2PtC_2H_4$/g	0.069889	0.085820	0.088105	0.084915	0.086343
$\Delta H(5)$/kJ mol^{-1}	+8.42	+8.42	+7.86	+7.96	+7.98

$<\Delta H(5)> = +(8.1 \pm 0.2)$ kJ mol^{-1}

Enthalpies of solution of $(PhC{\equiv}CPh)(c)$ in $[21(PhC{\equiv}CPh) + 2000TOL](\ell)$ reaction (6)

$MPhC{\equiv}CPh$ /g	0.020641	0.026379	0.018723	0.020170	0.018090
$\Delta H(6)$/kJ mol^{-1}	+16.84	+18.42	+17.23	+18.10	+17.93

$<\Delta H(6)> = +(17.7 \pm 0.7)$ kJ mol^{-1}

Enthalpies of solution of $(C_2H_4)(g)$ in $[21(PhC{\equiv}CPh) + 2000TOL](\ell)$ reaction (7)

MC_2H_4/g	0.003183	0.003358	0.003185	0.003111	0.003547
$\Delta H(7)$/kJ mol^{-1}	-10.67	-10.53	-12.33	-10.78	-10.05

$<\Delta H(7)> = -(10.9 \pm 0.8)$ kJ mol^{-1}

Enthalpies of solution of $(PPh_3)_2Pt(PhC{\equiv}CPh)(c)$ in $[C_2H_4 + 21(PhC{\equiv}CPh) + 2000TOL](\ell)$, reaction 8

$M(PPh_3)_2Pt(PhC\,CPh)$/g	0.100137	0.103255	0.098430	0.098440	0.096614
$\Delta H(8)$/kJ mol^{-1}	+18.67	+19.91	+18.49	+19.02	+19.60

$<\Delta H(8)> = +(19.1 \pm 0.5)$ kJ mol^{-1}

Enthalpies of rearrangement $(PPh_3)_2Pt[(Cl)_2C{=}C(Cl)_2](c) \rightarrow (PPh_3)_2Pt(Cl)[ClC{=}C(Cl)_2](c)$, reaction 9

$M(PPh_3)_2Pt[(Cl)_2C{=}C(Cl)_2]$/g	0.005002	0.004318	0.004476	0.003850	0.003260
$\Delta H(11A)$/kJ mol^{-1}	+43.68	+39.75	+36.02	+40.50	+38.03
$\Delta H(11B)$/kJ mol^{-1}	+18.20	+16.86	+15.10	+19.25	+18.20

$<\Delta H(11A)> = +(39.6 \pm 2.2)$ kJ mol^{-1}

$<\Delta H(11B)> = +(17.5 \pm 1.4)$ kJ mol^{-1}

calorimeter. Small samples (∿ 5 mg) were encapsulated and treated as described in chapter 2.

The results are shown in Table 3.

5.2. Discussion

The enthalpies of reactions (12) and (13), ΔH(12) and ΔH(13),

$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + (CN)_2C{=}C(CN)_2(c) \rightarrow (PPh_3)_2Pt[(CN)_2C{=}C(CN)_2](c) + CH_2{=}CH_2(g) \qquad (12)$$

$$(PPh_3)_2Pt(CH_2{=}CH_2)(c) + PhC{\equiv}CPh(c) \rightarrow (PPh_3)_2Pt(PhC{\equiv}CPh)(c) + CH_2{=}CH_2(g) \qquad (13)$$

can be obtained from the relationships

$$\Delta H(12) = \Delta H(3) + \Delta H(4) - \Delta H(5) - \Delta H(6)$$

as $\Delta H(12) = -(74.6 \pm 3.6)\ \text{kJ mol}^{-1}$,

and $$\Delta H(13) = \Delta H(7) + \Delta H(8) - \Delta H(9) - \Delta H(10)$$

as $\Delta H(13) = +(17.6 \pm 2.2)\ \text{kJ mol}^{-1}$

To obtain values for the differences between the bond dissociation energies, the reaction should refer to the gas phase. Unfortunately, at present, an enthalpy datum is available only for the following process:

$$(CN)_2C{=}C(CN)_2(c) \rightarrow (CN)_2C{=}C(CN)_2(g) \qquad (14)$$

$\Delta H(14) = (81.2 \pm 5.9)\ \text{kJ mol}^{-1}$ 77

In the case of diphenylacetylene, the value for the phase change

$$Ph{-}C{\equiv}C{-}Ph(c) \quad Ph{-}C{\equiv}C{-}Ph(g), \qquad (15)$$

can be estimated as $\Delta H(15) = (100 \pm 10)\ \text{kJ mol}^{-1}$. This is based upon a knowledge of enthalpies of sublimation of similar hydrocarbons.

1-2 diphenylethane,	84 kJ mol^{-1}	78
cis-1-2 diphenylethene,	90 kJ mol^{-1}	78
anthracene,	105 kJ mol^{-1}	78
phenanthrene,	95 kJ mol^{-1}	78

The enthalpies of sublimation of the platinum complexes are assumed to be similar and therefore mutually self-balancing in a heat cycle.

Therefore, the gas-phase enthalpies

$$(PPh_3)_2Pt(CH_2{=}CH_2)(g) + (CN)_2C{=}C(CN)_2(g) \rightarrow (PPh_3)_2Pt[(CN)_2C{=}C(CN)_2](g) + CH_2{=}CH_2(g) \quad (16)$$

and

$$(PPh_3)_2Pt(CH_2{=}CH_2)(g) + PhC{\equiv}CPh(g) \rightarrow (PPh_3)_2Pt(PhC{\equiv}CPh)(g) + CH_2{=}CH_2(g) \quad (17)$$

may be calculated as

$$\Delta H(16) = \Delta H(12) - \Delta H(13) = -(155.8 \pm 8.0)\ \text{kJ mol}^{-1}$$

and

$$\Delta H(17) = \Delta H(13) - \Delta H(15) = -(82 \pm 12)\ \text{kJ mol}^{-1}$$

The following differences between bond dissociation energies are derived:

$$D(\text{Pt-tetracyanoethylene}) - D(\text{Pt-ethylene}) = (156 \pm 8)\ \text{kJ mol}^{-1}$$

$$D(\text{Pt-diphenylacetylene}) - D(\text{Pt-ethylene}) = (82 \pm 12)\ \text{kJ mol}^{-1}$$

Kirkham <u>et.al.</u>(79) have measured the enthalpies of the replacement reaction

$$Pt(PPh_3)_2L(c) + CS_2(soln) \rightarrow Pt(PPh_3)_2(CS_2)(soln) + L(g)$$

where L is $CH_2{=}CH_2$, $CH_2{=}CH(Ph)$, cis-(Ph)HC=CH(Ph), or trans-(Ph)HC=CH(Ph), from which it is possible to calculate enthalpies of the following replacement reaction:

$$Pt(PPh_3)_2CH_2{=}CH_2(c) + \text{olefin}(g) \rightarrow Pt(PPh_3)_2\text{olefin}(c) + CH_2{=}CH_2(g)$$

These values, together with those for L = $(CN)_2C{=}C(CN)_2$ and PhC≡CPh, from this work, are shown in Table 5.

The data in Table 5 allows empirical derivations about the relative stability of the olefin complexes. Substitution of the hydrogen atom of the ethylene by phenyl, or electron withdrawing groups, increases the stability of the complexes very considerably. These findings can be interpreted in terms of the current views of the bonding, in these compounds, which are now reviewed.

5.2.(1) Bonding

The structural data available for zerovalent platinum-olefin, and acetylene, complexes shows them to be almost planar, but not completely so, as there is a small angle, α, between the C-M-C plane and the P-M-P plane. The substituents, which are bound to the carbon atoms involved in the multiple bond, are bent away from the metal, M. See Fig.2 and Table 4. Moreover, the olefin or acetylene bond becomes lengthened on coordination to the platinum. A bonding description must, therefore, be able to account for these observations.

The most successful of the bonding models has been that proposed by Dewar, Chatt and Duncanson,(80) as modified by Nelson.(81) The model is very similar to that described for the compounds $(EEt_2)_2PdCl_2$. The model again involves the use of a dp^2 hybrid orbital from d_{xy}, p_x and p_y orbitals of the metal atom. These overlap with the π bonding system, of the olefin or acetylene, to give a metal-olefin σ-interaction. The metal also has available filled d-orbitals which can overlap with antibonding orbitals of the olefins (Fig.1).

Acetylenes do have available further π orbitals which can give a second σ bond by overlap with the hybrid $(d_{xz} + d_{yz})$. A π bond can also be formed with the antibonding π orbitals on the acetylene and the metal orbitals from $(d_{xz}-d_{yz})$ (Fig.1).

Now depending on the nature of the substituents, attached to the carbon atoms involved in the multiple bond, the interaction between the metal and multiple bond will vary. Thus, electronegative substituents, on the olefin, such as the cyano-group, decrease the σ-donor capacity of the olefin, but increase the π acceptor character; this results from antibonding orbitals of lower energy and thereby increased donation of metal electrons, to the olefin. Conversely, inductive substituents, like methyl, would be expected to increase the σ-donor character of the olefin, compared with 'neutral' substituents, such as hydrogen. However, the net observed effect, on the olefinic bond, would be expected to be the same, in that increasing σ-donor ability would result in olefin bond weakening, i.e. lengthening, whilst increasing π acceptor ability would reduce the bonding order in the olefin, once again resulting in bond lengthening. The observed X-ray structures have always shown this lengthening phenomena, as can be seen from Table 4.(82)

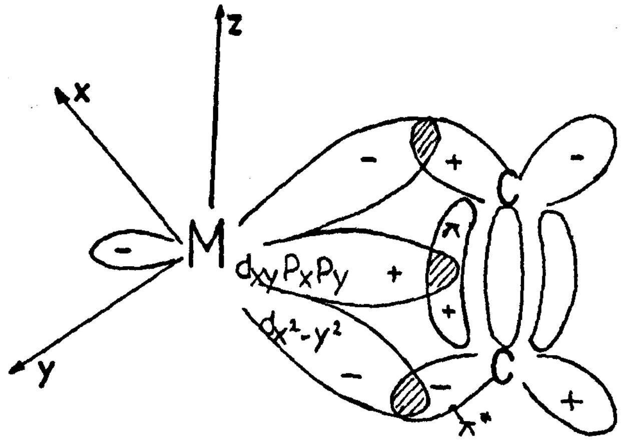
Table 4

COMPLEX			Multiple bond length Å	
	α	β	COMPLEX	FREE
$(PPh_3)_2Pt[(CN)_2C=C(CN)_2]$	8.3	41.5	1.49	1.31
$(PPh_3)_2Ni(CH_2=CH_2)$	12.0	42.0	1.46	1.33
$(PPh_3)_2Pt[(Cl)_2C=(Cl)_2]$	12.3	47.0	1.62	-
$(PPh_3)_2Pt[(Cl)_2C=C(CN)_2]$	1.9	40.6	1.42	-
$(PPh_3)_2Pt[CN-C\equiv C-CN]$	8.0	-	1.40	1.19
$(PPh_3)_2Pt(PhC\equiv CPh)$	14.0	3.9	1.32	1.19

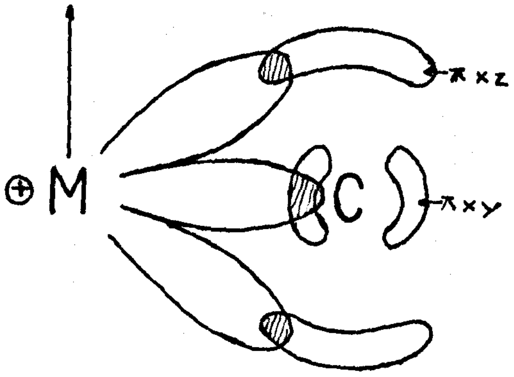
where α and β refer to the dihedral angle of the C-M-C and P-M-P planes and the C-M-C bond angle, respectively; see Fig.2.

The higher electron density in the antibonding orbitals also implies a shift towards sp^3 hybridisation on the carbon atoms of olefins, giving a tendency towards tetrahedral structure, hence, the substituents on the olefin move away from the plane perpendicular to the olefin-platinum plane.

FIG. 1



Bonding picture for olefines & acetylenes



Additional bonding in acetylenes

FIG. 2

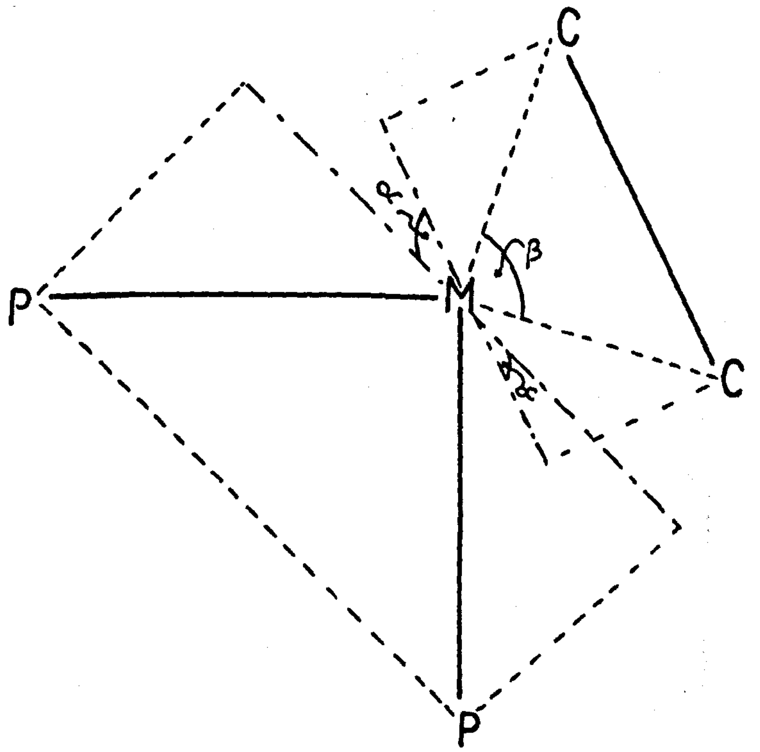
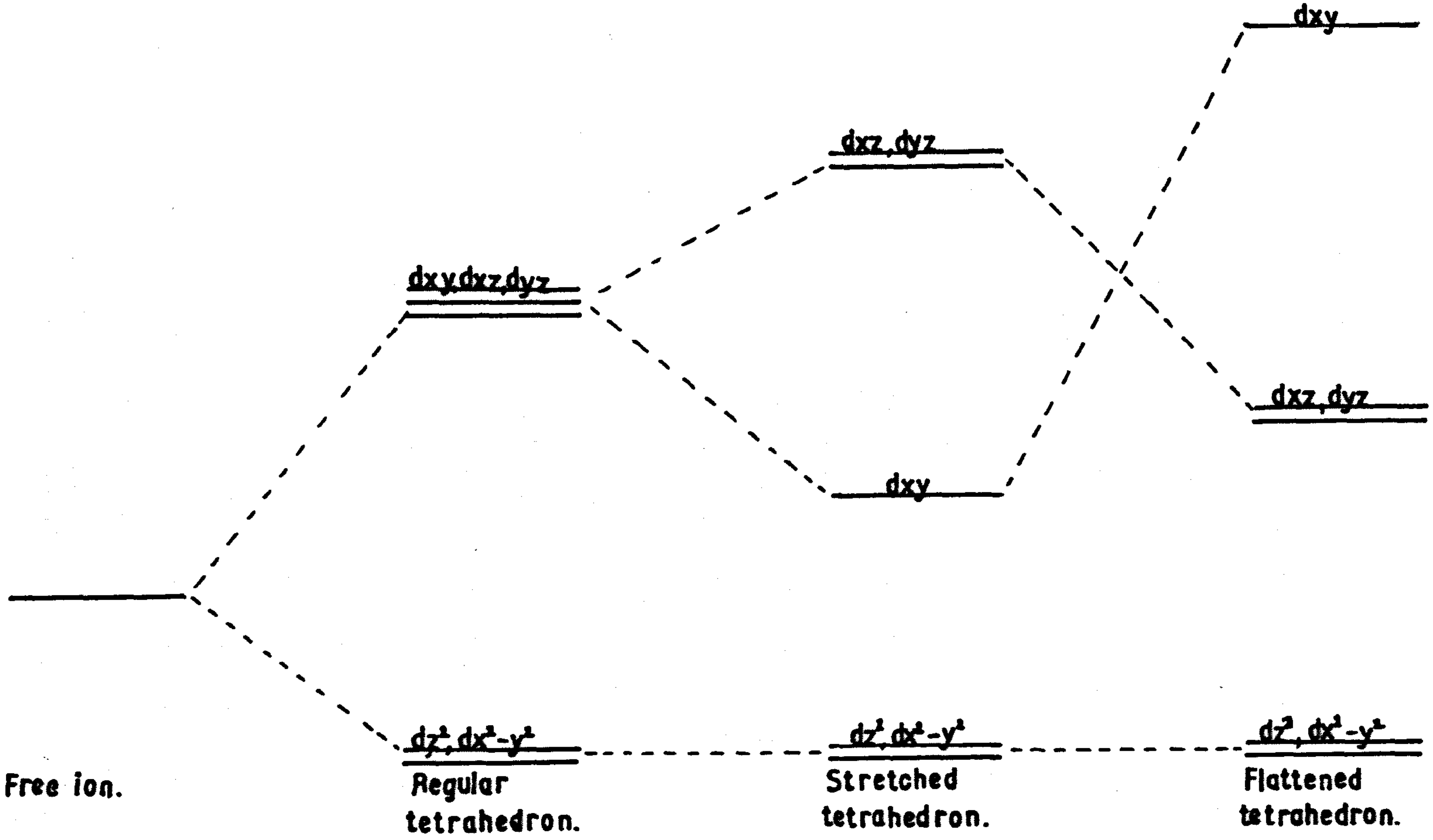


FIG. 3



Tetrahedral configuration of square-Planar complexes of platinum

A further aspect, that has been observed, is the pseudo-planar structure (Fig.2) of these complexes. This can be explained from electronic considerations of the platinum. The d^{10} configuration, of the zerovalent platinum, would be expected to be tetrahedral, in order to minimize bond pair/bond pair repulsions. However, assuming back donation does occur, then less than 10 electrons are effectively occupying the metal orbitals. The Jahn-Teller effect can then be incorporated, to offer a possible explanation, whereby the electron distribution becomes distorted to either of two extreme types (Fig.3): (a) flattened tetrahedron and (b) stretched tetrahedron. Assuming a pseudo d^8 configuration results from back donation of the metal electrons, then the flattened tetrahedron is the most favoured, since the gain in ligand field stabilisation is the highest for this structure.

The synergic interaction between metal and olefin implies that different olefins and acetylenes would have differing metal-carbon bond strengths, depending upon the balance of the metal-olefin, pi and sigma donations. An expected series for the compound $X_2C{=}CX_2$ would be

$$X = H < CN < F < Cl \quad {}^{(83)}$$

This assumes that the carbon-carbon multiple bond lengths reflect inversely the metal-carbon bond strengths.

Support for this idea of back donation has been established using electron spectroscopy (E.S.C.A.) techniques,$^{(84)}$ where binding energies of the $Pt(4f^{7}/_{2})$ electrons were found to increase on going from K_2PtCl_4 to $KPt(Cl)_3(CH_2{=}CH_2)$.

However, later authors,$^{(85)}$ also using E.S.C.A. techniques, established that the binding energies of the platinum $\Delta f^{5}/_{2}$ and $\Delta f^{7}/_{2}$ electrons were independent of the nature of the substituent, R, in the complexes $(PPh_3)_2Pt(R_2C{=}CR_2)$, where R = H, Cl, F or CN, leading to the conclusion that in $(PPh_3)_2Pt(\text{olefin})$, the phosphine-platinum moiety is so basic, that olefin substituents play but a minor part. A further logical conclusion is, therefore, that the platinum-olefin bond strength is the same for all olefins. This is not in agreement with the data shown in Table 5.

Table 5

Enthalpies of reaction $(PPh_3)_2Pt(CH_2{=}CH_2)(c) + L(g) \rightarrow (PPh_3)_2PtL(c) + CH_2{=}CH_2(g)$

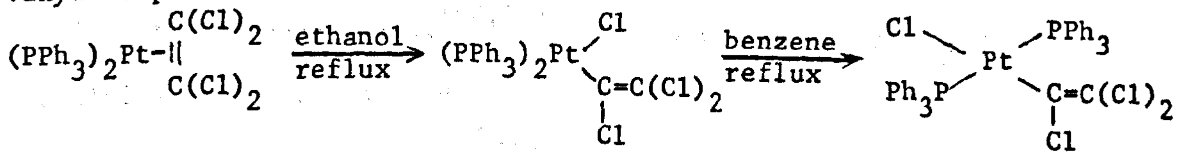
	ΔH/ kJ mol^{-1}	Ref.
$CH_2{=}CHC_6H_5$	- 41.3 ± 5	86
cis-C_6H_5-CH=CH-C_6H_5	- 90.2 ± 5	86
trans-C_6H_5-CH=CH-C_6H_5	-118.5 ± 5	86
$(CN)_2C{=}C(CN)_2$	-155.8 ± 8	This thesis
C_6H_5-C≡C-C_6H_5	- 82.0 ± 12	" "

The data in Table 5 also allow empirical derivations to be made about the relative stability of the olefin complexes. Substitution of the hydrogen atom of ethylene by phenyl, or electron-withdrawing groups, increases the stability of the complexes very considerably. Hence the enthalpies, and presumably bond dissociation energies, would be expected to vary.

5.3. Thermal study of $(PPh_3)_2Pt[(Cl)_2C{=}C(Cl)_2]$

The tetrachloroethylene complex was studied on the differential scanning calorimeter. The complex showed two endothermic peaks at 468 K and 485 K. At 468 K the compound melted and then resolidified. There was an overall weight loss of 2.5% and a colour change of white to orange. At temperatures above ∿ 560 K considerable decomposition occurred. The literature(87) value for the melting point is given as

463 K. Further work on the tetrachloroethylene complex, revealed that it could be converted to the cis-vinyl complex by refluxing in ethanol. Refluxing the cis-vinyl compound in benzene gave the trans-vinyl complex:



These vinyl complexes had decomposition temperatures of 559 K and 562 K for the cis and trans-configurations, respectively.(88)

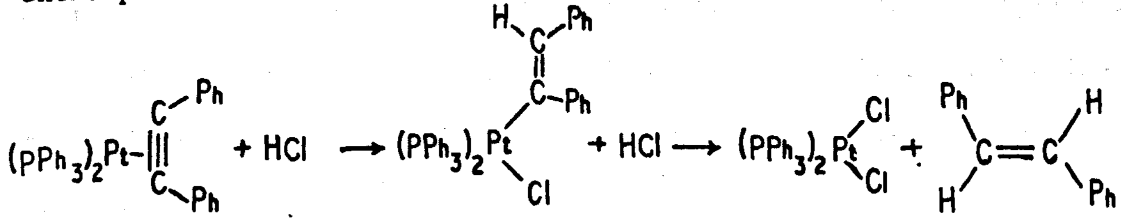
Therefore, it would seem likely that, when the tetrachloroethylene complex is heated in the scanning calorimeter, the first peak represents conversion of the π-complex to the cis-vinyl complex, whilst interconversion of the cis to the trans isomer results in the second peak. The enthalpy changes for these changes are + 39.6 ± 2.2 kJ mol^{-1} and 17.5 ± 1.4 kJ mol^{-1}, respetively.

The very small weight loss may be due to slight decomposition, since Ugo *et.al.*,(89) noted a red material formed by attempted recrystallisation of many of the platinum complexes; it may also help to explain the orange colouration accompanying the transformation.

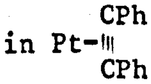
Chapter 6

The platinum-carbon bond strength in $(PPh_3)_2Pt(Cl)(PhC{=}CHPh)$

In chloroform solution, $(PPh_3)_2Pt(PhC{\equiv}CPh)$ reacts with gaseous HCl in a two stage process.(90,91) From measurements at 298 K of the enthalpies of the two stages:

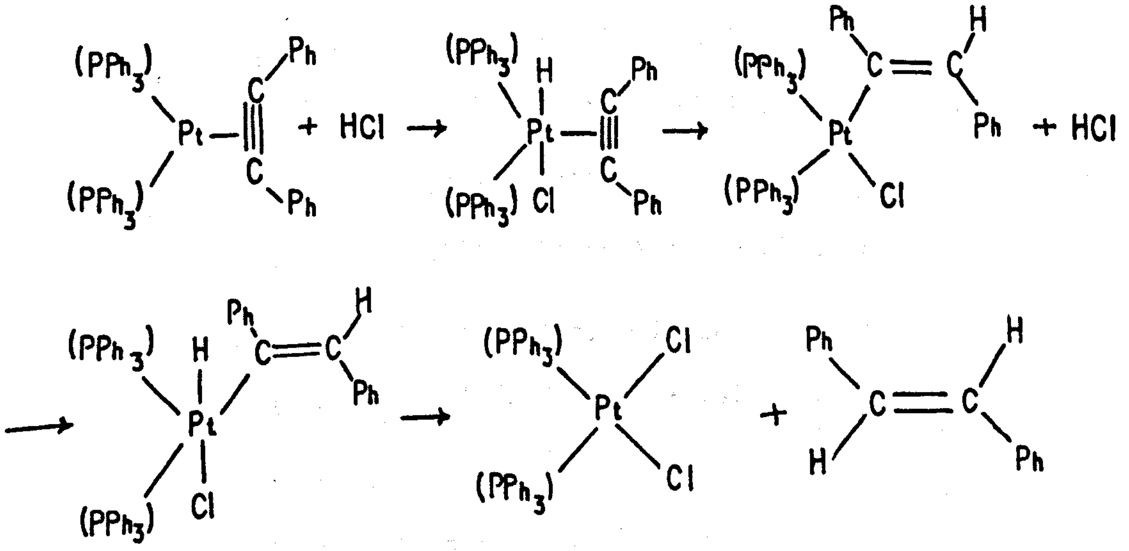


and also by estimation of the enthalpies of transitions to the gas phase, the bond strengths of the Pt-Cl and Pt-(CPh=C(H)Ph) bonds can be calculated relative to the strength of the platinum-acetylene bond; for convenience this bond is subsequently written as Pt-Tolane in

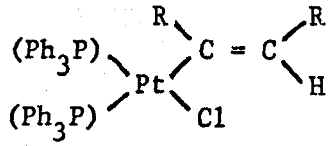


$\mathrm{Pt}-\overset{\mathrm{CPh}}{\underset{\mathrm{CPh}}{|||}}$.

The reaction mechanism, which was suggested(91) by Tripathy and Roundhill, involved the formation of a six-coordinate intermediate.



This fitted the then available data. However, following the preparation of the intermediate vinyl complex (Mann et.al.(90)), a cis hydrogen, in the complex, was found, and not a trans one as first suggested.



Also, the semi-empirical calculations, by Wheelock et.al.,$^{(92)}$ do not favour a six coordinate intermediate. This is in accord with expectations of the bonding model proposed for the olefin and acetylene complexes.

Alternative mechanisms proposed were protonation, or a hydride type of reaction. Support for both is based upon known, analogous, reaction paths.

The thermochemical measurements undertaken, while unable to provide additional mechanistic information can, however, provide a guide to the relative strengths of bonds in these compounds.

The reactions were studied according to the following schemes.

For stage 1,

$$(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + HCl(g) \rightarrow (PPh_3)_2Pt(Cl)(PhC{=}CHPh)(c) \tag{1}$$

$$\begin{aligned}&(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + 7350CHCl_3(\ell) \rightarrow\\ &\qquad [(PPh_3)_2Pt(PhC{\equiv}CPh) + 7350CHCl_3](\ell)\end{aligned} \tag{2}$$

$$\begin{aligned}&[(PPh_3)_2Pt(PhC{=}CPh) + 7350CHCl_3](\ell) + HCl(g) \rightarrow\\ &\qquad [(PPh_3)_2Pt(Cl)(PhC{=}CHPh) + 7350CHCl_3](\ell)\end{aligned} \tag{3}$$

$$\begin{aligned}&(PPh_3)_2Pt(Cl)(PhC{=}CHPh)(c) + 7350CHCl_3(\ell) \rightarrow\\ &\qquad [(PPh_3)_2Pt(Cl)(PhC{=}CHPh) + 7350CHCl_3](\ell)\end{aligned} \tag{4}$$

For stage 2,

$$\begin{aligned}&(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + 2HCl(g) \rightarrow\\ &\qquad cis\text{-}(PPh_3)_2PtCl_2(c) + trans\text{-}PhHC{=}CHPh(c)\end{aligned} \tag{5}$$

$$\begin{aligned}&(0.5 + x)(PPh_3)_2Pt(PhC{\equiv}CPh)(c) + 13{,}000CHCl_3(\ell) \rightarrow\\ &\qquad [(0.5 + x)(PPh_3)_2Pt(PhC{\equiv}CPh) + 13{,}000CHCl_3](\ell)\end{aligned} \tag{6}$$

$$\begin{aligned}&[(0.5 + x)(\mathrm{PPh_3})_2\mathrm{Pt}((\mathrm{PhC{\equiv}CPh}) + 13{,}000\mathrm{CHCl_3}](\ell) + \mathrm{HCl}(g) \rightarrow\\ &\quad [(0.5-x)(\mathrm{PPh_3})_2\mathrm{PtCl_2} + 2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{\equiv}CPh)} +\\ &\quad (0.5-x)\text{trans-}\mathrm{PhHC{=}CHPh} + 13{,}000\mathrm{CHCl_3}](\ell)\end{aligned}\tag{7}$$

$$\begin{aligned}&(0.5-x)\text{trans-}\mathrm{PhHC{=}CHPh}(c) + [(0.5-x)(\mathrm{PPh_3})_2\mathrm{PtCl_2} + 2x(\mathrm{PPh_3})_2\mathrm{PtCl}\\ &\quad (\mathrm{PhC{=}CHPh}) + 13{,}000\mathrm{CHCl_3}](\ell) \rightarrow [(0.5-x)\text{trans-}\mathrm{PhHC{=}CHPh} +\\ &\quad (0.5-x)(\mathrm{PPh_3})_2\mathrm{PtCl_2} + 2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)} + 13{,}000\mathrm{CHCl_3}](\ell)\end{aligned}\tag{8}$$

$$\begin{aligned}&(0.5-x)\text{cis-}(\mathrm{PPh_3})_2\mathrm{PtCl_2}(c) + [2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)} + 13{,}000\mathrm{CHCl_3}](\ell)\\ &\quad \rightarrow [(0.5-x)\text{cis}(\mathrm{PPh_3})_2\mathrm{PtCl_2} + 2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)} +\\ &\quad 13{,}000\mathrm{CHCl_3}](\ell)\end{aligned}\tag{9}$$

$$\begin{aligned}&2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)}(c) + 13{,}000\mathrm{CHCl_3}(\ell) \rightarrow\\ &\quad [2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)} + 13{,}000\mathrm{CHCL_3}](\ell)\end{aligned}\tag{10}$$

$$2x(\mathrm{PPh_3})_2\mathrm{Pt(Cl)(PhC{=}CHPh)}(c) \rightarrow 2x(\mathrm{PPh_3})_2\mathrm{Pt(PhC{\equiv}CPh)}(c) + 2x\mathrm{HCl}(g)\tag{11}$$

6.1. Experimental

The complex $(PPh_3)_2Pt(PhC{\equiv}CPh)$ was prepared(90) by hydrazine reduction of cis-$(PPh_3)_2PtCl_2$, followed by addition of diphenylacetylene in ethanol. The product was recrystallised from chloroform/hexane.

The final product cis-$(PPh_3)_2PtCl_2$ was prepared,(93) as described previously, from potassium tetrachloroplatinite and triphenylphosphine by refluxing together in xylene.

A sample of the intermediate vinyl complex was produced by reaction of the acetylene complex, in chloroform, with a calculated amount of hydrogen chloride gas, delivered from a syringe. The resulting solid was recrystallised from either dichloromethane/pentane to give the complex (A), or from methanol to give a second complex (B). The compound (A) was subjected to thermal analysis on the D.S.C. when it was converted to (B) (the enthalpy of isomerisation, A → B was measured in this way).

Analyses are given in Table 1.

Table 1

COMPOUND	M.P./K		ANALYSIS			
	FOUND	LIT.	FOUND		CALCULATED	
			C%	H%	C%	H%
$(PPh_3)_2Pt(PhC\equiv CPh)$	432	433(75)	66.8	4.50	66.9	4.49
$(PPh_3)_2PtCl_2$	566	566(87) >572(93)	55.0	3.90	54.7	3.82
$(PPh_3)_2Pt(Cl)(PhC{=}C(H)Ph)$ (A)	452	489-490(90)				
$(PPh_3)_2Pt(Cl)(PhC{=}C(H)Ph)$ (B)	536					

Other compounds used were, potassium tetrachloroplatinite, prepared from platinum metal(94) (Johnson Matthey), HCl gas (Air Products) used directly from the cylinder; chloroform (Koch Light) was distilled b.p. 331-333 K, 740 mm Hg; diphenylacetylene (Koch Light) was recrystallised twice from ethanol m.p. 334 K; trans-stilbene (Fluka puriss for scintillation) was used directly m.p. 396-398 K.

6.2. Procedures

Ampoules were loaded, under nitrogen, with the following quantities of chemicals:

reaction (2)	$(PPh_3)_2Pt(PhC\equiv CPh)$	0.04g, 4.45×10^{-5} mol
reaction (4)	$(PPh_3)_2Pt(Cl)(PhC{=}CHPh)$	0.04g, 4.28×10^{-5} mol
reaction (6)	$(PPh_3)_2Pt(PhC\equiv CPh)$	0.022g, 2.45×10^{-5} mol
reaction (8)	trans-(PhHC=CHPh)	0.0052g, 2.88×10^{-5} mol
reaction (9)	cis$(PPh_3)_2PtCl_2$	0.019g, 2.40×10^{-5} mol

In each case five ampoules of type (6) (Chapter 2) were loaded. In addition, several ampoules were filled with nitrogen, and others with hydrogen chloride gas.

The following reactions were run consecutively: reactions (2) and (3); reactions (6) and (7); and reactions (8) and (9).

In reactions (1) and (5) the weights taken were such that there was a slight excess of the complex, $(PPh_3)_2Pt(PhC{\equiv}CPh)$, always present, so that after reaction no HCl gas remained in solution. This avoided the need for measurement of the heats of solution of hydrogen chloride. The solution of the products of reaction (1), therefore, contained both the vinyl complex and a small amount of the acetylene complex.

For the second stage, reaction (5), insufficient HCl was added to convert both the small amount of acetylene complex and the whole quantity of the vinyl complex to the dichlorocomplex. A small amount of the vinyl complex remained in the final solution.

A thermal correction was made for the heat which would have evolved if reaction, of this remaining quantity of vinyl complex, to the dichlorocomplex had occurred.

The 25 ml vessel was used throughout and chloroform was saturated with nitrogen prior to use. Corrected temperature rises for reactions (2), (4), (6), (8) and (9) were calculated by Dickenson's extrapolation and for reactions (3) and (7), by computer calculation. The enthalpy of reaction (10), $\Delta H(10)$, is assumed to be equal to $2\times\Delta H(4)$, and the enthalpy of reaction (11), $\Delta H(11)$, is derived from the enthalpy of reaction (11).

All other procedures were the same as those described previously.

Table 2 shows the enthalpies for each reaction given in the scheme and Table 3 shows the enthalpy data for reaction (5) for each sample taken.

Table 2

Enthalpies of solution of $(Ph_3P)_2Pt(PhC{\equiv}CPh)(c)$ in $[7350CHCl_3]$ reaction 2

$M(Ph_3P)_2PtPhC{\equiv}CPh/g$	0.034420	0.043874	0.037330	0.042751
$\Delta H(3)/kJ\ mol^{-1}$	+3.8	+2.7	+2.2	+2.2

$<\Delta H(2)> = +(2.7 \pm 0.4)\ kJ\ mol^{-1}$

Enthalpies of solution of $HCl(g)$ in $[(Ph_3P)_2Pt(PhC{\equiv}CPh) + 7350CHCl_3]$ reaction 3

$MHCl/g$	0.001703	0.001703	0.001703	0.001703
$\Delta H(4)/kJ\ mol^{-1}$	-82.3	-89.9	-104.6	-84.8

$<\Delta H(3)> = -(90.4 \pm 5.0)\ kJ\ mol^{-1}$

Enthalpies of solution of

$(Ph_3P)_2Pt(Cl)CPh{=}CHPh(c)$ in $[7350CHCl_3](\ell)$ reaction 4

$M(Ph_3P)_2Pt(Cl)CPh{=}CHPh/g$	0.040896	0.033855	0.036333	0.037496
$\Delta H(5)/kJ\ mol^{-1}$ +3.	+3.0	+2.9	+2.1	+2.2

$<\Delta H(4)> = +(2.5\quad 0.3)\ kJ\ mol^{-1}$

Enthalpies of solution of

$(Ph_3P)_2Pt(PhC{\equiv}CPh)(c)$ in $[13{,}000CHCl_3](\ell)$ reaction 6

$M(Ph_3P)_2Pt(PhC{\equiv}CPh)/g$	0.021709	0.021288	0.022414	0.022407
$\Delta H(7)/kJ\ mol^{-1}$	+1.8	+1.2	+1.5	+1.9

$<\Delta H(6)> = =(1.6 \pm 0.2)\ kJ\ mol^{-1}$

Enthalpies of solution of trans-stilbene(c) in

$[(0.5-x)(Ph_3P)_2PtCl_2 + 2x(Ph_3P)_2Pt(Cl)(CPh{=}CHPh) + 13{,}000CHCl_3](\ell)$ reaction 8

$MPhHC{=}CHPh\ /g$	0.005337	0.005177	0.005639	0.004872
$\Delta H(9)/kJ\ mol^{-1}$	+23.3	+18.9	+18.6	+20.9

$<\Delta H(8)> = +(20.2 \pm 1.0)\ kJ\ mol^{-1}$

Enthalpies of solution of cis-$(Ph_3P)_2PtCl_2(c)$ in

$[(2x(Ph_3P)_2Pt(Cl)(CPh{=}CHPh) + 13{,}000CHCL_3](\ell)$ reaction 9

$M(Ph_3P)_2PtCl_2/g$	0.018941	0.019408	0.018548	0.018703
$\Delta H(10)/kJ\ mol^{-1}$	+2.1	+2.4	+1.9	+1.1

$<\Delta H(9) > = +(1.9 \pm 0.2)\ kJ\ mol^{-1}$

Table 3

Enthalpies of solution of

HCl(g) in $[(Ph_3P)_2Pt(PhC{\equiv}CPh) + 13,000CHCl_3](\ell)$, reaction 7.

MHCl/g	0.001703	0.001703	0.001703	0.001703	0.001703
$M\ (Ph_3P)_2Pt$ $(PhC{\equiv}CPh)$/g	0.021709	0.021288	0.024307	0.022414	0.022407
x/g	0.0202	0.0101	0.0824	0.0371	0.0369
$-\Delta H(7)$/kJ mol^{-1}HCl	112.3	97.2	107.5	108.4	112.3
$(0.5-x)\Delta H(6)$kJ	0.8	0.8	0.7	0.8	0.8
$(0.5-x)\Delta H(8)$kJ	9.7	9.9	8.4	9.4	9.4
$(0.5-x)\Delta H(9)$kJ	0.9	0.9	0.8	0.9	0.9
$2x\Delta H(10)$kJ	0.0	0.0	0.2	0.1	0.1
$2x\Delta H(11)$kJ	3.6	1.8	14.9	6.5	6.5
$\Delta H(5)$kJ mol^{-1}	-247.0	-215.1	-242.6	-240.9	-249.2

$\langle\Delta H(5)\rangle = -(239.0 \pm 6)$ kJ mol^{-1}

Table 4

Enthalpies of isomerisation of $(Ph_3P)_2Pt(Cl)(PhC{=}CHPh)$

$M((Ph_3P)_2Pt(Cl)(CPh{=}CHPh)$/g	0.002735	0.003482	0.004024	0.004234	0.002922	0.003114
ΔH(1st transition)/kJ mol^{-1}	+15.90	+15.9	+14.2	+18.4	+16.7	+13.6
ΔH(2nd transition)/kJ mol^{-1}	-28.5	-25.5	-26.8	-29.3	-30.1	-28.0

$\langle\Delta H(\text{1st transition})\rangle = +(15.8 \pm 0.8)$ kJ mol^{-1}

$\langle\Delta H(\text{2nd transition})\rangle = -(28.0 \pm 0.8)$ kJ mol^{-1}

In this latter case the corrections vary for each sample. Table 4 shows the enthalpies of isomerisation of the complex $(PPh_3)_2Pt(Cl)(PhC{=}CHPh)$.

6.3. Discussion

The enthalpy of reaction (1), ΔH(1), is given by

$$\Delta H(1) = \Delta H(3) - \Delta H(4) + \Delta H(2)$$

$$\langle\Delta H(1)\rangle = -(90.2 \pm 6)\ \text{kJ mol}^{-1}$$

The enthalpy of reaction (5), ΔH(5), is given by

$$\Delta H(5) = \frac{1}{(0.5-x)}\ [\Delta H(7) + (0.5-x)\Delta H(6) - (0.5-x)\Delta H(8) - (0.5x)\Delta H(9) - 2x\Delta H(10) + 2x\Delta H(11)]$$

$$\langle\Delta H(5)\rangle = -(239 \pm 6.0)\ \text{kJ mol}^{-1}$$

Enthalpies of sublimation of the complexes $(PPh_3)_2Pt(PhC{\equiv}CPh)$, $(PPh_3)_2Pt(Cl)(PhC{=}CHPh)$ and cis-$(PPh_3)_2PtCl_2$ are not known, but to analyse the data further, it is assumed that they have very similar values. Using an estimated value for the enthalpy of sublimation of 100 ± 5 kJ mol^{-1}, for trans-stilbene gives the value ΔH(12) = $-(139 \pm 16)$ kJ mol^{-1} for the gas phase reaction (12)

$$(PPh_3)_2Pt(PhC{\equiv}CPh)(g) + 2HCl(g) \rightarrow (PPh_3)_2PtCl_2(g) + \text{trans-}CHPh{=}CHPh(g) \qquad (12)$$

In terms of bond dissociation energies for the overall reaction, the relationship may be written

$$\Delta H(1) + \Delta H(12) = D(\text{Pt-Tolane}) - [D_1(\text{Pt-Cl}) + D_2(\text{Pt-Cl})] - [D_1\text{C-H}) + D_2(\text{C-H})] + 2D(\text{H-Cl}) \qquad (13)$$

Where D_1(Pt-Cl) and D_2(Pt-Cl) are the first and second bond dissociation energies in $(PPh_3)_2PtCl_2$ and $[D_1(C\text{-}H) + D_2(C\text{-}H)]$ is the sum of the first and second bond dissociation energies in trans stilbene, given by

$$[D_1(\text{C-H}) + D_2(\text{C-H})] = \Delta H_f^o(PhC{\equiv}CPh,g) - \Delta H_f^o(\text{trans-}CHPh{=}CHPh,g) + 2\Delta H_f^o(H,g).$$

Using the following values for enthalpies of formation

$\Delta H_f^o(H,g) = +(217.97 \pm 0.01)$ kJ mol^{-1} (95); ΔH_f^o(trans-CHPh=CHPh,c) = +(136.9 ± 1.0) kJ mol^{-1} (96); ΔH_f^o(PhC≡CPh,c) = +(312.4 ± 1.2) kJ mol^{-1} (96); and an estimated value for the enthalpy of sublimation of diphenylacetylene of 100 ± 5 kJ mol^{-1} (the same as that estimated for trans-stilbene) the value is derived

$$[D_1(C\text{-}H) + D_2(C\text{-}H)] = (611.4 \pm 12.2) \text{ kJ mol}^{-1}$$

Substitution of this value, and the value D(H-Cl) = 431.57 ± 0.01 kJ mol^{-1} (97) into the equation (13) gives:

$$[D_1(Pt\text{-}Cl) + D_2(Pt\text{-}Cl)] - D(Pt\text{-}Tolane) = 391 \pm 17 \text{ kJ mol}^{-1}$$

For the first stage of the reaction between $(PPh_3)_2Pt(PhC{\equiv}CPh)$ and HCl, the relationship (14) may be written

$$\Delta H(1) = D(Pt\text{-}Tolane) - [D(Pt\text{-}CPh{\equiv}CPh) + D_2(Pt\text{-}Cl) + D_2(C\text{-}H)] + D(H\text{-}Cl), \quad (14)$$

where D(Pt-PhC=CHPh) and D_2(Pt-Cl) are the enthalpies of the successive gas-phase reactions

$$(PPh_3)_2Pt(Cl)(PhC{=}CHPh) \rightarrow (PPh_3)_2PtCl + PhC{=}CHPh \rightarrow (PPh_3)_2Pt + Cl.$$

No value is available for D_2(C-H) but the approximation $D_2(C\text{-}H) = \frac{1}{2}[D_1(C\text{-}H) + D_2(C\text{-}H)]$ gives the value D_2(C-H) = (305.7 ± 6.1) kJ mol^{-1}. Substitution into equation (14) gives

$$D(Pt\text{-}PhC{=}CHPh) + D_2(Pt\text{-}Cl) - D(Pt\text{-}Tolane) = (216.1 \pm 12) \text{ kJ mol}^{-1}$$

Using recent values for the enthalpies of formation (98) of $PtCl_2$(c), $\Delta H_f^o(PtCl_2,c) = -(110.9 \pm 1.0)$ kJ mol^{-1}, and Pt(g), $\Delta H_f^o(Pt,g) = +(565 \pm 5)$ kJ mol^{-1}, the value $[D_1(Pt\text{-}Cl) + D_2(Pt\text{-}Cl)] = (780 \pm 6)$ kJ mol^{-1}, is obtained. Assuming the bond dissociation energies of the platinum-chloride bonds, in gaseous $(PPh_3)_2PtCl_2$, to be the same as those in gaseous $PtCl_2$, and also the relationship $D_1(Pt\text{-}Cl) = \frac{1}{2}[D_1(Pt\text{-}Cl) + D_2(Pt\text{-}Cl)]$, then values for bond dissociation energies, shown in Table 5, can be derived.

Table 5

BOND	COMPOUND	D(Pt-L)/kJ mol^{-1}	
Pt-Cl	$PtCl_2$	390 ± 3	
Pt-Tolane	$(Ph_3P)_2Pt(PhC{\equiv}CPh)$	389 ± 23	
Pt-(PhC=CHPh)	$(Ph_3P)_2Pt(Cl)(PhC{=}CHPh)$	215 ± 23	
Pt-Ph	$(Et_3P)_2Pt(Cl)Ph$	264 ± 15	ref. 99
Pt-(CO)Ph	$(Ph_3P)_2Pt(Cl)\overset{O}{\underset{Ph}{c}}$	172 ± 20	ref. 100

It seems, therefore, that the bond dissociation energies for (Pt-Cl) and (Pt-Tolane) are quite similar.

Finally, measurements of the enthalpies of transformation of the two compounds, A and B, yielded the results $A(c) \rightarrow A(\ell)$ $\Delta H_{453} = +(15.8 \pm 0.8)$ kJ mol^{-1} and $A(\ell) \rightarrow B(c)$ $\Delta H_{491} = -(28.0 \pm 0.8)$ kJ mol^{-1}. For the transformation, $A(c) \rightarrow B(c)$, the value can be calculated, therefore, as $\Delta H(A_c \rightarrow B_c) = -(12.1 \pm 1.6)$ kJ mol^{-1}. This is comparable to the value -(13.4) kJ mol^{-1},(101) for the cis→trans isomerisation of $(PPhMe_2)_2Pt(Cl)Me$ and to the assumption that A and B are simply cis and trans isomers, respectively, of $(PPh_3)_2Pt(Cl)(PhC{=}CHPh)$.

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Appendix 1, Enthalpies of formation of compounds (ancillary data)

The following is a list of enthalpies of formation of compounds used as ancillary data in this thesis. Vales are in kJ mol^{-1}.

Compound (state)	ΔH_f^o	Ref.
$H_2O(g)$	-285.830	C.O.D.A.T.A., 1973.
$CO_2{}^{(a)}(g)$	-393.509	N.B.S. 270-3, 1968.
$NH_4Cl(c)$	-314.43	N.B.S. 270-3, 1968 (ref.62)
$NH_4{}^+(aq)$	-133.13	M. Mansson *et.al.* (ref.53)
$H(g)$	217.97	N.B.S. 270-3, 1968 (ref.62)
$[HCl\ in\ 111H_2O](\ell)$	-210.66	C.A.T.C.H. Tables (ref.43)
$PdCl_2(c)$	-163.2	R.N. Goldberg, L.G. Hepler (ref.36)
$PdCl_4{}^{2-}(aq)$	-523.0	R.N. Goldberg, L.G. Hepler (ref.36)
$(NH_4)_2PdCl_4(c)$	-841.0	This thesis
$Pt(g)$	565	S.J. Ashcroft, C.T. Mortimer (ref.98)
$PtCl_2(c)$	-110.9	S.J. Ashcroft, C.T. Mortimer (ref.98)
$Et_2S(\ell)$	-119.07	W.D. Good *et.al.* (ref.64)
(g)	- 30.97	H.L. Finke *et.al.*(ref.66)
$Et_2Se(\ell)$	- 96.2	W.N. Merten *et.al.*(ref.65)
(g)	- 66.6	H.A. Skinner (ref.67)
$Et_2Te(\ell)$	-100.0	estimate
(g)		
$CH_2{=}CH_2(g)$	- 52.26	J.D. Cox, G. Pilcher (ref.44)
$[CH_3CHO\ in\ 1000H_2O](\ell)$	-165.893	J.D. Cox, G. Pilcher (ref.44)
$C_6H_5C{\equiv}CC_6H_5(c)$	312.4	J.D. Cox, G. Pilcher (ref.96)
(c→g) ΔHsub	100.0	estimate
trans-$(C_6H_5)HC{=}CH(C_6H_5(c)$	136.9	J.D. Cox, G. Pilcher (ref.96)
(c→g) ΔHsub	100.0	estimate
$(C_6H_5)H_2C{-}CH_2(C_6H_5)$(c→g) ΔHsub	84.0	J.D. Cox, G. Pilcher (ref.78)

Compound (state)	ΔH_f^o	Ref.
cis$(C_6H_5)HC{=}CH(C_6H_5)$ (c→g)	ΔHsub 95.0	J.D. Cox, G. Pilcher (ref.78)
Anthracene (c→g)	ΔHsub 105.0	J.D. Cox, G. Pilcher (ref.78)
Phenanthrene (c→g)	ΔHsub 95.0	J.D. Cox, G. Pilcher (ref.78)
$(CN)_2C{=}C(CN)_2$ (c→g)	ΔHsub 81.2	R.H. Boyd (ref.77)

(a) ΔH_f^o CO_2 was not used in this thesis, but values, for other compounds based on static bomb and rotating bomb measurements, depend on this value.

Appendix 2. Glossary of terms

Enthalpy

The First Law of Thermodynamics (or Law of Conservation of Energy) states that the energy of a system is a state function and is single valued. It is necessary to define the properties of a system which describe that system, both in its initial and final states, before interpretation of the accompanying energy change. In addition to heat being exchanged with the surroundings, a system may also perform work. The energy change is given by the sum of the two terms, heat and work, which are recognised as being interconvertible forms of energy. The change in internal energy of the system

$$\Delta U = q - m \qquad (1)$$

where ΔU is the energy change, q is the heat exchanged with the surroundings and m is the work done by the system.

By definition, the derivative of a state function is a complete differential, so that equation (2) represents such a differential

$$dU = \delta q - \delta m \qquad (2)$$

Neither δq nor δm need be complete differentials. For example, if only pressure-volume work is performed by the system.

$$\delta m = PdV$$

Integration of PdV cannot be carried out unless P is known as a function of V. Therefore, for PV work, δm may possess several values and m(PV) is not a state function.

However, d(PV) can be integrated and a new state function formulated, namely, enthalpy (H).

$$dH = dU + d(PV)$$

In the important case where the initial and final pressures are equal, not necessarily at a constant pressure throughout the change, "enthalpy at constant pressure" is referred to:

$$\Delta H = \Delta U + P\Delta V$$

If there is no volume change the heat absorbed is equal to the change in internal energy:

$$q = \Delta U$$

The state functional property of enthalpy is embodied in the Law of Constant Heat Summation as proposed by Hess(99), whereby enthalpies of reaction may be derived from enthalpies of other reactions, provided they combine to yield the required reaction.

Now, since enthalpy has a temperature dependence and also a pressure dependence (see above) then in order to make reactions thermochemically relevant to one another a reference system is used. A '*standard state*' is used and defined as being the naturally occurring isotopic mixture of the element at 25° C and 1 atmosphere pressure or unit fugacity for a gas. Similarly the standard state of a compound is that state in which the compound exists at 25° C and 1 atmosphere pressure. For allotropes one is generally agreed to be the standard state.

Thus the *standard enthalpy of formation* ΔH^o_f of a compound may be defined as the change in heat content in forming one mole of the compound, in its standard state, from its constituent elements in their standard states.

Often it is useful to know the enthalpy of formation of the compound in the gaseous state, this can be accomplished by incorporation of the *molar enthalpy of vaporisation* for a liquid or the *molar enthalpy of sublimation* for solids.

From these terms it is possible to calculate the *bond dissociation energy* D(A-B) of the bond (A-B) in the gas phase reaction

$$AB \rightarrow A + B$$

from the relationship

$$D(A-B) = \Delta H_f^o(A,g) + \Delta H_f^o(B,g) - \Delta H_f^o(AB,g).$$

The symbol D referring, simply, to the enthalpy change at 25^o C. The true bond dissociation energy $D_o^{\ o}$ is defined as the energy change $\Delta E_o^{\ o}$, at absolute zero of temperature, in the ideal gase state, for the reaction AB → A + B, the products being in their ground states. The subscript$_o$ refers to the zero'th vibrational level of the molecule. Generally the values of $D_o^{\ o}$ and D are not too different, and usually corrections are not warranted, due to the imprecise nature of the measurement used, also heat capacity data is often lacking.

If a molecule such as AB_x is considered, where x(A-B) bonds are broken in the gas phase reaction

$$AB_x \quad A + xB$$

The enthalpy of reaction is measured as $x\bar{D}$(A-B) using the same notation as above. Thus the enthalpy obtained when divided by x gives the *mean bond dissociation energy*, $\bar{D}$(A-B). This mean is not necessarily the value for removal of the first or subsequent groups, since different energies of reorganisation may be involved, after each B group is removed.