THERMOCHEMISTRY OF SOME PLATINUM COMPLEXES

by

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I would like to thank all the staff of the chemistry department for generously answering innumerable requests, for everything from chemical principles to paper clips.

I am especially grateful to Professor Colin Mortimer, whose impetus, optimism and clear thinking made this work possible.

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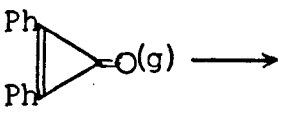
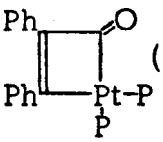
ABSTRACT

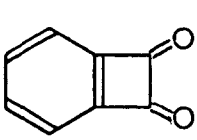
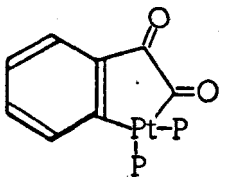
The heats of a number of reactions of platinum complexes have been measured by solution calorimetry. These results have been used, in conjunction with measured heats of sublimation, to derive the heats of the following reactions . (In the equations, P stands for PPh_3, and P* stands for PMe_2Ph.)

(1) $P_2Pt(C_2H_4)(s) + CS_2(g) \longrightarrow P_2Pt(CS_2)(s) + C_2H_4(g)$

The heat of reaction (1), $\Delta H(1) = -44.0 \pm 1.7$ kJ mol^{-1}, indicates that the bond dissociation energy $D(Pt-CS_2)$ is greater than $D(Pt-C_2H_4)$ by 44 kJ mol^{-1}.

The heats of reactions (2) and (3), $\Delta H(2) = -94.8 \pm 5.5$ kJ mol^{-1}, $\Delta H(3) = -57.4 \pm 4.8$ kJ mol^{-1}, in which platinum is inserted into cyclic ketenes to produce cyclic platina-ketenes, suggest that the relief of ring strain in converting the 3-membered into the 4-membered ring is rather greater than that when converting the 4-membered ring into the 5-membered.

(2) $P_2Pt(stilbene)(s)$ +  (g) ⟶  (s) + stilbene (g)

(3) $P_2Pt(stilbene)(s)$ +  (g) ⟶  + stilbene (g)

From the heats of reactions (4) and (5), $\Delta H(4) = -114.1 \pm 2.0$ kJ mol^{-1}, $\Delta H(5) = -42.1 \pm 1.9$ kJ mol^{-1}, it has been calculated that the heat of isomerisation from cis to trans-P_2PtI_2 is -19 ± 5 kJ mol^{-1}. This

result and the heat of reaction (6), $\Delta H(6) = -78.9 \pm 2.0$ kJ mol^{-1}, have been used to show that the bond dissociation energies $D(Pt-CH_3)$ and $D(Pt-I)$ in these complexes are very similar.

(4) $P_2Pt(C_2H_4)(s) + I_2(s) \longrightarrow$ trans-$P_2PtI_2(s) + C_2H_4(g)$

(5) $P_2Pt(C_2H_4)(s) + C_2H_4I_2(s) \longrightarrow$ cis-$P_2PtI_2(s) + 2C_2H_4(g)$

(6) $P_2Pt(C_2H_4)(s) + CH_3I(g) \longrightarrow$ cis-$P_2Pt(CH_3)I(s) + C_2H_4(g)$

From the heat of reaction (7), $\Delta H(7) = -141.9 \pm 6.3$ kJ mol^{-1}, the value $D(Pt-tcne) = 142$ kJ mol^{-1} in $P_2{*}Pt(CH_3)Cl(tcne)$, where tcne stands for tetracyanoethene, is obtained. This is much less than the value of $D(Pt-tcne)$ in $P_2Pt(tcne)$.

(7) $P_2{*}Pt(CH_3)Cl(s) + tcne(g) \longrightarrow P_2{*}Pt(CH_3)Cl(tcne)(s)$

(8) $P_2PtHCl(s) + tcne(g) \longrightarrow P_2Pt(tcne)(s) + HCl(g)$

From the heats of reactions (7) and (8), $\Delta H(8) = -112 \pm 6.0$ kJ mol^{-1}, it has been shown that in complexes of the type P_2PtRCl, the value of $D(Pt-CH_3)$, when $R = CH_3$, is much less than $D(Pt-H)$, when $R = H$.

The heat of reaction (9), $\Delta H(9) = -78.9 \pm 2.3$ kJ mol^{-1}, has been determined by reacting $PtCl_3$(9-methyladenineH) and potassium tetrachloro--platinate (II) separately with aqueous potassium cyanide.

(9) 9-MeAdHCl(aq) + K_2PtCl_4(aq) $\longrightarrow$ $PtCl_3$(9-MeAdH)(s) + 2KCl(aq)

The heats of sublimation of trans-stilbene, $\Delta H_{sub} = 95.4 \pm 3.1$ kJ mol^{-1}, benzocyclobutenedione, $\Delta H_{sub} = 88.6 \pm 1.9$ kJ mol^{-1}, and phenylcyclobutenedione, $\Delta H_{sub} = 105.2 \pm 3.6$ kJ mol^{-1}, have been measured by a Knudsen technique, using glass effusion cells in a thermobalance.

INTRODUCTION

Interest and research in the organometallic chemistry of platinum springs both from the wide variety of compounds which can be prepared and from their present or potential use as homogeneous catalysts and anti--cancer drugs. Preparative and structural chemistry has been followed by calorimetry designed to measure the strengths of bonds between platinum and organic ligands (1-9).

The aim of the present work was to determine the dissociation energies of a number of bonds made by platinum in its complexes, by the measurement of heats of reaction using solution calorimetry. Many of the reactions are related to bis(triphenylphosphine)(ethene) platinum (0), $Pt(PPh_3)_2(C_2H_4)$, the "ethene compound", as indicated in figure 1. The reactions may be classified into three groups.

(1) Substitution of ethene by another alkene or unsaturated compound, the oxidation number of the platinum remaining zero. Examples are the reactions of the ethene complex with carbon disulphide or tetracyanoethene (tcne).

(2) Cycloplatination reactions, in which the first stage is a simple substitution, the ethene or other alkene being replaced by a C=C group which forms part of a three- or four-membered ring, for example phenylcyclobutenedione, pcbd. This stage may be followed by the insertion of the platinum into the ring, the platinum-olefin bond being replaced by two platinum-carbon bonds which have principally a σ-character, but which may have a consid--erable π component because of the delocalisation of the electrons in the ring and its substituents. In this second step the oxidation number of the

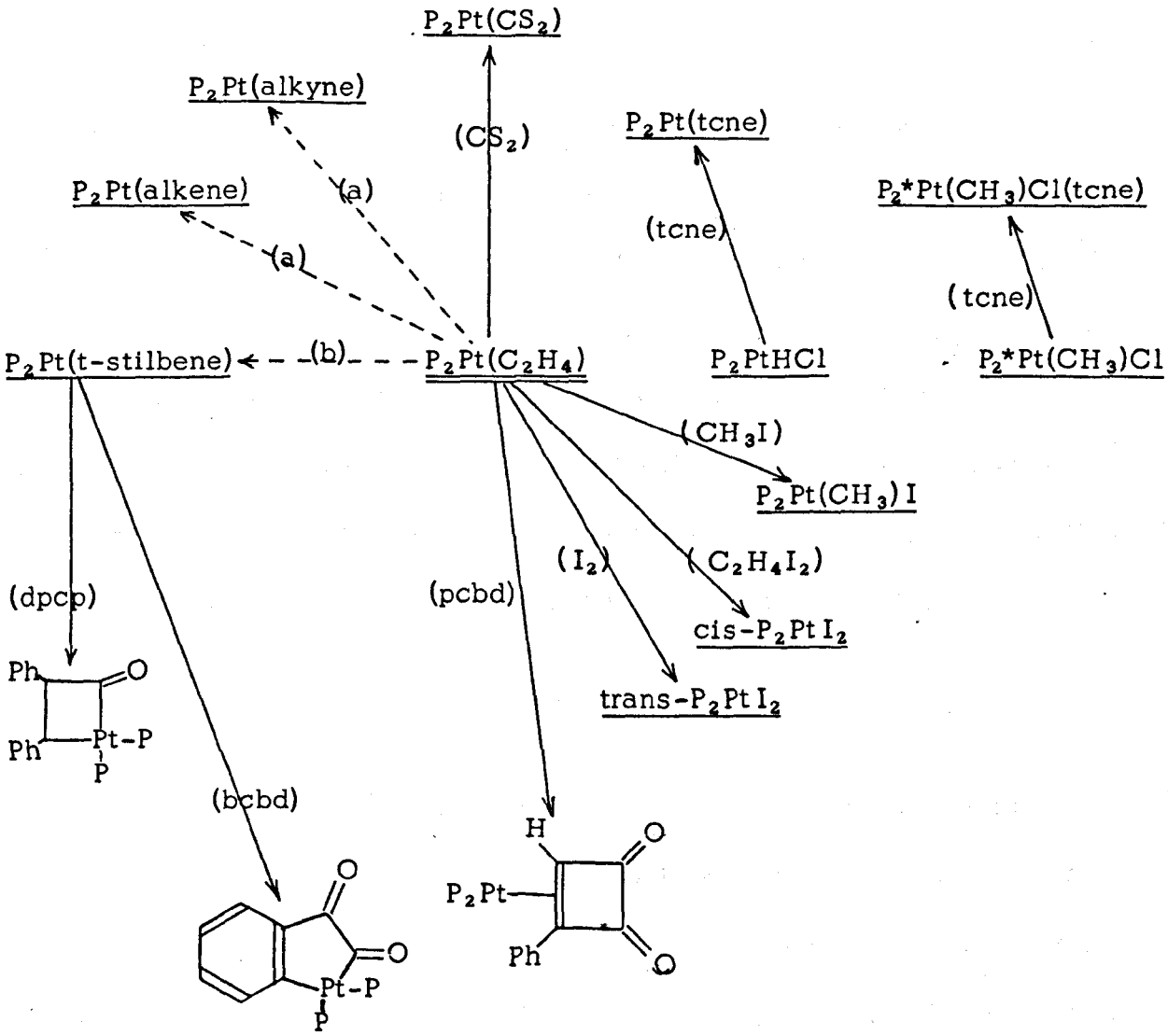


Figure 1. Some reactions of platinum compounds for which heats of reaction have been determined.

Reactions investigated in this work are indicated by full lines, while those that have been investigated by other workers are shown by broken lines. (a) signifies Evans et al. (1-4), (b) signifies Lister et al.(5-7).

platinum is increased from zero to +2. This is illustrated by the reaction (on the left of figure 1) between P_2Pt(trans-stilbene) and diphenylcyclo--propenone, dpcp.

(3) Oxidative addition reactions, in which the platinum forms new bonds by addition or substitution, and is again oxidised to the +2 state. An example is the reaction of the ethene compound with iodomethane to form $P_2Pt(CH_3)I$.

The reverse of these oxidative addition reactions, a reductive elim--ination, is illustrated by the reaction between P_2PtHCl and tcne, in which hydrogen chloride is eliminated. In the similar compound $P_2Pt(CH_3)Cl$ reaction with tcne yields the intermediate addition compound $P_2Pt(CH_3)Cl$(tcne). Thermochemical data for these reactions may provide information about the reasons for the differences between them.

The most usual approach to the description of bonding in the alkene compounds of platinum is that developed by Dewar, Chatt and Duncanson (10,11) and modified by Hartley (12). This theory suggests that the bond consists of two distinct components, σ and π (figure 2). The σ bond is made by overlap of a filled π orbital of the ethene with an unfilled $5d6p^2$ ($5d_{xy}+6p_x+6p_y$) hybrid orbital of the platinum. The π bond consists of a movement of charge in the reverse direction, through overlap of a $5d_{x^2-y^2}$ orbital of platinum with the unfilled antibonding π^* orbital of ethene.

The observed structure of the ethene compound can be largely explained by this theory. X-ray analysis (13) shows that it consists of discrete monomeric molecules, in which the platinum atom lies in the centre of a distorted square whose corners are the phosphorus and ethene carbon atoms. The 'square' is not quite planar, as the P-Pt-P and C-Pt-C

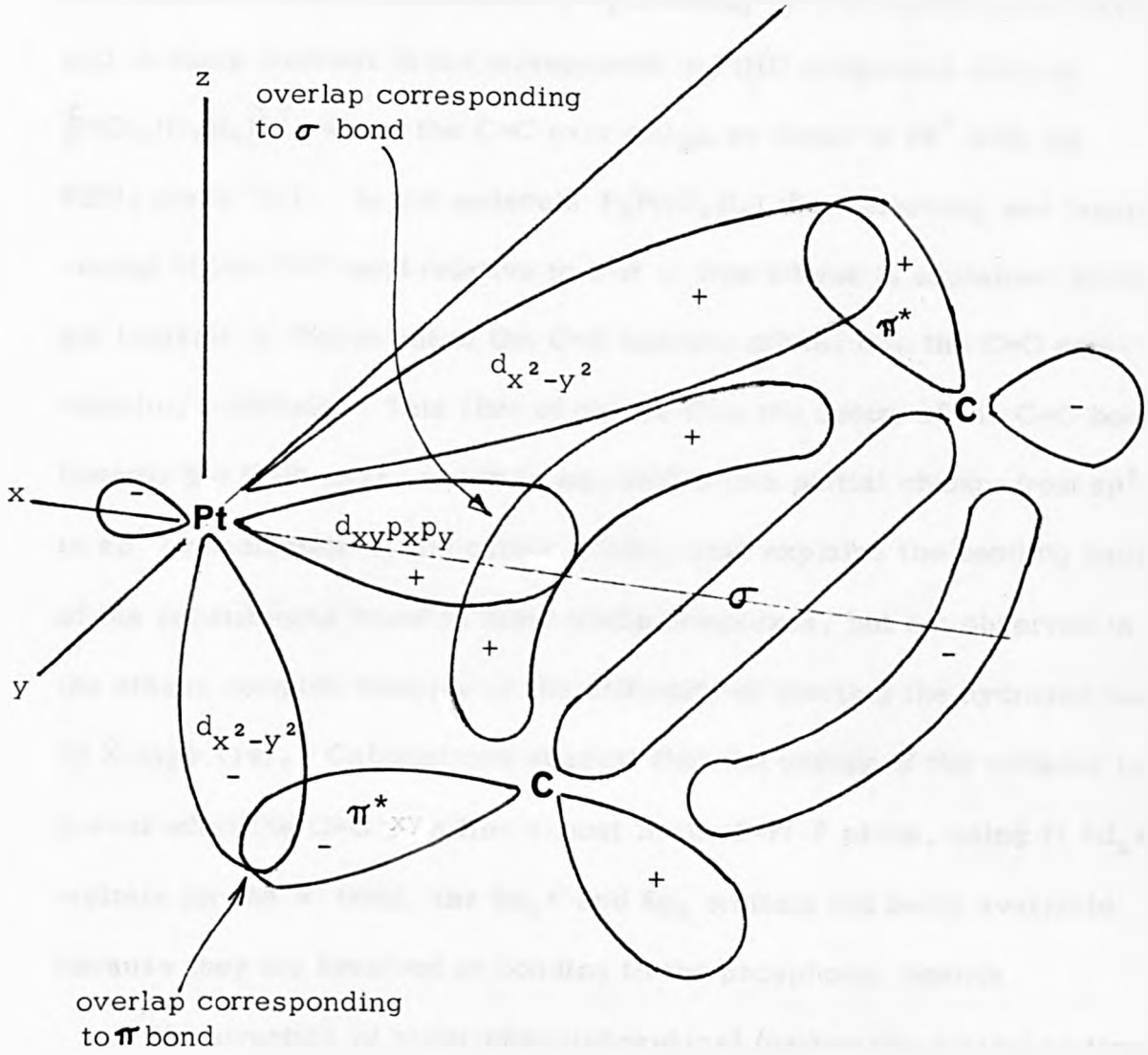


Figure 2. Schematic diagram of bonding in $P_2Pt(C_2H_4)$.

planes are offset by 1.6^{o}, a smaller deviation than those found in the structurally-similar compounds $P_2Pt\{C_2(CN)_4\}$ (8^{o}) or $P_2Pt(C_2Cl_4)$ (12^{o}), and in sharp contrast to the arrangement in Pt(II) complexes such as $[PtCl_3(C_2H_4)]^-$, where the C=C axis makes an angle of 84^{o} with the $PtCl_3$ plane (11). In the molecule $P_2Pt(C_2H_4)$ the weakening and length--ening of the C=C bond relative to that in free ethene is explained by the net transfer of charge out of the C=C bonding orbital into the C=C anti--bonding orbitals. This flow of charge from the centre of the C=C bond towards the C-Pt axes, which is equivalent to a partial change from sp^2 to sp^3 hybridisation of the carbon atoms, also explains the bending back of the substituents found in other olefin complexes, but not observed in the ethene complex because of the difficulty of locating the hydrogen nuclei by X-rays.(14). Calculations suggest that the energy of the complex is lowest when the C=C axis lies almost in the P-Pt-P plane, using Pt $5d_{x^2-y^2}$ orbitals for the π bond, the $5d_{z^2}$ and $6p_z$ orbitals not being available because they are involved in bonding to the phosphorus ligands.

The structure of bis(triphenylphosphine) (carbon disulphide) platinum (0), $P_2Pt(CS_2)$, is also known (15,16) and one intention of this work was to relate this information to the strength of the Pt-CS_2 bond.

A combination of structural and bond-strength data for compounds involved in the cycloplatination reactions may help to indicate which the reaction proceeds to the platina-cyclic product with some reagents but with others stops at the first stage of simple substitution.

A further aspect of the work reported in this thesis is the determination of the heat of the reaction between an aqueous solution of an organic base, 9-methyl adenine, and potassium tetrachloroplatinate (II). This reaction is thought to resemble the interaction of DNA with those platinum (II) complexes which have been found to suppress the growth of tumours.

To clarify the meanings of the phrases heat of reaction, heat of formation, bond strength, bond energy and bond dissociation energy, definitions of these terms are now considered.

Heats of reaction.

The heat, or enthalpy change, of a reaction, $\Delta H_{r,T}$ is the difference in heat content between the products and reactants, that is, the quantity of heat absorbed when the reactants are converted into products at constant temperature. To define the enthalpy change one must specify the following.

1. The amount of reaction, by choosing one reagent or product and quoting the heat per mole of that species,

2. The physical states of all the substances involved, i.e. whether they are solids, liquids or gases, whether pure or in solution, and the concentration of the solution, and

3. The temperature of the reaction.

Since the heat content is a function of state, the enthalpy change of a chemical reaction is independent, real or hypothetical, by which the reaction proceeds. The enthalpy change of the reverse reaction is equal in size and opposite in sign to that of the forward reaction. Thus the enthalpy change of any reaction, however impossible to realise, may be found if those for a series which together lead from the same starting state to the same final state can be measured.

The standard state of a gas is that of the hypothetical ideal gas at one atmosphere pressure, when the heat content is the same as that of the real gas at zero pressure. The standard state of a liquid or solid is the pure substance, liquid or crystalline, under one atmosphere pressure.

Enthalpy changes of reactions between substances in their standard states are standard heats of reaction, denoted $\Delta H^{\circ}_{r,T}$. The temperature remains to be specified; in this thesis if there is no subscript the enth--alpy change is that for 25°C, 298.15 K.

The standard heat of formation of a substance is the heat of the reaction in which it is formed from its constituents, all being in their standard states. From heats of formation, any other standard heat of reaction may be calculated by the the formula

$$\Delta H^{\circ}_{r} = \Sigma \Delta H^{\circ}_{f} \text{ (products)} - \Sigma \Delta H^{\circ}_{f} \text{ (reactants)}$$

When standard heats of formation are not known, heats of reaction must be measured directly or calculated from cycles of equivalent reactions.

In this thesis the quantity of reaction almost always refers to one mole of substance, calculations being based on IUPAC 1975 atomic weights (17).

The states of pure substances are defined by the symbols (s), (l), and (g) for solid, liquid and gas. The solids were usually microcryst--alline, the crystals being visible under a microscope but possibly differing slightly in energy from a single crystal of defined form. Solutions are denoted by square brackets containing the symbols for the principal chemical substances present and their molar ratios, there being no significance in the order in which the substances are listed. No attempt has been made to show all the chemical species that may be formed by interaction in solution, so that, for example, a solution of one mole of hydrogen chloride in a thousand moles of water would be written as $[HCl, 1\,000\ H_2O](l)$, although it contains hydrated hydrogen and chloride

ions etc.

Measurements at temperatures other than 298.15 K may be converted to that temperature by using Kirchhoff's equation

$$\Delta H_{r,T_1} - \Delta H_{r,T_2} = \int_{T_1}^{T_2} \Delta C_p \, dT$$

where $\Delta C_p = \Sigma C_p$ (products) $- \Sigma C_p$ (reactants)

The value of ΔC_p may be found by measuring the energy equivalent of the mixture before and after reaction, or from tables of heat capacities, which, however, do not include values for most solutions or for the less common pure substances. For small temperature differences $(T_2 - T_1)$, ΔC_p may be assumed to be constant over the temperature range,[18] and the best single value to use is that for the mean temperature $(T_1 + T_2)/2$. Over wider temperature ranges the specific heats vary enough to make necessary a more detailed expression for each specific heat capacity, such as the following, in which A, B, and C are experimentally-determined constants.

$$C_p = A + B.T + C.T^2$$

If exact values of the heat contents of reactants and products at the temperatures concerned have been published they may be used in place of Kirchhoff's equation, since

$$\Delta H_{r,T_2} = \Sigma\left[\Delta H_{T_1-T_2}\right] \text{(reactants)} + \Delta H_{r,T_1} + \Sigma\left[\Delta H_{T_2-T_1}\right] \text{(products)}$$

The calorimetry reported in this thesis has all been carried out over a small temperature range close to 298.15 K (see page 59), so a constant value of ΔC_p might be used for correction to that standard temperature. In fact even these corrections were not made, because of the lack of data and because all measurements were made at a temperature

within approximately 0.1 K of 298.15 K, as explained on page 59. Similarly no attempt has been made to convert enthalpies measured at 298 K to hypothetical values at absolute zero, since heat capacity data are not available.

Bond strengths and bond energies.

The idea of the strength of a bond between atoms in a molecule may be a composite one, based on the concepts of the length, resistance to stretching, and resistance to breaking of a bond. These rather ill-defined properties are essentially different. However, although the experiments by which they may be measured are of different kinds, one may observe correlations between the results derived from them

The lengths of bonds are found be measuring internuclear distances in crystal structures derived from X-ray diffraction. Electron density maps may also show the distribution of charge between the nuclei.

Force constants of bonds are derived from infra-red and Raman spectroscopy.

The resistance to breaking of a bond may be defined in two distinct ways.

1. Thermochemical bond energies, or bond energy terms, E, are defined by equating their sum to the heat of formation of a gaseous mole-cule from its separate gaseous atoms. E is not a direct measure of the strength of the bond between the atoms as they are present in the molecule, but represents a fraction of the difference in energy between the free atoms in their ground states and the molecule, in which the distribution of elec-tronic charge around each atom is very different. In this way E is unlike the ionic lattice energy, which in many cases is successfully calculated,

using Coulomb's law, by assuming that the free ion retains its shape and charge within the lattice. Bond energy terms correspond to single measurable quantities only in the simplest cases, i.e. diatomic molecules. In a slightly more complicated molecule such as water, the two O-H bonds are allocated equal energy.

$$H_2O\,(g) \longrightarrow 2\,H\,(g) + O\,(g)\,, \quad \Delta H_r = 2E(O\text{-}H) = 934\ kJ\ mol^{-1} \qquad (19)$$

When there is more than one type of bond within the molecule, the energy may not be divided with any certainty between them, except by assuming that their energy remains the same from one molecule to another. This assumption gives results which are almost self-consistent in simple molecules, but has to be modified to allow for multiple bonds, different oxidation numbers, and different geometries. The larger and more complex a molecule is, the less suitable is the method of bond energy terms for arriving at the strength of a single bond of a particular kind within it. The calculation requires knowledge of the heat of formation of the compound, of the heats of atomisation of all the elements concerned, and of the bond energy terms appropriate to all the other bonds in the molecule. All the errors in these quantities contribute to the uncertainty of the unknown term.

2. The bond dissociation energy, D, is more specific; it is the internal energy change, ΔU_o, for breaking a particular bond while leaving the rest of the molecule united although probably somewhat reorganised, the reaction being carried out at 0K. Measuring the change at the temperature zero removes any contribution from rotation or translation, but the difference in the zero-point energy of vibration of reactants and products remains, and must be subtracted from ΔU_o if the purely electronic

energy change associated with the breaking of the bond is to be evaluated (19).

The energies required to break successive bonds between identical pairs of atoms within a single molecule are not the same. One cannot, for example, speak of "the bond dissociation energy, D(O-H)" in general since even in water there are two different values:-

$$H_2O\,(g) \longrightarrow OH\,(g) + H\,(g)\ , \quad \Delta U_o = D_1 = 497\ kJ\ mol^{-1}$$
$$OH\,(g) \longrightarrow O\,(g) + H\,(g)\ , \quad \Delta U_o = D_2 = 421\ kJ\ mol^{-1} \quad (19)$$

Similarly the value of D(O-H) will not be the same in ethanol as in acetic acid.

Many thermochemical measurements (including all the heats of reaction described in this thesis) are made at constant pressure and some temperature T, so the thermodynamic function that may be derived from them is the change in heat content.

$$\Delta H_T = \Delta U_T + p\Delta V$$

To show the relative sizes of the terms in the equation above, one may consider a reaction at 298 K in which one mole of gas which obeys the gas laws is formed. In this case

$$p\Delta V = R.T = 2476\ J\ mol^{-1} \simeq 2.5\ kJ\ mol^{-1}\ .$$

Since ΔU is commonly several tens of kJ mol^{-1} for a reaction involving breaking bonds, the difference between ΔH and ΔU is relatively small. If the reaction causes no change in the number of moles of gas, the $p\Delta V$ term is due entirely to deviations from the gas laws, or to differences in the molar volumes of the solids and liquids consumed and formed. Its value is then much smaller, $\simeq 10^{-3} R.T$, i.e. 1 to 10 J mol^{-1}, and may

be ignored. In practice even where this is not the case many thermochem-
-ists refer to heat content changes, ΔH, as "bond dissociation energies",
a convention which will be followed in this thesis.

Calorimetric methods of determining bond dissociation energies.

(1) Dissociation energies from heats of formation.

The bond dissociation energy , D(A-B), is the heat of a chemical reaction.

$$AB\ (g) \longrightarrow A\ (g) + B\ (g)$$

It is related to the heats of formation of the species involved as follows.

$$\Delta H_r = \Delta H_f\,(A,g) + \Delta H_f\,(B,g) - \Delta H_f\,(AB,g)$$

A value of D(A-B) can be calculated if the heats of formation of AB, A and B are known. Where the species A and B are stable entities, it may be possible to use calorimetry either to determine the enthalpy of the dissoc--iation process directly or to determine the enthalpies of formation of AB, A and B in separate experiments. Thus the bond dissociation energy corresponding to the heat of the reaction below may be determined by measuring the heats of formation of the ligand L, the complex PtX_2L, and the complex without that ligand, PtX_2.

$$PtX_2L\ (g) \longrightarrow PtX_2\ (g) + L\ (g)$$

Such a method seems particularly suitable for complexes of the type $Pt(PPh_3)_2$(alkene), because bis(triphenylphosphine) platinum (O), $Pt(PPh_3)_2$, is sufficiently stable to be isolated and purified (20) as are the alkenes and some product complexes. The heats of formation of the more common alkenes and other unsaturated compounds which act as ligands are of course already known, leaving only those of the platinum compounds to be deter--mined. Having established a value for the heat of formation of $Pt(PPh_3)_2$, determination of each bond dissociation energy would require only one

further heat of formation, supported by heats of sublimation and vapor-
-isation.

The heats of formation of the platinum complexes might be found from heats of combustion. Kharchevnikov and Rabinovich (8) have measured the heats of combustion of five platinum (IV) complexes containing iodide, methyl and cyclopentadienyl radicals, and pyridine ligands, apparently using static bomb calorimeters. They analysed the products of combustion quantitatively for carbon dioxide, nitric acid, crystalline iodine and crystalline platinum. Water was the only other product they reported. Unfortunately several arguments suggest that the prospects of obtaining accurate bond dissociation energies by measuring heats of com-
-bustion of platinum (0) complexes containing phosphines are not bright.

Firstly: bomb calorimetry undertaken with the aim of determining bond energies must be extremely accurate, particularly if the compound has a large molecular mass and heat of combustion. One can estimate the heat of combustion of, for example, the ethene complex $P_2Pt(C_2H_4)$, from the known values for triphenyl phosphine and ethene. If the estimated heat of combustion is $\simeq 21\,000$ kJ mol^{-1}, the energy of a single bond which might be $\simeq 300$ kJ mol^{-1} is only 1.5 % of the total, so that an uncertainty of only 0.15 % in the heats of combustion of the product and reactant complexes would lead to an uncertainty of 10 to 20 %, i.e. 30 to 60 kJ mol^{-1}, in the bond dissociation energy. This need for accuracy is a well-known feature of bomb calorimetry, which has particular relevance here due to the probable difficulty of achieving complete combustion, and of obtaining pure samples of the complexes. Many must be used as prepared, since they are unstable not only with respect to reaction with oxygen, but to decomposition during chromatography or adduct formation during recrystallisation.

Secondly: it has been found that the platinum phosphine complexes are not cleanly and completely oxidised during CHN microanalysis (21). This difficulty has been largely overcome, by using maximum temperatures (980-990^{o}C) and oxygen flow (60-80 cm^3 min^{-1}), with a layer of tungsten (VI) oxide covering the sample so that hydrogen and carbon are now sufficiently well oxidised for analysis results to fall within the usual error of the instrument, i.e. 0.3 %. However in spite of the higher oxygen pressure, conditions within a bomb calorimeter are otherwise less likely to achieve complete oxidation. Bomb calorimetry of metal complexes is notoriously difficult; Long and Norrish (22) in fifty separate combustions of zinc diethyl used twenty variations of technique but still failed to achieve complete combustion, and so admitted an uncertainty of "several tenths of one percent". While this failure may have been partly caused by their glass-ampoule technique, similar difficulties were encountered by Pope and Skinner (23) who, when reporting their work on tetraphenyl tin, stated that "a technique which would guarantee successful combustion was not found".

Thirdly: a further difficulty is due to uncertainty about the final state of platinum after combustion of its complexes, in spite of Kharchevnikov and Rabinovich's results, particularly when the complexes contain phosph--orus which may lead to the formation of platinum phosphide.

Although platinum is the standard material for crucibles and bomb linings, and might therefore be thought to be left as the metal, its oxides PtO, PtO_2, PtO_3 and possibly Pt_2O_3 are known(24). If the metal is held at high temperatures in air or oxygen the thickness of the (PtO_2) oxide layer increases very slowly, its growth rate being limited by diffusion, unless the pressure is low enough for the oxide to evaporate (25). The fate of this volatile oxide depends on the temperature of the surface on

which it condenses. At higher temperatures it decomposes to platinum metal, while on cooler surfaces it condenses as the dioxide (26). These observations of the bulk metal have only limited relevance to the behaviour of burning complexes, though they do suggest that the apparent inertness of platinum towards oxygen is due to the kinetics of transport in the solid state rather than to thermodynamic stability.

More pertinent are measurements of oxygen uptake by platinum sponge (27). When heated to 430-600°C in 8.5 to 310 atm. of oxygen, the solid took up between 7.8 and 9.4 % of oxygen, corresponding to oxygen to platinum atomic ratios between 1 : 1 and 4 : 3. Lafitte and Grandadam (28) found that platinum sponge heated to 450-460°C for six hours under 40 atmospheres of oxygen took up only approximately 2% of oxygen by weight, but platinum black held for a longer period at the same temperature under 130 atmospheres took up nearly 14 % by weight. In the latter conditions most of the metal was oxidised to PtO_2, which could be separated from the PtO residue. Taken together, these observations suggest that the final state of the platinum from a complex burned in a bomb would be uncertain, and considerable care would have to be taken over the analysis of the products, which might contain Pt, PtO, and PtO_2, as well as platinum phosphide.

Cox and Pilcher (18) recommend for all work of high accuracy the use of a moving bomb, with the aim of producing an analysable and reproducible homogeneous solution of reaction products. The advantage of this type of apparatus is only realised if a suitable solvent can be found. Lafitte and Grandadam (28) were able to dissolve PtO, but not PtO_2, in aqua regia; a liquid that would dissolve the products of combustion of platinum complexes without attacking the bomb itself might well be hard

to find.

One further finding that supports these pessimistic conclusions: the mass of residue left after combustion microanalysis of complexes has usually been greater than the calculated platinum content, presumably due to the formation of platinum phosphide, even when the carbon and hydrogen analysis showed that the compound was reasonably pure and that the organic content had burned completely.

It is possible that reaction schemes may be devised by which heats of formation of compounds of the type PtX_2L may be determined by measurement of the heats of solution reactions rather than by combustion, but none has yet been reported.

(2) Dissociation energies from heats of reaction.

The direct determination of bond dissociation energies from heats of reaction in which only the particular bond of interest is broken usually has the advantage that the quantity of heat being measured is of the same order of magnitude as the bond dissociation energy itself; it follows that the uncertainty produced by a given percentage error in the experimental observation is not a disproportionately large fraction of the calculated bond energy.

(a). Differential Scanning Calorimetry.

Perhaps the type of reaction most directly relevant to the determination of bond dissociation energies is the dissociation of a solid or liquid complex.

$$MX_2L \longrightarrow MX_2\,(s) + L\,(g)$$

Enthalpies of reactions of this sort may be measured by differential scanning calorimetry (DSC). It is applicable only when the complex dissociates by a clearly-defined reaction which is not complicated by simultaneous

melting or boiling, or by more drastic decomposition. The measured enthalpy change is calculated from the area traced by a recorder pen. The determination of the area by planimeter, whose readings are reproducible to only 5 - 10 %, or by cutting and weighing, is responsible for considerable uncertainty. In spite of these limitations DSC may be used with great effect, provided that it is possible to obtain values for heats of sublimation of solid species, as shown by McNaughton (29). Unfortunately, scanning calorimetry is not suitable for the determination of bond energies in the complexes studied in this thesis, since they melt and decompose simult--aneously to ill-defined products.

(b). Solution calorimetry.

Alternatively, it may be possible to use a suitably designed calorimeter to measure the heat of a reaction in solution, in which the bond of interest is made or broken. The reaction may consist of addition or replacement, e.g.

$$P_2Pt\ (s) + CS_2\ (l) \longrightarrow P_2Pt(CS_2)\ (\text{in } CS_2 \text{ solution})$$

$$P_2Pt(C_2H_4)\ (s) + C_2(CN)_4\ (\text{solution}) \longrightarrow P_2Pt\{C_2(CN)_4\}\ (\text{solution})$$

The reactions of this sort that have been studied in this work have the following characteristics.

(i) The quantities of heat are small; rarely more than 5 Joules and frequently less than 1 Joule. This follows from the comparatively small masses of platinum complex available for a series of measurements, and in some cases from the limited solubility of the compounds.

(ii) The reactions may be exothermic, as are the heats of most of the reactions involving addition or replacement of ligands, and heats of solution of gases, or endothermic, as is the case for the heats of solution of most solids.

(iii) The rate of reaction and consequently the rate of heat change varies widely, the process being substantially complete in anything from a few seconds to many minutes or occasionally hours.

The calorimeter should be of a design capable of measuring such heat changes to an accuracy of ± 0.1 %. In addition, it must be such as to allow the following operations.

(i) Addition of accurately-known small masses of pure gases, liquids or solids into the reaction vessel.

(ii) Use of a volatile solvent and exclusion of oxygen and water vapour which may react with one or more components. The calorimeter must therefore be sealed and must contain as little vapour space as possible.

(iii) Use of reactive solvents and reagents, such as acids, oxidising and complexing agents, all of which must be resisted by the materials used for the calorimeter vessel, stirrers and so on.

No single calorimeter can answer these conflicting requirements, particularly if it must be simple and rapid to use, so that a complete investigation, which may require six or more repetitions of up to five contributing reactions, may be carried out in reasonable time. The following is a brief review of various types of calorimeter with an indication of their advantages and disadvantages with regard to their use in measuring the heats of the reactions of platinum complexes set out the the introduction, figure 1.

Calorimeters for reactions in solution.

The principal difficulty in calorimetry, particularly when such small quantities of heat ore involved, lies in distinguishing between heat and temperature changes produced by the process under study and those produced by other processes such as stirring and by flow of heat from the environment. Many calorimeters are designed to minimise this heat flow, but the most obvious solution, that of completely insulating the calorimeter from the environment, is not possible, since no barrier is a completely effective insulator, and the calorimeter must have a removable lid, a stirrer, thermometer and heater, all of which provide channels for the flow of heat.

Adiabatic calorimeters minimise heat flow by surrounding the calorimeter with a 'shield' whose temperature is made to follow that of the calorimeter contents as closely as possible. Stubblefield (30) used a thirty-junction thermel between his tantalum calorimeter and shield with a proportional controller supplying heat to the shield. The temperature of the shield was apparently within 10^{-5} °C of that of the calorimeter except during calibration or reaction (an important exception) and the heat flow resulting from any discrepancy was reduced by polishing both shield and calorimeter and evacuating the space between the two to 10^{-4} to 10^{-5} torr. There was apparently no provision for cooling the shield to follow an endothermic reaction; an outer jacket was held at a constant 23°C, approximately 2° below the inner one, so that a reduction of the heat supply to the inner shield would presumably produce slow cooling.

Prosen and Kilday's adiabatic solution calorimeter (31) was similar in its use of thermel-controlled adiabatic shield, vacuum insulation, and outer jacket at constant temperature. Again, the temperature of the

shield did not consistently match that of the calorimeter; during fast reactions differences of 2.5×10^{-3}°C, and during calibrations up to 1×10^{-3} °C occurred. The heat leakage modulus was 3×10^{-3} min^{-1}, three times higher than that claimed by Stubblefield, in spite of special heaters attached to the various tubes carrying stirrer and leads through the shield. However, the total correction for heat losses, found by integrating the area on a graph of temperature discrepancy against time, was only 3×10^{-4} Joules. Again, there was no specific provision for endothermic reactions. This calorimeter contained 300 cm^3 of liquid and was used for strongly exothermic reactions such as that between sulphuric acid and sodium hydroxide solutions, in which 50 to 100 Joules of heat were produced. In this context the heat losses were negligible; even the 0.02 J uncertainty in the energy of opening the sample container was barely significant. A smaller adiabatic calorimeter with an equally effective shield and less energetic sample introduction would be suitable for at least the exothermic reactions of complexes.

Isothermal calorimeters also reduce heat flow by minimising the tem-perature difference between the calorimeter and its surroundings, but by a process which is the opposite of that just described. Here it is the calorimeter which is heated or cooled to keep its temperature equal to that of theisothermal jacket.

The phase-change or Bunsen calorimeter uses a mixture of liquid and solid, such as water and ice, to maintain the constant temperature and to indicate the quantity of heat evolved in the calorimeter reaction. The replacement of ice by diphenyl ether, whose melting point is 300.02 K, makes the method suitable for measuring heats which can be corrected to

298.15 K without serious error; the smaller specific latent heat of the ether also makes the method more sensitive. If the calorimeter is sur-rounded by a vacuum jacket and a closely-controlled thermostat very little melting or freezing of the ether occurs except as a result of heat absorbed or evolved by the calorimeter contents. The quantity of heat is measured by observing the difference in volume caused by the phase change; an equal volume of mercury is displaced and measured either by weighing or by observing its motion in a capillary.

The phase change calorimeter has been used for slow reactions such as polymerisation (32), measuring quantities of heat up to 125 J or more if precautions are taken to keep the 'mantle' of solid intact. When used for these quantities of heat, weighing and capillary observation give similar precision (33); a calorimeter designed for smaller heats might achieve greater precision by using a finer capillary, or a series of different tubes, none of which would need to be finer than those routinely used for thermometers. As the length of the measurable section is 200 to 300 mm, and the precision of measurements with a travelling microscope approximately 0.01 mm, measurements might conceivably be made to a precision of 0.005%. The advantages of this type of calorimeter are its simplicity and independence from expensive electronic equipment (if electrical calibration is dispensed with) and its ability to measure large or small amounts of heat, absorbed or evolved, from fast or slow reactions. The principal disadvantage appears to be the time and care needed for preparation before each measurement; Giguère et al. (34) suggest that 20 to 60 minutes are needed to form the mantle, and a further five hours must pass before the solid and liquid are in equilibrium.

Compensating calorimeters are also isothermal, the effect of the chemical event being counterbalanced as closely as possible by electrical

heating or cooling. They are commonly used in studying heats of mixing of non-polar liquids, where the enthalpy changes are so small that they would be masked by heat leaks in a non-isothermal apparatus (35). The supply of heat need not be automatic; after a trial to establish the rate and approximate heat change of an endothermic reaction, a quantity of heat that will minimise the temperature change is supplied when each subsequent reaction is carried out. The inevitable small differences between the chemical and electrical effects may be measured and corrected for just as in the adiabatic calorimeters described earlier.

While this type of apparatus removes the need for heat capacity measurements or cooling corrections, it is well suited only to endothermic reactions of moderate rate. Slow exothermic reactions may be compensated by Peltier cooling, as shown by Christensen, Johnson and Izatt (36) who regulated the flow of heat from intrinsically rapid reactions by using a titration technique. Rather than calibrating the Peltier cooling, they maintained it at a constant level, normally balanced by separate Joule heating to keep the temperature of the calorimeter contents constant to within 2×10^{-4} K. Heats of reaction were measured as the decrease in this automatically-controlled heating that was necessary to maintain constant temperature. Their technique seems well adapted to reactions between solutions, though the quoted uncertainties, at 0.2 % of 56 kJ mol^{-1}, and 1% of 0.9 kJ mol^{-1}, are not as low as many that have been reported.

This technique might be applied to heats of reaction, and of solution of the gaseous and liquid reagents involved in studies of metal complexes, as these could all be slowed down by titration. Heats of solution of solid ligands and complexes could be measured only in a modified apparatus fitted with a powerful heater to offset the frequently rapid absorbtion of

heat during the solution process. The limited solubility of the complexes would impose an upper limit on the concentration of the solution that could be prepared and used for titration, in conflict with the small volumes of relatively concentrated solutions that are recommended for titration calorimetry.

While describing means of reducing the effects of heat loss, one may mention Domen's ingenious 'heat loss compensated calorimeter',(37) in which the core is surrounded by a thermally-isolated jacket of identical heat capacity. Heat flow between core and jacket, and between jacket and environment, is reduced by evacuating the intervening spaces and by choice of supports in the usual way, but the unusual feature is that the apparent temperature changes are measured by two thermistors (presum--ably identical), one in the jacket and one in the core, forming opposite arms of a Wheatstone bridge. Heat lost from the core to the jacket has the same effect on the apparent temperature as it would if it had remained in the core. Beyond the jacket the outer shield may be isothermal or may be made to follow the jacket temperature; Domen suggests that the corrections for heat flow or the change in shield temperature will be made smaller and more regular by the presence of the jacket, whose temperature changes much more slowly than that of the core. This calorimeter was designed for measuring radiation doses; it is not clear that it could be adapted to deal with a vessel and its contents whose heat capacity varied, nor with the need for stirrers,etc., to penetrate the jacket. It is worth noting that a jacket of heat capacity equal to that of a vessel containing 25 or 100 cm^3 of water could be made from copper only a few millimetres thick at a distance of 10 to 20 mm from the vessel.

Heat flow calorimeters. In the design of some calorimeters the aim of reducing heat loss, which, as has been shown, is never entirely successful, is abandoned. Instead the flow is measured. The simplest device of this sort is that developed by Junkers (38), in which the heat is transferred to a steadily flowing stream of water from a thermostat. The flow rate and change in temperature of the water are measured. Much more commonly used are 'microcalorimeters' of the Tian-Calvet type (39,40) in which the heat flows from the vessel or'cell' along multiple thermocouple wires attached to silver plates covering as much of the surface of the cell as possible. The flow of heat is not measured directly, but is proportional to the combined emf of the thermocouples, which are connected in series. The relation between emf and heat flow is established by electrically heating the cell. Early versions relied on the constancy of temperature of a copper block, surrounding the cell, to which alternate junctions of the thermel were fixed. Any change in the temperature of the block appeared as an uncertainty in the measurement of heat flow. The sensitivity of the calorimeter and its ability to deal with slow reactions have been enormously increased by comparing the emf of the thermel with that of an identical element on a comparison cell, the two cells being symmetrically placed in the same copper block. Variations in temperature of the block no longer contribute to the readings, provided that the temperatures of the surroundings of the two cells do not differ.

In order to deal with energetic reactions while retaining the sensit--ivity provided by the multiple thermocouples, most of the temperature change may be offset by heating or cooling, as in the compensating calorimeters already described. The arrangement of cells in opposed pairs gives a wider choice of ways of achieving the compensation; an

exothermic change in the experimental cell, for example, may be counter--acted either by Peltier cooling of that cell, or by Joule heating of a standard resistor in the opposing cell. It is claimed that the thermels conduct sufficiently well to make the measurement nearly isothermal (40), and the opposing cells of a pair are supposed to be identical, so that there should be little error due to differences in heat capacity between the experimental and comparison cells. Nevertheless, greater accuracy would be obtained by counteracting the heat effect within the reaction cell itself, so that a heater should be included in any reaction vessel to be used for endothermic reactions. The characteristics of a commercial microcalorimeter, fitted with 15 cm^3 cells, are set out in table 1. (41)

Table 1. Characteristics of the SETARAM ms 70 microcalorimeter.

	Power/W	Instantaneous energy/J
Threshold	10^{-5}	2×10^{-3}
Maximum	0.5	50
Reproducibility	0.5 % + threshold	0.5 % + threshold

i.e. for 0.1 J instantaneous energy, reproducibility = 0.0025 J, (2.5 %)

for 5.0 J instantaneous energy, reproducibility = 0.027 J, (0.54%)

These measurements are no more reproducible than those given by some other forms of calorimeter, and the Calvet, like the phase-change calorimeter, takes several hours to equilibrate before each measurement. So it is the instrument of first choice only for very slow reactions whose enthalpy changes cannot be determined more rapidly.

Isoperibol calorimeters. Differing both from calorimeters which are designed to prevent heat flow, and those where the flow itself is the measured quantity, are those in the 'constant temperature environment' category. The name 'isoperibol' for this type seems to have been invented by Kubaschewski and Hultgren (42), while many designs can be traced back to Sunner and Wadsö's 1959 paper (43). Calorimeters of this sort are designed to have a heat loss which is small and measurable, so that it may be accurately corrected for. Sunner and Wadsö set out to make an apparatus that would be simple, versatile and easy to operate, for reactions taking less than an hour and giving up to 200 Joules. The accuracy aimed at was 0.1% or 0.2 J, whichever was the larger. In their comparison of six or so different 100 cm^3 calorimeters the most important criteria were the following.

(i) Reproducibility of results.

(ii) Freedom from corrosion by a variety of reagents.

(iii) The speed of equilibration after setting up the calorimeter and after a change in temperature due to reaction or calibration.

The last factor was particularly important, and appeared to depend on three factors:

(a) The existence of a clearly-defined boundary between the calorimeter vessel on the one hand and the constant-temperature jacket on the other.

(b) The absence of large masses of material which formed part of the vessel yet were distant from the calorimeter liquid.

(c) The use of materials of high thermal conductivity.

The best performance was given by a light brass can, coated with chromium and teflon against corrosion, suspended by its thin glass neck from the lid of a larger can, the space between the two being evacuated to

a pressure of less than 10^{-4} torr by rotary and diffusion pumps (figure 3). The combined ampoule-holder and stirrer was made of stainless steel, coated with 0.12 mm of teflon. A thermistor, for temperature measurement, and the calibrating heater were housed in separate tubes, presumably also made of brass, placed on opposite sides of the vessel approximately half-way between the centre and the walls. Epoxy resin was used to seal these components into the tubes, andto attach the glass neck to the metal can. A teflon-coated brass washer separated the contents of the can from the air in the glass neck.

Sunner and Wadsö's paper also describes the advantages of mould-blown thin-walled glass ampoules, which break under a small and reprod--ucible force, said to be equivalent to 10 g, and produce minimal energy changes when broken. (If the upper limit for the distance that the glass might deform before breaking is 1 mm, and the mean force exerted over this distance is half that equivalent to 10 g, i.e. approximately 0.05 N, then the work done in breaking two faces is given by

$$W = 2 \times 10^{-3} \times 0.05 = 10^{-4} \text{ J}.$$

This is negligible in comparison with the energy changes to be measured, and much smaller than the other effects of opening the ampoule, listed in the Experimental section of this thesis, pages 53 ff. In a later paper Hill et al. (44) give the enthalpy of breaking as the much higher figure of 5×10^{-3} J, but without making clear either the sign of the heat effect or whether it was simply mechanical energy of breaking or the total effect occurring when an empty ampoule was broken into the calorimetric liquid.

The Sunner and Wadsö calorimeter was found to equilibrate within two minutes of the end of a heating period, presumably because of its low

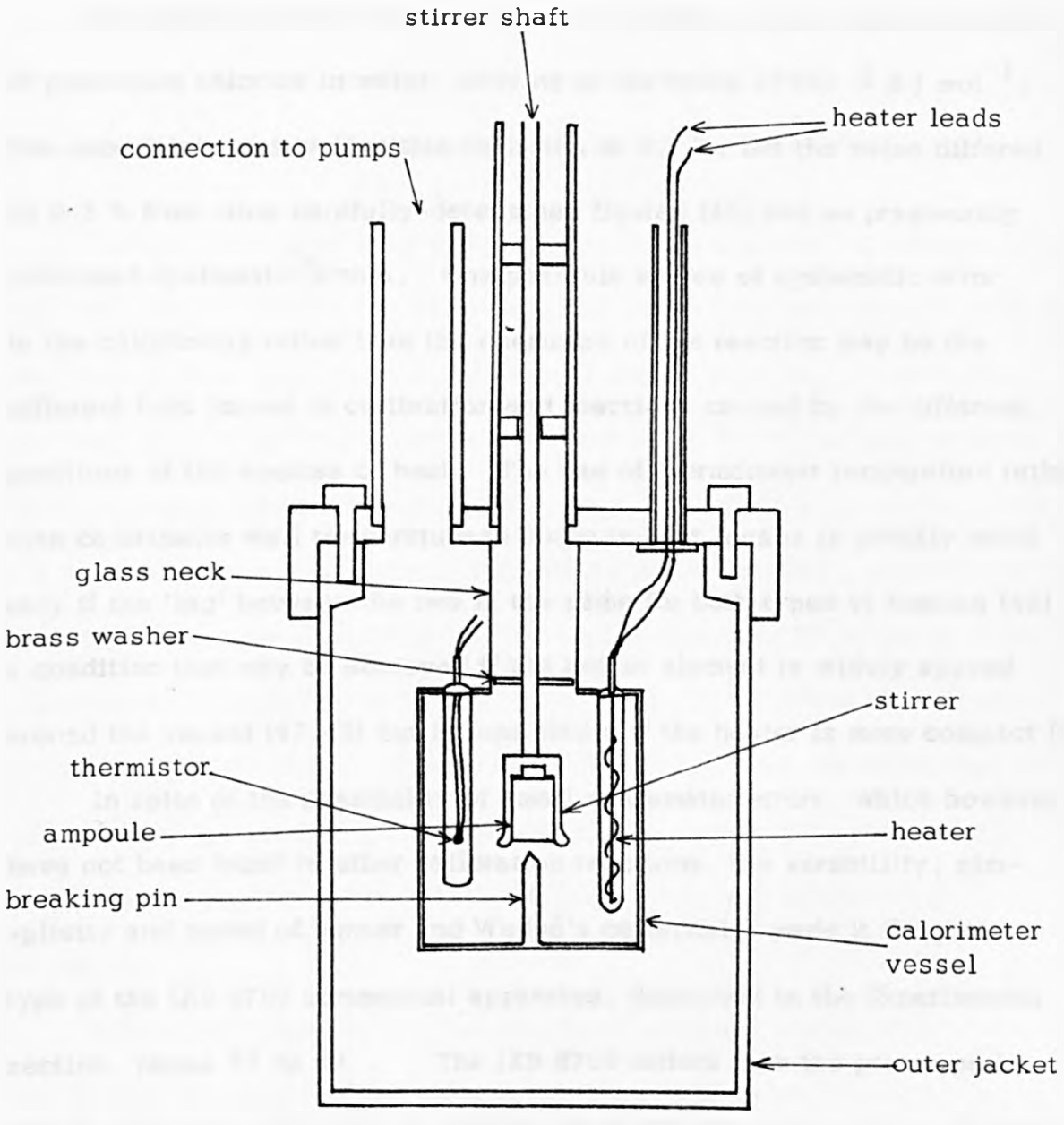


Figure 3. The Sunner and Wadsö prototype isoperibol calorimeter.

mass and high thermal conductivity, and the effectiveness of the glass neck and washer acting as a boundary.

The authors tested their calorimeter by measuring the heat of solution of potassium chloride in water, arriving at the value 17502 $\pm$ 8 J mol^{-1}. The uncertainty was well within their aim of 0.1 %, but the value differed by 0.5 % from other carefully-determined figures (45) and so presumably contained systematic errors. One possible source of systematic error in the calorimetry rather than the chemistry of the reaction may be the different heat losses in calibration and reaction, caused by the different positions of the sources of heat. The use of thermometer temperature rather than calorimeter wall temperature to compute heat losses is strictly valid only if the 'lag' between the two is the same for both types of heating (46), a condition that may be achieved if the heater element is widely spaced around the vessel (47,48) but is less likely if the heater is more compact (49).

In spite of the possibility of small systematic errors, which however have not been found in other calibration reactions, the versatility, simplicity and speed of Sunner and Wadsö's calorimeter made it the prototype of the LKB 8700 commercial apparatus, described in the Experimental section, pages 37 to 39 . The LKB 8700 differs from the prototype in having thevessel and wells for heater and thermistor made entirely of glass, whose transparency, resistance to attack and cheapness are useful, at the expense of some loss of heat conduction. The disc at the base of the neck is omitted, presumably because it added to the difficulty of loading the vessel.

Many further modifications to the LKB system have been made. Gerding, Leyden and Sunner (50) replaced the ampoule by a pipette whose bulb-full of liquid was immersed in the calorimeter fluid and was therefore almost in thermal equilibrium with the rest of the calorimeter before being

opened to allow the liquids to react. Grenthe, Ots and Ginstrup (51) added gold titration pipettes so that liquid reagent could be added at a rate controlled by pistons outside the calorimeter, the titrant being brought to thermostat temperature in a heat exchanger on the lid of the can. These pipettes were later fitted with valves to prevent diffusion before addition (52).

Two methods have been developed to obtain temperature measurements less laboriously than by the LKB thermistor and Wheatstone bridge (page 49). Brunette, Prosen and Goldberg (53) used a quartz oscillator thermometer, and were able to achieve a temperature resolution of 10^{-5} K with the help of an unusually stable reference frequency. Earlier workers (54) had found the crystal thermometer to be less precise than thermistors, probably because their oscillator was less stable. The crystal thermometer achieves great precision at the expense of speed; a reading to 10^{-5}K takes 100 seconds. Its advantages are that it can easily provide digital data for paper tape and computer analysis, and that it is inherently an integrating device whose output is suitable for the Regnault-Pfaundler method of temperature correction.

Automatic digital output has also been achieved by Nichols, Skold and Wadsö (55) by passing a constant current through the thermistor and using a digital voltmeter to measure the potential across the ends. The voltmeter output was printed on paper tape every five seconds throughout an experiment.

The LKB 8700 is not perfectly suited to measure the small quantities of heat associated with these reactions of platinum complexes. If Sunner and Wadsö's aim of a precision of 0.2 J was not bettered, the uncertainty would lie between 4 % and 200 % for heat effects between 5 and 0.1 J.

The LKB 8700 manual (56) claims a precision of 0.02 %, but the meaning of this figure is not clear as there is no indication of the range of heats to which the percentage might apply. The system is chosen because it is in practice sufficiently precise to make the uncertainty in measuring the heat no larger than the uncertainty in the chemical changes that produce it, as recommended by Churney et al.(57). If the platinum complexes could be made sufficiently pure and could be analysed to the standards commonly achieved for samples used in bomb calorimetry, a different choice of apparatus might be appropriate.

Treatment of data from isoperibol calorimeters.

The accuracy of isoperibol calorimetry depends on the precision with which the effects of heat flow between the calorimeter and its environ--ment may be calculated. The importance of these effects in different circumstances may be judged from figures 4, 5 and 6. Figure 4 represents the temperatures observed during a rapid and strongly exothermic reaction such as that between 'tris' and hydrochloric acid carried out in the 100 cm^3 vessel of an LKB 8700 calorimeter. Figure 5 shows a weakly exothermic and slower reaction carried out in a 25 cm^3 vessel full of an organic solvent, and figure 6 shows an electrical calibration approximately equivalent in energy to the reaction of figure 5, carried out under the same conditions.

In each of the three diagrams, S represents the start of time and temperature readings, B is the beginning and E the end of the temperature increase due to reaction or calibration, while L is the last reading. The period from t_S to t_B is known as the fore-period, t_B to t_E the main or reaction period, and t_E to t_L the final or after-period. The temperature difference $T_E - T_B$ is all that would have to be measured if no heat effects other than the reaction itself contributed to the change in temperature; in that case the temperature would remain constant before and again after the reaction. Clearly, in figure 4, $(T_E - T_B)$ is a close approximation to the effect of the reaction, only a small correction being needed to allow for the effects represented by the slopes of the lines during the fore- and after-periods. In the situations represented by figures 5 and 6, these slopes are much more dramatic, and the overall temperature change, $(T_E - T_B)$, during the reaction period is much greater than that caused by the reaction alone (designated θ); the difference, ΔT_x, being due to

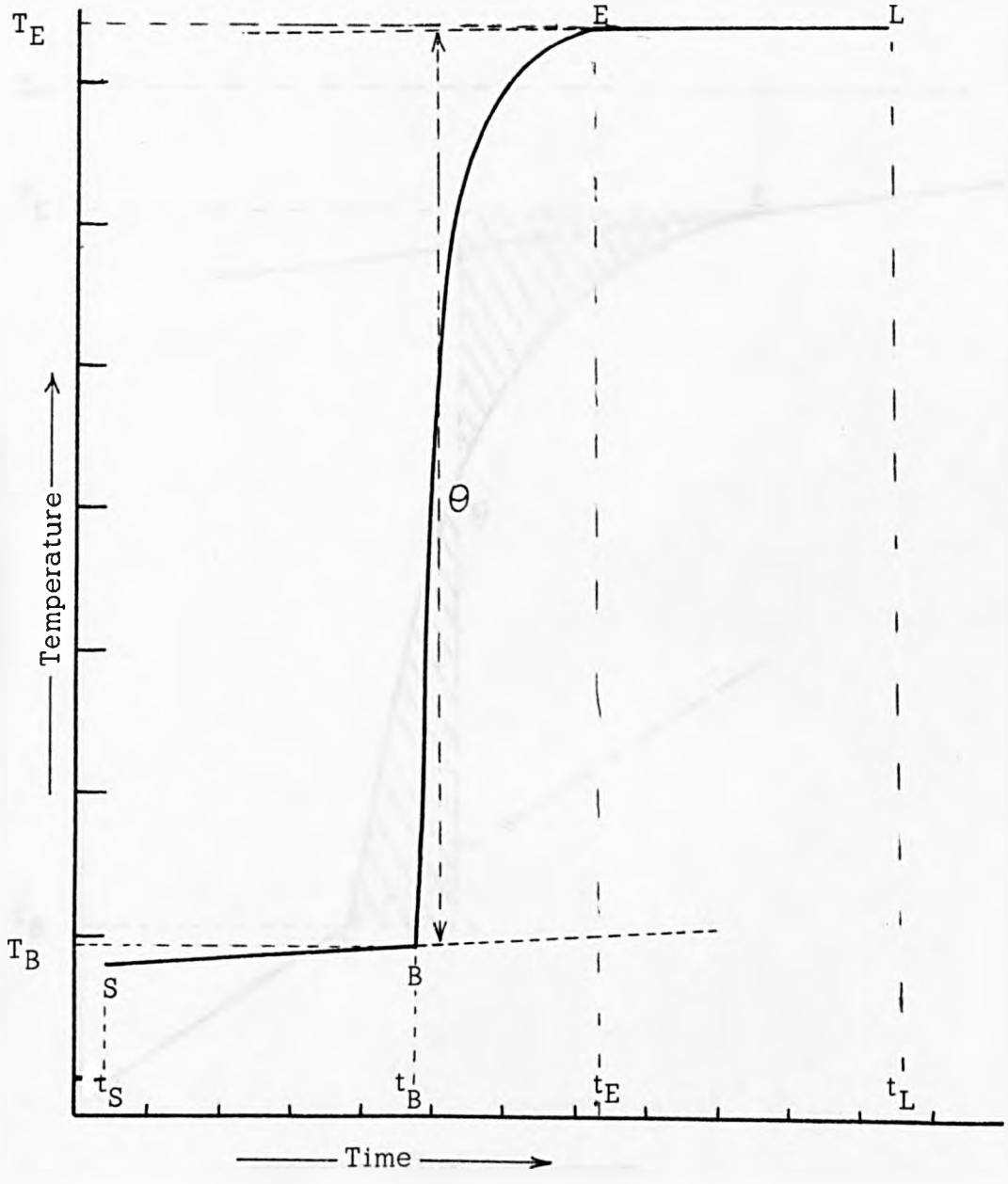


Figure 4. Temperature : time graph typical of a rapid and strongly exothermic reaction.

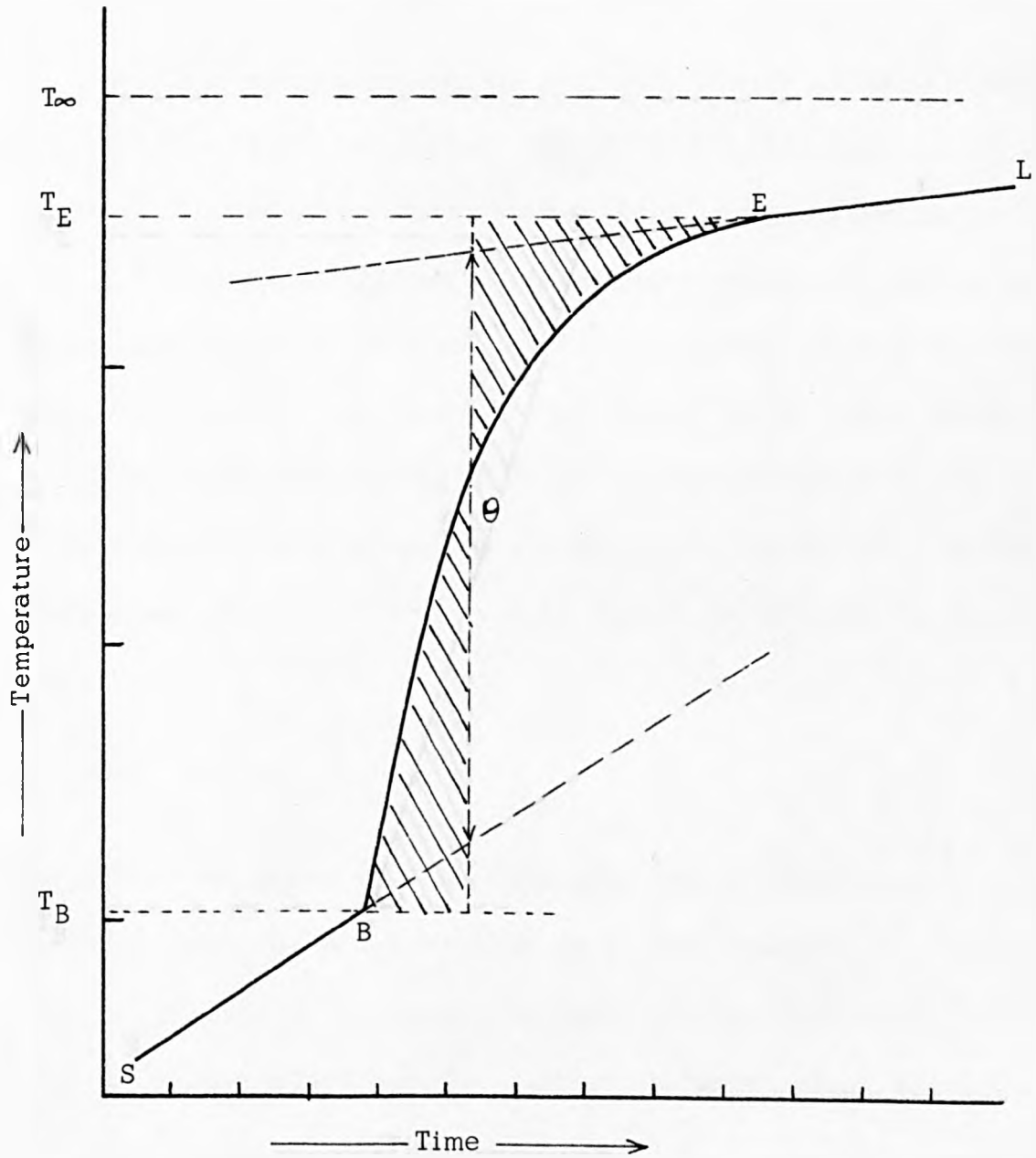


Figure 5. Temperature : time graph typical of a weakly exothermic reaction.

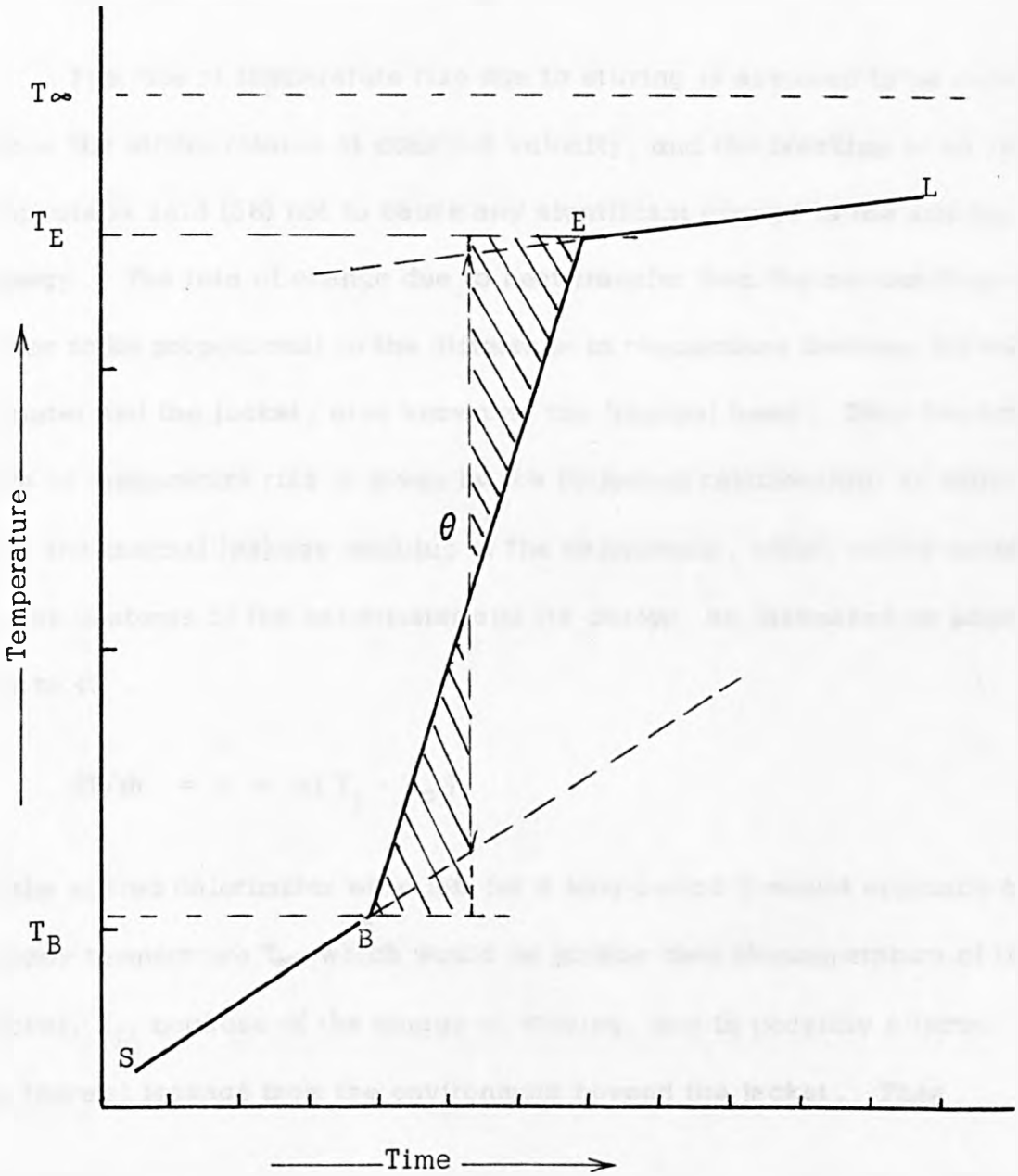


Figure 6. Temperature : time graph for electrical calibration corresponding to the reaction shown in figure 5.

stirring and to heat entering from the surroundings. Thus

$$T_E - T_B = \Delta T = \theta + \Delta T_x$$

The rate of temperature rise due to stirring is assumed to be constant, since the stirrer rotates at constant velocity, and the breaking of an LKB ampoule is said (58) not to cause any significant change in the stirring energy. The rate of change due to heat transfer from the surroundings is taken to be proportional to the difference in temperature between the calor--imeter and the jacket, also known as the 'thermal head'. Thus the total rate of temperature rise is given by the following relationship, in which k is the thermal leakage modulus of the calorimeter, which varies according to the contents of the calorimeter and its design, as discussed on pages 40 to 43 .

$$dT/dt = u + k(T_j - T_c) \qquad (1)$$

If the stirred calorimeter were left for a long period it would approach a steady temperature T_∞, which would be greater than thetemperature of the jacket, T_j, because of the energy of stirring, and is possibly affected by thermal leakage from the environment beyond the jacket. Then

$$dT/dt = 0 = u + k(T_j - T_\infty) \qquad (2)$$

$$T_j = T_\infty - u/k \qquad (3)$$

Equation (3) may be combined with equation (1) to give

$$dT/dt = k(T_\infty - T_c) \qquad (4)$$

The extraneous temperature change, ΔT_x, is the integral of the rate of change given by equation (4) :

$$\Delta T_x = \int_{t_s}^{t_f} k\,(T - T_c)\,dt \qquad (5)$$

$$= k\,(T - T_m)\,\Delta t \qquad (6)$$

where T_m is the mean temperature during the reaction period and Δt is the duration of this period. If the slope at F, the middle of the fore-period, is g_F, and that at A, the middle of the after-period, is g_A, then

$$g_F = k\,(T_\infty - T_F)$$

$$g_A = k\,(T_\infty - T_A).$$

These equations may be used to substitute for T_∞, an unmeasured quantity, in equation (6) to evaluate ΔT_x and so the corrected temperature change, θ.

$$\Delta T_x = [g_F - k(T_m - T_F)]\Delta t$$

$$\Delta T_x = [g_A - k(T_m - T_A)]\Delta t$$

$$\theta = \Delta T - \Delta T_x = \Delta T - [g_F - k(T_m - T_F)]\Delta t$$

$$\theta = \Delta T - [g_A - k(T_m - T_A)]\Delta t$$

These two estimates of the corrected temperature change, using the slopes from the fore- and after-periods, should be the same if the heat leakage constant has not altered during the reaction. The mean temperature during the reaction period, T_m, is evaluated by dividing the curve of the reaction period into a sufficiently large number of straight lines and taking the weighted mean of these. The slopes g_F and g_A are best found by least-squares straight lines fitted to the data from the fore- and after-periods. This treatment, called the Regnault-Pfaundler method, is suitable for any rate of reaction, provided that sufficient readings exist to define the fore-main and after-periods.

An alternative treatment proposed by Dickinson (59,60), depends on finding an 'extrapolation time', t_x, such that

$$\Delta T_x = k\int_{t_B}^{t_E} (T - T)\,dt = g_B(t_x - t_B) + g_E(t_E - t_x).$$

This condition is approximately satisfied if the two cross-hatched areas in figure 5 or 6 are equal. (Appendix 1 shows that the areas described by Dickinson are not exactly those that should be used in finding t_x.)

A value of t_x may be found by counting squares on temperature: time graphs, but this is so laborious that the Dickinson method is preferred to the Regnault-Pfaundler only if there is some other way to equalise the areas. If the reaction curve is exponential, t_x is the time at which 63% of the total temperature change has occurred. This rule can be used when the reaction is so rapid that sufficient data for the Regnault-Pfaundler integration cannot be obtained, while the shortness of the reaction period minimises errors caused by any departure of the temperature : time curve from an exactly exponential form. Electrical calibration gives rise to a straight-line relation between time and temperature (figure 6), so that the shaded areas are made equal if t_x is exactly half-way between t_B and t_E. Once t_x has been found, the corrected temperature change, θ, is the difference, PQ, between the temperatures corresponding to the intercepts of the extrapolated fore- and after-periods with t_x.

The Dickinson and Regnault-Pfaundler methods may be used with any scale of temperature, or any temperature-indicating measurement which is closely proportional to temperature. Even the resistance of a thermistor, which is only approximately inversely proportional to temperature, may be used if the corrected ΔR values are 'normalised' as described on page 53 (58). Nevertheless Olofsson et al. (61) and Mansson (62) analysed their results by converting resistances to temperatures , using an empirical equation to

relate the two variables. They then fitted the fore- and after-periods to an integrated form of Newton's law, rather than assuming a straight-line relationship, before applying the Regnault-Pfaundler correction. More recently Vagera (63) has published a FORTRAN programme for calculating corrected temperature changes, also assuming exponential fore- and after-periods. Yet Coops et al. (60) have shown that the difference in temperatures calculated from linear and exponential equations for a fore-period as long as ten minutes was less than 10^{-4} K, and the effect of small errors is almost removed if the temperatures and times of fore- and after-periods are approx--imately the same for calibration and reaction, so the simpler linear relation may be used without loss of accuracy. Oloffson et al. and Mannson were working with bomb calorimeters which produced a rapid burst of heat that could not be duplicated by the calibration, so could achieve the accuracy essential in bomb calorimetry only by using the exponential forms.

Electrical calibration.

In order to convert temperature or resistance changes into the desired energy changes, the effective energy equivalent, ε, of the full calorimeter must be known. If the temperature change has been calculated, ε corresponds approximately to the heat capacity, in $J\,K^{-1}$, of whatever parts of the calorimeter and its contents experience the same temperature changes as the thermometer. If the normalised thermistor resistance or some other function of temperature is used without conversion, ε is simply a calibration constant relating the function to energy. Its value is different each time the calorimeter is loaded, due to the different masses of solvent and reagents in the vessel, so an electrical calibration must accompany each reaction. Since ε may also vary with the temperature of the calorimeter and its surroundings, and with the lag between the evolution of energy and its effects, the calibration and reaction should cover the same range of temperature and time.

The calibration may precede or follow the reaction, according to whether the reaction is made to start or finish at the standard temperature for which the enthalpy change is required. The cycles (a) and (b) of figure 7, in which R and P represent reactants and products respectively, show the two alternatives for an exothermic reaction and its calibration, designed to measure the enthalpy change at 298 K in a non-isothermal calorimeter.

The enthalpy changes shown in the cycles refer to the following.

ΔH_r : the reaction.

ΔH_{298} : the isothermal reaction at 298 K, i.e. the desired heat of reaction.

ΔH_{cR} : the calibration of calorimeter plus reactants, i.e. before reaction.

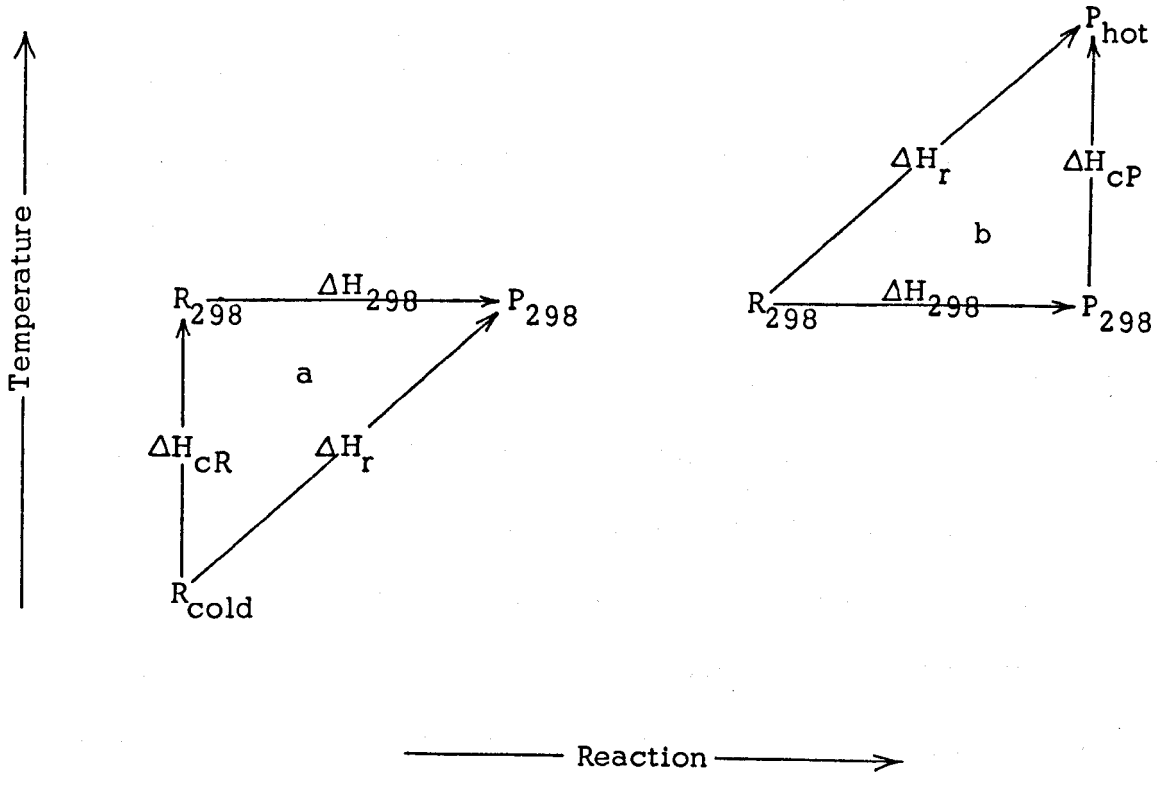


Figure 7. Cycles to illustrate calibration before (a) and after (b) reaction.

ΔH_{cP} : the calibration of calorimeter plus products, i.e. after reaction.

Hess's law may be applied to each of the cycles, as follows.

$$\Delta H_{298} = - \Delta H_{cR} + \Delta H_r$$

$$\Delta H_{298} = \Delta H_r - \Delta H_{cP}$$

If heat losses have been allowed for, the enthalpy change ΔH_r during the non-isothermal reaction is zero. Therefore calibration before reaction gives the desired ΔH_{298} if the reaction is initiated below, and ends at, 298 K, while calibration after reaction gives ΔH_{298} if the reaction is initiated at the standard temperature and ends at a higher temperature. There are reasons for preferring the former arrangement, corresponding to cycle (a).

Firstly: the reaction starts rapidly but often finishes slowly, so that its beginning shows as an obvious change of slope even if the temperature of the calorimeter is so far from T_∞ that the temperature : time line is already quite steep. The end of the reaction produces a much less dramatic change of slope which can best be detected if it occurs when there is little temperature change due to leakage, i.e. when the calorimeter temperature is close to T_∞, which in turn is arranged to be close to 298 K.

Secondly: This reason is relevant only in the unusual, but not unknown, event of a fault in the connection or action of the calibrating heater. If calibration precedes reaction such a fault is detected and corr--ected before the ampoule is broken, so little time is lost, whereas a reaction designed to be followed by calibration would be wasted if the heater failed.

Thirdly : it may be useful to remove and examine or analyse the contents of the calorimeter soon after reaction, and this is only possible if calibration precedes reaction.

EXPERIMENTAL

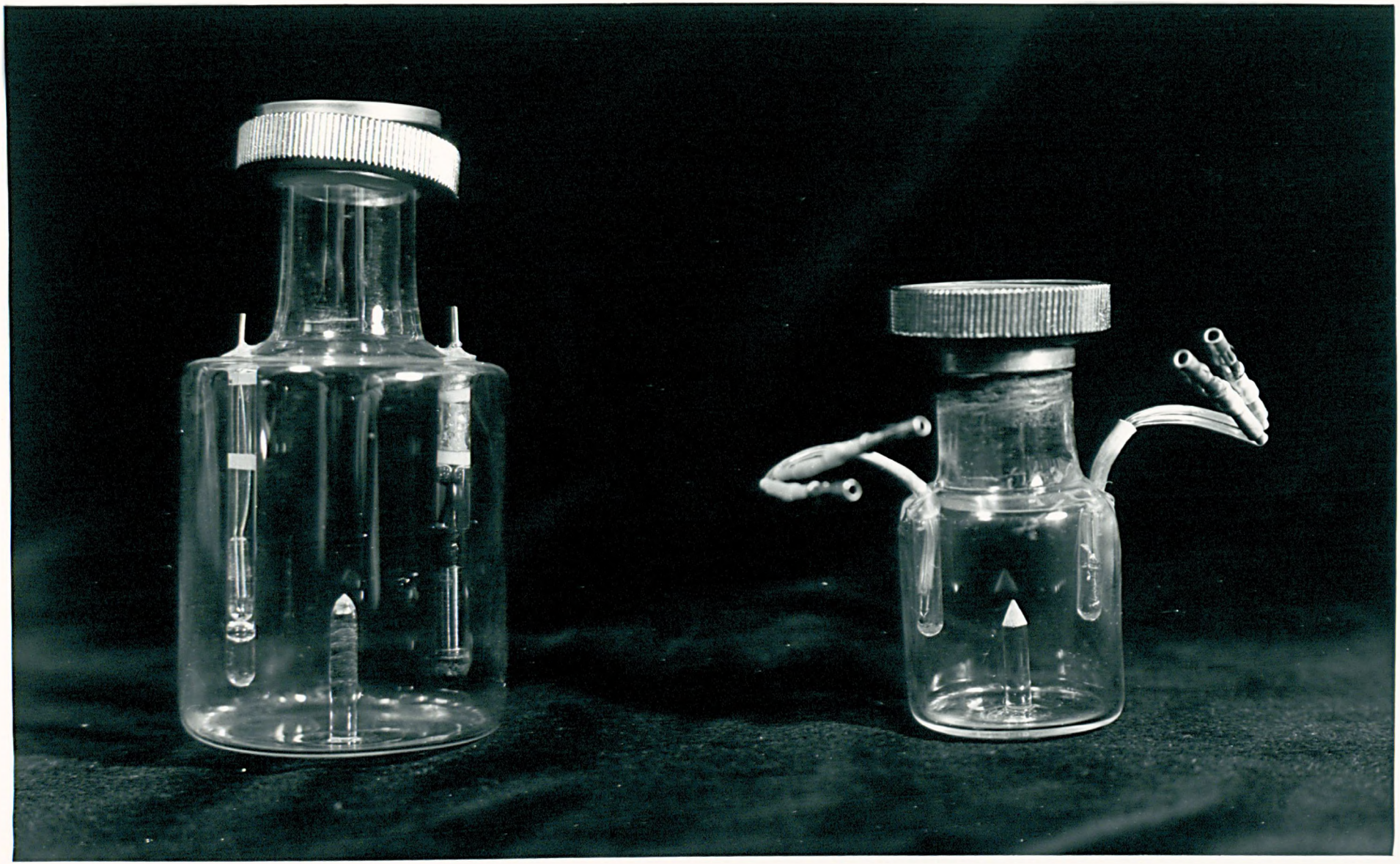
The LKB 8700 calorimeter, description.

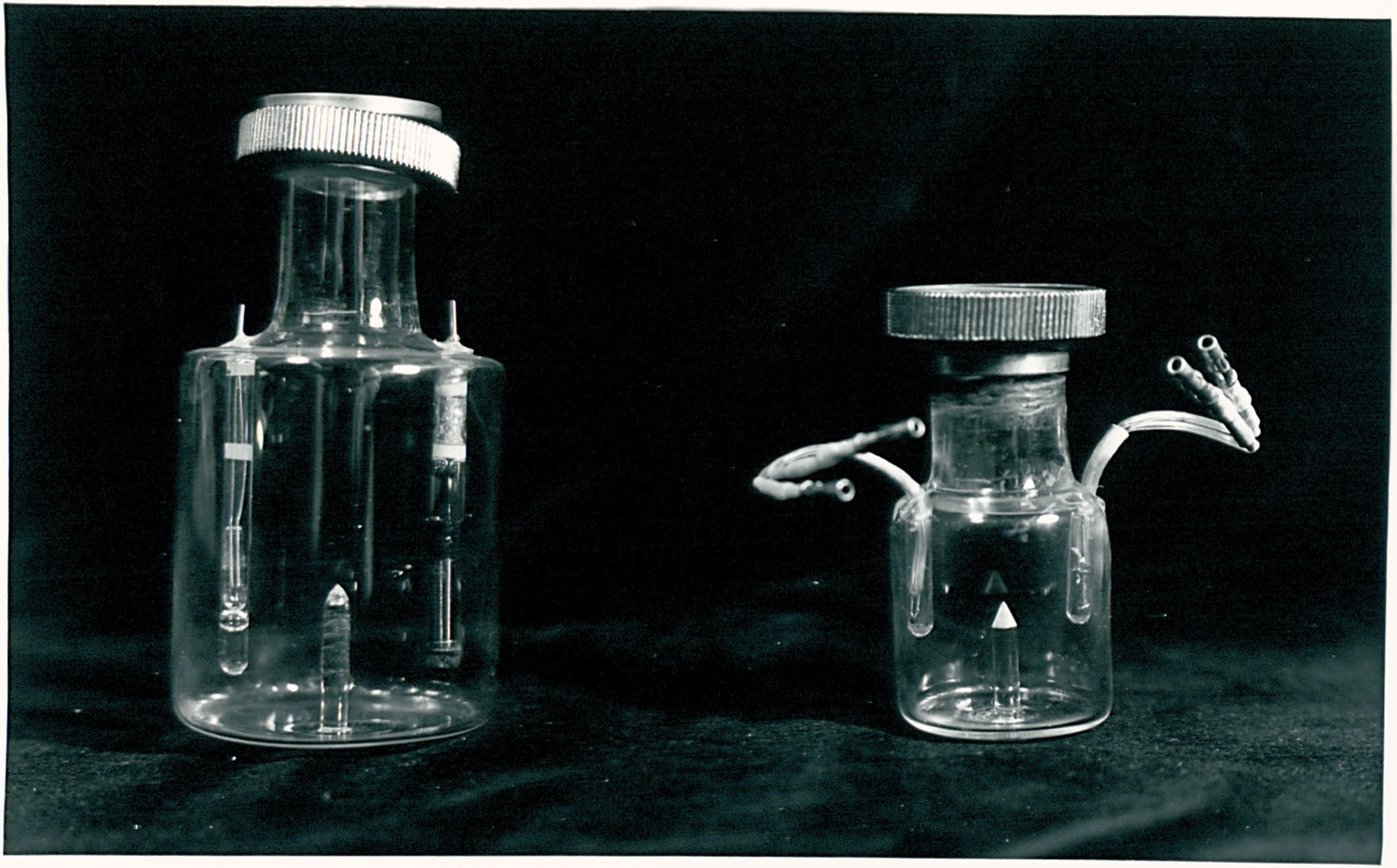
All reaction calorimetry was carried out in the LKB 8700 precision calorimetry system, designed for the measurement of heats of reactions between a small volume of one reagent, which may be solid, liquid or gaseous, with a larger volume of liquid reagent or solution at temperatures from -10 to +60°C.

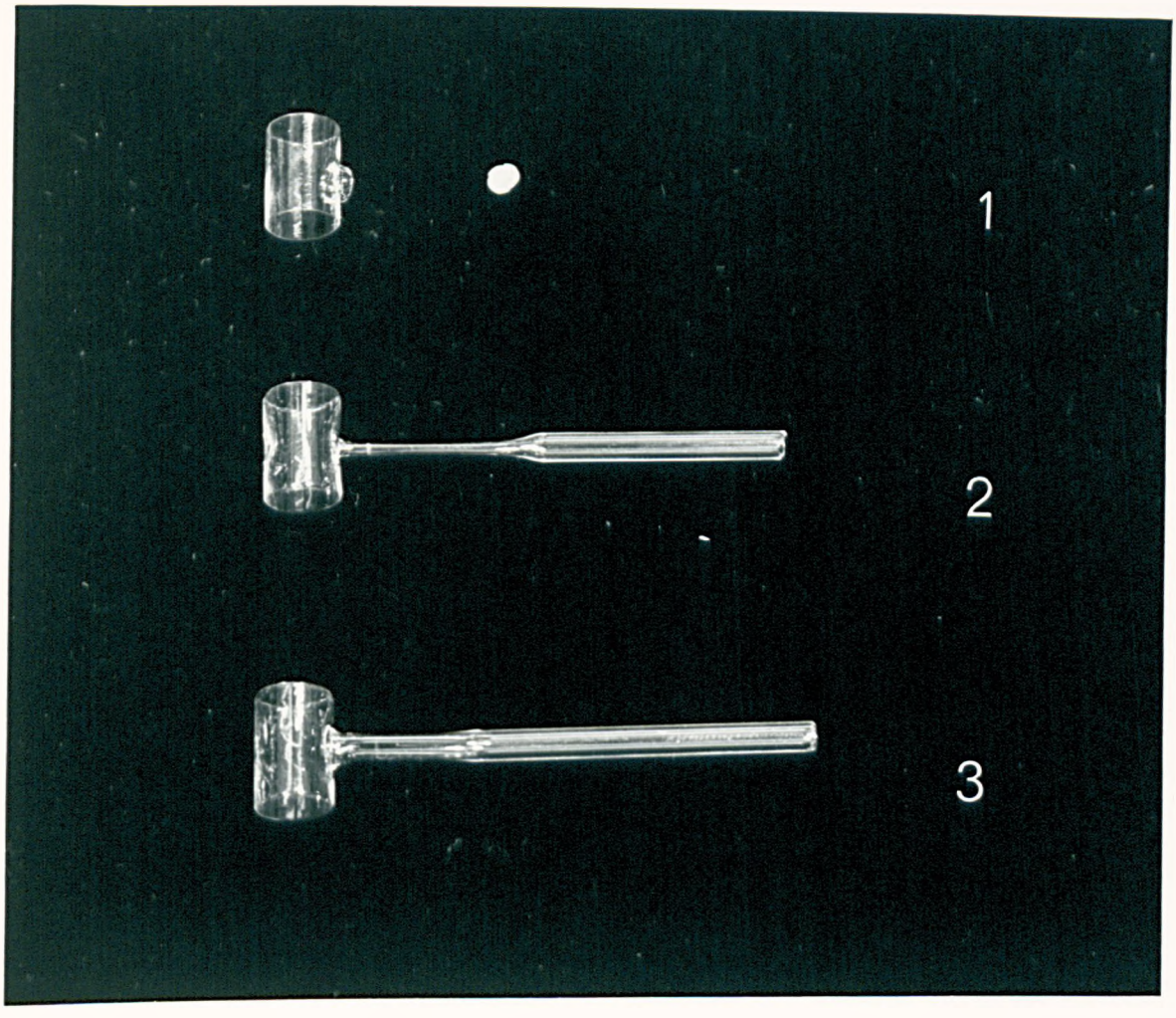
The heart of the system is the pyrex calorimeter vessel, of 25 cm^3 or 100 cm^3 capacity, (figure 8), with two wells, one containing a therm--istor for temperature measurement, the other a coiled wire resistance heater for calibrations. The wells are filled with liquid paraffin to conduct heat between the heater or thermistor and the glass walls. Those in the comm--ercially-produced 100 cm^3 vessel are capped with low-melting alloy heat traps and gold pins to make connection to detachable leads, while those in the Keele-made 25 cm^3 vessel have no heat traps, the leads being permanently soldered to thermistor and heater. From the base of the calorimeter vessel rises a glass rod tipped with sapphire * for piercing the ampoule to start the reaction. A gold stirrer at the centre of the vessel is driven by a shaft through the calorimeter lid at 125, 250 or 500 rpm. It also holds the ampoule, and can be lowered manually or automatically to break the ends of the ampoule against the sapphire.

The three types of ampoule (figure 9) are mould-blown cylinders (43) of thin (0.1 mm) pyrex glass, of about 1.1 cm^3 capacity. They

* The pin in the 25 cm^3 vessel was replaced by a plain pyrex rod in August 1977.



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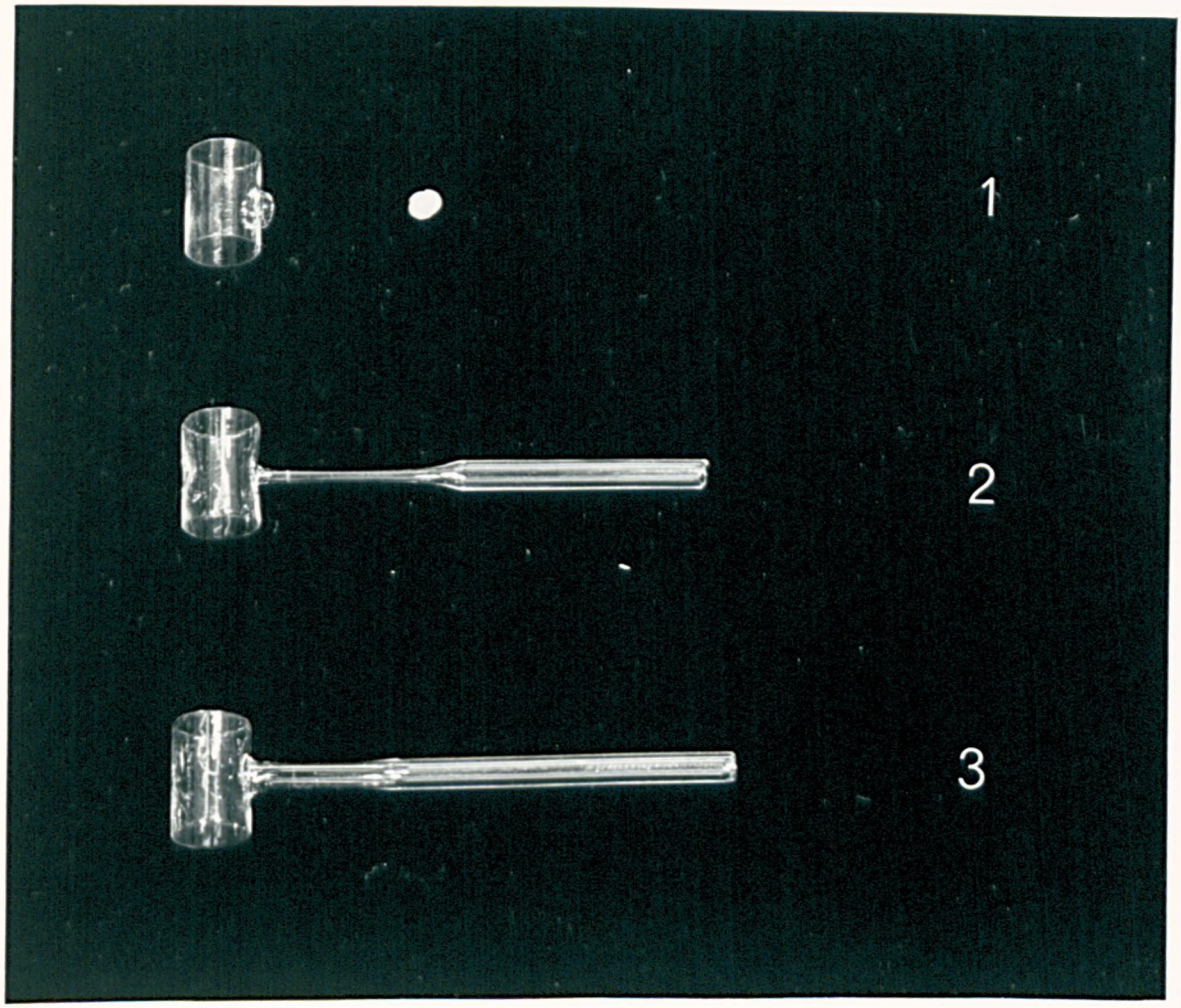
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differ in the shape of the neck and method of sealing. Type 1 has a short neck which is sealed with a silicone-rubber plug and a layer of wax; type 2, used for gases and liquids, has a 1 mm wide neck which is sealed with oxygen-gas flames; and type 3, used for solids, has a 2.5 mm wide neck, also flame-sealed.

The calorimeter vessel is surrounded by a chromium-plated brass can which is lowered into an 18 litre thermostatted waterbath. The temp -erature of the bath is maintained by a constant flow of cooling water and electrical heating regulated by a proportional controller. If the temperature of the room and the cooling water do not vary by more than 0.5°C, the temperature of the waterbath is said not to change by more than 0.001°C in 8 hours or more (56); during the 20 to 60 minute course of a single measurement the variation should be smaller.

The control unit of the LKB 8700 contains equipment for calibration and temperature measurement. The resistance of the thermistor, which is about 2 000 ohm at 298 K and decreases by about 4% (80 ohm) per degree, is measured by a Wheatstone bridge reading to 0.01 ohm, corresponding to approximately 10^{-4} K, and a Hewlett-Packard 419A DC voltmeter that indicates the off-balance signal from the bridge. A null-detector senses the balance-point of the bridge, and operates a stopwatch whose slave pointer indicates the time, to 0.01 minute, at which balance was reached, without interrupting the continuous time measurement.

Calibration heating of the calorimeter is controlled by a constant-current source and a 10 kHz quartz-crystal oscillator which enables heating times of 1 to 99 seconds (in 1 s steps) or 10 to 990 seconds (in 10 s steps) to be chosen. The accuracy claimed is 0.003 s. The resistance of the heater is measured by a precision DC potentiometer, range 0.990 to 1.011

volt and resolution better than 20 microvolt, i.e. to a precision of better than 1 part in 50 000. This is done by passing a current of approximately 0.02 amp through a standard 50 ohm resistor and the heater in series, adjusting this current to give a p.d. of exactly 1 volt across the standard resistor, and then measuring the p.d. across the heater while leaving the current unaltered. The resistance of the heater is then given by the relationship

$$R = (50 \times \text{p.d. across heater}) / 1.000 \quad \text{ohm}$$

The same potentiometer, which is standardised by a Weston cell built into the control unit, is used to standardise the calibration current to provide heating power at 20, 50, 100, 200 or 500 mW.

The heat leakage modulus, k.

The rate of heat flow between calorimeter vessel and jacket is particularly important when small quantities of heat are to be measured.

The leakage modulus, calculated from the following relationship, may be measured for any experimental arrangement of calorimeter and contents, and may be used to compare with other calorimeters.

$$dT/dt = k (T_{\infty} - T_C)$$

The leakage modulus of the Keele-made 25 cm^3 vessel filled with an organic solvent (1,2,4-trichlorobenzene) has been measured for a temperature 'head' (the difference between the temperature of the vessel and the infinity temperature) corresponding to a difference of 5 - 10 ohms in the resistance of the thermistor, and has been found to be approximately 4×10^{-2} min^{-1}. This may be compared with the 1×10^{-3} min^{-1} of Christensen et al.'s Dewar vessel (64), the 1×10^{-3} min^{-1} of Stubblefield's adiabatic tantalum vessel (30), whose jacket was evacuated to 10^{-4} to 10^{-5} torr, and with the figures given by Prosen and Kilday (31), which varied from 1×10^{-2} min^{-1} at 760 torr pressure to 3×10^{-3} min^{-1} at 10^{-3} torr, with no further decrease when the pressure was further reduced.

Thus the leakage of the Keele calorimeter appears to be four times greater than even the unevacuated Prosen calorimeter, and 10 to 40 times greater than the evacuated ones. Part of this discrepancy is probably due to the small size of the Keele vessel; at 25 cm^3 it contains only 1/4 to 1/12 of the volume of the others mentioned. If the vessels were identically shaped, and if one can assume that the heat loss is proportional to the surface area while the heat capacity is proportional to volume, then the leakage modulus of the smaller vessel should be $\sqrt[3]{12} \simeq 2.3$ times

greater than that of the larger. In fact the neck, leads and stirrer are relatively larger in the 25 cm^3 vessel, and so may cause a proportionally greater heat loss from this smaller vessel. Further, the calorimeters described in the literature have presumably been tested when filled with water (the figures appeared in papers concerned with reactions in aqueous solutions) whose high specific heat capacity reduces the leakage modulus. A small calorimeter filled with an organic solvent has a higher modulus due to the solvent and to the proportionally greater mass of glass, since the specific heat capacities of both these materials are considerably less than that of water. The change of liquid alone is estimated to cause a 2.5 x increase in the modulus.

Thus the difference between the leakage modulus of the Keele vessel and that of Prosen's vessel before evacuation is fully explained. Improvement of the modulus of the Keele vessel must depend on evacuation of the jacket. The effects of evacuation on radiation, conduction and convection may be considered separately.

Heat losses by radiation are presumably almost unaffected by reduction in pressure. Once the emittance of the surfaces of the vessel and can have been reduced as far as possible by polishing, the only way to reduce radiative heat loss still further is by surrounding the vessel with a radiation shield. One shield can be expected to reduce radiation loss by at least half, but even the lightest aluminium foil shield adds several minutes to the time taken for equilibration after heat generation, and so is probably not worthwhile at room temperature, where radiation forms only a minor part of the total heat flow.

Gaseous conduction is expected to be independent of pressure, since the conductance is given by the following relationship, in which

k is the heat flow across unit cube under unit temperature difference, m is the mass of a molecule and n the number of molecules per unit volume, l is the mean free path, $\bar{c}$ the root mean square velocity, and C_v the specific heat capacity at constant volume.

$$k = mn\,\bar{c}\,l\,C_v \qquad (65)$$

The value of n is directly, and the value of l is inversely, proportional to pressure, while the other terms are unaffected. Presumably this independence of k from the effect of pressure breaks down when the mean free path is determined largely by collisions with the apparatus rather than with other gas molecules, i.e. when l is of the same order of magnitude as the air gap between calorimeter and jacket. The mean free path in nitrogen at 298 K and 760 torr is 6.5×10^{-5} mm (66), so the pressure at which it would be approximately 20 mm is given by

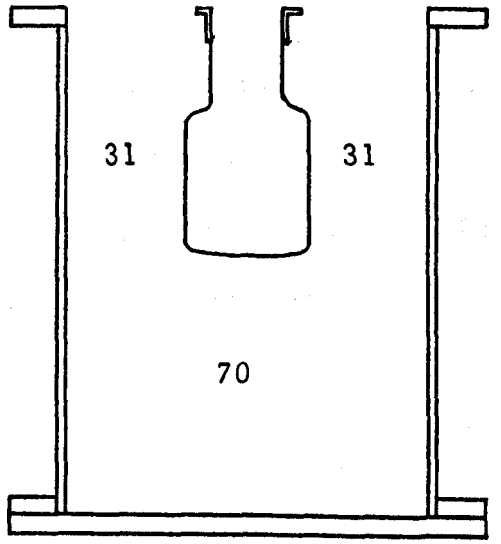
$$p = (6.5 \times 10^{-5} \times 760) / 20 = 2.5 \times 10^{-3} \text{ torr}$$

Between approximately 10^{-2} torr and atmospheric pressure one would expect little change in heat flow by conduction; below approximately 10^{-3} torr the conduction should decrease in proportion to the pressure. These deductions may be compared with Prosen and Kilday's measurements.

The observed constancy of thermal leakage below 10^{-3} torr suggests that the contribution of gaseous conduction is not significant at these pressures. The decrease of thermal leakage from 10^{-2} to 3×10^{-3} min^{-1} that they noted as the pressure was reduced from 760 to 10^{-3} torr was presumably due to a decrease in convection, which is the least acceptable form of heat loss, since it does not follow Newton's law of cooling, on which the calculation of corrections is based.

To reduce convection at atmospheric pressure most writers recommend that the width of the gap between calorimeter and jacket should not be greater than 10 to 15 mm, apparently following White(46). The gaps between the 25 cm^3 vessel and the 100 cm^3 vessel and the LKB can are larger than 15 mm (figure 10) , so that convection might be expected to make an important contribution to heat leakage. However Ginnings and West (67) show that the onset of convection depends on the temperature difference across which the heat is flowing. To remove convection and so ensure that heat loss is proportional to temperature difference, $(T_j - T_c)$, at room temperature and pressure, the quantity $L^3 (T_j - T_c)$ must be less than about 11 cm^3 K, where L is the thickness of the air gap. For differences of only 0.1 K the gap should be less than $\sqrt[3]{110} \simeq 4.8$ cm, while for differences of 1 K it should be less than 2.2 cm. Thus the only gap that should give rise to convection at small temperature differences is that below the 25 cm^3 vessel. It is not clear that convection is making an important contribution to heat leakage from either of the LKB vessels, but evacuation by rotary pump should reduce convection to negligible proportions, and more effective evacuation would also decrease gaseous conduction.

The LKB 8700 system is designed to allow evacuation of the can, via an unsuitably narrow (11 mm internal diameter) tube which could easily be replaced by a larger connection. An attempt to evacuate the can when the calorimeter was filled with dichloroethane caused an imm--ediate and dramatic drop in temperature which was attributed to evaporation of the solvent caused by leakage from the vessel into the can. The existence of a leak had already been suspected, for the smell of solvent could always be detected in the can after calorimetry. As the O ring at



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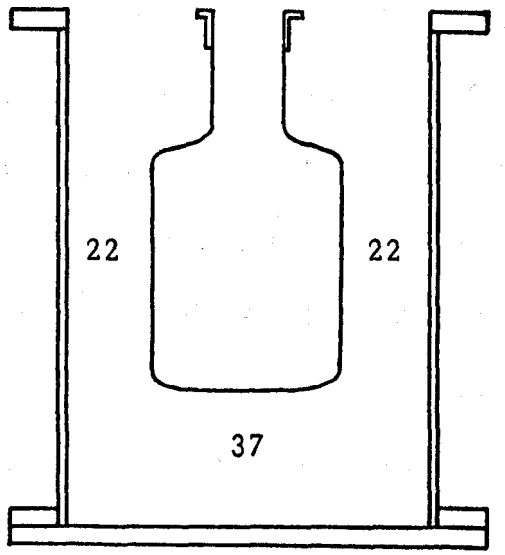


Figure 10. The L.K.B. 8700 25 cm^3 and 100 cm^3 calorimeter vessels and jacket, showing the dimensions (in mm) of the air gap surrounding each vessel.

the neck of the vessel was new and well greased, and the vessel was intact, the leak must have been through the resin seal between the glass neck and the metal top of the vessel. Although epoxy resin withstands aqueous solutions it is softened by chorinated hydrocarbons, and cannot be expected to hold vacuum in their presence. The attempt to evacuate the can was abandoned. If a new vessel, with a glass flange (figure 11) rather than a metal one was made, the can might safely be evacuated.

Heater errors.

The calibrating heater may be a source of unsuspected errors in calorimetry (68). One set of errors arises from the heat liberated in the leads by the current flowing throught them. This heat is proportional to the resistance of the leads, which for the Keele vessels has been found to be 0.04 to 0.08 ohm. As the resistance of the heater itself is 50 ohm, the heat generated in the leads is 0.08 to 0.16 % of the total. A worked example in the LKB handbook (56) suggests that the resistance of the leads should be subtracted from the total resistance before multiplying by the square of the current to arrive at the calibration energy, implying that all the heat generated in the lead flows into the jacket rather than into the vessel itself. Many authors assume that half this heat flows into the vessel and half into the jacket. Which is the truer picture of events depends on the effectiveness of the thermal connection made by the ends of the leads. The detachable leads from the 100 cm^3 vessel make good thermal contact with the jacket lid via massive pins and sockets, while the connections to the vessel are much more slender, consistent with the assumption that most if not all of the heat from the leads flows into the jacket. If the assumption was false, as may well be the case for the

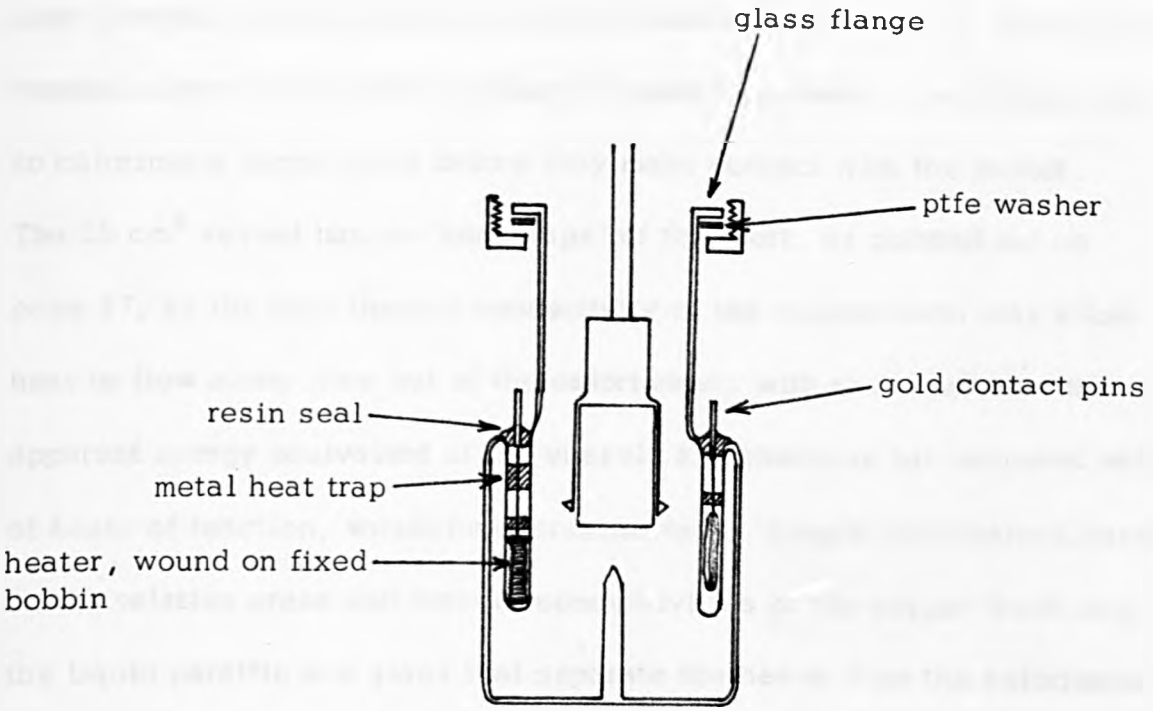


Figure 11. Proposed new 25 cm^3 vessel for LKB 8700 calorimeter.

25 cm^3 vessel, where the leads are permanently soldered to the heater, the calibration energy would be underestimated by up to 0.16 %.

A further, and potentially more important, error may arise from heat flowing from the heater through the leads to the jacket. In the 100 cm^3 vessel a layer of low-melting alloy 'tempers' the leads, i.e. brings them to calorimeter temperature before they make contact with the jacket. The 25 cm^3 vessel has no 'heat traps' of this sort, as pointed out on page 37, so the high thermal conductivity of the copper leads may allow heat to flow along them out of the calorimeter, with the result that the apparent energy equivalent of the vessel, and therefore all measured values of heats of reaction, would be overestimated. Simple calculations, based on the relative areas and thermal conductivities of the copper leads and the liquid paraffin and glass that separate the heater from the calorimeter liquid, suggest that this overestimation may lie in the range 1 to 10 %. The results from the standard 'tris' reaction (pages 61 to 63) show that both systematic and variable errors occur in the 25 cm^3 vessel to a much greater extent than in the 100 cm^3, the discrepancy being in the direction that would be caused by leakage along the heater leads. It is likely that the performance of the smaller vessel would be considerably improved by surrounding the leads with a 'heat trap' made of low-melting alloy or dental amalgam, and sealing the heater well with araldite surrounding gold pins as in the 100 cm^3 vessel. (figure 11)

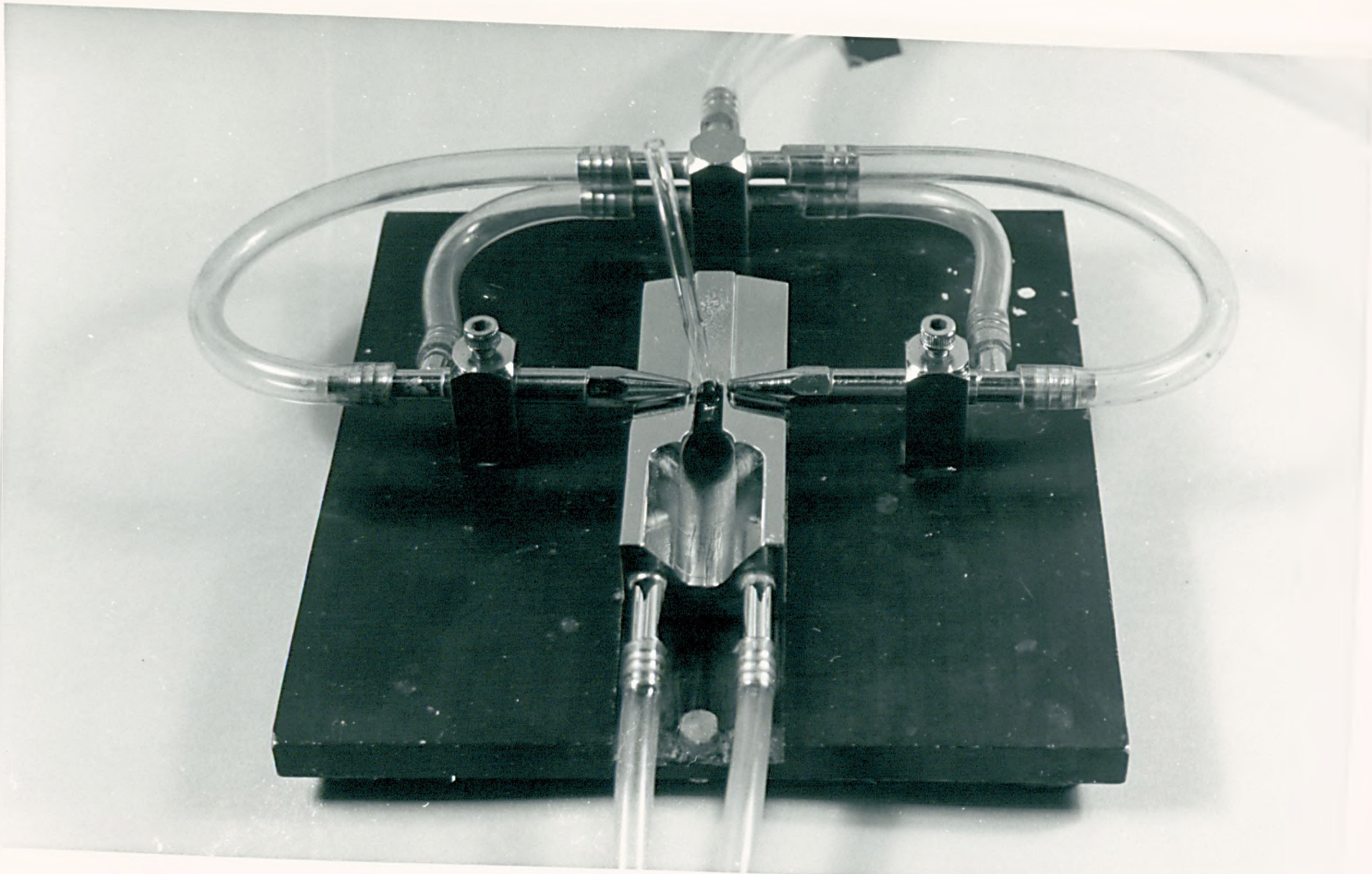
Calorimetry : Procedure.

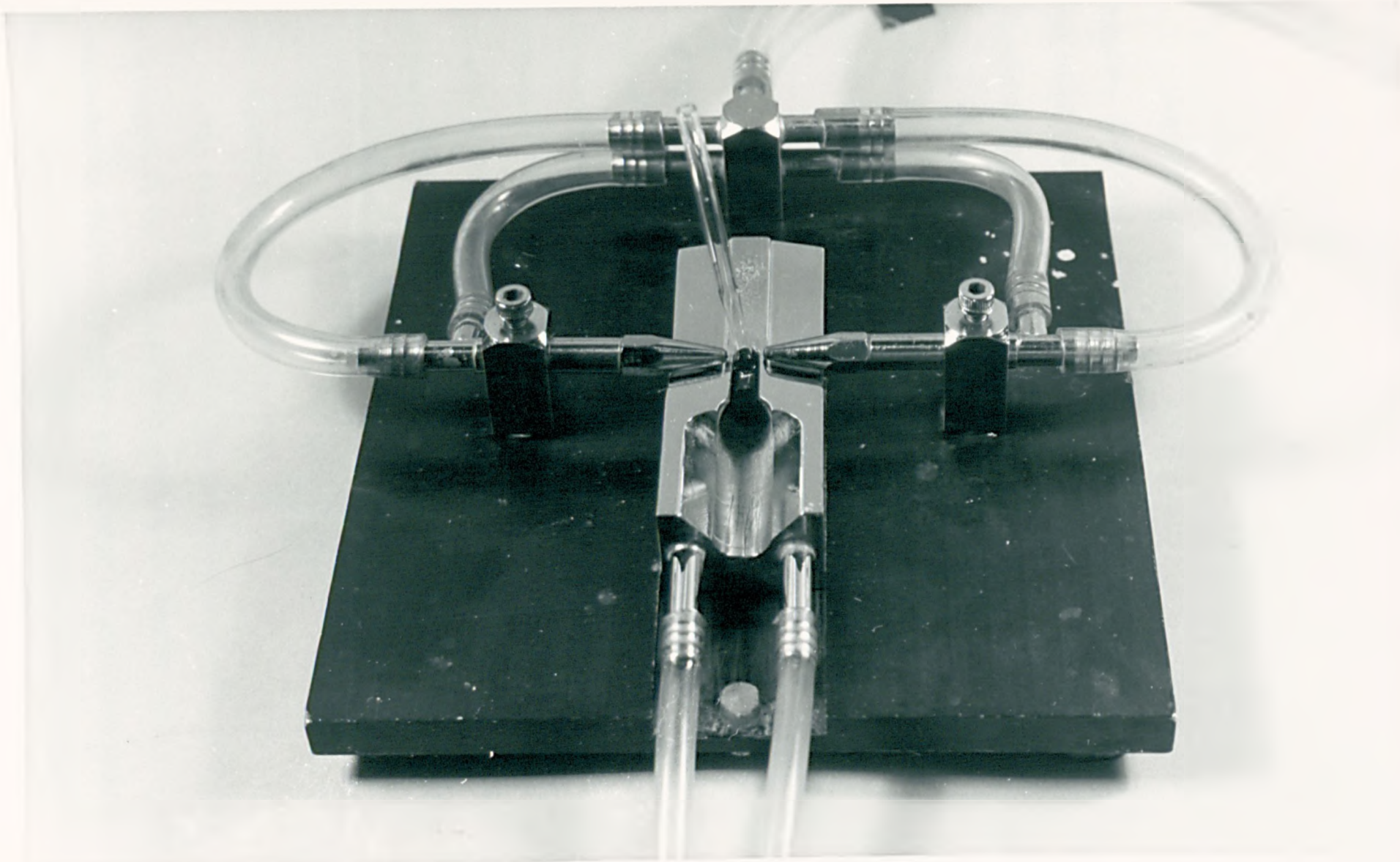
The experimental methods set out here were used for every reaction described in this thesis. Such modifications as were needed for particular reactions are described in the accounts of those reactions.

Ampoule filling and weighing.

When the calorimeter contained aqueous solutions the neckless ampoules, type 1 of figure 9, were used. For reactions in organic solvents the long-necked ampoules, type 2 for liquids and gases, and type 3 for solids, were used. Before and during weighing the ampoules were handled only with tweezers or cotton gloves.

Solid reagents were ground to free-flowing powders and poured into the ampoules through a simple glass funnel. In some cases, partic--ularly when the long-necked ampoules were used, the filling operation was impeded by the tendency of the solid to 'stick' in the funnel. Part of this tendency was presumably caused by electrostatic effects, as it could be lessened by clamping a weak radioactive source, as supplied for micro--balances, near the ampoule during filling. When long-necked ampoules were used for oxygen-sensitive compounds they were filled with nitrogen before sealing by placing them in numbered partitions in a vacuum dessicator, and twice evacuating and filling the dessicator with nitrogen. On removal from the dessicator the ampoules were rapidly plugged with rubber tubing and glass rod, and sealed using the LKB burner. In this device (figure 12) the ampoule is almost surrounded by a water-cooled metal block, to minimise the temperature rise during sealing. Nevertheless it was found to be necessary momentarily to open the upper end of the ampoule neck





while the flame was played on the glass; if not, the heat produced a pressure rise sufficient to prevent a seal from being made.

The masses of involatile solids were found by weighing the empty ampoule and the filled ampoule before flushing with nitrogen and sealing.

Liquids were introduced into the ampoules through a long hypodermic needle. The mass used was found by weighing the empty ampoule and the filled ampoule and its detached neck after sealing, making a correction for the differing masses of air and nitrogen where necessary.

When gaseous reagents were used the ampoules were filled by means of the vacuum dessicator, pump and gas supply as described for nitrogen on the previous page.

The Stanton balance used had a capacity of 30 g, and the smallest division on the optical scale corresponded to 0.01 mg. The weights, Stanton 2032 NPL A' 51, were certified by the National Physical Laboratory to have an accuracy of ± 0.01 mg, and a density, for the purposes of buoyancy corrections, of 8.4 g cm^{-3} (69). The buoyancy correction was applied to the masses of 'tris' used in the standardisation reaction (pages 57 to 63), but not to the masses of other substances since the magnitude of the correction (0.074 %)(70) was insignificant in comparison with the uncertainties of the measurements, including the weighing.

The calorimeter solution and reaction.

The solvent was stored in the LKB burette unit under nitrogen, and a measured 25 cm^3 or 100 cm^3 was run into the reaction vessel through a calibrated tap pipette. Solutes were weighed out into glass sample tubes with the same precision as the reagents in the ampoules, and were dissolved in the solvent as it was run into the vessel. An ampoule was placed in

the stirrer and the vessel was screwed into position. Connections to the thermistor and heater were made by gold-plated pins and sockets, using short leads of known resistance. The can was then clamped round the vessel, and was lowered into the water-bath. A stirring rate suitable for the reaction in hand was chosen. In general the lowest practicable stirring rate should be chosen, in order to minimise the heat of stirring and, more importantly, the change in heat of stirring caused by breaking the ampoule. This was particularly necessary when the 25 cm^3 vessel made in this laboratory was used, because the sapphire-tipped pin was slightly shorter than the ampoule, part of whose walls had therefore to be broken before the upper face of the ampoule was pierced and the solvent could wash out all the solid reagent.* The LKB-made 100 cm^3 vessel had a longer pin which broke both faces while usually leaving the side walls almost intact, so that the pattern and heat of stirring were altered as little as possible. In spite of these considerations, in many solid-liquid reactions it was necessary to use a high rate of stirring to accelerate the dissolution of the solid.

The infinity resistance of the thermistor under the conditions of a particular reaction was found by leaving the calorimeter until the resistance ceased to change appreciably. The calorimeter was then cooled by blowing air through the tube in the top of the can so that the expected heat of reaction would bring the resistance close to, but still a little above, the infinity resistance. When investigating an untried reaction this heat effect was approximately determined by a trial reaction, using a 'Servoscribe' chart recorder coupled to the Wheatstone bridge output rather than taking readings by hand. The trial also showed whether the rate of reaction was sufficient to provide more precise measurements, and whether the product

* The pyrex pin fitted in August 1977 was long enough to remove this difficulty

of reaction was soluble in the chosen solvent.

The time and power for calibration were then chosen to produce a resistance : time curve that resembled that of the reaction as closely as possible. The heater current was calibrated, and the heater resistance measured, following the LKB procedures (56). The resistance of the leads to the heater had previously been measured, and this value was subtracted from the measured heater resistance to obtain that of the heater alone, before calculating the precise calibration energy from the relationship:

$$E = i^2 Rt$$

Once the calibration time and heating power had been set, the stopwatch was started and a number (at least eight) of readings of time and resistance were taken, until it was clear that the resistance was changing slowly and steadily, at a constant rate typical of the chosen starting value. For each of these readings the resistance was set on the Wheatstone bridge, and when the meter passed through zero the null detector operated the slave pointer on the stopwatch so that a pair of readings of time and resistance could be made. The bridge was then quickly set to a new resistance value and the slave pointer reset for the next reading. The intervals between measured resistances were chosen to give time intervals of 0.20 to 0.50 minutes ; shorter intervals were found to lead to haste and error, while longer ones were unnecessarily tedious and gave scope for greater departure from linearity in the resistance : time curves.

Calibration.

After the fore-period was established the calibration heating was started, using the 'mode of operation' switch set to 'calibrate, auto'. As many readings as possible were taken during the calibration; where

the reaction or calibration was rapid it was found to be essential to choose these resistances in advance, and if only one or two could be made in a very restricted time one was chosen to correspond to approximately 50 % (for calibration) or 63 % (for reaction) of the total resistance change, thus providing a figure for Dickinson's method of evaluating the corrected resistance change (page 33). After the heating period further resistance and time measurements were made until the rate of change had remained substantially constant for eight or more readings, which formed the after-period.

The calorimeter was then cooled again, and a new fore-period was measured over the same resistance values as those used in the calibration. The reaction was initiated manually by pressing down the stirrer shaft until the fracture of both faces of the ampoule had been felt. When this was first done an anomalous heating effect was observed, which was attributed to friction between the stirrer or ampoule walls and the base of the vessel. In all subsequent experiments the stirring was stopped for the two or three seconds of the breaking process ; not by switching off the motor, because this produced a 'spike' of electrical noise which gave a spurious reading on the null detector, but by taking the stirrer momentarily out of gear. Resistance and time readings were taken for the reaction period just as for the calibration, and were continued until the rate of change was constant. Endothermic reactions were carried out in the same way, but the reaction was started at the end of the after-period of the calibration, which therefore also served as the fore-period of the reaction. Representative calibration and reaction curves are shown in figures 13 to 15.

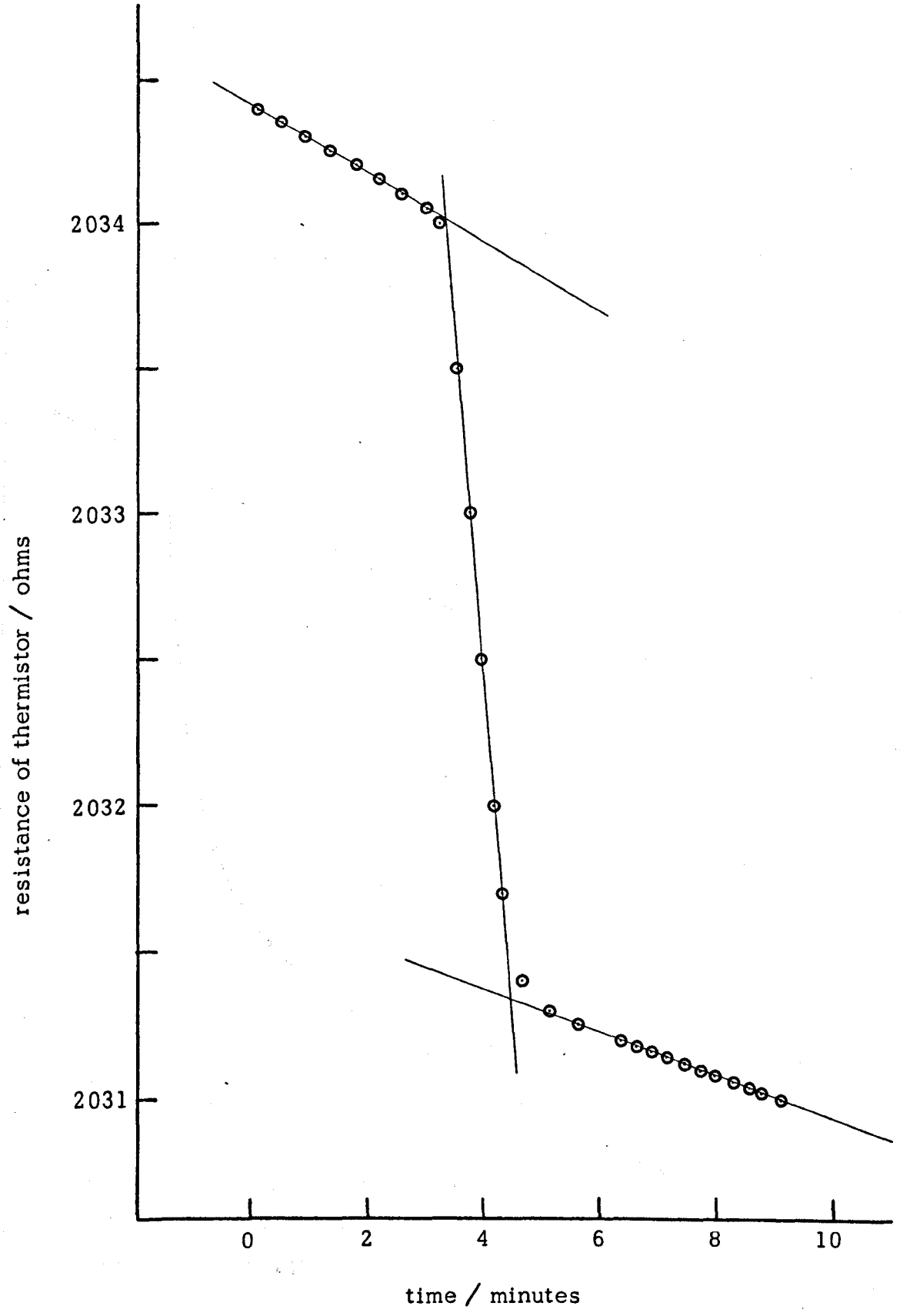


Figure 13. Resistance : time curve for calibration corresponding to the reaction shown in figure 14.

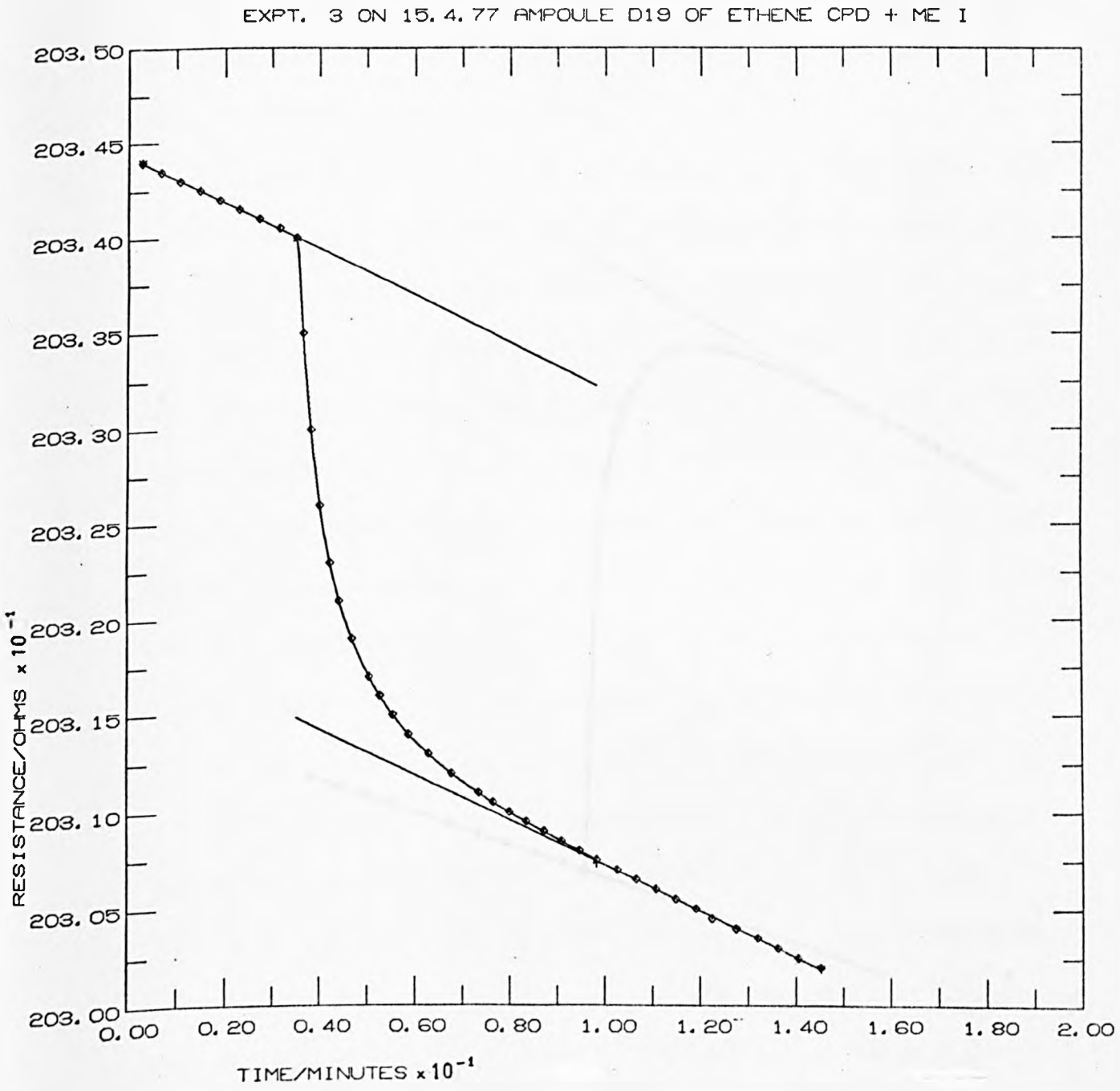


Figure 14. Resistance : time curve for exothermic reaction.

(Output from RPTEMP programme.)

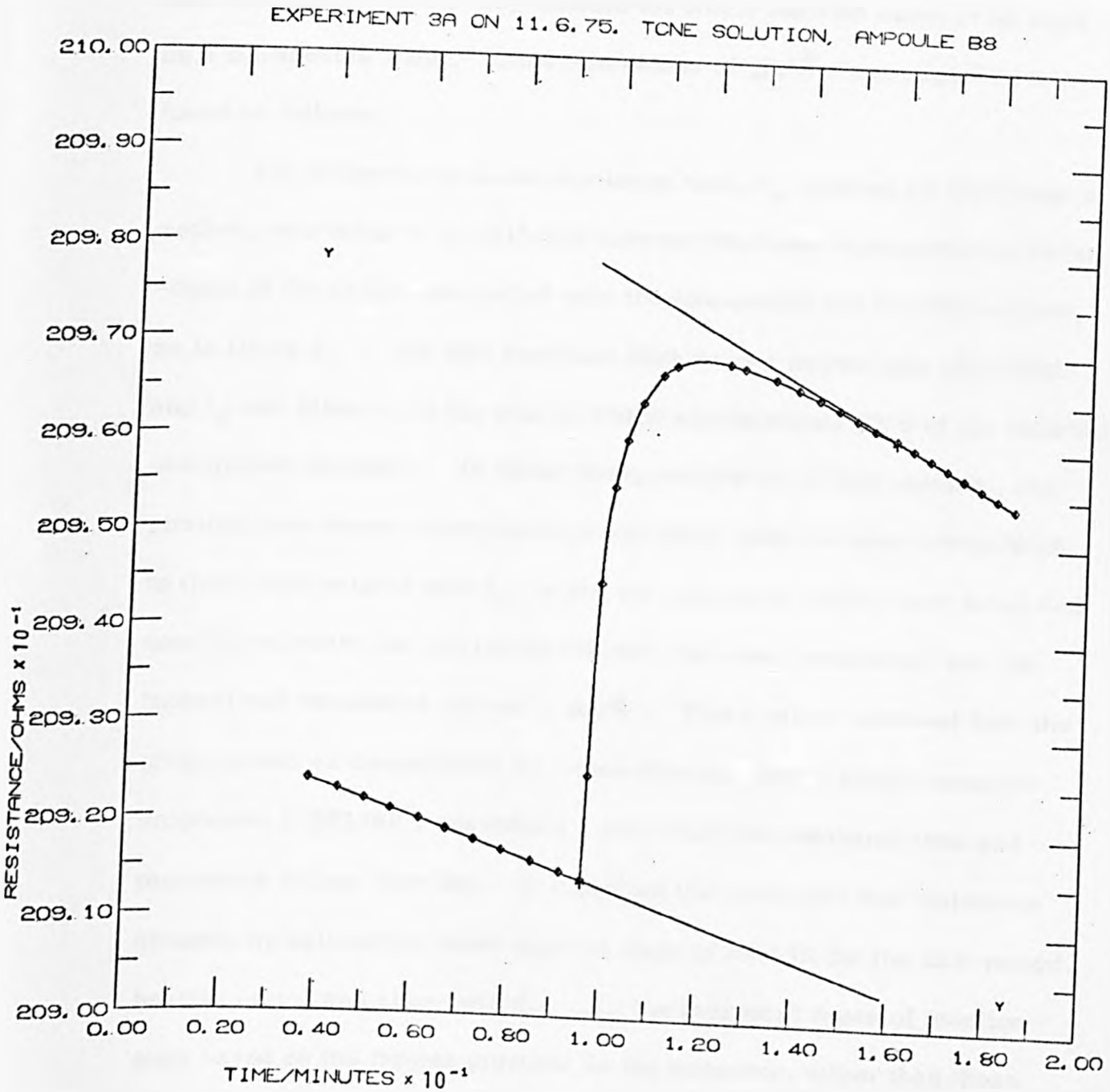


Figure 15. Resistance : time curve for endothermic reaction.

(Output from RPTEMP programme .)

Analysis of measurements.

The preliminary treatment of all the readings was the same; a graph of resistance against time was drawn, using a scale of 10 mm per minute and up to 100 mm per ohm. Although these scales entailed plotting and reading to 0.1 mm, they enabled the whole reaction curve to be seen on a manageable sheet. Corrected values of $\Delta R/\bar{R}$ (see page 53) were found as follows:

For calibrations the extrapolation time, t_x, needed for Dickinson's method, was taken to be half-way between the times represented by the inter--cepts of the calibration period with the fore-period and the after-period, as in figure 6. For fast reactions Dickinson's method was also used, and t_x was taken to be the time at which approximately 63 % of the resistance change had occurred. In either case, calibration or fast reaction, the straight lines representing the fore- and after- periods were extrapolated to their intersections with t_x, where the resistance values were noted and used to calculate the resistance change, the mean resistance, and the 'normalised resistance change', $\Delta R/\bar{R}$. These values obtained from the graph served as comparisons for those obtained from a simple computer programme ('DELTAR', appendix 2) into which the measured time and resistance values were fed. It computed the intercepts and resistance changes by calculating least-squares lines of best fit for the fore-period, heating period and after-period. All the presented heats of reaction were based on the figures provided by the computer, rather than those obtained from the graphs. For interest, the calculations of the heat of the 'tris' reaction (page 61) were carried out using resistance values derived from both the hand-drawn graphs and the computer programme. The results, shown in table 4, agree exactly.

For reactions that were not so rapid the first step was again to draw a graph, which served to identify errors in reading and to show which points could definitely be included in the after-period rather than the reaction. A more elaborate computer programme ("RPTEMP,") (71) based on the Regnault Pfaundler correction by Dr P. Borrell was used. The programme determines the point at which the reaction ends and the after-period begins by comparing three resistance readings in turn with the extrapolated least-squares straight line drawn through those points that are definitely in the after-period. If all three readings differ from the line by more than a specified number - usually three - of standard deviations, these points are designated part of the reaction curve, and are used in the Regnault-Pfaundler integration described on page 32 . If however the points lie within these limits the latest is incorporated in an expanded after-period for which a new straight line is calculated, and the point of divergence is found.

Calculation of the enthalpy change.

Ideally the reaction and calibration would produce identical corrected temperature changes, showing that the enthalpy changes from the two processes were of identical magnitude. In practice there is a small difference between the changes, and the calibration energy must be multiplied by the ratio of the corrected temperature changes to obtain the heat of reaction. To do this the relation between temperature and ther--mistor resistance must be known. The resistance of the thermistor does not vary linearly with temperature - the relation appears not to correspond to any simple mathematical function, but approximates to the following formula, in which A and B are empirical constants.

$$R = A e^{-B/T}$$

From this relationship various functions approximately proportional to the temperature change have been derived and experimentally tested (58). The extent to which they deviate from exact proportionality is shown in table 2. In all the work reported here the function $\Delta R/\bar{R}$, known as the 'normalised resistance change' was used for the calculation of enthalpies.

Table 2. Deviations from linearity of expressions relating change in thermistor resistance to change in temperature.

	expression taken as proportional to T				
	$(\Delta R \bar{T}^2)/\bar{R}$	$\Delta R/\bar{R}$	ΔR	$\frac{\ln(R_1/R_2)}{\ln R_1 . \ln R_2}$	$\ln R_1/R_2$
Deviation from linearity, % per ohm:-	0.001	0.01	0.07	0.005	0.01

(R_1, R_2, and $\bar{R}$ denote initial, final and mean resistances respectively, $\bar{T}$ denotes mean temperature.)

Heat effects other than reaction.

Even after allowing for heat leakage the resistance and temperature changes are not entirely due to the reaction being studied. Other heat effects unclude the following.

1. Mechanical work done in breaking the ampoule. This unavoidable effect is claimed by LKB to be less than 2 millicalories (0.008 J) for 90 % of the ampoules. The need to disengage the stirrer during breaking has already been mentioned.

2. Heat absorbed by evaporation of solvent into the gas released from the ampoule, which is an appreciable quantity if the solvent is volatile.

The observed magnitude of this effect agrees quite well with the value calculated from vapour pressures and heats of vaporisation, as the following example shows.

Calculation of the heat effect due to breaking an ampoule of nitrogen into 1,2-dichloroethane.

It is assumed that the ampoule is completely filled with dry nitrogen at atmospheric pressure (750 torr) and that this gas becomes saturated with solvent vapour by evaporation of solvent in such a way that the heat of evaporation is drawn from the calorimeter contents.

Vapour pressure of solvent: $\log p = - \frac{0.05223\,A}{T} + B$ (72)

where A = 35 598 and B = 8.126,

i.e. $p = 77.6$ mmHg

Heat of vaporisation $\simeq$ 34 300 J mol^{-1} at 25°C.

If the 1.1 cm^3 of gas liberated from the ampoule expands to $(1.1 \times 750+77.6)/750 = 1.214$ cm^3 as the solvent evaporates, and a fraction proportional to the partial vapour pressure of the new volume is solvent vapour, then the number of moles of solvent evaporating is calculated to be $\simeq 5.1 \times 10^{-6}$, and the heat absorbed during the evaporation is 0.174 J.

This figure may be compared with the experimental average of the heat of ampoule breaking in 1,2-dichloroethane, which is 0.183 $\pm$ 0.017 J, so that the theoretical value lies well within the experimental uncertainty of the measured values.

The combined effect of breaking the ampoule and evaporation of the solvent were evaluated for each solvent used in the current work by breaking ampoules filled with the same gas, air or nitrogen, as was

contained in the ampoules used in the reactions themselves. The mean observed heat effect was then subtracted from all apparent heats of reaction to obtain 'corrected' heats of reaction.

3. Decrease in vapour pressure due to solution of ampoule contents, leading to condensation and heat evolution. This effect may also be calculated, using the known molar ratios of solvent and solute.

a. For the formation of a 10^{-4} mole ratio solution in 1,2-dichloroethane. The vapour pressure at 298 K = 78 torr, and $H_{vap.} = 34300\ J\ mol^{-1}$ while the air space in the vessel is approximately 10 cm^3. If the change in svp is proportional to the change in the molar fraction of solvent, the number of moles evaporating $= (78 \times 10^{-4} \times 10)/(760 \times 24790) = 4.14 \times 10^{-9}$ moles, and the heat evolved $= 1.4 \times 10^{-4}$ J.

b. For the formation of a solution of 5 g of 'tris' per litre of aqueous acid. The mole fraction of water decreases by approximately 7.43×10^{-4}. The svp of water at 298 K is 24 torr, and the heat of vaporisation is approximately 44 000 $J\ mol^{-1}$, so that the heat evolved is $\simeq 4.2 \times 10^{-4}$ J.

Neither of these quantities are significant when compared with other errors in the associated measurements.

Other extraneous effects are discussed in the descriptions of the reactions in which they occurred.

Uncertainties.

The uncertainties of experimentally-derived values quoted in this thesis are, according to thermochemical convention (73) equal to twice the estimate of the standard deviation of the mean, i.e.

$$\text{uncertainty} = 2 \times \sqrt{(x_i - \bar{x})/n(n-1)}$$

The uncertainties of literature values usually follow the same convention, but their derivation is frequently not described.

Where an overall heat of reaction has been calculated from more than one measured value, by an equation of the form

$$\Delta H_T = a\Delta H_1 + b\Delta H_2 + c\Delta H_3$$

the standard deviation of the mean for the combined reaction has been calculated using the following relationship (73).

$$s_T = \sqrt{(a.s_1)^2 + (b.s_2)^2 + (c.s_3)^2}$$

The uncertainty quoted for the combined reaction has been twice the standard deviation so calculated.

THE TEST REACTION

Although solution calorimeters are commonly calibrated electrically at every use, so that the enthalpies of the reactions being studied are compared with accurately measured quantities of energy, it is recommen--ded that each calorimeter and its method of operation are tested by measuring the enthalpy of a standard reaction (44). The IUPAC subcommission on calibration and test materials (74) chose as a standard for the calorimetry of reactions in solution the reaction of tris(hydroxymethyl)aminomethane, 'tris' or 'THAM', with 0.1 M aqueous hydrochloric acid, using the reference material supplied by the National Bureau of Standards in Washington as NBS 724 or 724a.

$$(CH_2OH)_3CNH_2\ (s) + HCl\ (aq) \longrightarrow (CH_2OH)_3CNH_3^+Cl^-\ (aq)$$

The recommended concentration is 5 g 'tris' per dm^3 of aqueous acid.

Experimental.

A fresh sample of tris (Sigma 'Trizma Base T 1503', stated purity 99.9 %) was stored at room temperature over saturated magnesium nitrate solution, as recommended by Hill et al. (44). The purity was determined by titration with standard hydrochloric acid diluted from a BDH CVS ampoule to a concentration of 0.1 ± 0.0001 mol dm^{-3}. Class 'A' glassware was used throughout the purity determination, except for the pipette, which was calibrated by weighing. The water used was glass-distilled and thermo--statted at 20.0°C. The indicator chosen was bromocresol green, whose pK_a is 4.7, corresponding exactly to the pH of a 0.1 mol dm^{-3} solution of tris hydrochloride (75,70). The purity as determined by the titrations

(five aliquots) was 100.02 ± 0.12 %, the uncertainty quoted includes the stated error of the flasks and hydrochloric acid concentration as well as the uncertainty of the titration readings. Figures for the calibration of glassware, titrations and calculations are shown in table 3.

The heat of the tris reaction was determined in the 25 cm^3 and 100 cm^3 calorimeter vessels, using the recommended concentrations and applying the methods already described. The stirrer speed was set to 'high', since that speed was usually necessary for the measurement of the reactions of platinum complexes. The reaction of tris with hydrochloric acid was very rapid, so the highest possible calibration power (500 mW) was used in order to produce a correspondingly short heating period.

When an air-filled ampoule was broken into 0.1 mol dm^{-3} hydro--chloric acid, no heat effect, other than a small change in the slope of the resistance : time graph, could be detected, so no correction for heat of ampoule breaking was applied to the observed heats of reaction. The results of calorimetry are shown in tables 4 and 5.

Correction of results of the tris reaction for non-standard temperature.

As in these measurements calibration preceded reaction the cal--culated enthalpy change refers to an isothermal reaction taking place at a temperature which is taken to be the mean temperature of the after-period. The mean resistance of the thermistor during the after-period was 2035.33 ohm. To find the temperature which is equivalent to this resistance, the calorimeter was left overnight starting from an initial resistance close to R_∞, with no stirring, so that the temperature of the thermistor would be as close as possible to that of the thermostat. The temperature of the

laboratory was 23.2°C. At the end of this period the thermistor resistance was 2030.43 ohm, and the corresponding temperature of the bath, as measured by a 20 - 27°C x 0.01 °C mercury-in-glass thermometer cor--rected for the emergent stem, was 25.056°C. The temperature coefficient of the resistance of the thermistor was approximately 80 ohm per °C (56), so the temperature corresponding to 2035.33 ohm, i.e. the temperature for which the enthalpy change was measured, was 24.995°C.

The temperature coefficient of the enthalpy of the tris reaction is 174 J mol^{-1} K^{-1}, (76) so that the correction to be applied to the measured enthalpies is -0.87 J mol^{-1}. As this is much smaller than the uncertainty of the reaction it has not been applied to the measured results.

Conditions were much the same for the other solution reactions reported here. The thermostat temperature was always 25.05 to 25.06°C, and the infinity resistance of the the thermistor corresponded to a slightly higher temperature, i.e. 25.05 to 25.10 °C. The resistance at the end of each reaction was 5 to 10 ohm above the infinity value R_∞, corresponding to a temperature 0.06 to 0.12°C below the thermostat, i.e. within approx--imately 0.05° of 25.00°C, 298.15 K. The change in heat capacities

$$\Delta C_p = \Sigma C_p \text{ (products)} - \Sigma C_p \text{ (reactants)}$$

is not known for the reactions investigated, so no certain correction may be made, but if C_p is of the order of 200 J mol^{-1} K^{-1}, the correction to $\Delta H_{298.15}$ that would be needed for the temperature differences set out above would be approximately 10 J mol^{-1}, which is much smaller than the uncertainty of the measurements and has therefore been ignored.

Table 3. Estimation of the purity of tris.

Calibration of pipette:

Mean mass of 25 cm^3 aliquots of distilled water at 20.0°C = 24.9183 ± 0.0062 g.

Volume of 1 g of water at 20.0°C = 1.0028 cm^3 (70)

So true volume delivered by pipette at 20.0°C = 24.9881 ± 0.0119 cm^3

Nominal purity of tris, using masses corrected for the buoyancy of air, = 0.100074 mol dm^{-3}.

So nominal quantity of tris in each aliquot = 2.50066×10^{-3} mole.

Calibration of burette:

Mass of a nominal 25.045 cm^3 of distilled water at 22.0°C from the burette = 24.9423 g. Volume of 1 g water at 22.0°C = 1.0032 cm^3.

So true volume delivered in calibration = 25.0221 cm^3.

Titration of nominal 25 cm^3 aliquots of tris solution with 0.1000 mol dm^{-3} HCl (aq), using 2 drops bromocresol green indicator to green end-point.

Volumes of acid added /cm^3: 25.03, 25.04, 25.05, 25.04_5, 25.03_5

Mean titre = 25.04 cm^3. Blank titre : 0.005 cm^3.

So mean titre of tris = 25.035 ± 0.007 cm^3.

True volume delivered = (25.035 x 25.0221/ 25.045) = 25.012 cm^3

Quantity of HCl reacting with each aliquot of tris = 25.012×10^{-4} mole.

Therefore purity of tris = $(25.012 \times 10^{-4} / 2.50066 \times 10^{-3}) \times 100$

= 100.02 ± 0.12 %

Table 4. Reaction of 'tris' with 100 cm^3 of 0.1000 mol dm^{-3} HCl (aq).

Ampoule number	Mass of tris / g	Heat of reaction / J	Heat of reaction / kJ mol^{-1} (computed)	(graph)
C2	0.50003	-122.670	-29.718	-29.730
C3	0.50120	-122.817	-29.684	-29.701
C4	0.50118	-122.931	-29.712	-29.752
C5	0.50103	-122.750	-29.678	-29.632
C6	0.49918	-122.324	-29.684	-29.638
C7	0.50079	-122.838	-29.713	-29.696

Mean ΔH = -29.698 ± 0.015 kJ mol^{-1} (computed)

-29.698 ± 0.014 kJ mol^{-1} (graph)

Table 5. Reaction of 'tris' with 25 cm^3 of 0.1000 mol dm^{-3} HCl (aq).

Ampoule number	Mass of tris / g	Heat of reaction / J	Heat of reaction / kJ mol^{-1}
D15	0.12540	-31.5857	-30.511
D16	0.12518	-31.3075	-30.296
D17	0.12517	-31.0610	-30.060
D18	0.12499	-30.9006	-29.948
D19	0.12515	-31.0855	-30.088
D20	0.12537	-31.1518	-30.100
D21	0.12547	-31.1937	-30.116

Mean ΔH = -30.16 ± 0.14 kJ mol^{-1}

Discussion of the 'tris' reaction.

Results of several determinations of the heat of the 'tris' reaction, mostly using the NBS standard material, are shown in table 6. They differ by only 0.12 %, but the variation between different workers' results is much greater than the experimental uncertainties (2 sdm) , except the uncertainty quoted by Prosen and Kilday, who included an estimate of systematic errors in their figure.

Table 6. Literature values for the enthalpy of the 'tris' reaction.

Authors	Enthalpy of reaction / J mol^{-1}		reference
Gunn	29735	± 2	77
Hill, Ojelund, Wadsö	29743	7	44
Prosen and Kilday	29771	31	76
Nichols, Skold, Wadsö	29768	3	55

Some authors have found values very different from these; although Prosen and Kilday were able to show that one very high result (30718 J mol^{-1}, i.e. 3 % above the accepted figure) was only obtained if the calorimeter was sealed, other workers have found values varying from 29732 to 29983 J mol^{-1} without any agreement as to whether the variation should be attrib--uted to the calorimetry, the method of preparing the sample, or its origin (78). Rychly and Pekarek (78) found a difference of 51 J mol^{-1} between crushed and uncrushed samples of the same (Merck) solid, and a smaller but still significant difference between crushed and uncrushed NBS 724 a. While the NBS samples, if prepared for calorimetry as recommended, appears to have always given results in the range 29720 to 29790 kJ mol^{-1}, it is

not certain that other samples of apparently pure solid will not show a wider variation however accurate the calorimetry.

The results obtained in this work may be compared with the literature values.

Those obtained in the 100 cm^3 vessel are approximately 0.2 % below the NBS certified figure; the uncertainty of 15 J mol^{-1} is rather greater than those obtained at Lund or the NBS which usually fall in the range 3 to 11 J mol^{-1}. It may be relevant to note that if the resistance of the leads were not subtracted from the total resistance in calculating the calibration energy the result would be 29746 J mol^{-1}, which is within the usual range even for the NBS sample.

Results obtained from the 25 cm^3 vessel are approximately 1.3 % higher than the certified figure, with an uncertainty of 0.46 %, showing that there are considerable systematic and random errors in the use of this vessel. The most likely source of systematic error is leakage of heat along the heater leads, as described on page 44 . As the heater is free to move in its well, so changing its thermal connection to the calorimeter fluid, the leakage may vary from one measurement to another, and so account for part of the random error. Suggestions for the improvement of the apparatus are set out on page 44.

While these errors are large compared to those expected from a standardisation reaction, they are not so serious when applied to the heats of reaction of the platinum compounds. In particular, systematic errors are partially removed when thermochemical values are found by subtracting one experimentally-measured heat from another.

The precision of heats of reaction of platinum complexes and the test reaction.

The precision of the results for this standard reaction is likely to be much better than the precision of the other reactions studied, particularly when these are expressed as heats of reaction per mole, for several reasons:

a. None of the reagents were as pure as the sample of 'tris'.

b. Most reactions were carried out in 1,2-dichloroethane, which is more volatile than water and has a lower specific heat capacity.

c. The heats of reaction were considerably smaller than the heat evolved in the standard reaction, principally because a smaller mass of reagent was used.

d. The molar masses of the platinum complexes are high, so that the observed heats are multiplied by a very large factor, typically 3 $\times 10^4$, to obtain the molar heats.

The reaction of $P_2Pt(C_2H_4)$ with carbon disulphide.

Introduction

The bond dissociation energy of the Pt-CS_2 bond is of interest as part of a series of values for different unsaturated compounds which may be used to test theories of bonding. It may also help to explain the difficulty of forming complexes of carbon dioxide, which might be expected to resemble those of CS_2. Although CO_2 will react with platinum (0) com--plexes, it apparently does so only in the presence of oxygen, to form carbonato complexes of the type $P_2Pt(CO_3)$ rather than a Pt (0) complex analogous to the CS_2 complex, $P_2Pt(CS_2)$. (79)

Bis(triphenylphosphine)(carbon disulphide) platinum (0), $P_2Pt(CS_2)$, was first made by Baird and Wilkinson (80,81) in 1966 by reacting CS_2 with a suspension of $Pt(PPh_3)_2$ in ether. Its structure, as determined by Mason and Rae(16) is shown in figure 16. The bond lengths and angles in the co-ordinated carbon disulphide may be compared with those in the free molecule, where the C-S bond lengths are 0.1554 nm and the SCS angle is 180°. The S_2-C_1 bond length in the complex is 0.174 nm, implying a considerable weakening relative to that in the free molecule, caused by donation of charge from platinum to the CS_2 π^* antibonding orbitals. The mean C-S bond length in the complex, 0.163 nm, and the SCS angle of 136.2° are very similar to those in the first excited state of CS_2. Mason (82) has pointed out that the Dewar-Chatt-Duncanson theory of bonding in π complexes of unsaturated ligands implies that the electron distribution in the coordinated molecules shall resemble that in the excited state of the free molecule, or in some cases in the molecular anion. The difference in the platinum-phosphorus bond lengths in the complex may be

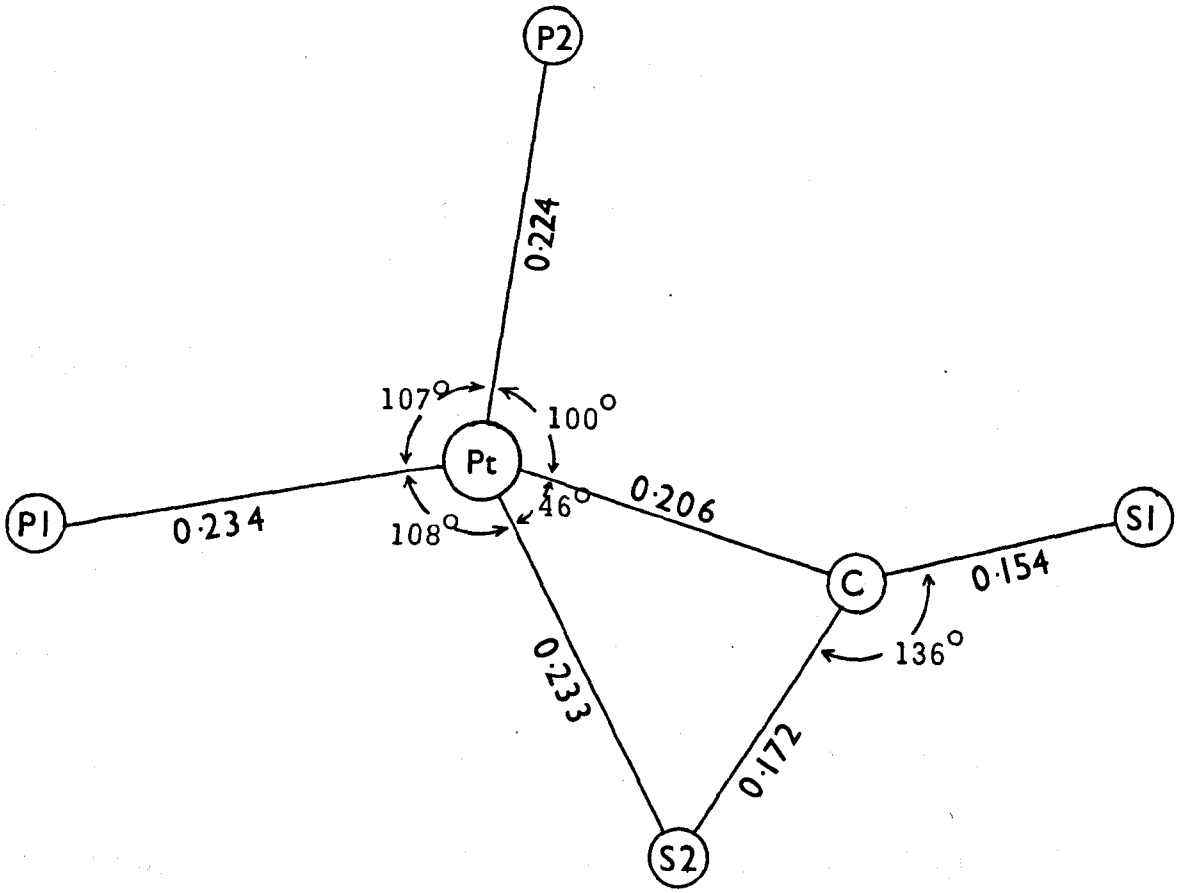


Figure 16. Molecular structure of $P_2Pt(CS_2)$, with bond lengths (in nanometres) and angles. The phenyl groups of the phosphines have been omitted for clarity.

due to the different trans effects of the carbon and sulphur atoms. Since the carbon pπ orbital contributes much more than does the sulphur to the antibonding π^* molecular orbital of CS_2 (15), the platinum orbitals may be expected to overlap more with carbon than with sulphur, and so will form weaker π bonds to the phosphorus which is trans to the carbon.

Procedure and results.

The heat , ΔH (1), of reaction (1) has been determined from measurements of the heats, $\Delta H(2)$ to $\Delta H(5)$, of reactions (2) to (5), and incorporation of a value for $\Delta H(6)$, the heat of vaporisation of carbon disulphide. The solvent was 1,2-dichloroethane, dce.

(1) $P_2Pt(C_2H_4)$ (s) + CS_2 (g) $\longrightarrow$ $P_2Pt(CS_2)$ (s) + C_2H_4 (g)

(2) 80 CS_2 (l) + 3200 dce (l) $\longrightarrow$ [80 CS_2, 3200 dce] (l)

(3) $P_2Pt(C_2H_4)$ (s) + [80 CS_2, 3200 dce] (l) $\longrightarrow$ [$P_2Pt(CS_2)$, C_2H_4, 79 CS_2, 3200 dce] (l)

(4) $P_2Pt(CS_2)$(s) + [79 CS_2, 3200 dce] (l) $\longrightarrow$ [$P_2Pt(CS_2)$, 79 CS_2, 3200 dce] (l)

(5) C_2H_4(g) + [$P_2Pt(CS_2)$, 79 CS_2, 3200 dce] (l) $\longrightarrow$ [$P_2Pt(CS_2)$, C_2H_4, 79 CS_2, 3200 dce] (l)

(6) CS_2 (l) $\longrightarrow$ CS_2 (g)

The relations between the reactions are shown in the following cycle:

$$
\begin{array}{lcl}
P_2Pt(C_2H_4)\,(s) + CS_2\,(g) & \xrightarrow{\Delta H(1)} & P_2Pt(CS_2)\,(s) + C_2H_4\,(g) \\
\uparrow \Delta H(6) & & \downarrow \Delta H(4) \qquad \downarrow \Delta H(5) \\
CS_2\,(l) & & \\
\downarrow \Delta H(2) & & \\
P_2Pt(C_2H_4)\,(s) + [CS_2, dce]\,(l) & \xrightarrow{\Delta H(3)} & [P_2Pt(CS_2), CS_2, C_2H_4, dce]\,(l)
\end{array}
$$

The heat of reaction (1) is given by the following equation.

$$\Delta H(1) = \Delta H(2) + \Delta H(3) - \Delta H(4) - \Delta H(5) - \Delta H(6)$$
$$= (-3.97) + (-15.77) - (+15.39) - (-10.94) - (+27.70)$$
$$= -44.0 \pm 1.3 \text{ kJ mol}^{-1}$$

Experimental

As the ethene complex is unstable in solution in the presence of oxygen, the reaction with carbon disulphide was carried out by breaking an ampoule of solid ethene complex into excess carbon disulphide dissolved in a suitable solvent. For the same reason air was excluded from the ampoules and the solvent as far as possible in this and other reactions involving the ethene complex. The solvent chosen was 1,2-dichloro--ethane, selected after a number of others, including dichloromethane, trichloromethane, dibromomethane, nitromethane and nitrobenzene, had been rejected either because they were too volatile to allow precise calor--imetry or because the carbon disulphide complex did not dissolve in them. The choice of a chlorinated hydrocarbon solvent precluded the use of rubber-stoppered ampoules in calorimetry, because the bungs were rapidly attacked by the solvent and flew out of the ampoules soon after immersion in the calorimeter solution. Before use the dce (May and Baker) was dried over magnesium sulphate, purged with nitrogen, and distilled under nitrogen, the central fraction boiling within a 0.1 ^{o}C range, e.g. 82.16^{o} to 82.23^{o}C at 748.25 torr, being collected. The purity of the distilled solvent was tested by gas chromatography; no impurity peak greater than (5×10^{-4}) x the height of the dce peak could be detected. The dce was stored in the LKB solvent burette under nitrogen and purged again at every use. All the nitrogen used for this and other experimental work was

B.O.C. "Oxygen Free" grade, nominally containing less than 10 parts per million of oxygen.

The proportions of carbon disulphide, ethene complex and solvent were chosen to give as rapid a reaction as possible, hence the large excess of carbon disulphide, while keeping down the volatility of the liquid and producing a homogeneous solution of the products.

Reaction (2). Solution of CS_2 in dce.

Carbon disulphide (Hopkin and Williams) was purged with, and distilled under, nitrogen. The fraction boiling at 45.90 ± 0.01°C under a pressure of 759.0 torr was collected and stored under nitrogen. A 0.500 cm^3 capillary-necked bulb pipette was used to measure the carbon di--sulphide both when filling ampoules and when preparing the calorimeter solution for heats of reaction. This large volume of the liquid was used because of the difficulty of flame-sealing an accurately-known small mass of such a volatile substance into the LKB ampoules. The mass of CS_2 used was found by subtracting the mass of the empty ampoule from that of the filled ampoule and detached stem after sealing, allowance being made for the mass of air displaced by the liquid.

No correction was made for the heat of breaking, since there was no obvious way in which the opposing effects of CS_2 vapour con--densing and dce evaporating could be evaluated. A correction would not affect the heat of reaction by more than 0.02 kJ mol^{-1}.

Results of calorimetry are shown in table 7.

Reaction (3). Reaction of $P_2Pt(C_2H_4)$ with carbon disulphide.

The ethene complex was provided by Dr R. Puddephatt of Liverpool University, and was analysed at Keele (found C= 58.45 %, H = 4.48%,

calculated C = 61.04 %, H = 4.58 %). This and all other analyses quoted were carried out on a Perkin-Elmer model 240 Elemental Analyser. Each sample of platinum placed in the combustion boat for analysis was covered with 10 mg of pre-dried tungsten (VI) oxide to ensure complete oxidation in the furnace. A 'blank' combustion in which the boat contained only tungsten oxide gave no measurable readings for carbon or hydrogen.

Ampoules containing approximately 10^{-4} moles of the CS_2 complex were broken into a solution of 0.5 cm^3 of carbon disulphide in 25 cm^3 of dce.

The reaction was not complete until at least 10 minutes after breaking the ampoule; this low rate of reaction and the small quantity of heat evolved caused the reaction period to merge into the after-period. Both the RPTEMP computer programme and graphical methods of analysis rest on the assumption that the plot of resistance against time in the after-period is a straight line. While this assumption is usually almost correct for short periods, it does not hold for more than a very few minutes. The rate of fall of resistance decreases as the temperature of the calorimeter fluid approaches the infinity temperature. In order to improve on the arbitrary choice of the end of the reaction period, the RPTEMP programme was modified, for this reaction only, to include an exponential rather than a straight-line after-period, thus conforming more closely both to the observations and to the behaviour corresponding to Newton's law of cooling. The values of resistance changes for the reaction were obtained from computer-drawn graphs generated by this modified programme. The results of calorimetry are shown in table 8.

Reaction (4). Solution of $P_2Pt(CS_2)$ in carbon disulphide and dce.

A sample of the CS_2 complex was made by adding 0.6 g of $P_2Pt(C_2H_4)$

to 10 cm^3 of dce and 1 cm^3 of carbon disulphide in a 100 cm^3 beaker in a glove bag that had been repeatedly evacuated and refilled with nitrogen. The liquids had been purged with and stored under nitrogen. The complex was precipitated by the addition of 50 cm^3 ofdiethyl ether and filtered before removal from the bag. Infra-red spectra of the product showed peaks at 1139 and 1156-60 cm^{-1} in nujol and 1148 cm^{-1} in trichloro--methane, close to the literature values of 1141 and 1160 cm^{-1} in nujol and 1147 cm^{-1} in dichloromethane (81). The melting point was 143-160°C, literature 145-165 (decomp.)(80). There was no sign of the infra-red absorbtion at 818 cm^{-1} that is typical of the dioxygen complex P_2PtO_2. The results of calorimetry are shown in table 9.

Reaction (5). Solution of ethene in carbon disulphide and dce.

Attempts to measure this heat of solution by using the narrow-necked flame-sealed ampoules intended for gases proved unsatisfactory. There was considerable uncertainty as to the mass of gas contained in the ampoule, since the temperature of the gas at the moment of sealing could not be known. The seal itself was often faulty, with signs of soot indicating that the ethene had been decomposedby the heat. These difficulties were reflected in the results, which showed an uncertainty of 2 kJ mol^{-1}.

An alternative method, based on Evans' technique for the calorimetry of gaseous reactions (1) was used. A 25 cm^3 calorimeter vessel (figure 17) was fitted with a ground-glass B6 socket into which was sealed with de Khotinski cement a cone that was drawn into a fine tube inside the vessel, and was covered with a rubber serum cap outside. A 1 cm^3 glass syringe was held in the brass tube attached to the calorimeter can, and from the syringe a 50 mm hypodermic needle was passed through a glass guide into the serum cap. The delivery tube brought the gas to a point near the pin

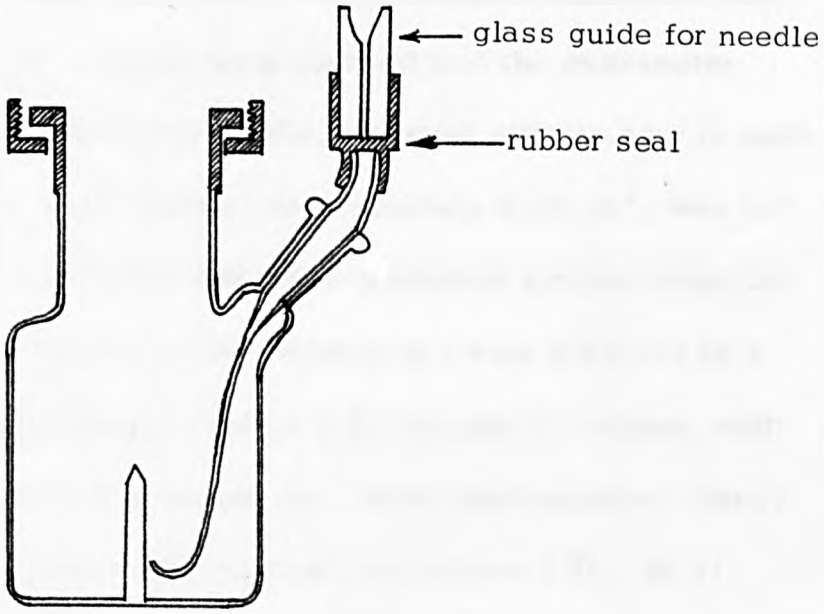


Figure 17. 25 cm^3 calorimeter vessel adapted for gas injection.

in the centre of the vessel. Any gas that did not dissolve immediately it left the tube was caught in a glass bell held in the stirrer.

Ethene (BDH, $\geqslant$ 99.8 %) was taken directly into the syringe from the cylinder by driving the hypodermic needle through the wall of a length of pressure tubing attached to the valves. After repeated flushing of the syringe, a number of 1 cm^3 samples were injected into the calorimeter vessel. Most of the gas dissolved rapidly, but even after an hour or more in contact with the dce a small volume, approximately 0.06 cm^3, was left in the 'bell'. This gas was withdrawn into a graduated syringe where its volume was measured. Samples of the residual gas were analysed by a Pye series 104 gas chromatograph, using a 4 ft.'Poropac Q' column, with katharometer detector and helium carrier gas, which distinguished clearly between air (21 - 23 seconds retention time) and ethene (75 - 80 s). The samples showed the same retention time as air, with only very minute traces of ethene.

After calorimetry the volume of undissolved gas was measured in the way just outlined; the volume of ethene dissolved was taken to be the volume injected minus the residue. The results of calorimetry are shown in table 10.

Reaction (6). Vaporisation of carbon disulphide.

The literature value for the heat of vaporisation at 298 K is + 6.61 kcal mol^{-1},(84) which is equivalent to + 27.7 kJ mol^{-1}.

Discussion.

The heat of reaction (1), between gaseous carbon disulphide and solid $P_2Pt(C_2H_4)$ to form gaseous ethene and solid $P_2Pt(CS_2)$, has been determined.

$$\Delta H(1) = -44.0 \pm 1.3 \text{ kJ mol}^{-1}$$

The difference in bond dissociation energies, $D(Pt - C_2H_4) - D(Pt - CS_2)$, is equal to the heat, $\Delta H(8)$, of the reaction between gaseous reactants to form gaseous products.

$$(8) \quad P_2Pt(C_2H_4)\,(g) + CS_2\,(g) \longrightarrow P_2Pt(CS_2)\,(g) + C_2H_4\,(g)$$

Thus one may write

$$D(Pt-C_2H_4) - D(Pt-CS_2) = \Delta H(7) - \Delta H_{sub}\,P_2Pt(C_2H_4) + \Delta H_{sub}\,P_2Pt(CS_2)$$

The heats of sublimation are not known, but may be assumed to be approx--imately equal, the assumption being supported by the findings of McNaughton, (29) who measured heats of sublimation of a number of halide complexes ofcobalt, nickel and copper. The values were affected most by the identity of the metal, rather less by the nature of the halogen, and least by the olefin substituent; complexes differing only in the last respect having heats of sublimation within 2 kJ mol^{-1} of one another. Therefore

$$D(Pt - C_2H_4) - D(Pt - CS_2) \simeq -44 \text{ kJ mol}^{-1}$$

i.e. the $Pt - CS_2$ bond is approximately 44 kJ mol^{-1} stronger than the $Pt - C_2H_4$ bond in complexes containing bis(triphenylphosphine).

Table 7. Reaction (2). Solution of carbon disulphide in dce.

Ampoule number	Mass of CS_2/ g	Heat of reaction/J	Heat of reaction / kJ mol^{-1}
1	0.7655	39.980	3.977
2	0.7626	39.863	3.980
3	0.7339	38.213	3.965
4	0.7722	40.490	3.922
5	0.7758	40.469	3.972
6	0.7556	39.117	3.942
7	0.7544	39.321	3.969

Mean $\Delta H(2) = +3.97 \pm 0.01$ kJ mol^{-1}

Table 8. Reaction (3). Reaction of $P_2Pt(C_2H_4)$ with CS_2 in dce.

Ampoule number	Mass of $P_2Pt(C_2H_4)$/mg	Corrected heat of reaction/ J	Heat of reaction / kJ mol^{-1}
1	89.75	-2.0376	-16.98
2	94.80	-2.0414	-16.10
3	84.65	-1.6006	-14.14
4	101.05	-2.2118	-16.37
5	131.05	-2.6748	-15.26

Mean $\Delta H(3) = -15.77 \pm 0.98$ kJ mol^{-1}

Table 9. Reaction (4). Solution of $P_2Pt(CS_2)$ in CS_2 and dce.

Ampoule number	Mass of $P_2Pt(CS_2)$/mg	Corrected heat of solution/J	Heat of reaction / kJ mol^{-1}
1	51.25	0.9882	15.34
2	61.45	1.1689	15.14
3	87.50	1.6414	14.93
4	70.65	1.4394	16.21
5	70.45	1.3560	15.32

Mean $\Delta H(4) = +15.39 \pm 0.44$ kJ mol^{-1}

Table 10. Reaction (5). Solution of ethene in CS_2 and dce.

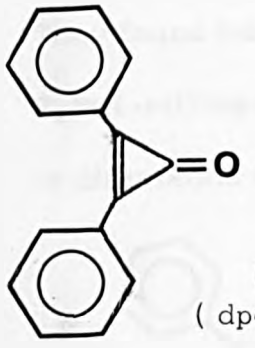
Injection number	Mass of ethene/mg	heat of solution/J	heat of solution / kJ mol^{-1}
1	0.975	-0.3584	-10.32
2	"	-0.3696	-10.64
3	"	-0.3512	-10.11
4	"	-0.4132	-11.89
5	"	-0.4080	-11.74

Mean $\Delta H(5) = -10.94 \pm 0.74$ kJ mol^{-1}

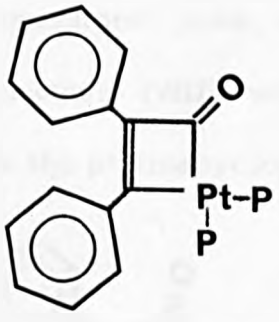
Cycloplatination reactions.

Introduction

Diphenylcyclopropenone, dpcp, (I), reacts rapidly at room temperature with tetrakis(triphenylphosphine) platinum (0) to form the platinacyclo--butenone, (II) (85).

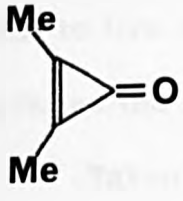


(I)
(dpcp)

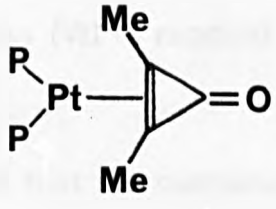


(II)

The reaction contrasts with that of another unsaturated 3-carbon ring compound, 1,2-dimethylcyclopropenone, (III), which reacts with $P_2Pt(C_2H_4)$ to form a π complex, (IV) (86).

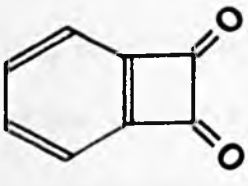


(III)

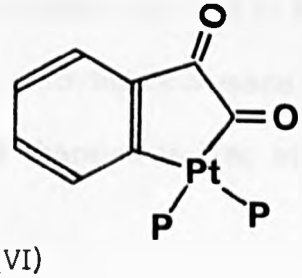


(IV)

Benzocyclobutenedione, bcbd, (V), resembles dpcp in its reaction with tetrakis(triphenylphosphine) platinum (0), forming the platinacyclopentene--dione, (VI) (87).

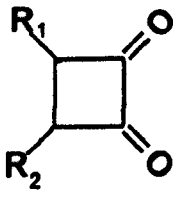


(V) (bcbd)



(VI)

Hamner, Kemmitt and Smith (88) reacted a number of cyclobutene--diones with bis(triphenylphosphine)(trans-stilbene) platinum (0).



(VII)

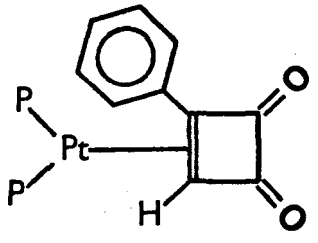
a. R_1 = Ph, R_2 = H ., (pcbd)

b. R_1 = Ph, R_2 = OMe

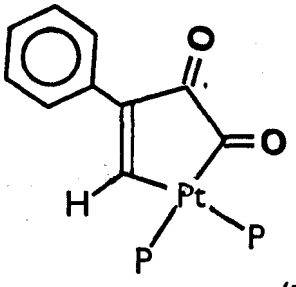
c. R_1 = R_2 = OMe

d. R_1 = Ph, R_2 = Me

They found that (VII a), phenylcyclobutenedione, pcbd, when reacted with P_2Pt(t-stilbene) in ether formed a π compound (VIII), which when dissolved in chloroform rearranged slowly to form the platinacyclopentenedione (IX).



(VIII)



(IX)

The compounds (VII b) and (VII c) passed rapidly through the π stage, (VIII) to form compounds analogous to (IX), whereas (VII d) reacted only as far as the π complex without opening the ring.

Taken together these observations suggest that the outcome of the reactions of cyclic alkenes and alkenones with platinum (0) depends both upon the degree of strain in the ring and upon the nature of the substit--uents.

Calorimetric work on these compounds was intended to establish the enthalpies of the two stages of the reactions leading to π or platina-ring compounds, and to make clearer the contributions made by the energies of the σ and π bonds to platinum and the changes in ring strain accompanying the ring-opening.

The reaction of P_2Pt(trans-stilbene) with diphenylcyclopropenone.

The heat, $\Delta H(1)$, of reaction (1) has been derived from measure--ments of the heats, $\Delta H(2)$ to $\Delta H(5)$, of reactions (2) to (5), in which $P_2Pt(dpcp)$ denotes the platinacyclobutenone, (II) on page 75, and stilbene denotes the trans isomer.

(1) $P_2Pt(stilbene)(s) + dpcp\ (s) \longrightarrow P_2Pt(dpcp)(s) + stilbene\ (s)$

(2) $dpcp\ (s) + [dpcp, 10^4 dce]\ (l) \longrightarrow [2dpcp, 10^4\ dce]\ (l)$

(3) $P_2Pt(stilbene)(s) + [2dpcp, 10^4 dce]\ (l) \longrightarrow [P_2Pt(dpcp), stilbene, dpcp, 10^4 dce]\ (l)$

(4) $P_2Pt(dpcp)(s) + [stilbene, dpcp, 10^4 dce](l) \longrightarrow [P_2Pt(dpcp), stilbene, dpcp, 10^4 dce]\ (l)$

(5) $stilbene\ (s) + [dpcp, 10^4 dce](l) \longrightarrow [stilbene, dpcp, 10^4 dce]\ (l)$

The relations between these reactions are shown in the following cycle.

$$\begin{array}{lllll} P_2Pt(stilbene)\ (s) & + & dpcp\ (s) & \xrightarrow{\Delta H(1)} & P_2Pt(dpcp)\ (s) + stilbene\ (s) \\ & & \downarrow \Delta H(2) & & \downarrow \Delta H(4) \qquad \searrow \Delta H(5) \\ P_2Pt(stilbene)\ (s) & + & [dpcp, dce]\ (l) & \xrightarrow{\Delta H(3)} & [P_2Pt(dpcp), stilbene, dce]\ (l) \end{array}$$

The heat of reaction (1) is given by the following equation.

$$\begin{aligned} \Delta H(1) &= \Delta H(2) + \Delta H(3) - \Delta H(4) - \Delta H(5) \\ &= (+36.4) + (-53.2) - (+7.99) - (+23.97) \\ &= -48.8 \pm 1.8\ kJ\ mol^{-1} \end{aligned}$$

Experimental.

The dpcp as supplied (by Aldrich) was said to be 98% pure, with a melting point of 119-121 °C. The observed melting point was 121.8 to 122.5 °C, preceded by signs of incipient melting from 116°C. The crude compound was recrystallised by dissolving in boiling hexane , cooling to 0°C and washing with fresh hexane before drying in vacuo. The recryst--allised solid melted sharply at 121.5°C.

Baddley et al. (85) made the platinum-dpcp complex from tetrakis--(triphenylphosphine) platinum (0) in dichloromethane, by a reaction which took approximately 10 minutes and gave only 60% yield, so there was some doubt about the occurrence, speed and completeness of the reaction starting from the stilbene complex. (The stilbene complex, P_2Pt(stilbene), was obtained from Dr J. Burgess of Leicester University, and was analysed at Keele. found C = 66.57 %, H = 4.66 %, calculated C = 66.73 %, H = 4.70 %) A trial reaction using a two-fold molar excess of dpcp in dce showed that the reaction was complete in approximately 90 seconds,and produced approximately 45 kJ mol^{-1}.

This substantial heat of reaction, $\Delta H(3)$, which more precise calorimetry showed should be - 53.2 kJ mol^{-1}, is sufficiently exothermic to itself provide strong evidence for the completeness of the reaction. From the well-known equations relating the free energy change to the enthalpy and entropy changes, and to the equilibrium constant of the reaction, it is clear that a partial reaction, for which $K \simeq 1$, could only occur if the negative contribution of ΔH to the free energy change was offset by a large increase in entropy; in this case $53200/298 \simeq 178$ $JK^{-1}mol^{-1}$.

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} = - RT \ln K_p$$

Sizeable increases in entropy are uncommon unless there is an increase

in the number of moles of gas, and even in a case such as vaporisation of a liquid, where one mole of gas is produced, the entropy increase is not more than approximately 90 $J K^{-1} mol^{-1}$. The reaction under consideration does not, of course, involve the production of gas, and although the dissolution of a solid may be accompanied by an increase of entropy, it is hardly conceivable that this would be sufficiently large to counter more than a very small part of the negative free energy change due to the observed enthalpy change. It was therefore assumed that the reaction was complete under the conditions in the calorimeter.

Reaction (2). Solution of dpcp in dce.

Ampoules containing approximately 3×10^{-5} moles of recrystallised dpcp were broken into a solution of the same quantity of dpcp in 25 cm^3 of dce. Results are shown in table 11.

Reaction (3). Reaction of P_2Pt(stilbene) with dpcp in dce.

Ampoules containing approximately 3×10^{-5} moles of stilbene complex were broken into a solution containing twice that quantity of dpcp in 25 cm^3 of dce. Results are shown in table 12.

Reaction (4). Solution of P_2Pt(dpcp) in stilbene, dpcp and dce.

The product complex was prepared by dissolving the ethene complex with twice the number of moles of dpcp in a small volume of dce, and stirring the solution at room temperature for 7 minutes. The pale yellow solid was precipitated by the addition of a much larger volume of 40-60° petrol and cooling to 0°C. It was filtered, washed with petrol, and dried in vacuo. The whole operation was carried out under nitrogen using nitrogen-purged solvents. The melting point of the product was 156.5 - 161°C,

and the infra-red spectrum showed a single strong absorbtion at 1650 cm^{-1}. These findings should be compared with those of Baddley et al.(85) who reported the melting point of the platinacyclobutenone product to be 158-160°C, and stated that "the only band observed in the range 1500 to 2200 cm^{-1} of the infra-red spectrum was a strong absorbtion at 1652 cm^{-1}".

Ampoules containing approximately 3×10^{-5} moles of this product were broken into a solution of the same nnmber of moles of stilbene, and of dpcp, in 25 cm^3 of dce. The results of calorimetry are shown in table 13.

Reaction (5). Solution of stilbene in dpcp and dce.

Ampoules containing approximately 3×10^{-5} moles of stilbene were broken into a solution containing the same number of moles of dpcp in 25 cm^3 of dce. Results are shown in table 14.

The reaction of P_2Pt(stilbene) with benzocyclobutenedione.

The heat, $\Delta H(6)$, of reaction (6) has been derived from measurements of the heats, $\Delta H(7)$ to $\Delta H(10)$, of reactions (7) to (10), in which P_2Pt(bcbd) stands for the platinapentenedione complex (VI) on page 75.

(6) $P_2Pt(stilbene)(s) + bcbd\ (s) \longrightarrow P_2Pt(bcbd)(s) + stilbene\ (s)$

(7) $bcbd\ (s) + [9\,bcbd, 10^4\,dce]\ (l) \longrightarrow [10\,bcbd, 10^4\,dce]\ (l)$

(8) $P_2Pt(stilbene)(s) + [10\,bcbd, 10^4\,dce]\ (l) \longrightarrow [P_2Pt(bcbd), stilbene, 9\,bcbd, 10^4\,dce]\ (l)$

(9) $P_2Pt(bcbd)(s) + [stilbene, 9\,bcbd, 10^4\,dce]\ (l) \longrightarrow [P_2Pt(bcbd), stilbene, 9\,bcbd, 10^4\,dce]\ (l)$

(10) $stilbene\ (s) + [9\,bcbd, 10^4\,dce]\ (l) \longrightarrow [stilbene, 9\,bcbd, 10^4\,dce]\ (l)$

The relations between these reactions are shown in the following cycle.

$$\begin{array}{lcl} P_2Pt(stilbene)\ (s) + bcbd\ (s) & \xrightarrow{H(6)} & P_2Pt(bcbd)\ (s) + stilbene\ (s) \\ \Big\downarrow \Delta H(7) & & \Big\downarrow \Delta H(9) \quad \Big\downarrow \Delta H(10) \\ P_2Pt(stilbene)\ (s) + [bcbd, dce]\ (l) & \xrightarrow{H(8)} & [P_2Pt(bcbd), stilbene, dce]\ (l) \end{array}$$

The heat of reaction (6) is therefore given by the equation below.

$$\begin{aligned} \Delta H(6) &= \Delta H(7) + \Delta H(8) - \Delta H(9) - \Delta H(10) \\ &= (+16.7) + (-55.47) - (+24.4) - (+0.77) \\ &= -63.9 \pm 3.2\ kJ\ mol^{-1} \end{aligned}$$

Experimental.

Benzocyclobutenedione, bcbd, was obtained from Dr J. Burgess of Leicester University. Results of microanalysis agree with calculation within experimental error (found C = 72.73%, H = 3.05%, calculated C = 73.29%, H = 2.91 %).

Trials showed that solid P_2Pt(stilbene) reacted completely with a ten-fold molar excess of bcbd in dce within one minute, and the temperature : time curve gave no sign of a second reaction. The heat of breaking of a nitrogen-filled ampoule into pure dce was determined and was used to correct subsequent measurements. Reagents in solution were protected from oxygen, using the same precautions as described for the carbon disulphide reaction.

Reaction (7). Solution of bcbd in bcbd and dce.

Ampoules containing approximately 3×10^{-5} moles of bcbd were broken into a solution of 27×10^{-5} moles of bcbd in dce. The results of calorimetry are shown in table 15.

Reaction (8). Reaction of P_2Pt(stilbene) with bcbd in dce.

Ampoules containing approximately 3×10^{-5} moles of P_2Pt(stilbene) were broken into a solution of 3×10^{-4} moles of bcbd in 25 cm^3 of dce. The red solid product was recovered from the calorimeter solution by rotary evaporation followed by recrystallisation from dichloromethane with 40-60 petrol, in which the excess bcbd and stilbene were both soluble, and was analysed on the Perkin-Elmer Differential Scanning Calorimeter, model DSC 1, which showed an endothermic reaction, presumably melting and decomposition, starting at 213°C (literature melting point 205-212°C, with decomposition) (86). The infra-red spectrum (KBr disc) showed a broad absorbtion at 1640-1690 cm^{-1}, with shoulders at 1640,1660 and

1687 cm^{-1} (literature 1640,1660, and 1686 cm^{-1}) (87). The results of calorimetry are shown in table 16.

Reaction (9). Solution of P_2Pt(bcbd) in stilbene, bcbd and dce.

Solid bcbd was recovered from the calorimetry solutions by rotary evaporation followed by recrystallisation from hexane and vacuum drying. The melting point of the recovered solid was 120-130°C, com--pared with the original sample (Burgess) which melted at 116-126°C, and the literature value of 132°C (89). This recovered bcbd was used to make the solutions for heat of solution calorimetry.

The bcbd complex was prepared by reacting recovered bcbd with an equimolar mass of $P_2Pt(C_2H_4)$ in dichloromethane, and precipitating the resulting red solid with 40-60 petrol. The heat of solution was measured by breaking ampoules containing 3×10^{-5} moles of P_2Pt(bcbd) into a solution of 27×10^{-5} moles of bcbd and 3×10^{-5} moles of stilbene in 25 cm^3 of dce. The results of calorimetry are shown in table 17.

Reaction (10). Solution of stilbene in bcbd and dce.

Ampoules containing 3×10^{-5} moles of stilbene were broken into a solution of 2.7×10^{-4} moles of bcbd in 25 cm^3 of dce. The stilbene used was Fluka A. G. trans-stilbene , scintillation grade. Results of calorimetry are shown in table 18.

Discussion : the reactions of P_2Pt(stilbene) with dpcp and with bcbd.

The heat, $\Delta H(1)$, of reaction (1), in which solid dpcp reacts with solid P_2Pt(stilbene) to form solid P_2Pt(dpcp) and trans-stilbene, has been determined.

$$\Delta H(1) = - 48.8 \pm 1.8 \text{ kJ mol}^{-1}$$

Using heats of sublimation of dpcp and of stilbene (page 163) one can derive the heat, $\Delta H(11)$, of reaction (11).

(11) $P_2Pt(\text{stilbene})(s) + \text{dpcp}(g) \longrightarrow P_2Pt(\text{dpcp})(s) + \text{stilbene}(g)$

$$\Delta H(11) = \Delta H(1) - \Delta H_{sub}(\text{dpcp}) + \Delta H_{sub}(\text{stilbene})$$
$$= -94.8 \text{kJ mol}^{-1}$$

Similarly the heat, $\Delta H(6)$, of reaction (6), in which solid bcbd reacts with solid P_2Pt(stilbene) to form solid products, has been determined.

$$\Delta H(6) = - 63.9 \pm 3.2 \text{ kJ mol}^{-1}$$

The heat, $\Delta H(12)$, of reaction (12) may be calculated from this result and from values for the heats of sublimation of bcbd and of stilbene (page 163).

(12) $P_2Pt(\text{stilbene})(s) + \text{bcbd}(g) \longrightarrow P_2Pt(\text{bcbd})(s) + \text{stilbene}(g)$

$$\Delta H(12) = \Delta H(6) - \Delta H_{sub}(\text{bcbd}) + \Delta H_{sub}(\text{stilbene})$$
$$= -57.4 \text{ kJ mol}^{-1}$$

These two reactions, (11) and (12), may be compared with similar ring-extending reactions, (13) and (14), of the corresponding cyclic alkenes.

(13) C_3H_4 (g) + CH_2 (g) —— C_4H_6 (g)

(14) C_4H_6 (g) + CH_2 (g) —— C_5H_8 (g)

In these reactions cyclopropene is converted to cyclobutene, which is converted in turn into cyclopentene. (Data are not available for reactions between the cyclic ketenes that would correspond more closely to the substances involved in the platination reactions.) The difference between the heats, $\Delta H(13)$ and $\Delta H(14)$, of reactions (13) and (14) may be found from heats of formation (18).

$$\Delta H(14) - \Delta H(13) = 2.0 \pm 3.3 \text{ kJ mol}^{-1}$$

It indicates that the relief of angular ring strain in these alkenes is very similar in converting the 3-membered ring to the 4-membered ring, and in converting the 4-membered ring to the 5-membered ring.

The value for the difference between the heats of the two cyclo--platination reactions (11) and (12) would perhaps be altered by the incor--poration of the heats of sublimation of the cycloplatina products, but these heats are not available.

$$\Delta H(12) - \Delta H(11) = + 37.4 \text{ kJ mol}^{-1}$$

However, this difference is likely to remain larger than that for the ring-expansion of the cycloalkenes. These observations have two implications.

(a). The difference between the ring strain energies of dpcp (I) and its cycloplatina product (II) is larger than that between bcbd (V) and its cycloplatina product (VI). In this respect the insertion of a platinum atom into the ketenes differs from the insertion of a carbon atom into the alkenes.

(b) Any additional stabilisation of the platinapentenedione molecule (VI), due to delocalisation of electrons between the platinum atom and

the adjacent benzene ring would tend to make reaction (12) more exothermic than reaction (11), so any such effect appears to be more than offset by the effects of ring strain.

It should be noted that the values of $\Delta H(11)$ and $\Delta H(12)$, and the difference between them, are influenced by the values of the heats of sublimation of dpcp and bcbd. The heat of sublimation of bcbd was measured as part of this work (pages 161-3), while that of dpcp was determined, with some difficulty, by Hopkins et al.(90).

The comparative strain energies are considered first. Hopkins, Bostwick and Alexander (90) have measured the heat of formation of dpcp.

$$\Delta H_f^{\circ}(\text{dpcp, g}) = + 552 \pm 8 \text{ kJ mol}^{-1}$$

Using the Laidler method, incorporating parameters recommended by Cox and Pilcher (18), they have derived a strain energy of at least 326 kJ mol^{-1} for this molecule. Unfortunately there is no value available for the heat of formation of bcbd from which a strain energy may be calculated, so that it is not yet possible to carry this analysis of ring strain further.

Secondly, the stabilisation energies. The structure of the platina--cyclobutenone (II), shown in figure 18 with bond lengths in nanometres, indicates that the C=C double bond and the remaining C-C single bond of the parent cyclopropenone retain their character. The C=O distance is also normal. No interaction between the platinum and the oxygen atoms is expected due to the long distance, 0.295 nm, between them. The implication of these data is that there is little stabilisation due to electron delocalisation in the ring. No structural data are available for the corresponding 5-membered platina ring compound (VI), so that again it is not yet possible to develop the consideration of stabilisation due to delocalisation of electrons.

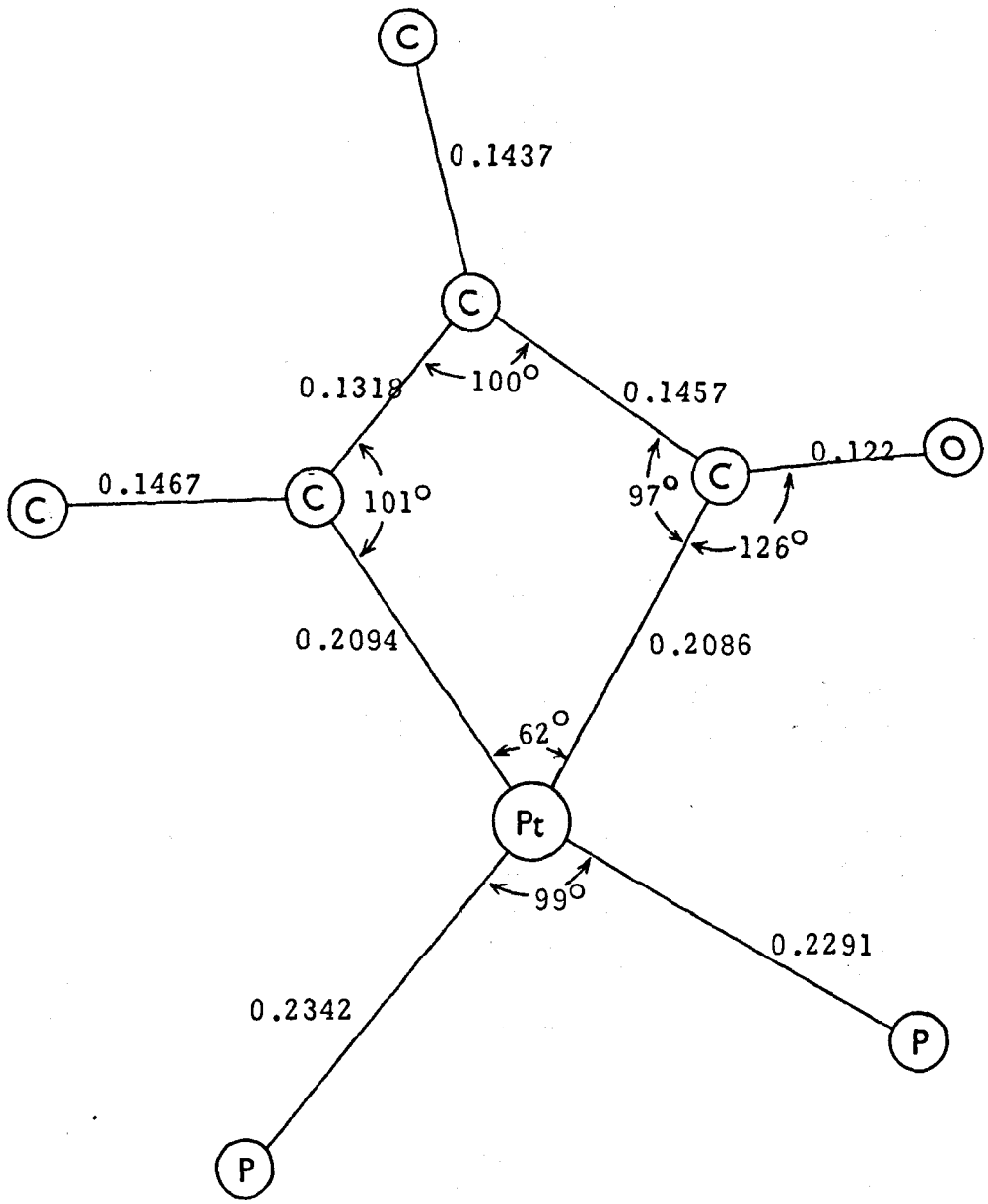


Figure 18. Molecular structure of the platinacyclobutenone, $P_2Pt(dpcp)$. Bond lengths are in nanometres. The phenyl rings have been omitted for clarity.

Table 11. Reaction (2). Solution of dpcp in dce.

Ampoule number	Mass of dpcp/mg	Corrected heat of solution / J	Heat of solution/kJ mol^{-1}
C1	6.99	1.2104	35.713
C2	6.61	1.1276	35.182
C3	5.43	0.9830	37.332
C4	6.19	1.0972	36.558
C5	7.12	1.2043	34.885
C6	5.89	1.1064	38.741

Mean $\Delta H(2) = + 36.4 \pm 1.2$ kJ mol^{-1}

Table 12. Reaction (3). Reaction of P_2Pt(stilbene) with dpcp in dce.

Ampoule number	Mass of P_2Pt(stilbene)/mg	Corrected heat of reaction / J	Heat of reaction/kJ mol^{-1}
C8	27.56	-1.6623	-54.28
C9	27.04	-1.6134	-53.70
C11	28.60	-1.6318	-51.35
C12	28.04	-1.6432	-52.74
C13	26.46	-1.6137	-52.20

Mean $\Delta H(3) = - 53.2 \pm 1.1$ kJ mol^{-1}

Table 13. Reaction (4). Solution of P_2Pt(dpcp) in stilbene, dpcp and dce.

Ampoule number	Mass of P_2Pt(dpcp)/mg	Corrected heat of solution / J	Heat of solution/kJ mol^{-1}
C8	26.46	0.1889	6.61
B1	25.49	0.2293	8.33
B2	29.09	0.2512	8.00
B3	22.93	0.1651	6.67
B4	21.95	0.1709	7.21
B6	23.34	0.1986	7.88

Mean $\Delta H(4) = + 7.99 \pm 0.77$ kJ mol^{-1}

Table 14. Reaction (5). Solution of stilbene in dpcp and dce.

Ampoule number	Mass of stilbene/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
C2	7.50	1.0255	24.65
C3	5.91	0.7830	23.88
C4	5.43	0.7006	23.26
C5	6.82	0.9180	24.26
C6	5.38	0.6982	23.39
C7	9.32	1.2445	24.07
C1	6.12	0.8335	24.25

Mean $\Delta H(5) = + 23.97 \pm 0.38$ kJ mol^{-1}

Table 15. Reaction (7). Solution of bcbd in bcbd and dce.

Ampoule number	mass of bcbd/mg	corrected heat of solution / J	heat of solution/J
A 11	3.99	0.5088	16.85
A 12	6.13	0.7841	16.76
A 13	5.33	0.6931	17.18
A 14	4.40	0.5375	16.14
A 15	4.72	0.5944	16.64
A 16	4.47	0.5626	16.63

Mean $\Delta H(7) = +16.70 \pm 0.28$ kJ mol^{-1}

Table 16. Reaction (8). Reaction of P_2Pt(stilbene) with bcbd in dce.

ampoule number	mass of P_2Pt(stilbene)/mg	corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
A 2	28.61	-1.6777	-52.77
A 3	30.08	-1.7536	-52.46
A 4	25.53	-1.6215	-57.16
A 5	31.42	-1.9294	-55.26
A 6	27.17	-1.7100	-56.64
A 7	28.50	-1.8540	-58.54

Mean $\Delta H(8) = - 55.47 \pm 2.0$ kJ mol^{-1}

Table 17. Reaction (9). Solution of $P_2Pt(bcbd)$ in stilbene, bcbd and dce.

ampoule number	mass of $P_2Pt(bcbd)$/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
A 1a	25.78	0.1329	4.39
A 2	25.74	0.1635	5.41
A 1b	27.40	0.0120	0.37
A 4	25.88	0.0358	1.18
A 5	24.90	0.0161	0.55
A 6	26.60	-0.1223	-3.92
A 7	27.03	-0.0696	-2.19

Mean $\Delta H(9) = + 0.77 \pm 2.5$ kJ mol^{-1}

Table 18. Reaction (10). Solution of stilbene in bcbd and dce.

ampoule number	mass of stilbene/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
A 9	6.75	1.0908	24.60
A 10	5.66	0.9276	24.13
A 11	7.28	1.1427	24.09
A 12	5.93	0.9634	24.12
A 13	7.51	1.1966	24.64
A 14	5.19	0.8687	24.27
A 15	6.19	1.0192	24.73

Mean $\Delta H(10) = + 24.37 \pm 0.21$ kJ mol^{-1}

The reaction between $P_2Pt(C_2H_4)$ and pcbd.

The heat, $\Delta H(15)$, of reaction (15) has been determined by measure--ment of the heats, $\Delta H(16)$ and $\Delta H(17)$, of reactions (16) and (17), com--bined with an estimate of the heat, $\Delta H(18)$, of reaction (18), and by taking the value for the heat, $\Delta H(19)$, of reaction (19) to be equal to the heat, $\Delta H(5)$ of reaction (5) on page 66.

(15) $P_2Pt(C_2H_4)$ (s) + pcbd (s) $\longrightarrow$ $P_2Pt(pcbd)$ (s) + C_2H_4 (g)

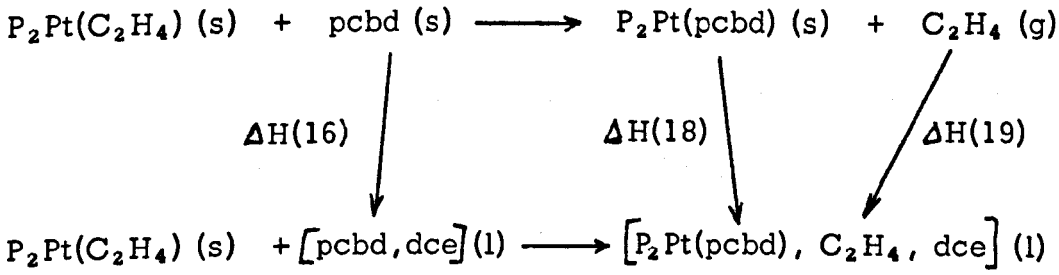
(16) pcbd (s) + 10^4dce (l) $\longrightarrow$ [pcbd, 10^4dce] (l)

(17) $P_2Pt(C_2H_4)$ (s) + [pcbd, 10^4dce] (l) $\longrightarrow$ [$P_2Pt(C_2H_4)$, C_2H_4, 10^4dce] (l)

(18) $P_2Pt(pcbd)$ (s) + [C_2H_4, 10^4dce] (l) $\longrightarrow$ [$P_2Pt(pcbd)$, C_2H_4, 10^4dce] (l)

(19) C_2H_4 (g) + 10^4dce (l) $\longrightarrow$ [C_2H_4, 10^4dce] (l)

In these equations $P_2Pt(pcbd)$ stands for the π complex (VIII) on page 76. The relations between the reactions are shown in the following cycle.



The heat of reaction (15) is therefore given by the following equation.

$$\Delta H(15) = \Delta H(16) + \Delta H(17) - \Delta H(18) - \Delta H(19)$$
$$= +(21.85) + (-13.47) - (+9) - (-10.94)$$
$$= +10.3 \pm 9 \text{ kJ mol}^{-1}$$

Experimental

The ethene complex, $P_2Pt(C_2H_4)$, was supplied by Dr R. Puddephatt of Liverpool University, and the pcbd by Dr J. Burgess of Leicester Univ--ersity. Analyses are shown below.

		found/%	calculated/%
$P_2Pt(C_2H_4)$	C	60.28	61.04
	H	4.76	4.58
pcbd	C	76.70	75.94
	H	3.65	3.82

A trial reaction between equal numbers of moles of the two reactants in dce was very rapid, being completed in less than one minute, and was slightly exothermic.

Reaction (16). Solution of pcbd in dce.

Ampoules containing 3×10^{-5} moles of pcbd were broken into 25 cm^3 of pure dce. Calorimetric results are shown in table 19.

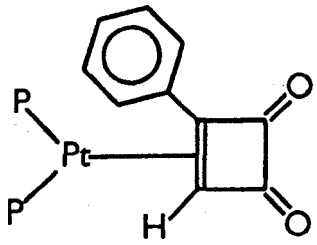
Reaction (17). Reaction of $P_2Pt(C_2H_4)$ with pcbd in dce.

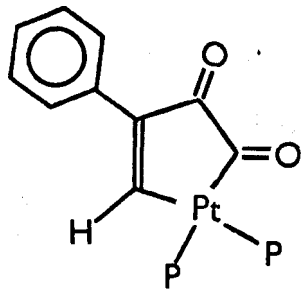
Ampoules containing 3×10^{-5} moles of $P_2Pt(C_2H_4)$ were broken into a solution of the same number of moles of pcbd in 25 cm^3 of dce. In each case a small excess (mean 3.1 %) of pcbd was present so that the quantity of reaction was determined by the ethene complex, which had the greater molar mass and could therefore be weighed out more precisely.

Although the resistance : time graphs did not suggest more than a single rapid reaction, the solution of the products changed colour, from yellow to brownish-orange, within a few hours of its removal from the cal--orimeter. Because of this, and other reasons based on the small value of the observed enthalpy change, it was suspected that only the first of

two consecutive reactions had occurred in the calorimeter.

In order to determine which of the two structures, (VIII) and (IX), was formed in the reaction whose enthalpy was measured, solutions of the reaction products were examined in a JEOL JNM FX 100 pulsed Fourier transform nmr spectrometer. Hamner et al. (88) have reported the nmr spectra of both these possible products; their findings are set out below.





(VIII)		(IX)
4.75	δ* / ppm	9.20
48.8	J(Pt-H) / Hz	21.5
6.7	J(P-H) / Hz	17.0

(* chemical shift measured downfield from Me_4Si)

Ideally the spectrometer would have been used to follow the course of the reaction under exactly the same conditions as those in the calorimeter, but the low concentration of complex and the strong absorbtion caused by the solvent (dce) prevented the production of useful spectra. Even when deuterochloroform was used in place of dce, clear signals from the complex were only obtained by accumulating data over a period of several hours, so the course of the early stages of the reaction could not be followed. The operating temperature of the spectrometer, 30°C, was somewhat higher than the calorimetric temperature.

After five hours from the time of mixing of equimolar quantities of

$P_2Pt(C_2H_4)$ and pcbd in deuterochloroform, the spectrum showed two relevant features, both due to the protons shown in structures (VIII) and (IX).

(i) A set of signals centred on $\delta \simeq$ 4.5 ppm, attributed to structure (VIII).

(ii) A weaker set of signals centred on $\delta \simeq$ 8.9 ppm, attributed to structure (IX).

The differences between these chemical shifts and those measured by Hamner et al. (88) were probably due to the difference in the concentrations of the solutions used for spectrometry. Further details of the signals in these two regions, which clearly indicate that they are due to the protons bonded to the carbon atoms nearest to platinum, are given below.

(i) In the 4.5 ppm region there were features due to coupling of the proton with platinum and with phosphorus nuclei. Coupling with ^{195}Pt (33.8 %) produced a central peak flanked by two smaller peaks separated by 47.5 Hz (lit. 48.8 Hz). Two of these three peaks were split by coupling to the two ^{31}P (100 %) nuclei, which have different coupling constants (approximately 6.3 and 7.3 Hz, lit. 6.7 Hz) and therefore give rise to a doublet of doublets which under coarser resolution would resemble a triplet, as reported by Hamner et al.. The third peak was not similarly split, perhaps due to the method of accumulating data in the spectrometer.

(ii) In the 8.9 ppm region four major peaks were produced by the effect of 'cis' and'trans' phosphorus nuclei, with apparent coupling constants of 8.3 and 16.6 Hz (lit. 8.5 and 17.0). Each major peak was flanked by two satellites due to ^{195}Pt with a coupling constant of 21.0 (lit. 21.5).

Over the following eight hours the intensity of the signals at 4.5 ppm decreased while those at 9 ppm grew stronger. These observations suggest

that a slow reaction from (VIII) to (IX) was occurring throughout the 14 or so hours after mixing the $P_2Pt(C_2H_4)$ and pcbd. This reaction was consid--erably less than half completed after three hours or so at 30°C, judging from the intensity of the nmr absorbtion, and rather more than half completed at ten hours. Unless the reaction in dce was quite different from that in deuterochloroform, it can safely be assumed that a negligible proportion of structure (IX) was produced in the first few minutes of the reaction at 25°C in the calorimeter, so the measured enthalpy, ΔH(17), refers to the reaction that produced structure (VIII). Results of calorimetry are shown in table 20.

Reaction (18). Solution of P_2Pt(pcbd) in ethene and dce.

In view of the existence of a second stage of reaction, from (VIII) to (IX), as shown by the changes in colour and nmr spectra, a sample of solid P_2Pt(pcbd) was not isolated. The heat of reaction (18) may be estimated from the heats of solution in dce of other solid complexes, which vary from 0 to + 17 kJ mol^{-1}. The value of ΔH(18) is therefore estimated to be + 9 ± 9 kJ mol^{-1}.

Discussion : the reaction of $P_2Pt(C_2H_4)$ with pcbd.

The heat, $\Delta H(20)$, of reaction (20) might be determined from the heat of reaction (15), the measured heat of sublimation of pcbd, and the unmeasured heats of sublimation of the platinum complexes $P_2Pt(C_2H_4)$ and $P_2Pt(pcbd)$.

(20) $P_2Pt(C_2H_4)\,(g) + pcbd\,(g) \longrightarrow P_2Pt(pcbd)\,(g) + C_2H_4\,(g)$

$$\Delta H(20) = \Delta H(15) - \Delta H_{sub}[P_2Pt(C_2H_4)] - \Delta H_{sub}(pcbd) + \Delta H_{sub}[P_2Pt(pcbd)]$$

$$= -94.9 - \Delta H_{sub}[P_2Pt(C_2H_4)] + \Delta H_{sub}[P_2Pt(pcbd)]$$

If these last two heats of sublimation are not very different, the heat of reaction (20) is known.

$$\Delta H(20) \simeq -95.\ kJ\ mol^{-1}$$

This heat of reaction is equal to the difference in the bond dissoc-iation energies of the Pt - C_2H_4 and the Pt - pcbd bonds, i.e.

$$D(Pt-C_2H_4) - D(Pt-pcbd) = -95\ kJ\ mol^{-1}$$

Thus it appears that the bond dissociation energy of the Pt - pcbd bond in the π complex (VIII) is $\simeq$ 95 kJ mol^{-1} greater than that of the Pt - C_2H_4 bond in $P_2Pt(C_2H_4)$.

Table 19. Reaction (16). Solution of pcbd in dce.

ampoule number	mass of pcbd/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
D 15	5.77	0.8015	21.97
D 16	5.72	0.8026	22.19
D 17	5.14	0.7072	21.76
D 18	4.59	0.6343	21.86
D 19	5.60	0.7678	21.69
D 20	4.68	0.6402	21.63

Mean $\Delta H(16) = + 21.85 \pm 0.17$ kJ mol^{-1}

Table 20. Reaction (17). Reaction of $P_2Pt(C_2H_4)$ with pcbd in dce.

ampoule number	mass of $P_2Pt(C_2H_4)$/mg	corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
D 6	23.79	-0.4326	-13.60
D 7	25.71	-0.4328	-12.59
D 8	26.54	-0.4678	-13.18
D 10	26.78	-0.4561	-12.74
D 11	21.43	-0.4072	-14.21

Mean $\Delta H(17) = - 13.47 \pm 0.64$ kJ mol^{-1}

Oxidation reactions ; the reactions of $P_2Pt(C_2H_4)$ with iodine and with alkyl iodides.

Introduction

Birk, Halpern and Pickard (91) reported that the complex $P_2Pt(C_2H_4)$ reacted in benzenesolution at 25°C with iodomethane and with 1,2-diiodo--ethane according to equations (1) and (2).

(1) $P_2Pt(C_2H_4) + CH_3I \longrightarrow P_2PtCH_3I + C_2H_4$

(2) $P_2Pt(C_2H_4) + C_2H_4I_2 \longrightarrow P_2PtI_2 + 2C_2H_4$

They did not state whether the cis or trans isomers of the products were formed. Their kinetic measurements implied that the $P_2Pt(C_2H_4)$ was 90% dissociated into P_2Pt and C_2H_4 in solutions where the ethene concentration was 3×10^{-3} mol dm^{-3}, leading to very rapid reaction of the P_2Pt with the other reagents, which also replaced the bound ethene in a slower reaction. In dilute solutions initially free of dissolved ethene the reactions might be expected to be rapid and complete, and if suitable for calorimetry would provide data for comparing the bond dissociation energies $D(P_2IPt - CH_3)$ and $D(P_2IPt - I)$.

In experiments designed to support their formulation of the tris- and tetrakis(triphenylphosphine) complexes of platinum (0), Malatesta and Ugo (92) titrated these compounds with iodine in benzene solution, forming P_2PtI_2. The reactions were evidently fast and complete, and in view of the dissociation of both $P_2Pt(C_2H_4)$ and P_3Pt, suggested that the reaction (3) might be suitable for solution calorimetry.

(3) $P_2Pt(C_2H_4) + I_2 \longrightarrow P_2PtI_2 + C_2H_4$

The results from this reaction would provide a check on those of reaction (2).

The reaction of $P_2Pt(C_2H_4)$ with iodine.

The heat, $\Delta H(4)$, of reaction (4) has been determined by assuming that the heat, $\Delta H(5)$ may be taken to be the same as the previously-determined heat, $\Delta H(5)$ on page 66, and by measuring the heats, $\Delta H(6)$ to $\Delta H(8)$, of reactions (6) to (8). In these equations the formula $t\text{-}P_2PtI_2$ denotes the trans isomer of bis(triphenylphosphine) diiodo platinum (II).

(4) $P_2Pt(C_2H_4)(s) + I_2(s) \longrightarrow t\text{-}P_2PtI_2(s) + C_2H_4(g)$

(5) $C_2H_4(g) + [t\text{-}P_2PtI_2, 10^4 dce](l) \longrightarrow [t\text{-}P_2PtI_2, C_2H_4, 10^4 dce](l)$

(6) $I_2(s) + 10^4 dce(l) \longrightarrow [I_2, 10^4 dce](l)$

(7) $P_2Pt(C_2H_4)(s) + [I_2, 10^4 dce](l) \longrightarrow [t\text{-}P_2PtI_2, C_2H_4, 10^4 dce](l)$

(8) $t\text{-}P_2PtI_2(s) + 10^4 dce(l) \longrightarrow [t\text{-}P_2PtI_2, 10^4 dce](l)$

The relations between these reactions are shown in the following cycle.

$$\begin{array}{lcl} P_2Pt(C_2H_4)(s) + I_2(s) & \xrightarrow{\Delta H(4)} & t\text{-}P_2PtI_2(s) + C_2H_4(g) \\ \Delta H(6) \downarrow & & \downarrow \Delta H(8) \quad \downarrow \Delta H(5) \\ P_2Pt(C_2H_4)(s) + [I_2, dce](l) & \xrightarrow{\Delta H(7)} & [t\text{-}P_2PtI_2, C_2H_4, 10^4 dce](l) \end{array}$$

The heat of reaction (4) is given by the equation below.

$$\begin{aligned} \Delta H(4) &= \Delta H(6) + \Delta H(7) - \Delta H(8) - \Delta H(5) \\ &= (+22.32) + (-138.4) - (+9.0) - (-10.94) \\ &= -114.1 \pm 2.0 \text{ kJ mol}^{-1} \end{aligned}$$

Experimental

A trial, using 1 : 1 molar ratio of iodine and $P_2Pt(C_2H_4)$ in dce indicated that the reaction was complete in 30 seconds or so, and produced approximately 126 kJ mol^{-1}. Excess of iodine was avoided because of the complication that would have resulted from unreacted iodine complexing with iodine atoms bonded to platinum, a reaction similar to that between iodine molecules and free iodide ions to form I_3^- ions.

Reaction (6). Solution of iodine in dce.

Ampoules containing 3×10^{-5} moles of iodine, I_2, (BDH, 99.5% pure) were broken into 25 cm^3 of dce. The method of weighing was mod--ified because of the volatility of iodine. The mass of solid was found by subtracting the mass of the empty ampoule from that of the filled ampoule after it had been twice evacuated, flushed with nitrogen, and sealed. A correction was made for the different densities of air and nitrogen. Results from calorimetry are shown in table 21.

Reaction (7). Reaction of $P_2Pt(C_2H_4)$ with iodine in dce.

Ampoules of $P_2Pt(C_2H_4)$ were broken into solutions containing 3×10^{-5} moles of iodine, I_2, in dce. Each ampoule contained a mass of ethene complex calculated to give a very small molar excess (from 0.5 to 2.5 %) over the corresponding mass of iodine already in solution, these excesses being so small that their heats of solution would produce a negligible error in the measured heat of reaction. The reaction produced a deep orange solution, and an orange solid, the trans-iodide complex $t\text{-}P_2PtI_2$, was left after rotary evaporation. Results of calorimetry are shown in table 22.

Reaction (8). Solution of t-P_2PtI_2 in dce.

The solutions from calorimetry of the reaction between $P_2Pt(C_2H_4)$ and iodine were combined, and the calculated amount of iodine was added to combine with the unreacted excess of $P_2Pt(C_2H_4)$. The solution was evaporated to dryness, and the resulting solid was recrystallised from dichloromethane with ethanol and again from dichloromethane with 40-60 petrol before being washed with diethyl ether and vacuum dried. The infra--red spectrum of the iodide complex prepared in this way showed only the weak absorbtion at 540 cm^{-1} that is characteristic of the trans isomer (93). Ampoules containing 3×10^{-5} moles of this solid were broken into 25 cm^3 of dce. The results of calorimetry are shown in table 23.

The reaction of $P_2Pt(C_2H_4)$ with 1,2-diiodoethane.

The heat, $\Delta H(9)$, of reaction (9) has been determined by measuring the heats, $\Delta H(10)$ to $\Delta H(12)$, of reactions (10) to (12) and by assuming that the heat, $\Delta H(13)$, of reaction (13) is equal to twice the previously-determined heat of reaction (5) on page 66 . In these equations the formula $c\text{-}P_2PtI_2$ denotes the cis isomer of bis(triphenylphosphine) diiodo platinum (II).

(9) $P_2Pt(C_2H_4)(s) + C_2H_4I_2(s) \longrightarrow c\text{-}P_2PtI_2(s) + 2\,C_2H_4(g)$

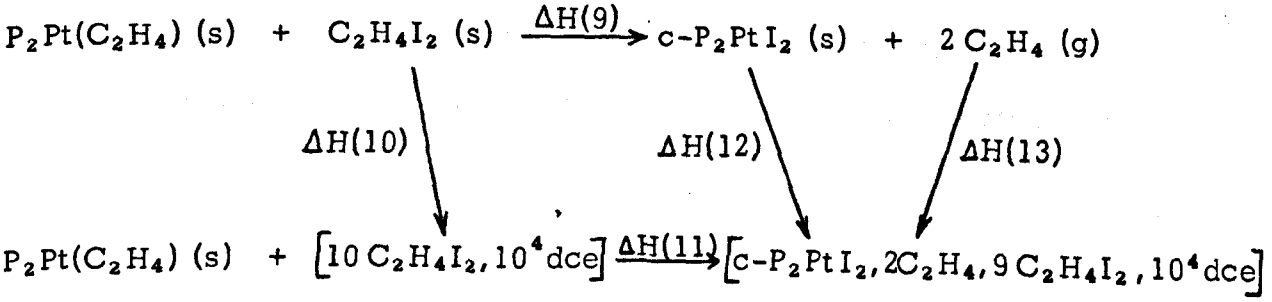
(10) $C_2H_4I_2(s) + [9\,C_2H_4I_2, 10^4 dce](l) \longrightarrow [10\,C_2H_4I_2, 10^4 dce](l)$

(11) $P_2Pt(C_2H_4)(s) + [10\,C_2H_4I_2, 10^4 dce](l) \longrightarrow [c\text{-}P_2PtI_2, 2\,C_2H_4, 9\,C_2H_4I_2, 10^4\ dce](l)$

(12) $c\text{-}P_2PtI_2(s) + [9\,C_2H_4I_2, 10^4 dce](l) \longrightarrow [c\text{-}P_2PtI_2, 9\,C_2H_4I_2, 10^4 dce](l)$

(13) $2\,C_2H_4(g) + [c\text{-}P_2PtI_2, 9\,C_2H_4I_2, 10^4 dce] \longrightarrow [c\text{-}P_2PtI_2, 2\,C_2H_4, 9\,C_2H_4I_2, 10^4 dce](l)$

The relations between these reactions are shown in the following cycle.



The heat of reaction (9) is therefore given by the equation below.

$$\Delta H(9) = \Delta H(10) + \Delta H(11) - \Delta H(12) - \Delta H(13)$$

$$= (+18.9) + (-73.9) - (+9.0) - (2 \times -10.9)$$

$$= -42.1 \pm 1.9\ kJ\ mol^{-1}$$

Experimental.

A trial reaction of $P_2Pt(C_2H_4)$ with a ten-fold molar excess of diiodoethane in dce was complete in approximately 30 seconds. Diiodo--ethane (Fluka A.G.) was claimed to be 98 % pure but was off-white and melted at 75.5 - 78.5°to a red-brown liquid (lit. white crystals or plates, m.p. 81 - 82 °C (94)) The compound is known to be unstable towards decomposition into ethene and iodine, particularly in daylight. Follow--ing Beilstein (94) the crude solid was recrystallised from hexane, washed with the same solvent, and dried in vacuo, all in subdued tungsten lighting. The white needles melted at 81.2 - 82.0 °C; solutions of this recryst--allised solid were colourless.

Reaction (10). Solution of diiodoethane in diiodoethane and dce.

Ampoules containing 3×10^{-5} moles of diiodoethane were broken into solutions containing 27×10^{-5} moles of the same solid in 25 cm^3 of dce. In some ampoules parts of the solid darkened during sealing, presumably because of heat and light from the flame, in spite of the use of the water-cooled carrier. The worst of these were rejected, since solutions made from them were noticeably pink, presumably due to the presence of free iodine. Results from the calorimetry of the others are shown in table 24.

Reaction (11). Reaction of $P_2Pt(C_2H_4)$ with diiodoethane in dce.

Ampoules containing 3×10^{-5} moles of $P_2Pt(C_2H_4)$ were broken into solutions containing 3×10^{-5} moles of diiodoethane in 25 cm^3 of dce. The usual procedure, that is to follow each measurement of the heat of solution of the dissolved reagent by measurement of the heat of

reaction, using the same calorimeter contents, was not followed because of the possibility that the diiodoethane used for the heat of solution might have been partially decomposed when the ampoule was sealed. Instead a solution of the pure solid that had not been exposed to heat and light was used for each reaction. The solution left after measuring the heat of reaction was yellow, presumably containing cis-P_2PtI_2. The infra-red spectrum of the solid complex obtained by rotary evaporation of the calorimeter solution at room temperature showed the strong absorb--tion at 540 cm^{-1} attributed by Mastin (93) to cis-bis(triphenylphosphine)-platinum dihalide complexes. Results from calorimetry are shown in table 25.

Reaction (12). Solution of c-P_2PtI_2 in $C_2H_4I_2$ and dce.

The heat, $\Delta H(12)$ of this reaction was assumed to be the same as the heat, $\Delta H(8)$ of reaction (8) on page 98.

Discussion : The reactions of $P_2Pt(C_2H_4)$ with iodine and with 1,2-diiodoethane, and the cis-trans isomerism of P_2PtI_2.

The heats, $\Delta H(4)$ and $\Delta H(9)$, of reactions (4) and (9), in which all reactants and products are in their standard states, have been deter-mined.

(4) $P_2Pt(C_2H_4)\,(s) + I_2\,(s) \longrightarrow t\text{-}P_2PtI_2\,(s) + C_2H_4\,(g)$

(9) $P_2Pt(C_2H_4)\,(s) + C_2H_4I_2\,(s) \longrightarrow c\text{-}P_2PtI_2\,(s) + 2\,C_2H_4\,(g)$

$$\Delta H(4) = -114.1 \pm 2.0 \text{ kJ mol}^{-1}$$

$$\Delta H(9) = -42.1 \pm 1.9 \text{ kJ mol}^{-1}$$

These heats may be combined with the selected values for the heats of formation of ethane and 1,2-diiodoethane (18) to derive the difference between the heats of formation of the isomeric products of reactions (4) and (9).

$$\Delta H^{\circ}_f(C_2H_4, g) = +52.1 \pm 0.4 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ}_f(C_2H_4I_2, g) = -0.8 \pm 4.6 \text{ kJ mol}^{-1}$$

$$\Delta H^{\circ}_f(\text{trans-}P_2PtI_2) - \Delta H^{\circ}_f(\text{cis-}P_2PtI_2) = -19.1 \pm 5.4 \text{ kJ mol}^{-1}$$

This conclusion may be compared with such information as has been published about the enthalpies of isomerisation of similar complexes.

Scott and Mastin (95) have followed the cis - trans isomerisation of $Pt(PEt_3)_2I_2$ at 130°C using scanning calorimetry. Their value for the enthalpy of isomerisation, reaction (14), is $\Delta H(14) = -13.4 \text{ kJ mol}^{-1}$.

(14) $cis\text{-}Pt(PEt_3)_2I_2\,(s) \longrightarrow trans\text{-}Pt(PEt_3)_2I_2\,(s)$

The value is not accompanied by any estimate of its precision, and the determination was made more difficult by overlap between the endothermic peaks attributed to the melting of the cis and trans isomers and the exo--thermic peak attributed to the isomerisation, so the above figure must be regarded as an approximation. The enthalpy of isomerisation of the triphenylphosphine complex might be expected to be rather larger than that of the triethylphosphine complex, due to the greater bulk of the phenyl groups. Chatt and Wilkins, (96), on the other hand found that replacement of one of the alkyl groups on an arsine ligand in a complex such as $Pt(AsR_3)Cl_2$ by a phenyl group produced a shift of the equilibrium constant towards the cis isomer, but did not state whether the correspon--ding change in the free energy of the reaction was due to an enthalpy or an entropy effect. Their measurements were made in solution, and included very few iodide complexes, only sufficient to show that in the iodides the position of equilibrium lay well towards the trans isomer. A typical figure that they gave is given below.

$$K_{298} = \frac{[trans]}{[cis]} \simeq 200, \qquad \Delta G \simeq -13 \text{ kJ mol}^{-1}$$

They also reported that the iodo complexesisomerised more easily than the chloro complexes.

When combined with this information, the results from calorimetry and infra-red spectroscopy suggest that the reaction of $P_2Pt(C_2H_4)$ with iodine in dce produced largely or entirely trans-P_2PtI_2, while under the same conditions $P_2Pt(C_2H_4)$ reacted with 1,2-diiodoethane to form the cis isomer, cis-P_2PtI_2. The heat of isomerisation of cis to trans-P_2PtI_2 is similar to, or slightly more exothermic than, the heats of the corresponding reactions reported in the literature, i.e. -19 ± 5 kJ mol^{-1}.

The reaction of $P_2Pt(C_2H_4)$ with iodomethane.

The heat, $\Delta H(15)$, of reaction (15) has been determined by measurement of the heats, $\Delta H(16)$ to $\Delta H(18)$, of reactions (16) to (18), by assuming that the heat, $\Delta H(19)$, of reaction (19) is the same as that of reaction (5) on page 66 , and by incorporating a literature value for the heat, $\Delta H(20)$, of reaction (20).

(15) $P_2Pt(C_2H_4)\,(s) + CH_3I\,(g) \longrightarrow c\text{-}P_2Pt(CH_3)I\,(s) + C_2H_4\,(g)$

(16) $CH_3I\,(l) + [99\,CH_3I, 10^4\,dce](l) \longrightarrow [100\,CH_3I, 10^4\,dce]\,(l)$

(17) $P_2Pt(C_2H_4)\,(s) + [99\,CH_3I, 10^4\,dce](l) \longrightarrow [c\text{-}P_2Pt(CH_3)I, C_2H_4, 99\,CH_3I, 10^4\,dce]\,(l)$

(18) $P_2Pt(CH_3)I\,(s) + [99\,CH_3I, 10^4\,dce\,(l) \longrightarrow [c\text{-}P_2Pt(CH_3)I, 99\,CH_3I, 10^4\,dce]\,(l)$

(19) $C_2H_4\,(g) + [c\text{-}P_2Pt(CH_3)I, 99\,CH_3I, 10^4\,dce](l) \longrightarrow [c\text{-}P_2Pt(CH_3)I, C_2H_4, 99\,CH_3I, 10^4\,dce]\,(l)$

(20) $CH_3I\,(l) \longrightarrow CH_3I\,(g)$

In these equations the formula $c\text{-}P_2Pt(CH_3)I$ stands for the cis isomer of bis(triphenylphosphine)methyl iodo platinum (II). The relations between the reactions are shown in the following cycle.

$$\begin{array}{lcl}
P_2Pt(C_2H_4)\,(s) + CH_3I\,(g) & \xrightarrow{\Delta H(15)} & c\text{-}P_2Pt(CH_3)I\,(s) + C_2H_4\,(g) \\
\Delta H(20)\uparrow & & \searrow \Delta H(18) \quad \searrow \Delta H(19) \\
CH_3I\,(l) & & \\
\Delta H(16)\downarrow & & \\
P_2Pt(C_2H_4)\,(s) + 100\,CH_3I, 10^4\,dce\,(l) & \xrightarrow{\Delta H(17)} & [c\text{-}P_2Pt(CH_3)I, C_2H_4, 99\,CH_3I, 10^4\,dce]\,(l)
\end{array}$$

The heat of reaction (15) is therefore given by the following equation.

$$\Delta H(15) = -\Delta H(20) + \Delta H(16) + \Delta H(17) - \Delta H(18) - \Delta H(19)$$

$$= -(+28.03) + (+1.21) + (-45.9) - (+17.14) - (-10.94)$$

$$= -78.9 \pm 2.0 \text{ kJ mol}^{-1}$$

Experimental

Iodomethane (May and Baker) was distilled under nitrogen in semi-darkness, the fraction boiling at 41.90°C being collected. Before and after distillation the liquid was colourless, suggesting the absence of free iodine, the most likely impurity. A trial reaction using a hundred fold molar excess of iodomethane was complete in approximately 90 seconds. A specially-made capillary pipette was used to prepare solutions of 2.97×10^{-3} moles of iodomethane in 25 cm^3 of dce for subsequent calor-imetry.

Reaction (16). Solution of iodomethane in iodomethane and dce.

Flame-sealed ampoules were not used to contain iodomethane because of its instability to light and heat, and its volatility. Instead a modification of the gas-injection calorimeter (figure 17) was used in conjunction with a 10 microlitre syringe fitted with a 75 mm needle. The body of the syringe was held in the brass tube of the calorimeter can, that is, below the level of the thermostat water, so that its contents were brought to calorimeter temperature before injection. Until the moment of injection the piston was supported at precisely the 10 microlitre mark by an aluminium stop. The reproducibility of the mass delivered by the syringe in this way was tested by weighing ; the mean mass of five del-iveries was 22.05 ± 0.04 mg. As the uncertainty is 0.18 % of the mean, this injection method was thought to be acceptably precise.

The results of calorimetry, shown in table 26, have the lowest uncer--tainty of any, other than the standard 'tris' reaction, of any reported here.

Reaction (17). Reaction of $P_2Pt(C_2H_4)$ with iodomethane in dce.

Ampoules containing 1.2×10^{-4} moles of ethene complex were broken into solutions containing 1.2×10^{-2} moles of iodomethane in 100 cm^3 of dce. The infra-red spectrum of the solid complex $P_2Pt(CH_3)I$ recovered from the calorimeter solution by rotary evaporation showed the strong absorbtion at 540 cm^{-1} typical of cis isomers of bis(triphenylphos--phine) platinum (II) complexes (93). The calorimetry results are shown in table 27.

Reaction (18). Solution of c-$P_2Pt(CH_3)I$ in iodomethane and dce.

A sample of the complex was prepared in a closed system under nitrogen by adding 0.231 g of ethene complex , $P_2Pt(C_2H_4)$ to a solution of 0.2 cm^3 of iodomethane (a ten-fold molar excess) in 20 cm^3 of dce that had been vacuum-degassed. After the mixture had been stirred for an hour at room temperature the liquids were evaporated under vacuum . The crude solid product was recrystallised from dichloromethane with ethanol and vacuum-dried at 45°C. The microanalysis showed satisfac--tory agreement with calculated values. (found C = 51.94 %, H = 4.03 %, calculated C = 51.58 %, H = 3.86 %).

Ampoules containing 3×10^{-5} moles of the complex prepared in this way were broken into solutions containing 3×10^{-3} moles of iodo--methane in 25 cm^3 of dce. The results of calorimetry are shown in table 28.

Reaction (20). Vaporisation of iodomethane.

The heat of vaporisation of iodomethane was found by Thompson and Linnett (97) to be + 6.7 ± 0.3 kcal mol^{-1}, equivalent to + 28.03 ± 1.3 kJ mol^{-1}.

Discussion : Comparison of the bond dissociation energies D_1(Pt - X) in cis-P_2PtIX where X = I or CH_3.

A value of the heat, ΔH(21), of reaction (21) may be derived by combining the literature heat of sublimation of iodine, ΔH(22), with the calculated heat of reaction (4) (page 98).

(22) I_2 (s) ⟶ I_2 (g)

$\Delta H(22) = + 62.44$ kJ mol^{-1} (84)

(21) $P_2Pt(C_2H_4)$ (s) + I_2 (g) ⟶ t-P_2PtI_2 (s) + C_2H_4 (g)

$\Delta H(21) = - 176.5 \pm 2.0$ kJ mol^{-1}

The heat, ΔH(23), of reaction (23), in which the product is the cis isomer of P_2PtI_2, may be obtained by incorporating the value of - 19.1 kJ mol^{-1} for the heat of cis-trans isomerisation of the complex.

(23) $P_2Pt(C_2H_4)$ (s) + I_2 (g) ⟶ c-P_2PtI_2 (s) + C_2H_4 (g)

$\Delta H(23) = - 157.4 \pm 5.4$ kJ mol^{-1}

If W kJ mol^{-1} is the heat of sublimation of $P_2Pt(C_2H_4)$, and Y kJ mol^{-1} is the heat of sublimation of cis-P_2PtI_2, then the heat, ΔH(24),

of the gas-phase reaction (24) is given by the equation which follows.

(24) $P_2Pt(C_2H_4)$ (g) + I_2 (g) ⟶ c-P_2PtI_2 (g) + C_2H_4 (g)

$$\Delta H(24) = - 157.4 - W + Y \quad kJ\ mol^{-1}$$

Similarly if Z kJ mol^{-1} is the heat of sublimation of cis-$P_2Pt(CH_3)I$, the heat, $\Delta H(25)$ of the gas-phase reaction (25) between $P_2Pt(C_2H_4)$ and iodomethane may be derived from the value of $\Delta H(15)$ on page 106.

(25) $P_2Pt(C_2H_4)$ (g) + CH_3I (g) ⟶ c-$P_2Pt(CH_3)I$ (g) + C_2H_4 (g)

$$\Delta H(25) = - 78.9 - W + Z \quad kJ\ mol^{-1}$$

Each of these heats, $\Delta H(24)$ and $\Delta H(25)$, may be equated to the difference in the dissociation energies of the bonds made and broken in the reaction to which it refers.

(26) $D(Pt-C_2H_4) + D(I-I) - D_1(Pt-I) - D_2(Pt-I) = - 157.4 - W + Y$

(27) $D(Pt-C_2H_4) + D(CH_3-I) - D_1(Pt-CH_3) - D_2(Pt-I) = - 78.9 - W + Z$

The bond dissociation energies D(I-I) in I_2 and $D(CH_3-I)$ in iodomethane are known.

$$D(I-I) = 152.549 \pm 0.008\ kJ\ mol^{-1} \quad (98)$$

$$D(CH_3-I) = 236 \pm 4\ kJ\ mol^{-1} \quad (99)$$

If Y and Z, the heats of sublimation of c-P_2PtI_2 and c-P_2PtCH_3I are assumed to be equal, the difference between the bond dissociation energies $D_1(Pt-CH_3)$ and $D_1(Pt-I)$ may be calculated. These bond dissociation energies are the heats of the reactions set out below.

$D_1(Pt - CH_3)$ is the heat of the reaction

$$c\text{-}P_2Pt(CH_3)I\ (g) \longrightarrow P_2PtI\ (g) + CH_3\ (g)$$

$D_1(Pt - I)$ is the heat of the reaction

$$c\text{-}P_2PtI_2\ (g) \longrightarrow P_2PtI\ (g) + I\ (g)$$

$$D_1(Pt - CH_3) - D_1(Pt - I) = + 5 \pm 6\ kJ\ mol^{-1}$$

From this result it appears that the bond dissociation energies of the two bonds Pt - I in $c\text{-}P_2PtI_2$ and Pt - CH_3 in $c\text{-}P_2Pt(CH_3)I$ are very similar.

Table 21. Reaction (6). Solution of iodine in dce.

ampoule number	mass of iodine/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
D 10	8.02	0.6891	21.81
D 15	8.61	0.7632	22.50
D 16	8.12	0.6714	20.98
D 17	8.87	0.8092	23.15
D 18	9.12	0.8110	22.57
D 19	9.61	0.8255	21.80
D 20	7.58	0.6764	22.65
D 21	11.74	1.0687	23.10

Mean $\Delta H(6) = + 22.32 \pm 0.52$ kJ mol^{-1}

Table 22. Reaction (7). Reaction of $P_2Pt(C_2H_4)$ with iodine in dce.

ampoule number	mass / mg of $P_2Pt(C_2H_4)$, I_2		corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
D 4	22.32	7.58	-4.1335	-138.41
D 5	27.14	9.12	-4.9057	-136.53
D 6	24.11	8.02	-4.4607	-141.17
D 8	34.77	11.74	-6.3306	-136.86
D 9	24.52	8.12	-4.4650	-139.57
D 11	28.68	9.61	-5.1294	-135.47
D 12	25.57	8.61	-4.7236	-139.24
D 14	26.42	8.87	-4.8916	-139.97

Mean $\Delta H(7) = - 138.4 \pm 1.4$ kJ mol^{-1}

Table 23. Reaction (8). Solution of t-P_2PtI_2 in dce.

ampoule number	mass of t-P_2PtI_2/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
A 9	28.57	0.2512	8.56
A 10	29.26	0.2126	7.07
A 11	28.25	0.2743	9.45
A 15	37.06	0.3956	10.39
A 16	28.00	0.2679	9.31

Mean $\Delta H(8) = + 9.0 \pm 1.1$ kJ mol^{-1}

Table 24. Reaction (10) Solution of $C_2H_4I_2$ in $C_2H_4I_2$ and dce.

ampoule number	mass of $C_2H_4I_2$/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
B 1	8.82	0.5845	18.680
B 2	9.00	0.5678	17.782
B 3	12.38	0.8562	19.494
B 4	10.60	0.7445	19.797
B 5	11.80	0.7938	18.961
B 6	14.72	0.9490	18.172
B 7	11.75	0.8062	19.339

Mean $\Delta H(10) = + 18.89 \pm 0.55$ kJ mol^{-1}

Table 25. Reaction (11). Reaction of $P_2Pt(C_2H_4)$ with $C_2H_4I_2$ in dce.

ampoule number	mass of $P_2Pt(C_2H_4)$/mg	corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
D 15	23.74	-2.3259	-73.260
D 16	26.83	-2.5938	-72.286
D 17	27.38	-2.6827	-73.263
D 18	23.57	-2.3615	-74.915
D 20	23.45	-2.3302	-74.301
D 21	23.45	-2.3732	-75.671

Mean $\Delta H(11) = -73.9 \pm 1.0$ kJ mol^{-1}

Table 26. Reaction (16). Solution of iodomethane in iodomethane and dce.

Injection number	mass of iodomethane / mg	heat of solution / J	heat of solution / kJ mol^{-1}
1	22.05	0.1900	1.223
2	"	0.1818	1.170
3	"	0.1928	1.241
4	"	0.1883	1.212
5	"	0.1798	1.158
6	"	0.1946	1.253

Mean $\Delta H(16) = +1.21 \pm 0.03$ kJ mol^{-1}

Table 27. Reaction (17). Reaction of $P_2Pt(C_2H_4)$ with iodomethane in dce.

ampoule number	mass of $P_2Pt(C_2H_4)$/mg	corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
D 15	111.61	-6.5085	-43.603
D 16	97.03	-6.2943	-48.503
D 17	102.22	-6.3419	-46.391
D 18	102.58	-6.2540	-45.587
D 19	95.88	-5.8172	-45.366
D 20	100.89	-6.1689	-45.720

Mean $\Delta H(17) = -45.9 \pm 1.3$ kJ mol^{-1}

Table 28. Reaction (18). Solution of c-$P_2Pt(CH_3)I$ in iodomethane and dce.

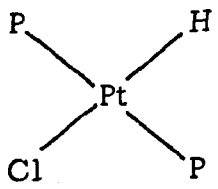
ampoule number	mass of c-$P_2Pt(CH_3)I$/mg	corrected heat of solution / J	heat of solution/ kJ mol^{-1}
A 1	20.51	0.4152	17.44
A 3	24.72	0.4926	17.17
A 4	16.38	0.3392	17.84
A 5	19.33	0.3702	16.50
A 7	14.19	0.2761	16.76

Mean $\Delta H(18) = +17.14 \pm 0.48$ kJ mol^{-1}

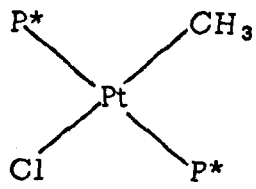
The reactions of P_2PtHCl and $P^*_2Pt(CH_3)Cl$ with tetracyanoethene.

Introduction.

The reactions of tetracyanoethene, tcne, with platinum complexes differ significantly from the analogous reactions of unsaturated hydrocarbons and fluorocarbons, which were investigated earlier(100). For example, tcne was the first substituted alkene found to displace an alkyne (phenylacetylene) from a platinum (0) complex of the type P_2Pt(alkyne); alkynes commonly displace alkenes. These observations and evidence from thermochemistry, crystal structures and infra-red spectroscopy (1,2,101-3), suggest that the platinum (0) - tcne bond is unusually strong. Tcne also forms complexes with platinum (II).



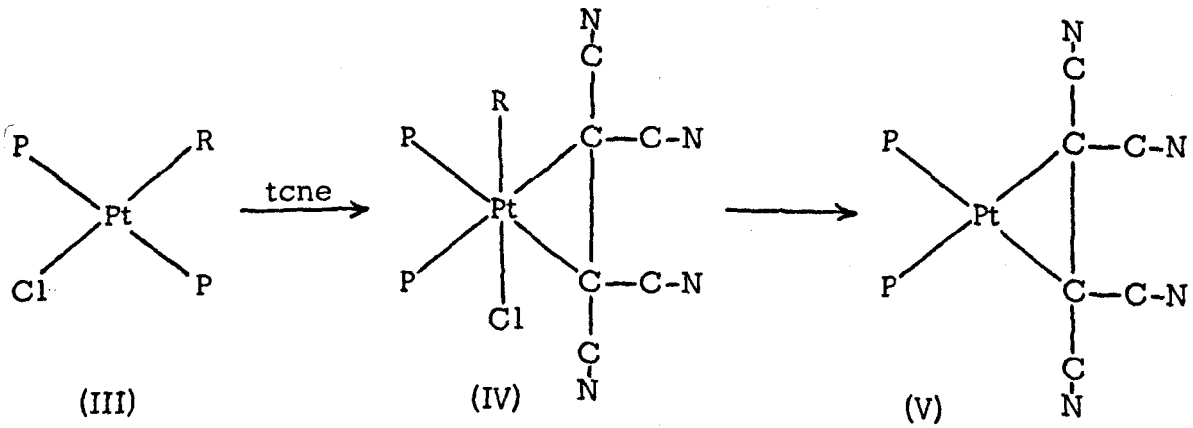
(I)



(II)

(As before, P stands for triphenylphosphine, and P* for dimethylphenylphosphine.)

Chlorohydridobis(triphenylphosphine) platinum (II), P_2PtHCl, (I), and chlorobis(dimethylphenylphosphine)methyl platinum (II), $P^*_2Pt(CH_3)Cl$, (II), both react with tcne according to the scheme shown below.



(III) (IV) (V)

The first stage is a simple addition. The second stage is formally a red--uction; in the intermediate compound (IV) the tcne is bonded to platinum (II) whereas in compounds of type (V) tcne is bonded to platinum (0).

The reaction of P_2PtHCl passes rapidly through the addition stage (IV), which is not isolated, to the substitution product (V). On the other hand $P_2^*Pt(CH_3)Cl$ reacts only as far as (IV). Clark and Puddephatt (103) suggested that the reason for the difference in the relative rates of the two stages lies in the weakness of the Pt-H bond compared with the $Pt-CH_3$ bond. The calorimetric work on these substances was intended to provide evidence for or against this argument, as well as to indicate the strength of Pt-tcne bonds.

The reaction of P_2PtHCl with tcne.

The heat, $\Delta H(1)$, of reaction (1) has been determined by measure--ment of the heats, $\Delta H(2)$ to $\Delta H(5)$, of reactions (2) to (5), and incorpor--ation of a value for $\Delta H(6)$, the heat of sublimation of tcne.

(1) $P_2PtHCl\ (s) + tcne\ (g) \longrightarrow P_2Pt(tcne)\ (s) + HCl\ (g)$

(2) $tcne\ (s) + [49\,tcne, 10^4\,dce]\ (l) \longrightarrow [50\,tcne, 10^4\,dce]\ (l)$

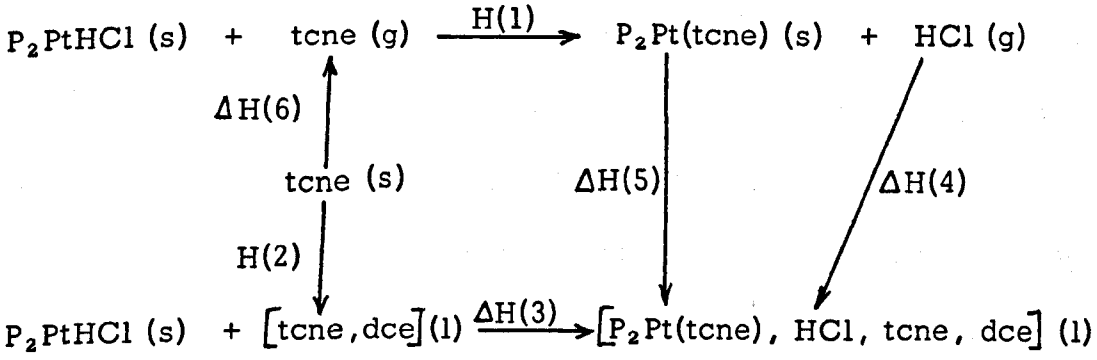
(3) $P_2PtHCl\ (s) + [50\,tcne, 10^4\,dce]\ (l) \longrightarrow [P_2Pt(tcne), HCl, 49\,tcne, 10^4\,dce]\ (l)$

(4) $HCl\ (g) + [P_2Pt(tcne), 49\,tcne, 10^4\,dce]\ (l) \longrightarrow [P_2Pt(tcne), HCl, 49\,tcne, 10^4\,dce]\ (l)$

(5) $P_2Pt(tcne)\ (s) + [49\,tcne, 10^4\,dce]\ (l) \longrightarrow [P_2Pt(tcne), 49\,tcne, 10^4\,dce]\ (l)$

(6) $tcne\ (s) \longrightarrow tcne\ (g)$

The relations between these reactions are shown in the following cycle.



The heat of reaction (1) is therefore given by the following equation.

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

$$= -(+81.2) + (+19.9) + (-60.0) - (-13.7) - (+4.5)$$

$$= -112.2 \pm 6.0\ kJ\ mol^{-1}$$

Experimental

The complex P_2PtHCl was prepared by Dr R. Puddephatt of Liverpool University, and analysed at Keele. (found C = 57.45%, H = 4.14%, calculated C = 57.19%, H = 4.13%). Tcne (Emanuel) was purified by recrystallisation from dichloromethane followed by vacuum sublimation, and was stored over solid sodium hydroxide.

Trials showed that the complex reacted rapidly and exothermically with a fifty-fold excess of tcne in dce. Physical and chemical tests were carried out to determine whether under the conditions in the calorimeter the reaction was an addition, to form a six-coordinate complex (IV) or a sub--stitution of tcne for chloride and hydride to form a four-coordinate complex (V) and hydrogen chloride.

The nmr spectrum of P_2PtHCl in dce before reaction showed a triplet at 26.1 ppm, typical of the chemical shift of a hydride proton attached directly to platinum and split by coupling to ^{31}P (104,105). This signal disappeared completely after the addition of tcne, suggesting that the hydrogen had been displaced from the platinum.

The infra-red spectrum of the starting complex in nujol showed peaks at 270 cm^{-1} (Pt - Cl stretch), 832 cm^{-1} (Pt - H bend) and 2214 cm^{-1} (Pt - H stretch). In the spectrum of the solid product complex the strong absorbtion by C≡N masked the Pt - H stretching region, but no absorbtion was detected at 832 or 270 cm^{-1}. Infra-red spectroscopy of the solution was inconclusive, due to powerful absorbtion by the solvent.

When tcne and complex solutions of the low concentrations used in calorimetry were mixed, no bubbles were seen, but a sharp smell of hydrogen chloride could be detected. The same reaction was carried out on a vacuum line, and the evolved gas was collected in an infra-red cell,

where it gave the characteristic spectrum of hydrogen chloride (106), i.e. a doublet centred on 2890 cm^{-1} and subsidiary peaks at intervals of approximately 23 cm^{-1}.

Thus chemical tests, infra-red spectroscopy and nmr spectroscopy all confirmed that the product formed in the calorimeter was $P_2Pt(tcne)$ rather than addition complex of type (IV).

Reaction (2). Solution of tcne in tcne and dce.

Ampoules containing 1.5×10^{-4} moles of tcne were broken into a solution of 1.35×10^{-3} moles of tcne in 25 cm^3 of dce. Equation (2) indicates that the quantity of tcne in each ampoule should be only 3×10^{-5} moles, i.e. less than 4 mg. A slightly larger quantity was used to avoid the errors involved in weighing such small masses. The final concentration of tcne was the same as that required by equation (2), and the initial concentration was only 8% different from that required, so it was assumed that the measured molar heat of solution would be an accurate estimate of $\Delta H(2)$. The results of calorimetry are shown in table 29.

Reaction (3). Reaction between P_2PtHCl and tcne in dce.

Ampoules containing 3×10^{-5} moles of the complex were broken into solutions of 1.5×10^{-3} moles of tcne in 25 cm^3 of dce. The results of calorimetry are shown in table 30.

Reaction (4). Solution of hydrogen chloride in $P_2Pt(tcne)$, tcne and dce.

Ampoules were evacuated and filled with hydrogen chloride (BDH) at atmospheric temperature and pressure (21.5°C and 751.15 torr) before sealing. They were broken into solutions containing 3×10^{-5} moles of $P_2Pt(tcne)$ and 1.47×10^{-3} moles of tcne in 25 cm^3 of dce. Only the lower

face of the ampoule was broken, so that hydrogen chloride did not escape without dissolving. The gas dissolved rapidly, the exothermic reaction being complete in approximately 15 seconds. In most cases there was a small bubble of gas, never more than 0.1 cm^3, left undissolved after calor--imetry. This gas was found not to be hydrogen chloride; its volume was measured by drawing it into a calibrated 1 cm^3 syringe and was subtracted from the total volume of the ampoule to arrive at the quantity of hydrogen chloride that had dissolved. Results of calorimetry are shown in table 31.

Reaction (5). Solution of $P_2Pt(tcne)$ in tcne and dce.

Ampoules containing 3×10^{-5} moles of $P_2Pt(tcne)$ were broken into solutions of 1.47×10^{-3} moles of tcne in 25 cm^3 of dce. The results of calorimetry are shown in table 32.

Reaction (6). Sublimation of tcne.

The value found by Boyd (107) using the McLeod gauge technique, is $+ 81.2 \pm 5.8$ kJ mol^{-1}.

The reaction of $P_2^*Pt(CH_3)Cl$ with tcne.

The heat, $\Delta H(7)$, of reaction (7) has been determined by measure--ment of the heats, $\Delta H(2)$, $\Delta H(8)$ and $\Delta H(9)$, of reactions 2, 8 and 9, and incorporation of the previously-described literature value of $\Delta H(6)$, the heat of sublimation of tcne.

(7) $P_2^*Pt(CH_3)Cl$ (s) + tcne (g) $\longrightarrow$ $P_2^*Pt(CH_3)Cl(tcne)$ (s)

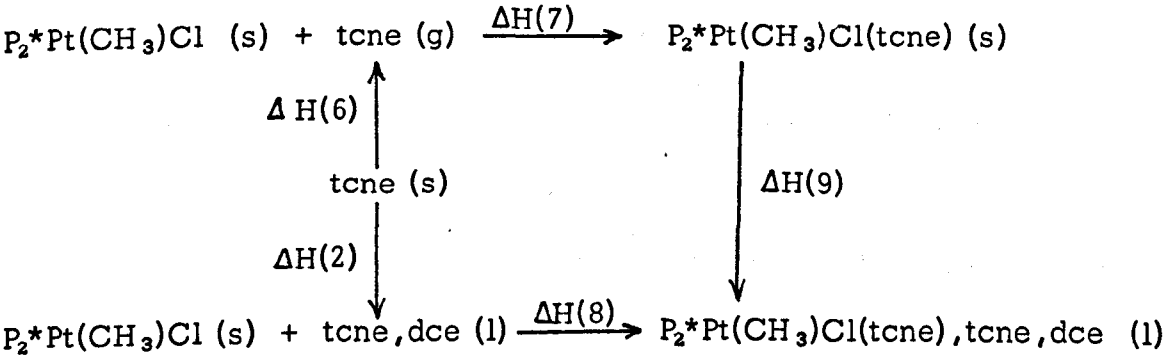
(2) tcne (s) + [49 tcne, 10^4 dce] (l) $\longrightarrow$ [50 tcne, 10^4 dce] (l)

(8) $P_2^*Pt(CH_3)Cl$ (s) + [50 tcne, 10^4 dce] (l) $\longrightarrow$ [$P_2^*Pt(CH_3)Cl$(tcne), 49 tcne, 10^4 dce] (l)

(9) $P_2^*Pt(CH_3)Cl$(tcne) (s) + [49 tcne, 10^4 dce] (l) $\longrightarrow$ [$P_2^*Pt(CH_3)Cl$(tcne), 49 tcne, 10^4 dce] (l)

(6) tcne (s) $\longrightarrow$ tcne (g)

The relations between these reactions are shown in the cycle below.



The heat of reaction (7) is therefore given by the following equation.

$$\Delta H(7) = -\Delta H(6) + \Delta H(2) + \Delta H(8) - \Delta H(9)$$

$$= -(+81.2) + (+19.9) + (-71.7) - (+8.92)$$

$$= -141.9 \pm 6.3 \text{ kJ mol}^{-1}$$

Experimental

The complex P_2*Pt(CH_3)Cl was supplied by Dr R. Puddephatt of Liverpool University and analysed at Keele. (found C = 39.21%, H = 4.97%, calculated C = 39.13%, H = 4.83%). The tcne was as used for the previous reaction. Trials showed that the complex reacted rapidly and exothermically with a fifty-fold excess of tcne in dce.

Reactions (2) and (6). Solution and sublimation of tcne.

The determination of the heats of these reactions has already been described, on pages 120 and 121.

Reaction (8). Reaction of P_2*Pt(CH_3)Cl with tcne in dce.

Ampoules containing 3×10^{-5} moles of the complex were broken into solutions of 1.5×10^{-3} moles of tcne in 25 cm^3 of dce. Results of calor-imetry are shown in table 33.

Reaction (9). Solution of P_2*Pt(CH_3)Cl(tcne) in tcne and dce.

This product complex was prepared by dissolving equimolar masses (0.4 mmole) of P_2*Pt(CH_3)Cl and tcne in separate volumes of nitrogen-purged dichloromethane and mixing the colourless solutions at room temperature in the absence of oxygen to form a pale yellow solution. The solvent was evaporated and the solid was dried under a jet of nitrogen. Ampoules containing 3×10^{-5} moles of the complex were broken into solutions of 1.47×10^{-3} moles of tcne in 25 cm^3 of dce. Results from calorimetry are shown in table 34.

Discussion : the bond dissociation energy, D(Pt - tcne) in P_2*Pt(CH_3)Cl(tcne).

The heat, ΔH(10), of the gas-phase reaction (10) may be assumed to be equal and opposite to the heat, ΔH(7), of reaction (7) on page 122 if the heats of sublimation of the complexes P_2*Pt(CH_3)Cl and P_2*Pt(CH_3)Cl(tcne) are similar.

(10) P_2*Pt(CH_3)Cl(tcne) (g) ⟶ P_2*Pt(CH_3)Cl (g) + tcne (g)

Since in reaction (10) only a single bond is broken, the heat of reaction is equal to the bond dissociation energy.

$$D(\text{Pt-tcne}) = \Delta H(10) = 142 \text{ kJ mol}^{-1}$$

This rather small value for dissociation energy of the bond between tcne and platinum (II) may be compared with the bond dissociation energy of bonds between tcne and platinum (0).

The complex P_2Pt(tcne), (V) on page 116, has the molecular structure shown in figure 19 (102). The dihedral angle between the planes P_1PtP_2 and C_1PtC_2 is 10^o, and the CN-C_1-C_2-CN planes are bent away from the perpen--dicular to the C_1PtC_2 plane by the same amount. The C_1-C_2 bond length is 0.152 nm, much closer to the 0.154 nm of a normal C-C single bond than to the 0.135 nm bypical of double bonds. The C-CN bond length is 0.140 nm, significantly shorter than the length in uncoordinated tcne, which is 0.1449 nm. The two Pt-P bond lengths are almost equal, as are the two Pt-C distances.

The Pt-tcne bonding may be described in terms of the Dewar-Chatt-Duncanson model (9,10,11). Tcne has little tendency to donate electrons; it is one of the strongest π acids known (108) so the tcne⟶Pt(0) σ bond is likely to be very weak, while the Pt dπ ⟶ tcne p π* bond is extremely

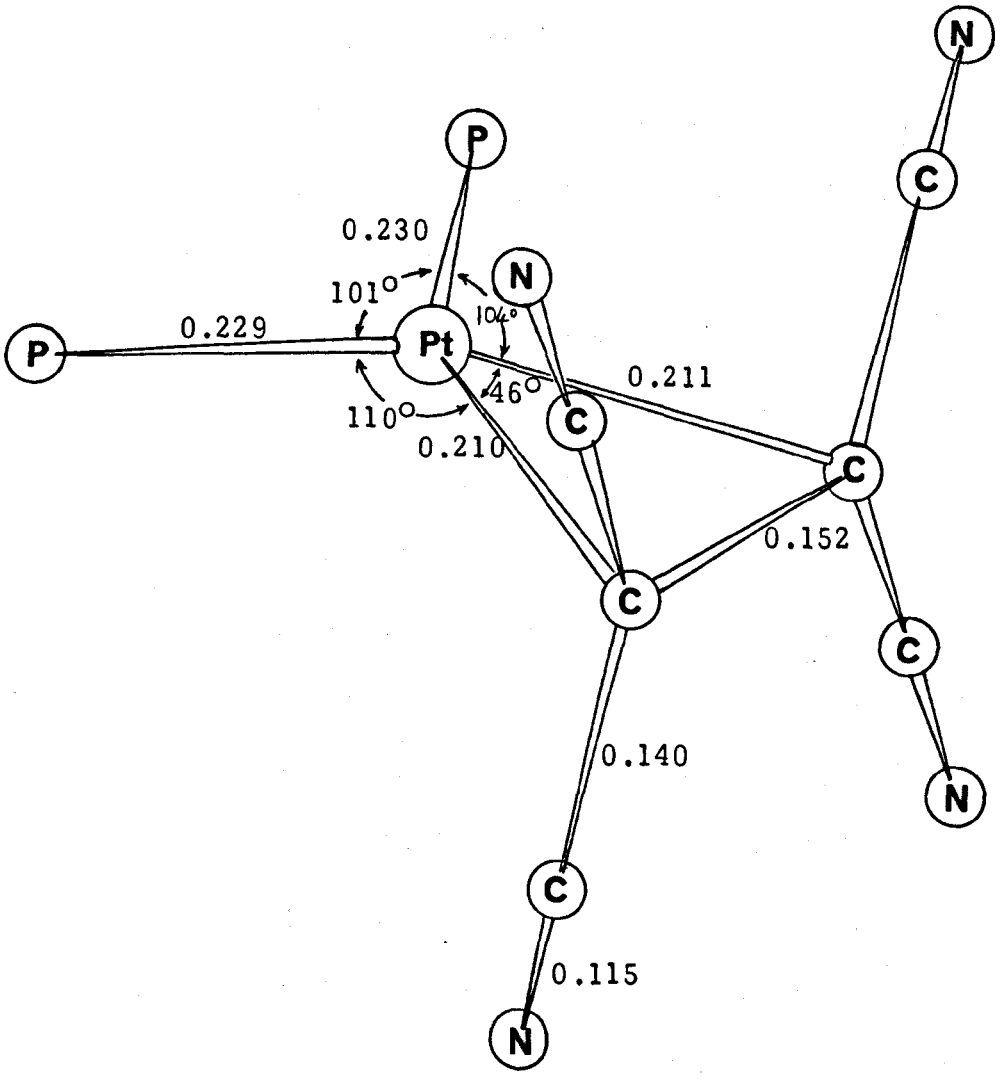


Figure 19. Molecular structure of $P_2Pt(tcne)$, with bond angles, and bond lengths in nanometres. The phenyl rings have been omitted for clarity.

strong. The electron pair in the π bond is located almost entirely in the tcne $p\pi^*$ antibonding orbital, so the single C-C bond length is explained. Molecular orbital calculations have shown that adding electron density to the antibonding orbital should increase the order, and therefore decrease the length, of the C-CN bond, as observed (109). The bending of the substituents on the alkene away from the plane of the C_1-C_2 bond is the expected effect of transferring electrons to the antibonding orbital, where they are concentrated nearer the Pt-C_1 and Pt-C_2 axes, so that the distrib--ution of charge around the carbon atoms is almost equivalent to sp^3 hybrid--isation (12). Nuclear magnetic resonance provides further evidence for the almost complete transfer of charge from platinum to tcne (103). The spectrum of the complex $P_2Pt(tcne)$ is similar to those of platinum (II) com--plexes of the type P_2PtX_2. As the π component is thought to be responsible for the strength of all Pt(0)–alkene bonds, it is not surprising that an acceptor as powerful as tcne should form very strong bonds of this sort. Evans, Mortimer and Puddephatt (2) found that D(Pt-tcne) in $P_2Pt(tcne)$ was greater than D(Pt-C_2H_4) in $P_2Pt(C_2H_4)$ by about 156 kJ mol^{-1}, thus putting a figure to the predictions of Uguagliati and Baddley (101).

Bonding in complexes of tcne with platinum (II).

Comparatively little is known about the structures of platinum(II) - tcne complexes and the strengths of the bonds within them. Clark and Puddephatt(103) prepared several complexes of the type $Pt(PR_3)(CH_3)X(tcne)$ and found that they were much more stable than the analogous complexes in which tcne was replaced by fluoro-alkenes. The nmr spectra of these complexes resembled those of platinum (IV) rather than platinum (II) compounds. These observations were attributed to the ability of the tcne to oxidise the metal, so it appears that the strength of the bond is, as in platinum (0)

complexes, principally due to the π component.

Since bonding to tcne in complexes of both oxidation states is largely due to a movement of electrons from the metal towards tcne, and platinum (II) is a less effective electron donor than platinum (0), the bond dissociation energy D(Pt - tcne) in P_2*Pt(CH_3)Cl(tcne) may be expected to be less than in P_2Pt(tcne). These conclusions may be compared with the experimentally-derived values.

D(Pt - tcne) in P_2*(CH_3)Cl(tcne) = 142 kJ mol^{-1} (this work, page 122)

D(Pt - tcne) in P_2Pt(tcne) = D(Pt - C_2H_4) + 156 kJ mol (Evans et al. (2))

As the bond dissociation energy D(Pt - C_2H_4) in P_2Pt(C_2H_4) is probably approximately 300 kJ mol^{-1}, the bond dissociation energy in P_2*Pt(CH_3)Cl(tcne) is evidently very much less than in P_2Pt(C_2H_4), as expected.

The reactions of P_2PtHCl and P_2*Pt(CH_3)Cl with tcne.

The following section of the discussion is concerned with explan--ations for the observation that P_2PtHCl reacts with tcne to form P_2Pt(tcne) , (V), by elimination of hydrogen chloride, while P_2*Pt(CH_3)Cl forms the addition compound P_2*Pt(CH_3)Cl(tcne), (IV). Two types of thermochemical argument may be considered.

a. The bond dissociation energies in the starting complexes, I and II, may be compared with one another and with those in the final product, V.

The measured enthalpy of the reaction (1), page 118 , is - 112.2 $\pm$ 6.0 kJ mol^{-1}.

(1) $P_2PtHCl\ (s) + tcne\ (g) \longrightarrow P_2Pt(tcne)\ (s) + HCl\ (g)$

Assuming that the heats of sublimation of the two solid complexes in the above reaction are approximately equal, one may attribute this enthalpy of reaction to the difference in bond dissociation energies of the bonds broken and formed.

(i) $\Delta H(1) = D_1(Pt - H) + D_2(Pt-Cl) - D(Pt-tcne) - D(H-Cl) = -112\ kJ\ mol^{-1}$

In this equation $D_1(Pt-H)$ and $D_2(Pt-Cl)$ are the heats of the successive gas-phase reactions below.

$$P_2Pt\,HCl \longrightarrow P_2PtCl + H \longrightarrow P_2Pt + H + Cl$$

Evans, Mortimer and Puddephatt (4) estimated the heat, $\Delta H(10)$ of the gas-phase reaction (10).

(10) $P_2Pt(tolane)\ (g) + HCl\ (g) \longrightarrow P_2Pt(CPh{=}CHPh)Cl$

$$\Delta H(10) = -90 \pm 6\ kJ\ mol^{-1}$$

(In this reaction a $\sigma\pi$ bond to platinum is replaced by a Pt-C σ bond.) This value may be equated to the difference in bond dissociation energies of the bonds broken and formed.

(ii) $D(Pt-tolane) + D(H-Cl) - D_1(Pt-C) - D_2(Pt-Cl) - D(C-H) = -90\ kJ\ mol^{-1}$

In this equation $D_1(Pt-C)$ and $D_2(Pt-Cl)$ are the heats of the successive gas-phase reactions below.

$P_2Pt(CPh{=}CHPh)Cl\ (g) \longrightarrow P_2PtCl\ (g) + CPh{=}CHPh\ (g)$

$P_2PtCl\ (g) \longrightarrow P_2Pt\ (g) + Cl\ (g)$

Combination of (i) and (ii) above leads to the following relationship.

(iii) $D_1(Pt-H) - D_1(Pt-C) + D(Pt\text{-tolane}) - D(Pt\text{-tcne}) - D(C-H) = -202\ kJ\ mol^{-1}$

Evans et al. have obtained the following relationships, from which the difference in bond dissociation energies, D(Pt-tolane) - D(Pt-tcne) may be obtained.

$$D(Pt\text{-tolane}) - D(Pt\text{-}C_2H_4) = 82 \pm 12\ kJ\ mol^{-1} \quad (3)$$

$$D(Pt\text{-tcne}) - D(Pt\text{-}C_2H_4) = 156 \pm 8\ kJ\ mol^{-1} \quad (2)$$

therefore $D(Pt\text{-tolane}) - D(Pt\text{-tcne}) = -74 \pm 14\ kJ\ mol^{-1}$

They have also calculated the bond dissociation energy D(C-H) in $P_2Pt(CPh{=}CHPh)Cl$.

$$D(C-H) = 306\ kJ\ mol^{-1} \quad (4)$$

By combining these values with equation (iii) above the following relationship is obtained.

$$D(Pt-H) - D(Pt-C) = 178\ kJ\ mol^{-1}$$

In view of the estimates and the approximations used in deriving this result no importance should be attached to its precise value. Nevertheless it suggests that in complexes of the type P_2PtXCl, the Pt-H bond (X = H) is considerably stronger than the Pt-C bond (X = CPh=CHPh). If the strength of the Pt-CH_3 bond in $P_2{*}Pt(CH_3)Cl$ is similar to that of the Pt - CPh=CHPh bond, then it also is considerably weaker than in Pt-H bond in P_2PtHCl, and so offers no explanation for the different reactions of the two complexes I and II.

The discussion so far has dealt with the energies of the bonds

broken in the reactions. The bonds which are formed may also be compared. The real or hypothetical reactions that produce $P_2Pt(tcne)$ or $P_2{}^*Pt(tcne)$ both involve the formation of a Pt-tcne bond, which may be assumed to have very similar bond dissociation energies in each of these products. The other bond formed is either H-Cl or CH_3-Cl, whose bond dissociation energies are given below.

$$D(H\text{-}Cl) = 431.57 \text{ kJ mol}^{-1} \qquad (110)$$

$$D(CH_3\text{-}Cl) = 351. \text{ kJ mol}^{-1} \qquad (111)$$

The greater strength of the H-Cl bond partially offsets the difference between the bond dissociation energies D(Pt-H) and D(Pt-CH_3) already noted, as it would tend to favour the elimination of HCl in the formation of a complex of type V rather than IV.

b. Explanations for the fact that reactions may stop at IV or proceed to V should be based on the properties of the 6-coordinate complexes, IV. The relative bond dissociation energies of the Pt-CH_3 and Pt-H bonds are not necessarily the same in the 4-coordinate and the 6-coordinate complexes. Since the methyl group is known to be a better electron donor than the hydrogen atom, it may make a greater contribution to the Pt→tcne π bond and the stability of the addition compound IV, so decreasing the difference between D(Pt-CH_3) and D(Pt-H) in that type of compound. Even so, it appears that the explanation for the difference in the courses of the reactions of tcne with $P_2^*Pt(CH_3)Cl$ and P_2PtHCl does not lie in the strengths of the bonds between these ligands and platinum. It may be that there is a kinetic, rather than a thermodynamic, reason for the difference.

Table 29. Reaction (2). Solution of tcne in tcne and dce.

ampoule number	mass of tcne/mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
A 7	20.4	2.8780	18.071
A 8	20.2	3.0027	19.041
A 9	20.1	2.7366	17.440
A 10	20.4	3.3574	21.082
B 6	19.15	3.1024	20.752
B 7	31.5	5.1721	21.031
B 8	26.3	4.3208	21.044
B 9	20.67	3.3840	20.971

Mean $\Delta H(2) = + 19.9 \pm 1.1$ kJ mol^{-1}

Table 30. Reaction (3). Reaction between P_2PtHCl and tcne in dce.

ampoule number	mass of P_2PtHCl/mg	corrected heat of solution / J	heat of solution/ kJ mol^{-1}
A 2	23.1	-1.8023	-58.994
A 3	23.7	-1.8756	-59.840
A 4	23.7	-1.9040	-60.645
A 5	23.9	-1.9112	-60.467
A 6	23.59	-1.8694	-59.920

Mean $\Delta H(3) = - 60.0 \pm 0.60$ kJ mol^{-1}

Table 31. Reaction (4). Solution of HCl in $P_2Pt(tcne)$, tcne, and dce.

ampoule number	mass of HCl/mg	heat of solution/J	heat of solution/kJ mol^{-1}
B 2	1.57	0.5887	13.639
B 4	1.56	0.5940	13.898
B 5	1.54	0.5883	13.905
B 6	1.54	0.5636	13.320
B 7	1.62	0.6087	13.700

Mean $\Delta H(4) = -13.69 \pm 0.21$ kJ mol^{-1}

Table 32. Reaction (5). Solution of $P_2Pt(tcne)$ in tcne and dce.

ampoule number	mass of $P_2Pt(tcne)$/mg	corrected heat of solution / J	heat of solution /kJ mol^{-1}
A 1	26.4	0.14231	4.570
A 2	25.8	0.09200	3.023
A 3	27.85	0.15265	4.647
A 4	35.4	0.22661	5.427
A 6	27.6	0.18660	5.732
A 7	30.0	0.15506	4.382
A 8	26.43	0.12397	3.977

Mean $\Delta H(5) = +4.54 \pm 0.68$ kJ mol^{-1}

Table 33. Reaction (8). Reaction of P_2*Pt(CH_3)Cl with tcne in dce.

ampoule number	mass of P_2*Pt(CH_3)Cl/mg	corrected heat of reaction / J	heat of reaction/kJ mol^{-1}
B 1	17.0	-2.2435	-68.874
B 2	17.6	-2.5504	-75.626
B 3	17.0	-2.3152	-71.074
B 4	17.0	-2.3198	-71.214
B 5	17.3	-2.3739	-71.611

Mean $\Delta H(8) = -71.7 \pm 2.2$ kJ mol^{-1}

Table 34. Reaction (9). Solution of P_2*Pt(CH_3)Cl(tcne) in tcne and dce.

ampoule number	mass of P_2*Pt(CH_3)Cl(tcne) / mg	corrected heat of solution / J	heat of solution/kJ mol^{-1}
A 17	16.74	0.23501	9.125
A 18	16.72	0.24868	9.667
A 19	16.58	0.22685	8.893
A 20	16.35	0.22254	8.847
A 21	16.71	0.22127	8.607
A 22	16.33	0.20505	8.161
A 23	16.23	0.22871	9.159

Mean $\Delta H(9) = +8.92 \pm 0.36$ kJ mol^{-1}

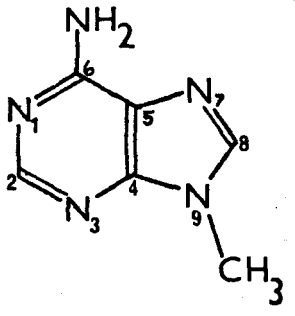
The reaction of potassium tetrachloroplatinate (II) with 9-methyl adeninium chloride.

Introduction.

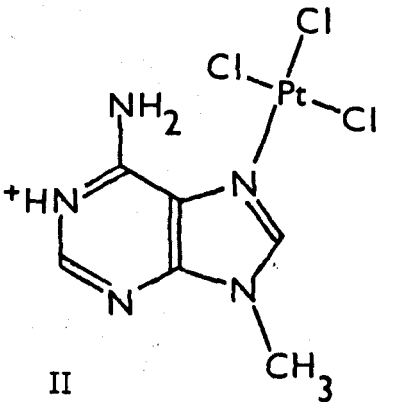
In 1969 Rosenberg, Van Camp, Tsovko and Mansour (112) reported that various coordination compounds of platinum, especially cis-$Pt(NH_3)_2Cl_2$, were able to check the growth of tumours. A number of different compounds of platinum (II), all containing at least two labile ligands (Cl) in cis positions, have been found to prevent the growth of several types of tumours or even to cause them to regress, both in vivo and in tissue culture. Although the compounds have some damaging side-effects, their toxicity is not proportional to their therapeutic effect (113). The compounds appear to prevent formation of DNA by coordination to potential ligands, usually nitrogen, on the purine bases. It has been suggested that a single platinum atom bonds to both strands of the DNA helix, so preventing division and replication.

When the purine forms part of the DNA molecule there are several possible points of attachment, N(1), N(3) and N(7), as well as any suitable substituent on C(6), but not N(9), to which the sugar is attached. Crystallographic and nmr studies to find which of the possible sites for bonding are used have been carried out on isolated nucleosides or even the free bases. Kong and Theophanides (114,115) found that both N(1) and N(7) of adenosine were coordinated, but to different platinum atoms, when Pt(dien)Cl_2 was reacted with the nucleoside in water. The purines guanosine, xanthosine and inosine all coordinated through N(7). In order to obtain a simple compound suitable for crystal structure determination

without opening the N(9) position to attack by platinum, Terzis et al. (116,117) chose 9-methyladenine , I, which reacted over a period of days with potassium tetrachloroplatinate (II) to form the 9-methyladenium complex, II, whose structure is shown in figure 20.



I



II

If the heat of this reaction was known, the heat of formation of $PtCl_3$(9-MeAdH) might be calculated, so adding some thermodynamic information to the analytical and structural data on the subject. The reaction is far too slow for calorimetry, but its heat may be found by reacting potassium tetrachloroplatinate (II) and $PtCl_3$(9-MeAdH) in turn with aqueous cyanide, which displaces other ligands to form potassium tetracyanoplatinate (II).

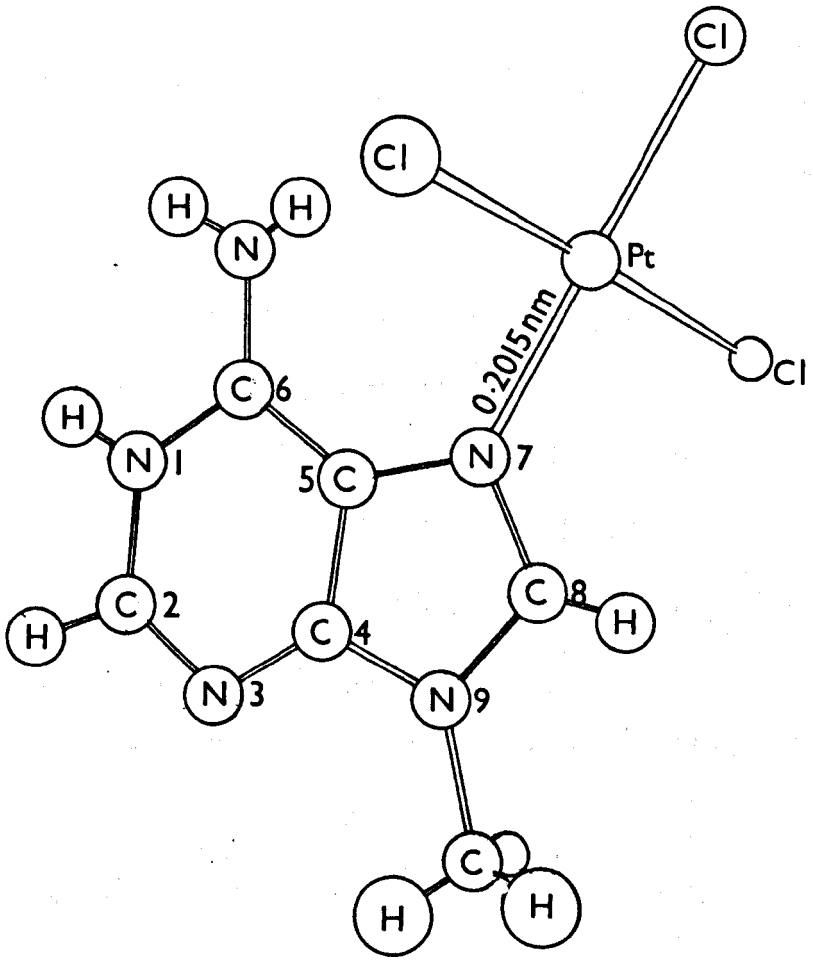


Figure 20. Molecular structure of $PtCl_3$(9-methyladenineH).

The $PtCl_3$ plane makes an angle of 62.6° with the adenine plane.

Procedure and results.

The heat, $\Delta H(1)$, of reaction (1) may be derived from the heats, $\Delta H(2)$ to $\Delta H(8)$, of reactions (2) to (8).

(1) $9\text{-MeAdHCl}, 10^4 H_2O\ (l) + [K_2PtCl_4, 10^4 H_2O](l) \longrightarrow [PtCl_3(9\text{-MeAdH})(s) + 2KCl, 2 \times 10^4 H_2O](l)$

(2) $9\text{-MeAdHCl}\ (s) + 10^4 H_2O\ (l) \longrightarrow [9\text{-MeAdHCl}, 10^4 H_2O](l)$

(3) $K_2PtCl_4\ (s) + 10^4 H_2O\ (l) \longrightarrow [K_2PtCl_4, 10^4 H_2O]\ (l)$

(4) $K_2PtCl_4\ (s) + [100KCN, 10^4 H_2O](l) \longrightarrow [K_2Pt(CN)_4, 4KCl, 96KCN, 10^4 H_2O](l)$

(5) $9\text{-MeAdHCl}\ (s) + [K_2Pt(CN)_4, 4KCl, 96KCN, 10^4 H_2O](l) \longrightarrow [9\text{-MeAdHCl}, K_2Pt(CN)_4, 4KCl, 96KCN, 10^4 H_2O]\ (l)$

(6) $2KCl\ (s) + [9\text{-MeAdHCl}, K_2Pt(CN)_4, 2KCl, 96KCN, 10^4 H_2O]\ (l) \longrightarrow 9\text{-MeAdHCl}, K_2Pt(CN)_4, 4KCl, 96KCN, 10^4 H_2O]\ (l)$

(7) $PtCl_3(9\text{-MeAdH})\ (s) + [100KCN, 10^4 H_2O]\ (l) \longrightarrow [9\text{-MeAdHCl}, K_2Pt(CN)_4, 2KCl, 96KCN, 10^4 H_2O]\ (l)$

(8) $2\ KCl\ (s) + 2 \times 10^4 H_2O\ (l) \longrightarrow [2KCl, 2 \times 10^4 H_2O]\ (l)$

Of these heats, $\Delta H(3)$ has been obtained from the literature (118), while $\Delta H(4)$ and $\Delta H(7)$ have been measured. The heats, $\Delta H(6)$ and $\Delta H(8)$ of reactions (6) and (8) have been assumed to be equal, so that their com--bined contribution to $\Delta H(1)$ is zero. As no 9-methyl adenine was available, the heat, $\Delta H(2)$ of reaction (2), has been assumed to be equal to the heat, $\Delta H(9)$ of reaction (9), which has been measured. Similarly $\Delta H(5)$ was assumed to be equal to $\Delta H(10)$, which was measured.

(9) $AdHCl\ (s) + 10^4 H_2O\ (l) \longrightarrow [AdHCl, 10^4 H_2O]\ (l)$

(10) $AdHCl\ (s) + [100KCN, 10^4 H_2O]\ (l) \longrightarrow [AdHCl, 100KCN, 10^4 H_2O](l)$

The heat of reaction (1) is given by the following equation.

$$\Delta H(1) = -\Delta H(2) - \Delta H(3) + \Delta H(4) + \Delta H(5) - \Delta H(6) - \Delta H(7) + \Delta H(8)$$

$$= -(+43.51) - (+47.7) + (-407.2) + (+10.2) - X - (-409.3) + X$$

$$= -78.9 \pm 2.3 \text{ kJ mol}^{-1}$$

Reaction (3). Solution of potassium tetrachloroplatinate (II) in water.

The literature values for the standard heats of formation of crystalline and aqueous ("dilute") potassium tetrachloroplatinate (II) are -1063.6 and -1015.9 kJ mol^{-1} respectively, so that the heat of solution is + 47.7 kJ mol^{-1}. (118).

Reaction (4). Reaction of potassium tetrachloroplatinate (II) with aqueous potassium cyanide.

The potassium cyanide (BDH) was heated to 100°C in vacuo for several hours to remove any ammonium acetate that had been formed by hydrolysis. The distilled water used as solvent was boiled for several hours while nitrogen was bubbled through it, before cooling and storing it under nitrogen. Ampoules containing 1.4×10^{-4} moles of potassium tetrachloroplatinate (II) (Johnson Matthey) were broken into a solution of 1.4×10^{-2} moles of potassium cyanide in 25 cm^3 of water. Results of calorimetry are shown in table 35.

Reactions (6) and (8). Solution of potassium chloride.

In reaction (8) two moles of potassium chloride are dissolved in 2×10^4 moles of water, while in reaction (6) the same quantity of potassium chloride is dissolved in a solution containing 10^4 moles of water and

9-MeAdHCl, K_2PtCl_4, KCl and KCN whose total concentration is approximately equivalent to 102 moles of potassium chloride. The heat of reaction (6), which is not known, has been taken to be approximately equal to the heat of reaction (8). To ascertain whether this assumption is reasonable one may refer to the heats of solution of potassium chloride in solutions whose concentrations are similar to those which are involved in reactions (6) and (8). The heats of solution of potassium chloride at infinite dilution (equiv--alent to reaction (8)) and at a KCl : water ratio of 1 : 100 (equivalent to reaction (6)) are + 17.22 and + 17.41 kJ mol^{-1} respectively, (118) the difference being $\simeq$ 0.2 kJ mol^{-1}. This difference is less than the uncertainties of the other measurements reported here, so the assumption that $\Delta H(6)$ and $\Delta H(8)$ are equal appears to be reasonable.

Reaction (7). Reaction of $PtCl_3$(9-MeAdH) with aqueous potassium cyanide.

The complex $PtCl_3$(9-MeAdH) was given by Professor T. Theophanides of the University of Montreal. Ampoules containing 1.4×10^{-4} moles of this complex were broken into a solution of 1.4×10^{-2} moles of potassium cyanide in 25 cm^3 of water. Results from calorimetry are shown in table 36.

Reaction (9). Solution of adenine hydrochloride in water.

Ampoules containing 1.4×10^{-4} moles of adenine hydrochloride (Koch Light) were broken into 25 cm^3 of water. Results from calorimetry are shown in table 37.

Reaction (10). Solution of adenine hydrochloride in aqueous potassium cyanide.

Ampoules containing 1.4×10^{-4} moles of adenine hydrochloride were broken into a solution of 1.4×10^{-2} moles of potassium cyanide in 25 cm^3 of water. Results from calorimetry are shown in table 38.

Discussion

It is in principle possible to obtain the heats of various reactions between 9-MeAdHCl and K_2PtCl_4, in which the different combinations of reactants and products are in the solid state or in solution. Of these, reaction (1), in which the platinum complex $PtCl_3$(9-MeAdH) is solid but the other reagents and products are in aqueous solution, was thought to be the most relevant to reactions in living tissue, in which this or similar complexes are thought to be attached to the DNA macromolecule where they are largely protected from free water. The value found for $\Delta H(1)$ indicates that there is a significant exothermic enthalpy term contributing to the free energy change of the reaction.

$$\Delta H(1) = -79 \text{ kJ mol}^{-1}$$

The same is likely to be true of other reactions in which a chlorine atom bonded to platinum (II) is displaced by the nitrogen of a nucleotide.

The heat, $\Delta H(11)$ of reaction (11), in which the reactants and products are in their standard states may be found by incorporating literature values for $\Delta H(3)$ and $\Delta H(8)$ (118).

(11) 9-MeAdHCl (s) + K_2PtCl_4 (s) $\longrightarrow$ $PtCl_3$(9-MeAdH) (s) + 2KCl (s)

$$\Delta H(11) = -22.2 \text{ kJ mol}^{-1}$$

From this value and literature values of the standard heats of formation of KCl and K_2PtCl_4 (118) the standard heat of formation of $PtCl_3$(9-MeAdHCl) might be calculated if the standard heat of formation of 9-MeAdHCl was determined by bomb calorimetry.

$$\Delta H_f^\circ [PtCl_3(9\text{-MeAdH}), s] = \Delta H_f^\circ (9\text{-MeAdHCl}, s) - 214.0 \text{ kJ mol}^{-1}$$

From this value, once found, a bond energy term for the Pt - (9-MeAdH) bond might be derived.

Table 35. Reaction (4). Reaction of potassium tetrachloroplatinate (II) with aqueous potassium cyanide.

ampoule number	mass of K_2PtCl_4/mg	heat of reaction/J	heat of reaction/kJ mol^{-1}
A 1	58.45	-57.013	-404.76
A 2	58.01	-57.298	-410.01
A 3	57.46	-56.111	-405.36
A 4	56.89	-56.022	-408.77
A 5	57.00	-55.672	-405.43
A 7	57.38	-56.553	-409.12

Mean $\Delta H(4) = -407.2 \pm 1.9$ kJ mol^{-1}

Table 36. Reaction (7). Reaction of $PtCl_3$(9-MeAdHCl) with aqueous potassium cyanide.

ampoule number	mass of complex/mg	heat of reaction/J	heat of reaction/kJ mol^{-1}
A 8	62.75	-56.624	-407.53
A 9	61.87	-56.242	-410.53
A 9b	62.73	-56.674	-408.02
A 10	62.72	-56.989	-410.35
A 11	62.71	-56.713	-408.42
A 12	61.61	-56.043	-410.74

Mean $\Delta H(7) = -409.3 \pm 1.2$ kJ mol^{-1}

Table 37. Reaction (9). Solution of adenine hydrochloride in water.

ampoule number	mass of adenine hydrochloride/mg	heat of solution/J	heat of solution/kJ mol^{-1}
A 2	24.72	5.9374	43.910
A 3	24.78	5.9355	43.258
A 4	25.78	6.2414	43.723
A 5	25.63	6.1812	43.555
A 6	25.24	6.0417	43.230
A 8	25.88	6.2213	43.414

Mean $\Delta H(9) = + 43.51 \pm 0.22$ kJ mol^{-1}

Table 38. Reaction (10). Solution of adenine hydrochloride in aqueous potassium cyanide.

ampoule number	mass of adenine hydrochloride/mg	heat of solution/J	heat of solution/kJ mol^{-1}
A 9	25.50	1.4616	10.351
A 10	23.89	1.2712	9.610
A 12	25.70	1.4931	10.492

Mean $\Delta H(8) = + 10.2 \pm 0.5$ kJ mol^{-1}

Heats of sublimation.

Introduction

Bond dissociation energies are the heats of reactions of isolated molecules, i.e. those in the gas phase. Since calorimetrically-determined enthalpy changes, even when corrected for heats of solution, refer to ligands and complexes which are often solid or liquid, bond dissociation energies can only be calculated if heats of vaporisation and sublimation are known. Values for heats of vaporisation of all the liquids used in this work may be found in the literature, but the heats of sublimation of several of the solid ligands and all of the complexes have not previously been investigated.

The standard heat of sublimation $\Delta H^{o}_{sub,298.15}$ is the enthalpy change at 298.15 K for the process involving solid and gas in their standard states:-

solid under 1 atm. pressure $\longrightarrow$ ideal gas at 1 atm. pressure.

This is the same as the enthalpy change for the process

solid under 1 atm. pressure $\longrightarrow$ real gas at zero pressure.

In practice the enthalpy change that is measured is usually that for the process

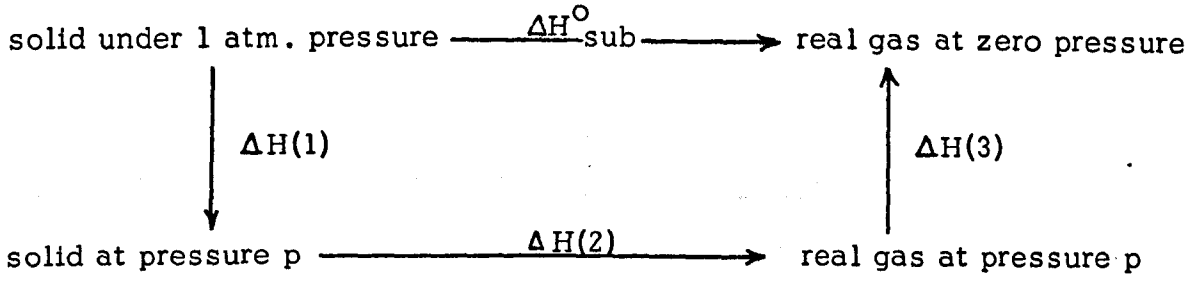
solid under pressure p $\longrightarrow$ real gas at pressure p

where the value of p is one atmosphere or less, depending on the experim--ental method being used, and is most commonly the saturated vapour pressure of the substance under investigation.

The experimental enthalpy change, $\Delta H(2)$ and the standard

enthalpy change , ΔH°_{sub}, form parts of a cycle (18) from which the following relationship is derived.

$$\Delta H^{\circ}_{sub} = \Delta H(1) + \Delta H(2) + \Delta H(3)$$



In this cycle $\Delta H(1)$ and $\Delta H(3)$ have the following values.

$$\Delta H(1) = \int_1^p \left[- T (\partial V/\partial T)_p + V \right] dp$$

$$\Delta H(3) = \int_p^{\circ} \left[- T (\partial V/\partial T)_p + V \right] dp$$

Of these terms, $\Delta H(1)$ is almost always small; the molar volume of a solid is $- 100\ cm^3$, so that even if p is almost zero $\Delta H(1)$ will only be $\simeq 0.1$ litre atmosphere $\simeq 10\ J\ mol^{-1}$. The second term $\Delta H(3)$ is significantly larger only if $p \gg 0$, but as the solid ligands and complexes all have vapour pressures even at the temperatures of measurement of 10^{-3} atmospheres or less, $\Delta H(3)$ is also negligible if p is the saturated vapour pressure.

If measurements are made at a temperature T_1 other than 298.15 K they should be corrected to that temperature using the equation below.

$$\Delta H^{\circ}_{sub,298} = \Delta H_{sub,T_1} + \int_{T_1}^{298} \left[C_p(g) - C_p(s) \right] dT$$

If the difference in the heat capacities of the solid and the gas is indepen-
-dent of pressure, the following relationship may be used.

$$\Delta H^{o}_{sub,298.15} = \Delta H_{sub,T_1} + (298.15 - T_1)\left[C_p(g) - C_p(s)\right]$$

If the heat capacities are unknown one has little choice but to ignore the correction, or to assume that it is small compared to the experimental error of the determination of the enthalpy.

Experimental methods for determining heats of sublimation.

These enthalpy changes may either be measured directly, in some form of calorimeter, or be calculated from the variation of vapour pressure with temperature.

Direct calorimetry.

No calorimeters appear to have been designed specifically for the measurement of heats of sublimation: of those intended for heats of vaporisation some are also suitable for solids. All operate isothermally, the energy absorbed by the evaporating liquid or solid being supplied by a calibrated heater to keep the temperature constant and equal to that of the surroundings. Those of Osborne and Ginnings (119) and of Konicek (120) were essentially inverted U tubes, one arm forming the calorimeter from which the substance was vaporised, the other, held at a lower temp--erature, acting as a receiver. The rate of evaporation was controlled by a throttle valve (119) or by changing the temperature of the receiver (120) so that evaporative cooling might be matched by electrical heating. The mass of substance was determined by detaching and weighing the cooled receiver. Konicek's results for fourteen fairly volatile liquids showed uncertainties of 0.1 to 0.25 kJ mol^{-1}, no solids were investigated.

In Wadsö 's calorimeters (121,122) the substance was vaporised into a stream of nitrogen, and its mass was measured by weighing the calorimeter before and after each period of evaporation. Again the method was used for reasonably volatile liquids; the author set a lower limit of 0.5 torr to the vapour pressure because of zero errors caused by high gas flow rates or by heat losses if the time of measurement was extended to deal with less volatile substances.

Morawetz and Sunner (123,124) claimed that their calorimeter could be used to determine heats of vaporisation at vapour pressures down to 10^{-2} or even 10^{-3} torr. In order that the small masses of evaporating substances might be measured on a microbalance the calorimeter was itself reduced in size; the rate of evaporation was controlled by varying the diameter of the effusion hole in the calorimeter lid. Systematic errors of up to 2.5 kJ mol^{-1} were attributed to the fact that the substances were evaporating into an unknown pressure between that of the applied vacuum and the saturated vapour pressure. Morawetz (124, 125) later applied corrections which reduced the uncertainty of the determinations to 0.2 to 0.4 kJ mol^{-1}. His most recent 'triplet calorimeter' (125) has been tested on substances whose vapour pressures range from 10^{2} to 10^{-4} torr; the precision of the heats of vaporisation was better than 0.4 kJ mol^{-1}. In principle this calorimeter could be used for substances with vapour pressures as low as 10^{-6} torr, for which both theoretical and practical reasons suggest that the precision would be considerably worse.

Sabbah, Chastel and Lafitte (126) used a Tian-Calvet microcalorimeter for the direct measurement of heats of vaporisation at 298 K of substances whose vapour pressures ranged from 0.05 to 100 torr, with uncertainties of 0.3 kJ mol^{-1} for the more volatile substances and 1.7 kJ mol^{-1} for the least volatile.

Enthalpies of sublimation from vapour pressures.

The Clapeyron equation relates the heat of sublimation to the variation of saturated vapour pressure with temperature (18).

$$\Delta H_{sub,T_1} = T_1 \, (dp/dt)(V_g - V_s)$$

In the equation p is the pressure of vapour in equilibrium with the solid at temperature T_1, and V_g and V_s are the molar volumes of the substance in gaseous and solid forms at a pressure p and the same temperature T_1. A rigorous evaluation of the heat of sublimation requires knowledge of the exact equation of state of the vapour concerned, and of the density of the solid at the relevant temperature and pressure. The most common proced--ure, however, is to assume that the volume of the solid may be ignored, and that the vapour obeys the gas laws. Since the pressures concerned are less than 1 torr, both assumptions are reasonable, as the following example shows.

The molar volume of solid stilbene is approximately 0.186 litre, while that of the vapour at 298 K and 1 torr is 1.86×10^4 litre, so the error incurred by neglecting V_s is only 10^{-3} %.

Applying the gas laws to the vapour leads to the following relation--ships.

$$\Delta H_{sub,T_1} = R T_1^2 \, (d \ln p / dT)$$

$$= - R \frac{(d \ln p)}{(d \, 1/T)} \qquad (1)$$

Thus to calculate the heat of sublimation only the variation of vapour pressure with temperature need be measured.

Methods of measuring the vapour pressure of solids.

a. Static methods.

The low volatility of most solids precludes the use of the manometric methods that are usually applied to liquids. The depression of a mercury column by the vapour at low pressures is to small to be measured accurately, and less dense manometric liquids may not be used because they dissolve or react with the substance being investigated.

Douglas and Krause (127) avoided this difficulty by measuring the pressure in a container of argon before and after briefly connecting it to another flask which held the solid , iodine, and its vapour. The saturated vapour pressure of the iodine was calculated from the volumes of the two containers and the change in pressure of the argon. Menzies (128) used a McLeod gauge to measure the pressure of argon in equilibrium with the vapour being studied, which was prevented from entering the gauge by cooling the capillary between vapour and argon. Boyd (107) found the heat of sublimation of tcne by a similar technique.

Mechanical methods of measuring low pressures, such as the pendulum tensimeter (129) and the Rodebush trapdoor (130) , estimate the force exerted on a plate of known area by the vapour; they demand intricate apparatus and may produce widely-ranging results (131).

All static measurements are sensitive to the presence of impurities in the sample. The use of gas chromatography (132-4) rather than direct pressure measurements removed the effect of impurity. The fact that absolute vapour pressures were not known was not a disadvantage since only relative measurements at different temperatures were needed for calculating heats of vaporisation. Apart from the gas chromatograph itself only a thermostatted flask and some simple glassware were needed to produce

results which agreed with known values, for substances with vapour pressures in the range 5 to 200 torr, to an uncertainty of approximately 1 kJ mol^{-1}. The application of gas chromatography to less volatile sub--stances was limited by the sensitivity of the detector to low concentrations; it is possible that more recently developed techniques, particularly that of concentrating the vapour by 'trapping' before introducing it on to the column, would extend the usefulness of the method.

b. Gas saturation methods.

These rely on the existence of a sensitive method for determining the quantity of vapour contained in a much larger volume of inert gas which is drawn over the solid or liquid sufficiently slowly to become saturated. Thus Davies and Jones (135) determined the heat of sublimation of benzoic, salicylic and other solid acids to a precision of 0.1 kJ mol^{-1} over a temperature range at which the vapour pressures were 0.05 to 2 torr. The acids condensed from the flowing gas were washed out and titrated with aqueous base. Few substances can be analysed so simply; more usually a new technique must be used for each solid investigated. Looney and Downing (136) measured the heat of sublimation of tcne by trapping the vapour in NN-dimethylaniline and colorimetrically determining the concentration of the resulting red dye. Their result, 78.0 kJ mol^{-1}, differs by 3.2 kJ mol^{-1} from Boyd's (107). Gerry and Gillespie (137) showed that a straightforward use of the gas saturation method to measure vapour pressures involved unjustified assumptions; a more rigorous treat--ment gave significantly different results but required knowledge of various properties unknown for all but a very few substances.

c. Vapour pressures from rates of effusion or sublimation.

Vapour pressures of solids, and heats of sublimation have most frequently been determined still less directly, by effusion. According to Knudsen (138) the rate of mass loss (m') through a hole of area (a) is related to the vapour pressure (p) by the following relationship, in which M is the molar mass of the effusing vapour.

$$p = \frac{m'}{a}\left(\frac{2\pi RT}{M}\right)^{\frac{1}{2}}$$

The equation only holds if the hole has negligible depth and is small compared with the mean free path of the molecules. Clausing (139) derived a correction for the finite depth of the hole, and the treatment was extended by Freeman and Searcy (140) to apply to the force exerted by the effusing molecules, as well as to the pressure. Since the correction consists of a multiplication factor, whose value is constant for a given ratio of length to diameter of the hole, it need not be taken into account when heats of sublimation, rather than vapour pressures themselves, are required. Similarly, although the need to know the area of the effusion hole and the molecular mass of the vapour are sources of difficulty when pressure measurements are needed, they do not enter into the calculation of heats of sublimation, and so need not be determined, provided that they remain constant over the range of temperatures used in the experiment.

The area of the hole is important, however, since it affects the pressure inside the effusion cell, and so determines whether the measured quantity of heat corresponds more closely to ΔH, as it will if the pressure is constant and equal to the saturated vapour pressure, or to ΔU, as it will if the pressure tends to zero. The pressure inside the cell is given by the following relationship.(126).

$$P = \frac{\alpha}{\alpha + a/A} \cdot P_{(eqm.)}$$

In this equation α is a sublimation coefficient often assumed to be unity, A is the surface area of the subliming solid, and $p_{(eqm.)}$ is the saturated vapour pressure. Clearly when $a/A = 10^{-2}$, the pressure in the cell is close to the saturated vapour pressure, and the measured heat corresponds to ΔH.

Early users of the Knudsen method withdrew the effusion cell from the vacuum chamber for weighing, a process made unnecessary by hanging the cell from a silica spring scale within the chamber. Use of the Dupont thermobalance, reported in the experimental section that follows, (pages 154 ff) is a simple modification of the technique.

From equation (1) on page 146, it is clear that the heat of sublim--ation may be found by multiplying the slope of a graph of ln p against 1/T by the gas constant, R. Separating the temperature-dependent terms from the constant terms in the Knudsen equation, (2) on page 149, produces the following relationship, which shows that a graph of ln $(m'\sqrt{T})$ against 1/T may equally well be used to evaluate the heat of sublimation.

$$(3) \qquad \ln p = \ln(m'\sqrt{T}) + \ln\left(\frac{2\pi R}{2M}\right)^{\frac{1}{2}}$$

The method that has previously been used at Keele to determine heats of sublimation has been described by Ashcroft (141) who applied it to various standard organic compounds and to acetylacetonate complexes of transition metals. (For details of the method see the experimental section, pages 154 to 157.) Figures quoted in his paper illustrate the large variation between the heats of sublimation determined by different

workers using different methods to study the same substance. Values ranged from 23 to 116 kJ mol^{-1} in the most dramatic case, and from 106 to 127 kJ mol^{-1} or from 67 to 91 kJ mol^{-1} even for substances treated as standards. Ashcroft's technique consisted of measuring the rate of sub-limation into a vacuum, and treating the results in the same way as those from effusion. An immediate difficulty is that the Clapeyron equation refers to the pressure of vapour in equilibrium with the solid, yet there can not be equilibrium over the solid in an open dish in a pumped system.

The justification of the method relies on three assumptions:-

Firstly: that the rate of loss of mass per unit surface area of the substance is related to the vapour pressure of the substance by Langmuir's equation (142), in which α is a sublimation coefficient assumed to be 1.

$$m' = \alpha\left(\frac{M}{2\pi R T}\right)^{\frac{1}{2}}.p$$

Secondly: that the simplefied form of the Clausius-Clapeyron equation (1) on page 146 may be applied.

Thirdly: that the surface area of the solid remains constant throughout the experiment. This third assumption is obviously not valid; the surface area inevitably changes during sublimation due simply to loss of material, and further changes may be caused by recrystallisation, which is likely to occur when the substance is heated. Also it is not correct to think of the surface as uniform; the probability of a molecule presumably depends on its site on the face, edge or corner of a crystal, and on the presence of dislocations, whose numbers are altered by heating. In practice the change of surface area is minimised by keeping the total loss of mass as small as possible, i.e. by restricting both the time and the upper temperature of the sublimation process. Ashcroft recommended

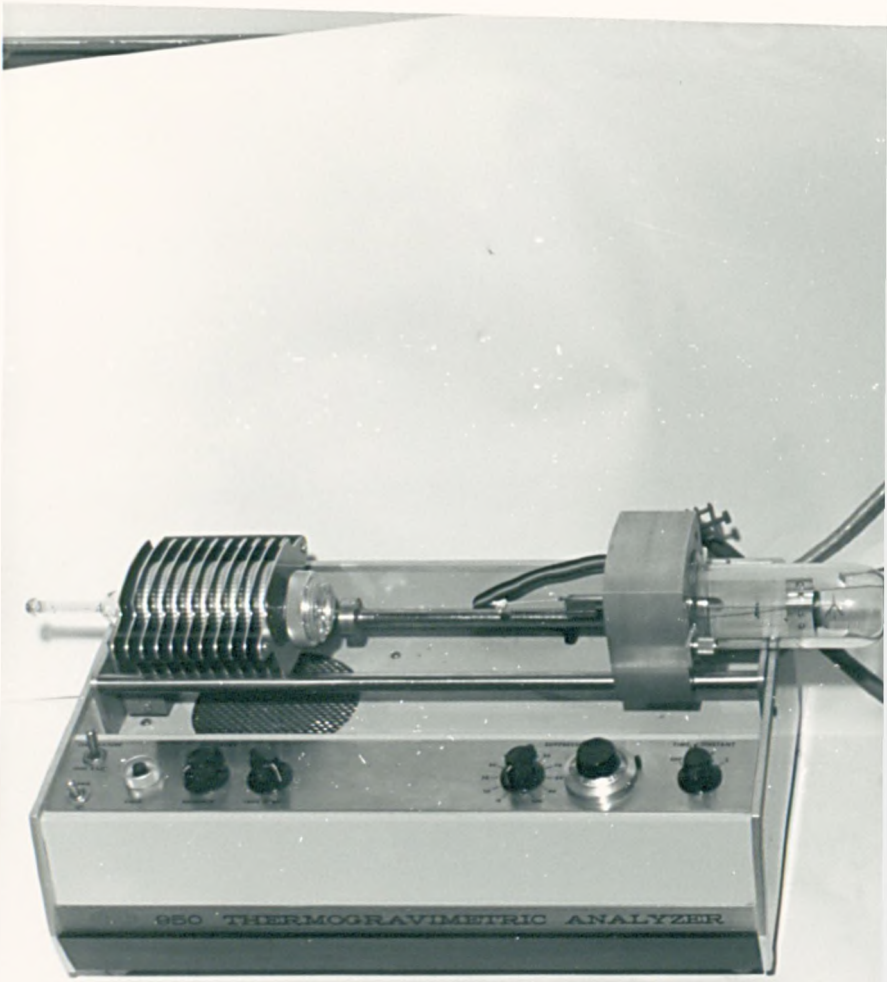
that the mass sublimed should be kept below 5 %, and preferably below 2 %, of the total mass to achieve ΔH_{sub} values "reproducible to about 5 %." The need to restrict the loss militates against precision in the readings, since the slopes of mass : time graphs may be measured prec--isely only if they cover an appreciable range on both axes. Furthermore a large number of readings of rates of mass loss at different temperatures is needed to establish the heat of sublimation accurately, but these cannot be achieved without significant mass losses.

Thermobalance : description.

The 'Dupont 950 Thermogravimetric Analyzer' is a thermobalance designed for use with the same firm's '900 Differential Thermal Analyzer'. It may be set to follow the variation of mass either with temperature or, as in this work, with time.

The balance, figures 21, 22 and 23, is essentially a taut-band galvanometer, the pointer being replaced by a balance beam. One arm of the beam is extended by a quartz rod from which the specimen, contained in a light aluminium or platinum boat, is hung; the other arm carries counterweights and a slit signal flag. The flag is held in position between a fixed lamp and photocells, and the current through the meter coils nec--essary to do this indicates the out-of-balance force on the beam; it is amplified and shown on the Y axis of an XY plotter. The specimen and quartz rod are surrounded by a pyrex or silica tube which may be evacuated, and which slides into a 500 W resistance furnace controlled by a thermo--couple close to the specimen. The furnace is designed to maintain temperatures between room temperature and 1200^{o}C and heating rates of 0.5 to 30^{o}C per minute; the controls are therefore coarser than if they had been designed for lower temperatures. The smallest division on the (uncalibrated) temperature dial corresponds to approximately 2.5^{o}C.

Although the balance is intended to take specimens of a gramme or more, in practice it oscillates if loaded with more than 0.3 to 0.4 g. The maximum sensitivity is 0.2 mg per inch of movement on the chart paper; at this setting the entire Y scale of the chart represents a change in mass of 1.4 mg. When used to plot the variation of mass with time, the scale of the X axis of the recorder may be set to various values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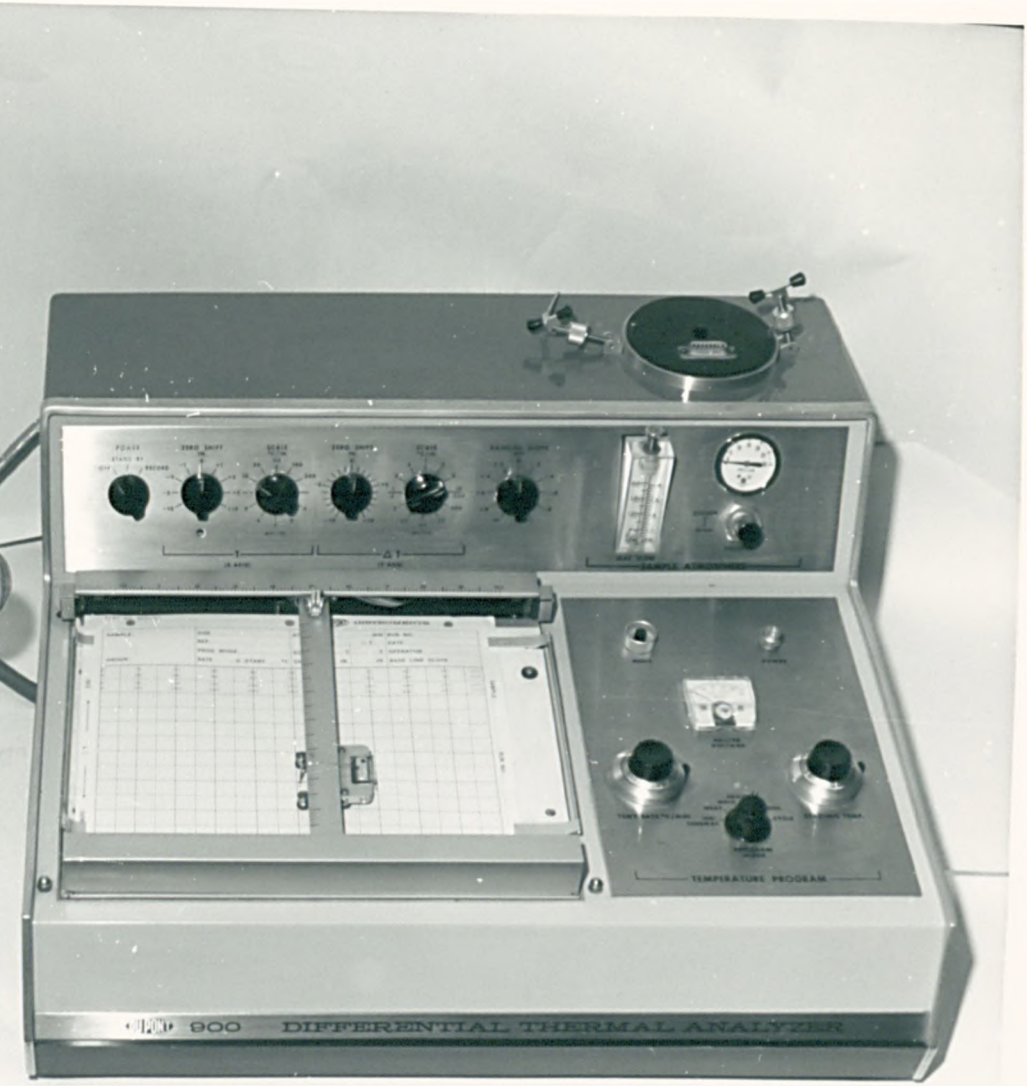
TEMPERATURE PROGRAM
900 DIFFERENTIAL THERMAL ANALYZER

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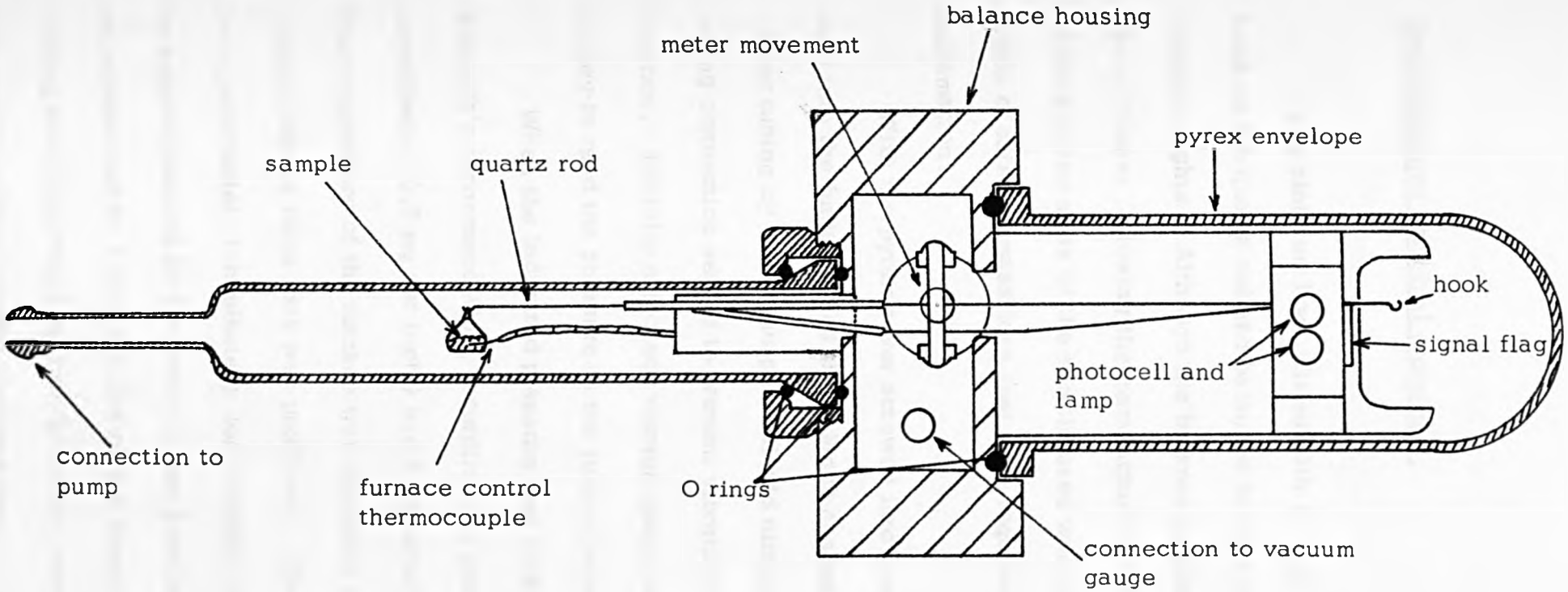


Figure 23. The Dupont 950 Thermobalance.

between 0.05 and 10 inches per minute.

Thermobalance, original procedure.

The platinum boat, filled with 30 - 100 mg of powdered solid, was hung on the quartz rod and balanced to the nearest 5 mg using wire counterweights. Although the balance had been calibrated against a class M mass following the manufacturers' instructions (143), no record of the precise mass of the sample used was kept, since it was only the ratios of rates of mass loss that were required for evaluating heats of sublimation.

With the pyrex cover screwed into place, the specimen was inser--ted into the furnace, and the balance assembly was evacuated through rubber tubing by rotary pump and liquid nitrogen traps. The lengthy rubber tubing connection served to prevent vibration from the pump affecting the balance. Initially a McLeod vacuum gauge was attached to the pumping trolley to read the pressure in the tubing between the pump and the traps.

When the indicated pressure was less than 0.04 mm Hg, following Ashcroft's recommendation, recording was started, using maximum mass sensitivity (0.2 mg per inch) and a speed of 0.5 inches per minute. The temperature of the furnace was gradually raised until a low but meas--urable rate of mass loss was produced. The temperature was held steady for approximately ten minutes; long enough for thermal equilibrium to be approached and for the rate of mass loss to reach a steady value, as represented by a straight line on the mass : time plot. The furnace setting was then raised by two divisions, corresponding to about 5°C, and held until a further straight line was seen. In this way a series of

lines was obtained, the slope of each being characteristic of a particular setting of the furnace.

The temperature corresponding to each furnace setting was read from a calibration graph, obtained as follows.

A 0.1°C mercury in glass thermometer was tested in ice and water and in refluxing distilled water. After applying the emergent stem correc--tion and boiling point: pressure data (144) the thermometer was found to be correct to within the precision to which it could be read, i.e. 0.02°C, at 0 and 100°C. This thermometer was held in the centre of the furnace, surrounded by a glass tube similar to that covering the balance beam, and a series of thermometer and furnace-setting readings was made between room temperature and 110°C.

Attempts to measure the heat of sublimation of trans-stilbene in this way were unsatisfactory, for several reasons.

Firstly, the furnace was not able to maintain a constant temperature below approximately 60°C, while stilbene and other ligands were volatile enough to sublime below that temperature.

Secondly, the temperature recordings were imprecise, because no direct measurements of temperature were made during each experiment, so that readings relied upon careful setting of the furnace control and reference to the calibration curve.

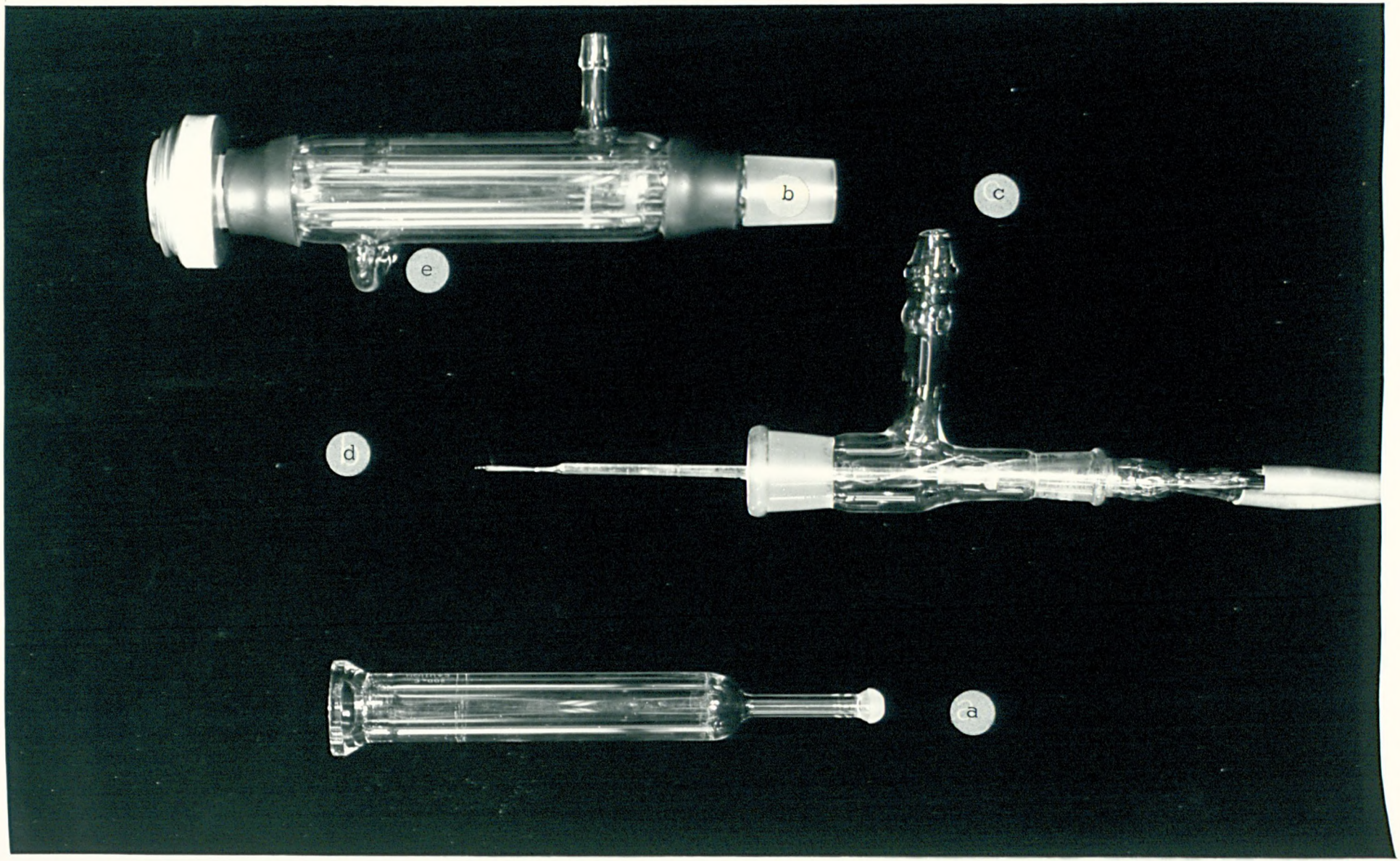
Thirdly, the vacuum gauge was likely to give an over-optimistic estimate of the pressure in the balance housing, since the two were sep--arated by a metre or so of narrow-bore tubing. The same tubing, and the neck of the pyrex tube surrounding the specimen, could be expected seriously to restrict the pumping rate and the ultimate pressure in the balance, since their internal diameter of about 6 mm was similar to, or

less than, the mean free path of nitrogen molecules at the pressures nec-
-essary for sublimation.

To overcome these difficulties the apparatus was modified as follows. The original glass tube (a, figure 24) was replaced by one carrying a B24 cone (b) to which was fitted a T piece (c) carrying a large-diameter vacuum connection and a B14 socket. Into this socket fitted either a standard adaptor for a thermometer, or an extended cone (d) into which was sealed a fine copper-constantan thermocouple. The couple was connected to a Servoscribe RE 511 20 potentiometric recorder, operated on its 2 mV or 5 mV range, to give a continuous record of the temperature close to the specimen. The combination of the thermocouple and recorder was calibrated against the previously-tested thermometer by immersing both in a vigorously-stirred water-bath and taking pairs of readings every five degrees over the full range from 0 to 100°C. The readings were plotted on a calibration graph, and were also analysed by a computer programme which calculated the cubic curve of best fit through the points.

For temperatures below about 95°C, heating was provided not by the furnace but by a water-jacket (e, figure 24) surrounding the glass tube. The water was pumped from an insulated thermostatted bath whose small volume made possible the rapid temperature changes that were needed.

The vacuum gauge was moved to the side of the balance housing remote from the pump connection, so that its reading of pressure would be equal to, or higher than, the pressure surrounding the specimen. For the connection between the pump and the balance, which was as short as possible, 13 mm internal diameter rubber tubing was used. The greater rigidity of this tubing led to increased transmission of vibration from the pump via the vacuum train to the balance; this was largely overcome by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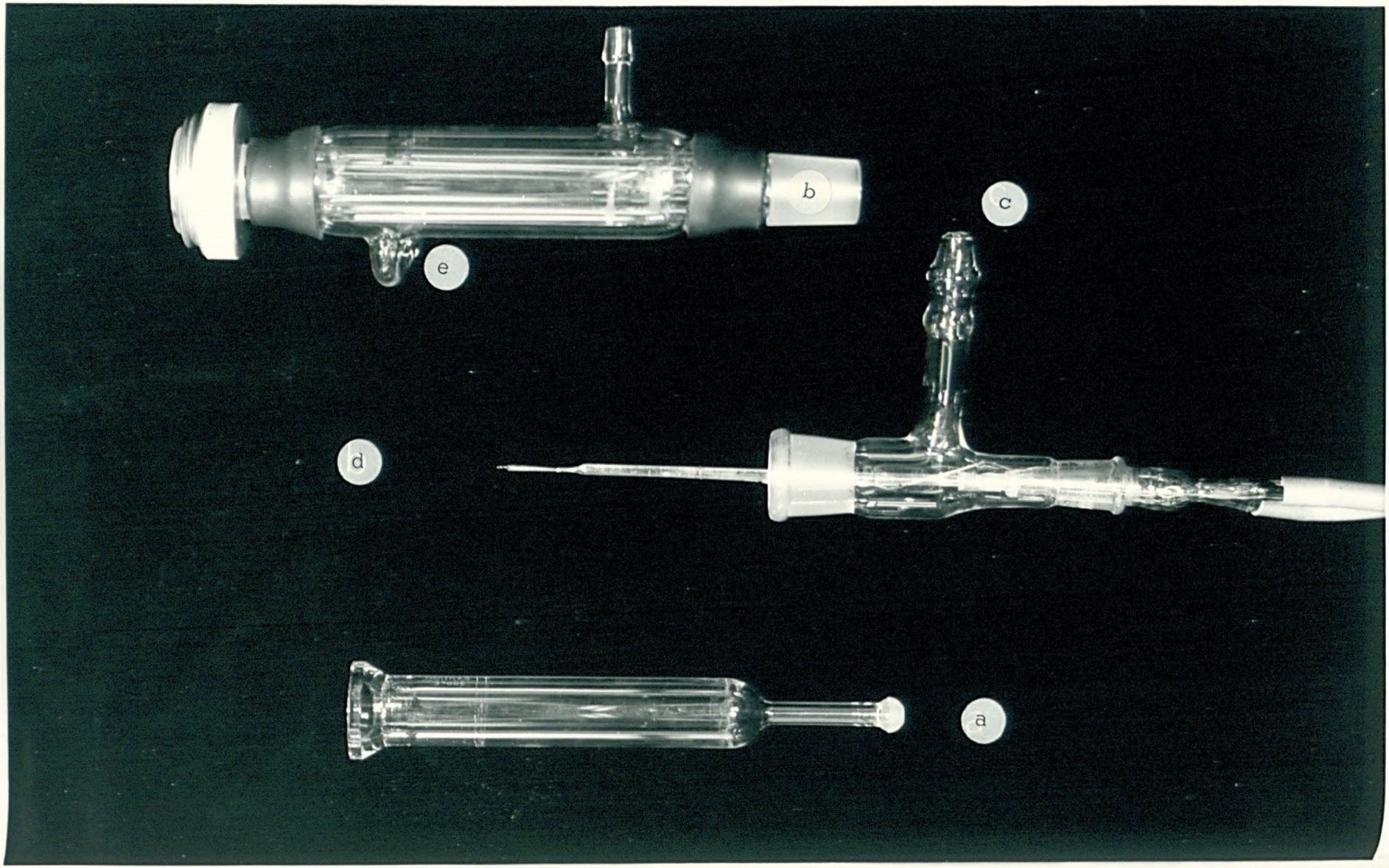
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a

standing the pump on the floor rather than on the trolley carrying the glassware and by damping the oscillations of the rubber tube leading from the pump with several kilogrammes of lead. The improved vacuum system rapidly achieved pressures in the balance of 0.005 to 0.01 torr.

Although these modifications led to increased precision and reproducibility of readings, it was still not possible to obtain a value of the heat of sublimation of stilbene, since the plot of $\ln(\text{slope}\sqrt{T})$ against $1000/T$ was strongly curved (figure 25). The curvature was little altered by changing the mass of stilbene, by powdering it to increase the surface area, or by reversing the direction in which the temperature range was scanned. Clearly one or more of the assumptions on which the method was based did not apply to this substance under these conditions. The lack of effect when the order of temperatures was reversed indicated that the curvature was not due simply to the decrease in surface area during the measurements, for if it had been, the curvature would also have been reversed.

In all subsequent measurements a small modification of the app--aratus altered the method from free evaporation to the better-known effusion technique.

Thermobalance, effusion method.

The open dish hanging from the balance arm was replaced by an LKB neckless ampoule, figure 26, which was plugged with silicone rubber after being half-filled with powdered solid, so that the only remaining orifice was a minute hole pierced in the end wall with a white-hot tungsten wire. As the diameter of the wire was approximately 0.19 mm, and the wire fitted the smaller holes nicely, these had a diameter of about 0.2 mm.

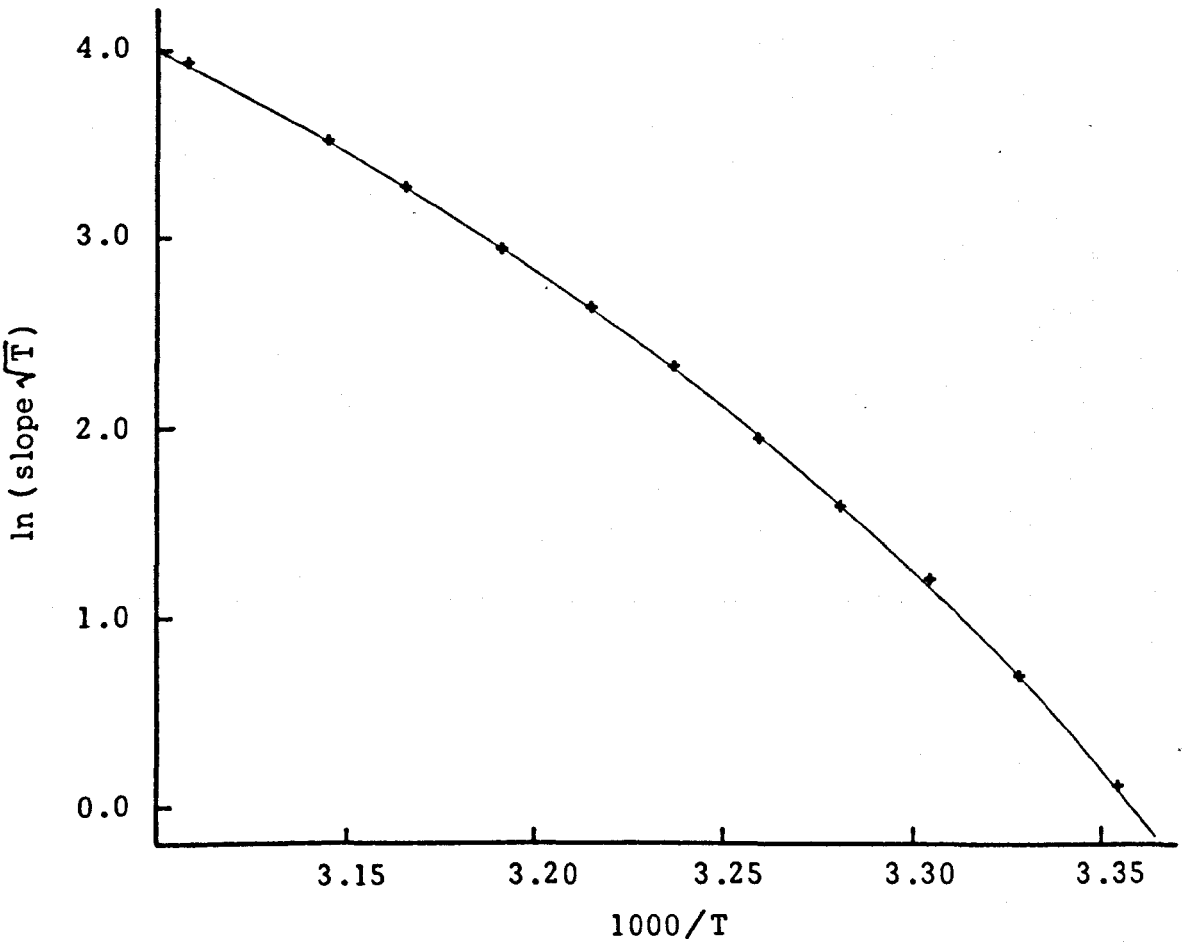
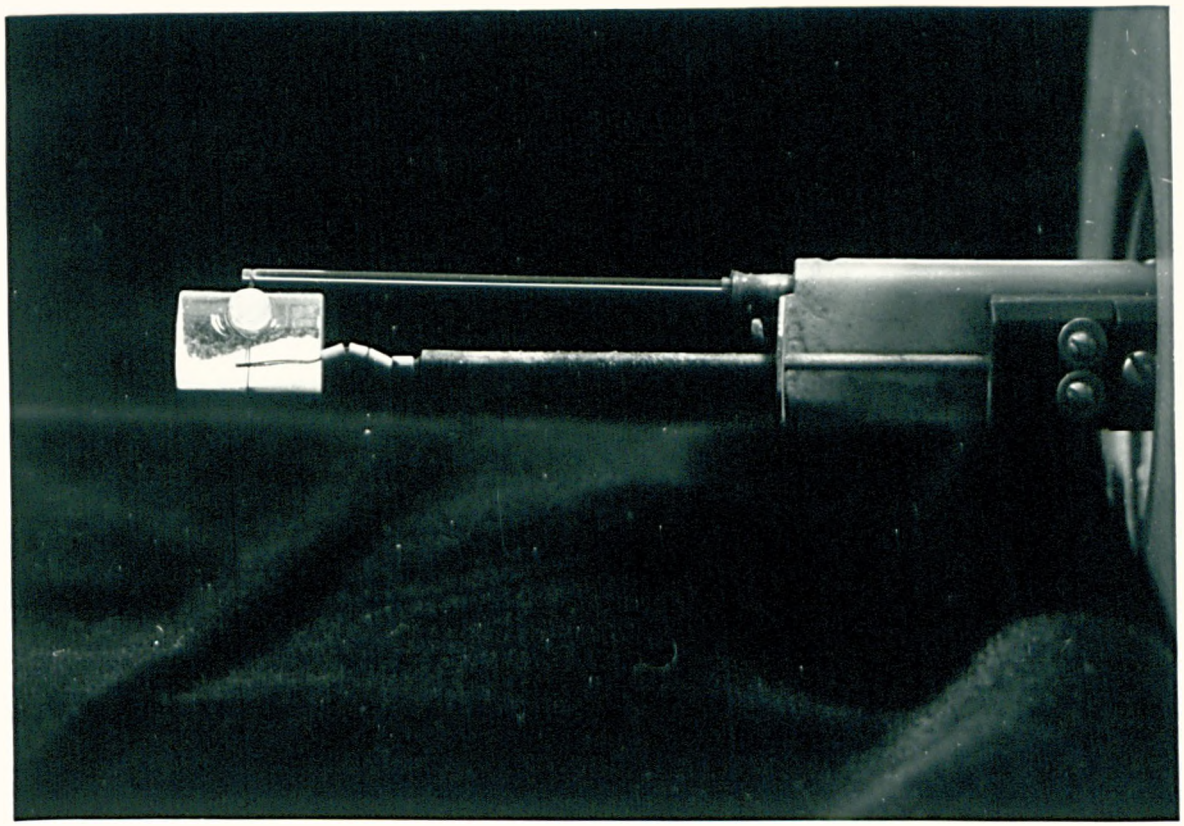


Figure 25. Graph for heat of sublimation of trans-stilbene, open dish method, 25.8.76.



The thickness of the glass varied from 0.17 to 0.28 mm; any excess glass built up on the outside of the hole during the piercing operation was removed by gently grinding with silicon carbide paper. The pierced ampoules were examined under the microscope and only those which allowed free passage for effusion were used.

Temperature and mass readings were made as for the open dish method, allowing about 10 minutes for effusion at each temperature.

As shown on page 150 , the pressure inside the effusion cell depends on the ratio of the areas of the effusion hole, a, and the subliming surface, A. In this case $a \simeq 3 \times 10^{-2}$ mm^2, and A was at least equal to the exposed area of the layer of solid inside the cell, i.e. $\simeq 70$ mm^2, and was probably much greater, so $a/A \leq 10^{-4}$ and the pressure in the cell may be assumed to be very close to the saturated vapour pressure.

When this effusion method was used there was no need to restrict measurements to small mass losses, as had been necessary when the open dish method was used, since the calculation of the heat of sublimation was no longer dependent on the assumption of constant surface area. Therefore a large proportion of the total mass of sample in the ampoule could be sublimed in the course of one or more series of temperature and mass readings, bringing two advantages over the open dish method. Firstly the range of temperature could be extended to include high rates of sublimation which could be measured more precisely than lower rates. Secondly any impurities in the sample gave rise to only a small proportion of the total loss of mass, and so had little effect on the calculated heat of sublimation.

Analysis of results from the effusion method.

The mass : time graphs were drawn by the XY plotter on paper subdivided in single millimetres, the lines on the paper being accurately aligned with the axes of the plotter. The slopes, which were proportional to the rates of loss of mass at the various temperatures, were calculated by extrapolating the straight-line portions to the edges of the paper, where the intercepts were read as accurately as possible, i.e. to $\pm$ 0.1 mm. Temperatures were read in the first instance from the calibration curve of the thermocouple . Values of ln (slope$\sqrt{T}$) were plotted against 1000/T, and the sublimation energy was obtained from the slope of the line of best fit. A basic computer programme, incorporating the cubic equation relating thermocouple emf to temperature, was written to calculate the sublimation energy directly from the measured thermocouple emfs and the slopes of the lines on the XY plotter. ("DUPONT", appendix 3)

Usually twelve pairs of readings were obtained from each ampoule of solid. In some cases all twelve points lay close to a straight line, whose slope, as estimated from a hand-drawn graph, was satisfactorily close to that calculated by the DUPONT programme. An example is shown in figure 27.

Other sets of results, as shown in figure 28, produced a wider scatter, sometimes suggesting a curved line, in the points corresponding to the lowest temperatures and rates of sublimation, even when the higher-temperature points lay precisely on a straight line. It is not surprising that the low temperature points were more widely spread, since small irregularities in the line drawn by the thermobalance, due to vibration, irregular movement of the pen carriage on the slidewire, or even variations in the thickness of the line, caused proportionally large changes in the

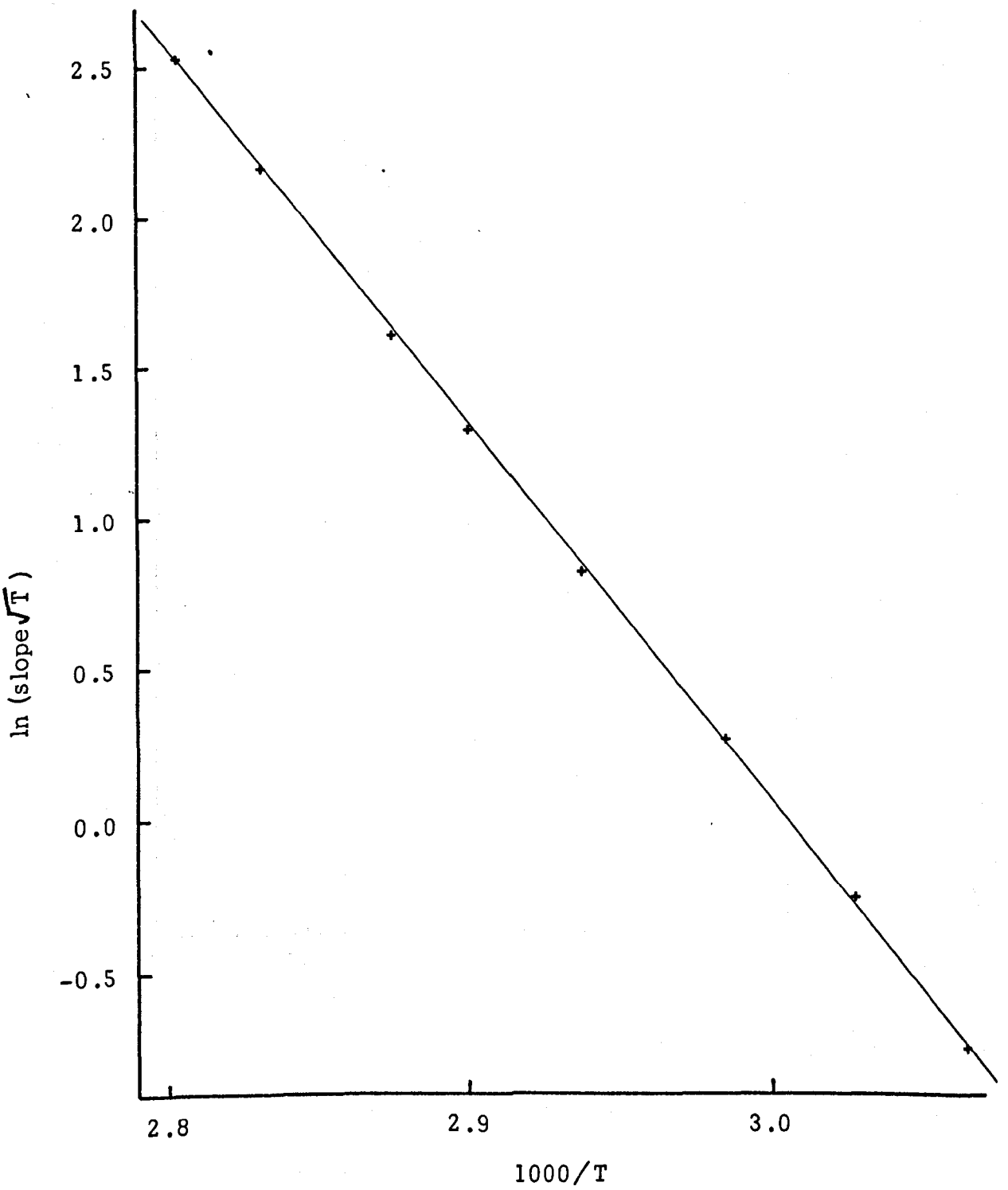


Figure 27. Graph for heat of sublimation of trans-stilbene, effusion method, 22.9.76.

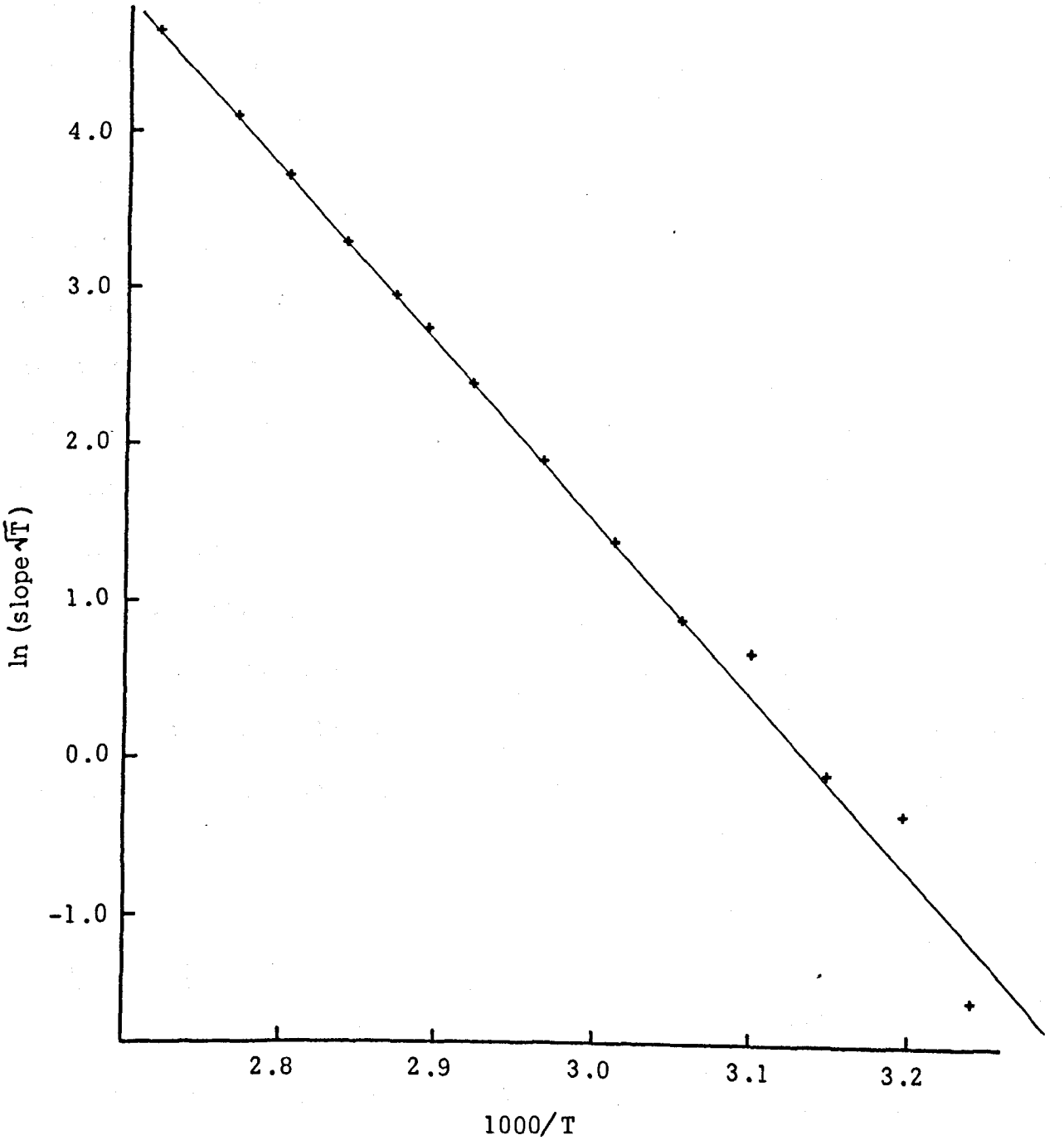


Figure 28. Graph for heat of sublimation of benzocyclobutenedione, effusion method, 22.2.77.

very small slopes that corresponded to these temperatures. These errors in the slopes were converted by the logarithmic equation to large errors in the final plot used for measuring the heat of sublimation.

When the sets of results which showed this scatter at low temperatures were analysed, the slope computed from all the points did not correspond to that obtained from the high-temperature points which lay on a straight line. Although omission of the low-temperature points may be justified because they are subject to such large errors, the choice of which points to omit was subjective. A further computer programme was therefore designed to include all data but to give most weight to the higher temperature readings whose slopes could be most precisely determined, and least weight to the less precise low-temperature readings. Each pair of readings was weighted in proportion to the measured rate of mass loss. Dr A. Hewitt kindly supplied the mathematics for the weighting in this programme,"WTDUP2", which appears in appendix 4.

Application of the effusion method.

In order to test the method, the heats of sublimation of benzoic and salicylic acids were determined. These substances were chosen because their precise heats of sublimation may be found in the literature (18), and because pure samples were available. The benzoic acid was National Bureau of Standards standard sample 39 h, and the salicylic acid was supplied by May and Baker (= 99.5 % pure). Results from the effusion of these substances are shown in tables 39 and 40. The mean values for the measured heats of sublimation are given below.

Benzoic acid: measured heat of sublimation = 91.6 ± 1.7 kJ mol^{-1}

literature heat of sublimation = 91.4 ± 0.4 kJ mol^{-1}

Salicylic acid: measured heat of sublimation = 96.5 ± 5.1 kJ mol^{-1}

literature heat of sublimation = 95.14 ± 0.04 kJ mol^{-1}

Both measured heats are within experimental error of the literature values, and so suggested that the method was not subject to large systematic errors. The results are much less precise than the literature values, but it was thought that even measurements of rather low precision would be useful if the method could be applied to the ligands involved in reactions with platinum complexes.

The heats of sublimation of trans-stilbene, benzocyclobutene--dione and phenylcyclobutenedione were therefore determined by the effusion method, the results being shown in tables 41, 42, and 43. The solids were as used for calorimetry. Attempts to measure the heat of sublimation of diphenylcyclopropenone, dpcp, gave inconsistent results. Hopkins et al. (90) have measured the heat of sublimation of this compound by the Knudsen method, using five temperatures between 50 and 70°C.

$$\Delta H_{sub}(\text{dpcp, s}) = 141.4 \pm 4.2 \text{ kJ mol}^{-1}$$

Table 39. Sublimation of benzoic acid.

date of experiment	number of points	temperature range / K	heat of sublimation / kJ mol^{-1} unweighted	weighted
24. 9.76	13	306-360	85.2	90.1
27. 9.76	15	311-360	92.9	91.3
11.10.76	11	320-361	93.7	94.1
12.10.76	11	294-339	93.2	91.0

Mean ΔH_{sub} = 91.6 ± 1.7 kJ mol^{-1}

Table 40. Sublimation of salicylic acid.

date of experiment	number of points	temperature range / K	heat of sublimation / kJ mol^{-1} unweighted	weighted
13.10.76	10	331-366	102.8	101.5
14.10.76	17	306-360	95.5	95.0
19.10.76	13	306-356	94.2	93.0

Mean ΔH_{sub} = 96.5 ± 5.1 kJ mol^{-1}

Table 41. Sublimation of trans-stilbene.

date of experiment	number of points	temperature range / K	heat of sublimation / kJ mol^{-1} unweighted	weighted
10. 9.76	7	312-349	98.0*	95.4
14. 9.76	12	317-353	88.8	90.8
16. 9.76	8	317-354	87.0	90.6
21.10.76	13	306-360	99.4	98.0
22.10.76	13	306-360	97.6	98.9
25.10.76	15	306-360	101.4	98.7

Mean ΔH_{sub} = 95.4 ± 3.1 kJ mol^{-1}

Table 42. Sublimation of benzocyclobutenedione, bcbd.

date of experiment	number of points	temperature range / K	heat of sublimation / kJ mol^{-1} unweighted	weighted
7.2.77	12	312-367	80.7	85.7
8.2.77	12	307-359	79.3	84.5
11.2.77	12	315-366	88.7	91.0
14.2.77	14	313-366	91.2	91.5
17.2.77	19	309-367	90.2	89.7
22.2.77	15	309-368	90.1	89.2
23.2.77 1	11	307-352	89.4	86.7
23.2.77 2	11	300-347	96.7	90.7

Mean $\Delta H_{sub} = 88.6 \pm 1.9$ kJ mol^{-1}

Table 43. Sublimation of phenylcyclobutenedione, pcbd.

date of experiment	number of points	temperature range / K	heat of sublimation / kJ mol^{-1} unweighted	weighted
1.3.77	14	321-377	103.2	110.2
2.3.77 1	14	322-383	95.3	101.7
2.3.77 2	12	326-379	91.3	100.6
3.3.77	9	324-379	100.9	102.0
4.3.77	11	321-361	103.0	106.9
7.3.77	10	321-360	103.7	110.1

Mean $\Delta H_{sub} = 105.2 \pm 3.6$ kJ mol^{-1}

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Appendix 1. The Dickinson method for finding the corrected temperature change in isoperibol calorimetry.

In his paper on combustion bomb calorimetry (59) Dickinson pro--posed that the condition for finding a time t_x at which the corrected temperature change should be measured was that the areas between the T:t curve and the lines T_B and T_E are equal on either side of it, see figure 29. T_B and T_E are the temperatures at the beginning and end of the reaction period. Neither Dickinson, in his original article, nor Coops et al. (60) in their discussion indicate that this criterion for the choice of t_x is an approximation, however Vagera's computer programme (63) incorporates the more nearly exact criterion, which is perhaps also used by other thermochemists. The following argument is intended to show the difference between the two methods of choosing t_x.

In figure 29 the curved line SBWEL is the actual trace of the temperature change, and the more nearly rectilinear path SBPQEL is the hypothetical trace of an instantaneous reaction, giving chemically identical products, occurring at a time t_x. The lines BP and EQ are the extrapolations of the fore- and after-periods, which may be linear, or exponential, or may correspond to some other empirical function. It must be shown that the change T_P to T_Q is the same as the temperature change that would be caused by the reaction in the absence of heat leakage or heat effects from stirring.

It is assumed that the rate of change of temperature is proportional to the heat flow, which is in turn proportional to the temperature 'head', i.e. that the heat capacity is constant over the temperature range and that Newton's law of cooling applies.

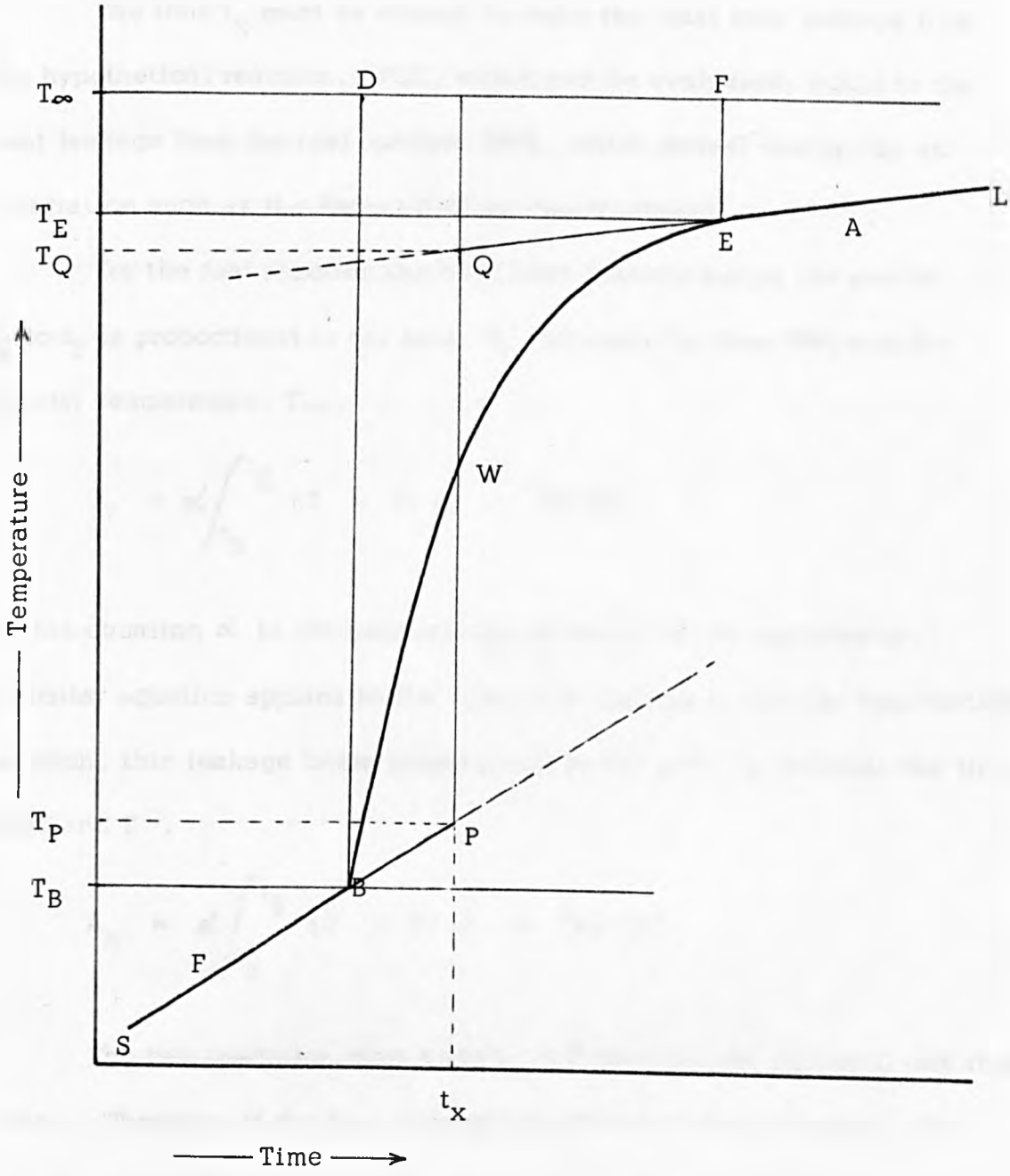

Figure 29. Graph of temperature against time for an exothermic reaction, to illustrate Dickinson's method of finding the corrected temperature change.

In this case an area on the graph of temperature against time is propor--tional to q, a quantity of heat lost or gained other than by reaction.

The time t_x must be chosen to make the total heat leakage from the hypothetical reaction, BPQE, which can be evaluated, equal to the heat leakage from the real reaction BWE, which cannot (except by an integration such as the Regnault-Pfaundler treatment).

For the real reaction the total heat leakage during the period t_B to t_E is proportional to the area, A_r, between the line BWE and the infinity temperature, T_∞.

$$A_r = \alpha \int_{t_B}^{t_E} (T - T) \, dt = \text{DBWEF}$$

In this equation α is the heat leakage constant of the calorimeter. A similar equation applies to the total heat leakage during the hypothetical reaction, this leakage being proportional to the area A_h between the line BPQE and T .

$$A_h = \alpha \int_{t_B}^{t_E} (T - T) \, dt = \text{DBPQEF}$$

The two reactions start and finish from the same chemical and thermal state. Therefore if the heat losses from the two are made equal, the only other heat effects, i.e. the heat of reaction, must also be equal. The heat losses are equal if the areas A_r and A_h are equal. These two areas differ in opposite senses by the areas BPW and EQW, so that if these smaller areas are equal, then A_r and A_h are also equal. It then follows that the temperature change $(T_Q - T_P)$, due to the hypothetical reaction, is identical to the temperature change that would be produced by the real reaction in the absence of heat leakage.

Thus t_x must be chosen to make equal the areas defined by the

extrapolations ,BP and EQ , of the fore- and after-periods, not the areas defined by the temperature-horizontals T_E and T_B , as suggested by Dickinson and by Coops et al..

The difference between the two criteria for choosing t_x is perhaps not important in combustion calorimetry, where the fore- and after-periods slope very little, but it may become more significant in calorimeters of lower thermal capacity and higher heat leakage modulus, particularly when small quantities of heat are being measured.

The values of T_Q and T_P are found by extrapolating the fore- and after-periods, either as straight lines by graph or computer, or as expon--ential curves.

Appendix 2. DELTAR programme for evaluating the normalised resistance change for rapid reactions and calibrations.

```
COPY FROM DC (A,CH09)

 50    PRINT "REF.:";
 55    REM   REFERENCE NUMBER AND DATE OF EXPERIMENT
 60    INPUT D
 70    PRINT
 80    PRINT
100    PRINT "FORE-PERIOD READINGS:-"
105    GOSUB 400
110    PRINT "N1 = "; N1
115    REM   NUMBER OF READINGS IN FORE-PERIOD
120    PRINT
130    PRINT "T=";
140    INPUT T
141    REM  T = THE TIME TO PRODUCE EQUAL AREAS, USING
142    REM  DICKINSON S METHOD.
150    LET R1=Y3+B1*(T-X3)
160    PRINT
170    PRINT "R1 = ";R1;" OHMS."
180    PRINT
190    PRINT
200    PRINT "AFTER-PERIOD READINGS:-"
205    GOSUB 400
210    PRINT "N2 = ";N1
215    REM   NUMBER OF READINGS IN AFTER-PERIOD
220    PRINT
230    LET R2=Y3+B1*(T-X3)
240    PRINT "R2 = ";R2;" OHMS."
250    LET R3=R2-R1
260    PRINT
270    PRINT "R CHANGE AT ";T;" MINUTES = ";R3;" OHM."
280    PRINT
290    PRINT "OMITTED PART OF R :";
300    INPUT R4
```

```
310   LET R4=R4+(R1/2 + R2/2)
320   PRINT
330   PRINT "NORMALISED R CHANGE = ";R3;"/";R4;" = ";R3/R4
335   GOTO 650
400   LET X1=0
410   LET X2=0
420   LET Y1=0
430   LET Y2=0
440   LET Z=0
450   LET N1=0
455   INPUT X,Y
456   REM  READINGS OF TIME AND RESISTANCE.  TO SAVE TYPING
457   REM  OMIT DECIMAL POINTS FROM ALL READINGS (RESTORED
458   REM  BY LINES 464 AND 466) AND OMIT CONSTANT PART OF
459   REM  RESISTANCE (RESTORED BY LINE 300).
460   IF X<0 THEN 540
464   LET X=X/100
466   LET Y=Y/100
470   LET N1=N1+1
480   LET X1=X1+X
490   LET X2=X2+X*X
500   LET Y1=Y1+Y
510   LET Y2=Y2+Y*Y
520   LET Z=Z+X*Y
530   GOTO 455
540   LET X3=X1/N1
550   LET Y3=Y1/N1
560   LET S1=X2-X1*X3
570   LET S=Z-X1*Y3
580   LET B1=S/S1
590   PRINT
600   PRINT
610   RETURN
650   END
```

Appendix 3. DUPONT programme for calculating heats of sublimation from thermocouple emfs and rates of mass loss in effusion exper-
-iments.

```
COPY FROM DC (A,CH09)

10   DIM C(20),K(20),S(20),T(20),X(20),Y(20)
20   PRINT "HEAT OF SUBLIMATION BY THERMOBALANCE; EXPT:";
30   INPUT E
40   PRINT
50   PRINT "NUMBER OF PAIRS OF READINGS =";
60   INPUT N
70   PRINT
80   LET X1=0
90   LET Y1=0
100  LET X2=0
110  LET Y2=0
120  LET Z=0
160  PRINT "CHART READINGS AND SLOPES"
170  FOR I=1 TO N
180     INPUT C(I),S(I)
190   LET K(I)=272.35+1.3513*C(I)-6.78936?-3*(C(I))^2
191   LET T(I)=K(I)+9.57871?-5*(C(I))^3-5.4587?-7*(C(I))^4
192   REM CALIBRATION OF T.COUPLE AND 5 MV SCALE ON 21.9.76
200      LET X(I)= 1000/T(I)
210      LET Y(I)=LOG(S(I)*SQR(T(I)))
220      LET X1=X1+X(I)
230      LET X2=X2+X(I)*X(I)
240      LET Y1=Y1+Y(I)
250      LET Y2=Y2+Y(I)*Y(I)
260      LET Z=Z+X(I)*Y(I)
270      NEXT I
280   PRINT
290   PRINT "CHART READING  TEMPERATURE   SLOPE    ";
300   PRINT"       X(=1000/T)   Y(=LOG(S*RT.T))"
310   PRINT
320   FOR I=1 TO N
```

```
330      PRINT C(I),T(I),S(I),X(I),Y(I)
340      NEXT I
350   LET X3=X1/N
360   LET Y3=Y1/N
370   LET M=(Z-X1*Y3)/(X2-X1*X1/N)
380   LET C=(X2*Y1-X1*Z)/(N*X2-X1*X1)
390   LET R=(Y2-2*M*Z-2*C*Y1+2*M*C*X1+M*M*X2+N*C*C)/(N-2)
400   LET V=N*R/(N*X2-X1*X1)
410   LET T=X2*R/(N*X2-X1*X1)
420   PRINT
430   PRINT "SLOPE,M = ";M;" (STANDARD ERROR = ";SQR(V);")"
440   PRINT "      C = ";C;" (STANDARD ERROR = ";SQR(T);")"
450   PRINT
460   PRINT "HEAT OF SUBLIMATION = ";-M*8.3143;" KJ/MOL."
470   PRINT "                +/- ";16.6286*SQR(V);" KJ/MOL"
480   PRINT
490   PRINT "MEAN X = ";X3;"       MEAN Y = ";Y3
500   END
```

Appendix 4. WTDUP2 programme for calculating heats of sublimation from thermocouple emfs and rates of mass loss in effusion experiments, giving more weight to readings at higher temperatures and rates of effusion.

```
COPY FROM DC (B,CH09)

10   DIM C(20),K(20),S(20),T(20),X(20),Y(20)
20   PRINT "HEAT OF SUBLIMATION BY THERMOBALANCE; EXPT:";
30   INPUT E
35   PRINT "DATA WEIGHTED BY SLOPE"
40   PRINT
50   PRINT "NUMBER OF PAIRS OF READINGS =";
60   INPUT N
70   PRINT
80   LET X1=0
90   LET Y1=0
100  LET X2=0
110  LET Y2=0
120  LET Z=0
150  LET W=0
160  PRINT "CHART READINGS AND SLOPES"
170  FOR I=1 TO N
180     INPUT C(I),S(I)
190   LET K(I)=272.35+1.3513*C(I)-6.78936?-3*(C(I))^2
191   LET T(I)=K(I)+9.57871?-5*(C(I))^3-5.4587?-7*(C(I))^4
192   REM CALIBRATION OF T.COUPLE AND 5 MV SCALE ON 21.9.76
200      LET X(I)= 1000/T(I)
210      LET Y(I)=LOG(S(I)*SQR(T(I)))
220      LET X1=X1+X(I)*S(I)
230      LET X2=X2+X(I)*S(I)*X(I)
240      LET Y1=Y1+Y(I)*S(I)
250      LET Y2=Y2+Y(I)*S(I)*Y(I)
260      LET Z=Z+X(I)*Y(I)*S(I)
265   LET W = W+S(I)
270      NEXT I
280   PRINT
290   PRINT "CHART READING  TEMPERATURE   SLOPE    ";
```

```
300   PRINT"      X(=1000/T)   Y(=LOG(S*RT.T))"
310   PRINT
320   FOR I=1 TO N
330      PRINT C(I),T(I),S(I),X(I),Y(I)
340      NEXT I
350   LET X3=X1/N/W
360   LET Y3=Y1/N/W
365   LET D3=W*X2-X1*X1
370   LET M=W*Z/D3 - Y1*X1/D3
380   LET C=X2*Y1/D3 -X1*Z/D3
390   LET R=(Y2-2*M*Z-2*C*Y1+2*M*C*X1+M*M*X2+W*C*C)/(W-2)
400   LET V=W*R/D3
410   LET T=X2*R/D3
420   PRINT
430   PRINT "SLOPE,M = ";M;" (STANDARD ERROR = ";SQR(V);")"
440   PRINT "      C = ";C;" (STANDARD ERROR = ";SQR(T);")"
450   PRINT
460   PRINT "HEAT OF SUBLIMATION = ";-M*8.3143;" KJ/MOL."
470   PRINT "                +/- ";16.6286*SQR(V);" KJ/MOL"
480   END
```

&