A REDETERMINATION OF HEATS OF FORMATION OF SOME COMPOUNDS OF BIOLOGICAL INTEREST

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ABSTRACT

The energies of combustion of thoroughly dried samples of l-histidine, uracil and cytosine were measured at 298.15 K by oxygen-bomb combustion calorimetry. The enthalpies of formation for these compounds were redetermined. It appears that a ten-fold improvement in the accuracy of the results was obtained.

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CHAPTER 1

INTRODUCTION

1.1 General

Thermochemistry is concerned with the energy changes of chemical reactions and of associated physical processes which involve substances of known composition. It began in the period 1780-1840 with the work of Lavoisier on combustion and the measurements by Lavoisier and Hess of the heat evolved in chemical reactions, and came into prominence in the second half of the nineteenth century when it was believed (falsely) that the driving force of the chemical reaction was determined solely by the heat of the reaction. With the realisation that the entropy change was an additional factor, the study of thermochemistry seemed to go into decline. The former impetus was not regained until the late 1920's when it was realised that thermochemical data was useful in chemical technology and in helping to understand the nature of chemical bonding, a field which, at that time, abounded with theories.

It was apparent that calculations of heat balances in chemical reactions of interest to engineers, and calculations of bond energies of interest to theoreticians, required greater accuracy than the then available calorimeters could give. This in turn required a high standard of preparation and purification of chemical substances, and careful and rigorous assessment of experimental conditions. All these were developed and incorporated in the work of Rossini and co-workers at the American National Bureau of Standards, Washington, D.C. Their guidelines are still valid; their standard of experimental work has seldom been surpassed; and they still remain the source of the primary standard chemicals used in thermochemistry.

One of the aims of thermochemistry has been to provide an experimental set of data for the compiling of a table of values from which may be calculated the heat of every possible chemical reaction. One of the most useful quantities in this regard is the standard enthalpy of formation, ΔH_f^o , which is defined as the enthalpy of reaction for the formation of one mole of the substance from its elements in their natural state at 1 atmosphere pressure (now 101.325kPa) and at the standard temperature. If the enthalpies of formation of both reactants and products are known, the heat of reaction may be calculated from the equation:

$$\Delta H = \sum \Delta H_f^o \text{ (products)} - \sum \Delta H_f^o \text{ (reactants)} \qquad (1)$$

A common way to obtain the standard enthalpy of formation of organic substances has been to calculate it from the heat released when that substance is burned in air. These measurements, known as heats of combustion, are made in a bomb calorimeter. The method of calculating ΔH_f^o values is given in Section 1.3.

Values of the heats of combustion, and enthalpies of formation of some organic compounds of biological interest are shown in Table 1.1. It will be seen that the values are exothermic and very large. This is some advantage as far as the heat of combustion measurements are concerned, for it means a large temperature rise, and thus (in principle) the possibility of a very accurate experiment. This becomes critical when enthalpies of formation are used to calculate enthalpies of reaction. The enthalpy of reaction is usually at least one order of magnitude smaller than the heat of combustion, ΔH_f^o. Thus for an accuracy of 0.1 - 1% in that quantity we need to know ΔH_f^o to 0.01% — 0.1%; a very demanding task.

Indeed, the modern tendency is to use, wherever possible, calorimeters that can measure the heat of reaction directly.

There are some reactions, notably biochemical ones, for which direct measurements are impossible, and for which heat of formation data is the only way to proceed. For this reason we decided to study the heats of combustion of cytosine, uracil, and l-histidine; three compounds

Table 1.1

Some Literature Values of ΔH_c° (298.15 K)

Compound	ΔH_c° (298.15 K) / kJ mol^{-1}	
l-phenylalanine (s)	4646.3 ± 0.8	[1]
l-tryptophan (s)	5929.6 ± 0.8	
l-isoleucine	3578.2 ± 0.8	
l-threonine	2053.9 ± 0.8	
l-alanine	1576.9 ± 2.0	
l-glycine	966.1 ± 0.8	
l-methionine	3176.5 ± 0.8	
l-glutamine	2572.3 ± 0.6	[2]
l-glutamic acid	2246.8 ± 0.7	
l-valine	2920.1 ± 0.5	

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[1] Tsuzuki, Harper and Hunt, Journal of Physical Chemistry, 62, 1958, 1594.

[2] Tsuzuki and Hunt, Journal of Physical Chemistry, 61, 1957, 1668.

widely used in biochemical reactions.

1.2 Principles of Calorimetry

The standard enthalpy change of a chemical reaction may be obtained directly from calorimetry or indirectly from the temperature dependence of the equilibrium constant K since

$$\frac{\partial \ln K}{\partial \, {}^{1}/_{T}} = - \Delta H^{\circ}/R \qquad (2)$$

This latter method has been shown to be inferior[3], and ought only to be used where calorimetry is impractical. In calorimetry, the heat which is produced can be manipulated in a variety of ways. For instance, in an isothermal calorimeter, the heat produced melts a certain amount of solid. By comparing the amount of liquid so produced, with that when a known amount of heat is released (usually in the form of Joule heating) the heat of reaction can be calculated. In an adiabatic calorimeter, on the other hand, the experiment is done so that no heat whatsoever is released to the surroundings. This causes a rise in the temperature of the system as a whole. Again a known amount of heat is put into the system, and now, by a comparison of the temperature changes the heat of reaction may be obtained.

In practice, it is very difficult to make a system which is totally adiabatic. There is inevitably some loss of heat to the surroundings. For this reason, the most commonly used calorimeter in combustion experiments is the isoperibol, or isothermal-environment calorimeter, in which the surroundings are held at constant temperature, and the calorimeter is insulated to some extent from these surroundings. The rate of heat exchange between calorimeter and surroundings is small and calculable by the laws of heat flow. These calculations, which were required for this work, are exemplified in Section 1.5.

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[3] R.C. Wilhoit in Biochemical Microcalorimetry, Ed. H.D. Brown, Academic Press, 1969.

The essential requirements for a calorimeter of the above type are as follows:

(a) the calorimeter must have a very sensitive thermometer capable of measuring the moving temperature of the calorimeter without permitting significant unmeasurable transfer of heat to the surroundings. The thermometer used in this work, a quartz-crystal oscillator, was capable of a resolution of 10^{-4}K, thus satisfying this criterion;

(b) the calorimeter should be designed so that all parts come quickly to thermal equilibrium. This was achieved by having a vessel filled with water. The water was continually stirred;

(c) heat exchange between the calorimeter and its surroundings must be under close control. In this calorimeter this was achieved by a thermistor bridge circuit which activated a heating circuit which in turn maintained the water in the jacket at a constant temperature above the water which housed the reaction vessel;

(d) the chemical species must be capable of purification, and the chemical reaction must occur in a stoichiometric fashion;

(e) the calorimeter must be capable of precise calibration. For many calorimeters this means incorporating an electrical heating circuit. In bomb calorimetry it is customary to use combustion of benzoic acid as the calibrant. This was the procedure followed here;

(f) the calorimeter must have some means of initiating the chemical reaction. In combustion calorimetry this is generally done by supplying an electric spark to ignite the reactant.

1.3 The Relationship between the Heat of Combustion and the Enthalpy and Internal Energy of Combustion

According to the first law of thermodynamics, the internal energy change, ΔU, is related to the heat absorbed by the system, q, and the work done by the system, w, by the relationship $\Delta U = q - w$. If that work is done by expansion, i.e. if $w = \int pdV$, then $\Delta U = q - \int pdV$.

Thus for the case $dV = 0$ (i.e. constant volume), $\Delta U = q$, i.e. the heat produced at constant volume is equal to the change in the internal energy.

In a bomb calorimeter, where the above condition holds, the heat which is released on combustion equals the internal energy change. Appropriate corrections (see Section 1.4) will convert this into the standard energy change of combustion.

The change in the enthalpy function is defined by the equation

$$\begin{aligned} \Delta H &\equiv \Delta U + \Delta(PV) \qquad (3)\\ &= \Delta U + \int pdV + \int Vdp \\ &= q + \int Vdp \end{aligned}$$

If $dp = 0$, i.e. at constant pressure,

$\Delta H = q$, so that the heat produced at constant pressure is equal to the enthalpy change of the reaction. Under those circumstances the heat of combustion is properly called the enthalpy of combustion. Notice that the thermodynamic function to which the heat is equal depends upon the process.

It is, of course, by (3), possible to convert one function into another. For the purposes of tabulation it is desirable to refer all reactions to some standard state or conditions. Both of these aspects are illustrated in Section 1.4.

1.4 Thermodynamics of Bomb Calorimetry

The ultimate aim of bomb calorimetry experiments is to obtain the standard enthalpy of formation, ΔH_f^o, of the compound. If this compound has the general formula $C_aH_bO_cN_d$, the standard enthalpy of formation refers to the process

$$aC(s)(1atm) + \frac{b}{2}H_2(g)(1atm) + \frac{c}{2}O_2(g)(1atm) + \frac{d}{2}N_2(g)(1atm) \xrightarrow{\qquad} C_aH_bO_cN_d\ (s\ or\ l)\ (1atm) \qquad (4)$$

conducted at a specified temperature, in this case 25°C.

The standard enthalpy of formation may be calculated from the standard heats of combustion. These may be written as

$$C_aH_bO_cN_d\ (\text{s or l}) + \left(a + \frac{b}{4} - \frac{c}{2}\right)O_2(g) \xrightarrow[25^\circ C]{1\ atm} aCO_2(g) + \frac{b}{2}H_2O(l) + \frac{d}{2}N_2(g) \quad (5)$$

$$aC(s) + aO_2(g) \xrightarrow[25^\circ C]{1atm} aCO_2(g) \quad (6)$$

$$\frac{b}{2}H_2(g) + \frac{b}{4}O_2(g) \xrightarrow[25^\circ C]{1atm} \frac{b}{2}H_2O(l) \quad (7)$$

$$\Delta H_f^\circ = -\Delta H_c^\circ(2) + \Delta H_c^\circ(3) + \Delta H_c^\circ(4) \quad (8)$$

It is the standard enthalpy of combustion of process (5) which is found from bomb calorimetry.

In bomb calorimetry, the reaction process is carried out under constant volume conditions. Thus the experimental quantity obtained is the standard internal energy of combustion, ΔU_c°. This is related to ΔH_c° by the equation

$$\begin{aligned}\Delta H_c^\circ &= \Delta U_c^\circ + \Delta(PV)\\ &= \Delta U_c^\circ + \Delta nRT \quad (9)\end{aligned}$$

where $\Delta n = \sum_p n_g - \sum_r n_g$

and $\sum_p n_g$ = total number of moles of products in gaseous phase

$\sum_r n_g$ = total number of moles of reactants in gaseous phase.

Thus ΔU_c° is found by experiment and ΔH_c° is obtained from equation (9). This number, together with the known values of ΔH_c° (6) and ΔH_c° (5) can then be used to obtain ΔH_f°, using equation (8).

However, ΔU_c° itself must be calculated from the actual bomb experiment. The experimental conditions differ from the standard state conditions in the following respects

(i) The reaction is carried out at 30 atmospheres,

(ii) The temperature of the system before the reaction is carried out is different from the temperature after the reaction is completed and at least one of these temperatures is different from the standard temperature of 25°C,

(iii) A small amount of water is added to the system before the reaction is carried out. Some of this water evaporates. Some of the gaseous species present in the bomb, both before and after the reaction will dissolve in the water remaining in the liquid phase. Both evaporation and dissolving processes involve an internal energy change,

(iv) Some of the products formed are not those specified in equations (5) - (8). In particular, nitrous and nitric acids are formed. Corrections for this must also be made.

(v) Consideration must be given to the energy released on combustion of the fuse. In this work, the fuse was made of platinum wire and firing cotton. Only the latter contributed to the energy changes in the calorimeter.

In order to correct for the effects of the above five items, a knowledge of the heat of combustion of the firing cotton, the heat of evaporation of water, the heats of solution of oxygen, carbon dioxide, nitrous and nitric acids and the heats of formation of nitrous and nitric acids is required. A knowledge is also required of the heat capacity of the reactants and the products, and the heat capacity (more correctly energy equivalent) of the bomb calorimeter. (This latter value has been found using the heat of combustion of benzoic acid.) Finally, the value of $\left(\frac{\partial U}{\partial p}\right)_T$ for all reactants and products is required.

A procedure for making these corrections has been laid down by Washburn[4]. A computer program has been written based on Washburn's method. An outline of his method is as follows:

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[4] Washburn, E.W., J. Research National Bureau of Standards, 10, 525 (1933), as reported in Experimental Thermochemistry, Rossini, F.D., (Ed.), Interscience Publishers, New York, 1956, at Ch. 5, p. 75.

(i) From a knowledge of the free volume of the bomb, the initial and final pressures, and the pVT behaviour of the initial and final gas mixtures, and from a knowledge of the total amount of water added; the number of moles of each of the gaseous species both before and after reaction and the number of moles of gases dissolved in the aqueous phase at 30 atmospheres and 25°C is calculated.

(ii) The number of moles of each species in each phase found from (i) both before and after reaction is then used to calculate (at 1 atmosphere) the energy changes due to dissolving and evaporation. This essentially allows for the energies of mixing the reactants in their standard states, and the energies of unmixing the products.

(iii) The energy required to compress the reactants from 1 atmosphere to 30 atmospheres and decompress the products from 30 atmospheres to 1 atmosphere is calculated from $\left(\frac{\partial U}{\partial p}\right)_T$ data,

(iv) The energy required to bring the reactants at 30 atmospheres from 25°C to the initial temperature T_i and that required to bring the products at 30 atmospheres from the final temperature T_f to 25°C is calculated from the heat capacities (at constant volume) of the reactants and products.

(v) The energy change due to the combustion reaction

$$\text{reactants } (30 \text{ atm}, T_i) \longrightarrow \text{products } (30\text{atm}, T_f)$$

is obtained from a knowledge of the energy equivalent of the calorimeter, $\mathcal{E}$(Calor), and the change in temperature $(T_f - T_i)$,

(vi) Corrections are made for the formation of HNO_2 and HNO_3.

(vii) Finally, a correction is made for the heat of combustion of the firing cotton.

The values used in making the corrections are shown in the Appendix. The contribution of each of the terms (ii) - (vii) for a typical experiment is given in Table 1.2. It can be seen that the overall correction, though small, is significant.

Table 1.2

Magnitudes of the Internal Energy Changes for l-Histidine, 12/11/76

[initial refers to before combustion
final refers to after combustion]

(ii)	initial vaporisation of a portion of the liquid water	+ 17.2J
	final condensation of any water vapour present	- 17.8J
	initial solution of a portion of the O_2 & N_2 gases in the water	- 0.5J
	final dissolution of dissolved O_2 & N_2 gases	+ 0.6J
	final dissolution of dissolved CO_2 gas	+ 4.9J
	total	+ 4.5J
(iii)	initial compression of substance	- 1.4J
	initial compression of liquid water	- 0.2J
	final decompression of aqueous solution	+ 0.4J
	initial compression of gases	- 72.6J
	final decompression of gases	+ 88.2J
	total	+ 14.5J
(iv)	reactants from 25°C to T_i	- 43.6J
	products from T_f to 25°C	- 2.3J
	total	- 46.0J
(v)	internal energy change on combustion	33 004.0J
(vi)	dilution of HNO_3 and HNO_2 to a concentration of 0.1M	- 0.4J
	decomposition of HNO_3 and HNO_2 to their component gases in standard states	+111.9J
	total	+111.5J
(vii)	contribution of firing cotton to internal energy change on combustion	- 63.1J

(Processes (ii), (iii), and (vi) comprise the Washburn corrections with a total internal energy change of 130.5J.)

1.5 Correction for Heat Losses during the Experiment

In a completely adiabatic process, the internal energy change occurring within the calorimeter during combustion, $\Delta U_{process}$, would be given by the equation

$$\Delta U_{process} = C\ (T_3 - T_1) = C\ \Delta T \tag{10}$$

where C refers to the heat capacity of the calorimeter system and T_1 and T_3 refer respectively to the temperature before and after combustion. This idealized process is represented by the path E T_1 G H, in Figure 1. The actual process which occurs is more likely to follow the path A B I C D. In this case during the course of the experiment, there is energy exchange between the system and the surroundings. This arises from several causes. There are firstly, those that depend on the temperature difference between the calorimeter and jacket, and calorimeter and room, such as conduction by solid connections, radiation and convection by the intervening gases. There is also evaporation, though this may be made negligible by efficient sealing. It is also appropriate to include the heat of stirring.

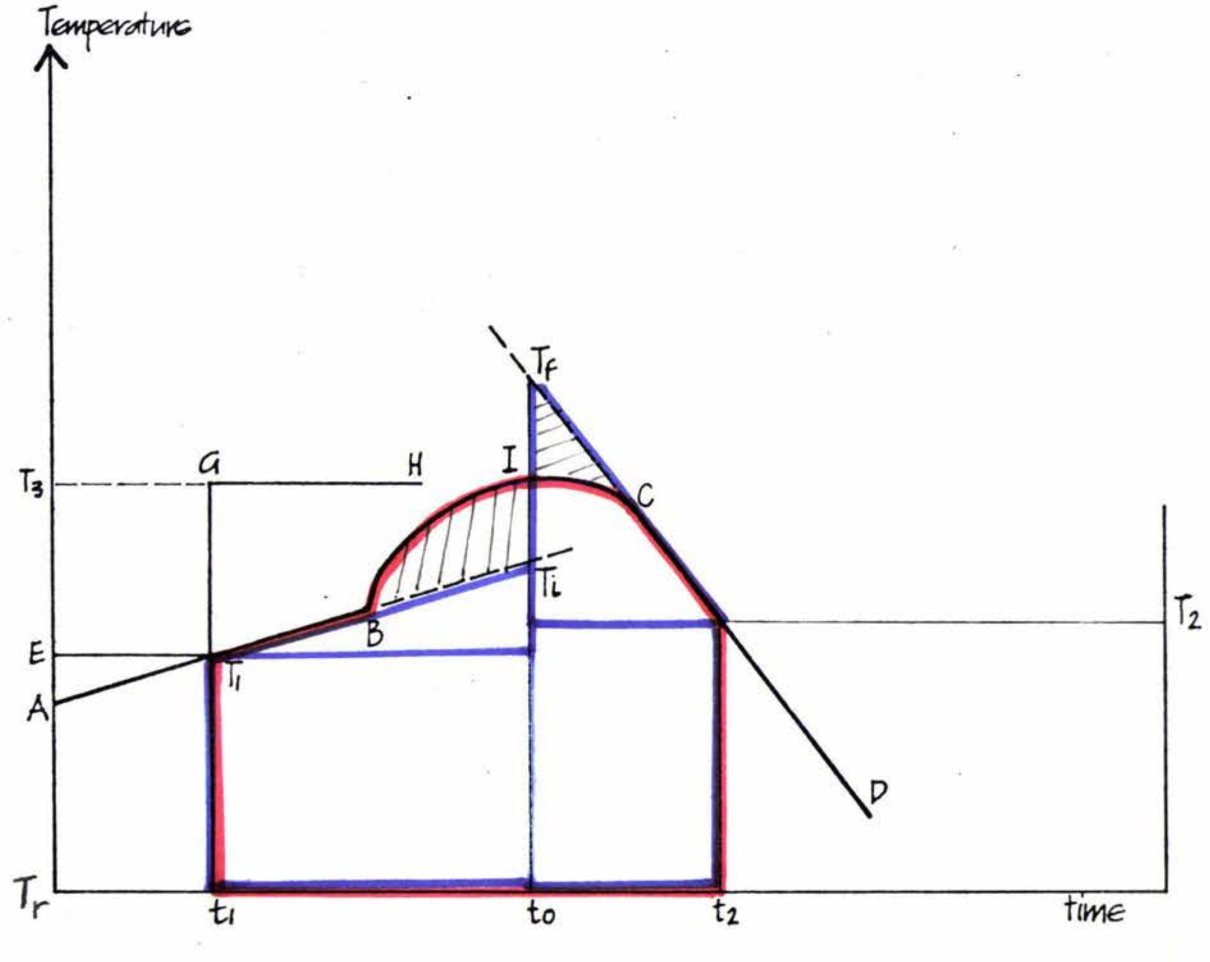
Provided that the temperature differences are small, we can assume that the heat exchange rate, $\dot{q}$, will be governed by Newton's law of cooling. If the work rate of the stirrer is designated $\dot{w}$, then the rate of energy exchange $\dot{U}_{ex}$ is given by

$$\dot{U}_{ex} = \dot{q} + \dot{w} \text{ and}$$

$$\dot{U}_{ex} = k_1\ (T_j - T_c) + \dot{w} + k_2\ (T_r - T_c)$$

where k_1 and k_2 are constants and T_j, T_c and T_r refer to the temperature of the jacket, the temperature of the calorimeter and the temperature of the room respectively. If the experiment is carried out such that $(T_j - T_c)$, $\dot{w}$, and T_r are all constant

$$\dot{U} = K + k_2\ (T_r - T_c) \tag{11}$$



The integral $\int_{t_1}^{t_2} (T_C - T_r)dt$ is the area bounded by red.

If the perpendicular $T_f t_o$ is dropped so that the shaded areas are equal, the area bounded by red is the sum of the rectangles and the triangles bounded by blue.

Thus $$\int_{t_1}^{t_2} (T_r - T_C)dt = -\int_{t_1}^{t_2} (T_C - T_r)dt = (T_r - T_1)(t_o - t_1) + (T_r - T_2)(t_2 - t_o)$$

$$+ \tfrac{1}{2}(T_1 - T_i)(t_o - t_1) + \tfrac{1}{2}(T_2 - T_f)(t_2 - t_o)$$

Figure 1
Measurement of ΔT

The actual process can be conveniently divided into three parts. There is a fore period, AB, and an after period, CD, where the only processes occurring are those involving energy exchange. If these periods are short enough AB and CD can be assumed linear without great loss of accuracy. During the period BIC, in addition to the exchange processes, there is also a temperature change due to the combustion process itself. This period is sometimes known as the reaction or main period.

We can calculate the effect of the energy exchange on the final temperature if we proceed as follows:

Somewhere along the fore line we choose a point (T_1, t_1), where the process is deemed to begin, and along the after line we choose a point (T_2, t_2), where the process is deemed to end. We then consider two processes whereby we pass from T_1 to T_2.

Process 1 Direct

$$\text{System } T_1 \longrightarrow \text{system } T_2 \tag{A}$$

Process 2 Indirectly via T_3, the temperature the system would reach were it adiabatic.

$$\text{System } T_1 \longrightarrow \text{system } T_3 \tag{B}$$

$$\text{System } T_3 \longrightarrow \text{system } T_2 \tag{C}$$

Now the first law requires

$$\Delta U_{ex}(A) = \Delta U_{ex}(B) + \Delta U_{ex}(C)$$

where $\Delta U_{ex}(A)$ refers to the energy exchange due to the processes (A).

Now, according to our assumption $\Delta U_{ex}(B) = 0$

Whence $\Delta U_{ex}(A) = C(T_2 - T_1) = \Delta U_{ex}(C) = C(T_2 - T_3)$.

Now $\Delta T = T_3 - T_1$ i.e. the temperature differences that would occur in the adiabatic case (which is the value we require in (10)) is given by

$$\begin{aligned} \Delta T &= (T_2 - T_1) + (T_3 - T_2) \\ &= (T_2 - T_1) - \Delta U_{ex}/C \end{aligned} \tag{12}$$

And, from (11)

$$\Delta U_{ex}/C = \int_{t_1}^{t_2} \left[K/C + k_2/C \quad (T_r - T_c) \right] dt \tag{13}$$

The terms K/C, k_2/C can be eliminated by considering the rate of energy exchange in the fore period and the rate of energy exchange in the after period.

Since $\dot{U} = C\dot{T}$ we obtain from (11)

$$\dot{T}_{fore} = K/C + k_2/C \ (T_r - T_{fore}) \tag{14}$$

$$\dot{T}_{after} = K/C + k_2/C \ (T_r - T_{after}) \tag{15}$$

where $\dot{T}_{fore}$ and $\dot{T}_{after}$ refer to the rate of change in the fore and after period at temperatures T_{fore} and T_{after} respectively. Solving (14) and (15) yields K/C and k_2/C.

The evaluation of the integral in (13) can be simplified if AB and CD are extended as in the diagram, and a perpendicular $T_f \, I \, T_i \, t_0$ is dropped such that the area B T_i I is the same as the area I T_f C. (see p. 12) Since AB and CD extended are linear, we have

$$T_f = T_2 - \dot{T}_{after} \ (t_2 - t_0) \tag{16}$$

$$T_i = T_1 + \dot{T}_{fore} \ (t_1 - t_0) \tag{17}$$

Using the values of K/C and k_2/C found from (14) and (15), and using (16) and (17) to obtain T_2 and T_1 in equation (12) in terms of T_f and T_i, and substituting these in equation (13) leads to the result

$$\Delta T = T_f - T_i + \frac{(\dot{T}_{after} - \dot{T}_{fore})}{(T_{after} - T_{fore})} \left[(T_{after} - T_f)(t_2 - t_0) + (T_{fore} - T_i)(t_0 - t_1) - \frac{1}{2} \left\{ \dot{T}_{after} \ (t_2 - t_0)^2 - \dot{T}_{fore} \ (t_0 - t_1)^2 \right\} \right] \tag{18}$$

If it is further assumed that $T_{after} \sim T_f$, $T_{fore} \sim T_i$, $(t_2 - t_0) \sim (t_0 - t_1) = \delta t$, and if we write $T_{after} - T_{fore} = \Delta^1 T \sim \Delta T$, $\dot{T}_{after} - \dot{T}_{fore} = \Delta \dot{T}$, we obtain $\Delta T = (T_f - T_i) - \frac{(\Delta \dot{T})^2 (\delta t)^2}{2 \Delta^1 T}$ $(19)^5$

In this work, since our temperatures can be measured to 10^{-4} K, we may neglect the second term of (19) if its magnitude is around 10^{-5} K. Since $\Delta T \sim 2$ K this will be achieved if $\Delta \dot{T} \sim 10^{-3}$ K mm^{-1}, and $\delta t \sim 10$ minutes. Since t_1 and t_2 are arbitrary the only restriction this puts on the experiment is the time from T_f to C.

The condition for $\Delta \dot{T}$ lays a further constraint on the experiment, the others being constant temperature difference between the jacket and the calorimeter, the linearity of the slopes, and the constancy of the temperature of the room. In this work, it was required that the room temperature be constant to ± 0.5 K, the difference between water and jacket temperature to be constant to ± 0.1 K. The linearity of the after slope was judged satisfactory if it gave T_f to within 0.0005 K. (If the condition for the fore slope was not met, one did not fire.) These four criteria proved to be very rigorous as about half of the experiments done were rejected on one or more of these bases.

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[5] Equation (19) was originally derived for the writer by Dr I.R. McKinnon, Senior Lecturer, Monash University.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus

The combustion measurements in this work were made using a Gallenkamp "Adiabatic" Bomb Calorimeter (CB-110), but with the mercury thermometer replaced by a quartz thermometer. The entire apparatus was housed in a room maintained at a constant temperature of 25.0 ± 0.5°C. (But see p. 4 for comment on "adiabatic" calorimeters.)

A basic outline of the apparatus is shown in Figure 2. It is made up of a pressurized combustion chamber, or bomb, A, which (after loading) is placed on three legs in a water filled can, B. The can is also positioned on three legs so as to leave an air space of about one centimetre between it and the outer jacket, C. This outer jacket, C, and the jacket lid, D, are filled with water so that a layer of water three centimeters deep surrounds the can. A firing circuit is housed in the rest of the apparatus and makes connection with the bomb at F. The circuit diagram of the firing system is given in Figure 3.

The combustion chamber is shown in more detail in Figure 4. It consists of a bomb cap, A, and body of capacity of about $300 cm^3$, B, made from stainless steel (BS 1506-845B). The head is screwed to the body via a sealing nut, D, and a rubber "O" ring. The head supports the two firing electrodes, one of which, E, is insulated from the bomb, while the other, F, is connected to the bomb. This electrode is earthed through a contact between the can and the water jacket, and contains a Schröder valve, through which oxygen is introduced to the bomb. A safety valve is used in conjunction with the needle valve on the oxygen cylinder. The earthed electrode, F, supports the pellet to be combusted via a nickel chromium crucible, L, which in turn is supported by a support ring, M. The pellet is attached to the electrodes by 0.08mm diameter platinum wire by means of firing cotton.

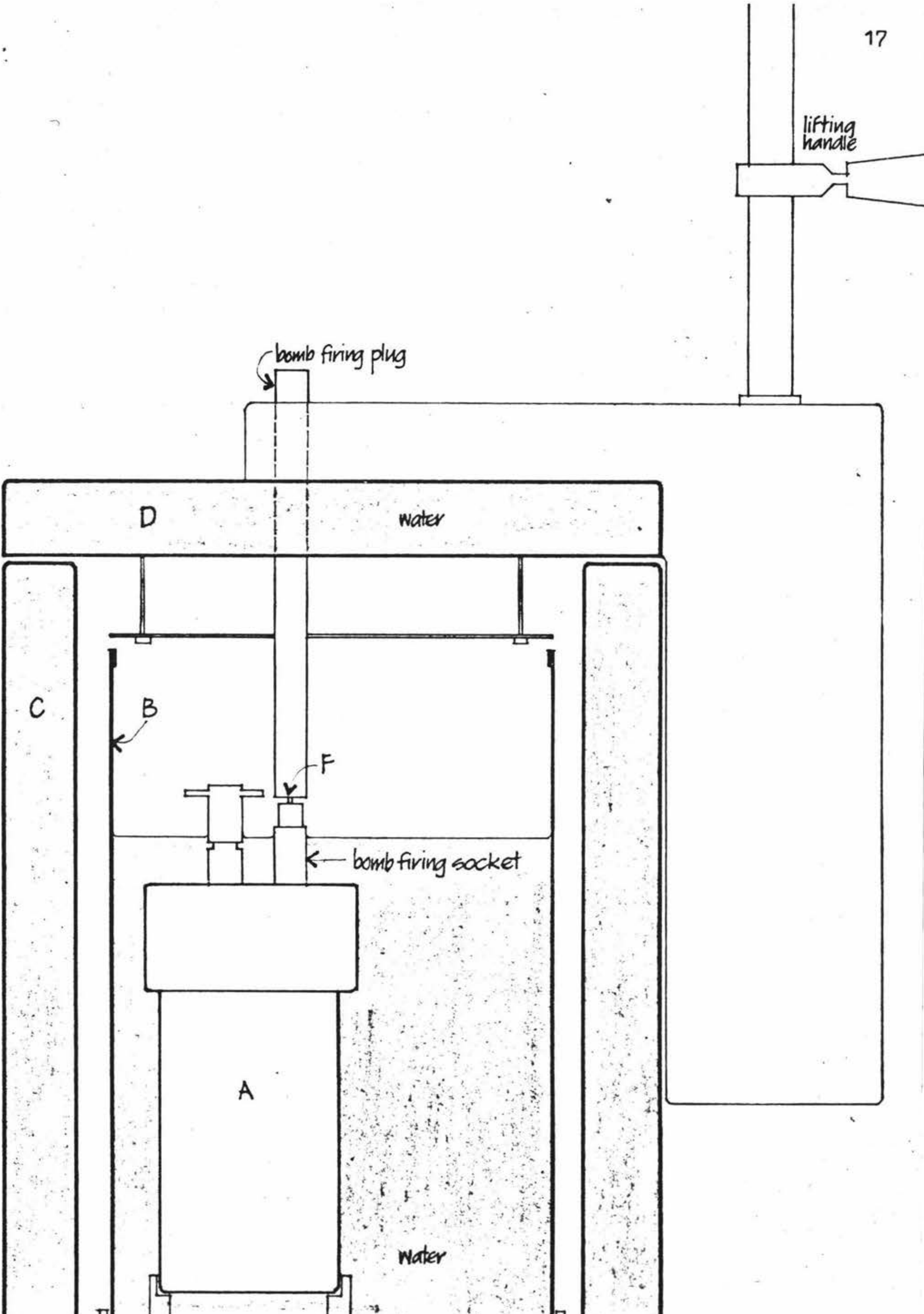


Figure 2
Basic Outline of Apparatus

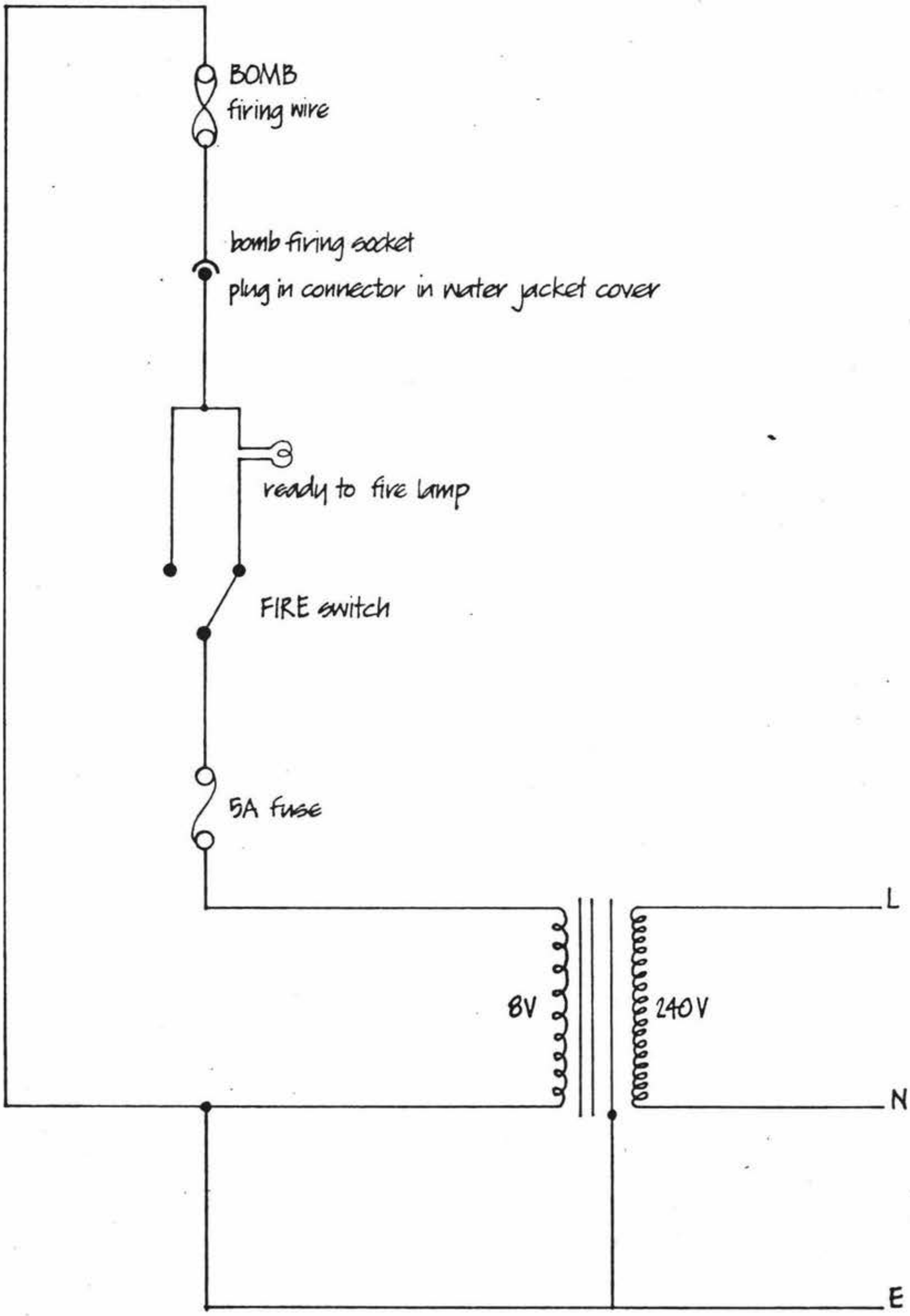


Figure 3
Circuit diagram of firing system.

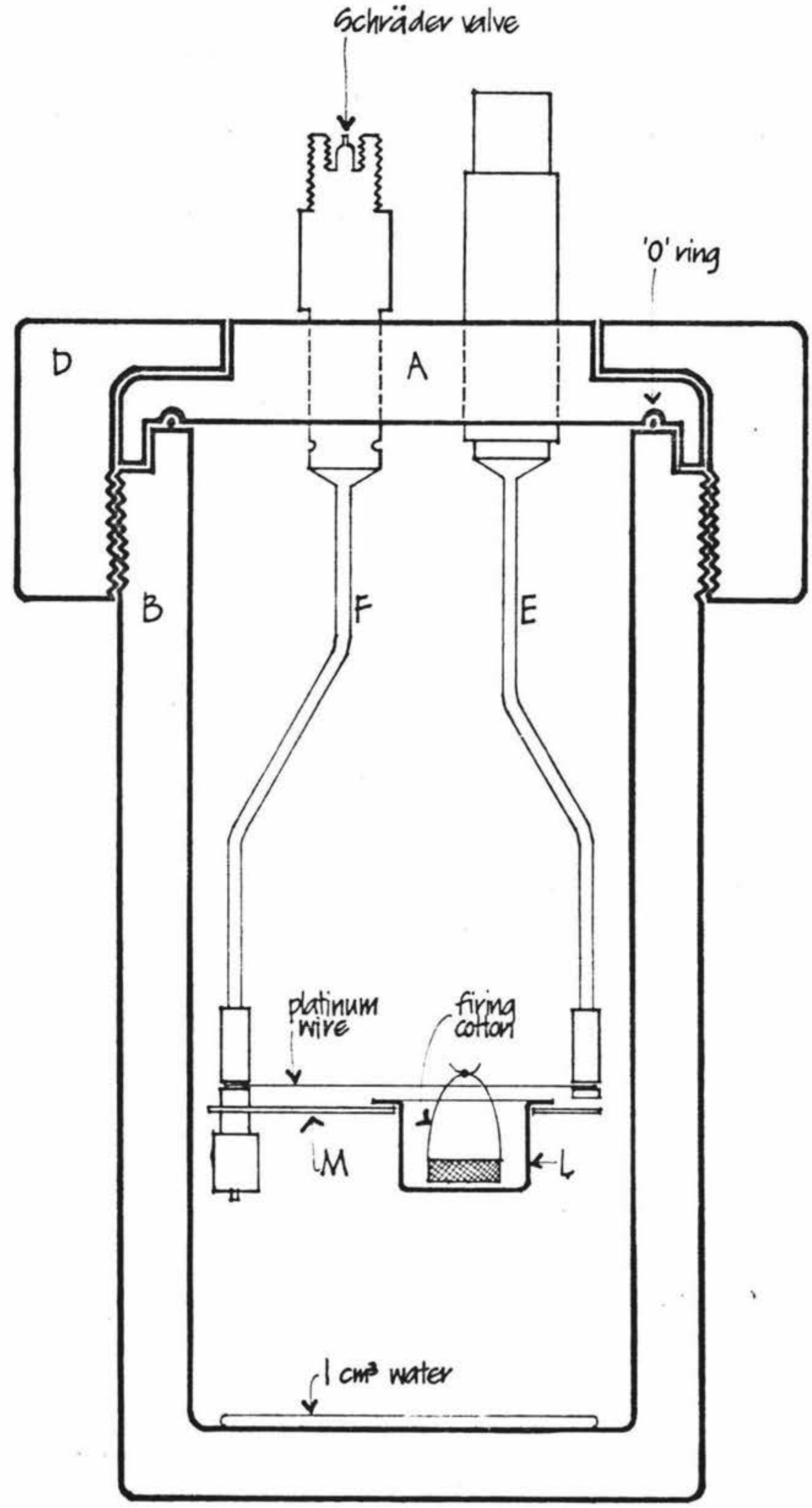


Figure 4
Combustion Chamber

More details of the bomb calorimeter and the enclosing water jacket are given in Figure 5. The can, B, has a capacity of about 2100cm^3; this volume of water is stirred by a stirrer, S, driven by a constant speed motor. The water in the jacket, C, and in the lid, D, is kept at a uniform temperature by a pump, P, which circulates it. The water jacket is maintained at a temperature that is a fixed amount above the temperature of the water in the can by means of matched thermistors, M, which control heaters in the water jacket. The thermistors form two arms of a Wheatstone bridge (Figure 6). When their resistance differs by more than a specified amount, the off balance voltage which results activates these heaters.

It is necessary to increase the conductivity of the water by the addition of small amounts of sodium carbonate so as to give a current of between 6 and 7A when the electrode heaters are switched into operation.

The outer surface of the can is polished to minimise heat losses by radiation, and is separated from the inner surface of the thermostatically controlled jacket, which is also highly polished, by an air gap of 1.0 to 1.5cm (Figure 5).

It is necessary to remove the heat produced from the circulating pump by flowing tap water through a cooling coil placed in that jacket and a flow rate of 345cm^3 min^{-1} was used. A constant flow rate was found to be critical, and it was monitored by a glass float meter to ± 5cm^3 min^{-1}.

The temperature sensing device was an Hewlett Packard quartz thermometer (HP-2801A). This compares the frequencies of a quartz crystal housed in the probe which is placed in the can and a reference crystal housed in a constant temperature oven under the oscillator. The frequency changes as the temperature varies. Beats occur when the two crystals are at differing temperatures and the instrument relates the frequency of these beats directly to temperature. It was calibrated at the ice point of water.

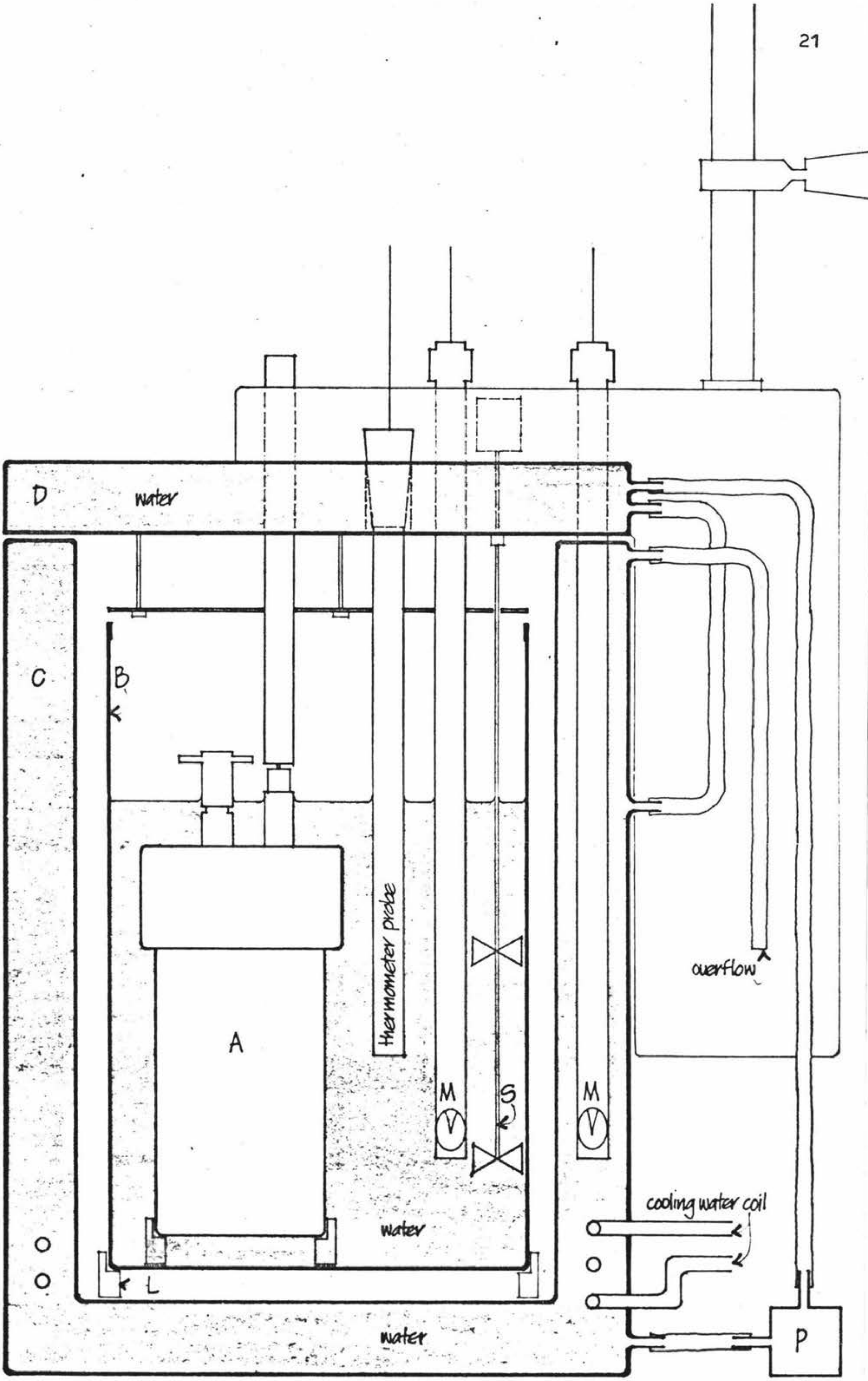


Figure 5
Detailed diagram of Apparatus

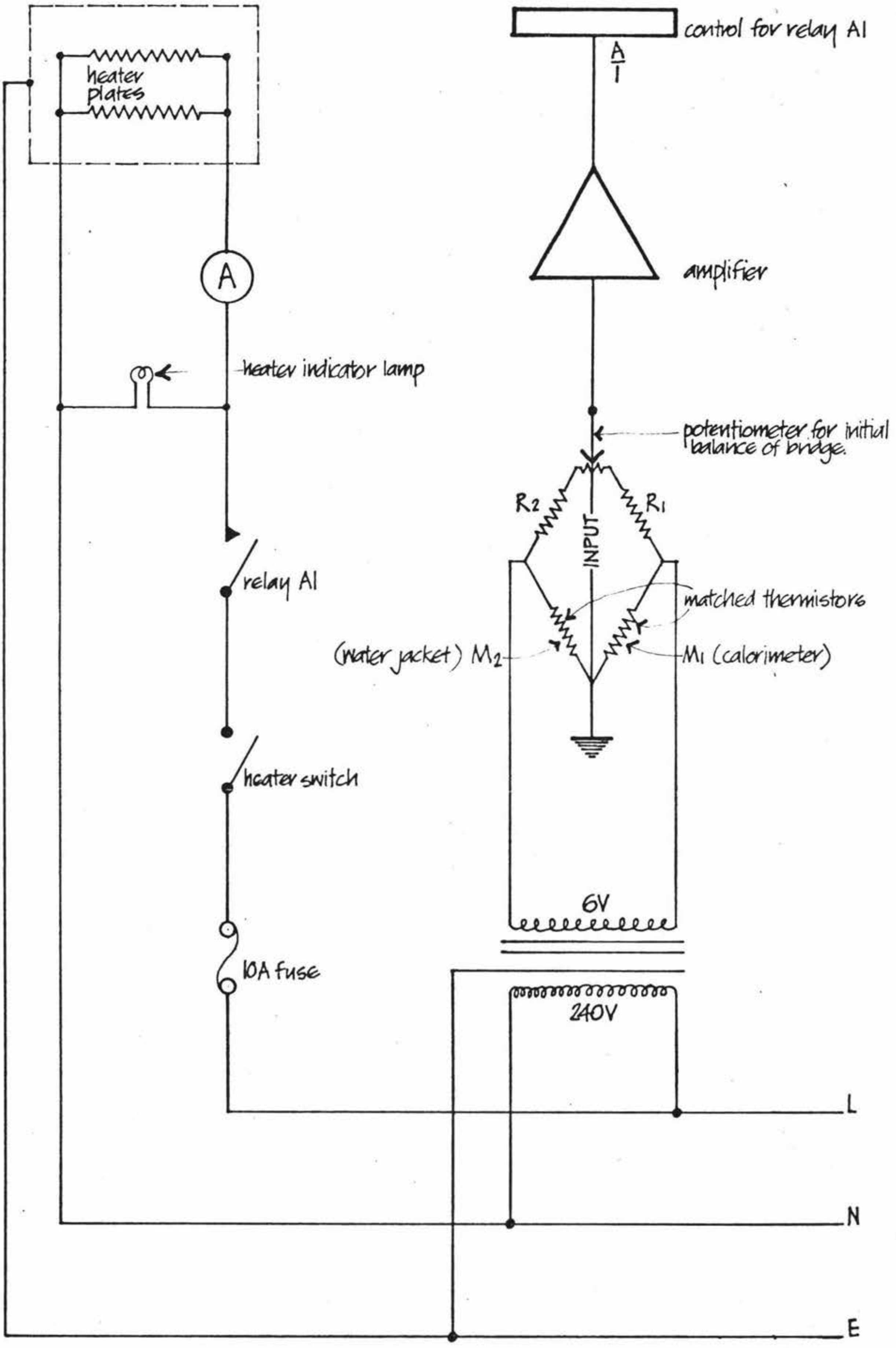


Figure 6
Circuit diagram of Jacket Temperature Control.

The sample is prepared for combustion by pelletisation in a pellet press. An outline of this press is given in Figure 7. A hardened steel punch and die form the samples into pellets. Firing cotton is compacted into the sample during this operation.

2.2 Procedure

2.2.1 Preparation of the Sample

The substances to be combusted were thoroughly dried using the following procedure. The substance was stored for a few days in a vacuum desiccator over "Drierite" (anhydrous calcium sulphate). The substance was then formed into pellets and further dried, again in the vacuum desiccator. The pellets were then crushed and left a further 24 hours in the desiccator. The final pellet was made incorporating a weighed amount of firing cotton (about 9cm long), and placed in the desiccator for at least a further three hours before weighing.

The pellet was weighed in a nickle/chromium crucible on a M5 Mettler Balance (No. 190760 Max. 20g.) to five places after the decimal. The mass of the samples were corrected to in vacuo. This required a knowledge of the density, and an estimate of the density of each substance to be combusted was made by weighing a pellet and measuring the diameter and height of the pellet. The crucible and pellet were then placed on the ring support and the cotton attached to the platinum wire that connects the electrodes.

2.2.2 Loading the Bomb

A small amount of water ($1.000 cm^3$) was accurately pippetted into the bomb, then the cap applied and the sealing nut closed to hand tightness. Industrial grade oxygen ($\geqslant 99.5\%$ oxygen, ~ 200ppm $H_2O(g)$ by volume, <50ppm hydrogen by volume, trace N_2) was introduced into the bomb, firstly to flush out the air, then finally to a pressure such that at 25°C the pressure inside the bomb would be 30atm (3039 kPa).

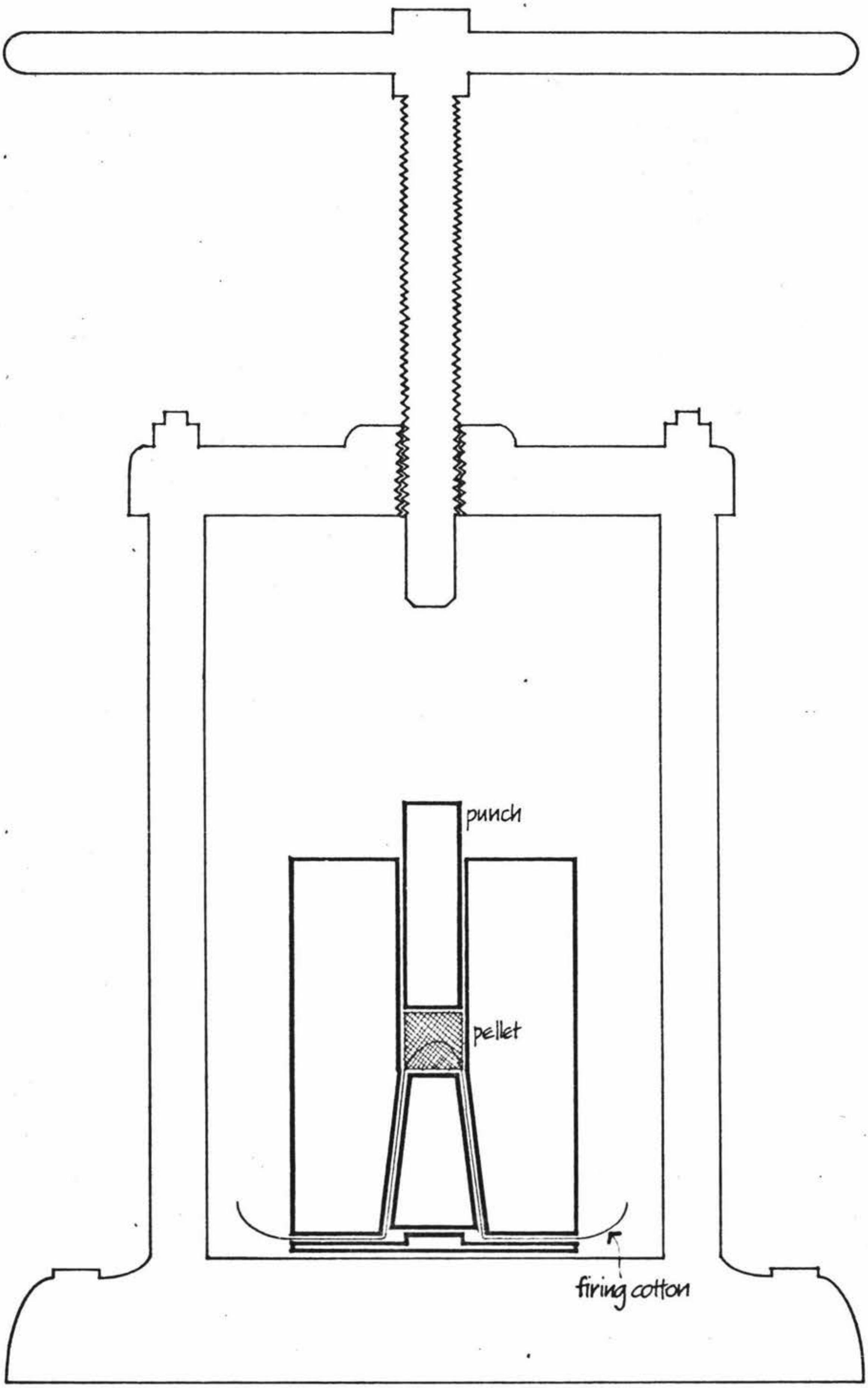


Figure 7
Pellet Press.

The bomb was tested for leaks by immersing it in water which was warmed to about 22.5°C (to assist in bringing the bomb towards the desired commencing temperature).

2.2.3 Loading the Calorimeter Can

Prior to placing the bomb in the calorimeter can, the can was filled with a quantity of previously warmed water to a total mass of 3 000.0 ± 0.1g using a top pan balance (Mettler P5). The water had been heated so that its temperature after the bomb had been placed in the can would be about 22.5°C. The bomb was wiped dry and immediately lowered into the can.

As soon as the bomb was in position, the total calorimeter can assembly was placed inside the water jacket. The lid was lowered over the can, the thermometer probe inserted, and stirring commenced. Finally the temperature controlling circuit of the water jacket was adjusted until the temperature of the water jacket was 0.4 ± 0.1°C above that of the calorimeter at the balance point for the bridge.

2.2.4 Taking a Measurement

After being left to stabilise for half to one hour, the temperature of the calorimeter was recorded each minute until a linear variation with time over a 20 minute period was obtained. The sample was ignited by means of the firing system and the ensuing temperature rise, caused by the combustion reaction, was measured every fifteen seconds for five minutes. The temperature was then further monitored at minute intervals until again a linear slope was obtained. This usually took thirty minutes from the time of firing, but in some cases it took up to an hour. An hour after firing the bomb was removed from the calorimeter and, after release of pressure, the interior was inspected. If soot was present, incomplete combustion was assumed, and the run discarded.

2.2.5 Determination of the Amount of Acid Formed

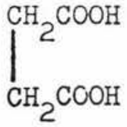
During the combustion process small amounts of nitric and nitrous acids were formed. These were removed from the bomb by several washings to a total of 50 - 70cm^3 of distilled water. These washings were titrated with standardized 0.1M sodium hydroxide using methyl orange as indicator. The sodium hydroxide had been standardized with hydrochloric acid which in turn had been standardized with the primary standard, borax.

2.3 Purification of Materials

Benzoic Acid, C_6H_5COOH

National Bureau of Standards sample 39i of benzoic acid was used in the calibrations. This had been refined by fractional freezing at N.B.S. specifically for use as a calorimetric standard.

Succinic Acid,



$$\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$$

Several batches of May and Baker Reagent grade succinic acid were purified for combustion by following the method set out below and recommended by Vanderzee et al.[6]

After recrystallisation four times from deionised water, drying at 80°C for 1 hour, grinding in an agate pestle and mortar, and then drying at 102°C for 20 hours, 112°C for 2 hours, and 118°C for 3 hours, the crystals were stored in a desiccator over "Drierite" for at least a week.

The crystals were then compacted into pellets and replaced in the desiccator for at least 2 days before being broken into coarse fragments and returned to the desiccator for storage. Vanderzee reports a mass loss by the pellets of 0.043%, mostly in their first 18 hours in the desiccator. This was retested and a mass loss of 0.021% was obtained after 4 hours in

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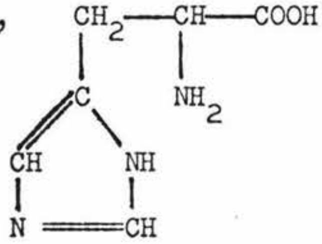
[6] Vanderzee, C.E., Månsson, M., Sunner, S., The Energy of Combustion of Succunic Acid, J. Chem. Thermodyn. 1972, 4(4), 533-40.

the desiccator, increasing to 0.025% for the first 30 hours, and 0.029% in 50 hours.

Each pellet that was prepared for combustion from the coarse fragments mentioned above was stored for at least 2-3 hours before use.

<u>l-histidine,</u>

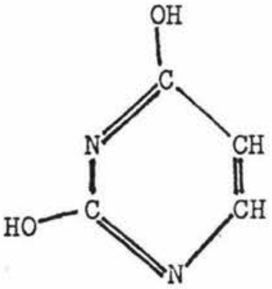


One batch was recrystallized twice from deionised water and large (~1/2cm) straw coloured crystals were obtained.

On comparison with combustion runs with unrecrystallized Fluka puriss. l-histidine no change was apparent.

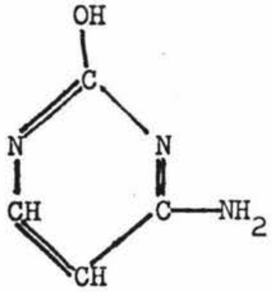
All crystals were pellet dried in a manner similar to succinic acid, but without heating.

<u>Uracil,</u>



Samples of Uracil were taken directly from the bottle of Fluka puriss. uracil and pellet dried before use.

<u>Cytosine,</u>



Similarly, cytosine was pellet dried without recrystallization from the Fluka puriss. cytosine before use.

2.4 Calibration with Benzoic Acid

The energy change associated with the change in temperature during combustion may be obtained from energy of combustion experiments with benzoic acid. The quantity that is symbolized ε(Calor) is essentially the heat capacity of the bomb calorimetric system (excluding the contents of the bomb) *under the conditions of the bomb experiment*. During the experiment, the pressure of the bomb changes in going from the initial to the final state, and therefore the elastic strain on the bomb proper and the compression on the crucible and other parts change. Strictly, therefore, the term "heat capacity" is inappropriate, and "energy equivalent" is preferred.

The value of ε(Calor) is obtained from a knowledge of the energy of combustion of benzoic acid *under standard bomb conditions*, ΔU_B, a knowledge of the energy changes associated with other isothermal processes going on in the bomb during combustion, and the measurement of the change in temperature during combustion. The overall energy change, $\Delta U_{I.B.P.}$, going on in the bomb at 30 atmospheres and 25°C is given by

$$\Delta U_{I.B.P.} = \Delta U_{Bz}\cdot m_{Bz} - \Delta U_{decomp}\,(HNO_3)\cdot n_{HNO_3} - \Delta U_{decomp}\,(HNO_2)\cdot n_{HNO_2} - \Delta U_{dilution}\cdot(n_{HNO_3} + n_{HNO_2}) + \frac{\Delta U_c^\circ\,(fuse)}{M}\cdot m_{fuse} \qquad (20)$$

Here and subsequently, unless otherwise specified, the symbols used are those of Hubbard, Scott and Waddington[7] except that internal energy is represented by U, the temperature change including the correction for heat transfer between the system and the surroundings is represented by $\Delta T = T_f - T_i$ (i.e. $t_f - t_i - \Delta t_{corr}$ is represented by ΔT), and the assumption that $T_f \sim t_f$ is made for the calculation of $\Delta U_{I.B.P.}$

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[7] Hubbard, W.N., Scott, D.W., Waddington, G. In *Experimental Thermochemistry*, Chap. 5, pp. 75-128. E.D. Rossini, editor. Interscience: New York, 1956.

The symbol ΔU_{Bz} refers to the energy of combustion of benzoic acid under the conditions of the bomb experiment. In general these differed from standard bomb conditions. Under standard bomb conditions the sample is burned in a bomb of constant volume in pure oxygen at an initial absolute pressure of 30 atmospheres and at a temperature of 25°C. The number of grammes burned is numerically equal to three times the volume of the bomb (in litres), and the number of grammes of water placed in the bomb before combustion is numerically equal to three times the volume of the bomb (in litres). ΔU_{Bz} is related to the energy of combustion of benzoic acid under standard bomb conditions, ΔU_B, by the equation

$$\Delta U_{Bz} = \Delta U_B \left[1 + 10^{-6} \left\{ 20(p_i - 30) + 42\left(\frac{m_{Bz}}{V_{bomb}} - 3\right) + 30\left(\frac{m_{H_2O}}{V_{bomb}} - 3\right) - 45\,(t - 25) \right\} \right] \tag{21}$$

Here p_i, m_{Bz}, V_{bomb}, m_{H_2O}, and t refer respectively to the initial pressure of the oxygen (in atmospheres), the mass of benzene (in grammes), the volume of the bomb (in litres), the mass of water (in grammes), and the temperature to which the reaction is referred. (In this work $t = 25$°C.)

The terms ΔU_{decomp} (acid) and $\Delta U_{dilution}$ refer to the energy of decomposition of one mole of the acid specified, and the energy of dilution of nitrous and nitric acid in total. The term $\Delta U_c^\circ(\text{fuse})/M$ refers to the energy of combustion of the firing cotton per gramme. Values for ΔU_B, $\Delta U_c^\circ(\text{fuse})/M$, ΔU_{decomp} (HNO_3), and ΔU_{decomp} (HNO_2) were taken as -26434 J g^{-1} [8], -17489 J g^{-1} [9], 58886 J mol^{-1} [10], and -27614 J mol^{-1} [10] respectively. The firing cotton was assumed to have the same empirical formula (viz. $CH_{1.686}O_{0.843}$)[11] as filter paper fuse.

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[8] National Bureau of Standards Certificate (accompanying calorimetric standard benzoic acid, sample 39i).

[9] Gallenkamp Autobomb Automatic Adiabatic Bomb Calorimeter handbook.

[10] Hubbard *et al.*, *op. cit.*, p. 100.

[11] *ibid.*, p. 81.

The number of moles of HNO_3 is given in Table (2-1). It was assumed $n_{HNO_2} = 4 \times 10^{-3}\, n_{HNO_3}$[12]. The energy of dilution in each case was read from a graph of the data of wt.% (HNO_3 + HNO_2) vs $\Delta U_{dilution}$[13].

The energy equivalent of the system (minus contents) is given by the equation

$$\mathcal{E}(\mathrm{Calor}) = \frac{\Delta U_{I.B.P.} - (25 - T_f)(\mathcal{E}^f_{(cont)} - \mathcal{E}^i_{(cont)})}{-\Delta T} - \mathcal{E}^i_{(cont)} \quad (22)$$

Here $\mathcal{E}^i_{(cont)}$ and $\mathcal{E}^f_{(cont)}$ refer respectively to the heat capacity of the contents of the bomb before and after combustion, and T_f is the temperature of the system after combustion.

The values of $\mathcal{E}$(Calor) obtained from five experiments are given in Table 2-1. The mean value 10730 J K^{-1} was used in subsequent experiments.

2.5 Test of Apparatus: Energy of Combustion of Succinic Acid

The energy of combustion of succinic acid has been measured by a number of workers. The consistency of the results of these studies and the large measure of agreement between different groups has led to the suggestion that succinic acid be used as a secondary standard. Recently this possibility has been thoroughly investigated by Vanderzee and others, who find that provided care is taken in the drying process, accurate and reproducible measurements can indeed be made. To further enhance this view, these workers summarized, and where appropriate recalculated to standard state conditions, the results of others. This summary is shown in Table 2.2.

It was decided to check the calibration of our machine by measuring the energy of combustion of succinic acid. The results are given in Table 2.3. The process by which the value of ($\Delta U^\circ_c/M$) was calculated

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[12] *ibid.*, p. 142.

[13] *ibid.*, p. 91.

Table 2.1

Data for Combustion Experiments with Benzoic Acid

Equation of the reaction $C_7H_6O_2(s) + 7\frac{1}{2}O_2(g) \longrightarrow 7\ CO_2(g) + 3\ H_2O(l)$.

Date	Mass/g	Mass of fuse/g	Final temperature/°C	$\Delta T/K$	Quantity of HNO_3/mol	$\varepsilon(\text{Calor})/JK^{-1}$
16/6/76	0.98178	0.00352	25.0393	2.4215	0.00008	10731.0
18/6/76	1.00231	0.00313	25.3788	2.4702	0.00008	10736.0
6/7/76	0.99705	0.00325	24.6682	2.4597	0.000086	10726.7
23/7/76	0.89856	0.00425	25.3262	2.2190	0.000063	10725.3
26/7/76	0.97742	0.00342	25.2272	2.4102	0.000078	10732.8

mean $\varepsilon(\text{Calor}) = 10730\ JK^{-1}$

standard deviation = ± 9 JK^{-1}

standard error = ± 4 JK^{-1}

Table 2.2

Summary of Values for the Standard Specific Energy of Combustion of Succinic Acid at 298.15K

Investigators	$-\Delta U_c^\circ/M/Jg^{-1}$
Verkade, Hartmann, and Coops	12638.6 ± 5.0
Beckers	12639.0 ± 4.2
Keffler	12636.1 ± 4.2
Roth and Becker	12637.2 ± 3.3
Huffman	12637.6 ± 2.5
Pilcher and Sutton	12638.1 ± 1.8
Cass and Springall	12635.7 ± 4.2
Keith and Mackle	12635.3 ± 5.0
Bills and Cotton	12636.1 ± 4.2
Wilhoit and Shiao	12634.0 ± 4.2
Adams, Carson, and Laye	12637.4 ± 5.0
Good	12637.9 ± 1.7
Ducros	12639.0 ± 3.3
Wong and Westrum	12634.8 ± 1.7
Vanderzee, Månsson, and Sunner[14]	12639.3 ± 2.3
Kitzinger and Hems[15]	12635 ± 2
Zaikin and Nazaruk[16]	12639.4 ± 1.7
This study, Table 2.3	12638.6 ± 16.8

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[14] Vanderzee, C.E., Månsson, M., Sunner, S. J. Chem. Thermodyn. 1972, 4(4), 533-40 (see Table 3, p. 538 of this paper for all preceding values.)

[15] Kitzinger, C., Hems, R. Biochem. J. <u>71</u>, 395 (1959).

[16] Zaikin, I.D., Nazaruk, L.N. Russ. J. Phys. Chem. 1970, 44, 1376.

Table 2.3

Data for Combustion Experiments with Succinic Acid

Equation of the reaction $C_4H_6O_4(s) + 3\frac{1}{2}O_2(g) \longrightarrow 4\ CO_2(g) + 3\ H_2O(l)$

Date	Mass/g	Mass of fuse/g	Final Temperature/°C	$\Delta T/K$	Quantity of HNO_3/mol	$\frac{\Delta U_c^\circ}{M}/Jg^{-1}$
24/ 8/76	0.86812	0.00289	23.9670	1.0286	0.00002	-12655.3
8/ 9/76	1.84653	0.00330	24.7029	2.1844	0.00004	-12662.8
15/ 9/76	1.93735	0.00364	24.7069	2.2871	0.000040	-12635.1
16/ 9/76	1.87906	0.00346	24.0235	2.2158	0.00005	-12620.4
1/10/76	1.97614	0.00333	25.0155	2.3305	0.000053	-12625.4
4/10/76	1.93995	0.00346	25.0864	2.2894	0.000048	-12632.6

mean $\frac{\Delta U_c^\circ}{M}$ (298.15K) = -12638.6 J g^{-1} standard deviation = ± 16.8 J g^{-1}

is described in detail in the introduction and is expanded in the next section. At this stage it is pertinent to point out that our mean result, listed also in Table 2.3, is in excellent agreement with others.

CHAPTER 3

RESULTS

3.1 Measurement of ΔT

The manner in which the temperature changes during the course of a combustion experiment is typified in Figure 8. The fore period AB extends over about an hour. Notice that about half this time elapsed before a constant slope of 2.3×10^{-4} Kmin^{-1} was obtained. The main period, BD, (shown on an expanded scale) shows typical behaviour, as does the after period, DE. Here the constant slope is - 4.3×10^{-4} K min^{-1}. From applying the equal area rule to the period BD, t_o was at 1.3 min. after FIRE, and from AB and DE, T_i and T_f, and thus ΔT, were found to be 22.8170°C, 25.2272°C and 2.4102 K respectively.

3.2 Calculation of $\Delta U_c^o/M$

The values of ΔT, the mass of material, and the amount of nitric acid formed after each experiment are given for each compound in Tables 3.2 - 3.4. Also given is the specific energy of combustion, $\frac{\Delta U_c^o}{M}$, calculated for this data, making the appropriate corrections. With reference to page 9 the corrections involved the following additional data:

(i) In order to calculate the free volume of the bomb, allowance had to be made for the volume of its contents. This required a knowledge of the volume of the pellet, which was obtained from the mass of the pellet and its density. There were no density figures available for any of the substances. To obtain a figure, pellets of each compound were made and weighed, and their diameter and height measured using a micrometer. The densities so estimated are given in Table 3.1.

(ii) - (iv), (vi), (vii) The values of the physical data used to calculate the corrections were those of Hubbard, Scott and Waddington[17], except for the solubility constant of carbon dioxide, where the value

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[17] Hubbard _et al._, _op. cit._ pp. 83-101.

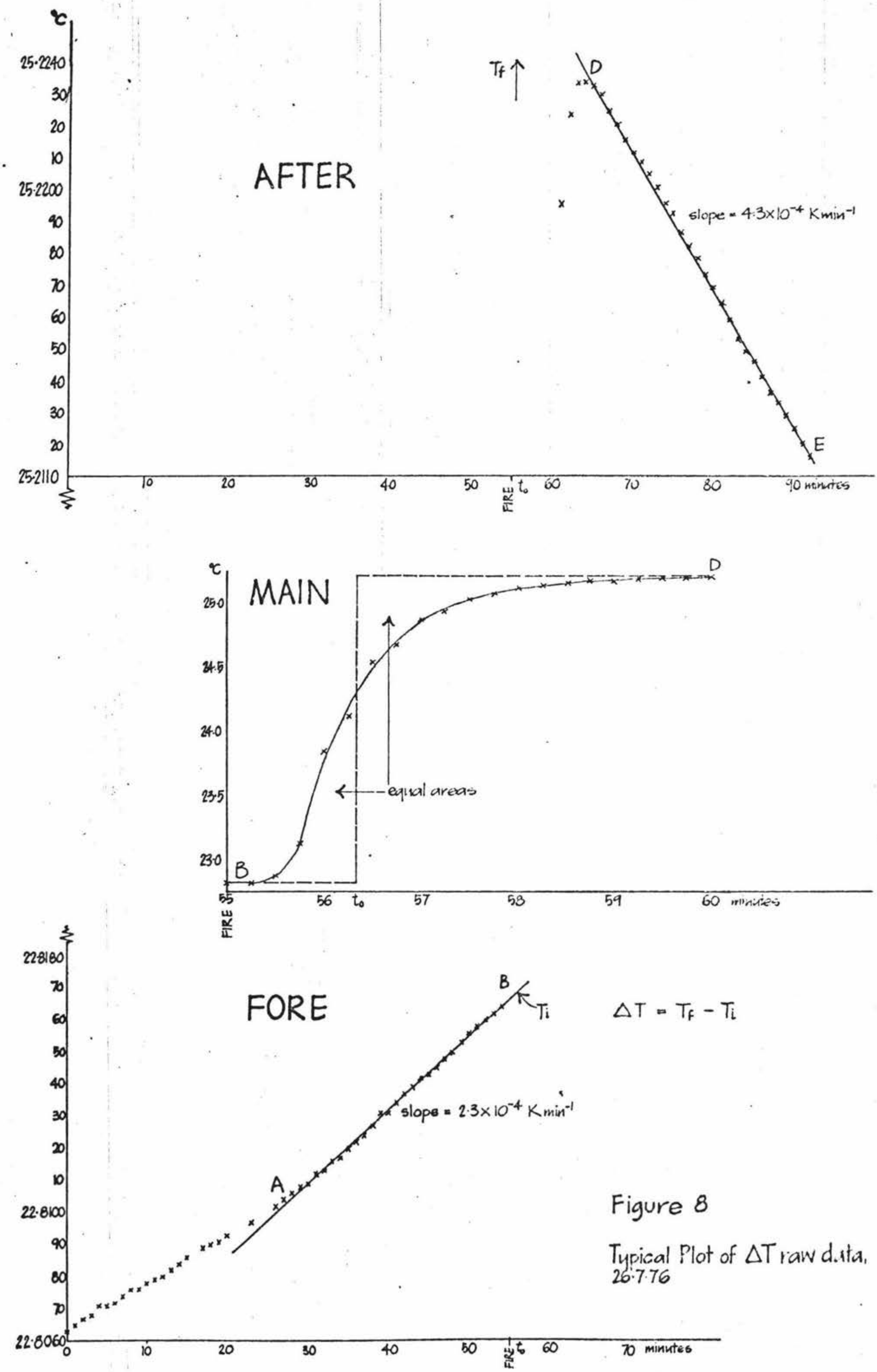

Figure 8

Typical Plot of ΔT raw data, 26·7·76

Table 3.1

Density Values Used in Calculations

	Density/g cm^{-3}	
	Approximate Estimate	Literature Value
benzoic acid	1.2	1.26
succinic acid	1.4	1.56
l-histidine	1.2 ± 0.2	
uracil	1.3 ± 0.2	
cytosine	1.2 ± 0.2	

[Note: For benzoic acid and succinic acid the results were compared with values reported in bomb calorimetry literature. In view of the large discrepancies a high error rate of about 20% was assumed where no literature value was available.]

Table 3.2

Data for Combustion Experiments with l-histidine

Equation of the Reaction:

$$C_6H_9O_2N_3(s) + \frac{29}{4}O_2(g) \longrightarrow 6CO_2(g) + \frac{9}{2}H_2O(l) + \frac{3}{2}N_2(g)$$

Date	Mass/g	Mass of fuse/g	Final temperature/°C	ΔT/K	Quantity of Nitric Acid/mol	$\frac{\Delta U_c^\circ}{M}$/Jg^{-1}
14/10/76	1.74607	0.00453	25.5545	3.3502	0.00186	-20494.1
22/10/76	1.18197	0.00411	24.2234	2.2714	0.00141	-20501.47
8/11/76	1.14488	0.00416	25.3867	2.2023	0.00130	-20524.0
12/11/76	1.60772	0.00361	25.1434	3.0736	0.00190	-20495.0

Mean $\frac{\Delta U_c^\circ}{M}$ (298.15K) = -20504 Jg^{-1} Standard deviation = ± 14 Jg^{-1}

Table 3.3

Data for Combustion Experiments with Uracil

Equation of the Reaction:

$$C_4H_4O_2N_2(s) + 4O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l) + N_2(g)$$

Date	Mass/g	Mass of Fuse/g	Final Temperature/°C	ΔT/K	Quantity of HNO_3/mol	$\frac{\Delta U_c^\circ}{M}$/$Jg^{-1}$
29/11/76	1.65754	0.00315	24.2021	2.3877	0.00144	-15377.0
1/12/76	1.57658	0.00376	24.8883	2.2708	0.00133	-15368.4
14/ 2/77	1.74850	0.00439	25.1869	2.5186	0.00155	-15364.9
17/ 2/77	1.60152	0.00364	25.3689	2.3123	0.001394	-15406.5

Mean $\frac{\Delta U_c^\circ}{M}$ (298.15K) = -15379 Jg^{-1} Standard Deviation = ± 19 Jg^{-1}

Table 3.4

Data for Combustion Experiments with Cytosine

Equation of the Reaction:

$$C_4H_5ON_3(s) + \frac{19}{4}O_2(g) \longrightarrow 4CO_2(g) + \frac{5}{2}H_2O(l) + \frac{3}{2}N_2(g)$$

Date	Mass/g	Mass of Fuse/g	Final Temperature/°C	$\Delta T/K$	Quantity of HNO_3/mol	$\frac{\Delta U_c^\circ}{M}$ /Jg^{-1}
22/3/77	0.85257	0.00387	24.6260	1.4925	0.001272	-18626.7
25/3/77	0.91998	0.00402	24.0032	1.6100	0.001385	-18619.6
29/3/77	1.41458	0.00368	24.8964	2.4716	0.002065	-18627.0
15/4/77	0.84604	0.00310	24.7724	1.4797	0.001288	-18622.9

Mean $\frac{\Delta U_c^\circ}{M}$ (298.15K) = $-18624\ Jg^{-1}$ Standard Deviation = $\pm 4\ Jg^{-1}$

$\Delta U_{\text{solution}}$ (CO_2) = - 17280 J mol^{-1} at 25°C is now preferred[18]. These values are listed in the computer printout (see Appendix). In the absence of any information it is assumed that the heat capacity, C_v, for each substance is the same. Similarly the internal energy change with pressure for each substance is assumed to be the same. The errors arising from these assumptions are small (see Section 3.4).

(v) The energy equivalent of the calorimeter was of course taken from the benzoic acid experiments to be 10730 ± 4 JK^{-1}.

3.3 Calculation of ΔU_c^o, ΔH_c^o, ΔH_f^o

The standard energy of combustion, ΔU_c^o was obtained using molar masses based on the ^{12}C atomic mass scale. The standard enthalpy change on combustion, ΔH_c^o, was obtained from ΔU_c^o using equation (9). (See page 7).

The standard enthalpy of formation was obtained from equation (8).

The values for ΔH_f^o (CO_2, g, 1atm, 25°C), and ΔH_f^o (H_2O, l, 1atm, 25°C) were taken as - 393.15 ± 0.13 and - 285.830 ± 0.042 kJ mol^{-1} respectively[19].

Values of the three quantities are shown in Table 3-5.

3.4 Analysis of Errors

Errors have been classified under six headings:

1. Error in the mass of the substances

   The error in each of the weighings is ± 10^{-5}g, giving rise to a percentage error of 0.0005%. However, because of the large error in the density (~ 20%), the error in the true mass (i.e. mass in vacuo) is ± 3 x 10^{-4}g, or 0.02%.

2. Error in the temperature measurements

   In a typical experiment, the error in the fore slope is about 3%,

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[18] Hu et al., Journal of Chemical Thermodynamics, 1972(4), pp. 283-299.

[19] CODATA Recommended Key Values for Thermodynamics, CODATA Bulletin No. 17, ICSU CODATA, Paris, 1976.

Table 3.5

Standard Enthalpy of Formation, ΔH_f° (298.15K)

Compound	l-histidine	Uracil	Cytosine
Formula	$C_6H_9O_2N_3$	$C_4H_4O_2N_2$	$C_4H_5ON_3$
Relative Molar Mass/g mol^{-1}	155.154	112.086	111.100
$\frac{\Delta U_c^\circ}{M}$(298.15K)/$Jg^{-1}$	-20504 ± 14	-15379 ± 19	-18624 ± 4
ΔU_c° (298.15K)/$kJmol^{-1}$	-3181.2 ± 2.2	-1723.8 ± 2.1	-2069.1 ± 0.4
ΔH_c° (298.15K)/$kJmol^{-1}$	-3180.6 ± 2.2	-1721.3 ± 2.1	-2067.2 ± 0.4
ΔH_f° (298.15K)/$kJmol^{-1}$	- 466.7 ± 0.5	- 424.4 ± 0.7	- 221.4 ± 0.2

and in the after slope around 20%. This leads to an error in T_i and T_f of 0.00005°C and 0.0005°C respectively. The error in ΔT is therefore ± 0.0006 K or 0.02%. In all experiments t_o was found to occur at 1.33 minutes after firing, with an error of 0.02 min., and thus makes a negligible contribution to the error in ΔT. (See Figure 8, page 36 for an example.)

3. Error in $\mathcal{E}$(Calor)

The error in $\mathcal{E}$(Calor) was taken as the standard error of the benzoic acid results, ± 4 JK^{-1}, or 0.04%.

4. Errors arising from Washburn correction factors

(i) Errors arising from solution, dissolution, and evaporation. The main experimental source of error is the volume of the bomb. The value of 0.2961 l ± 0.0001 l introduces an error of 0.03%. In view of the small overall contribution of this term, this error was neglected.

(ii) Errors arising from compression and decompression of the materials. Again, because of the small magnitude, error contributions of these terms were also able to be neglected. For example the error in the estimated term $\left(\frac{\partial U}{\partial p}\right)_T$ makes the greatest contribution and the value of $\left(\frac{\partial U}{\partial p}\right)_T$ for each compound was estimated from Hubbard's illustration[20]. Assuming this gives an error of 15% (from a consideration of the mean of Hubbard's three values and the value given for succinic acid[21]), the error in the term arising from the initial compression of the compound is ± 0.2 J.

(iii) Errors due to dilution and decomposition of nitric and nitrous acids. The contribution of the dilution term is again negligible, as is the decomposition of nitrous acid term. The error in the determination of the number of moles of nitric acid formed is 1.2%, giving an error in the decomposition of nitric acid term of ± 1.3 J.

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[20] Hubbard, W.N., Scott, D.W., Waddington, E., op. cit., p. 90.

[21] Vanderzee, C.E., Mansson, M., Sunner, S., op. cit., p. 535.

5. Errors arising from temperature changes

As the experiments are arranged so that T_f is near 25°C, the error for the products from T_f to 25°C term is neglected.

A significant source of error occurred for the heat capacity of the compounds. These are unknown, and it was assumed they were all the same as succinic acid[22]. Hubbard's example[23] also gives values for C_p and consideration of all these values suggested an error of 30%. This introduces an error of 5% for the energy equivalent of the contents of the bomb in the initial state and thus an error of ± 2 J for the term, reactants from 25°C to T_i.

6. Error due to combustion of fuse

The error in the determination of the mass of the fuse is 0.2%, giving an error in the combustion of the fuse term of ± 0.2 J.

From items 4 - 6, the total error in the correction factors is ± 4 J. (See Table 1.2, page 10, parts (ii), (iii), (iv), (vi) and (vii)). The error in ΔT and $\mathcal{E}$(Calor) leads to an error of 0.06% or ± 20 J for the internal energy change on combustion. (See Table 1.2 part (v)). Consideration of all the errors (Table 3.6) leads to a combined error of 0.1% (about 20 Jg^{-1}) in $\frac{\Delta U_c^\circ}{M}$.

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[22] ibid., p. 535.

[23] Hubbard, W.N., Scott, D.W., Waddington, G., op. cit., p. 93.

Table 3.6

Errors

1.	Mass	0.02%			0.1%
2.	ΔT	0.02%	0.06% (± 20 J)	0.07%	
3.	$\mathcal{E}$(Calor)	0.04%			
4 - 6	Correction Factors		(± 4 J)		

CHAPTER 4

DISCUSSION

The primary purpose of this investigation was to redetermine the heats of formation of some compounds of biological interest previously measured by Humphrey in 1971[24]. Humphrey described the thermometer as 'difficult to read, especially in obtaining the third decimal place'. With the replacement of this mercury in glass thermometer by a Hewlett-Packard Quartz thermometer having a resolution of 10^{-4} K it seemed likely that errors involved in the original measurements could be decreased. (No plots or raw data from the calorimeter temperature versus time graphs for the 1971 work have been able to be obtained.)

The cytosine combusted in this investigation was anhydrous and therefore not able to be meaningfully compared with the cytosine.H_2O previously combusted. The result of this research was -221.4 ± 0.2 kJ mol^{-1} for ΔH_f° (298.15 K); that previously obtained being -536.7 ± 0.6 kJ mol^{-1} for ΔH_f° (298.15 K).

The results for the remaining two compounds combusted, l-histidine and uracil, are compared in Table 4.1 with the values obtained in 1971 by Humphrey.

Some evidence that the recent values are more reliable than the 1971 values may be suggested by the test results obtained in each case. (Table 4.2) Naphthalene was chosen from the test substances used by Humphrey because the value he obtained for this was closest to the literature value. From a comparison of the results in Table 4.2 it seems possible that the introduction of the new thermometer may have improved the results obtained by a factor of ten.

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[24] Humphrey, R.S., The Thermochemistry of Organic Compounds Involved in Metabolic Processes, unpublished project for B.Sc.(Hons.), Massey University, 1971.

Table 4.1

Comparison of Values of ΔH_f° (298.15 K)

ΔH_f° (298.15 K) / kJ mol^{-1}	1-Histidine	Uracil
Humphrey[25]	-478.6 ± 0.6	-421.3 ± 0.5
This work	-466.7 ± 0.5	-424.4 ± 0.7

---

[25] *ibid.*, Tables V and IV (between pp. 16 and 17).

Table 4.2

Comparison of Research Results with Literature Values

Test Substance	Result ΔH_c° (298.15 K) kJ mol^{-1}	Literature Value ΔH_c° (298.15 K) kJ mol^{-1}	% Difference
Naphthalene (Humphrey)[26]	-5153.4 ± 2.9	-5156.8	0.066
Succinic acid (this work)	-1491.3 ± 2.0	-1491.2 ± 0.2	0.007

---

[26] *ibid.*, Table II (between pp. 16 and 17).

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APPENDIX

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C CALCULATION OF BOMB CALORIMETER "WASHBURN CORRECTIONS" FOR ORGANIC
C NITROGEN COMPOUNDS BASED ON HUBBARD ET AL
C
C $SET SEQ LINE INFO
FILE  5=INPUT,UNIT=READER

FILE  3=OUTPUT,UNIT=PRINTER


      DIMENSION AM(3),CAM(3),RHO(3),A(3),B(3),C(3),D(3),AN(3),V(3),AI(3
      DIMENSION Y(3),Q(3),DEDP(3),CP(3),Z(20)
C ITEMS 1-18 ARE DATA FOR MATERIALS COMPRISING THE TOTAL SUBSTANCE THAT
C UNDERGOES COMBUSTION
C (SUBSTANCE=> COMPOUND+AUXILIARY COMPOUND+FUSE)
C1 FORMULA OF COMPOUND IS C(A(1)) H(B(1)) O(C(1)) N(D(1))
C2 AM(1) IS MASS OF COMPOUND
C3 CAM(1) IS MOLAR MASS OF COMPOUND
C5 RHO(1) IS DENSITY OF COMPOUND IN GRAMS PER LITRE
C7 FORMULA OF AUXILLARY COMPOUND IS C(A(2)) H(B(2)) O(C(2)) N(D(2))
C8 AM(2) IS MASS OF AUXILLARY MATERIAL
C9 CAM(2) IS MOLAR MASS OF AUXILLARY MATERIAL
C11 RHO(2) IS DENSITY OF AUXILLARY MATERIAL
C13 FORMULA OF FUSE IS C(A(3)) H(B(3)) O(C(3)) N(D(3))
C14 AM(3) IS MASS OF FUSE
C15 CAM(3) IS MOLAR MASS OF FUSE
C17 RHO(3) IS DENSITY OF FUSE
      WRITE(3,1548)
 1548 FORMAT('0 "WASHBURN CORRECTIONS" ')
      WRITE(3,1552)
 1552 FORMAT('0   COMPOUND:                                        S.R.WILSON'
      WRITE(3,1554)
 1554 FORMAT('0                    CYTOSINE 22/3/77')
      WRITE(3,1556)
 1556 FORMAT('0  AUXILIARY MATERIAL  -NONE')
      WRITE(3,1558)
 1558 FORMAT('0  FUSE  -COTTON')
      DO 1000 I=1,3
 1000 AI(I)=1.
      READ(5,1501) AMAIR,TROOM,PATM
      WRITE(3,1559) AMAIR,TROOM,PATM
 1559 FORMAT('0  AMAIR=',F10.5,' GRAM   TROOM=',F3.0,'   PATM=',F5.1)
      READ(5,1501) CAM(1),RHO(1)
      AM(1)=(1.2929*PATM*273.15)/(1000*760*(273.15+TROOM) )
      AM(1)=AM(1)*(1/RHO(1)-1/8.4)
      AM(1)=AMAIR*(1+AM(1))
      WRITE(3,1560) AM(1),CAM(1),RHO(1)
      DO 1500 I=2,3
      READ(5,1501) AM(I),CAM(I),RHO(I)
 1501 FORMAT(3E15.10)
      WRITE(3,1560) AM(I),CAM(I), RHO(I)
 1560 FORMAT('0',F10.5,' GRAM  ',F9.3,' G/MOL  ',F9.2,' G/CM3 ')
 1500 CONTINUE
      DO 1502 I=1,3
      READ(5,1503) A(I),B(I),C(I),D(I)
 1503 FORMAT(4E15.10)

      WRITE(3,1561) A(I),B(I),C(I),D(I)
 1561 FORMAT('0    C(',F6.3,')  H(',F6.3,')  O(',F6.3,')  N(',F6.3,')')
 1502 CONTINUE
C AN(I) IS NO OF MOLES OF COMPOUND(1), AUXCMPD(2), OR FUSE(3),(4,10,16)
C V(I) IS VOLUMEIN LITRES OF CMPD(1),AUX CMPD(2),OR FUSE(3), (6,12,18)
      DO 1600 I=1,3
      AN(I)=AM(I)/CAM(I)
 1600 V(I)=AM(I)/(RHO(I)*1000.)
C STEPS 19-25 CALCULATE SUBSCRIPTS OF THE EMPIRICAL FORMULA
C C(AE)H(BE)O(CE)N(DE) SO THAT ANSUB WHICH IS NO MOLES TOTAL SUBSTANCE=
   19 AE=F(AN,A)
   20 BE=F(AN,B)
   21 CE=F(AN,C)
```

```
   22 DE=F(AN,D)
   23 AMSUB=F(AI,AM)
   24 CAMSB=12.011*AE+1.008*BE+15.999*CE+14.006*DE
   25 ANSUB=AMSUB/CAMSB
C ITEMS 26-36 DEAL WITH INITIAL AMOUNTS OF O2,N2,H2O IN BOMB AND
C THEIR DISTRIBUTION BETWEEN THE GASEOUS AND LIQUID PHASES
   26 READ(5,1501) VBOMB,VH2O,PGAS
      WRITE(3,1760) VBOMB,VH2O,PGAS
 1760 FORMAT('0  VBOMB=',F7.4,'    VH2O=',F7.4,'    PGAS=',F6.2)
      ROH2O=0.99756
C PREFIX A MEANS INITIAL STATE. SUFFIX L,V,T MEAN LIQUID,VAPOUR,TOTAL
C HO IS WATER,CO ISCARBON DIOXIDE,N NITROGEN,NO NITROGEN+OXYGEN MIXTURE
   29 AMHOT=ROH2O*VH2O*1000.
   30 ANHOT=AMHOT/18.016
      VCORR=F(AI,V)
   31 AVGAS=VBOMB-VH2O-VCORR
   32 ANHOV=0.02304+0.00008*PGAS
      ANHOV=ANHOV*AVGAS/18.016
   33 ANHOL=ANHOT-ANHOV
   34 ANGAS=PGAS*AVGAS
      TEMP=25.
      AMU=890.-11.3*TEMP
      AMU=AMU*PGAS/1000000.
      AMU=1.-AMU
      AMU=AMU*(TEMP+273.15)*0.082054
      ANGAS=ANGAS/AMU
      APHO=0.03
      AKO2=0.00117
   35 ANNOD=0.01807*AKO2*ANHOL
      ANNOD=ANNOD*(PGAS-APHO)
   36 ANNOT=ANGAS-ANHOV+ANNOD
C ITEMS 37-67 DEAL WITH ALL COMPOUNDS IN THEIR FINAL STATE IN BOMB
C E PREFIX DENOTES FINAL STATE,NO3 IS HNO3,NO2 IS HNO2
      READ(5,1501) ENNO3
      ENNO2=0.004*ENNO3
      WRITE(3,1860) ENNO3
 1860 FORMAT('0  ENNO3=',F8.6)
   39 ENN=DE/2.*ANSUB-0.5*(ENNO2+ENNO3)
   40 ENHOL=ANHOT-0.5*(ENNO2+ENNO3)-ANHOV+BE/2.*ANSUB
C EMSO IS MASS OF SOLUTION . WTWNT ISWEIGHT% OF NITRIC &NITROUS ACIDS
   41 EMSO=18.016*ENHOL+63.*ENNO3+47.*ENNO2
   43 WTCNT=6302.*ENNO3+4702.*ENNO2
      WTCNT=WTCNT/EMSO
   44 EROSO=ROH2O+0.0054*WTCNT
   45 EVSO=EMSO/(1000.*EROSO)
C EVSO IS FINAL VOLUME OF SOLUTION ENORM IS NORMALITY OF HNO3+HNO2
   47 ENORM=ENNO3+ENNO2
      ENORM=ENORM/EVSO

   49 EVGAS=VBOMB-EVSO
   50 ENCOT=AE*ANSUB
   51 EKCO=340.+10.*ENORM
      EKCO=EKCO/10000.
   52 DCO2=0.854
      N=1
   53 ECOS=DCO2*EKCO
      ENCOD=0.082054*(TEMP+273.15)*ECOS*EVSO
   54 ENCOD=ENCOD/EVGAS
      DEN=1.+ENCOD
      ENCOD=ENCOD/DEN*ENCOT
   55 ENCOG=ENCOT-ENCOD
   56 ENNOT=ANNOT-(AE+BE/4.-CE/2.)*ANSUB-1.25*ENNO3-0.75*ENNO2
      EKO=(ENNO3+ENNO2)/2.
      EKO=11.26+1.05*(1.0-EKO)
   57 EKO=EKO/10000.
   58 EDO=0.926
```

```
  59 EKOS=EDO*EKO
  60 ENNOD=0.082054*(TEMP+273.15)*EKOS*EVSU/EVGAS
     DEN=1.+ENNOD
     ENNOD=ENNOD/DEN
     ENOM=ENNOT+ENN
     ENNOD=ENNOD*ENOM
  61 ENNOG=ENNOT-ENNOD
  62 ENGAS=ENNOG+ENCOG+ANHOV+ENN
  63 XCO=ENCOG/ENGAS
 631 XNO=ENNOG/ENGAS
 632 XN=ENN/ENGAS
     IF(N-1) 126,126,127
 126 N=N+1
     DCO2=873.-190.*XCO
     DCO2=DCO2/1000.
     GO TO 53
 127 CONTINUE
  64 EMUO=890.-11.3*TEMP
     EMUO=EMUO/1000000.
     EMUGS=EMUO*(1.+3.21*XCO*(1.+1.33*XCO))
  65 EPGAS=EVGAS/(0.082054*(TEMP+273.15)*ENGAS)
     EPGAS=EPGAS+EMUGS
     EPGAS=1./EPGAS
  66 G=1.-0.006*WTCNT
     ACO=0.00048
     CO=0.02304
     AO=0.00008
     ENHOV=XCO*(ACO-AO)
  67 ENHOV=AO+ENHOV
     ENHOV=ENHOV*EPGAS
     ENHOV=CO+ENHOV
     ENHOV=ENHOV*G*EVGAS/18.016
C ITEMS 68-80 TABULATE ENERGY FACTORS AND CALORIMETRIC DATA
  68 READ(5,1501) DEDP(1),DEDP(2),DEDP(3)
     WRITE(3,1960) DEDP(1),DEDP(2),DEDP(3)
1960 FORMAT('0  &U/&P(1)=',F7.4,'  &U/&P(2)=',F7.4,'  &U/&P(3)=',F7.4)
  69 DEDPS=-186.-8.*WTCNT
     DEDPS=DEDPS/100000.
  70 UDIL=102-96*WTCNT**0.25
  71 READ(5,1501) UAUX,UFUSE
     WRITE(3,1962) UDIL,UAUX,UFUSE
1962 FORMAT('0  >UDIL HNO3=',F4.0,'    >UAUX=',F9.5,'    >UFUSE=',F10.1)
  74 READ(5,1501) UCALR,AMPT,AMGL
     WRITE(3,1964) UCALR,AMPT,AMGL

1964 FORMAT('0  ε(CALOR)=',F7.2,'  AMPT=',F8.5,'    AMGL=',F8.5)
C UDIL IS DILUTION ENERGY NACIDS, UAUX IS ENERGY CHANGE DUE TO AUX CMPD
C UFUSE IS ENERGY CHANGE DUE TO FUSE, UCALR IS ENERGY EQUIVALENT OF BOM
C AMPT IS MASS OF PLATINUM, AMGL IS MASS OF GLASS AMPOULE.
     READ(5,1501) CP(1),CP(2),CP(3)
     WRITE(3,1966) CP(1),CP(2),CP(3)
1966 FORMAT('    CP(1)=',F6.3,'    CP(2)=',F6.3,'    CP (3)=',F6.3)
     READ(5,1501) CVO,CVCO,CVN
     WRITE(3,1968) CVO,CVCO,CVN
1968 FORMAT('0  CV(O2)=',F6.3,'    CV(CO2)=',F6.3,'   CV(N2)=',F6.3)
     READ(5,1501) E,UIGN
     WRITE(3,1970) E,UIGN
1970 FORMAT('0  E=',F4.0,'              >U(IGN)=',F5.2)
     AZ=0.997-0.012*WTCNT
  75 AUCN=CVO*ANNOT+0.997*AMHOT+E*ANHOV
     SUM=F(AM,CP)
     AUCN=AUCN+SUM
  76 EUCN=CVO*ENNOT+CVCO*ENCOT+AZ*(EMSU+18.*ENHOV)+E*ENHOV+0.325*AMPT
C AUCN IS INITIAL ENERGY EQUIVALENT OF CONTENTS OF BOMB
C EUCN IS THE FINAL ENERGY EQUIVALENT OF THE CONTENTS OF THE BOMB
     EUCN=EUCN+CVN *ENN
  78 READ(5,1501) TIN,TFIN,DELT
     WRITE(3,1972) TIN,TFIN,DELT
1972 FORMAT('0  TINITIAL=',F5.1,' TFINAL=',F8.4,' TI-TF+>T=-',F6.4)
```

```
C ITEMS 81-100 CALCULATE CHANGES IN INTERNAL ENERGY
   81 AUVHO=9922.*ANHOV
      Z(1)=AUVHO
   82 AUCHO=-0.0335*ANHOL*(PGAS-1.)
      Z(2)=AUCHO
   83 AUCSB=F(DEDP,AM)
      AUCSB=AUCSB*(PGAS-1.)
      Z(3)=AUCSB
   84 AUDNO=-3200.*ANNOD
      Z(4)=AUDNO
   85 AUCGS=-1.574*PGAS*ANGAS
      Z(5)=AUCGS
   86 AIBP=-1.*DELT*(UCALR+AUCN)+(EUCN-AUCN)*(TEMP-TFIN)
      Z(6)=AIBP
   87 EUCOS=(4050.-200.*ENORM)*ENCOD
      Z(7)=EUCOS
   88 EUNOS=(3200.-530.*ENORM)*ENNOD
      Z(8)=EUNOS
   89 EUCSU=DEDPS*EMSU*(1.-EPGAS)
      Z(9)=EUCSU
   90 EUMAC=UOIL*(ENNO3+ENNO2)
      Z(10)=EUMAC
   92 EUBAC=14074.*ENNO3-6600.*ENNO2
      Z(11)=EUBAC
   93 EUCGS=1.574*(XNO+0.908*XN +2.691*XCO +1.69*XCO*XCO)
      EUCGS=EUCGS*EPGAS*ENGAS
      Z(12)=EUCGS
   94 EUVHO=-9922.*ENHOV
      Z(13)=EUVHO
      UOSU=0.
      DO 95 I=1,13
      WRITE(3,2060) Z(I)
 2060 FORMAT(7F9.2)
   95 UOSU=UOSU+Z(I)
      UOAX=UAOX
      UOFSE=UFUSE
   96 UOAX=UOAX*AN(2)

   97 UOFSE=UOFSE*AN(3)
      WRITE(3,2062) UOFSE
 2062 FORMAT(' UOFSE=',F8.2)
   98 UOC=UOSU-UOAX-UOFSE
   99 UOCG=UOC/AM(1)
  100 UOCM=UOC/(1000.*AN(1))
      WRITE(3,1562) UOCG
 1562 FORMAT('0                    >U(COMPOUND)/M=',F9.2,'CAL/G')
      END

##############################################################

      FUNCTION F(Y,Q)
      DIMENSION Y(3),Q(3)
      X=0.
      DO 1 I=1,3
      IF(Y(I)) 3,4,3
    3 IF(Q(I)) 5,4,5
    4 PROD=0.
      GO TO 1
    5 PROD=Y(I)*Q(I)
    1 X=X+PROD
      F=X
      RETURN
      END
```

```
"WASHBURN CORRECTIONS"
 COMPOUND:                                              S.R.WILSON
           CYTOSINE 22/3/77
AUXILIARY MATERIAL  -NONE
FUSE  -COTTON
AMAIR=   0.85184 GRAM   TROOM=22.     PATM=762.4
 0.85257 GRAM     111.101 G/MOL        1.20 G/CM3
 0.00000 GRAM       0.000 G/MOL        0.00 G/CM3
 0.00387 GRAM      27.198 G/MOL        1.50 G/CM3
  C( 4.000)  H( 5.000)  O( 1.000)  N( 3.000)
  C( 0.000)  H( 0.000)  O( 0.000)  N( 0.000)
  C( 1.000)  H( 1.686)  O( 0.843)  N( 0.000)
VBOMB= 0.2961   VH2O= 0.0010     PGAS= 30.00
ENNO3=0.001272
&U/&P(1)=-0.0070  &U/&P(2)=-0.0070  &U/&P(3)=-0.0070
>UDIL HNO3=-46.    >UAUX=  0.00000    >UFUSE= -113690.0
E(CALOR)=2564.60  AMPT= 0.00000     AMGL= 0.00000
CP(1)= 0.300   CP(2)= 0.000   CP (3)= 0.400
CV(O2)= 5.056  CV(CO2)= 7.251  CV(N2)= 4.996
B=550.             >U(IGN)= 0.00
TINITIAL= 22.0 TFINAL= 24.6260 TI-TF+>T=-1.4925
    4.12
   -0.05
   -0.17
   -0.11
  -17.36
-3832.59
    0.40
    0.12
    0.09
   -0.06
   17.87
   20.16
   -4.14
UUFSE=   -16.18
                 >U(COMPOUND)/M= -4451.88CAL/G
```