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THE THERMOCHEMISTRY OF SOME SILICON AND SOME
ARSENIC COMPOUNDS

by

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ABSTRACT

Heats of reaction, at 25°, in the liquid phase have been measured in an adiabatic reaction calorimeter.

The heat of hydrolysis of liquid silicon tetrachloride in an excess of aqueous hydrofluoric acid has been measured. This datum has been used to calculate $\Delta H_f^\circ(\text{SiCl}_4, \text{liq.}) = -170.2 \pm 0.8 \text{ kcal./mole.}$ The mean bond dissociation energy, $\bar{D}(\text{Si-Cl}) = 97.2 \pm 0.7 \text{ kcal./mole,}$ is derived, together with the heat of formation of the radical, $\Delta H_f^\circ(\text{SiCl}_3, \text{g}) = 86.1 \pm 4.8 \text{ kcal./mole.}$

The heats of hydrolysis of trimethylchlorsilane in water, and of hexamethyldisilazane in an aqueous solution of excess hydrogen chloride have been measured. These data are used to calculate the values $\Delta H_f^\circ(\text{Me}_3\text{SiCl}, \text{liq.}) = -97.50 \pm 1.37 \text{ kcal./mole}$ and $\Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{NH}, \text{liq.}] = -123.76 \pm 1.40 \text{ kcal./mole.}$ These values, together with other heats of formation are used to derive bond dissociation energies for bonds involving silicon atoms.

The heats of reaction between bromine, in carbon tetrachloride, and two forms of arsenic (cryst., α , rhomb.) and (amorph., β) to give arsenic tribromide in solution have been measured. The heat of formation, $\Delta H_f^\circ(\text{AsBr}_3, \text{cryst.}) = -47.57 \pm 0.10 \text{ kcal./mole,}$ and the heat of transition, $\Delta H = +3.24 \pm 0.03 \text{ kcal./g.-atom,}$ for the process $\text{As}(\text{cryst., } \alpha, \text{ rhomb.}) \rightarrow \text{As}(\text{amorph., } \beta)$ have been calculated. The heats of hydrolysis of arsenic tribromide, arsenious oxide, and

arsenic oxide in an aqueous solution of sodium hydroxide, and the heat of oxidation of sodium arsenite to sodium arsenate, using liquid bromine, have also been measured. The data are used to calculate the following heats of formation: $\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst.}, \text{octa.}) = -160.30 \pm 0.22$; $\Delta H_f^\circ(\text{As}_2\text{O}_5, \text{cryst.}) = -222.14 \pm 0.35$; $\Delta H_f^\circ[\text{NaAsO}_2, \text{in } 64 \text{ NaOH}, 2000 \text{ H}_2\text{O}] (\text{liq.}) = -164.57 \pm 0.20$; $\Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{in } 60 \text{ NaOH}, 2002 \text{ H}_2\text{O}] (\text{liq.}) = -389.97 \pm 0.30 \text{ kcal./mole.}$

The heat of combustion of arsenic (cryst., α , rhomb.) has been measured in a rotating-bomb calorimeter and used to derive $\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst.}, \text{octa.}) = -160.14 \pm 1.60 \text{ kcal./mole.}$

The mean bond dissociation energy $\bar{D}(\text{As-O}) = 77.6 \pm 0.1 \text{ kcal./mole}$ is calculated for arsenious oxide.

An appendix on the heat of combustion of cyclo-octadecanonaene, ([18]-annulene), is also included.

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CHAPTER I

Introduction

All chemical and physical processes involve energy changes, and it is those energy changes which accompany changes of state and chemical reactions which constitute the subject matter of thermochemistry.

In order to derive useful thermochemical data of a system it is necessary to refer the energy content of the system to some reference state in which the energy content is arbitrarily set equal to zero. For this purpose it is assumed that the heat contents of elements, in their standard states, is zero.

The standard state of an element is the naturally occurring isotopic mixture of the element at 25°C and 1 atm. pressure, or unit fugacity for a gas. Similarly the standard state of a compound is that state in which the compound normally exists at 25°C and 1 atm. pressure. Where two or more allotropic forms of an element exist, or where there is more than one crystalline form of a compound, one of these has generally been agreed to be the standard state.

Thus the standard heat of formation, ΔH_f° , of a compound may be defined as the change in heat content in forming one mole of the compound, in its standard state, from its constituent elements in their standard states. The standard state values are denoted by the superscript $^\circ$. Thus, ΔH° is the change in heat content under

standard conditions. For compounds which are not gases in their standard states it is sometimes useful to know the heat of formation of the compound in the gaseous state. This may be calculated by incorporating the molar latent heat of vaporisation in the case of a liquid, or of sublimation, where the compound is a solid. The molar latent heat may be defined as the change in heat content, at 25°C , 1 atm. pressure, for the process liquid \rightarrow gas and is denoted by $\Delta H_{\text{vap.}}$; for solid \rightarrow liquid, ΔH_{fusion} ; and for solid \rightarrow gas, $\Delta H_{\text{sub.}}$. The heat of formation of a gaseous compound $\Delta H_f^{\circ}(\text{g})$, is given by the sum $\Delta H_f^{\circ}(\text{liq.}) + \Delta H_{\text{vap.}}$.

In general terms the heat of any reaction may be equated to the difference between the sum of the heats of formation of the products and the sum of the heats of formation of the reactants, i.e.

$$\Delta H_r = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$$

From a knowledge of the heat of a reaction, in which all the participants except one have known heats of formation, the heat of formation of the remaining compound may be calculated using Hess's Law.

In a reaction $\text{AB} \rightarrow \text{A} + \text{B}$, the products A and B may be either molecules, atoms or radicals. If they are atoms, then the terms $\Delta H_f^{\circ}(\text{A}, \text{g})$ and $\Delta H_f^{\circ}(\text{B}, \text{g})$ are the heats of formation of the atoms (sometimes called the heat of atomisation of the element) which is defined as the change in heat content when one gram-atom of the element, in its standard state, is converted into free atoms, in their ground-state at 25°C , 1 atm. pressure. If on the other hand the products A and B are radicals then the terms $\Delta H_f^{\circ}(\text{A}, \text{g})$ and $\Delta H_f^{\circ}(\text{B}, \text{g})$ refer to the heats of formation of

the radicals.

Using these terms it now becomes possible to calculate bond dissociation energies from the relationship

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

for the gas-phase reaction $AB \rightarrow A + B$. The bond dissociation energy $D_0^\circ(A - B)$ of the bond $(A - B)$ is defined as the energy change ΔE_0° , at absolute zero of temperature, in the ideal gas state, for the reaction $AB \rightarrow A + B$, the products being in their ground states. The subscript $_0$ refers to the zero'th vibrational level of the molecule. Often, the change in heat content, ΔH , at 25°C , of this reaction has been used as a measure of the dissociation energy, designated D , to avoid confusion with D_0° values. Generally, these two values, D_0° and D do not differ greatly, many of the data obtained by measurement of the latter quantity are not sufficiently precise to warrant the correction, for which in many cases the heat capacity information is often lacking.

If we consider the molecule AB_x , for the gas-phase reaction $AB_x \rightarrow A + xB$ where $x(A - B)$ bonds are broken, the heat of the reaction is $x\bar{D}(A - B)$. Here, $\bar{D}(A - B)$ is the mean bond dissociation energy. This mean value is not necessarily the same as the energy required to remove the first or subsequent groups, since there may be different energies of reorganisation of the radical remaining after removal of each B group.

Similarly, the bond dissociation energy of a bond between given atoms may vary considerably amongst molecules containing this bond,

since the bond may differ in character from molecule to molecule.

Two types of methods for determining bond dissociation energies can be distinguished. One is to determine the energy change for the reaction $AB \rightarrow A + B$ either directly or by way of a set of equilibrium measurements. The other method is to measure the rate of some process and relate it to thermodynamic properties by an assumption about the mechanism of the process. More specifically, some of the experimental methods which have been used are (a) thermal equilibria, (b) kinetic, (c) electron impact, (d) spectroscopic, and (e) the calorimetric method. The general outlines of these methods are as follows.

(a) Thermal Equilibria

The heat of dissociation may be deduced thermodynamically if the equilibrium concentrations of AB, A and B are known over a range of temperature. Using the Van't Hoff isochore,

$$\frac{d \ln K}{d(1/T)} = \frac{-\Delta H}{R},$$

a graph of $\ln K$ against $\frac{1}{T}$ may be plotted, whose slope is $-\frac{\Delta H}{R}$. This method suffers the disadvantage that a large temperature range is required. It is necessary to calculate ΔH_0 , the heat of dissociation at $0^\circ K$, from ΔH at high temperature.

It is also possible to derive ΔH from equilibrium measurements at one temperature provided the entropy change is known, using

$$-R \ln K = \frac{\Delta(G^\circ - H_0^\circ)}{T} + \frac{\Delta H_0^\circ}{T},$$

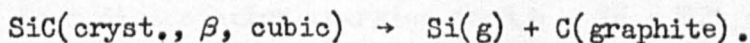
where $\frac{\Delta(G^\circ - H_o^\circ)}{T}$ is the "free energy function" which may be calculated from molecular data by the methods of quantum statistical mechanics.

The inherent difficulty in these methods lies in the determination of the concentrations, which often cannot be measured directly. Experimental techniques have involved, for example, manometric, effusion and equilibrium flow methods.

Davis, Anthrop and Searcy¹ measured the vapour pressures of both silicon and silicon carbide using Knudsen effusion cells. The reaction vessel, used in this method, has a hole in it leading to an evacuated space. The rate at which gaseous molecules pass through the hole depends only on the mean component of velocity of the molecules and the number present, and may be calculated to be

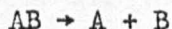
$$\frac{ap}{(2\pi mkT)^{\frac{1}{2}}} \text{ molecules per second,}$$

where a is the area of the hole, p , the pressure, m , the mass of the molecule, and k , the Boltzmann constant. Combination of the data measured with known entropies yielded a value of 108.4 ± 3 kcal./mole for the heat of sublimation of silicon to silicon atoms at 25°C , and a value of $\Delta H = 126.0 \pm 3$ kcal./mole for the reaction



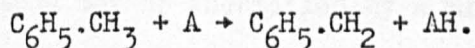
(b) Kinetic Methods

Commonly, in a kinetic study of the reaction



it is assumed that the activation energy for the recombination of radicals is zero, and therefore that the activation energy of the dissociation reaction is equal to the heat of reaction.

Szwarc² devised a method of ensuring that complicating side reactions do not confuse the kinetics of unimolecular dissociation. He found that toluene reacts with many radicals thus,



The radicals A and B, formed during a dissociation reaction, carried out in a flow system using toluene as carrier gas, are largely surrounded by toluene molecules. They react preferentially with the toluene producing the stable molecules AH and BH, thus preventing back reaction and possible chain reactions. Under the experimental conditions the benzyl radicals do not react in the hot zone and eventually dimerize outside the main reaction zone. The rate of the initial dissociation may be measured from the amounts of AH, BH or dibenzyl which are formed.

Trotman-Dickenson et al.³ used this approach to investigate the kinetics of pyrolysis of a number of hydrazines and benzylamines. These workers obtained values of 57.1, 51.9 and 49.6 kcal./mole for the N - N bond dissociation energies in $\text{H}_2\text{N} - \text{NH}_2$, $\text{H}_2\text{N} - \text{NHCH}_3$ and $\text{H}_2\text{N} - \text{N}(\text{CH}_3)_2$, and 59.8 and 57.7 kcal./mole for $\text{D}(\text{PhCH}_2 - \text{NH}_2)$ and $\text{D}(\text{PhCH}_2 - \text{NHCH}_3)$. From these and available heats of formation, the values $\Delta\text{H}_\text{f}^\circ(\text{NH}_2, \text{g}) = 39.8$, $\Delta\text{H}_\text{f}^\circ(\text{NHCH}_3, \text{g}) = 34.5$ and $\Delta\text{H}_\text{f}^\circ(\text{N}(\text{CH}_3)_2) = 29.5$ kcal./mole were derived.

(c) Electron Impact

In this method electrons of known energy are allowed to interact with molecules to produce ionization and dissociation. Under certain conditions the lowest electron energy required to produce a given ion by dissociation and ionization is equal to the sum of the dissociation energy and the ionization potential of the fragment. The fragments produced may be identified by a mass spectrometer. The method can be applied to both polyatomic and diatomic molecules, but for the former, identification of the process taking place is often difficult and the required ionization potentials of radicals are not always known sufficiently accurately.

Recently, Steele, Nichols and Stone⁴ have obtained the value $D(\text{Cl}_3\text{Si} - \text{Cl}) = 106 \pm 4$ kcal./mole from electron impact data for the dissociation energy of the first silicon-chlorine bond. These authors have also reported similar measurements on the alkyl silanes, RSiH_3 , and alkylchlorosilanes, RSiCl_3 , (where $\text{R} = \text{Me}, \text{Et}, \text{}^i\text{Pr}, \text{}^t\text{Bu}$) giving values for the dissociation energies of carbon - silicon bonds.

The status of both this method and the kinetic method has been critically assessed by Sehon and Szwarc.⁵

(d) Spectroscopic Methods.

Spectroscopy can give values for the dissociation energies of simple diatomic molecules. Accurate values may be obtained for a few molecules (hydrogen, oxygen, halogens) from the convergence limit of the absorption spectrum, at which the bands due to quantized vibrations

give place to a continuum. The limit corresponds to the energy at which the amplitude of the vibration becomes so great that the atoms separate. The products are usually one ground-state and one excited atom, ~~but~~ ^{if} the energy of excitation can be allowed for ~~and~~ the ground-state energy of formation of the two atoms ^{may be} obtained. For many molecules the absorption bands cannot be observed, or show no convergence; a value for the dissociation energy can still be obtained by extrapolation from the bands of the observed emission spectrum. The result depends on the method of extrapolation and on the number of bands that can be observed, and may provide only an upper limit to the true value of the dissociation energy.

The dissociation energy of chlorine has been established spectroscopically, the absorption spectrum being mainly continuous. Weak bands have, however, been observed^{6,7} giving a convergence limit at $20,850 \pm 20 \text{ cm.}^{-1}$. Allowing for the excitation of the chlorine atom this corresponds to $D(\text{Cl} - \text{Cl}) = 2.476 \text{ ev.}$ and $\Delta H_f^\circ(\text{Cl}, \text{g}) = 28.94 \text{ kcal./g.-atom.}$

(e) Calorimetric

Direct calorimetric measurement of the heat absorbed when dissociation takes place is rarely possible. In a few instances it is possible to measure the exothermic recombination of atoms or radicals. For example, Bichowsky and Copeland⁸ were able to measure the heat of recombination of hydrogen atoms by direct calorimetry. However, calorimetry contributes to the determination of dissociation energies by

providing accurate heat of formation data, which may be used in conjunction with heats of formation of radicals, determined by other methods, to derive dissociation energies.

From the point of view of experimental techniques it is convenient to divide reactions, for which changes in heat content are measured, into two main types. These are (i) combustion reactions, in which a compound is completely oxidised, usually by gaseous oxygen; and (ii) all other reactions such as hydrolysis, halogenation and hydrogenation. The techniques are referred to as combustion calorimetry and reaction calorimetry, respectively.

The heat of combustion, ΔH_c° , is the change in heat content per mole when a compound, in its standard state, reacts with oxygen to form gaseous carbon dioxide at 1 atm. pressure, and liquid water at 25°C. If elements other than carbon, hydrogen and oxygen are present in the compound, then all other products must also be in their standard states.

This process is not realisable exactly in practice, but ΔH_c° can be derived precisely by applying certain corrections to the value of the heat evolved, when the substance is burned in oxygen under pressure in a bomb. These corrections will be discussed later.

Three main types of combustion calorimeters are in general use, the flame, the static-bomb, and the rotating-bomb calorimeter.

Flame Calorimeter

This type of calorimeter is used to measure the heats of

combustion of gases or vapours, generally in oxygen, at constant pressure.

Oxygen and the sample under investigation are led into the reaction chamber through separate inlet tubes at controlled rates. The gases are ignited by a spark at the burner, and the water produced by the reaction is condensed and collected in a chamber.

The carbon dioxide produced is collected and weighed. This provides a measure of the amount of reaction.

Rossini⁹ has obtained highly accurate data for the reaction between hydrogen and oxygen to form water in a flame calorimeter. This reaction is now used to calibrate such calorimeters.

The flame calorimeter has not been widely used but several important studies have been carried out with it; e.g. heats of combustion of carbon monoxide, methane,¹⁰ ethane, propane,¹¹ and the butanes.¹²

More recently, Pilcher, et al.^{13,14} have successfully adapted the flame calorimetric technique to some volatile ethers to obtain reliable ΔH_c° and ΔH_f° values.

Static-Bomb Calorimeter

The modern static-bomb is based on that designed by Prosen and Rossini.¹⁵ The combustion of an organic compound is usually a fast reaction under the conditions in the bomb. The isothermal calorimeter of Dickinson's¹⁶ design is suitable for the study of these fast reactions. This calorimeter is isothermal in the limited sense that the external water jacket is maintained at a constant temperature.

The static-bomb calorimeter is suitable for accurate

measurement of heats of combustion only when the products of combustion and their thermodynamic states can be uniquely defined. It can be used for the precise measurement of the heats of combustion of compounds containing C, H, O and/or N. In the case of compounds containing no other than these elements it is usual and sufficient to analyse the bomb gases for CO_2 , and the bomb liquid for nitric acid. In general, it cannot be used to obtain precise heats of combustion of organic compounds containing halogens, sulphur, or metals.

However, by adopting special techniques (e.g. raising the pressure of oxygen in the bomb from the usual 30 atm. to 40 atm.), Davies, Pope and Skinner¹⁷ burned some alkyls of tin satisfactorily. They found only traces of unburnt tin (determined by weighing as less than 1% of the total tin content) in the combustion products, and only one oxide of tin, SnO_2 , (determined by X-ray analysis). The precision of their results was ca. $\pm 0.03\%$.

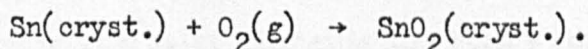
Pope and Skinner¹⁸ also used a static-bomb calorimeter to obtain ΔH_f° values of -48.4 ± 0.8 and -72.7 kcal./mole for liquid Et_4Ge and Pr_4Ge , in terms of the heat of formation¹⁹ of GeO_2 (cryst., hexa), the metal oxide formed in these combustions.

Although the heats of combustion of a number of metals, in oxygen, have been measured in static-bomb calorimeters the derived heats of formation of the corresponding metal oxides are usually accurate to only $\pm 0.5\%$. Combustion is generally incomplete, and it is necessary to determine the amount of oxides formed, together with their crystalline

forms. The difficulties of this analysis limits the accuracy of the derived heat of formation of the oxide.

A recent example ~~is~~ the work of Mah and Adami,²⁰ who burned crystalline Ge to GeO_2 (cryst., hexa) using paraffin as a kindling agent. The combustions were reported to be 97.8 - 98.8% complete, as determined from weight increase of the residue on ignition. A value of ΔH_f° (GeO_2 , cryst., hexa.) = -129.08 ± 0.13 kcal./mole was obtained.

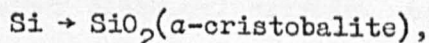
Likewise, Humphrey and O'Brien²¹ have derived the heat of formation of SnO_2 (cryst.) from measurements of ΔH_c° for the reaction,



After correcting for traces of unburned tin, (1 - 4%), they derived ΔH_f° (SnO_2 , cryst.) = -138.82 ± 0.09 kcal./mole.

Attempts to determine ΔH_c° values for non-metal oxides, by combustion of the element in oxygen, have been made, but again imprecise analysis limits the accuracy of the results. The difficulties are reflected in the published values for ΔH_c° of elemental boron, which range from -270 to -368 kcal./mole B_2O_3 . In a recent determination Gal'chenko et al.²² preheated boron to 1000° in the bomb to assist combustion, and obtained ΔH_f° (B_2O_3 , amorph.) = -299.1 ± 1.8 kcal./mole.

Due to unsatisfactory analysis of both elemental silicon and the products of its combustion in oxygen, Humphrey and King²³ obtained a value ΔH_c° = -209.33 ± 0.25 kcal./mole for the process,

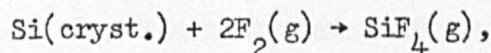


which is now known to be some 8 kcal./mole in error.

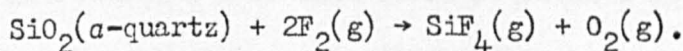
Static-bomb combustion calorimetry has been more successful in determining the heat of combustion of phosphorus. Holmes²⁴ burned *a*-white phosphorus, coated with a film of Perspex, in oxygen. Corrections were made for the partial hydration of the product, P_4O_{10} , by the water formed on combustion of the protective Perspex coating, and for traces of unburnt phosphorus remaining in the crucible (estimated by oxidation with I_2 , or by HNO_3). The derived value of $\Delta H_f^\circ(P_4O_{10}, \text{cryst., hexa.})$ was -713.2 ± 1 kcal./mole.

A new approach to static-bomb calorimetry is that developed by Hubbard and co-workers, of charging the bomb with fluorine gas instead of oxygen.

This technique enabled Hubbard et al.²⁵ to obtain a "clean" combustion of elemental silicon



and also of silica under the same conditions



From the difference between these heats of fluorination the value $\Delta H_f^\circ(SiO_2, a\text{-quartz}) = -217.72 \pm 0.34$ kcal./mole was obtained. By using a similar technique these workers have also determined the heats of formation of SiF_4 ,²⁵ UF_4 ,²⁶ and BF_3 .²⁷

Heats of explosion of unstable gaseous hydrides, when mixed with stibine in a copper block calorimeter²⁸ have been measured by

Gunn and co-workers. The heats of formation of SiH_4 , Si_2H_6 , GeH_4 and Ge_2H_6 ,²⁹ and Si_3H_8 and Ge_3H_8 ³⁰ have been determined in this way.

Baibuz and Medvedev³¹ used a spherical bomb of Monel metal (10 l. capacity) to measure heats of explosion and have derived the heats of formation of some fluorine-chlorine substituted methanes.

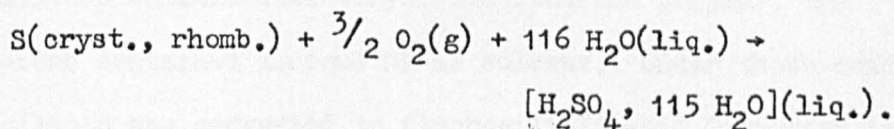
Rotating-Bomb Calorimeter

In the combustion in a static bomb of an organosulphur compound, in oxygen, the final thermodynamic state cannot be uniquely defined. A mist of sulphuric acid forms over the inner surface of the bomb. The concentration of this acid is not identical at different places in the bomb, and, since the heat of dilution of sulphuric acid is large, and is not a linear function of concentration, significant errors may be introduced.

In an attempt to overcome these difficulties Popov and Schirokikh³² in 1933 developed a bomb that could be oscillated during the combustion period. This technique was later extended by Smith and Sunner,³³ who introduced a bomb that could be rotated about its vertical and horizontal axes at the same time. This technique enables the inside surfaces of the bomb to be washed by the liquid placed inside the bomb, ensuring homogeneity of the final products in solution. A modern development of such a bomb has been described by Good, Scott, and Waddington.³⁴ The rotating-bomb used in work reported in this thesis is described later.

Good, Lacina, and McCullough³⁵ used a similar bomb to measure

the heat of formation of dilute sulphuric acid by direct combustion of rhombic sulphur,



The ΔH_c° value was reported as -143.85 ± 0.06 kcal./mole leading to $\Delta H_f^\circ[\text{H}_2\text{SO}_4, 115 \text{H}_2\text{O}](\text{liq.}) = -212.17 \pm 0.06$ kcal./mole. The results for the same reaction obtained by Månsson and Sunner³⁶ are in close agreement.

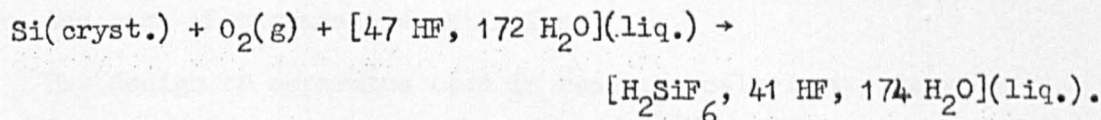
With a sound value for $\Delta H_f^\circ[\text{H}_2\text{SO}_4, 115 \text{H}_2\text{O}](\text{liq.})$ it became possible to determine the heats of formation of many organosulphur compounds using the techniques of rotating-bomb calorimetry. A review of this topic has been published by Mackle and O'Hare.³⁷

Likewise, with organofluorine compounds the accuracy of the results obtained from heats of combustion measurements depends on accurate knowledge of the heats of formation of HF (g) and HF(aq.). A discussion of the status of these heats of formation is given later.

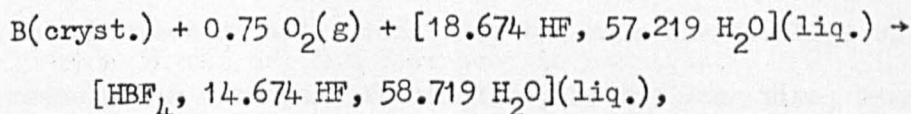
Conventional bomb calorimetry applied to organoboron and organosilicon compounds has not yielded very satisfactory results. A method developed by Good,³⁸ which involves mixing the boron or silicon compound with an organic fluorine containing compound as a combustion promoter, and burning the mixture in the rotating-bomb calorimeter containing aqueous HF as solvent has given good results. Under these conditions, no solid products of combustion remain after rotation of the bomb. The final product is a homogeneous solution of HBF_4 or H_2SiF_6 in aqueous HF,

and combustion of the original compound is complete.

Good³⁸ used this technique to measure the heat of combustion of pure silicon admixed with vinylidene fluoride polymer, the rotating-bomb contained aqueous HF as solvent. Under these conditions all the silicon was converted to fluorosilicic acid dissolved in HF solution. If SiO_2 was formed as a reaction intermediate it was totally dissolved by the aqueous HF on rotation. These experiments gave $\Delta H = -250.3 \pm 0.3$ kcal./mole for the reaction



The combustion of boron, in essentially the same manner, has been achieved by Good, Mansson and McCullough.³⁹ The measurements gave $\Delta H_c^\circ = -173.41 \pm 0.20$ kcal./g.-atom for the combustion reaction



which, together with other data, yields $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph.}) = -299.74 \pm 0.4$ kcal./mole (this may be compared with $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{amorph.}) = -299.1 \pm 1.8$ kcal./mole obtained from static-bomb combustion calorimetry²²) and $\Delta H_f^\circ(\text{B}_2\text{O}_3, \text{cryst.}) = -304.10 \pm 0.41$ kcal./mole, both these values being with reference to crystalline boron.

Values of ΔH_f° for $(\text{H}_2\text{SiF}_6, \text{aq.})$ ³⁸ and $(\text{HBF}_4, \text{aq.})$ ³⁹ obtained by this technique have made it possible to measure ΔH_c° and therefore ΔH_f° for organosilicon and organoboron compounds. Thus, Good,⁴⁰ using

a similar procedure to that used in the combustion of elemental silicon, was able to derive ΔH_f° for hexamethyldisiloxane, $\text{Me}_3\text{SiOSiMe}_3$, from combustion measurements.

Reaction Calorimetry

For a particular compound it is sometimes possible to study the heat of a reaction, other than combustion, which is more well-defined, which is accompanied by a much smaller heat change, and where the heats of formation of the reaction products are more well-established than in the case of degradative oxidation.

The design of apparatus used in reaction calorimetry depends to a large extent on the particular reaction studied. Dewar vessels have been used extensively, mainly because of their simplicity and low cost.

Sunner and Wadsworth⁴¹ designed and tested a number of vacuum-jacketed calorimeters and showed that the main disadvantage of glass Dewar vessels, as reaction calorimeters, is the long time, usually several hours, required for them to reach thermal equilibrium. They developed a brass calorimeter with a glass reaction vessel, which was accurate to $\pm 0.05\%$ and which equilibrated in less than two minutes.

For fast reactions (duration of reaction less than about 20 min.) constant-temperature environment calorimeters are preferable and have been mostly used. However, for the study of reactions of long duration, the adiabatic method is more suitable. The main advantages of this method may be briefly listed as follows.

(i) In the evaluation of the heat leakage correction in non-adiabatic calorimetry, the assumption is made that the leakage modulus, k , remains constant during an experiment. Errors due to variation in k , and to deviation of the heat exchange from Newton's Law are reduced in the adiabatic method since the multiplier of k , the thermal head (the difference between the jacket temperature and the calorimeter temperature) is small.

(ii) Maintenance of a small thermal head reduces convection in the air gap between the jacket and the calorimeter. It is thus permissible to use considerably wider air gaps, with correspondingly smaller leakage moduli, in the adiabatic method. This advantage may be employed in other methods by incorporating convection shields.

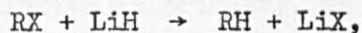
(iii) Troubles due to evaporation from an incompletely sealed calorimeter are less serious. It is, however, desirable to have tight sealing if possible.

(iv) The greatest advantage is in the application of the adiabatic method to prolonged reactions. In such cases the heat-loss corrections in other methods might be as large as, or even larger than, the total quantity of heat to be measured. In the adiabatic method the heat-loss term can be held to a small fraction of the total.

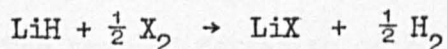
Using an adiabatic calorimeter similar to that described by Carson, Hartley, and Skinner,⁴² Carson et al.⁴³ studied the reductions in ethereal solution of methyl iodide,⁴³ benzyl bromide, benzyl iodide,⁴⁴

45

ethyl iodide and ethyl bromide by lithium aluminium hydride in the presence of lithium hydride. The reactions may be represented as



and by combining the enthalpy change of this reaction with that of the reaction



the heat of formation of the organic halide was derived in terms of the heat of formation of the corresponding hydrocarbon RH. From these studies the heat of formation of the benzyl radical and the bond dissociation energies $D(CH_3-I)$, $D(C_2H_5-I)$ and $D(C_2H_5-Br)$ were derived.

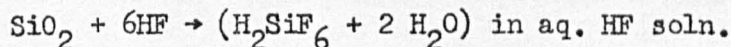
In recent years, great advances have also been made in the study of very slow reactions. The twin calorimeters of Buzzel and Sturtevant⁴⁶ and the microcalorimeter of Kitzinger and Benzinger⁴⁷ have been used extensively in studies of the enzyme hydrolysis of phosphates. Calvet⁴⁸ has used a twin micro-calorimeter for studies of many slow reactions, including thermogenesis processes lasting for several days.

Another interesting innovation in reaction calorimetry is the apparatus designed by Lacher et al.⁴⁹ These workers measured the heats of hydrogenation of a number of organic halides at elevated temperatures ($103^\circ - 248^\circ C$), using palladium-on-carbon catalyst. The calorimeter was an isothermal type in which the reaction heat was transferred to a surrounding liquid, which was cooled simultaneously by bubbling an inert gas through it. A steady state was obtained when

this cooling just balanced the heat evolved by the reaction.

The measurement of the heats of hydrolysis of inorganic compounds, using solution calorimetry, is an important approach to obtaining the heats of formation of these compounds. A rocking-bomb reaction calorimeter has been described by Gunn,⁵⁰ and used to measure the heats of hydrolysis of diborane and boron trichloride.⁵¹ The heat of formation of BF_3 has also been determined⁵² from its heat of hydrolysis in an aqueous solution of HF, when the product is a solution of fluoroboric acid. The heat of formation of BF_3 depends, therefore, on the value for $\Delta H_f^\circ(\text{HBF}_4, \text{aq.})$. Gunn et al. have also measured⁵³ the heats of solution and dilution of some ammonium salts in liquid ammonia at 25°C, demonstrating the versatility of this important new reaction calorimeter.

King⁵⁴ has reported measurements on the heat of solution of pure quartz in aqueous hydrofluoric acid, from which a value for the following reaction can be obtained.

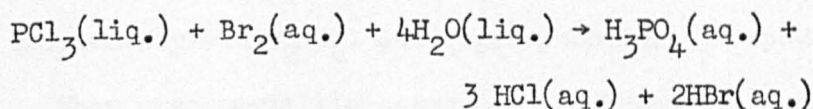


By incorporating the heat of combustion of silicon in oxygen, in the presence of aqueous HF, Good³⁸ derived the value $\Delta H_f^\circ(\text{SiO}_2, \alpha\text{-quartz}) = -217.5 \pm 0.5 \text{ kcal./mole}$, which is in close agreement with that obtained by Wise, et al.²⁵

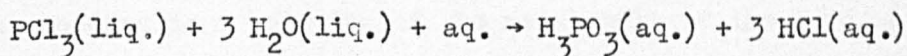
A similar approach has been adopted by Bills and Cotton^{55,56} to determine the heat of formation $\Delta H_f^\circ(\text{Et}_4\text{Ge, liq.}) = -50.0 \pm 1.9 \text{ kcal./mole}$. These authors measured the heat of combustion of tetraethylgermanium

in oxygen in the presence of aqueous HF, using a rotating-bomb calorimeter. By replacing the rotating-bomb with a wide-mouthed polythene bottle, they adapted the rotating-bomb calorimeter into a reaction calorimeter, and measured the heat of solution of germanium metal in a solution of both aqueous HF and H_2O_2 . They also measured the heat of solution of GeO_2 in aqueous HF for which the value $\Delta H_f^\circ(\text{GeO}_2, \text{cryst., hexa.}) = -132.2 \pm 1.2 \text{ kcal./mole}$ was obtained;¹⁹ upon which the heat of formation, $\Delta H_f^\circ(\text{Et}_4\text{Ge, liq.}) = -48.4 \pm 0.8 \text{ kcal./mole}$, obtained by Skinner¹⁸ is based.

Measurements of the heat of the reaction



by Neale and Williams,⁵⁷ and the heat of the hydrolysis



by Charnley and Skinner,⁵⁸ have been used in conjunction with the value reported by Holmes²⁴ for ΔH_c° (phosphorus) to provide a firm value of $\Delta H_f^\circ(\text{H}_3\text{PO}_3, \text{cryst.}) = -277.5 \pm 0.8 \text{ kcal./mole}$.

Heats of halogenation reactions have proved fruitful sources of accurate ΔH_f° values. Gross and Hayman⁵⁹ have developed a reaction calorimeter in which the heats of halogenation of some metals have been measured by burning the metals in chlorine vapour in a glass reaction chamber. Values for ΔH_f° for VCl_4 and HfCl_4 have been reported.

A different approach to heats of halogenation reactions is that of Duus and Mykytiuk⁶⁰ who obtained the heat of formation of

PF_3 by measuring the heat of fluorination of PCl_3 , using a fluidised bed of CaF_2 at 356°C .

Key Heats of Formation

Key heats of formation are important because they serve as stepping-stones in the indirect determination of the heats of formation of numerous other compounds.

The most widely used indirect method of determining heats of formation is that of combustion in oxygen. For simple organic compounds containing only C, H, O and N the products are CO_2 , H_2O and HNO_3 . When organohalogen compounds are burned the acids HX are formed. Organosulphur compounds yield H_2SO_4 , and organophosphorus compounds oxidise to H_3PO_4 . When organometallic compounds are burned in a static bomb, the metal oxides form, and, if the bomb is charged with an acid solution, the metal appears as a solution of the metal salt of the acid, e.g. PbNO_3 .^{61,62} In some cases the products of oxidation will be the complex fluoro-acid, e.g. H_2SiF_6 , H_2GeF_6 , HBF_4 .

The heats of formation of all these compounds are key data. Values for the heats of formation of the following are now well established; CO_2 , H_2O ,⁶³ HNO_3 ,⁶⁴ HBr ,⁶⁵ HCl ,⁶⁶ H_2SO_4 ^{35,36} and H_3PO_4 .²⁴ The heats of formation of metal oxides have been reviewed by Holley⁶⁷ and also by Skinner.⁶⁸

The heat of formation of HF is not as well established as those of the other haloacids. Armstrong and Jessup⁶⁹ measured the heat of combustion of ammonia in a fluorine flame-calorimeter, at

B(amorph.)

l

k

B(cryst.)

B_2H_6

B_2O_3 (cryst.)

f

B_2O_3 (amorph.)

j

e

a

HBO_2 (cryst.)

i

d

H_3BO_3 (aq.)

c

BF_3 (g)

H_3BO_3 (cryst.) g

$Me_3N.BH_3$

b

h

HBF_4 (aq.)

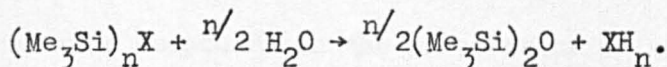
FIG. 1

constant pressure, to give $\Delta H_f^\circ(\text{HF}, g) = -64.63 \pm 0.07 \text{ kcal./mole}$. The heat of reaction of fluorine and excess hydrogen, measured⁷⁰ at 100° to avoid non-ideality corrections, gave $\Delta H_f^\circ(\text{HF}, g) = -64.46 \pm 0.1 \text{ kcal./mole}$. Hubbard et al.²⁷ obtained $\Delta H_f^\circ(\text{HF}, g) = -64.92 \pm 0.12 \text{ kcal./mole}$ by combining the measured heat of combustion of silica in fluorine with the heat of hydrolysis of SiF_4 , as determined from the equilibrium studies of Lenfesty et al.⁷¹ These values indicate that $\Delta H_f^\circ(\text{HF}, g)$ is more negative than that given in Circular 500,⁶⁶ of -64.2 kcal./mole . From the available data Skinner⁶⁸ has chosen $\Delta H_f^\circ(\text{HF}, g) = -64.7 \pm 0.5 \text{ kcal./mole}$ as the "best" value.

Reference has been made (pp.16 and 22) to the heats of formation of HBF_4 , H_2SiF_6 and H_2GeF_6 . Fig. 1 shows the dependence of the heats of formation of some boron compounds on $\Delta H_f^\circ(\text{HBF}_4, \text{aq.})$ ³⁹ which has been determined from the heat of combustion of crystalline boron (a, in the figure). This leads, with heat of solution measurements, to ΔH_f° values via b, for $\text{H}_3\text{BO}_3(\text{cryst.})$ ³⁹, c, for $\text{H}_3\text{BO}_3(\text{aq.})$,^{72,73} d, for $\text{HBO}_2(\text{cryst.})$,⁷³ e, for $\text{B}_2\text{O}_3(\text{amorph.})$,⁷² and, f, for $\text{B}_2\text{O}_3(\text{cryst.})$.⁷² The heat of formation of $\text{HBF}_4(\text{aq.})$ is also used to find ΔH_f° values for $\text{BF}_3(g)$,⁵² from the hydrolysis, g, and for $\text{Me}_3\text{NBH}_3(\text{cryst.})$ ³⁹ from its heat of combustion, h. The heat^{52,74} of decomposition, i, $\text{Me}_3\text{N} \cdot \text{BH}_3 \rightarrow \text{Me}_3\text{N} + \frac{1}{2} \text{B}_2\text{H}_6$, yields a value for the heat of formation of B_2H_6 . This is also known from its heat^{51,72} of hydrolysis, j, to $\text{H}_3\text{BO}_3(\text{aq.})$ or from the heat⁷⁵ of decomposition, k, to $\text{B}(\text{amorph.})$ and the heat of transformation, l, to $\text{B}(\text{cryst.})$.^{75,76}

A key datum in silicon thermochemistry is the heat of formation of $(\text{H}_2\text{SiF}_6, \text{aq.})$ which will enable the heats of formation of some silicon compounds to be determined. Thus, it is possible to determine the heat of formation of silicon tetrachloride from the heat of hydrolysis in an excess of aqueous hydrofluoric acid to an aqueous solution of fluorosilicic acid, hydrofluoric acid and hydrochloric acid. This determination is reported in this thesis.

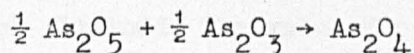
The heat of formation⁴⁰ of hexamethyldisiloxane, $\text{Me}_3\text{SiOSiMe}_3$, has also been determined from its heat of combustion, to $\text{H}_2\text{SiF}_6(\text{aq.})$, in a rotating bomb. This value may then be regarded as a secondary key thermochemical datum since this allows the heats of formation of other silicon compounds of the general formula $(\text{Me}_3\text{Si})_n\text{X}$, to be obtained, if it is possible to measure the heats of the hydrolysis reaction



Heat measurements of two such reactions, involving trimethylchlorosilane, Me_3SiCl , and hexamethyldisilazane, $\text{Me}_3\text{SiNHSiMe}_3$, are reported in this thesis.

The heats of formation of a number of arsenic compounds are based on the heat of formation of either crystalline arsenious oxide, or of sodium arsenite in an aqueous solution of sodium hydroxide. In arsenic thermochemistry these are key compounds. Long and Sackman⁷⁷ have shown by X-ray analysis that the products of the combustion of elemental arsenic, in a static bomb, are arsenic oxide, arsenious oxide and arsenic tetroxide formed from the combination of arsenic

and arsenious oxides.



These oxides appear as sublimates on the bomb walls and as a glass in the crucible. Variation of the initial oxygen pressure produces differing proportions of the oxides after combustion. They also found that some or all of the uncombined As_2O_3 in the bomb exists as an unusually active and soluble form. Heat of solution measurements on the bomb products indicated the presence of an oxide strongly endothermic with respect to ordinary $\text{As}_2\text{O}_3 - \text{As}_2\text{O}_5$ mixtures. These authors concluded that static-bomb combustion calorimetry was not suitable for this problem.

An aqueous solution of sodium arsenite is the reaction product of the hydrolysis,⁷⁸ and of the combustion in a rotating-bomb,⁷⁹ of trivalent arsenic compounds in the presence of an aqueous solution of sodium hydroxide.

The 'selected' value for the heat of formation of arsenious oxide given in Circular 500,⁶⁶ $\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -156.97 \text{ kcal./mole}$, is based on Schuman's⁸⁰ determinations of the free energy of formation from cell measurements, combined with Anderson's⁸¹ entropy data, and is supported by more recent work of Kirschning and Plieth.⁸²

De Passille⁸³ measured the heat of combustion of metallic arsenic in oxygen. By varying the pressure of oxygen, different ratios of arsenious oxide and arsenic oxide were produced, so that it was possible to calculate the heats of formation of both oxides. The

values $\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -154.7$, and $\Delta H_f^\circ(\text{As}_2\text{O}_5, \text{cryst.}) = -218.3$ kcal./mole were obtained. The value for arsenious oxide is the same as that obtained in much earlier work by Thomsen⁸⁴ (-154.7 kcal./mole), whilst the value obtained by Berthelot⁸⁵ (-156.4 kcal./mole) is closer to the 'selected' value. The 'selected' value for the heat of formation of arsenic oxide, -218.6 kcal./mole is slightly more negative than that obtained by de Passillé, but less so than Thomsen's value of -219.4 kcal./mole. The heats of formation of these oxides are, therefore, in doubt. It was with the object of providing sound values for these key data that investigations reported in this thesis were undertaken.

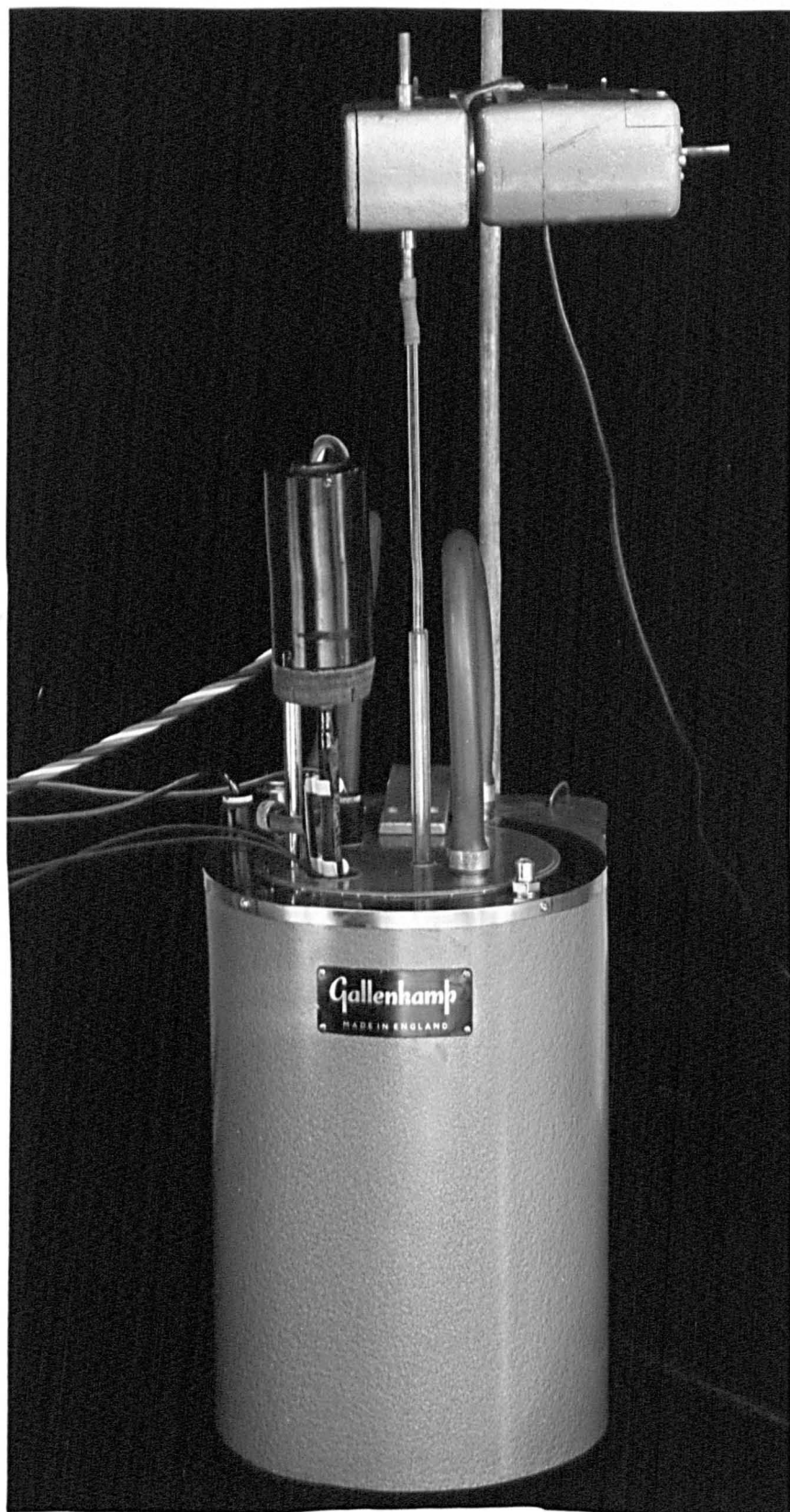


FIG.2

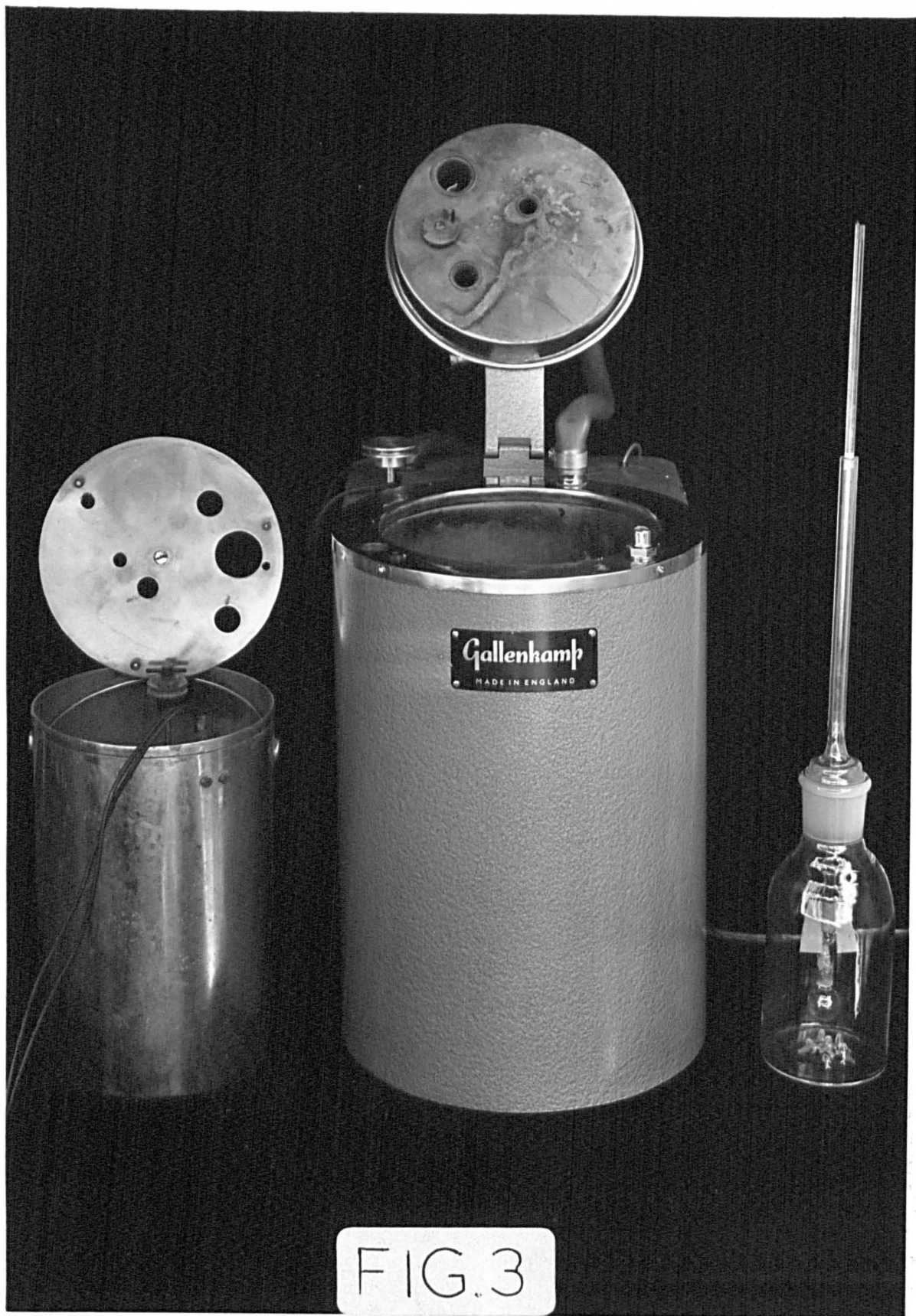


FIG. 3

CHAPTER II

Adiabatic Reaction Calorimeter

The calorimeter was manufactured by A. Gallenkamp and Co. Ltd. (type C.B.-040), Fig. 2, and was designed for use with a single valve, static combustion bomb. For the work reported in this thesis, only the adiabatic jacket and the calorimeter can, shown in Fig. 3, were used. Use of the adiabatic jacket in conjunction with a combustion bomb has been described elsewhere.⁸⁶ Three reaction vessels were used and these occupied the position normally taken by the combustion bomb.

The water-jacket

The adiabatic jacket and hollow lid (diam. 21.6 cm., height 33.0 cm.) were constructed of stainless steel, the inside surfaces being highly polished. An electrically driven centrifugal pump mounted at the rear circulated water through the jacket and lid. The jacket contained an overflow tube, two electrode heaters and an internal coil through which cooling water could be passed. A hole in the top of the jacket accommodated a thermistor, while a second hole allowed the jacket to be filled, and the level of water to be inspected.

Attached to the floor of the well in the jacket were three tufnol pegs that supported the calorimeter can centrally in the well. The jacket and calorimeter can were separated by an air space of 1.5 cm.

Two holes in the hinged, hollow lid permitted entry of the

platinum resistance thermometer, a thermistor, and the leads to the resistance heater, into the calorimeter can. A third hole supported the neck of the glass reaction vessel, or the ampoule support rod in the case of the copper reaction vessel.

The calorimeter can

The can and lid (diam. 14 cm., height 21.0 cm.) were made of stainless steel polished on the outside. Three metal pegs on the base of the can supported the reaction vessels in position and permitted free circulation of water round the vessels. A wire lifting handle facilitated lifting the can and contents into the water jacket. The can was also fitted with a stainless steel shaft equipped with two stirring rotors. A plastic sleeve minimised heat flow along the shaft. The stirrer was driven by the pump motor through pulleys, rubber belts, and an intermediate lay shaft for speed reduction. The stirrer operated at 400 r.p.m.

The control unit

The control circuit for the jacket temperature consisted of an energised Wheatstone Bridge with two thermistors representing two arms of the Bridge. One thermistor was placed in the jacket and the other in the calorimeter can. The other arms of the Bridge consisted of high stability resistances. When the jacket temperature fell below that of the calorimeter can and its contents (i.e. the system), the electrode heaters situated in the jacket were automatically operated by an out of balance signal from the Bridge. The temperature of the jacket

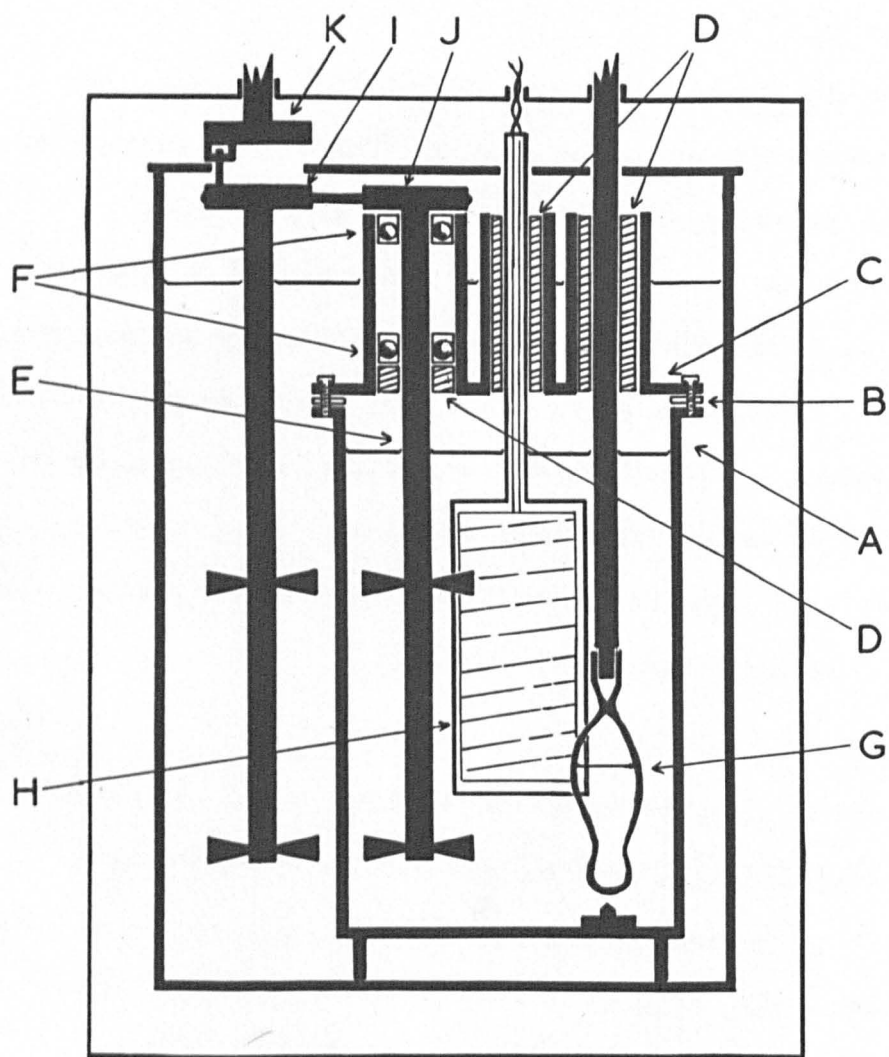


FIG.4

therefore followed that of the calorimeter can and its contents. The cooling coil in the jacket helped to ensure satisfactory jacket temperature control.

Reaction vessels

Three different reactions vessels were used.

Copper reaction vessel

The reaction vessel, Fig. 4, was a cylindrical copper can (A) (diam. 7.5 cm., height 12.0 cm.) fitted with a P.T.F.E. washer (B) and closed by a flanged lid (C). The lid was provided with three chimneys (internal diam. 1.9, 1.5, and 1.3 cm.) in which P.T.F.E. rings (D) were set, in order to close the system and prevent the escape of reactants. A stirrer shaft (E) supported by two stainless steel ball races (F) passed through the rings in the largest chimney. A P.T.F.E. rod, which passed through the rings in the intermediate-sized chimney held an inverted phial (G), to contain one of the reactants, which could be broken by pressing it on a spike in the base of the vessel. For some experiments the vessel also contained a resistance heater (H), the leads of which passed through a tube, which was supported by P.T.F.E. rings in the smallest chimney. When not in use for this purpose the chimney was closed by a P.T.F.E. plug. Except where otherwise indicated all copper surfaces were rhodium plated.

The vessel was immersed in water, to 1.0 cm. below the top of the chimneys, contained in the calorimeter can. The wheel (I) at the

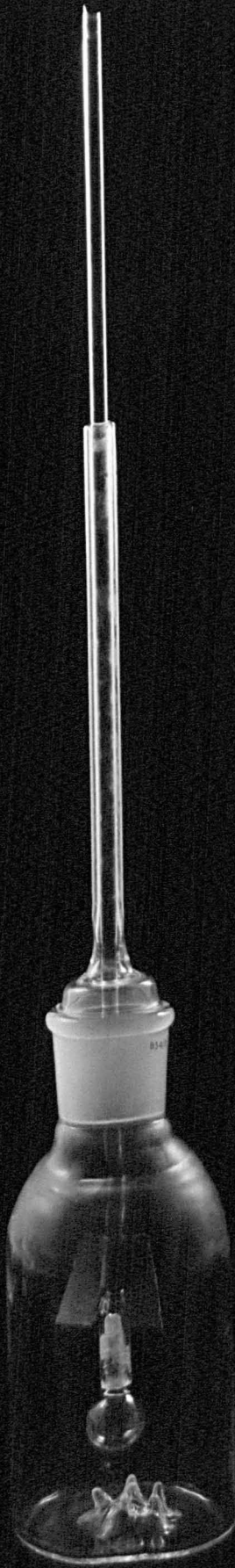


FIG.5

top of the shaft of the calorimeter can stirrer was connected by a rubber belt to a similar wheel (J) attached to the stirrer shaft (E) in the reaction vessel.

Three legs on the base of the vessel fixed its position on the pegs in the calorimeter can.

Glass reaction vessels

Reactions were performed in one of two Pyrex glass vessels, Fig. 5, which were of a similar design. The internal capacities of the two vessels were approximately 200 ml. and 400 ml. They were made from a length of Pyrex glass tubing by sealing one end and fusing into the other a B.34 Quickfit socket. To facilitate the breaking of glass ampoules in the reaction vessel at the commencement of a reaction, the base of the vessel was provided with five spikes. A combined stopper and stirrer guide for the reaction vessel was made from a B.34 Quickfit cone to which a piece of glass tubing (diam. 0.7 cm., length 11 cm.) had been joined.

A thin-walled ampoule, blown from glass tubing, was used to contain and separate one reactant from the other in the reaction vessel. The filled ampoule was fitted into a glass sheath attached to the end of the stirrer rod. A thin smear of Araldite adhesive produced a firm seal between ampoule and sheath.

The stirrer rod was made of glass (diam. 0.5 cm., length 35 cm.), at one end of which were fastened the stirrer blades. These blades were made of glass, for reactions involving large amounts of bromine, and of

rubber for reactions in which bromine was either absent or present only in small quantities. More efficient stirring could be achieved with the longer rubber stirrer blades, which could be folded when passing through the neck of the reaction vessel. This stirrer was driven at 60, 120, or 180 r.p.m. by a constant speed motor. The reaction time for slow reactions was shortened by using the fastest stirring speed (180 r.p.m.).

Temperature measuring system

The platinum resistance thermometer was of the nickel sheathed type (Cambridge No. C.654287). It had a fundamental interval of 9.8047. The thermometer was used in conjunction with a Smith's Difference Bridge (Cambridge, L.303552), and a Cambridge short period galvanometer. The thermometer resistance was therefore measured in a Wheatstone Bridge circuit, one arm of which consisted of the thermometer and a continuously variable resistance. With this arrangement the current through the instrument was the same at all temperatures. In this work a quick response, and adequate sensitivity, were essential in the galvanometer. Therefore an instrument having a period of 1.9 sec. and a deflection of 400 mm. at 1 metre for 1 μ amp. at maximum sensitivity (controlled by a Cambridge Universal Shunt) was used. This meant that a change of 0.00001 ohm in the resistance of the thermometer gave a deflection of 0.2 mm. on the scale.

Calibration

The energy equivalent, E_s (kcal./ohm) , of the calorimeter

system was determined by the dissipation of a measured amount of electrical energy through the calibration heater. The heater (101.00 ± 0.05 ohms) was constructed from manganin wire wound non-inductively on a mica sheet and encased in a thin oil-filled sheath. This heater was connected in series with a standard resistance of 1.0003 ohms, at 23° , and with a current supply. The current supply consisted of three banks, each of four, 40 amp. hr., 12v lead accumulators joined in series. The banks were connected in parallel to give a potential of 48v. In order to ensure that a steady current flowed through the heater the accumulators were discharged through a dummy heater for at least 2 hr. before a calibration experiment. The dummy heater consisted of a variable resistance adjusted to match the resistance of the calibration heater. The calibration heater was also connected by heavy copper leads (16 s.w.g., total length 4 yd., resistance 0.0298 ohm) to two standard resistances of 100.004 and $10,000.4$ ohms, joined in series. The circuit was similar to that described by Skinner, Sturtevant, and Sunner.⁸⁷ The current, i , flowing through, and the potential, e , across, the calibration heater were determined from the potentials across the 1 ohm and 100 ohm resistances, measured with a Pye precision vernier potentiometer capable of reading 0.00001 v, in conjunction with a cadmium cell (Pye and Co. Ltd.), having an e.m.f. of 1.01860 v at 20°C (temperature coefficient, -0.00004 volt per $^{\circ}\text{C}$).

The duration of current flow through the heater was measured by a transistorised Millisecond Stopclock, (type T.S.A.4, Venner

Electronics, Ltd.) to an accuracy of better than ± 0.01 sec.

The calorimeter can was filled with 2 l. of distilled water (combined weight, 3000 g.) and weighed to an accuracy of ± 0.05 g. using a precision balance capable of weighing up to 10 kg. Over a period of 8 hr. the loss of water, due to evaporation, from the can, when assembled in the adiabatic jacket was less than 0.5 g. i.e. $< 0.025\%$ of the total weight. The quantity of water used was sufficient to cover the reaction vessel to within 1 cm. from the top of its neck. The same amount of water was used throughout a given series of experiments.

The calorimeter can plus the standard amount of water was weighed and then positioned in the jacket well. The reaction vessel was then located on the pegs in the base of the calorimeter can. The lids of the calorimeter can and the jacket were then fitted into position. The leads to the calibration heater were passed through the appropriate hole as the lids were lowered. When the copper reaction vessel was in use the stirrer to the vessel was connected to the calorimeter can stirrer before the lids were fitted. In the case of the glass vessels the stirrer guide was passed through its holes in the lids as the lids were lowered. The stirrer motor, for the reaction vessel was clamped vertically above the stirrer guide and the stirrer rod was connected to the motor by a short length of rubber tubing. The platinum resistance thermometer, the two thermistors and the drive belt for the calorimeter stirrer were placed in position and the stirrer motors started. The adiabatic control circuit, together with the jacket water pump, were

then switched on. Finally, a steady flow of cold water was circulated through the cooling spiral in the jacket, and the leads from the calibration heater connected into the calibration circuit.

After the establishment of thermal equilibrium, resistance-time readings were taken every 2 min. over a period of 20 min. - the fore-period. Electrical energy was then dissipated during a heating period, and subsequently resistance-time readings were taken again every 2 min. for a further period of 20 min. - the after-period. The resistance-time readings taken during the fore and after-periods were expressed graphically.

The temperature of the calorimeter system normally rose during the fore and after-periods because the heat of stirring was greater than the heat losses to the cooling coil and to evaporation through apertures in the lids. This heat of stirring resulted mainly from friction between stirrer guide and stirrer rod. It was minimised by lubricating the stirrer rod with grease. Ideally, the slopes of the resistance-time graph over the fore and after-periods should be the same, indicating a steady rate of heating due to stirring. Generally, this situation was attained. In all experiments these slopes were always in the same sense and were never greater than 0.00010 ohm/2 min. During any one experiment the resistance-time slopes during the fore and after-periods never differed by more than 0.00003 ohm/2 min. Equilibrium between the reaction vessel and its contents and the water in the can was generally attained within the

first 10 minutes of the after-period.

The change in resistance, ΔR , of the platinum resistance thermometer was obtained from the resistance-time graph by extrapolating the fore and after-periods of the graph to the mid-point of the heating period. The resistance change during calibration was arranged to be as near as possible to the change in resistance occurring during a reaction.

The energy equivalent of the calorimeter system was then calculated as follows. The potential drop, e , across the calibration heater, was given by

$$e = \frac{10,100}{100} V_2 = 101 V_2$$

where V_2 was the potential across the 100 ohm standard resistance. The current through the 1 ohm resistance was equivalent to V_1 , the potential across this resistance. The current, i , passing through the calibration heater, was given by

$$i = V_1 - \frac{V_2}{100} = V_1 - 0.01 V_2.$$

The total heat, Q (kcal.), evolved during the dissipation of electrical energy was given by,

$$Q = \frac{(e) \times (i) \times (\text{heating time})}{J \times 10^{-3}}$$

Since calibration was normally performed after a reaction, the temperature of the system prior to calibration was in the range

25.0°C to 25.5°C. Table 1 shows the values obtained for the energy equivalent at three different temperatures. These values indicated that, within the experimental error, the energy equivalent of the system was independent of temperature within the range 24 - 26°C. In these calibrations the glass reaction vessel was charged with carbon tetrachloride.

Table 1

Energy Equivalent, E_s (kcal./ohm)

Temp.	<u>24°C</u>	<u>25°C</u>	<u>26°C</u>
	23.760	23.706	23.756
	23.713	23.745	23.714
	23.722	23.750	23.702
	23.739	23.724	23.735
Mean E_s (kcal./ohm)	23.733 \pm 0.010	23.731 \pm 0.010	23.727 \pm 0.012
\overline{sE}_s	\pm 0.042%	\pm 0.042%	\pm 0.051%

Initially, the copper reaction vessel was charged with water, and the energy equivalent of the system was determined with the calibration heater placed (a) in the reaction vessel and (b) in the calorimeter can. The mean values of the two energy equivalents differed by only 0.015%. In all subsequent determinations of the energy equivalent the

calibration heater was placed in the calorimeter can for convenience.

Reaction procedure

The calorimeter system was set up as described under calibration, the reaction vessel being loaded with the relevant reactants. The calibration heater was used to bring the temperature of the system up to 24.98°C , which was equivalent to a resistance reading on the Smith's Difference Bridge of about 20.632 ohm. The calorimeter was then allowed to stand for a period of 90 min. in order to attain thermal equilibrium. During this period the heat generated by the stirrers raised the temperature of the system to $25.00 \pm 0.01^{\circ}\text{C}$.

After thermal equilibrium had been established, resistance-time readings were taken over a fore and after-period in the same way as for a calibration. During the reaction-period readings were taken as often as possible in order to follow the course of the reaction.

Reactions were initiated by depressing the stirrer rod, in the case of the glass reaction vessels, and the ampoule support rod, in the case of the copper reaction vessel, onto spikes in the base of the vessel. The resistance change, ΔR , in the resistance of the platinum resistance thermometer was evaluated from the resistance-time graph. This change in resistance was taken as the difference between resistance readings at the time corresponding to the commencement of the reaction-period, and the reading obtained from the extrapolation of the after-period to the same time. Similarity between the slopes of the fore and after-periods of the graph was attained within the limits described

under calibration.

The temperature rises produced by reactions ranged from 0.005°C for some heats of solution to 0.5°C for some heats of reaction.

The majority of the reactions studied were exothermic, When reactions were endothermic (e.g. reactions 3 and 4, Chapter VI) the rate of stirring in the reaction vessel was reduced. As a result the heat loss from the calorimeter system to the cooling coil and through the apertures in the lids, was greater than the heat of stirring, and the temperature of the system fell throughout the experiment. It was assumed that this procedure would give a more accurate measure of the heat of an endothermic reaction. Had this procedure not been adopted the temperature change due to the endothermic reaction would have been in the opposite sense to that in the fore and after-periods. The cooling coil, in the adiabatic jacket, allowed the temperature of the jacket to follow this fall in temperature of the calorimeter system.

The heat of the reaction, ΔH , was given by the expression

$$-\Delta H = \frac{E_s \times \Delta R \times \text{Molecular Weight of sample}}{\text{Wt. of sample}} \text{ kcal./mole}$$

The calorimeter was tested by measuring the heat of solution of tris(hydroxymethyl)aminomethane (THAM, sample D, supplied by Dr. I. Wadsö, University of Lund, Lund, Sweden) in 0.100 M HCl, to give a final solution of concentration 5 g./l. Five experiments gave $\Delta H = -7104 \pm 4 \text{ cal./mole}$ compared with the recommended value of $-7104 \pm 3 \text{ cal./mole}$.⁸⁸

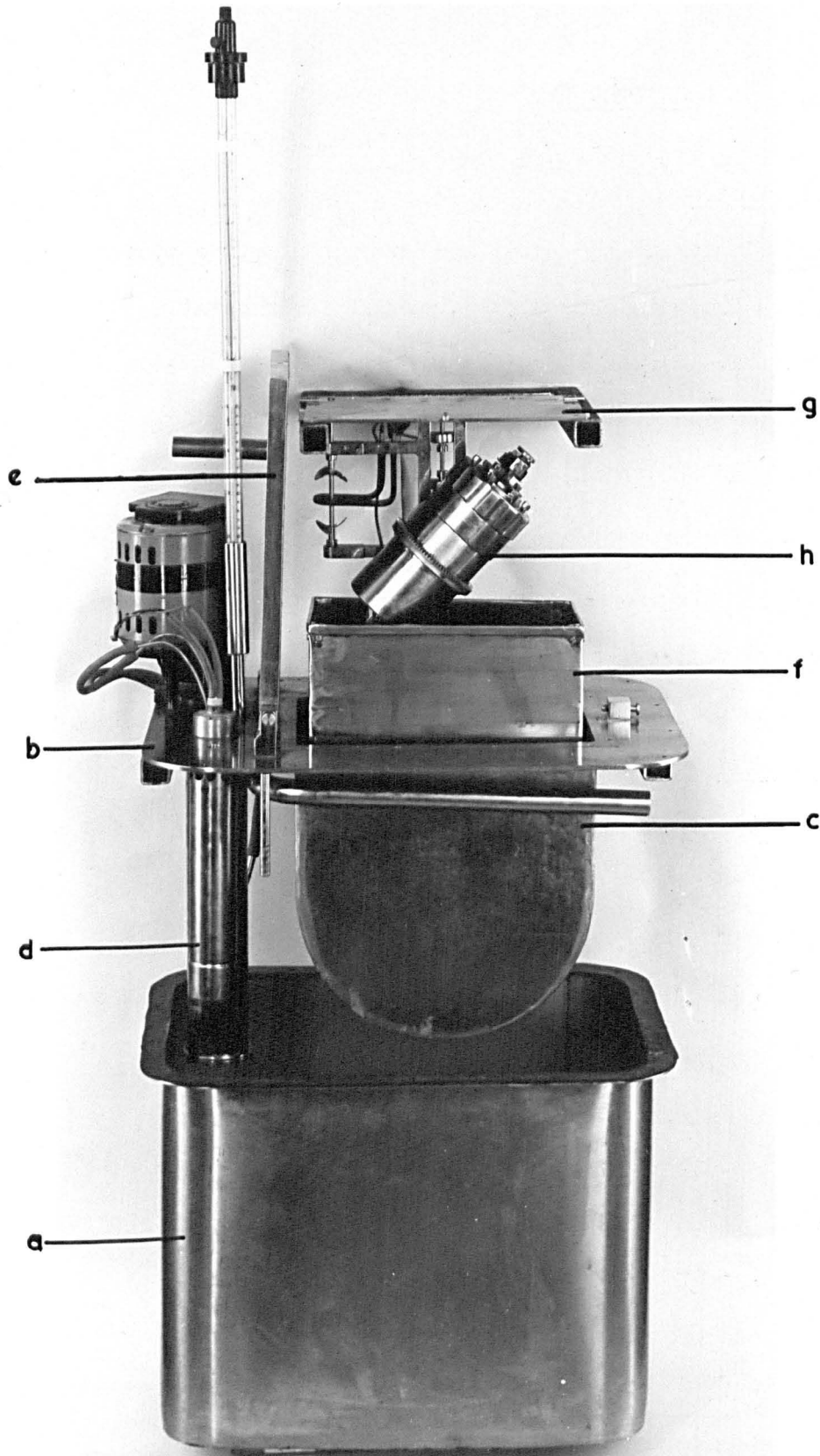


FIG.6

CHAPTER III

Rotating-Bomb Calorimeter

An "exploded" view of the rotating-bomb calorimetric system is shown in Fig. 6. The main components are, (a) thermostat can, (b) thermostat can lid, (c) the calorimeter can, (d) thermostating unit, (e) calorimeter can lid, (f) calorimeter vessel, (g) lid of calorimeter vessel, and (h) bomb.

Constant temperature jacket

(a) Thermostat can. This was constructed of high-grade, stainless steel plate (1 mm. thick), argon welded. There were no attachments to either the walls or the bottom of the can.

(b) Thermostat can lid. Stainless steel (4 mm. thick) of the same quality as that used in the construction of the can was used for the lid. Fourteen stainless steel nuts and bolts (4 mm. diam.) secured the lid to the can; a rubber gasket was placed between the surfaces.

The can was filled with water to within about 25 mm. from the top through an inspection hole in the lid.

(c) Calorimeter can (calorimeter well). The calorimeter can was made of welded, nickel-plated, copper plate (1.25 mm. thick). The can was fixed underneath the thermostat can lid, a 2 mm. rubber gasket being used to obtain a leakproof seal. Fitted to the inside wall of the can were three supports of reinforced phenolic resin from which the calorimeter vessel hung.

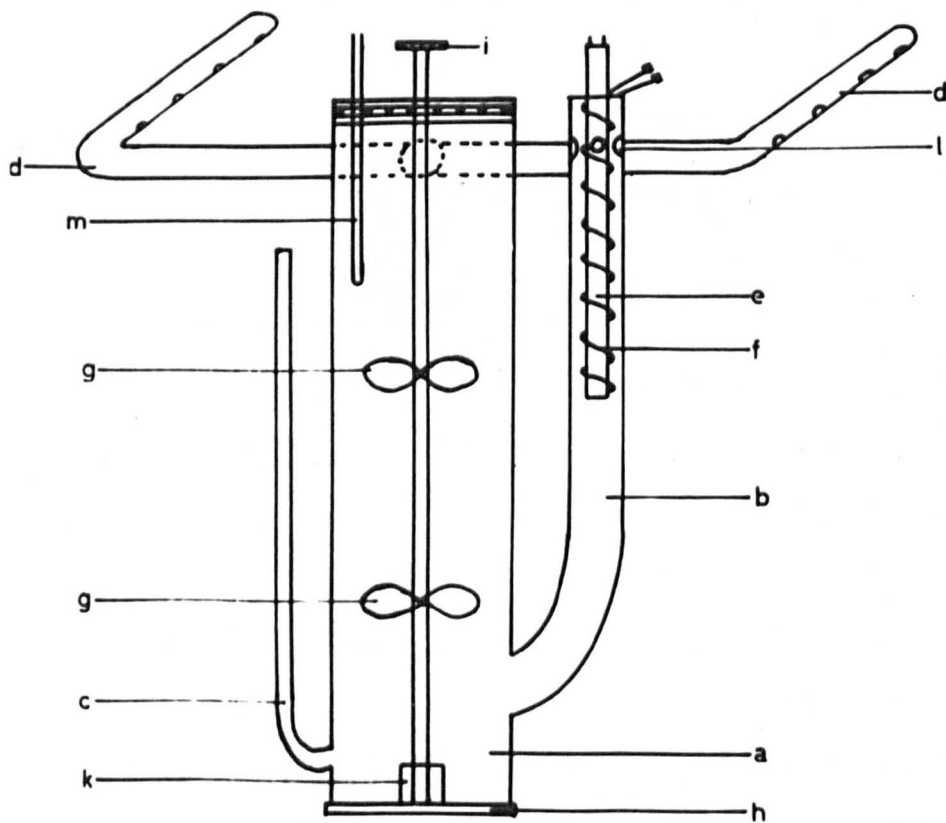


FIG. 7 Thermostatting Unit.

(d) Thermostatting unit. The thermostatting unit was placed at one end of the thermostat can and held in position, in the lid, by four screws. A diagrammatic representation of the unit is shown in Fig. 7. The unit consisted of a central vertical tube (a), to which two other vertical tubes (b and c) were attached, as well as a horizontal branched outlet tube (d). The two branches passed along each of the long sides of the calorimeter well.

A heater (e), around which a cooling coil (f) was wound was fitted inside tube (b). The heater and cooling coil constituted a separate unit which could be easily removed. The heater (650 watts) was enclosed in a straight, welded nickel tube. With a voltage of 30 - 50 v across the heater, the thermostat operated at 25 - 28°C. The particular voltage used depended on the rate of flow and temperature of the water passing through the cooling coil, room temperature, etc.

The main, central, tube (a) also accommodated a stirrer with two propellers (g), and, at the bottom, a centrifugal pump (h). The stirrer was fitted with a cogged wheel (i) at the top of its shaft and was driven by a geared motor mounted on the top of the thermostat can. The stirrer shaft was supported at the top by a ball-race (j) and at its base by a slide-bearing (k) of nylon.

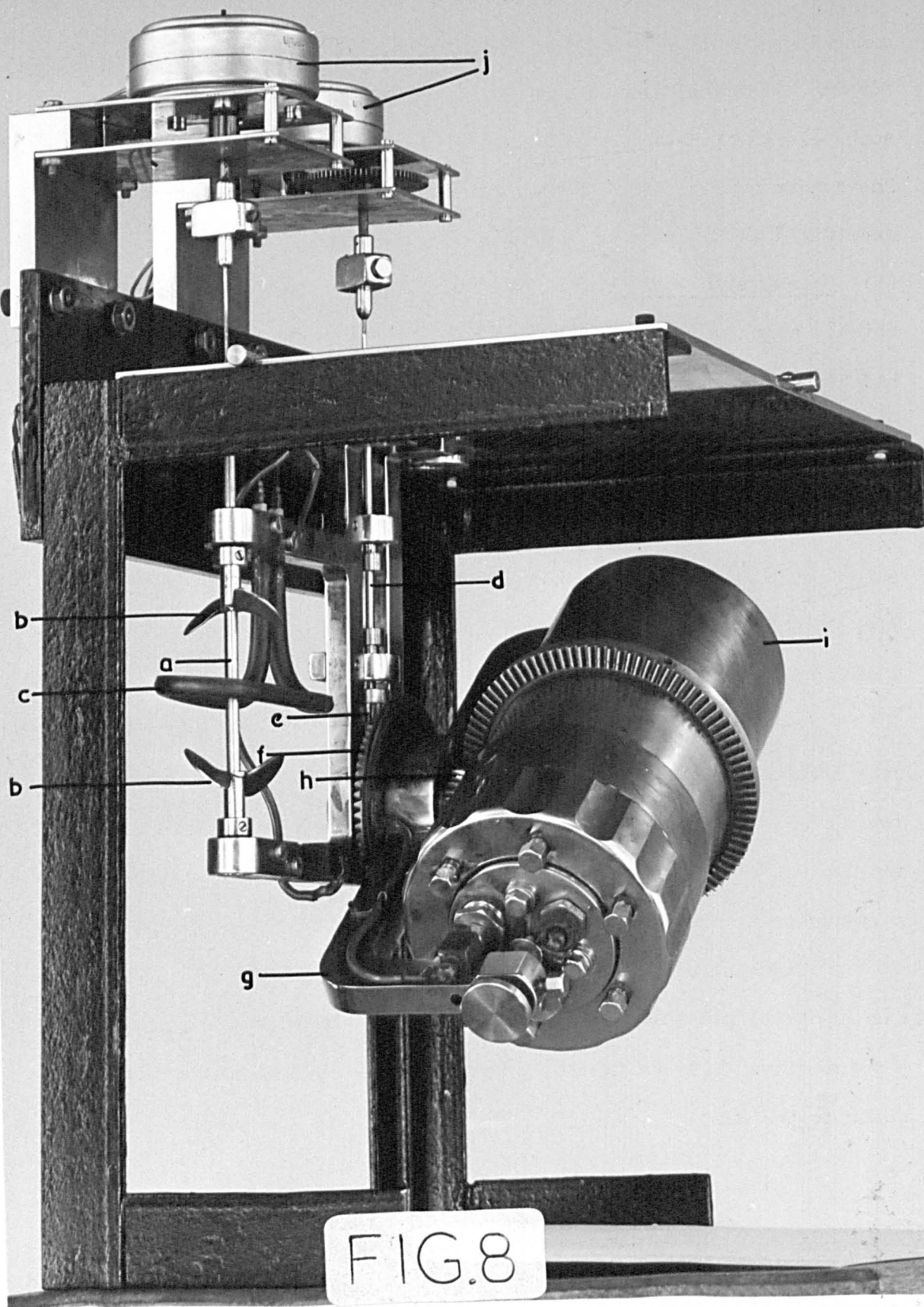
Water entered the unit through holes (l) in tube (b) and passed around the heating rod and into the central tube. From here the water passed up into the branched outlet tubes, each of which had a number of holes drilled on the underside, through which the water was forced.

Efficient circulation of water was obtained by this method. Water was also pumped through the narrow tube (c) into the lid of the calorimeter can.

The bulb of a Shandon, mercury-contact thermometer (m) was situated in the central tube. This activated a Sunvic, electronic relay that controlled the heater. By adjusting the voltage on the heater and the flow rate of water through the cooling coil, the on/off times (as indicated by a signal lamp) could be made equal and about 15 sec. The temperature variations in any one part in the thermostat were about $\pm 0.001^{\circ}\text{C}$ and between different places in the bath less than 0.002°C . To attain these conditions the stirrer was operated at 950 - 1000 r.p.m..

(e) Calorimeter can lid. This was made by soldering a top and a bottom plate of brass onto a framework of brass (12 mm. square). A central partition wall divided the lid into two halves. Two hinges at one end held the lid in position and also acted as the inlet and outlet for the circulating water. Two 9.3 mm. x 2.6 mm. rubber O-rings provided efficient seals at the hinges. Two lock pins enabled the lid to be held in a closed or open position. The lid, hinges and lock pins were nickel plated. A good seal was achieved between the lid and the thermostat can by fitting a chamois leather gasket.

Four holes in the lid accommodated the platinum resistance thermometer, the shafts of the bomb rotation and calorimeter stirrer motors, and the plug for the electrical connections to the bomb. The



hole for the resistance thermometer was threaded and equipped with a brass extension tube to support the thermometer. The three-pin plastic plug for the electrical connections to the bomb engaged a corresponding socket in the lid of the calorimeter vessel when the lid was closed. The synchronous motors for bomb rotation and for calorimeter stirring were fixed to the side of the lid.

(f) Calorimeter vessel. This was manufactured from plate (1.25 mm. thick), argon welded, nickel plated and highly polished. The vessel had brass adaptors at each corner to which the lid was secured with screws.

(g) Lid of calorimeter vessel. The lid was made of nickel-plated brass and was highly polished. The bomb rotation mechanism, the calorimeter heater, and stirrer were fixed to the underside of the lid. Fig. 8, shows the lid, with motors and bomb in position, mounted on a demonstration stand.

The stirrer, which was mounted in two stainless steel ball-races, consisted of a hollow shaft (a) fitted with two propellers (b). The top of the shaft, which protruded about 5 mm. above the surface of the lid was connected to a similar shaft from the stirrer motor by a self-centering crown clutch.

The manganin coil heater (12 v, 3 amp) in a strong copper sheath was so positioned that the heating coil encircled the stirrer shaft at a point midway between the two propellers. A transformer supplied the power to the heater.

The platinum resistance thermometer, used for temperature measurement of the calorimetric liquid, passed through a hole in the lid which was provided with a neoprene washer to ensure a firm fitting.

A plastic socket, for the electrical connections to the bomb, was screwed into the lid and held three metal connections, one to the heater, one to the ignition system, and one to earth.

Three short, steel bars which protruded from the lid fitted snugly into the phenolic resin supports when the calorimeter was in position. By this means, the calorimeter vessel hung inside the well and was separated from the walls of the well by a constant air space of 1.0 cm.⁸⁹

Bomb rotation mechanism.

The rotation mechanism, Fig. 8, was attached to the underside of the calorimeter lid, supported by stainless steel blocks.

The drive shaft (d) was mounted in two stainless steel ball-races. The upper end of the shaft passed through the lid, protruding about 3 mm., and was connected to the similar shaft of the rotation motor by a self-centering crown clutch.

At its lower end, the shaft was attached to a small mitred gear (e). This gear engaged a larger gear (f) which drove a yoke (g) mounted on a large stainless steel ball-race. A fixed horizontal shaft passed through the centre of this ball-race, ending in a cog (h). The bomb (i) was mounted within the yoke by two pivots at ends of the arms of the yoke. The two pivots, which had stainless steel ball bearings

at their ends to reduce friction, fitted into two centered indentations in either end of the bomb.

The rotation device gave the bomb a twofold rotation; the motor drove the shaft and mitred gear which in turn drove the yoke, giving the bomb an end-over-end rotation. As the bomb rotated, the gear ring, mounted around it, engaged the stationary cog (h), causing the bomb to rotate about its longitudinal axis. The ratio of end-over-end to longitudinal motion was 4:1.

The synchronous motors (j) for driving the calorimeter stirrer and the bomb rotation were manufactured by AEG (No. SSLK 375, 220 v, 50 cycles, 4 watts, 375 r.p.m.). Motors of low torque were chosen so that if the supports were wrongly adjusted and the shafts not central the resulting friction caused the motors to stop. The rotation motor was geared to give ca. 47 r.p.m.

The shafts of the motors were made of stainless steel rod, and were equipped at their ends with self-centering crown clutches for coupling into the corresponding clutches in the lid of the calorimeter. The shafts were carried in sliding sleeves, fitted with spring loaded catches, by which the positions of the shafts were fixed on the main drive shaft of the motors. The clutches were engaged by sliding the sleeves down to the lower position.

Bomb ignition system

A wire, from a connection in the plastic socket fixed in the lid of the calorimeter vessel, ran down the supports for the rotation

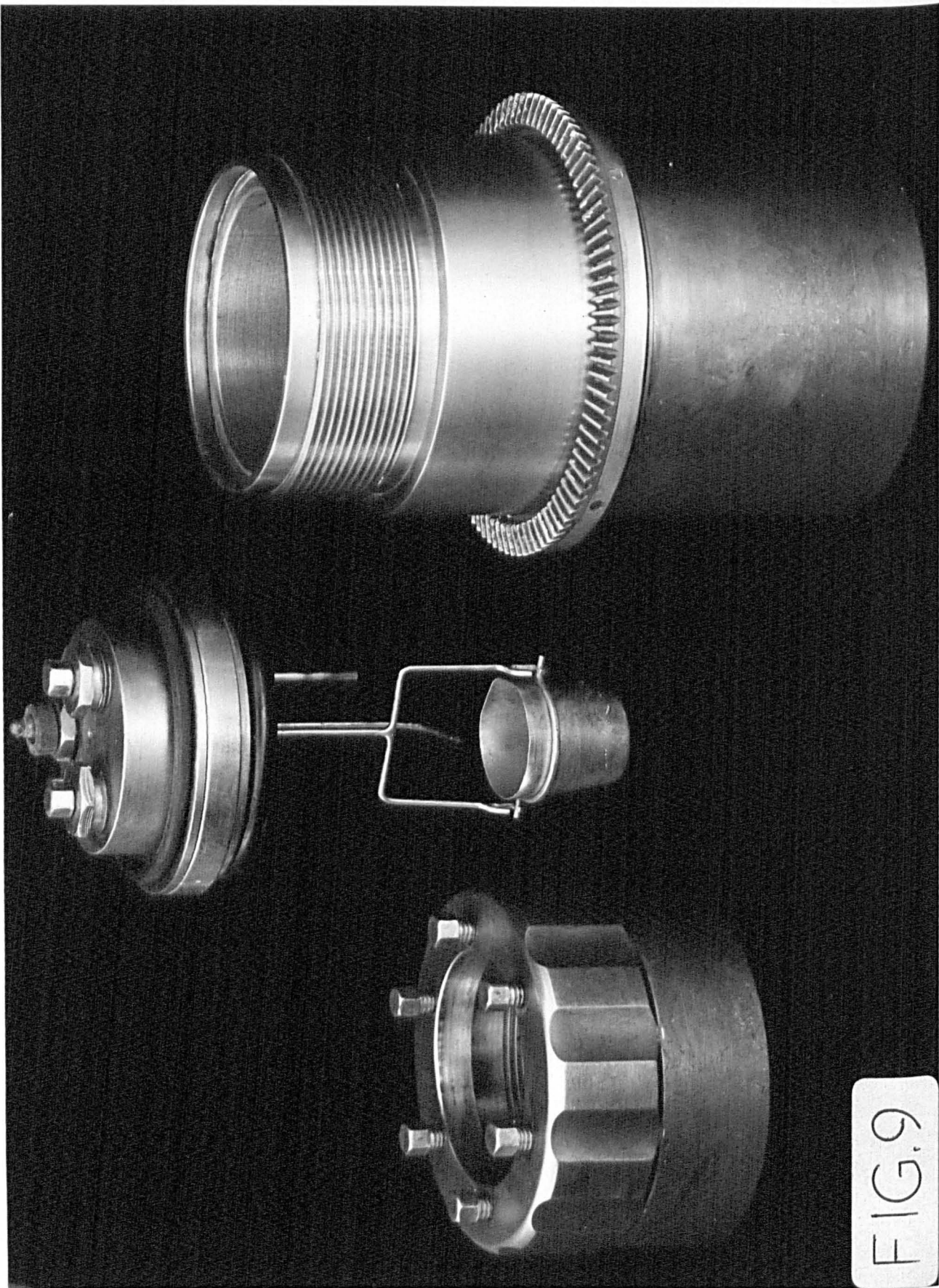


FIG. 9

system to a steel pointer. This pointer was held in contact with a brass ring fitted in the centre of the yoke. The ring was insulated from the yoke by a tufnol gasket. Another wire was led from this ring down one arm of the yoke to a steel strip (20 mm. x 3 mm.) mounted on a tufnol block. When the bomb was placed in the yoke, it was so positioned that a steel cap on top of the ignition electrode of the bomb made good contact with this steel strip.

Power to the ignition circuit was supplied by a transformer giving 12 v at 6 amp.

Bomb

The bomb was of conventional three-part type and Fig. 9 shows from left to right; the sealing sleeve, the bomb head with crucible, and the body of the bomb.

The inner surface of the body and the underside of the head were coated with a thin (0.20 mm.) layer of platinum to protect the surfaces from corrosion by combustion products. The internal volume of the bomb was 0.261 l.

The head was fitted with two platinum tubes (only one shown in Fig. 9), the longer one projecting about 20 mm. into the bomb, when the head was in position. These tubes were for gas inlet and outlet and were hard soldered to the bomb head before deposition of platinum on the surface of the head.

A platinum electrode, used for ignition of the sample, passed through the head into the bomb, and was insulated from the head by a

P.T.F.E. plug. A spring was fitted over this electrode and connected to a steel cap, which protruded from the head. The spring and cap were insulated from the head by a tufnol plug, which fitted inside a screw holding the ignition electrode in position.

A hole was tapped in the centre of the underside of the head and a plug was screwed into this hole. The crucible holder, which can be seen in Fig. 9, fitted into the plug and was held in position by a screw, passing through the side of the plug. From a horizontal cross-bar at the end of the central support, two vertical rods projected downwards, each terminating in a hook. The crucible ring was supported by these hooks. All these parts were of platinum/ruthenium alloy. The platinum combustion crucible sat loosely in the ring.

The bomb could be inverted so that the crucible and ring rotated smoothly, without disturbing the contents of the crucible.

At the top of the body of the bomb, there was a rim in which fitted a neoprene O-ring gasket, such that when the head was placed on top of the body a good seal was obtained.

The outside of the top of the body was threaded to take the sealing sleeve which screwed down over the head onto the body. The upper side of the head was protected by a loose steel ring onto which the screws of the sleeves clamped, and held the head firmly against the neoprene gasket. A large gear ring was fitted round the outside of the bomb.

The gas flow to and from the bomb was controlled by two valves.

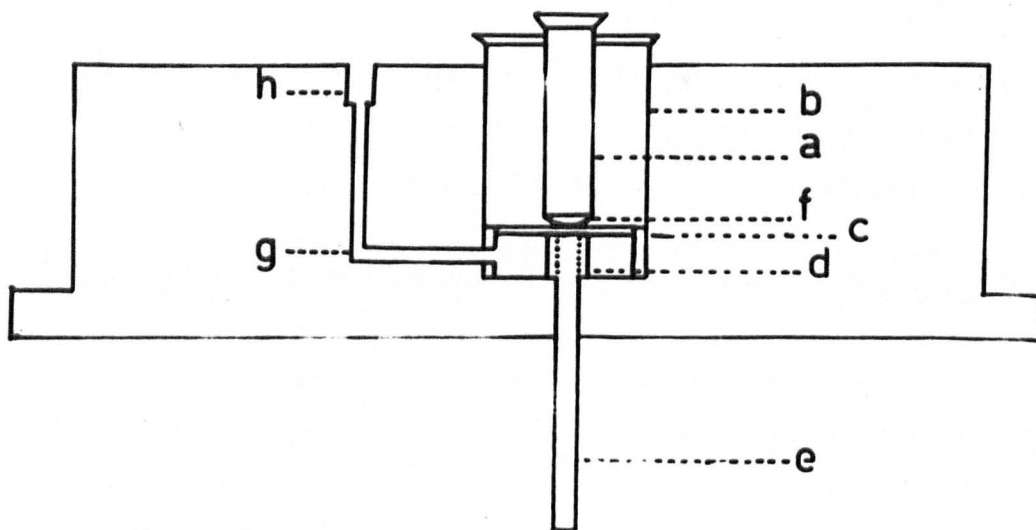


FIG. 10

Diagram of a bomb valve

The valves were of the same type as high pressure commercial valves, and a diagram of their construction is shown in Fig. 10. By use of a screw (a) which passed through a large central screw (b), a P.T.F.E. gasket (c) was pressed against a seat (d) in which the platinum tube (e) carrying the gas ended. In order to obtain a uniform pressure, the screw did not press directly on the gasket but on a hemispherical steel knob (f) which in turn pressed on the gasket. Only moderate tightening of the valve was necessary to ensure a good seal. With this type of valve the only part to wear out was the P.T.F.E. gasket which was easily replaced.

The gas supply to the valve came via a horizontal channel (g) in the bomb head leading from a threaded hole (h) drilled in the top of the head. A brass connection screwed into this hole, and the oxygen supply line was coupled directly to this connection. The gas outlet was of similar construction. When the bomb was filled and the valves closed, the brass connection was removed and the two holes closed by screws and nylon gaskets.

Temperature measuring system.

This was identical to that described under Adiabatic Reaction Calorimeter.

Calibration.

The energy equivalent of the calorimeter system was determined by measuring the temperature rise produced by burning weighed samples of B.D.H. thermochemical standard benzoic acid (batch no. 760161) in

the bomb. The heat of combustion of the benzoic acid was accurately known by comparison with a measured quantity of electrical energy and was certified as 6319.1 ± 0.7 cal./g., standard deviation $\pm 0.01\%$. The benzoic acid was supplied and burned in pellet form, the pellets being weighed in the crucible to 0.01 mg., and a correction applied to obtain the weight in vacuum taking 1.32 g./ml. as the density of benzoic acid. The crucible was then placed in the support ring hanging under the bomb head.

Thin platinum wire (0.08 mm. diam.) was connected between the ignition electrode and the central rod of the crucible holder. At its mid-point was fastened a weighed cotton thread which was placed in contact with the sample in the crucible.

Water (0.78 ml.) was placed in the bomb and the bomb assembled. The gas-inlet of the bomb was connected to a cylinder of oxygen and air was removed from the bomb by flushing it with oxygen for 10 minutes. The gas-outlet valve of the bomb was then closed and the bomb filled with oxygen to a pressure of 30 ± 0.1 atmospheres, measured on a Budenberg gauge. The bomb was carefully inverted so that the crucible stayed in the support, and was fitted into the yoke of the rotating mechanism such that the ignition head was in contact with the ignition strip. The ignition circuit was checked with a test-meter.

The calorimeter vessel was polished, and water, heated to about 24.5°C , was added. The whole was weighed to ± 0.05 g., the weight (9000 g.) being the same for each experiment.

Immediately after weighing, the bomb was placed in the calorimeter vessel and the lid of the vessel fixed in position by four screws. The calorimeter was placed in the well of the thermostat. The calorimeter lid was closed, and the platinum resistance thermometer, ignition and heater connections, together with the stirrer and rotation motors were put in position. The calorimeter stirrer was started.

The calorimeter was heated until a bridge reading corresponding to 24.95°C was attained and then left to attain thermal equilibrium (about 20 min.). When equilibrium had been established resistance-time readings were taken every two minutes for the fore-period.

At time 20 mins. the charge was ignited by applying a 12 v potential (6 amp) to the ignition circuit. This caused rapid heating of the platinum to its melting point thereby igniting the cotton, which in turn fired the sample. The melting of the platinum being practically instantaneous (as shown by an ammeter in the ignition circuit) the ignition energy was assumed to be constant for each experiment and was not measured.

At time 21 min. the bomb rotation motor was switched on and the bomb rotated for 4 min.

For the first three minutes of the reaction-period the times were noted at which the temperature reached certain preselected values. With practice these values could be chosen so that the time intervals during the reaction-period were separated by approximately twelve to fifteen seconds.

GRAPH SHOWING TEMPERATURE AGAINST TIME
FOR A TYPICAL COMBUSTION

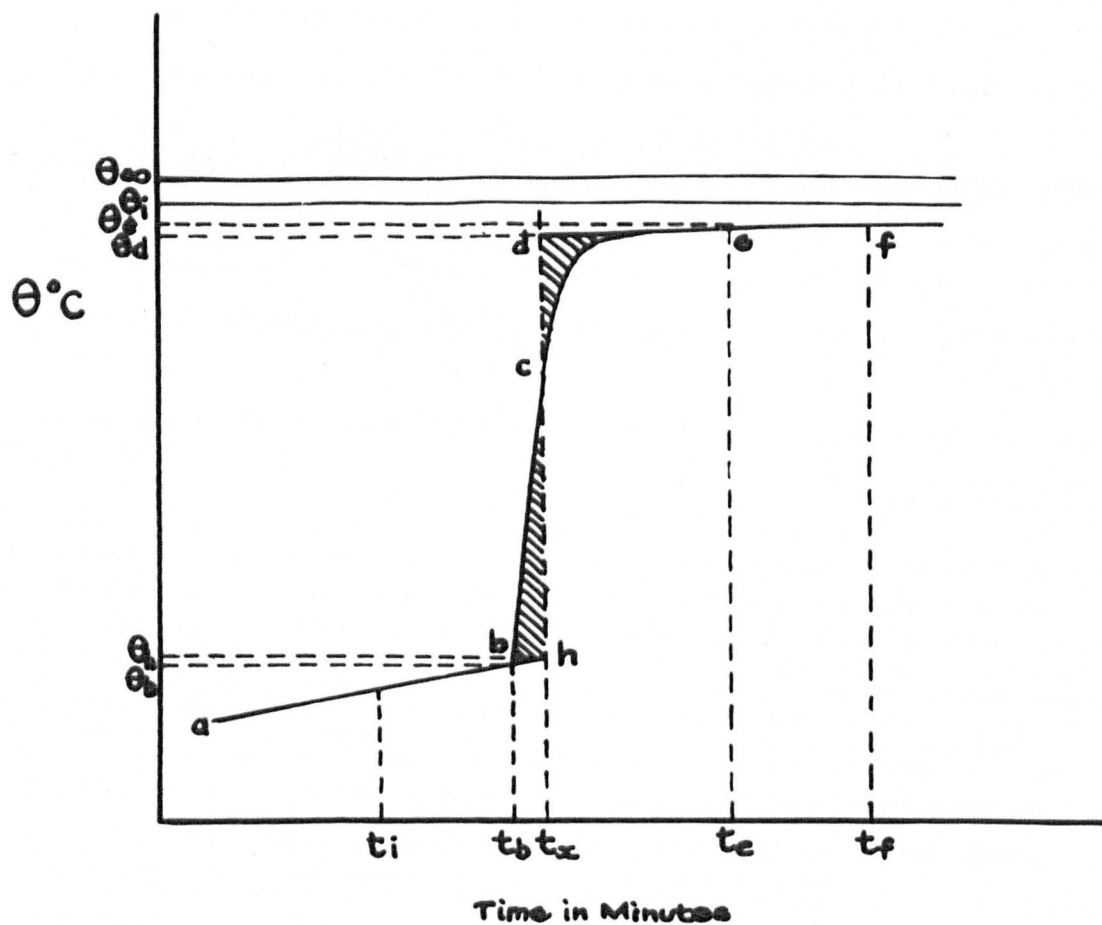


FIG. II

From 23 min. to 25 min. the resistance was read each half minute, and each minute from 25 min. to 36 min. During the after-period, which began at time 36 min., the resistance was read every 2 min. for a further 20 mins.

After dismantling the apparatus, the bomb gases were slowly released through the outlet valve, and the liquid in the bomb, plus the washings of all interior parts, was transferred to a volumetric flask to be analysed for nitric acid.

The energy equivalent of the system was then calculated from the corrected temperature rise and the mass of benzoic acid used and its known heat of combustion.

Calculation of the corrected temperature rise.

A combustion experiment may be divided into three parts: a fore-period of 20 mins. when the temperature change was due entirely to heat of stirring and thermal leakage; a reaction-period lasting 16 mins., when rapid temperature changes were produced by the combustion taking place in the bomb, the rate of temperature change falling off towards the end of this period as equilibrium was re-established; and an after-period of 20 mins. when heat of stirring and thermal leakage only were responsible for temperature changes.

A graph of temperature, θ , against time, t , Fig. 11, was plotted in order to calculate what proportion, $\Delta\theta$, of the observed temperature rise was due to thermal leakage and heat of stirring. Lines a - b and e - f correspond to the fore and after-periods, respectively.

The lines ab and fe are extrapolated to the points h and d at time t_x to determine $\Delta\theta$. This time was determined by the shape of the curve bce in the reaction-period. The time t_x was chosen such that the two shaded areas in the diagram were equal. It may be shown that when this condition applied, the temperature rise, $(\theta_d - \theta_h)$ is equal to the temperature rise which would have occurred if there had been no thermal leakage or heat of stirring. This was the corrected temperature rise, $\Delta\theta_{\text{corr.}}$.

Physically, this meant that if heat could have been put into the system at time t_x instantly and perfectly distributed at once, the temperature of the calorimeter would have followed the curve abcdef.

The method used here for determining t_x was proposed by Dickinson.¹⁶ It had the advantage of being less laborious, but may yield somewhat lower precision than other methods. A vertical component was constructed so that c cut the temperature-time curve at 63% of the observed temperature rise, $(\theta_b - \theta_e)$, and the time at which the temperature of the calorimeter reached this value was noted. Extrapolation of the after and fore-period curves to this time gave $\Delta\theta_{\text{corr.}}$.

The above method is adequate, but for higher precision the data are best treated by the Regnault-Pfaundler method.

The calculation can be carried out assuming that the rate, u , of the temperature rise of the calorimeter, due to heat of stirring, is constant, and that the thermal leakage is proportional to the difference between the temperatures of the jacket and calorimeter.

The total rate of temperature rise due to heat of stirring and thermal leakage is given by

$$\frac{d\theta}{dt} = u + k(\theta_j - \theta) \quad (1)$$

where k is the cooling constant of the calorimeter, θ_j , is the temperature of the jacket and θ is the temperature of the calorimeter.

Now, for the condition $\theta = \theta_\infty$, we have $\frac{d\theta}{dt} = 0$ and

$$\theta_j = \theta_\infty - \frac{u}{k}.$$

θ_∞ is the temperature the calorimeter would attain in an infinite time if θ_j and the rate of stirring remained constant.

Thus, from equation (1), we may write

$$\frac{d\theta}{dt} = k(\theta_\infty - \theta). \quad (2)$$

If R_i and R_f represent the values of $\frac{d\theta}{dt}$ at the mean temperature, θ_i and θ_f , of the fore and after-periods, then from equations (1) and (2)

$$k = \frac{R_i - R_f}{\theta_f - \theta_i} \quad (3)$$

and

$$u = R_f + k(\theta_f - \theta_j) \quad (4)$$

These calculated values of k and u should be virtually the same from

experiment to experiment and provide a useful check on the thermal reproducibility.

Integration of equation (2) yields

$$\begin{aligned}\Delta\theta &= -k \int_{t_b}^{t_e} (\theta_{\infty} - \theta) dt \\ &= -k(\theta_{\infty} - \theta_m)(t_e - t_b),\end{aligned}\tag{5}$$

where θ_m is the average temperature of the calorimeter wall in the reaction period. θ_m may be easily calculated. If $(n - 1)$ values of the temperature at equal time intervals are taken between $r = 2$ and $r = n - 1$, where $r = 1$ is t_b and $r = n$ is t_e , then

$$\begin{aligned}\theta_m &= \left\{ \sum_{r=2}^{n-1} \theta_r + \frac{\theta_b - \theta_e}{2} \right\} \frac{\Delta t}{t_e - t_b} \\ &= \frac{1}{n-1} \left\{ \sum_{r=2}^{n-1} \theta_r + \frac{\theta_b + \theta_e}{2} \right\}\end{aligned}\tag{6}$$

Thus, $\Delta\theta$ can be calculated from equation (5) and the corrected temperature rise is given by

$$\Delta\theta_{\text{corr.}} = (\theta_b - \theta_e) + \Delta\theta.\tag{7}$$

The energy equivalent of the calorimetric system

The energy equivalent, E , of a fixed calorimetric system is defined by the relation

$$E = \frac{Q}{\Delta\theta_{\text{corr.}}} \quad (8)$$

where Q is the heat added to the system, and $\Delta\theta_{\text{corr.}}$ is the corrected temperature rise of the system.

When the temperature rise is produced by combustion (or some other reaction), the situation is different. The calorimetric system is not fixed, since the reactants in the bomb are replaced by the products of the combustion reaction, so that, in general, the energy equivalent of the system changes. Also the combustion takes place over a range of temperature.

However, it may be shown⁹⁰ that the energy equivalent, E_i , of the fixed initial system, and the energy equivalent, E_f , of the fixed final system are given by

$$E_i = \frac{Q(\theta_e + \Delta\theta)}{\Delta\theta_{\text{corr.}}} \quad (9)$$

and

$$E_f = \frac{Q(\theta_b)}{\Delta\theta_{\text{corr.}}} \quad (10)$$

where Q_θ represents the quantity of heat which would have been evolved by the system if the reactions in the bomb had taken place at the

constant temperature θ . If m_s grams of benzoic acid were burned in the bomb then

$$E_i = \frac{m_s (-\Delta U_B(\theta_e + \Delta\theta)) + q_i + q_n}{\Delta\theta_{\text{corr.}}} \quad (11)$$

and

$$E_f = \frac{m_s (-\Delta U_B(\theta_b)) + q_i + q_n}{\Delta\theta_{\text{corr.}}} \quad (12)$$

where $-\Delta U_B(\theta)$ represents the heat of combustion, per gram of benzoic acid, at the temperature θ , and under the conditions of the actual bomb process; q_i is the energy used to ignite the charge, and q_n is the energy produced by the formation of nitric acid in the bomb.

When the heat of combustion of a compound is determined with a bomb calorimeter, neither E_i nor E_f can be applied directly. The material in the initial system will be other than benzoic acid, and the products of combustion in the final system will usually be different, and in different amounts from those when benzoic acid is burned. Thus, it is convenient to reduce the results of determinations of energy equivalent to the basis of a standard calorimeter system, which does not involve benzoic acid, or its products of combustion.

The standard calorimeter system may be defined arbitrarily in a number of different ways. For example, E_{si} , may be taken as the energy equivalent of the system with a specified mass of water in the calorimeter vessel, and with the bomb containing the firing fuse, and a specified quantity of oxygen, but no benzoic acid or other

combustible material. If E_i is the value of the energy equivalent of the initial system obtained in an experiment with benzoic acid, then the value, E_{si} , of the energy equivalent of the standard initial calorimeter system would be given by

$$E_{si} = E_i - E_{ci}, \quad (13)$$

where E_{ci} , would be calculated from the specific heat of benzoic acid and the mass used in the experiment, and the specific heats and differences in mass of any other materials present in different amounts than in the standard initial system.

Similarly, E_{sf} may be taken as the energy equivalent of the system with a specified quantity of water, the bomb containing only the crucible. Then, if E_f represents the energy equivalent of the final system as determined with benzoic acid, the energy equivalent of the standard final calorimetric system would be given by

$$E_{sf} = E_f - E_{cf}, \quad (14)$$

where E_{cf} would be calculated from the heat capacities of the oxygen, water, and carbon dioxide in the bomb at the end of the experiment with benzoic acid.

Combustion procedure

All the combustions were performed in the same manner as described for the calibration, each being initiated by a platinum wire, cotton thread, and an additional fuse of benzoic acid.

After a combustion, the corrected temperature rise was determined and used, in conjunction with the standard energy equivalent, to calculate the heat of the combustion process, ΔU_B . To derive ΔH_c° , the heat of combustion for the reaction under standard conditions, further corrections have to be applied. These result from the critical investigation into the actual bomb process and of the thermodynamics of the conditions existing in the bomb.

Corrections have to be applied to take account of the ancillary processes.

The heat evolved in the combustion of the cotton thread fuse was taken as 3.881 kcal./g.⁹⁰

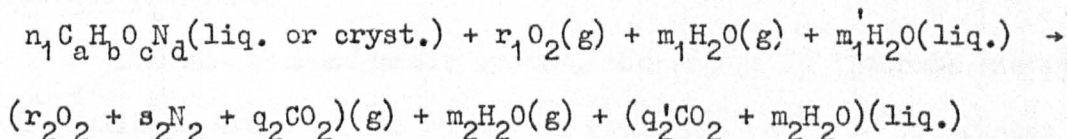
The amount of nitric acid, produced in the bomb by oxidation of nitrogen, present as impurity in the oxygen, was determined, for calibration experiments, by titration of the final bomb solution and washings against standard sodium hydroxide solution, using methyl orange indicator. The heat correction was then calculated using the value -13.81 kcal./mole⁹¹ for the heat of formation of 0.1N nitric acid from nitrogen and water. The nitric acid formed during the combustion of arsenic, in the presence of sodium hydroxide solution was completely neutralised by the sodium hydroxide solution on rotation. Therefore, the same oxygen supply was used for the calibration and combustion experiments. The mean correction, measured in the calibration experiments, was applied to all other combustion experiments.

Reduction to standard heat of combustion

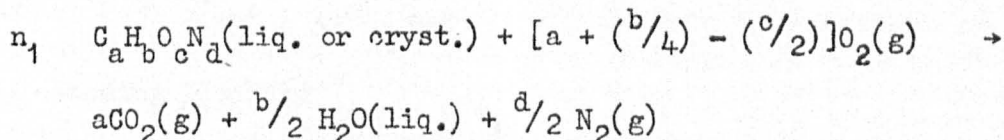
The heat evolved, $-\Delta U_B$, when the combustion of a substance takes place in the bomb calorimeter may differ significantly from the decrease in internal energy for the reaction under standard conditions $-\Delta U^\circ$. In 1933, this was pointed out by Washburn,⁹² who treated in detail the corrections to be applied to bomb calorimetric data, in order to obtain values of the standard change of internal energy. Such corrections are now termed "Washburn corrections".

Washburn's scheme applied to compounds which contained only carbon, hydrogen, and oxygen, but the treatment has been extended to include compounds which also contain sulphur,⁹³ nitrogen,⁹⁴ or one of the halogens.⁹⁵

For a compound $C_a H_b O_c N_d$, the process to which $-\Delta U_B$ refers, may be represented by the following equation, with all the reactants at pressure P_1 (water vapour at P_w) and temperature t_f , and all the products at a pressure P_2 (water vapour at P_w') and temperature t_f :



The thermodynamic standard reaction to which $-\Delta U^\circ$ refers may be written



with all the reactants and products in their thermodynamic standard states at temperature t_f .

The main quantities which must be calculated to obtain the difference between $-\Delta U^\circ$ and $-\Delta U_B$ are:

- (i) the change in energy of r_1 moles of oxygen from 0 atm. to P_1 atm;
- (ii) the change in energy of a mixture r_2 moles of oxygen from P_2 atm. to 0 atm. (plus that of s_2 moles of nitrogen, and q_2 moles of carbon dioxide);
- (iii) the energy of condensation of $(m_2 - m_1)$ moles of water;
- (iv) the energy of vaporisation of q'_2 moles of carbon dioxide from m'_2 moles of water.

In the combustion experiments reported in this thesis only items (i) and (ii) were calculated.

Correction to constant pressure

The value $-\Delta U^\circ$ obtained is the heat of combustion at constant volume, and it is necessary to convert this to an enthalpy value at constant pressure.

For any thermodynamic system, the change in internal energy, $-\Delta U^\circ$, will be equal to the change in enthalpy, $-\Delta H^\circ$, of the system less any work performed by the system. If the system is at constant pressure we may write

$$\Delta U^\circ = \Delta H^\circ - P\Delta V$$

or, assuming ideality

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$

$$\text{i.e. } \Delta H^\circ = \Delta U^\circ + \Delta nRT.$$

where Δn represents the change in the number of moles of gas present in the initial and final states.

Symbols and Units

In the subsequent chapters equations and tables are numbered for the individual chapter and not consecutively throughout.

Heat quantities are given in units of the thermochemical calorie, 1 cal. = 4.184 abs.J. exactly. The atomic weights used are those recommended by the International Union in 1961.⁹⁶ All heats of formation and reaction quoted from other sources have been recalculated, where necessary, in terms of these atomic weights. Weights used were calibrated against N.P.L. standards.

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

$$\bar{s} = \pm \sqrt{\frac{\sum(\bar{x} - x)^2}{n(n-1)}},$$

where x refers to an individual result. The standard deviation, expressed as a percentage of the mean value, is given by $(\frac{\bar{s}}{\bar{x}}) 100\%$. The uncertainty interval, within which future determinations, in other laboratories, of the same value may be expected to lie, is defined as $\pm 2\bar{s}$. When an "overall" standard deviation, \bar{s}' , was required, for example, in the combination of different heats of reaction, the value \bar{s}' was obtained from the expression, $\bar{s}' = (\bar{s}_1^2 + \bar{s}_2^2 + \dots)$, where \bar{s}_1 , \bar{s}_2 , ..., represent individual standard deviations.

The symbols used in the tables contained in Chapters IV, V, and VI have the following meanings:

$m(g)$ = mass of sample, in vacuo;

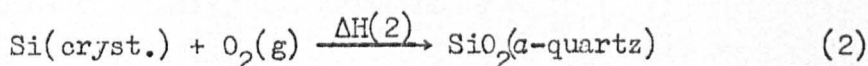
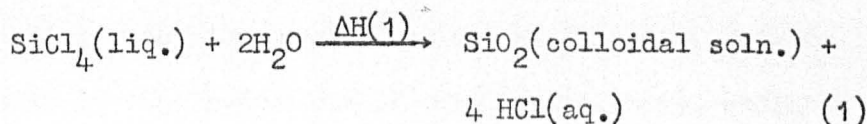
$\Delta R(\text{ohm})$ = change in resistance of the platinum resistance thermometer
proportional to the temperature rise;

$E_s(\text{kcal./ohm})$ = calibration constant.

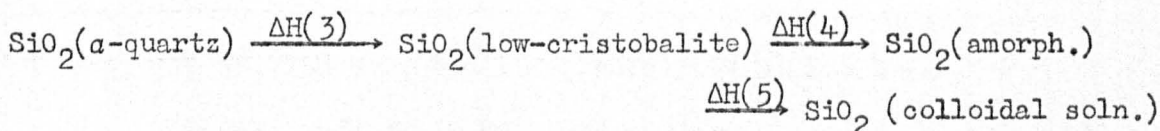
Other symbols, which are used, are defined in the appropriate
places in the text.

Hydrolysis of Silicon Tetrachloride

The currently accepted value for the heat of formation of silicon tetrachloride is based on measurements of the heats of the reactions:

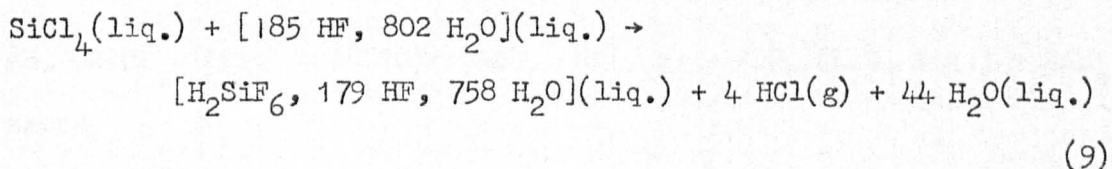
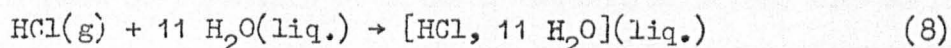
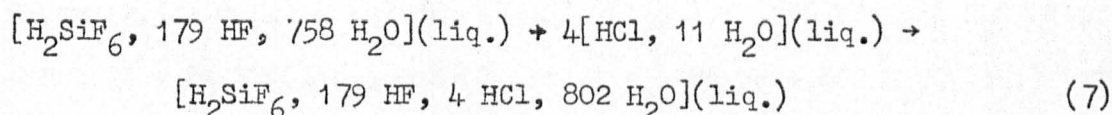
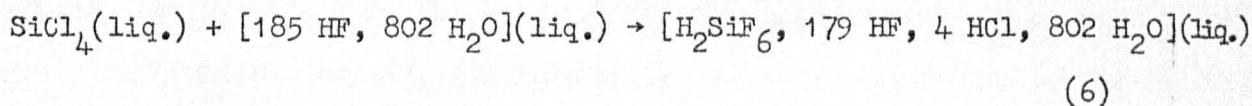


and on the heats of the transformations



The heat of hydrolysis, $\Delta H(1) = -70.11 \pm 0.15$ kcal./mole, was measured by Roth and Schwartz,⁹⁷ and confirmed by Chernick (reported by Flitercroft and Skinner⁹⁸). The heat of oxidation of silicon to α -quartz, $\Delta H(2)$, was measured by two independent methods as -217.75 ± 0.32 kcal./mole²⁵ and -217.5 ± 0.5 kcal./mole,³⁸ the mean value being -217.63 ± 0.32 kcal./mole. $\Delta H(3)$ and $\Delta H(4)$ were measured by Coughlin⁹⁹ and by Humphrey and King,²³ as $+0.35 \pm 0.55$ and $+1.19 \pm 0.05$ kcal./mole, respectively. The heat of transformation of amorphous silica to a colloidal solution is less certain, as the final state is not well defined. However, Thiessen and Koerner¹⁰⁰ measured the heats of hydration of amorphous silica to a number of distinct hydrates, including

$\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, $2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, and $\text{SiO}_2 \cdot \text{H}_2\text{O}$. The heats lie in the range -1.2 to -1.5 kcal./mole SiO_2 . It seems likely, therefore, that -1.5 kcal./mole is a minimum value for $\Delta H(5)$. Taking these values for $\Delta H(1)$ to $\Delta H(5)$, and the heats of formation: $\text{H}_2\text{O}(\text{liq.}) = 68.3149 \pm 0.0096$ kcal./mole,⁶³ and $\text{HCl}(\text{aq.}) = -40.02$ kcal./mole,^{66(a)} the heat of formation $\Delta H_f^\circ(\text{SiCl}_4, \text{liq.})$ is calculated to be -170.9 ± 0.7 kcal./mole. A more direct determination using the heat of reaction, $\Delta H(6)$, of silicon tetrachloride with aqueous hydrofluoric acid (reaction 6), which is well-defined thermochemically has been measured.

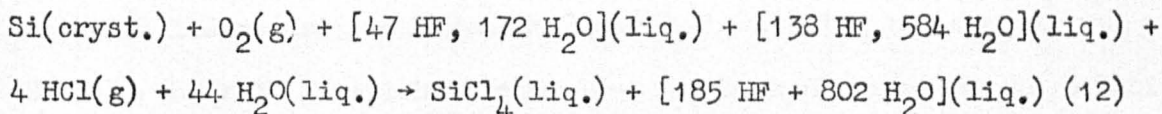
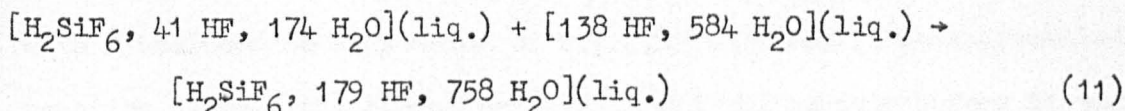
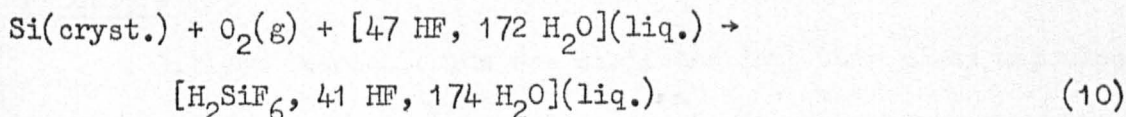


The heat, $\Delta H(7)$, of mixing an aqueous solution of hydrochloric acid with an aqueous solution of fluorosilicic acid and hydrofluoric acid (reaction 7) has also been measured. These data, together with the well-established heat of solution, $\Delta H(8) = 16.72 \pm 0.01$ kcal./mole^{66(a)} (reaction 8) make it possible to calculate the heat of reaction (9), from the relationship

$$\Delta H(9) = \Delta H(6) - \Delta H(7) - 4\Delta H(8).$$

Good³⁸ measured the heat, $\Delta H(10) = -250.3 \pm 0.3$ kcal./mole, of reaction (10), so that with the additional heat, $\Delta H(11)$, of the dilution reaction (11), it is possible to calculate $\Delta H(12)$ from the relationship

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



The heat of formation of silicon tetrachloride can then be calculated from the expression

$$\Delta H_f^\circ(\text{SiCl}_4, \text{liq.}) = \Delta H(12) + 4\Delta H_f^\circ(\text{HCl}, \text{g}) - 2\Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) + \Sigma \Delta H_s$$

where

$$\Sigma \Delta H_s = 47\Delta H_s[\text{HF in } 3.66 \text{ H}_2\text{O}](\text{liq.}) + 138\Delta H_s[\text{HF in } 4.24 \text{ H}_2\text{O}](\text{liq.}) - 185\Delta H_s[\text{HF in } 4.33 \text{ H}_2\text{O}](\text{liq.}).$$

The heats of formation, $\text{H}_2\text{O}(\text{liq.}) = -68.3149 \pm 0.0096$ ⁶³ and $\text{HCl}(\text{g}) = -22.061 \pm 0.01$,^{66(a)} and the heats of solution, $\text{HF}(\text{g})$ in $3.66 \text{ H}_2\text{O}$, -11.246 , $\text{HF}(\text{g})$ in $4.24 \text{ H}_2\text{O}$, -11.289 , and $\text{HF}(\text{g})$ in $4.33 \text{ H}_2\text{O}$, -11.293 kcal./mole^{66(a)} are also required. The calculated heat of formation of silicon

tetrachloride depends only on the heats of formation of liquid water and of gaseous hydrogen chloride, on the heats of solution of hydrogen chloride and hydrogen fluoride in water, and on the heats of reactions (6), (7), (10) and (11).

The heats of reactions (6) and (7) were measured in the adiabatic calorimeter using the copper reaction vessel.

Procedure

Silicon tetrachloride was distilled into thin glass ampoules on a vacuum line. The outside surfaces of the ampoules were coated with Flucalub-H (a suspension of P.T.F.E. in Freon). This prevented reaction between the hydrofluoric acid and the ampoule before it was broken. Independent measurements showed that, after the ampoule was broken, the rate at which it dissolved in the hydrofluoric acid solution was constant and slow. Correction for this heat was made by simply interpolating the rate of heating during the post reaction period to the time at which the ampoule was broken.

Reactions were initiated by breaking glass ampoules of silicon tetrachloride into a 20% solution of hydrofluoric acid (400 ml.). All reactions were performed in the rhodium-plated copper vessel.

Compounds

Silicon tetrachloride was supplied by B.D.H. Ltd., (redistilled). It was distilled, b.p. $57.5^{\circ}/748$ mm. (lit.¹⁰¹ $57^{\circ}/760$ mm.), a number of times through a 36 in. Fenske column in an atmosphere of oxygen free nitrogen. Hydrofluoric acid (40%) and hydrochloric acid (36%) were

supplied by B.D.H. Ltd., (AnalaR). They were diluted to the required concentrations before use.

Results

TABLE 1

SiCl_4 , M, 169.898

Experiment	1	2	3	4	5
m, (SiCl_4 , g.)	3.30250	4.79024	4.09586	5.10645	4.66000
ΔR (ohm)	0.07270	0.10555	0.09050	0.11335	0.10350
$-\Delta H$ kcal./mole	97.38	97.75	98.20	98.25	97.48

$$E_s = 26.038 \pm 0.013 \text{ kcal./ohm} \quad \text{Mean } \Delta H = -97.81 \pm 0.36 \text{ kcal./mole}$$

$$\overline{sE}_s = \pm 0.05\% \quad \overline{s\Delta H} = \pm 0.18\%$$

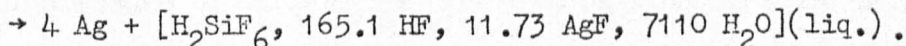
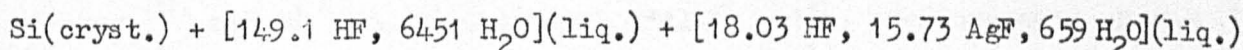
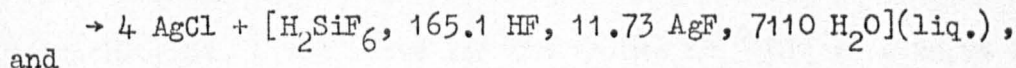
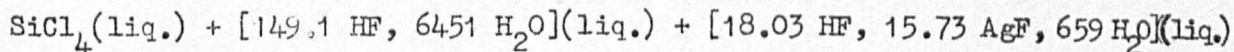
The heat of mixing of hydrochloric acid solution and an aqueous solution of fluorosilicic acid in hydrofluoric acid, $\Delta H(7)$, was measured as $+0.80 \pm 0.04$ kcal./mole. The errors $\overline{s\Delta H}(6)$ and $\overline{s\Delta H}(7)$, associated with the heats of these reactions, are twice the standard deviations of the mean values. The design of the calorimeter made it difficult to measure the heat of the dilution reaction (11). However, since the initial concentration of fluorosilicic acid in this reaction is already very low, the heat of dilution is likely to be very small and is neglected.

Discussion

Calculations using the values of $\Delta H(6)$ and $\Delta H(7)$ and other thermochemical data given above yield $\Delta H_f^\circ(\text{SiCl}_4, \text{liq.}) = -170.2 \pm 0.8$

kcal./mole. This value is close to that calculated from the heat of hydrolysis in aqueous solution, -170.9 ± 0.7 kcal./mole.

An entirely independent measurement of the heat of formation of SiCl_4 has been made by Schäfer and Heine.¹⁰² These workers measured the heats of the reactions,



This approach leads to a value for the heat of formation of SiCl_4 which is dependent only on the heat of formation $\Delta H_f^\circ(\text{AgCl, cryst.}) = -30.30$ kcal./mole.¹⁰³ This leads to the value $\Delta H_f^\circ(\text{SiCl}_4 \text{ liq.}) = -163.9$ kcal./mole. It was necessary to apply a number of corrections to the measured heats of reaction, so that these would refer to the reactions. In particular, it was found that in the reaction between SiCl_4 , HF, and AgF, there was a tendency for some HCl gas to be evolved, and also the precipitated AgCl trapped some unreacted SiCl_4 . In the reaction between Si, HF, and AgF, some hydrogen gas was evolved. Also the silicon contained about 0.3% of SiO_2 . Notwithstanding these difficulties the difference between the heat of formation obtained by Schäfer and Heine, and that reported in this thesis, is large.

Accepting the value $\Delta H_{\text{vap.}} = 7.0$ kcal./mole^{66(a)} for the heat

of vaporisation of silicon tetrachloride, the heat of formation

$\Delta H_f^\circ(\text{SiCl}_4, g) = -163.2 \pm 0.8 \text{ kcal./mole}$ is obtained.

The mean bond dissociation energy, $\bar{D}(\text{Si} - \text{Cl}) = 97.2 \pm 0.7 \text{ kcal./mole}$, can be calculated from the expression

$$\bar{D}(\text{Si} - \text{Cl}) = \frac{1}{4} \Delta H_f^\circ(\text{Si}, g) + \Delta H_f^\circ(\text{Cl}, g) - \frac{1}{4} \Delta H_f^\circ(\text{SiCl}_4, g)$$

This value is based on the heat of formation of gaseous silicon tetrachloride, given above and the values $\Delta H_f^\circ(\text{Cl}, g) = 28.94 \text{ kcal./g.-atom}$,¹⁰⁴ and $\Delta H_f^\circ(\text{Si}, g) = 110 \pm 2 \text{ kcal./g.-atom}$. Measurements of the vapour pressure of silicon and the dissociation pressure of silicon carbide¹ yielded values of 108.4 ± 3 and $112.6 \pm 3 \text{ kcal./g.-atom}$, respectively, for the heat of formation of gaseous silicon. The latter value also depends on a value for the heat of formation of silicon carbide of $-13 \pm 1 \text{ kcal./mole}$, which is in some doubt. However, until the discrepancy between the two values for the heat of formation of gaseous silicon is resolved, it is reasonable to take a mean value of $110 \pm 2 \text{ kcal./g.-atom}$.

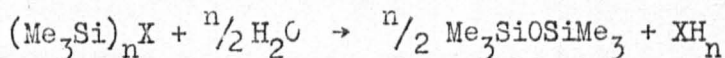
Steele, Nichols and Stone⁴ obtained the value $D(\text{Cl}_3\text{Si} - \text{Cl}) = 106 \pm 4 \text{ kcal./mole}$ from electron-impact data, for the dissociation energy of the first silicon - chlorine bond. From the expression

$$\Delta H_f^\circ(\text{SiCl}_3, g) = D(\text{Cl}_3\text{Si} - \text{Cl}) + \Delta H_f^\circ(\text{SiCl}_4, g) - \Delta H_f^\circ(\text{Cl}, g)$$

and the data given previously, the value $\Delta H_f^\circ(\text{SiCl}_3, g) = 86.1 \pm 4.8 \text{ kcal./mole}$ is calculated.

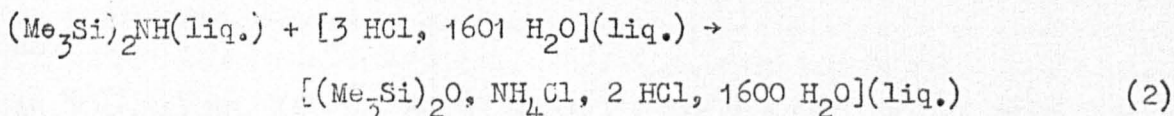
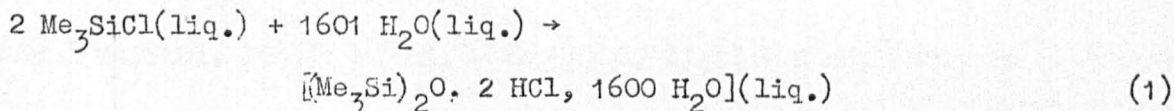
Hydrolysis of Trimethylchlorsilane and Hexamethyldisilazane

With the establishment⁴⁰ of the heat of formation of hexamethyldisiloxane, $(\text{Me}_3\text{Si})_2\text{O}$, it is possible to determine ΔH_f° values for compounds of the general formula $(\text{Me}_3\text{Si})_n\text{X}$ if the heat of the hydrolysis reaction

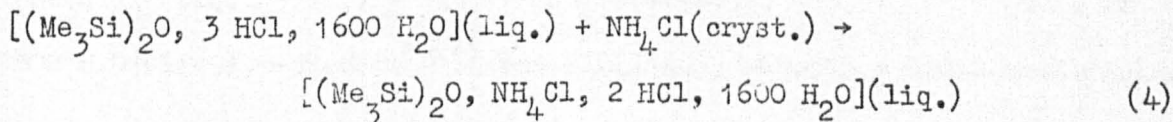
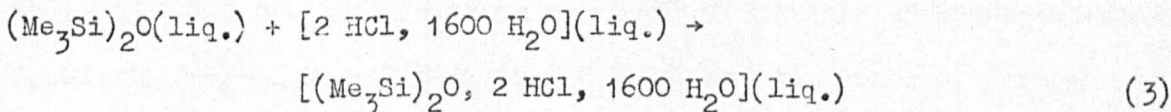


could be measured,

Both trimethylchlorsilane ($\text{X} = \text{Cl}$, $n = 1$) and hexamethyldisilazane ($\text{X} = \text{NH}$, $n = 2$) undergo hydrolysis of this type. The heats, $\Delta H(1)$ and $\Delta H(2)$, of the two reactions (1) and (2) were measured.



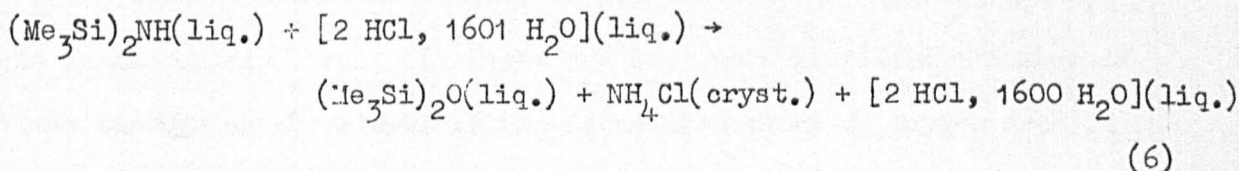
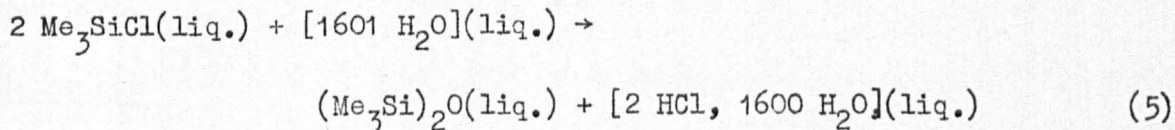
Two heats, $\Delta H(3)$ and $\Delta H(4)$, of solution (reactions 3 and 4) were also measured.



The heats, $\Delta H(5)$ and $\Delta H(6)$ of the idealised reactions (5) and (6) may then be calculated from the relations:

$$\Delta H(5) = \Delta H(1) - \Delta H(3); \text{ and}$$

$$\Delta H(6) = \Delta H(2) - \Delta H(3) - \Delta H(4).$$



The heats of formation of trimethylchlorsilane and hexamethyldisilazane may be derived from the following thermochemical relations;

$$\Delta H_f^\circ(\text{Me}_3\text{SiCl}, \text{liq.}) = \Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{O}, \text{liq.}] + 2 \Delta H_f^\circ[\text{HCl}, \text{in} \\ 800 \text{ H}_2\text{O}](\text{liq.}) - \Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) - \Delta H(5); \quad (7)$$

and

$$\Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{NH}, \text{liq.}] = \Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{O}, \text{liq.}] + \Delta H_f^\circ[\text{NH}_4\text{Cl}, \text{cryst.}] - \\ \Delta H_f^\circ[\text{HCl}, \text{in } 800 \text{ H}_2\text{O}](\text{liq.}) - \Delta H_f^\circ(\text{H}_2\text{O}, \text{liq.}) \\ - \Delta H(6) - \Delta H_d,$$

where $\Delta H_d = -0.054$ kcal./mole is the heat of dilution of hydrogen chloride $2[\text{HCl}, \text{in } \frac{1600}{3} \text{ H}_2\text{O}] \rightarrow 2[\text{HCl}, \text{in } 800 \text{ H}_2\text{O}]$; and the heats of formation: $(\text{Me}_3\text{Si})_2\text{O}(\text{liq.})$, -194.7 ± 1.3 ; 40 $\text{NH}_4\text{Cl}(\text{cryst.})$, -75.37 ; $^{66(a)}$ $[\text{HCl}, \text{in } 800 \text{ H}_2\text{O}](\text{liq.})$, -39.870 ; $^{66(a)}$ and $\text{H}_2\text{O}(\text{liq.})$, -68.315 ± 0.010 kcal./mole. 63

Procedure

Ampoules of trimethylchlorsilane and hexamethyldisilazane were broken into the appropriate solution to initiate reaction. Ampoules were filled with the relevant compound by distillation on a vacuum line. For both reactions the larger (400 ml.) glass reaction vessel was used.

Compounds

Trimethylchlorsilane (Hopkin and Williams, Ltd., pure grade) and hexamethyldisilazane (L. Light and Co.) were distilled a number of times through an 18" Fenske column in an atmosphere of oxygen-free nitrogen; b.p. $49.5^{\circ}/742$ mm. and $125.5^{\circ}/747$ mm. respectively (Lit. $57.3^{\circ}/760$ mm.¹⁰⁵ and $125.7 - 126.2^{\circ}/760$ mm.,¹⁰⁶ respectively). Hydrochloric acid (B.D.H., Ltd., AnalaR, 36%) was diluted to the required concentration before use.

Results

TABLE 1

Me_3SiCl M, 108.65

Experiment	1	2	3	4	5
m, (Me_3SiCl , g.)	2.49142	3.31605	3.60916	2.89255	2.82245
ΔH (ohm)	0.01001	0.01288	0.01438	0.01144	0.01111
E_s (kcal./ohm)	25.921	26.063	26.064	26.046	26.019
$-\Delta H$ (kcal./mole)	11.315	10.999	11.283	11.192	11.128

Mean $\Delta H = -11.18 \pm 0.06$ kcal./mole

$\bar{s}\Delta H = \pm 0.51\%$

TABLE 2

	(Me ₃ Si) ₂ NH M, 161.397					
Experiment	1	2	3	4	5	6
m[(Me ₃ Si) ₂ NH, g.]	2.62360	2.29795	3.18425	2.18954	2.19681	2.21713
ΔR(ohm)	0.02194	0.01911	0.02647	0.01815	0.01828	0.01843
-ΔH(kcal./mole)	34.671	34.478	34.465	34.368	34.499	34.464

$$E_s = 25.688 \pm 0.021 \text{ kcal./ohm} \quad \text{Mean } \Delta H = -34.49 \pm 0.04 \text{ kcal./mole}$$

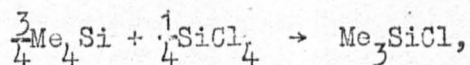
$$\overline{sE}_s = \pm 0.08\% \quad \overline{s\Delta H} = \pm 0.12\%$$

Reaction (3) was thermoneutral, and the heat, ΔH(4) of reaction (4) was measured as $+3.683 \pm 0.022$ kcal./mole.

Discussion

From equations (7) and (8) the following heats of formation are calculated, $\Delta H_f^\circ(\text{Me}_3\text{SiCl, liq.}) = -97.50 \pm 1.37$ kcal./mole, and $\Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{NH, liq.}] = -123.76 \pm 1.40$ kcal./mole. Incorporating the $\Delta H_{\text{vap.}}$ terms, $\Delta H_{\text{vap.}}(\text{Me}_3\text{SiCl}) = 7.22$ kcal./mole¹⁰⁵ and $\Delta H_{\text{vap.}}[(\text{Me}_3\text{Si})_2\text{NH}] = 9.9$ kcal./mole¹⁰⁷ then we calculate, $\Delta H_f^\circ(\text{Me}_3\text{SiCl, g}) = -90.28 \pm 1.37$ kcal./mole, and $\Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{NH, g}] = -113.86 \pm 1.40$ kcal./mole.

A value for D(Me₃Si - Cl) has not been determined experimentally. It is likely that D(Me₃Si - Cl) will be some 5 kcal./mole greater than D(Cl₃Si - Cl), since there is indirect evidence that the heat of the gas-phase redistribution reaction,



is in the region $\Delta H = -3$ to -7 kcal./mole. However, until this bond dissociation energy has been measured it seems reasonable to assume that $D(\text{Me}_3\text{Si} - \text{Cl}) = D(\text{Cl}_3\text{Si} - \text{Cl}) = 106 \pm 4$ kcal./mole,⁴ so that a lower limit for $\Delta H_f^\circ(\text{Me}_3\text{Si}, g) = -43.2 \pm 5$ kcal./mole may be calculated from the relation

$$\Delta H_f^\circ(\text{Me}_3\text{Si}, g) = D(\text{Me}_3\text{Si} - \text{Cl}) + \Delta H_f^\circ(\text{Me}_3\text{SiCl}, g) - \Delta H_f^\circ(\text{Cl}, g),$$

where $\Delta H_f^\circ(\text{Cl}, g) = 28.92 \pm 0.03$ kcal./g.-atom.¹⁰⁶

This in turn may be used to calculate $\bar{D}(\text{Si} - \text{N}) = 84.1$ kcal./mole for $(\text{Me}_3\text{Si})_2\text{NH}$ and $\bar{D}(\text{Si} - \text{O}) = 109.4$ kcal./mole for $(\text{Me}_3\text{Si})_2\text{O}$ from the following relations;

$$\bar{D}(\text{Si} - \text{N}) = \frac{1}{2} [\Delta H_f^\circ(\text{NH}, g) + 2 \Delta H_f^\circ(\text{Me}_3\text{Si}, g) - \Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{NH}, g]],$$

and

$$\bar{D}(\text{Si} - \text{O}) = \frac{1}{2} [\Delta H_f^\circ(\text{O}, g) + 2 \Delta H_f^\circ(\text{Me}_3\text{Si}, g) - \Delta H_f^\circ[(\text{Me}_3\text{Si})_2\text{O}, g]],$$

where $\Delta H_f^\circ(\text{NH}, g) = 81$,¹⁰⁹ $\Delta H_f^\circ(\text{O}, g) = 59.54$ kcal./g.-atom.¹⁰⁸

Table 4 gives the mean bond dissociation energies of some silicon compounds. The errors associated with these values do not include the uncertainties attached to the heats of formation of the radicals.

TABLE 3

(energy values in kcal./mole)

<u>Compound</u>	<u>$\Delta H_f^\circ(\text{liq.})$</u>	<u>$\Delta H_{\text{vap.}}$</u>	<u>$\Delta H_f^\circ(g)$</u>
SiH_4	-	-	$+7.3 \pm 0.3^{99}$
SiF_4	-	-	-386.0 ± 0.2^{110}
SiCl_4	-170.2 ± 0.8^{111}	$7.0^{66(a)}$	-163.2 ± 0.8
$(\text{Me}_3\text{Si})_2\text{O}$	-194.7 ± 1.3^{40}	8.92^{112}	-185.8 ± 1.3
$(\text{Me}_3\text{Si})_2\text{NH}$	-123.8 ± 1.4	9.9^{107}	-113.9 ± 1.4
$\text{Me}_3\text{Si}.\text{NEt}_2$	-76.2 ± 2.0^{113}	9.0^{113}	-67.2 ± 2.5
Et_4Si	-67.0 ± 1.0^{114}		
Si_2H_6	-	-	$+17.1 \pm 0.3^{29}$

TABLE 4

<u>Compound</u>	<u>Bond</u>	<u>$\bar{D}(\text{kcal./mole})$</u>
SiH_4	Si - H	49.1 ± 0.3
SiF_4	Si - F	142.5 ± 0.2
SiCl_4	Si - Cl	97.2 ± 0.3
$(\text{Me}_3\text{Si})_2\text{O}$	Si - O	109.4 ± 1.3
$(\text{Me}_3\text{Si})_2\text{NH}$	Si - N	84.1 ± 1.4
$\text{Me}_3\text{Si}.\text{NEt}_2$	Si - N	89.0 ± 2
Et_4Si	Si - Et	66.8 ± 4
Si_2H_6	Si - Si	81.3 ± 0.3

The following values were used in computing \bar{D} values;

$$\Delta H_f^\circ(\text{Si}, g) = 110 \pm 2; \Delta H_f^\circ(\text{H}, g) = 28.94;^{104} \Delta H_f^\circ(\text{F}, g) = 18.5 \text{ kcal./g.-atom.}^{104}$$

Pope and Skinner¹⁸ estimated $\bar{D}(\text{Si} - \text{Et})$ by comparing values of $\bar{D}(\text{M} - \text{Et})$ with $\bar{D}(\text{M} - \text{H})$ for $\text{M} = \text{C}, \text{Ge}, \text{Sn},$ and Pb , to be within the range 63 ± 4 kcal./mole. Heat of combustion measurements by Lautsch¹¹⁴ lead to $\Delta H_f^\circ(\text{Et}_4\text{Si}, \text{liq.}) = -67$ kcal./mole which corresponds to $\bar{D}(\text{Si} - \text{Et}) = 66.8$ kcal./mole, in fair agreement with expectation.

A value for $\Delta H_f^\circ(\text{NEt}_2, g) = 25 \pm 5$ kcal./mole was extrapolated from $\Delta H_f^\circ(\text{EtNH}, g) = 33 \pm 3$ kcal./mole¹¹⁵ by comparison with the series $\Delta H_f^\circ(\text{NH}_2, g) = 41 \pm 2$ kcal./mole^{115b} and $\Delta H_f^\circ(\text{MeNH}, g) = 37 \pm 3$ kcal./mole, and $\Delta H_f^\circ(\text{Me}_2\text{N}, g) = 34 \pm 3$ kcal./mole.¹¹⁵

The value $D(\text{H}_3\text{Si} - \text{H}) = 94 \pm 2$ kcal./mole⁴ may be used to derive $\Delta H_f^\circ(\text{SiH}_3, g) = 49.2$ kcal./mole from the relation

$$\Delta H_f^\circ(\text{SiH}_3, g) = D(\text{H}_3\text{Si} - \text{H}) + \Delta H_f^\circ(\text{SiH}_4, g) - \Delta H_f^\circ(\text{H}, g).$$

This value may be used to obtain the bond dissociation energy $D(\text{H}_3\text{Si} - \text{SiH}_3) = 81.3$ kcal./mole from the heat of formation $\Delta H_f^\circ(\text{Si}_2\text{H}_6, g) = +17.1 \pm 0.3$ kcal./mole,²⁹ using the expression

$$D(\text{H}_3\text{Si} - \text{SiH}_3) = 2\Delta H_f^\circ(\text{H}_3\text{Si}, g) - \Delta H_f^\circ(\text{Si}_2\text{H}_6, g).$$

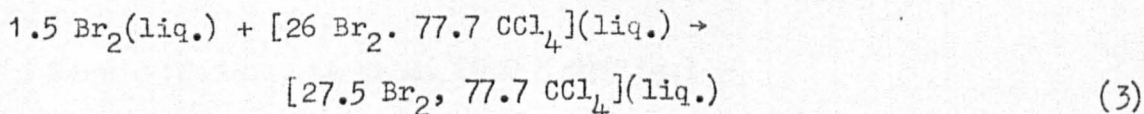
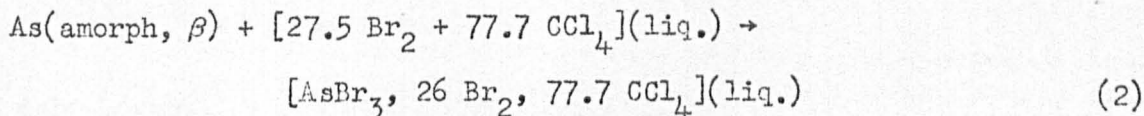
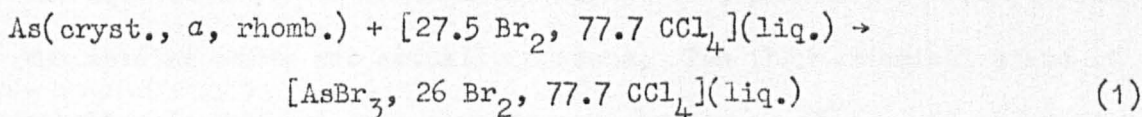
This value of $D(\text{H}_3\text{Si} - \text{SiH}_3) = 81.3$ kcal./mole may be compared with the value 82 kcal./mole¹¹⁶ obtained by Steele and Stone from electron impact data.

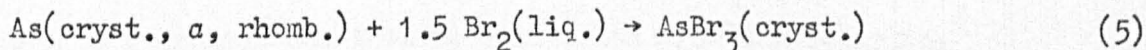
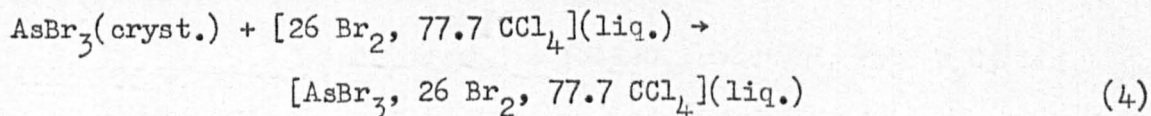
CHAPTER VI

Arsenic Tribromide, Arsenious and Arsenic Oxides and Aqueous Solutions of Sodium Arsenite and Sodium Arsenate.

Metallic arsenic dissolves in liquid bromine to give arsenic tribromide quantitatively.¹¹⁷ The reaction, which is almost explosive, may be moderated by dissolving the bromine in carbon tetrachloride, in which arsenic tribromide is also soluble. Measurement of the heat of this reaction, $\Delta H(1)$, together with the heats of solution of bromine and of arsenic tribromide, in a mixture of carbon tetrachloride and bromine, $\Delta H(3)$, and $\Delta H(4)$, respectively, yields the heat of reaction, $\Delta H(5)$ and the heat of formation of arsenic tribromide from the relation;

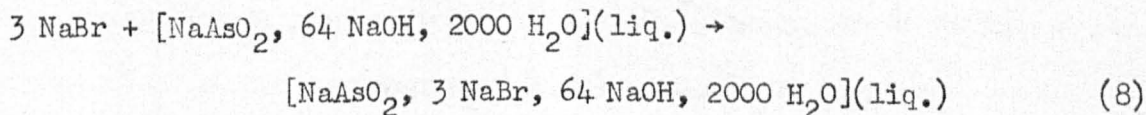
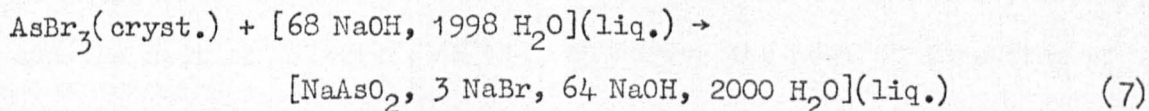
$$\Delta H_f^\circ(\text{AsBr}_3, \text{cryst.}) = \Delta H(5) = \Delta H(1) + \Delta H(3) - \Delta H(4).$$

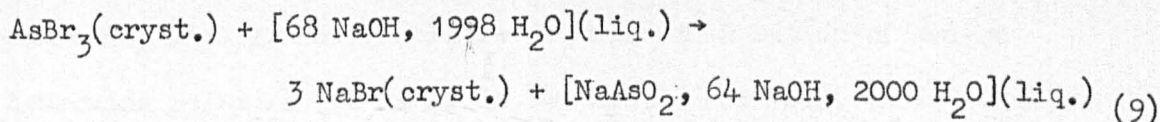




Measurement of the heat of reaction, $\Delta H(2)$, of amorphous arsenic in a solution of bromine in carbon tetrachloride, under the same conditions as those in reaction (1), yields the heat of transformation of crystalline to amorphous arsenic, $\Delta H(6) = \Delta H(1) - \Delta H(2)$.

The heat of hydrolysis of arsenic tribromide in sodium hydroxide solution, $\Delta H(7)$, and the heat of solution of sodium bromide in an aqueous solution of sodium arsenite and sodium hydroxide, $\Delta H(8)$, lead to the heat of reaction, $\Delta H(9)$, from the relation; $\Delta H(9) = \Delta H(7) - \Delta H(8)$. Use of the formula NaAsO_2 , to represent sodium arsenite in the aqueous solution is a purely formal one, and is not meant to indicate the species which are actually present. The thermochemical state of the solution is defined uniquely however, by the reactants and physical conditions.





The heat of formation of sodium arsenite in an aqueous solution of sodium hydroxide can then be calculated from the relation;

$$\Delta H_f^\circ[\text{NaAsO}_2, \text{ in } 64 \text{ NaOH}, 2000 \text{ H}_2\text{O}](\text{liq.}) = \Delta H(9) +$$

$$\Delta H_f^\circ(\text{AsBr}_3, \text{ cryst.}) - 3 \Delta H_f^\circ(\text{NaBr}, \text{ cryst.}) +$$

$$4 \Delta H_f^\circ[\text{NaOH}, \text{ in } 29.38 \text{ H}_2\text{O}](\text{liq.}) -$$

$$2 \Delta H_f^\circ(\text{H}_2\text{O}, \text{ liq.}) - \Delta H_d,$$

where $\Delta H_d = +0.45$ kcal./mole, is the heat of dilution of sodium hydroxide solution $[64 \text{ NaOH}, \text{ in } 1880 \text{ H}_2\text{O}] \rightarrow [64 \text{ NaOH}, \text{ in } 2000 \text{ H}_2\text{O}]$, and the heats of formation are; $[\text{NaOH}, \text{ in } 29.38 \text{ H}_2\text{O}](\text{liq.})$, -112.452 ± 0.006 ; ^{66(a)}, ¹¹⁸ $\text{H}_2\text{O}(\text{liq.})$, -68.3149 ± 0.0096 ^{66(a)} and $\text{NaBr}(\text{cryst.})$, -86.23 kcal./mole. The heat of formation of sodium bromide quoted here is 0.20 kcal./mole more negative than that given in reference ^{66(a)}, since the heat of formation of an aqueous solution of HBr , on which it is based, has been revised recently by this amount. ¹¹⁹

This thermochemical datum can then be used, in conjunction with the heat of reaction of arsenious oxide with sodium hydroxide, $\Delta H(10)$, and the heat of dilution, $\Delta H(11)$, to derive the heat of formation of arsenious oxide from the relation;

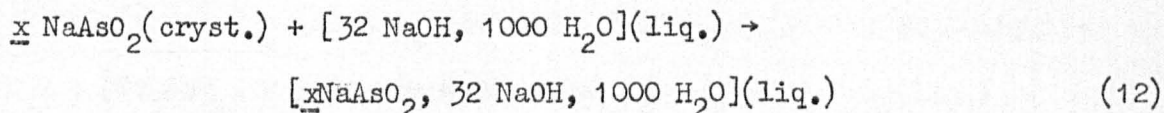
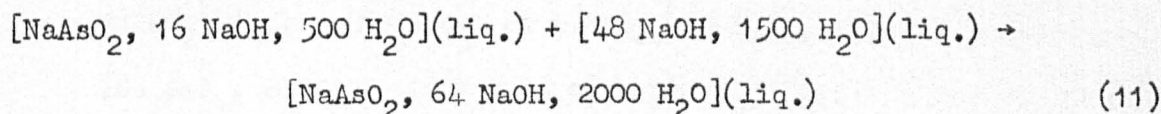
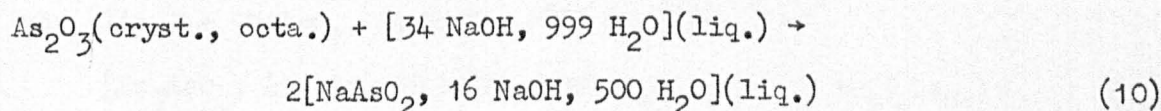
$$\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{ cryst., octa.}) = 2 \Delta H_f^\circ[\text{NaAsO}_2, \text{ in } 64 \text{ NaOH},$$

$$2000 \text{ H}_2\text{O}](\text{liq.}) + \Delta H_f^\circ(\text{H}_2\text{O}, \text{ liq.}) -$$

$$2 \Delta H_f^\circ[\text{NaOH}, \text{ in } 29.38 \text{ H}_2\text{O}](\text{liq.}) - \Delta H(10) +$$

$$2 \Delta H(11) + \Delta H_d,$$

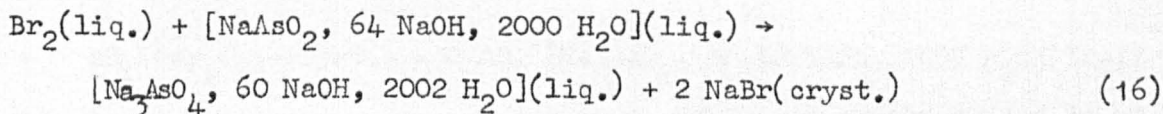
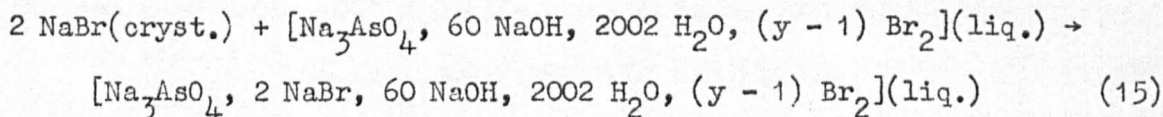
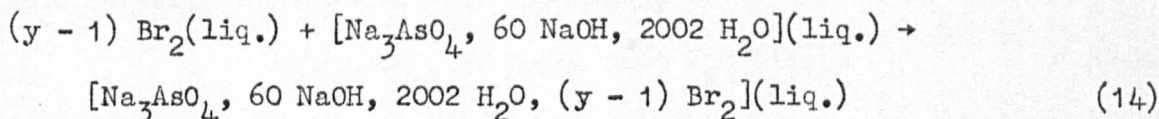
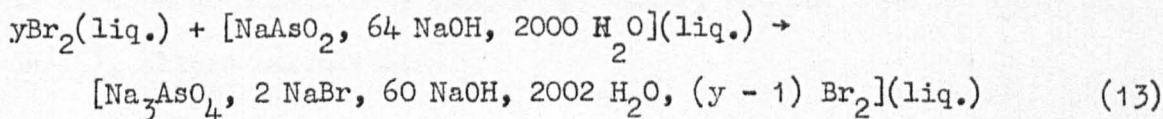
where $\Delta H_d = +0.22$ kcal./mole is the heat of dilution of sodium hydroxide solution $[32 \text{ NaOH, in } 940 \text{ H}_2\text{O}] \rightarrow [32 \text{ NaOH, in } 1000 \text{ H}_2\text{O}]$, and the heat of formation is; $[\text{NaOH, in } 29.38 \text{ H}_2\text{O}](\text{liq.}) - 112.452 \pm 0.006$ kcal./mole.^{66(a), 118}



Since the heat of reaction of arsenious oxide with sodium hydroxide solution (-12.03 kcal./mole) is so much less than that of arsenic tribromide (-62.69 kcal./mole), it was necessary to use larger quantities of the oxide to obtain a temperature rise which could be accurately measured. It was for this reason that the concentration of sodium arsenite in reaction (10) was four times greater than that in reaction (9). The heat of dilution, $\Delta H(11)$, was not measured. However, the heat of solution of sodium arsenite, $\Delta H(12)$, has been measured, where $\underline{x} = 0.5 - 1.0$. Within the limits of accuracy of the measurements, $\Delta H(12)$ is independent of \underline{x} , in this range. The heat, $\Delta H(11)$, is, therefore, likely to be small.

The heat of oxidation, $\Delta H(13)$, of a solution of sodium

arsenite to sodium arsenate, using an excess of liquid bromine, together with the heats of solution, $\Delta H(14)$ and $\Delta H(15)$, may be used to calculate the heat of the idealised reaction, $\Delta H(16)$, from the relation; $\Delta H(16) = \Delta H(13) - \Delta H(14) - \Delta H(15)$.



The heat of formation of sodium arsenate, in solution, may be calculated from the relation;

$$\Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{ in } 60 \text{ NaOH}, 2002 \text{ H}_2\text{O}](\text{liq.}) =$$

$$\Delta H_f^\circ[\text{NaAsO}_2, \text{ in } 64 \text{ NaOH}, 2000 \text{ H}_2\text{O}](\text{liq.}) -$$

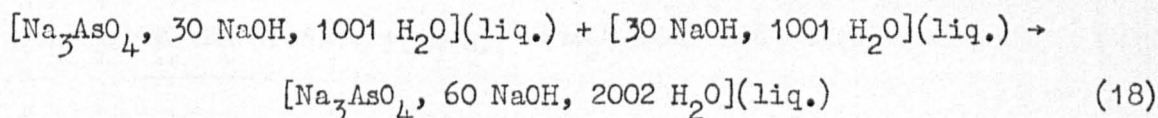
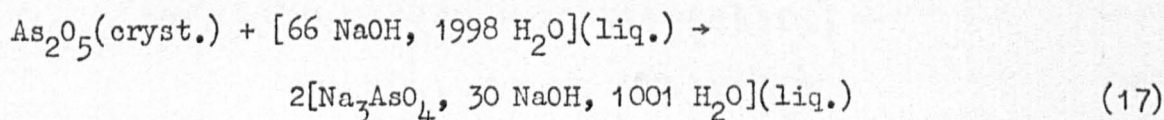
$$2 \Delta H_f^\circ(\text{H}_2\text{O}, \text{ liq.}) + 4 \Delta H_f^\circ[\text{NaOH}, \text{ in } 31.25 \text{ H}_2\text{O}](\text{liq.}) - 2 \Delta H_f^\circ(\text{NaBr}, \text{ cryst.}) +$$

$$\Delta H(16) - \Delta H_d,$$

where $\Delta H_d = +0.420 \text{ kcal./mole}$ is the heat of dilution of sodium

hydroxide solution $[60 \text{ NaOH, in } 1875 \text{ H}_2\text{O}] \rightarrow [60 \text{ NaOH, in } 2002 \text{ H}_2\text{O}]$, and the heat of formation is; $[\text{NaOH, in } 31.25 \text{ H}_2\text{O}](\text{liq.})$, $-112.446 \pm 0.006 \text{ kcal./mole.}$ ^{66(a),118}

Measurement of the heat of solution, $\Delta H(17)$, of arsenic oxide in an aqueous solution of sodium hydroxide, and the heat of dilution, $\Delta H(18)$, allows calculation



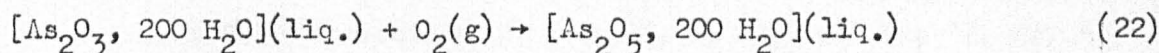
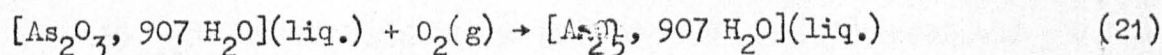
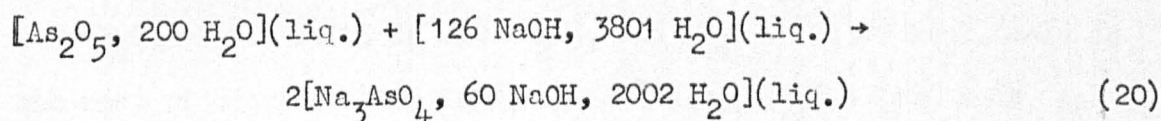
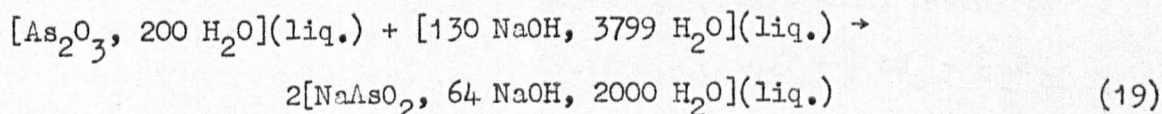
of the heat of formation of the oxide from the relation;

$$\begin{aligned} \Delta H_f^\circ(\text{As}_2\text{O}_5, \text{cryst.}) = & 2 \Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{ in } 60 \text{ NaOH, } 2002 \text{ H}_2\text{O}](\text{liq.}) \\ & + 3 \Delta H_f^\circ(\text{H}_2\text{O, liq.}) - 6 \Delta H_f^\circ[\text{NaOH, in } 30.27 \\ & \text{H}_2\text{O}](\text{liq.}) - \Delta H(17) - 2 \Delta H(18) + \Delta H_d, \end{aligned}$$

where $\Delta H_d = +0.48 \text{ kcal./mole}$ is the heat of dilution of sodium hydroxide solution $[60 \text{ NaOH, in } 1816 \text{ H}_2\text{O}] \rightarrow [60 \text{ NaOH, in } 2002 \text{ H}_2\text{O}]$, the heat of dilution, $\Delta H(18)$, is assumed to be negligible, and the heat of formation is $[\text{NaOH, in } 30.27 \text{ H}_2\text{O}](\text{liq.})$, $-112.450 \pm 0.006 \text{ kcal./mole.}$ ^{66(a), 118}

Finally, the heats of neutralisation, $\Delta H(19)$ and $\Delta H(20)$, were measured. The heat of the oxidation reaction, $\Delta H(21)$, has been given as $-76.6 \pm 0.2 \text{ kcal./mole.}$ ^{120,121} The arsenious oxide would be present as the virtually undissociated acid H_3AsO_3 , whilst the arsenic oxide would be present as two moles of the acid H_3AsO_4 , partially dissociated

to the ions H^+ and H_2AsO_4^- . Correction has been made for the heat of this ionisation, so that the value of $\Delta\text{H}(21)$ refers to an idealised reaction, in which the acids are completely associated.



Under the conditions in reaction (22) the arsenic would be about 24.3% ionised. The heat of ionisation of the first hydrogen atom of arsenic acid is -1.69 ± 0.04 kcal./mole,¹²² and if we assume that the heats of dilution of unionised arsenious and arsenic acids from the concentrations in reaction (21) to those in reaction (22) are the same, then we calculate $\Delta\text{H}(22) = -77.4 \pm 0.07$ kcal./mole, which refers to a reaction in which the arsenic acid is dissociated.

The difference between the heats of formation of sodium arsenate and sodium arsenite in solution can then be calculated from the relation;

$$\Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{ in } 60 \text{ NaOH, } 2002 \text{ H}_2\text{O}](\text{liq.}) - \Delta H_f^\circ[\text{NaAsO}_2 \text{ in } 64 \text{ NaOH, } 2000 \text{ H}_2\text{O}](\text{liq.}) = \frac{1}{2} \Delta H(20) + \frac{1}{2} \Delta H(22) - \frac{1}{2} \Delta H(19) - \Delta H_f^\circ(\text{H}_2\text{O, liq.}) + 3 \Delta H_f^\circ \text{NaOH, in } 30.17 \text{ H}_2\text{O}(\text{liq.}) - \Delta H_f^\circ[\text{NaOH, in } 29.22 \text{ H}_2\text{O}](\text{liq.}) + \frac{1}{2} \Delta H_d - \frac{1}{2} \Delta H_d',$$

where $\Delta H_d = + 0.78 \text{ kcal./mole}$ is the heat of dilution $[128 \text{ NaOH, in } 3470 \text{ H}_2\text{O}] \rightarrow [128 \text{ NaOH, in } 4000 \text{ H}_2\text{O}]$, and $\Delta H_d' = + 1.19 \text{ kcal./mole}$ is the heat of dilution $[120 \text{ NaOH, in } 3620 \text{ H}_2\text{O}](\text{liq.}) \rightarrow [120 \text{ NaOH, in } 4004 \text{ H}_2\text{O}]$, and the heats of formation are; $[\text{NaOH, in } 30.17 \text{ H}_2\text{O}]$, $-112.450 \pm 0.006 \text{ kcal./mole}$ and $[\text{NaOH, in } 29.22 \text{ H}_2\text{O}]$, $-112.452 \pm 0.006 \text{ kcal./mole}$.^{66(a), 118}

The heat of reactions (1 - 4, 7, 8, 10, 12 - 15, 17, 19, 20) have been measured. Details of these measurements are given in Tables 1 - 12.

Measurements of the heats of reactions 1, 2, 4, 12, 14, and 17 were made in collaboration with Mr. E. G. Tyler, B.A.

Procedure

Reactions were initiated by breaking glass ampoules of reactant into the relevant solution. The smaller reaction vessel, capacity 200 ml., was used for reactions (1 - 4). All other reactions were performed in the larger reaction vessel.

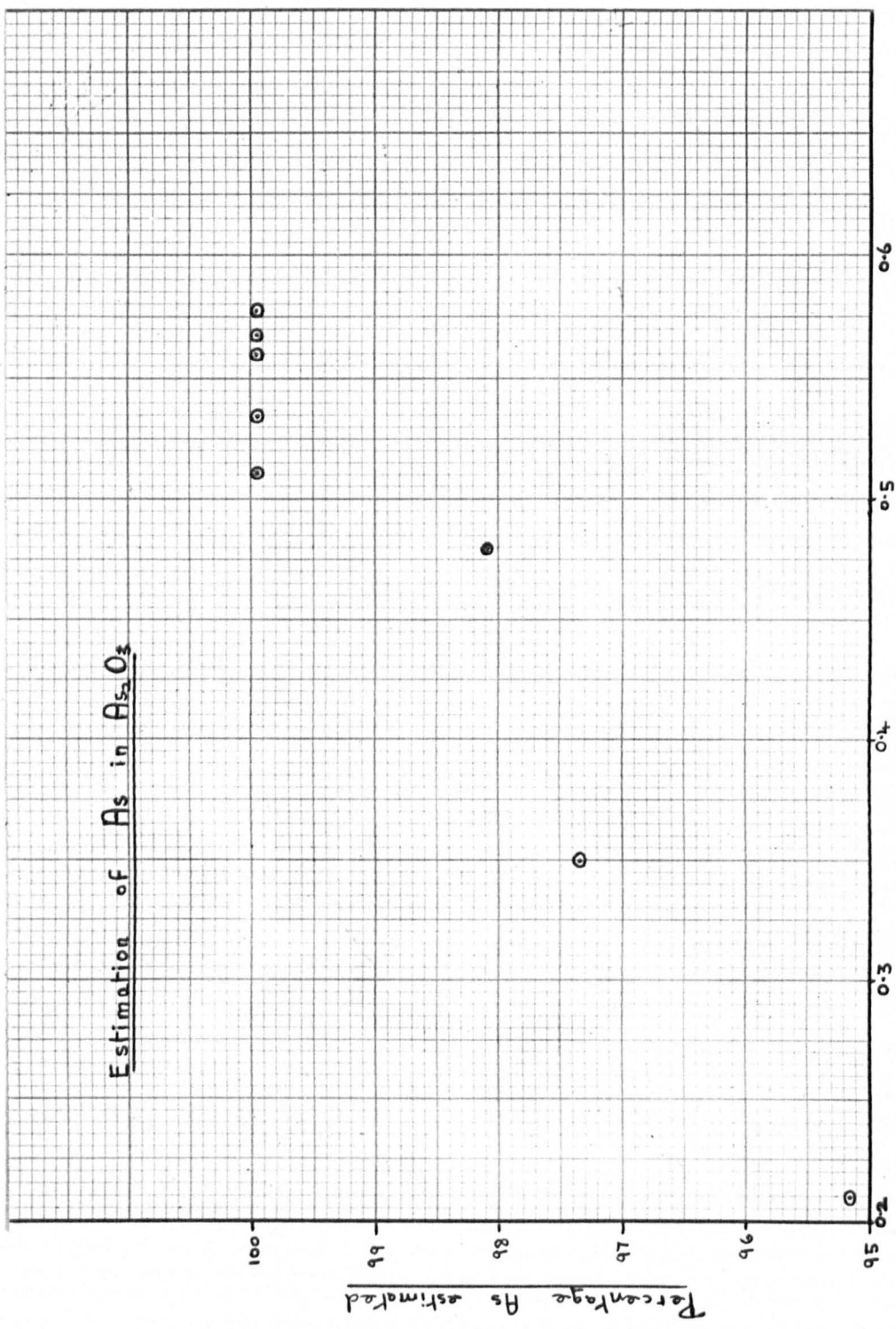
The concentrations of bromine in carbon tetrachloride and sodium hydroxide in water (ca. 2M) were chosen to minimise reaction

times which were never greater than 40 minutes. The reaction times for slow reactions were also reduced by using a high rate of stirring, (180 r.p.m.). For reactions (1 - 4), bromine (ca. 35 ml.) and carbon tetrachloride (ca. 175 ml.) were used. For reactions (7, 8, 10, 12 - 15 and 17) sodium hydroxide (ca. 30 g.) and water (400 ml.) were used.

In reaction (14) the heat of solution per mole of bromine, -10.145 kcal., was found to be independent of the quantity of bromine used over the molar range y (moles of bromine) = 2.3 to 17. The difference $\Delta H(13) - \Delta(14)$ was found to be constant, -84.41 kcal./mole, within the limits of accuracy of the calorimeter. If, however, $(y - 1)$ in reaction (13) was less than 1.3, then oxidation appeared incomplete. This was reflected in a lower value, -82.25 kcal./mole for the difference $\Delta H(13) - \Delta H(14)$ obtained under these conditions.

In reactions (19) and (20), ampoules containing aqueous solutions of arsenious oxide or arsenic oxide (ca. 30 ml.) were broken into sodium hydroxide solution (400 ml.). Complete breakage of a 30 ml. ampoule at the commencement of a reaction was difficult to achieve. Part of the arsenious or arsenic oxide solution was often trapped in the upper, unbroken, portion of the ampoule. To avoid this occurrence the glass stirrer rod, to which ampoules were sealed, was replaced by glass tubing of the same diameter and length. The lower end of this tubing projected into the ampoule. By passing a small quantity of nitrogen down the hollow stirrer shaft complete mixing of

FIG. 12



Estimation of As in As₂O₃

Calculated weight (g.) of As in As₂O₃ used for analysis

reactants was effected. The amount of nitrogen used did not produce an observable temperature change in the system.

Compounds

Arsenious oxide was supplied by B.D.H. Ltd., (AnalaR).

Before use the arsenious oxide was dried in an oven to constant weight at 105°C and then stored in a dessicator. Due to its high stability arsenious oxide was taken as a reference standard in arsenic analyses. Five consecutive analyses for arsenic in arsenious oxide, by the method described below, yielded the following results; 99.942%, 99.945%, 99.944%, 99.942%, 99.944%. In these analyses the amount of arsenic in the solutions analysed was 0.55 ± 0.04 g. For solutions containing less than 0.51 g. As the analyses showed considerable variation, see Fig. 12.

Analysis for arsenic relied upon the precipitation of a complex ammonium arsenate from alkaline solutions containing arsenic in the pentavalent state. The precipitation was effected by the addition of $\text{MgCl}_2 - \text{NH}_4\text{Cl}$ solution. The complex precipitate was collected in a Vitreosil filter crucible and subsequently converted to magnesium pyroarsenate, MgAs_2O_7 , in a muffle furnace at 850°C . This method of analysis has been described in detail by Vogel.¹²³

Arsenious oxide readily dissolved in 2N sodium hydroxide to yield a solution of sodium arsenite in which arsenic is present in the trivalent state. Oxidation of trivalent arsenic to pentavalent arsenic, prior to analysis, was performed with a 0.1N solution of potassium bromate.

To ensure the presence of the octahedral form in reaction (10) the arsenious oxide was recrystallised from concentrated hydrochloric acid,¹²⁴ the temperature of the final sample being kept below 70°C to prevent the possible conversion to the monoclinic form.

The aqueous solution of arsenious oxide used in reaction (19) was readily attacked by atmospheric carbon dioxide. This resulted in low and inconsistent values for $\Delta H(19)$. The oxide solution was, therefore, prepared by dissolving arsenious oxide in distilled water, free from carbon dioxide, under an atmosphere of nitrogen. The filling of ampoules was similarly performed under a nitrogen atmosphere.

Arsenic oxide was prepared from arsenious oxide by oxidising the latter with concentrated nitric acid. Arsenious oxide was dissolved in an excess of concentrated nitric acid and the resulting solution maintained at a temperature of 60°C for 48 hours. Evaporation of this solution under reduced pressure at 60°C yielded white solid arsenic acid which was converted into As_2O_5 by heating at 350°C until constant weight was attained. Analysis for pentavalent arsenic in As_2O_5 gave 100.000%. This analysis was carried out by the method previously described after first dissolving the arsenic oxide in 2N sodium hydroxide solution.

Aqueous arsenic oxide solution, used in reaction (20) was prepared in the same way as the arsenious oxide solution.

Arsenic, crystalline, α , orthorhombic, and amorphous, β , arsenic was supplied by L. Light. Both forms of arsenic were crushed into small

fragments, ca. 0.1 mm., before use. The fragmentation of the arsenic and the filling of ampoules was performed in a dry box filled with nitrogen.

Estimation of the percentage purity of both forms of arsenic was performed by the method previously described after dissolving the metallic arsenic in concentrated nitric acid. The resulting solution of arsenic acid contained arsenic in the pentavalent state. Both forms of arsenic were estimated to be 99.999% pure.

Arsenic tribromide was supplied by B.D.H. Ltd. It was purified by zone refining using a Baird and Tatlock semi-micro zone refiner. Each sample of zone refined arsenic tribromide was analysed for arsenic after dissolving the compound in 2N sodium hydroxide solution, and oxidising the resulting sodium arsenite solution with 0.1 N potassium bromate solution.

The resulting solution of sodium arsenate contained arsenic in the pentavalent state. Analyses ranged from 99.810% to 100.000% arsenic. Correction was made to the weight of arsenic tribromide used, on the assumption that the impurity made no contribution to the temperature change occurring in the reaction. The ampoules were filled with arsenic tribromide under a nitrogen atmosphere in a dry box.

Bromine was supplied by Hopkin and Williams (AnalaR) and was purified by two successive distillations on a vacuum line. The second distillate was collected in an ampoule attached to the vacuum line. The neck of this ampoule was provided with a constriction to

facilitate sealing of the ampoule when filled with bromine. By immersing the filled ampoule in liquid nitrogen the bromine was solidified and the constricted neck of the ampoule easily sealed with the aid of a blow pipe.

Other compounds were supplied by the manufacturers listed in parentheses. Carbon tetrachloride, sodium hydroxide (B.D.H. Ltd., AnalaR); sodium arsenite, sodium arsenate, (Hopkin and Williams, AnalaR); sodium bromide (Whiffen, pure grade).

Results

Derived Heats of Formation

$$\Delta H_f^\circ(\text{AsBr}_3, \text{cryst.}) = -47.57 \pm 0.10 \text{ kcal./mole}$$

$$\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -160.30 \pm 0.22 \text{ kcal./mole}$$

$$\Delta H_f^\circ(\text{As}_2\text{O}_5, \text{cryst.}) = -222.14 \pm 0.35 \text{ kcal./mole}$$

$$\Delta H_f^\circ[\text{NaAsO}_2, \text{in } 64 \text{ NaOH, } 2000 \text{ H}_2\text{O}](\text{liq.}) = -164.57 \pm 0.20 \text{ kcal./mole}$$

$$\Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{in } 60 \text{ NaOH, } 2002 \text{ H}_2\text{O}](\text{liq.}) = -389.97 \pm 0.30 \text{ kcal./mole}$$

$$\begin{aligned} \Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{in } 60 \text{ NaOH, } 2002 \text{ H}_2\text{O}](\text{liq.}) - \Delta H_f^\circ[\text{NaAsO}_2, \text{in } 64 \text{ NaOH,} \\ 2000 \text{ H}_2\text{O}](\text{liq.}) = -225.40 \pm 0.10 \text{ kcal./mole (as calculated from} \\ \text{the heats of reactions 19 and 20).} \end{aligned}$$

$$\begin{aligned} \text{Heat of transition for the process As(cryst., } \alpha, \text{ rhomb.)} \rightarrow \text{As(amorph., } \beta) = \\ +3.24 \pm 0.03 \text{ kcal./g.-atom.} \end{aligned}$$

TABLE 1

As, M, 74.922

Reaction (1)

Experiment	1	2	3	4	5
m,(As, cryst., g.)	1.66193	2.01080	1.80639	1.60754	1.87755
ΔR (ohm)	0.04114	0.04965	0.04472	0.03965	0.04639
E_s (kcal./ohm)	23.855	23.882	23.883	23.928	23.877
$-\Delta H(1)$ (kcal./g.-atom)	44.23	44.18	44.30	44.22	44.20

 d_{25} , 5.73 g./ml.Mean $\Delta H(1) = -44.22 \pm 0.02$ kcal./g.-atom $\overline{s}\Delta H(1) = \pm 0.04\%$ TABLE 2Reaction (2)

Experiment	1	2	3	4	5
m,(As, amorph., g.)	1.16956	1.36021	1.14862	1.00968	1.16287
ΔR (ohm)	0.03090	0.03583	0.03020	0.02658	0.03055
E_s (kcal./ohm)	23.969	23.998	24.007	24.140	24.093
$-\Delta H(2)$ (kcal./g.-atom)	47.45	47.36	47.29	47.61	47.42

 d_{25} , 4.70 g./ml.Mean $\Delta H(2) = -47.46 \pm 0.03$ kcal./g.-atom $\overline{s}\Delta H(2) = \pm 0.07\%$

TABLE 3 Br_2 , M, 159.818Reaction (3)

Experiment	1	2	3	4
m, (Br, g.)	6.86233	6.57066	6.93482	7.10903
ΔR (ohm)	0.00085	0.00056	0.00079	0.00071
E_s (kcal./ohm)	23.952	24.005	23.880	23.896
ΔH (kcal./g.-atom)	0.239	0.166	0.217	0.191

 d_{25} , 2.98 g./ml.Mean $\Delta H = +0.203 \pm 0.015$ kcal./g.-atomMean $\Delta H(3) = +0.61 \pm 0.045$ kcal./1.5 Br_2 mole $\bar{s}\Delta H(3) = \pm 7.38\%$ TABLE 4 AsBr_3 , M, 314.650Reaction (4)

Experiment	1	2	3	4
m, (AsBr_3 , g.)	7.49072	6.43524	6.51170	4.69047
% Purity	99.810	100.000	99.851	99.901
ΔR (ohm)	0.00392	0.00334	0.00340	0.00245
E_s (kcal./ohm)	24.182	24.141	24.157	24.141
$\Delta H(4)$ (kcal./mole)	3.978	3.941	3.965	3.967

 d_{25} , 3.40 g./ml.Mean $\Delta H(4) = +3.963 \pm 0.008$ kcal./mole $\bar{s}\Delta H(4) = \pm 0.20\%$

TABLE 5Reaction (7)

Experiment	1	2	3	4	5
m, (AsBr ₃ , g.)	4.09209	3.41880	3.54488	4.63351	3.67001
ΔR (ohm)	0.03100	0.02615	0.02687	0.03518	0.02793
E _s (kcal./ohm)	26.347	26.103	26.192	26.214	26.201
-ΔH(7) (kcal./mole)	62.80	62.82	62.47	62.63	62.75

$$\text{Mean } \Delta H(7) = -62.69 \pm 0.07 \text{ kcal./mole}$$

$$\overline{s}\Delta H(7) = \pm 0.10\%$$

TABLE 6Reaction (10)As₂O₃, M, 197.841

Experiment	1	2	3	4	5
m, (As ₂ O ₃ , g.)	4.84528	4.84004	4.80297	4.80578	3.10741
ΔR (ohm)	0.01135	0.01139	0.01110	0.01124	0.00721
E _s (kcal./ohm)	26.054	26.056	26.063	26.058	26.043
-ΔH(10) (kcal./mole)	12.08	12.13	11.92	12.06	11.96

$$\text{Mean } \Delta H(10) = -12.03 \pm 0.04 \text{ kcal./mole}$$

$$\overline{s}\Delta H(10) = \pm 0.33\%$$

TABLE 7NaAsO₂, M, 129.910Reaction (12)

Experiment	1	2	3	4
m, (NaAsO ₂ , g.)	3.06915	3.19370	6.29865	6.33335
ΔR (ohm)	0.00434	0.00461	0.00901	0.00915
E _s (kcal./ohm)	25.865	25.494	26.251	25.938
-ΔH(12) (kcal./mole)	4.79	4.90	4.92	4.91

$$\text{Mean } \Delta H(12) = -4.88 \pm 0.03 \text{ kcal./mole}$$

$$\overline{s}\Delta H(12) = \pm 0.61\%$$

TABLE 8Reaction (13)

Experiment	1	2	3	4	5
m, (As ₂ O ₃ , g.)	0.51070	0.50898	0.72356	0.63265	1.03389
m, (Br, g.)	7.80452	14.00835	3.46760	6.58197	3.88853
Y	9.45899	17.03536	2.96632	6.39312	2.32796
ΔR (ohm)	0.03365	0.04849	0.02914	0.03385	0.03896
E _s (kcal./ohm)	26.152	26.210	26.209	26.278	26.210
-ΔH(13) (kcal./mole)	170.46	247.01	104.42	139.09	97.70
-[ΔH(13) - ΔH(14)] (kcal./mole)	84.64	84.33	84.47	84.38	84.23

$$\text{Mean } [\Delta H(13) - \Delta H(14)] = -84.41 \pm 0.07 \text{ kcal./mole}$$

$$\overline{s}[\Delta H(13) - \Delta H(14)] = \pm 0.08\%$$

TABLE 9 Na_3AsO_4 , M, 207.889Reaction (14)

Experiment	1	2	3	4	5
$m, (\text{Na}_3\text{AsO}_4, \text{g.})$	1.3826	0.8550	2.7526	1.5050	2.3113
$m, (\text{Br}, \text{g.})$	8.99114	10.53976	4.16089	6.23974	2.35963
$\gamma-1$	8.45899	16.03536	1.96632	5.39312	1.32796
$\Delta R(\text{ohm})$	0.02179	0.02557	0.01009	0.01508	0.00574
$E_s(\text{kcal./ohm})$	26.196	26.185	26.209	26.209	26.100
$-\Delta H(14) (\text{kcal./mole})$	10.146	10.153	10.157	10.123	10.147

Mean $\Delta H(14) = -10.145 \pm 0.006 \text{ kcal./mole}$ $\overline{s\Delta H(14)} = \pm 0.06\%$ TABLE 10 As_2O_5 , M, 229.840Reaction (17)

Experiment	1	2	3	4	5
$m, (\text{As}_2\text{O}_5, \text{g.})$	2.79227	2.65002	2.77149	2.86436	2.72094
$\Delta R(\text{ohm})$	0.03988	0.03762	0.03957	0.04089	0.03856
$E_s(\text{kcal./ohm})$	26.477	26.563	26.528	26.572	26.640
$-\Delta H(17) (\text{kcal./mole})$	86.91	86.67	87.05	87.19	86.77

 $d_{25}, 4.09 \text{ g./ml.}$ Mean $\Delta H(17) = -86.97 \pm 0.09 \text{ kcal./mole}$ $\overline{s\Delta H(17)} = \pm 0.10\%$

TABLE 11Reaction (19)

Experiment	1	2	3	4	5
$m, (\text{As}_2\text{O}_3, \text{g.})$	0.37289	0.75527	0.97826	0.84798	0.75629
$\Delta R (\text{ohm})$	0.00135	0.00282	0.00346	0.00307	0.00375
$E_s (\text{kcal./ohm})$	25.215	25.342	25.980	25.863	25.680
$-\Delta H(19) (\text{kcal./mole})$	18.06	18.72	18.18	18.53	18.47

$$\text{Mean } \Delta H(19) = -18.39 \pm 0.11 \text{ kcal./mole}$$

$$\overline{s}\Delta H(19) = \pm 0.60\%$$

TABLE 12Reaction (20)

Experiment	1	2	3	4
$m, (\text{As}_2\text{O}_5, \text{g.})$	0.61303	0.58509	0.62961	0.61617
$\Delta R (\text{ohm})$	0.00832	0.00795	0.00851	0.00836
$E_s (\text{kcal./ohm})$	25.157	25.150	25.355	25.214
$-\Delta H(20) (\text{kcal./mole})$	78.47	78.54	78.77	78.63

$$\text{Mean } \Delta H(20) = -78.60 \pm 0.05 \text{ kcal./mole}$$

$$\overline{s}\Delta H(20) = \pm 0.06\%$$

The heats of reactions (8) and (15) were measured as, $\Delta H(8) = 0.18 \pm 0.02 \text{ kcal./3 NaBr}$, and $\Delta H(15) = -0.12 \pm 0.01 \text{ kcal./2 NaBr}$, respectively.

Discussion

The heats of solution of arsenious and arsenic oxides in approximately 2N sodium hydroxide solution have previously been measured by Long and Sackman¹²⁵ who obtained the values -12.16 ± 0.10 and -87.07 ± 0.28 kcal./mole, respectively. These values are close to the values reported in this work, $\Delta H(10) = -12.03 \pm 0.04$ kcal./mole, and $\Delta H(17) = -86.97 \pm 0.09$ kcal./mole, although the final concentrations obtained by Long and Sackman are slightly different from those obtained in reactions (10) and (17).

The heats of neutralisation of aqueous solutions of arsenious and arsenic oxides have been measured previously,⁷⁹ and it is noted that the value $\Delta H = -9.77 \pm 0.05$ kcal./mole for the heat of neutralisation of an aqueous solution of arsenious oxide in approximately 4N sodium hydroxide was erroneously reported. The value -9.77 kcal./mole refers to one mole of the product, sodium arsenite, so that the correct value per mole of arsenious oxide is -19.54 ± 0.10 kcal./mole. This value is 1.15 ± 0.20 kcal. more negative than that for the neutralisation in approximately 2N sodium hydroxide, $\Delta H(19) = -18.39 \pm 0.11$ kcal./mole. A similar difference of 1.40 ± 0.10 kcal./mole is observed between the heat of solution of crystalline arsenious oxide in approximately 4N sodium hydroxide solution, $\Delta H = -13.43 \pm 0.06$ kcal./mole¹²⁶ and the value reported here in approximately 2N sodium hydroxide solution of $\Delta H(10) = -12.03 \pm 0.04$ kcal./mole. This dependence of the heat of neutralisation of arsenious oxide on the concentration of sodium hydroxide is explained

by the fact that arsenious acid is a weak acid.

The previous value $\Delta H = -78.24 \pm 0.30$ kcal./mole⁷⁹ for the heat of neutralisation of an aqueous solution of arsenic oxide with approximately 4N sodium hydroxide solution is virtually the same, within the combined experimental errors, as the value of $\Delta H(20) = -78.60 \pm 0.05$ for the heat of neutralisation in approximately 2N sodium hydroxide. As a stronger acid, the heat of neutralisation of arsenic acid is less dependent on the alkali concentration.

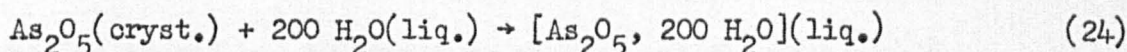
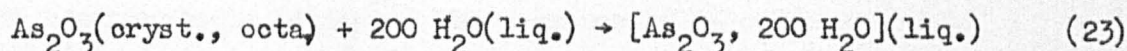
The heat of solution of bromine in approximately 2N sodium hydroxide, $\Delta H(14) = -10.145 \pm 0.006$ kcal./mole of bromine, compares with the values of -10.879 ± 0.084 kcal./mole in 0.1N sodium hydroxide, and -10.595 ± 0.203 kcal./mole in 0.032N sodium hydroxide solution reported by McDonald and Cobble.¹²⁷

The results reported in this thesis have been used to calculate the heat of formation of arsenic tribromide $\Delta H_f^\circ(\text{AsBr}_3, \text{cryst.}) = -47.57 \pm 0.10$ kcal./mole. This value can be compared with the value -46.61 kcal./mole^{66(a)} based on measurements made by Berthelot.¹²⁸ The derived heats of formation of the oxides, $\Delta H_f^\circ(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -160.30 \pm 0.22$ kcal./mole, and $\Delta H_f^\circ(\text{As}_2\text{O}_5, \text{cryst.}) = -222.14 \pm 0.35$ kcal./mole, are both more negative, to the extent of 3.4 kcal., and 3.6 kcal., respectively, than the 'selected' values.^{66(a)}

The heats of formation $\Delta H_f^\circ[\text{Na}_3\text{AsO}_4, \text{in } 60 \text{ NaOH, } 2002 \text{ H}_2\text{O}](\text{liq.}) = -389.97 \pm 0.30$ kcal./mole, and $\Delta H_f^\circ[\text{NaAsO}_2, \text{in } 64 \text{ NaOH, } 2000 \text{ H}_2\text{O}](\text{liq.}) = -164.57 \pm 0.20$ kcal./mole have been derived. The difference between

these two heats of formation -225.40 ± 0.15 kcal./mole is the same, within the combined limits of error, as the difference of -225.59 ± 0.10 kcal./mole, calculated from the heats of reactions (19), (20), and (22).

From the difference between the heats of reaction of sodium hydroxide and arsenious oxide, both crystalline and in aqueous solution, the heat of solution $\Delta H(23) = +6.36 \pm 0.12$ kcal./mole is obtained. Similarly, the value $\Delta H(24) = -8.37 \pm 0.10$ kcal./mole is calculated for arsenic oxide.



These compare with 'selected' values^{66(a)} of +7.3 and -6.0 kcal./mole, respectively.

The heat of the transformation $\text{As}(\text{cryst., } \alpha, \text{ rhomb.}) \rightarrow \text{As}(\text{amorph., } \beta.)$, $\Delta H(6) = +3.24 \pm 0.03$ kcal./g.-atom is more positive than the 'selected' value^{66(a)} of +1.0 kcal./mole.

CHAPTER VII

The Combustion of Arsenic

Heats of combustion of elemental arsenic have been measured, hitherto, only in static-bomb calorimeters.^{83,84,85} The combustion products consist of a mixture of solid arsenic oxides (As_2O_3 , As_2O_5 , As_2O_4) as sublimates on the bomb walls and as a glass in the crucible.¹²⁵ Long and Sackman have shown that some or all of the uncombined As_2O_3 in the bomb "exists in the form of an unusually active and soluble variety". They have further shown that a calorimetric determination on the bomb products indicates the presence of an oxide strongly endothermic with respect to ordinary As_2O_3 , As_2O_5 mixtures. The mixture is, therefore, difficult to analyse and thermochemically ill-defined. By using a rotating-bomb calorimeter, containing a solution of sodium hydroxide, it has been possible to measure the heat of combustion of arsenic, where the only product is a homogeneous, aqueous solution containing sodium arsenite, sodium arsenate, sodium carbonate (formed from the CO_2 produced by combustion of a benzoic acid fuse), and sodium hydroxide.

Procedure

Three separate series of experiments were performed.

(a) The energy equivalent, E_{si} , of the standard initial calorimeter, containing neither sample, water, nor oxygen, but containing a platinum

crucible, was determined by combustion of a sample of benzoic acid (B.D.H. Thermochemical Standard, batch No. 76016), having $-\Delta U_B = 6.3191 \pm 0.0007 \text{ kcal./g.}$, standard deviation, $\overline{sB} = \pm 0.011\%$ under recommended conditions. The recommended conditions⁹² were used, in that the bomb was charged with 0.78 ml. of water and oxygen at an initial pressure of 30 atm.

(b) The heat of combustion of arsenic (0.5 g.), contained in a fused silica crucible, was measured in the bomb charged with 50 ml. of water, 6.12 g. sodium hydroxide and oxygen at 30 atmospheres. An additional fuse of 3 benzoic acid pellets (ca. 0.5 g.) was used, the arsenic being placed in the centre of the well formed by leaning the pellets on the side of the crucible.

(c) A comparison experiment was made in which ca. 0.5 g. of benzoic acid, in a fused silica crucible, was burned in the rotating bomb in the presence of 50 ml. water, 6.12 g. sodium hydroxide, and 0.5 g. As in the form of As_2O_3 .

The amount of arsenic present as arsenite ions in the liquid phase after combustion was determined volumetrically by titration with 0.1 N potassium bromate solution. The bomb solution, and washings, was made up to 100 ml. in a graduated flask. Three samples (25 ml.) of this solution were analysed volumetrically for As^{III} . The As^{V} present in the bomb solution and washings was assumed to be the difference between the mass of arsenic burned and the mass of As^{III} as determined volumetrically.

In only one case did a solid white residue remain in the crucible after combustion. This was analysed for As^{III} , as above, after dissolution in hot sodium hydroxide solution. The analysis showed that As^{III} only was present in this residue.

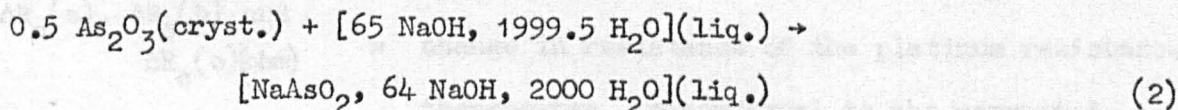
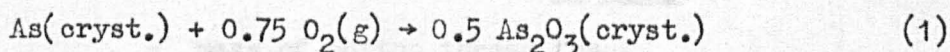
Compounds

Arsenic, crystalline, α , orthorhombic, was supplied by L. Light. It was burned in small pieces weighing approximately 0.5 g.

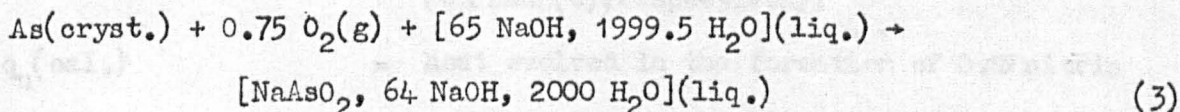
Sodium hydroxide was supplied by B.D.H. Ltd. (AnalaR).

Results

The overall process for the combustion of arsenic, if account is taken of the oxidation of a fraction of the sodium arsenite to sodium arsenate, may be considered to take place in stages represented by the scheme,

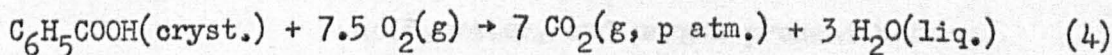


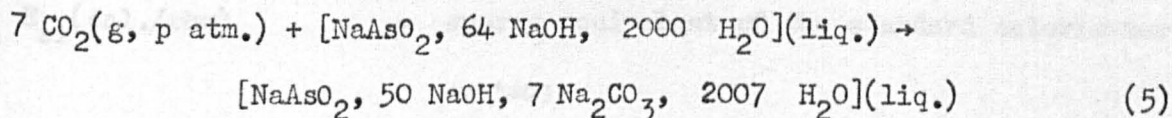
which, when combined, give the reaction



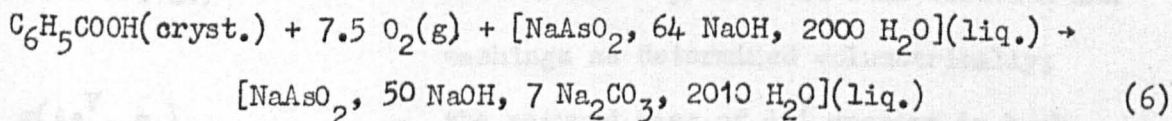
for which the change in internal energy is $\Delta U(3)$.

The combustion of benzoic acid, and the subsequent solution of carbon dioxide in the alkaline solution,





combine to give the reaction



Results of the measurements of heats of combustion experiments a, b, and c, are shown in Tables 1, 2 and 3. The symbols have the following meanings.

$m(\text{As, g.})$	= mass of arsenic, <u>in vacuo</u> ;
$m(\text{B.A., g.})$	= mass of benzoic acid, <u>in vacuo</u> ;
$m_1(\text{g.})$	= mass of cotton thread fuse;
$\Delta R_c(a), \Delta R_c(b)$ and $\Delta R_c(c)(\text{ohm})$	= change in resistance of the platinum resistance thermometer, proportional to the corrected temperature rise, for the experiments (a), (b), and (c), respectively;
$q_n(\text{cal.})$	= heat evolved in the formation of 0.1N nitric acid;
$q_1(\text{cal.})$	= heat of combustion of the cotton thread fuse, 3.881 kcal./g.;
$E_c(a)(\text{cal./ohm})$	= correction for energy absorbed by the benzoic acid, water, and oxygen present before combustion, over the temperature rise $\Delta R_c(a)(\text{ohm})$;

- $E_{si}(\text{cal./ohm})$ = energy equivalent of the standard calorimeter system;
- \overline{sE}_{si} = standard deviation of the mean of E_{si} ;
- $m(\text{As}^{\text{III}}, \text{g.})$ = mass of As^{III} present in bomb solution and washings as determined volumetrically;
- $m(\text{As}^{\text{V}}, \text{g.})$ = the assumed mass of As^{V} present in bomb solution and washings [i.e. $m(\text{As}, \text{g.}) - m(\text{As}^{\text{III}}, \text{g.})$];
- $m(\text{As}^{\text{III}}, \text{cryst., g.})$ = mass of As^{III} recovered from crucible after combustion;
- $q_{\text{B.A.}}(\text{cal.})$ = $m(\text{B.A.}, \text{g.}) \times \Delta U_{\text{B}}$, where $\Delta U_{\text{B}} = -6,319.1 \text{ cal./g.}$ benzoic acid;
- $q_{\text{sn}}(\text{cal.})$ = the heat evolved in the formation of an aqueous solution of sodium nitrate, produced by neutralisation of nitric acid formed by oxidation of nitrogen present as impurity in the oxygen, -27.0 kcal./mole ; ^{66(a)}
- $q_{\text{CO}_2}(\text{cal.})$ = heat evolved by solution of CO_2 in bomb solution; given by
- $$q_{\text{CO}_2} = [m(\text{CO}_2) \times m(\text{B.A.}) + m'(\text{CO}_2) \times m_1] \Delta U(5),$$
- where $m(\text{CO}_2)$ is the mass of CO_2 produced by combustion of 1 g. benzoic acid, 2.52272 g.;
- $m'(\text{CO}_2)$ is the mass of CO_2 produced by the combustion of 1g. of cotton thread fuse,

1.618 g.; and

$$\Delta U(5) = \frac{-[\Delta R_c(o) \times E_{si} - (q_{B.A.} + q_i + q_{sn})]}{[m(CO_2) \times m(B.A.) + m'(CO_2) \times m_i]}$$

$q_{oxid.}(\text{cal.})$

$$= \frac{10^{-3} \times m(As^V)}{M(As)} \times \Delta H_{oxid.}, \text{ where,}$$

$M(As)$ is the atomic weight of arsenic,

$$\begin{aligned} \Delta H_{oxid.} &= \Delta H_f^\circ [Na_3AsO_4, \text{ in } 62 \text{ NaOH, } 2001 \text{ H}_2\text{O}](\text{liq.}) \\ &\quad - \Delta H_f^\circ [NaAsO_2, \text{ in } 64 \text{ NaOH, } 2000 \text{ H}_2\text{O}](\text{liq.}) \\ &\quad - \Delta H_f^\circ (\text{H}_2\text{O, liq.}) - 2 \Delta H_f^\circ [\text{NaOH, in } \\ &\quad 31.25 \text{ H}_2\text{O}](\text{liq.}) + \Delta H_d = -68.8 \pm \\ &\quad 0.10 \text{ kcal./mole } Na_3AsO_4 \end{aligned}$$

where,

$$\begin{aligned} &\Delta H_f^\circ [Na_3AsO_4, \text{ in } 62 \text{ NaOH, } 2001 \text{ H}_2\text{O}](\text{liq.}) \\ &\quad - \Delta H_f^\circ [NaAsO_2, \text{ in } 64 \text{ NaOH, } 2000 \text{ H}_2\text{O}](\text{liq.}) = \\ &\quad -225.40 \pm 0.10 \text{ kcal./mole (Chap. VI, p. 99);} \end{aligned}$$

$\Delta H_d = +0.124 \text{ kcal./mole}$ is the heat of dilution $62 [\text{NaOH, in } 31.25 \text{ H}_2\text{O}] \rightarrow 62 [\text{NaOH, in } 32.27 \text{ H}_2\text{O}]$, and the heats of formation are $[\text{NaOH, in } 31.25 \text{ H}_2\text{O}], -112.446 \pm 0.006$, $[\text{NaOH, in } 32.27 \text{ H}_2\text{O}], -112.444 \pm 0.006 \text{ kcal./mole.}^{66(a)}$;

$q_w(\text{cal.})$

= the thermal correction corresponding to the conversion of the reactants and products to their standard states. It is difficult to

evaluate this quantity for eqn. (3) and correction was made only for the change of r_1 moles of oxygen from 0 atm. to P_1 atm. and the change in energy of r_2 moles of oxygen from P_2 to 0 atm.;

$E_o(b)$ = the isothermal correction due to the energy absorbed by the charge present in the bomb before combustion, over the temperature change, produced by the combustion of arsenic alone. The following values for specific heats were used; As, 0.0822; Pt, 0.324; Silica (fused), 0.200; NaOH solution, 0.908; benzoic acid 0.287; and oxygen 0.1555 cal./g.¹²⁹

The value, $\Delta U^o(3)$, is calculated from the relation

$$\begin{aligned}\Delta U^o(3) &= \Delta U(3) - E_c(b) + q_w \\ &= -[\Delta R_c(b) \times E_{si} - (q_{B.A.} + q_i + q_{sn} + q_{oxid.} + q_{CO_2}) - \\ &\quad E_c(b) + q_w] \frac{M(As)}{m(As)}.\end{aligned}$$

The standard heat of reaction, $\Delta H^o(3)$, may be derived from the relation

$$\Delta H^o(3) = \Delta U^o(3) + \Delta nRT,$$

where Δn is the difference between the number of moles of gas present before and after reaction (3).

TABLE 1

Experiment (a)

Experiment	1	2	3	4	5
$m(\text{B.A.}, \text{g.})^{\#}$	1.120225	1.124699	1.154652	1.124879	1.149250
$m_i(\text{g.})$	0.004547	0.003479	0.002642	0.002725	0.003413
$\Delta R_c(a)(\text{ohm})$	0.09962	0.09993	0.10238	0.09991	0.10206
$q_i(\text{cal.})$	17.66	13.50	10.25	10.58	13.25
$q_n(\text{cal.})$	1.33	1.28	1.04	1.20	0.41
$E_c(\text{cal./ohm})$	19.20	19.21	19.30	19.21	19.28
$E_{si}(\text{cal./ohm})$	71229.24	71248.98	71247.81	71245.63	71270.55

$$\#d_{25} = 1.320 \text{ g./ml.}$$

$$\text{Mean } E_{si} = 71248.44 \pm 6.6 \text{ cal./ohm}$$

$$\overline{SE}_{si} = \pm 0.009\%$$

TABLE 2

Experiment (b), As, M, 74.922

Experiment	1	2	3	4	5	6	7
m(As, g.)	0.507257	0.527930	0.502972	0.521124	0.505757	0.492545	0.516311
m(B.A., g.)	0.572835	0.558891	0.579306	0.570289	0.575140	0.569807	0.561519
m_1 (g.)	0.003528	0.003916	0.003313	0.003213	0.002924	0.003157	0.003782
$\Delta R_c(b)$ (ohm)	0.07181	0.07048	0.07266	0.07179	0.07218	0.07172	0.07174
m(As, ^V g.)	0.105311	0.110251	0.116385	0.114308	0.121792	0.12281	0.107997
m(As, ^{III} g.)	0.395203	0.417679	0.386587	0.406816	0.383965	0.369730	0.408314
m(As, ^{III} cryst..., g.)	0.006743	-	-	-	-	-	-
$q_{B.A.}$ (cal.)	3619.78	3531.67	3660.68	3603.70	3634.35	3600.65	3548.28
q_1 (cal.)	13.69	15.20	12.86	12.47	11.35	12.25	14.68
q_{sn} (cal.)	0.72	0.72	0.72	0.72	0.72	0.72	0.72
q_{CO_2} (cal.)	809.67	790.32	818.53	805.74	812.31	805.01	793.90
$q_{oxid.}$ (cal.)	96.71	101.25	106.88	104.97	111.84	112.78	99.17
q_w (cal.)	0.55	0.56	0.54	0.56	0.56	0.56	0.55
E_c (cal.)	5.02	5.02	5.02	5.02	5.02	5.02	5.02
$-\Delta U^0(3)$ kcal./ g.-atom As.	85.70	83.28	86.66	85.08	85.42	88.79	85.30

$$\text{Mean } \Delta U^0(3) = -85.85 \pm 1.60 \text{ kcal./g.-atom As}$$

$$\Delta n_{RT} = -0.23$$

$$\Delta H^0(3) = -86.08 \pm 1.60 \text{ kcal./g.-atom As}$$

TABLE 3

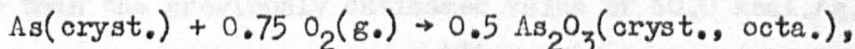
Experiment	Experiment (c)				
	1	2	3	4	5
m(B.A., g.)	0.565106	0.562945	0.557326	0.570226	0.571353
m _i (g.)	0.003456	0.003734	0.003421	0.003123	0.003434
$\Delta R_c(c)(ohm)$	0.06157	0.06125	0.06066	0.06204	0.06226
q _{B.A.} (cal.)	3570.94	3557.29	3521.78	3603.30	3610.42
q _i (cal.)	13.41	14.49	13.23	12.12	13.33
q _{sn} (cal.)	0.72	0.72	0.72	0.72	0.72
$-\Delta U(5) \text{ cal./g. CO}_2$	560.16	554.95	557.19	557.10	560.81

$$\text{Mean } \Delta U(5) = -558.04 \pm 1.3 \text{ cal./g. CO}_2$$

$$\bar{s}\Delta U(5) = \pm 0.23\%$$

Discussion

The heat of combustion, $\Delta H^\circ(3) = -86.08 \pm 1.6$ kcal./g.-atom As refers to the combustion of arsenic in oxygen, in the presence of sodium hydroxide, to form an aqueous solution of sodium arsenite in sodium hydroxide. The heat of reaction of As_2O_3 with sodium hydroxide has been measured as -12.03 ± 0.04 kcal./mole (Chap. VI, p.93), and thus we may calculate $\Delta H^\circ_f = -80.07 \pm 1.6$ kcal./g.-atom As for the reaction



leading to $\Delta H^\circ_f(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -160.14 \pm 1.6$ kcal./mole. This is in good agreement with the value $\Delta H^\circ_f(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -160.30 \pm 0.22$ kcal./mole. obtained by reaction calorimetry and reported in the previous Chapter.

The divergence between the value $\Delta H^\circ_f(\text{As}_2\text{O}_3, \text{cryst., octa.}) = -160.14 \pm 1.6$ kcal./mole and other values determined from combustion calorimetry (see p.25) may be attributed to the presence of an oxide in the combustion products, strongly endothermic with respect to ordinary $\text{As}_2\text{O}_3 - \text{As}_2\text{O}_5$ mixtures.¹²⁵ Use of a rotating bomb calorimeter obviates this problem.

Arsenious oxide exists in the gas phase, at 25°C, as the As_4O_6 molecule, and the heat of sublimation for the process $\text{As}_4\text{O}_6(\text{cryst., octa}) \rightarrow \text{As}_4\text{O}_6(\text{g})$ has been given as $\Delta H = +24.93$ kcal./mole,¹³⁰ hence the heat of formation of the gaseous As_4O_6 molecule is calculated as follows;
 $\Delta H^\circ_f(\text{As}_4\text{O}_6, \text{g}) = 2 \Delta H^\circ_f(\text{As}_2\text{O}_3, \text{cryst., octa.}) + 24.93 = -295.81 \pm 0.70$ kcal./mole.

The mean bond dissociation energy $\bar{D}(\text{As} - \text{O})$ in As_4O_6 is given by the relation;

$$\bar{D}(\text{As} - \text{O}) = \frac{1}{12} [4 \Delta H_f^\circ(\text{As}, g) + 6 \Delta H_f^\circ(\text{O}, g) - \Delta H_f^\circ(\text{As}_4\text{O}_6, g)]$$

Taking the values $\Delta H_f^\circ(\text{O}, g) = 59.54 \text{ kcal./g.-atom}^{108}$ and $\Delta H_f^\circ(\text{As}, g) = 69.4 \text{ kcal./g.-atom}$, the value $\bar{D}(\text{As} - \text{O}) = 77.6 \pm 0.1 \text{ kcal./mole}$ is calculated. The value $\Delta H_f^\circ(\text{As}, g) = 69.4 \text{ kcal./g.-atom}$, which is higher than the previously estimated value of $60.0 \text{ kcal./g.-atom}^{104}$ has been proposed by Sinke and Stull¹³¹ on the basis of a review by Brewer and Kane¹³² of available vapour pressure and spectroscopic data.

Conclusion

As a result of the work reported in this thesis, the thermochemistry of arsenic compounds has been put on a firmer basis. The way is now open to extend the use of rotating-bomb calorimetry and reaction calorimetry to a wide variety of arsenic compounds.

Measurements of heats of hydrolysis, using aqueous solutions of hydrofluoric acid in a reaction calorimeter, could yield the heats of formation of a number of other silicon compounds, such as the series $\text{SiH}_n\text{X}_{4-n}$, where X is a halogen. With the techniques of rotating-bomb calorimetry, which have already been applied successfully to some organo-silicon compounds, considerable developments in silicon thermochemistry may now be expected.

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