THERMOCHEMISTRY OF

GALLIUM ACETYLACETONATE

by

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A thesis presented for the degree of

Master of Philosophy

in the

University of Surrey.
In memory of my father

John Henry Walter

to whom this work is dedicated.
The work described in this thesis has been carried out in the Thermochemistry Laboratory, Chemistry Department, University of Surrey, under the supervision and guidance of the Reader in Inorganic Chemistry, Dr. R. J. Irving, to whom the author wishes to express his sincere thanks for the help and encouragement given throughout this course.

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Section R  RESULTS ................................ 79
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The standard heat of formation of crystalline gallium acetyl-
acetonate (GaAcac₃), has been determined by solution calorimetry.

The calorimeter was used to determine the heat of reaction \( \Delta H_R \) between gallium tri-chloride and acetylacetone. As this could not be measured directly, perchloric acid (60.4\%) was chosen as solvent for each chemical species and the above heat of reaction determined by application of Hess' Law. The standard heat of formation of GaAcac₃ was then calculated from the value of \( \Delta H_R \).

The experimental technique involved the measurement of smaller quantities of heat than had previously been met with this particular type of calorimeter. In order to achieve the required accuracy, an investigation of the physical behaviour of the instrumental system was made and several modifications introduced.

Two calculation methods have been discussed at some length from the user's viewpoint, and one of them, 'the change in thermistor resistance (\( \Delta R \))' method has been selected. Results were determined with the aid of a computer, and the programme justified by a series of calorimeter experiments.

The value of the standard heat of formation of GaAcac₃ was used to estimate both the homolytic and heterolytic gallium-oxygen bonding energies in this complex. Other subsidiary values calcu-
listed include the gas-phase enthalpy of reaction and the enthalpy of atomization. Results have been compared with those for aluminium acetylacetonate, and bond energy relationships between other physical properties suggested.
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1.1 PERIODIC CLASSIFICATION [1,2,3]:

Gallium belongs to the third main group of the Periodic System. The first two members, boron and aluminium, are widely distributed over the earth's crust; gallium, indium and thallium are considered very rare elements found only in small concentrations. Due to the close similarities between aluminium and gallium (analogous valence shell, identical ion charge, and only a small difference in ionic radii) gallium can substitute for aluminium ions in the crystal lattice of aluminium-based minerals. This is reflected in the fact that gallium (but not indium or thallium) is closely associated with aluminium in nature.

All elements in main group III have three electrons in excess of either the stable (two or eight electrons) or pseudo (eighteen electrons—Ni group type structure) inert gas structures and these three electrons can be lost relatively easily. Hence all elements of this group show a maximum valency of three, this being the only important state for boron and aluminium and the preferred valency for gallium and indium. Thallium, on the other hand, prefers the univalent state and this is the only state that exists in aqueous medium. The neutral atoms all show typical ns\(^2\)np valence electrons in this group (see table 1).

Group similarities are shown in table 1 where atomic weight and number increases are paralleled by increases in density, atomic volume and atomic and ionic size. Electron-deficient compounds are characteristic of this group, this tendency quite marked in compounds of boron (e.g., H\(_5\)NBF\(_3\)) but decreasing markedly down the
### Table I

**Properties of Main Group III Elements**

<table>
<thead>
<tr>
<th>Property</th>
<th>Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
</tr>
<tr>
<td>Atomic Number</td>
<td>5</td>
</tr>
<tr>
<td>Atomic Weight</td>
<td>10.82</td>
</tr>
<tr>
<td>Atomic Structure (outer configuration)</td>
<td>2s^2 2p^1</td>
</tr>
<tr>
<td>Density of solid g/cc at 20°C</td>
<td>2.33</td>
</tr>
<tr>
<td>Atomic Volume of solid (cc)</td>
<td>4.64</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>2300</td>
</tr>
<tr>
<td>Boiling Point (°C)</td>
<td>2550°</td>
</tr>
<tr>
<td>Covalent Radius (Å)</td>
<td>0.80</td>
</tr>
<tr>
<td>Crystal Radius M^3+ (Å)</td>
<td>0.20</td>
</tr>
<tr>
<td>Valency (favoured state underlined)</td>
<td>III</td>
</tr>
<tr>
<td>Ionization Energy M→M^3+ + 3e^- (Kcal/g atom)</td>
<td>1636.1</td>
</tr>
<tr>
<td>Standard Potential E(Volts) M→M^3+ + 3e^-</td>
<td>0.73</td>
</tr>
<tr>
<td>*Fajan Parameter $\phi$</td>
<td>15</td>
</tr>
</tbody>
</table>

*Fajan Parameter ($\phi$) = \( \frac{\text{cation charge}}{\text{cation radius}} \)

If $\phi \geq 2.2$, then a non-ionic compound is favoured.
Trivalent Ga, In and Tl all have chemical properties related to Al, e.g. hydroxides are amphoteric, salts are hydrolysed to some extent in solution, but the resemblance of In$^{3+}$ and especially of Ga$^{3+}$ is much closer to Al$^{3+}$ than to Tl$^{3+}$.

Discontinuities in properties exist between boron and aluminium which have no parallel in previous families. For example, boron has a very high melting point, a short liquid range and a definite non-metallic character (probably due to its small size and high concentration of nuclear charge) which tends towards covalent bond formation. Its homologues have relatively low melting points, long liquid ranges (especially gallium) and are typical metals.

They are able to exist in solution as free (i.e. hydrated) tri-positive ions. Boron cannot function this way. One would expect the ability to form covalent compounds to decrease from boron down the group in agreement with Fajan's rules. From calculated $f$ values (table 1), boron compounds would be expected to be very covalent whilst compounds of aluminium, gallium, indium and thallium would be largely covalent.

Boron is distinctly an acid-forming element. Al(III), Ga(III), In(III) and Tl(III) oxides are all amphoteric, their basic nature increasing with atomic weight. Tl(I) oxide is strongly basic.
The property differences between gallium, indium and thallium and their lighter homologues boron and aluminium are far more marked than is found with corresponding elements of main groups I and II. This has been explained from atomic structure considerations. Although the outermost electron shells have the same configuration (\(ns^2np^1\)), the \(s^2p^1\) valence shell in boron and aluminium immediately follows a stable inert gas configuration (2 and 8 electrons respectively) whereas the valence shell in gallium, indium and thallium is preceded by a \(n(s'p'd^{10})\) shell (18-electron - pseudo - inert gas structure containing a \(d^{10}\) orbital).

Thus the electropositive character rises considerably from boron to aluminium (as expected from similar trends in main groups I and II) but decreases from aluminium through gallium, indium to thallium. This irregular trend can be explained by reference to the gallium atom, which has a greatly increased nuclear charge over aluminium at the expense of additional electrons filling up the same principal quantum shell (\(M\) shell). Hence the gallium atom can retain its electrons more strongly than the aluminium atom; similar arguments can be used with indium and thallium.

Gallium, indium and thallium (as distinct from boron and aluminium) can readily be reduced from the typical group valence of three, to lower states. The only important valencies in boron and aluminium is 3; this is also the preferred state for gallium and indium but not thallium which tends to form univalent compounds, especially in aqueous media where univalent \(Tl\) is the only stable state.
The stabilisation of lower valencies with the heavier elements is thought to be due to the influence of the inert electron pair in the valence shell. $M^+$ is unknown for boron, has been shown to exist in gallium and indium, and is the preferred state for thallium.
Gallium and its compounds are finding ever increasing applications, for example in the semiconductor industry, as high temperature thermometers, in the formation of low melting alloys and cold soldering mixtures, as liquid seals in mass spectrometers, vacuum devices and diffusion pumps, and in the medical field.
1 Gallium metal when pure is soft, ductile and silvery-white with a bluish tinge. The most characteristic properties are its low melting point (29.8°C), its ability to remain as a supercooled liquid, its long liquid range and its very low vapour pressure (less than 1 mm Hg at 1400°C). In the liquid, gallium resembles mercury, but in contrast it wets glass readily.

At ordinary temperatures, gallium is stable in air but is vigorously attacked by chlorine and bromine. It is relatively resistant to mineral acids and is only attacked vigorously by hot concentrated hydrofluoric and perchloric acids. Alkalis will dissolve gallium with the evolution of hydrogen and consequent formation of alkali gallates. However, as the purity of gallium rises above 99.9% the reaction rate with both acids and alkalis decreases considerably [4].

2 Anhydrous gallium trichloride is a white substance crystallising in needlelike crystals; it has a density of 2.47 gm.cm\(^{-3}\) at 25°C, melts at 77.9°C, boils at 201.3°C and sublimes readily (vapour pressure 0.1 mm Hg at 23°C and 10 mm Hg at 78°C). Vapour density measurements show it to be 99.8% dimer at the boiling point (cf. Al\(_2\)Cl\(_6\)), 98.5% dimer at 200°C and 12% dimer at 498°C [5].

Anhydrous gallium trichloride is very hygroscopic; it fumes in moist air (forming hydrogen chloride by hydrolysis) and is gradually converted into a jellylike syrup. It dissolves very
exothermically in water and its solutions are acidic. However hydroxide can readily be deposited. The particular value of GaCl₃ in this thesis is that it can be obtained pure and from the rather restricted range of starting materials, is the obvious choice for the thermochemistry of gallium acetylacetonate because its heat of formation is known (-125.4 ±1.0 K. cal. mole⁻¹ [6]). The metal itself reacts too slowly under conditions suited to solution calorimetry.

3 Gallium Acetylacetonate (GaAcac₃):

3.1 General Properties: Gallium Acetylacetonate is an example of the chelate-neutral type complexes (non-electrolytes). It resembles Al(Acac)₃ to a very marked degree in its melting point and its volatile characteristics; it is decomposed by strong acids, is monomolecular in solution and possesses a crystal modification (α) which is isomorphous with the aluminium compound. Further properties and similarities appear in table (2). Gallium Acetylacetonate is very slightly soluble in water, more so in ethyl ether and alcohol and readily soluble in benzene, acetone, carbon disulphide or chloroform.

3.2 Structure: Its molecule consists of three chelate groups surrounding the central metal atom to form a regular octahedron of oxygen atoms. (diagram 1) Lingafelter and Braun [9] have recently measured the average non-variable interatomic distances and angles in a series of acetylacetonate complexes and these are shown in diagram (2). Calculated interatomic distances are shown in brackets. Metal-oxygen
### Properties of the Acetylacetones of Al, Ga and In [4,7,8,9,39]

<table>
<thead>
<tr>
<th>Property</th>
<th>Al(Acac)$_3$</th>
<th>Ga(Acac)$_3$</th>
<th>In(Acac)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Melting point (°C)</strong></td>
<td>192-4</td>
<td>194-5</td>
<td>186-7</td>
</tr>
<tr>
<td><strong>Boiling point (°C)</strong></td>
<td>315</td>
<td>decomposes</td>
<td>decomposes</td>
</tr>
<tr>
<td><strong>Volatile characteristics</strong></td>
<td>all sublime at 140° under 10 mm Hg. pressure</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Residue on subliming</strong></td>
<td>v. slight</td>
<td>slight</td>
<td>considerable</td>
</tr>
<tr>
<td><strong>Molecular weight determined</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Cryoscopically (f.p.)</td>
<td>monomolecular in solution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Ebullioscopically (b.p.)</td>
<td>monomolecular in gas phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Vapour density</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Crystal class</strong></td>
<td>α-monoclinic</td>
<td>α-monoclinic</td>
<td></td>
</tr>
<tr>
<td><strong>Molecules per cell</strong></td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>α</td>
<td>4</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>β</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ</td>
<td>16</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Metal-oxygen bond length (Å) calculated distances in brackets</strong></td>
<td>1.892</td>
<td>(2.013)</td>
<td>(2.203)</td>
</tr>
<tr>
<td><strong>Instability constant (pK)</strong></td>
<td>22.3</td>
<td>23.6</td>
<td>-</td>
</tr>
</tbody>
</table>
**Diagram 1**

Molecular structure of GaAcac$_3$

Three Acetylacetonate groups surround the metal ion to form an octahedron of oxygen atoms.

**Diagram 2**

Metal-Acetylacetonate complex showing average measured non-variable interatomic distances and angles (calculated interatomic distances in brackets)
bond lengths along with other properties of the acetylacetonates of Al, Ga and In are listed in table (2). Roof [10], in a study of Fe (Acac)$_3$, had previously established that the pairs of the M-O, C-O and C-C bond distances were of equal length, within limits of experimental error. He also pointed out that the C-C (1.39 Å, same as in benzene) and C-O (1.28 Å) distances were intermediate between those for the single and double bonds of each type respectively. The above evidence certainly suggests some kind of resonance in the chelate ring.

A 'benzenoid' six-membered ring type of resonance had earlier been proposed by Calvin and Wilson [11]. A study of the NMR and UV spectra of these metal chelate compounds by Holm and Cotton [12] provided no support for the benzenoid idea but showed some evidence for weak π bonding between metal and ligand. Their alternate suggestion for resonance in the chelate ring (also in agreement with the findings of Roof) is illustrated in diagram (3).

3.3 Mechanism of Metal Chelation: The chelate ligand is the anion of Acetylacetone. The fact that acetylacetone exhibits keto-enol tautomerism is of importance when considering its mode of attachment to a metal. The equilibrium constant for the reaction

$$\text{keto} \xrightarrow{\text{enol}} \text{k}$$

has been measured both for the pure liquid and for the gas phase.
**Diagram 3**

Resonance in Metal Acetylacetonate ring

I and II represented by III

**Diagram 4**

Mechanism of Metal Chelation

keto ↔ enol
\[ k_1 \text{ (pure liquid)} \quad 4.4 \quad [13] \]
\[ k_2 \text{ (gas phase)} \quad 11.0 \quad [14] \]

It is thought that the actual mechanism of metal chelation is the replacement of H (of the hydroxyl group) in the enol form by a metal [15] with the subsequent formation of the resonance stabilised six-membered ring of which the metal is part (diagram 4).
1 Reaction Heats and Enthalpy Changes: The solution calorimeter is a device that measures reaction heats liberated (-q) or absorbed (+q) in terms of temperature changes, under conditions of constant pressure.

The quantity of heat (q) necessary to change the state of a system is related to its internal energy (E) by the familiar first law statement:

\[ \Delta E = q + w = q - \int_1^2 P \, dV \]

That is, the sum of the heat introduced (q) and the work performed (w = \int_1^2 P dV) on a system when its state is altered, equals the change in internal energy of the system. Heat and work are regarded as positive when transferred from the surroundings to the system [16], as shown in diagram (5).

\[ \text{diagram (5)} \]

When the pressure is constant

\[ w = - \int_1^2 P \, dV = - P \Delta V \]

\[ \Delta E = q - P \Delta V \]

The internal energy (E) is also related to the enthalpy defining expression:

\[ H = E + PV \]

and for infinitesimal changes

\[ dH = dE + P \, dV + V \, dP \]
Again, for constant pressure, this reduces to:

\[ dH = dE + PdV \]

or

\[ \Delta H = \Delta E + P\Delta V \]  \hspace{1cm} (4)

Substituting equation (2)

\[ \Delta H = (q - P\Delta V) + P\Delta V = q \]

That is, reaction heats (q) obtained from the solution calorimeter can be directly equated to changes of enthalpy (\( \Delta H \)).

2 Applications of Hess' Law: Enthalpy is a function of state, and as such, changes in enthalpy are only dependent on the initial and final states of the system, and not on the path taken. Thus, the enthalpy change for the chemical reaction:

\[ A \xrightarrow{\Delta H} C \]  \hspace{1cm} (5)

can be derived from other chemical reactions (other paths), if the enthalpy changes for these processes are known. For example, other reactions may be:

\[ A \xrightarrow{\Delta H_1} B; \text{ and } B \xrightarrow{\Delta H_2} C \]  \hspace{1cm} (6)

then

\[ \Delta H = \Delta H_1 + \Delta H_2 \]  \hspace{1cm} (7)

This is a direct result of Hess' Law of constant heat summation.

The principle can be adopted in solution calorimetry work where it is not always convenient to measure the heat of a reaction directly.
as, for example in a reaction involving the formation of gallium acetylacetonate, such as:

\[ \text{Ga}(s) + 3\text{HAcac}(1) \xrightarrow{\Delta H} \text{GaAcac}_3(s) + \frac{3\text{H}_2(\text{g})}{2} \ldots \ldots \ldots (8) \]

The heat change in the above process is obtained indirectly by application of Hess' Law. Further, reactions used to determine bond energies are always referred to the gas state where the effect of intermolecular forces can be considered negligible (strictly, to the ideal gas state, but the difference between real and ideal gases at 1 atmosphere can be ignored for bond energy determinations). It becomes necessary to convert solution reactions, such as equation (8), to the gas state:

\[ \text{Ga}(g) + 3\text{HAcac}(g) \xrightarrow{\Delta H} \text{GaAcac}_3(g) + \frac{3\text{H}_2(g)}{2} \ldots \ldots \ldots (9) \]

and this can be accomplished by employing a Hess' Law treatment, if sufficient thermochemical data are available.

The solution calorimeter is useful for the bond energy studies of compounds whose heats of sublimation are known or can be readily measured. The metal acetylacetonates come under this category; they form a large series of compounds, many of which are volatile. They have the added advantage of possessing only one type of chelate metal linkage - the metal-oxygen bond which simplifies bond energy calculations (see section 1.4.3).

The heats of sublimation are not known for all of them, but for the non-ionic compounds the vaporisation process is a simple one.
compared with an ionic lattice and reasonable estimates can be made.

Being a large series, the possibility of inter-comparison between metal substituents exists. e.g. Hill [17] has measured the heats of formation of some transition metal acetylacetonates (chromium, iron and manganese) using a solution calorimeter, and related their bond strengths to various parameters of the metal, e.g. the number of d electrons, ionization potential and ionic radius. A comparison between aluminium and gallium is desirable because here there is no change in the number of d electrons in the outermost shell, and bond strength should only be related to ionization potential and ionic radius.

3 Bond Energies: One usually talks of the strengths of chemical bonds in terms of bond energy. Although this is a rather artificial concept, where energies are regarded as localised between individual atoms in a molecule, it is convenient and useful to express the total energy of a molecule as made up of individual bond energies.

For the molecule \( \Delta B_n \), where there exist \( n \) identical A-B bonds, the mean energy (for discussion see Mortimer [18], Cottrell [19]), of the bond A-B is simply \( \frac{1}{n} \) of the energy required to rupture the parent molecule into an atom of A and n atoms of B in the gas phase, according to the process:

\[
\Delta B_{n(g)} \xrightarrow{\text{Heat of}} A_{(g)} + n B_{(g)} \quad \cdots \cdots \cdots \cdots \cdots \ (10)
\]
where $\Delta H_{\text{atom}}$ is the enthalpy of atomisation of gaseous molecule $\text{AB}_n$

and therefore the bond energy relationship is:

$$E(\text{A-B}) = \frac{1}{n} \Delta H_{\text{atom}}$$  \hspace{1cm} (11)

where $E(\text{A-B})$ is the mean energy of the bond A–B.

When the gaseous molecule is a neutral complex, there are two approaches to bond energies. Take the example of a gaseous neutral metal–ligand complex $\text{ML}_n(g)$ [20]. This can either be formed from gaseous metal and ligand atoms, termed homolytic bond energy $E(\text{M-L})_{\text{homo}}$,

$$\text{M}^+_1(g) + n\text{L}^-_1(g) \xrightarrow{\Delta H_{f.i}} \text{M}_1\text{L}_n(g)$$  \hspace{1cm} (12)

where $E(\text{M-L})_{\text{homo}} = -\frac{1}{n} \Delta H_{f.i}$

or alternatively, it may be formed from a gaseous metal cation, and $n$ ligand anions, termed heterolytic bond energy $E(\text{M-L})_{\text{hetero}}$,

$$\text{M}^+_1(g) + n\text{L}^-_1(g) \xrightarrow{\Delta H_{f.r}} \text{M}_1\text{L}_n(g)$$  \hspace{1cm} (13)

where $E(\text{M-L})_{\text{hetero}} = -\frac{1}{n} \Delta H_{f.r}$

In the trivalent metal acetylacetonate series, where the metal is surrounded octahedrally by six indistinguishable oxygen atoms, the average homolytic strength of the metal–oxygen bond, $E(\text{M-O})_{\text{homo}}$, is obtained from the formation equation of the gaseous chelate complex involving the gaseous acetylacetonate radical, $[\text{C}_5\text{H}_7\text{O}_2]$,
according to:

\[
\begin{align*}
C_5H_7O_2(g) & \xrightarrow{D(C_5H_7O_2-H)} C_5H_7^02(g) + H(g) \ldots \ldots \ldots (14a) \\
M(g) + 3C_5H_7O_2(g) & \xrightarrow{\Delta H_{f.r}} M(C_5H_7O_2) \ldots \ldots \ldots (14b)
\end{align*}
\]

\[E(M-0)_{homo} = -\frac{1}{6} \Delta H_{f.r} \ldots \ldots \ldots \ldots \ldots \ldots (15)\]

\[\Delta H_{f.r} \text{ is given by the following relationship:} \]

\[\Delta H_{f.r} = \Delta H_f[Ga(C_5H_7O_2) \ldots (g)] - 3\Delta H_f[C_5H_7O_2(g)] - \Delta H_f[M(g)] \ldots \ldots \ldots (16)\]

where \(D(C_5H_7O_2-H)\) is the dissociation energy for the rupture of the oxygen-enolic hydrogen bond of acetylacetone and \(\Delta H_{f.r}\) is the enthalpy of formation of the gaseous complex from the radical. For the heterolytic case, the average heterolytic bond strength \(E(M-0)_{hetero}\) is obtained from the formation equation of the gaseous chelate complex according to:

\[
\begin{align*}
C_5H_7O_2(g) & \xrightarrow{E_L} C_5H_7O_2^-(g) \ldots \ldots \ldots (17a) \\
M^{3+}(g) + 3C_5H_7O_2(g) & \xrightarrow{\Delta H_{f.i}} M(C_5H_7O_2) \ldots \ldots \ldots (17b)
\end{align*}
\]

\[E(M-0)_{hetero} = -\frac{1}{6} \Delta H_{f.i} \ldots \ldots \ldots \ldots \ldots \ldots (18)\]

where \(E_L\) is the electron affinity of the ligand and \(\Delta H_{f.i}\) is the enthalpy of formation of the gaseous complex from the acetylacetone anion.
The two types of bond energies are related by the expression [17a]:

\[ 6E(M-O)_{hetero} = 6E(M-O)_{homo} + \sum_{i=1}^{3} I_i + 3(5/2RT) - 3E_L \ldots (19) \]

where \( \sum_{i=1}^{3} I_i \) is the ionization potential summation.

In this thesis, an attempt is made to establish values for both bond types in the neutral chelate complex of gallium acetylacetonate.
E.1 Preparation of Materials
1. THAM
2. Gallium Trichloride
3. Gallium Acetylacetone
4. Acetylacetone
5. Constant-Boiling Hydrochloric Acid
6. Perchloric Acid (60.4%)

E.2 Ampoule Filling & Weighing
1. Liquids
2. Solids
3. Gallium Tri-chloride
3.1 Dry box operations
3.2 Vacuum line sublimation of Gallium Tri-chloride

E.3 Reaction Scheme
1. Definition
2. Requirements
3. Method
4. Hess' Law Treatment
5. Justification for equating $\Delta H_4$ to Zero

E.4 Equipment
1. Introduction
2. Calorimeter
3. Calorimeter Stirrer
4. Ampoule Types
4.1 Restricted Glass-Seal Type
4.2 Plug Type
4.3 Vacuum Line Type
5. Constant Temperature Environment
6. Temperature Measuring System
6.1 The Temperature Sensor
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E.10 Chemical Standard for Reaction Calorimeters 77
1. **Tris (hydroxymethyl) aminomethane (THAM):** was recrystallised from a methanol : water (4 : 1) solution by the method used in the Thermochemical Laboratory at the University of Lund [21].

2. **Gallium Tri-chloride (GaCl₃) (stated 6N purity):** was purchased in vacuum seal containers (x 2 lots) from Messrs. Koch-Light Laboratories Limited.

3. **Gallium Acetylacetonate (GaAcac₃):** The following method was found suitable. Gallium tri-chloride was converted to the nitrate. A solution of the nitrate in water was adjusted to pH3, heated to 60-70 °C and a slight excess of acetylacetone added. The resulting mixture was shaken vigorously. Crystals of Gallium acetylacetonate separated. Several drops of dilute ammonia (1 ml./10 ml. water) were added, and again the container shaken. This procedure was repeated until the pH had risen to near 4. The crystals were filtered off and the filtrate retained. To the filtrate was added further drops of dilute ammonia until no further crystals appeared. (There is a danger that a white precipitate, presumably a hydrated oxide of gallium, will precipitate around pH4 even in the presence of excess acetylacetone.) The combined crystals were washed with cold water and dried in a dessicator. A yield of about 70% resulted. The crude product was recrystallised (x 3) from benzene, in which it was very soluble, dried and crushed finely in an agate mortar. The crystals were a light orange-beige colour.

**Analysis:**

- Calculated (%): C: 49.09; H: 5.77
- Found (%): C: 49.30; H: 5.49
4. Acetylacetone (EAcac): Reagent grade acetylacetone was distilled and a middle fraction collected (b.p. 134 - 136 °C).

5. Constant-Boiling Hydrochloric Acid: The concentration of reagent grade constant-boiling hydrochloric acid was determined by density measurements, using literature tables [22a].

\[
\text{HCl (20.29\% ; } d_{20} 1.0982 \text{ gm/ml) (HCl 7.950 H}_{2}\text{O)}
\]

6. Perchloric Acid (60.4\%): was similarly analysed [22b].

\[
\text{HClO}_4 (60.4\% ; d_{20} 1.537 \text{ gm/ml) (HClO}_4 3.656 \text{H}_2\text{O)}
\]
1 **Liquids:** A calibrated microsyringe (Burroughs-Wellcome 'Agla') was employed to fill 'restricted glass-seal' type ampoules (see section E.4.4) with either water, hydrochloric acid (HCl \(7.9504 \text{ H}_2\text{O}\)) or acetylacetone, as required. 

\[
\text{Wt.(Liq.)} = \text{Wt.(sealed amp. + stem)} - \text{Wt.(empty amp.)} \quad (20)
\]

2 **Solids:** Plug type ampoules, held in a polystyrene moulded block, were filled with sample (TEAM or GaAcac\(_3\)) via a small glass funnel placed directly in the ampoule neck.

3 **Gallium Trichloride:** It was necessary to transfer the compound from a vacuum seal container to calorimeter ampoules.

3.1 **Dry Box Operations:** proved unsatisfactory because slight fumes, presumably of hydrogen chloride gas, were noted on breaking the container, even when the dry box had been rigorously 'dried' for a week by:

(i) flushing with a stream of nitrogen dried through a concentrated sulphuric acid trap and magnesium perchlorate column, and

(ii) phosphorus pentoxide which was renewed every day or so.

3.2 **Vacuum Line Sublimation of Gallium Trichloride:** Gallium trichloride sublimes readily and an apparatus was designed for filling ampoules in vacuum. Initially silicone grease was used in some parts of the apparatus but this was slightly attacked by the GaCl\(_3\). A modified version shown in diagram (6) used teflon sleeves in place of silicone grease.
Diagram 6

Apparatus for Vacuum-Line Sublimation of Gallium Trichloride
1. **Definitions**: For the general reaction scheme:

\[ \Delta H_R = A + B \rightarrow C + D \]  

(21)

the standard heat of formation (\( \Delta H_f^0 \)) of any one substance can be calculated knowing the standard heats of formation of the other substances and the heat of the reaction (\( \Delta H_R \)).

The choice of reaction scheme is restricted by solution calorimeter requirements. For example, preliminary tests to determine the suitability of gallium metal indicated that dissolution in acids, even when catalysed by chloroplatinic acid [23] was not rapid enough for heats of solution measurements.

2. **Requirements**: The standard heat of formation of gallium acetylacetonate (GaAcac\(_3\)) can be determined from the reaction between GaAcac\(_3\) and hydrochloric acid yielding a solution of acetylacetone (HAcac) and gallium trichloride (GaCl\(_3\)) according to the equation:

\[ \text{GaAcac}_3 + 3\text{HCl} \rightarrow 3\text{HAcac} + \text{GaCl}_3 \]  

(22)

Preliminary tests showed that even in constant-boiling hydrochloric acid, GaAcac\(_3\) was only slowly decomposed; also the equilibration between HAcac, GaCl\(_3\) and constant boiling hydrochloric acid was not quickly realised. The initial hope that one of the reacting species (HCl) could function as solvent thus proved impractical. Satisfactory results were obtained on dissolving stoichiometric quantities of the above materials (GaAcac\(_3\), HCl, GaCl\(_3\) and HAcac) in 30.4\% perchloric acid. (HClO\(_4\), 3,658 H\(_2\)O) A restricted concentration range was necessary in order to achieve a compromise.
between rapid decomposition with fast equilibration and large heat outputs.

Solution heats were determined over this concentration range and strict control of stoichiometry was observed throughout the reaction scheme to eliminate problems associated with the undesirable heat of dilution of perchloric acid [22b].

**Diagram (7)**

**Reaction Scheme**

\[
\begin{align*}
23.85\text{H}_2\text{O}(1) + \text{GaCl}_3(3\text{c}) + 3\text{HAcac}(3\text{c}) &\rightarrow \Delta H \rightarrow 3(\text{HCl17.9504H}_2\text{O})_{(aq)} + \text{GaAcac}_3(3\text{c}) \\
\Delta H_1 &\rightarrow \Delta H_2 &\rightarrow \Delta H_3 &\rightarrow 3(\text{HCl17.9504H}_2\text{O})_{(aq)} + \text{GaAcac}_3(3\text{c}) \\
\text{HC10}_4 3.658\text{H}_2\text{O} &\rightarrow \Delta H_4 = 0 &\rightarrow \text{HC10}_4 3.658\text{H}_2\text{O} &\rightarrow \text{Solution A}_3 &\rightarrow \text{Solution B}_2
\end{align*}
\]

**Ampoule H2O + Solvent (1) (100.0ml) \rightarrow \Delta H_1 \rightarrow \text{Solution A}_1**

**Ampoule GaCl3 + Solution A1 \rightarrow \Delta H_2 \rightarrow \text{Solution A2**

**Ampoule HAcac + Solution A2 \rightarrow \Delta H_3 \rightarrow \text{Solution A3**

**Ampoule HCl + Solvent (2) (HCl 7.9504 H2O)(100.0ml) \rightarrow \Delta H_5 \rightarrow \text{Solution B1**

**Ampoule GaAcac3 + Solution B1 \rightarrow \Delta H_6 \rightarrow \text{Solution B2**
3 Method: The final choice of reaction scheme and the way the solvent was used to determine $\Delta H_R$ indirectly, is shown in diagram (7) and described below.

To a single volume (100.0 ml) of solvent, ampoules of $H_2O$, GaCl$_3$ and HAcac were added consecutively and the corresponding solution heats $\Delta H_1$, $\Delta H_2$, $\Delta H_3$ measured.

Ampoules of HCl 7.9504 $H_2O$ and GaAcac were added consecutively to a second volume of solvent (100.0 ml) and the corresponding heats $\Delta H_5$ and $\Delta H_6$ measured.

Strict control of stoichiometry (to better than 1 in 10$^3$) was maintained throughout one complete series of experiments.

4 Hess' Law Treatment: The reaction heat was calculated according to the Hess' Law relationship:

$$\Delta H_R = 23.851 \Delta H_1 + \Delta H_2 + 3 \Delta H_3 + \Delta H_4 - 3 \Delta H_5 - \Delta H_6 \ldots \ldots (23)$$

5 Justification for Equating $\Delta H_4$ to Zero: The above evaluation of $\Delta H_R$ relies upon the final solution on both sides of the equation (solutions $A_3$ and $B_2$) being identical. As a rough check as to the validity of this assumption, an ampoule of solution $A_3$ was broken into solution $B_2$ in the calorimeter. No detectable heat change was produced.
1 Introduction: The instrument used to carry out all the heats of solution work was a constant temperature environment non-isothermal calorimeter which has been adequately described previously [17b, 24, 25]. Only a brief description will be given here.

2 Calorimeter: The calorimeter, refer to diagram (8), consisted of a thin walled pyrex glass reaction vessel (A) of approximately 100 ml. capacity which contained a stout glass pin (B) pointing centrally upwards from the bottom, and two thin glass wells (C₁ and C₂) protruding downwards inside the body. The neck (D) was 'Aralited' to a threaded metal joint (E) which could be screwed into the metal submarine lid (F) containing two tubes, one of which (G) served as an exit for all lead wires from the calorimeter via (H), a precision plug and socket arrangement, (ITT Cannon Electric type DAK7W2); the other tube (I) was coned and suitable for evacuating the space between calorimeter and jacket (J) but was plugged at both ends and not used during these experiments. A water tight seal between submarine lid and jacket was effected by a neoprene 'O' ring (K) and a threaded metal retaining ring (L). All the above metal parts were chromium-plated.

3 Calorimeter Stirrer: The calorimeter stirring mechanism consisted of an all gold combined stirrer/ampoule holder (M) attached via a rigid teflon coupling (N) to a twin bearing shaft unit (O) which could easily be threaded into or withdrawn from
The Solution Calorimeter Full Scale
Diagram 10: Ampoule Modifications

a. restricted glass-seal type
b. plug type
c. vacuum line type
d. sealing technique
the central tube (P) in the submarine lid. The shaft unit was so arranged that an ampoule could be lowered onto the pin (B) and broken without interruption to the speed of stirring which was maintained at a constant speed by a synchronous motor unit mounted out of the way of all calorimeter operations. The unit, shown in diagram (9), comprises a tape recorder motor (£) with fan (R) and three-speed pulley (S₁) attached. A neoprene belt (T) drives three-speed pulley (S₂) at constant belt tension for positions 1, 2 and 3 of S₁ and S₂. Shaft (U) containing two bearings, supports the stirrer rod (Y) which could be raised or lowered whilst in motion by means of a grub screw (W) sliding in a slot (X) in the upper portion of Y.

The complete motor unit, pivoted about support (V) could easily be swung into position above the calorimeter and connected to the shaft unit (0), (diagram 8), via a neoprene coupling (Z).

Stirrer speed was adjusted, by changing positions of belt (T) to a speed (approximately 600 r.p.m.) such that (1) thermal equilibrium was attained in the calorimeter within one minute of the completion of a calibration and (2) the speed selected did not produce too large a heat of stirring, nor alter the slope of the resistance/time line after an empty ampoule was broken. (but see E.9.2).

4. Ampoule Types: The initial ampoule form was blown from thin walled pyrex tubing in a cylindrical brass mould of a design similar to that used by Sunner & Wadsö [24]. The following modifications (see diagram 10) of this 'normal' ampoule
were used:

4.1 'Restricted Glass-Seal' Type: The only alteration was a slight restriction of the stem of the ampoule at the neck to facilitate quicker and cleaner sealing off (diagram 10a). The ampoule was placed in a cooling tray containing an ice/water mixture and sealed with the aid of a miniature gas/oxygen flame (diagram 10d).

4.2 'Plug' Type: There is a possibility that in sealing off ampoules containing solids that the heat produced may slightly impair the state of its contents, either by melting or decomposition. A 'plug'-type ampoule (diagram 10b), was produced by cutting and slightly tapering the 'normal' ampoule at the neck and inserting a small plug cut from a section of a Viton '0' ring (Seatrist, Slough, Bucks.). No wax was needed to ensure complete sealing. The criterion for use of a Viton plug was that it did neither swell, nor take up weight on immersing in both calorimeter fluid and ampoule contents. Thus it was unsuitable for acetylacetone where a swelling of about 200% was produced.

4.3 Vacuum Line Type: An ampoule was required which:

(i) could be attached to a vacuum line, and yet be readily weighed to 5 places of decimals,

(ii) was strong enough to withstand a vacuum, but weak enough to fracture on the calorimeter ampoule breaker pin and further, produce negligible, or small constant heats of breaking. (section E.9.1) These requirements were met using an ampoule with dished ends to stand the pressure
difference and with a B7 socket attached to the end of the stem (diagram 10c).

5 Constant Temperature Environment: The assembled calorimeter was completely immersed in a well-stirred large thermostat bath, surrounded by several inches of vermiculite and packed in a wooden box. The thermostat was controlled by a toluene/mercury regulator and a fish tank heater (100 watts) coupled to a thermostatic proportionating head (Sunvic type TOL 33) and an electronic relay unit (Sunvic type EA 4T). The bath temperature ($25 \pm 0.002 \, ^{\circ}C$), could be observed on a mercury-in-glass thermometer (range 21-27 $^{\circ}C$, marked in hundredths) which was checked by a platinum resistance thermometer. (Tinsley type 5187H, N.P.L. calibrated.)

6 Temperature Measuring System:

6.1 The Temperature Sensor: used in the calorimeter was a thermistor (STC type FS2) possessing the following characteristics:

$$R_{25 \, ^{\circ}C} = 1579 \, \text{ohms}$$

$$R/T = -54 \, \text{ohms/degree}$$

$$C = 0.03 \, \text{minute} \quad \text{(see Appendix 1).}$$

It was situated inside well $C_1$ (refer diagram 3), surrounded by a medium of transformer oil to assist in a smooth but rapid attainment of calorimeter temperature. Several tests on the most suitable thermistor position have since been made; the chosen position was with the thermistor sensing tip touching the bottom of the glass well ($C_1$). This corresponded to a
position of minimum thermistor lag which although not essential (for a discussion on thermometric lag see [26a, 27, 28]), it is obviously desirable to reduce thermistor lag as much as possible.

6.2 Wheatstone Bridge Circuitry: The thermistor made up one arm of a conventional D.C. wheatstone bridge circuit, as shown in diagram (11). $R_1$, $R_2$ were precision (0.1%) non-inductively wound manganin wire resistors (Croydon substandards).

$R_4$ was a precision 6-dial decade resistance box (Croydon type R36) range 1-10,000 $\Omega$ in steps of 0.01 $\Omega$ made up of manganin wire non-inductively wound resistors similar to $R_1$, $R_2$.

$R_5$ was a stepwise variable resistance (Croydon), range $0 - 10^6 \Omega$ in powers of 10, in series with the galvanometer. The circuit was powered by a 2V accumulator at a current of 250 $\mu$A.

6.3 Null Detector Unit: The out-of-balance signal across the bridge was amplified by a photo-cell galvanometer amplifier (Tinsley type 5214) and fed to a galvanometer (Tinsley type MS2. 45E). Useful technical data for this system is as follows:

<table>
<thead>
<tr>
<th>Galvanometer</th>
<th>resistance</th>
<th>450 $\Omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>period</td>
<td>2.5 seconds</td>
<td></td>
</tr>
<tr>
<td>sensitivity</td>
<td>1000 mm/$\mu$A</td>
<td></td>
</tr>
</tbody>
</table>

### Table (3)

<table>
<thead>
<tr>
<th>Feedback Setting</th>
<th>Source Resistance ((\Omega))</th>
<th>Indicating Galvo Deflection (mm/$\mu$V)</th>
<th>Current Gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>1500</td>
<td>32</td>
<td>48</td>
</tr>
<tr>
<td>Max.</td>
<td>1500</td>
<td>?</td>
<td>3</td>
</tr>
</tbody>
</table>
Complete System (working conditions - bridge current 250 μA).

<table>
<thead>
<tr>
<th>Feedback Setting</th>
<th>Source Resistance (Ω)</th>
<th>Indicating Galvo Deflection mm/.01Ω change of resistance (R4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>1.2 K</td>
<td>.3</td>
</tr>
<tr>
<td>Normal</td>
<td></td>
<td>.4</td>
</tr>
<tr>
<td>Max.</td>
<td></td>
<td>1.2</td>
</tr>
</tbody>
</table>

Both amplifier and galvanometer lamps were powered by a constant voltage transformer (Advance type CV50F, 12V at 50W).

The null-detector unit, along with the Wheatstone bridge circuitry, calorimeter and bath is illustrated in diagram (14).

7 Electrical Calibration Unit and Associated Equipment:

7.1 The Calibration Heating Element (Rc): was a formerless non-inductively wound coil of enameled Karna wire with the following characteristics:

- resistance: 100.481 Ω (as measured at potential leads)
- resistance/ft: 108.00 Ω/ft.
- cross-section: .005 in.
- temperature coefficient: 10 ppm. (to 150 °C)
- maker: British Driver Harris, Stockport, Cheshire.

It was submerged in transformer oil in calorimeter well C2 (but see section E.8.4.1) and connected to the electrical calibration unit via enameled copper lead wires (cross-section .003 in.) with potential leads attached (enameled copper; cross-section .004 in.) at points midway between C2 and the submarine lid [260].
diagram 11  Thermistor Bridge Circuit

2V D.C.

diagram 12  Electrical Calibration Unit
diagram 13: Calibration Unit with Current Adjust Box ($R_p$), Timers and Potentiometer.

diagram 14: Calorimeter, Bath and Temperature Measuring System.
7.2 Electrical Calibration Unit and Power Measuring System:

The electrical calibration unit

(i) supplied any desired current between 0-100 mA to the
calibration heater \( R_E \) by the appropriate adjustment to
\( R_B \) (Croydon 4-dial precision resistance box type R84,
0-10,000 in steps of 1 ohm, and

(ii) provided a means of assessing the value of this current
\((\pm 1\mu A)\) or more correctly the power input to the
calorimeter. This was achieved by measuring the potential
drop \( E \) across a 10 Ω manganin wire wound resistor \( R_S \)
(Croydon (0.1%) substandard previously standardised using
an N.P.L. calibrated standard Croydon 10 Ω resistor type
RS1) during the time interval \( T \) electrical energy was
being supplied to the calorimeter.

Circuitry is illustrated in diagram (12). A 100 Ω dummy
resistor \( R_D \) was used to dissipate electrical energy
whilst not being supplied to the calorimeter.

Details of equipment used to measure \( E \) and \( T \) are listed in
table (4), and illustrated in diagram (13).
### Table (4)

**Calibration Unit Measuring Equipment**

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Type</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>D.C. Potentiometer</strong></td>
<td>type: P.10 Croydon precision vernier</td>
<td>ranges: 0-18 V; 0-1.8 V; in increments of 10 μV; 1 μV; accuracy: 1 in $10^5$</td>
</tr>
<tr>
<td>Weston Cadmium Standard Cell</td>
<td>type: S.C.2 Croydon precision double</td>
<td>1.01859 volts at 20 °C</td>
</tr>
<tr>
<td>Potentiometer Power Supply</td>
<td>type: P.10/3 Croydon precision mains operated</td>
<td>output voltage: 2.1 V at 24 mA; long term stability: 1 in $10^4$ per week</td>
</tr>
<tr>
<td>Galvanometer</td>
<td>type: SR4/45 Tinsley</td>
<td>resistance: 50 Ω; periodic time: 2 seconds; deflection/μA: 510 mm; deflection/μV: 6 mm at source resistance of 10 Ω</td>
</tr>
<tr>
<td>Stopclock</td>
<td>type: Jaquet solenoid actuated</td>
<td>range: 0.1 sec. to 15 min</td>
</tr>
<tr>
<td>Millisecond Stopclock</td>
<td>type: TSA1014/ABC Venner Electronics</td>
<td>range: 0.1 mS to 99,999 secs.; overall accuracy: better than 1 mS.</td>
</tr>
<tr>
<td>D.C. Power Supply for Electrical Calibration Unit</td>
<td>type: AA 0500 Ether Ltd. mains operated</td>
<td>output voltage: pre-set 5-30V (30V selected); stability: 1 in $2.10^4$</td>
</tr>
</tbody>
</table>
1 Preliminaries: Very few instrumental systems are designed ideally for the wide variety of purposes they are going to meet and the very stringent limits thereby imposed. When attempting to obtain ultimate sensitivity from temperature measuring equipment, a number of faults appear which are normally collected together and allowed for in the experimental error. A number of the measurements in this thesis involve such small quantities of heat that the instrumental error assumes an undue proportion of the total. Considerable effort then, has been directed towards a study of the physical behaviour of the temperature measuring system in an attempt to identify and minimize the sources of instrumental error.

2 Shielding of Bridge Circuit: Severe erratic variations of the galvanometer spot produced by electrostatic pickup, for example from nylon shirts, rubber soled boots, glasses or hands, were removed by complete shielding and earthing of the bridge circuitry including galvanometer and amplifier. Resistances $R_1$, $R_2$ (diagram 11) were placed in an aluminium case lagged with polystyrene. The battery was enclosed in aluminium foil. The interior of the resistance box $R_4$ and associated bridge circuit box were lined with foil. Electrostatic interference from hands near dials of resistance box $R_4$ was due to the metal dial prods acting as aerials near banks of coil type resistors. This effect was eliminated by running a metal braid from each dial to an unbroken E-shaped series of copper strips in the form of a printed
circuit passing close by all dial prods. The strips were glued to the bakelite baseboard of the resistance box and connected to the remaining shielding at a suitable take-off point. All shielding was interconnected and earthed at one point only to mains earth.

3 Zero Drift: In the present system, zero drift produced the largest single source of instrumental error. It took the form of slow wanderings of the galvanometer spot about the zero position under conditions of no input and usually occurred at a constant rate over a period of three or so minutes, then reversed itself and moved at a constant rate in the opposite direction. The effect was either to alter the slope of the resistance/time line as illustrated in diagram (15a) or introduce a curvature in it. In either case this produced extrapolation errors in the corrected resistance change (\( \Delta R \)).

The percentage error incurred depends on

(i) the magnitude of \( \Delta R \) and

(ii) the amount of extrapolation of the resistance/time graphs (see section E.8.1).

Typical error sizes produced two minutes after drift began (corresponding to a mean extrapolation time for all heat changes) are shown in table (5).

Zero instability in the present galvanometer system is independent of the position of the sensitivity control (amount of negative feedback) [29] and was found to vary according to temperature fluctuations in the circuitry (thermal emfs) of the photocell amplifier.
Thermally active components were detected and lagged with small blocks of polystyrene. As an added precaution, the whole photocell amplifier was placed in a box heavily padded with cotton wool. Furthermore, the zero position was inspected at least twice for every resistance/time line obtained and adjusted if required. The nett result was to virtually eliminate errors due to zero drift.

Table (5)

<table>
<thead>
<tr>
<th>( \Delta R )</th>
<th>Corresponding Heat change</th>
<th>Max. error (%) in ( \Delta R )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(( \Omega ))</td>
<td>Normal Drift (.02( \Omega ) per R/t Line)</td>
</tr>
<tr>
<td>20</td>
<td>30.8</td>
<td>.20</td>
</tr>
<tr>
<td>15</td>
<td>23.1</td>
<td>.27</td>
</tr>
<tr>
<td>10</td>
<td>15.4</td>
<td>.40</td>
</tr>
<tr>
<td>5</td>
<td>7.7</td>
<td>.80</td>
</tr>
<tr>
<td>2</td>
<td>3.1</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>1.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

4 Resistance Box Inconsistencies: Following removal of zero drift, other errors became apparent, notably random errors associated with the resistance box \( R_4 \) (diagram 11) and other minor errors which will be mentioned in the next section. The irregularities here were due to stray contact resistance in the 11-position rotary switches of the box \( R_4 \). This additional
resistance altered the normal time intervals taken for the
galvanometer spot to fall through the zero position. The
alterations occurred at definite positions of the dial switches,
i.e. when changing from one dial setting to the next dial,
e.g. 1585.00 to 1584.98 or 1585.30 to 1585.29 but these were not
consistent from experiment to experiment. Reference to diagram
(15b) shows the way in which switch contact resistance affected
the value of $\Delta R$.

Errors involved only became significant at low $\Delta R$ values, but as
two out of five series of experiments resulted in small heat
changes (1-2$\Delta R$), this type of error was considered important.

The contact resistance error was lowered to a level corresponding
to the ordinary spread of points about a resistance/time graph
(<0.001$\Delta R$) by spraying the switch contacts with special aerosol
cleansing fluid from time to time, and by careful attention when
altering positions of the switches.

Table (6) shows typical contact resistance errors both before and
after modification:

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$\Delta R$ & Corresponding heat change & Max. Error (%) in $\Delta R.$ & & \\
\hline
 & (\Omega) & (cals.) & Before Modification & After Modification & \\
\hline
 & Normal (.30 gauge/line) & Bad (.01 gauge/line) & Normal (.003 gauge/line) & Bad (.003 gauge/line) & \\
\hline
20 & 30.8 & .07 & .10 & Within & .03 \\
15 & 23.1 & .09 & .13 & normal & .04 \\
10 & 15.4 & .14 & .20 & spread & .06 \\
5 & 7.7 & .28 & .40 & of time & .12 \\
2 & 3.1 & .70 & 1.0 & intervals & .26 \\
1 & 1.5 & 1.4 & 2.0 & & .30 \\
\hline
\end{tabular}
\end{table}
A. Effect of Zero Drift on Lines
a. true line
b. zero drift at a constant rate
c. zero drift at a non-constant rate

B. Effect of Irregular Switch Contact Resistance on Lines

Diagram 16

Typical Temperature/Time Plot
Other Modifications: included

(i) the replacement of the thick galvanometer hair line for a thin one to facilitate readings, and

(ii) Capacitor by-passing of the relay contacts in the bath electronic relay unit to eliminate annoying 'flickings' of the galvanometer spot as the bath heater switched off and on.
The calorimeter was filled with 100.0 ml of solvent delivered by a calibrated pipette. An ampoule, with contents determined to .05 mg., was inserted into the ampoule holder of the stirrer shaft unit and the latter screwed into the calorimeter. Electrical connections were made to the calorimeter, which was then heated to just under 25 °C with the aid of a hair drier, assembled in its jacket and placed in the thermostat bath. After the system had attained an equilibrium state, a split-second stopwatch (Camerer-Cuss, range 0.01-30 min.) was started; readings of resistance (R) of thermistor, as read on box $R_4$ (diagram 11) and time (t) were taken at constant intervals of resistance by pressing the stopwatch the instant the galvanometer spot (section E.4.6.3) passed through the null point.

At a suitable time ($t_A$) the reaction period was begun either for a run by shattering the ampoule on the ampoule breaking pin, or for a calibration by depressing the relay switch ($S_R$) see diagram (12), which

1. allowed electrical energy to pass into the calorimeter and
2. operated both stopwatch and electronic timer.

For a run, it was only possible to obtain one or two points during the reaction period (the first point must be taken as quickly as possible for a fast reaction) whereas several points could be obtained during the reaction period of a calibration as well as several measurements of the potential drop (E) across the sub-standard resistor ($R_B$). The energy input for an electrical calibration was adjusted by $R_B$ so as to exactly match the heat output of a run. Calibrations were consistently performed after a
run. A series of R/t measurements lasting five to six minutes was
taken during the final period after the calorimeter and its con-
tents had attained thermal equilibrium, approximately one minute
after the reaction period had terminated.
Finally, the time interval (T), (as displayed on both stopclock
and electronic timer) during which electrical energy was supplied
to the calorimeter, was recorded.
1. Energy Content and Enthalpy Change: The energy content ($E$) of the calorimeter is defined as the heat required to raise the temperature of the complete calorimeter by one degree.

If $E$ calories raise calorimeter temperature 1°

then $\frac{E}{\Delta t} = \frac{Q}{E}$

Let $\frac{Q}{E} = \Delta t$ where $\Delta t$ = 'corrected' temperature change.

In a typical reaction, a quantity of heat $Q$ calories produces a 'corrected' temperature change of $\Delta t$ degrees.

$\Delta t = \frac{Q}{E}$  ........................................ (24)

If the above heat was produced by $M$ moles of reactant then the molar heat content (or enthalpy) change is defined by:

$\Delta h = \frac{Q}{M}$  ........................................ (25)

From equation (24)

$\Delta H = \frac{E}{\Delta t}$  ........................................ (26)

The energy content ($E$), can easily be determined by a simple calibration experiment.

Let $Q_c$ calories of electrical energy be dissipated in the calorimeter, producing a 'corrected' temperature rise of $\Delta t_c$ degrees, then:

$Q_c = \frac{E}{\Delta t_c}$  ........................................ (27)

If the electrical energy was generated by a current ($I$) across calorimeter heater ($R_H$) in $T$ seconds, it follows that:

$Q_c = \frac{I^2T}{4.1840}$ calories ........................ (28)

where 1 Thermochemical cal. = 4.1840 Joules.

The current ($I$) is evaluated by measuring the potential drop ($E$) across a substandard resistor ($R_S$) (diagram 12).

Equation (28) can therefore be rewritten as:

$Q_c = \frac{E^2T}{4.1840 x R_S^2}$ calories ........................ (29)
and from (27) \[ \mathcal{C} = \frac{E^{\text{TR}}_H}{4.1840 \times R_S^2 \Delta \theta_c} \text{ calories/degree (30)} \]

Therefore \[ \Delta H = \frac{kE^2 T \Delta \theta_r}{k \Delta \theta_c} \text{ calories/mole . (31)} \]

\[ \text{where } k = \frac{R_H}{4.1840 \times R_S^2} \]

2 The Corrected Temperature Change (\( \Delta \theta \)): The observed temperature change (\( \Delta \theta \)) during a calorimetric experiment is not the true or 'corrected' temperature change (\( \Delta \theta \)) of the reaction being studied because \( \Delta \theta \) is affected by other factors (for example, by heat leakage, heat of stirring, heat generated in the thermistor). In correcting for the total heat transfer between calorimeter and jacket, Newton's Law of Cooling is assumed to apply over the small temperature range in question. (The present calorimeter system, for example, is restricted to heat changes of 50 calories or 0.6 degrees.)

This can be written as follows:

\[ \frac{d \theta}{dt} = K (\theta_j - \theta) + u \ldots (32) \]

where \( \theta \) = temperature of calorimeter

\( \theta_j = \) temperature of jacket

\( \frac{d \theta}{dt} = \) rate of change of calorimeter temperature

\( K = \) thermal leakage constant

\( u = \) sum of contributions of the constant heat generated in the calorimeter.

Dickinson [30] used a similar equation to determine a method for
correcting the observed temperature change (\( \Delta \theta \)), illustrated in diagram (16).

Both pre- and post rater lines are extrapolated and a time (\( t_m \)) found such that areas 1 and 2 are equal. The corrected temperature change is then given by:

\[
\Delta \theta = \theta_1 - \theta_f
\]  

(33)

3 Temperature Change in Terms of Change in Thermistor Resistance:

The temperature (\( \theta \) in ° Kelvin) variation of thermistor resistance (R) may be expressed by:

\[
R = A e^{B/\theta}
\]  

(34)

where \( t \), \( B \) are constants.

differentiating

\[
\frac{dR}{d\theta} = \frac{-BR}{\theta^2}
\]

\[
\frac{\Delta R}{\Delta \theta} = \frac{-BR_m}{\theta_m^2}
\]  

(35)

where \( m \) indicates a mean value.

rearranging

\[
\Delta \theta = -\frac{\theta_m^2 \Delta E}{BR_m}
\]  

(36)

Alternatively the expression

\[
\theta = (\theta_2 - \theta_1) = \frac{B}{2.303} \left[ \log \frac{R_1}{R_2} \right]
\]

(37)

For a calorimetric experiment \( \theta_m^2 \), (\( \log R_1 \cdot \log R_2 \)) are nearly constant and equation (33) can be rewritten as:

\[
\Delta h = \frac{ke^2 T \Delta E}{m \cdot \rho \cdot c} \frac{R_m}{R}
\]  

(38)
or

$$\Delta H = \frac{kE^2T \log (R_1/R_2)_r}{M \log (R_1/R_2)_c} \ldots \ldots \ldots \ldots (39)$$

where subscripts r, c denote run and calibration respectively.

Equation (38) was used for all calorimetric calculations in this work.
General: Thermistor resistance decreases with increasing temperature. Hence graphs of thermistor resistance versus time are reversed from temperature/time graphs (diagram 16). Reference to diagram (17a) illustrates a resistance versus time plot for a typical run and calibration experiment.

The energy content of the calorimeter ($E$) is temperature sensitive and it is therefore highly desirable that the run and calibration heat changes be identical. In practice, moderate to large heat changes can be accurately matched with the exception that electrical heat inputs generally take place over a longer time interval than reaction heat outputs.

All reaction heats in this work were exothermic.

Log/Graphical versus Difference ($\Delta R$) Calculation Methods:

Waisb [31] has shown that the departure of the two equations (36) and (37) from the true expression relating thermistor resistance and temperature is both small and identical.

Previous work in the laboratory employed equation (39). The main disadvantage is that this 'log' method is a time consuming and tedious procedure involving at least two graphs, two Dickinson area plots and two log calculations for each determination of $\Delta H$.

One resorts to calculation short cuts such as:

(1) assuming the Dickinson time ($tm$) remains constant from reaction to reaction in a series, whereas it varies with the efficiency of fracturing the ampoule - see table (11).

(2) the calibration heater supplies energy to the calorimeter
at a constant rate and the assumption is therefore made
that for calorimeters possessing fast equilibrium times
(less than one minute) the value of \( t_m \) occurs at exactly
half the heating period \( (t_f) \); that is:

\[
\frac{t_k + t_e}{2} \quad \cdots \cdots \cdots \cdots \cdots \cdots (40)
\]

(for symbols refer to diagram (17b).

This is erroneous by an amount equal to the time lag \( (t_m - t_e) \) of
the calibration heater. Wadsö states this to be of the order of
a few seconds; such differences introduce negligible errors into
calibration calculations [31].

However, it has been the author's experience that calorimeters in
this laboratory do possess heater time lags (as high as 0.4 minute)
which affect the accuracy of calculations if \( t_e \) is taken in place
of \( t_m \).

Alternate to selecting \( t_m \) at half the reaction time, one may take
half the observed resistance change \( (\Delta r) \) and determine the point
\( t_m' \), at which this value \( (R_m) \) intersects with the reaction curve.
This can be evaluated graphically from a knowledge of suitable
reaction period data points, or by simple co-ordinate geometry,
assuming that straight lines can be drawn between the chosen data
points for both fast reactions and calibrations. Simple reaction
period data plotting for both runs and calibrations can readily
determine the most suitable data points to select. These were \( t_k R_k; t_1 R_1 \) for a run and \( t_1 R_1; t_2 R_2 \) for a calibration. (diagram 17a).
Pre- and post rater lines can then be extrapolated to \( t_m' \), the
corresponding resistance values, \( R_1 \) and \( R_f \) obtained and substi-
tuted into equation (38).
Typical Resistance/Time Plot for a Calorimetric Experiment

$r, c$ refers to run, calibration respectively.

Diagram 173

Resistance/Time Plot for a Calibration Experiment
displaying Computer Programme Symbols
Advantages to be gained by the use of equation (38) if computer facilities are available are as follows:

1. Graph plotting is entirely eliminated.
2. Calculation time is greatly reduced. Work involved is simply punching a data tape using a computer typewriter (flexowriter).
3. Log/graphical method is cumbersome and tedious. Difference ($\Delta R$) method is more direct and can be made use of in preliminary calculations such as:
   
   $\Delta R$ expected $\propto$ moles reactant $\left( M \right)$
   and $\Delta R$ calibration $\propto E^2 T$ (enables $E$ to be preset.)
4. $\log \left( R_1/R_2 \right)$ method involves systematic resistance box errors; $\Delta R$ method eliminates them.
5. Log/graphical calculations usually result in short cuts, and thereby inherent inaccuracies to determine $t$ for both runs and calibrations. $\Delta R$ calculations do not.

3 Computer Programme Method: All calculations were performed with the aid of an Elliot 503 Computer. Details of the Algol type programme appear below. For explanation of symbols, see diagrams (17a) and (17b). Suffixes $r$, $c$ refer to run, calibration respectively. Where a statement for a run and calibration coincide, only one equation is given.

Programme method is as follows:

1. Determine the equations of pre- and post rater lines by performing least squares calculations on $t[n]$, $R[n]$ data. Derive slopes $S_1$, $S_2$ and intercepts $I_1$, $I_2$ on Resistance
axis. Repeat for calibration.

(2) \( R_k \) calculated from pre-rater line:
\[
R_k = (t_k - S_1) + I_1
\]

(3) equation of the reaction period given by:
\[
S_{mr} = \frac{(r_1 - r_k)}{(t_1 - t_k)}; \quad b = r_1 - S_{mr} \cdot t_1
\]
\[
S_{mc} = \frac{(r_2 - r_1)}{(t_2 - t_1)}; \quad b = r_1 - S_{mc} \cdot t_1
\]
where \( b \) is the intercept on the Resistance axis.

(4) \( R_s \) calculated at point of intersection of reaction period and post rater lines.
\[
R_s = \frac{(I_2 S - b S_2)}{(S - S_1)}
\]

(5) \( R_m \) given by:
\[
R_m = R_k - f \cdot (R_k - R_s) = R_k - f (\Delta r)
\]
where \( f \) is defined as that fraction of the observed heat change (resistance change) that produces equal Dickinson areas 1 and 2.

\( f = 0.50 \) for calibration
\( f = 0.63 \) for a run assuming truly exponential heat (see section E.8.4.3).

That is, \( R_m \) occurs at 63% \( \Delta r \) for a run, and 50% \( \Delta r \) for a calibration.

(6) knowing \( R_m \) and \( S_m \), \( t_m \) can then be calculated:
\[
t_{mr} = t_k + \frac{(R_m - R_k)}{S_{mr}}
\]
\[
t_{mc} = t_2 + \frac{(R_m - R_2)}{S_{mc}}
\]

(7) \( R_1, R_f \) are derived by substituting \( t_m \) into the pre- and post rater equations respectively. The corrected
Resistance change is given by:

$$\Delta R = [R_1 - R_f] = [(t_m \cdot S_1 + I_1) - (t_m \cdot S_2 + I_2)] \cdot (48)$$

(8) $\Delta R, R_m$ values for run and calibration, substituted into equation (38).

4 Experimental Justifications of Computer Calculations:

4.1 Heater Time Lag at Different Heater Positions: It has been shown that the difference between $t_m$ and $t_2$ is dependent on the time lag associated with the calibration heater. Three similar series of calibrations were performed at the following positions of the heater.

1. suspended in transformer oil in the glass heater well,
2. same as (1) except that coils of the heater touched the glass well, and
3. heater sealed directly into the calorimeter.

Table (7) shows typical lag times $[t_m - t_2]$ at constant heat inputs for positions 1, 2 and 3 respectively and its effects on $\Delta R$. Note that position 3 gives the minimum possible lag time of 0.08 mins. or 4.8 seconds and hence the minimum error in $\Delta R$ if the value of $t_2$ is used. Position 2 represents the best compromise between the 'normal' (1) and the virtually 'lag-free' (3) heater positions.

4.2 Dickinson Areas versus Other Areas in $t_m$ Calculations:

It is a common practice to find a time ($t^*_m$) such that the areas 1 and 2 (dotted triangles) between pre- and post rater lines are equal, whereas a more justifiable time ($t_m$) occurs where the Dickinson areas 1 and 2 (heavy line triangles) can be
equated as illustrated in diagram (17b).

As some justification of the $t^*$ was considered necessary, differences between the two positions ($t^*$ and $t$) were calculated for a variety of heat changes in both run and calibration experiments. Reference to table (8) shows there is negligible difference in position between these two lines for the cases considered.

The Dickinson time involves simpler area calculations, and has been employed throughout this work.

4.3 Dickinson $t$ versus Computer $t$

(1) Calibrations: Comparison between columns 3 and 5 in table (8) reveals there to be small or negligible difference between Dickinson $t$ and computer calculated $t$ (section E.8.3).

(2) Runs: Here, however, Dickinson and computer $t$ times differ considerably. This is because the computer calculations shown in tables (8) and (9) assume that all run experiments occur exponentially; that is, $t$ occurs at a time for $63\% \Delta r$ (the observed resistance change; $f = 0.63$), whereas an analysis of all types of experiments performed here discloses $f_{average} = 0.55$, range 0.09. All run heat changes therefore occur at a rate faster than exponential as illustrated in column 4, table (9). Differences in $\Delta R$, (the corrected resistance change) due to different ways of calculating $t$ are clearly indicated. From the above analysis, the factor $f = 0.60$ was used in this thesis.
4.4 Selection of Position of $R_s$; It is relatively an easy matter to select the position ($R_s$) at which the reaction period terminates by graphical inspection, but complications arise for the general calorimetric experiment when this selection is governed by computer programme. The values of $t_m$ and $\Delta R$ are sensitive to changes in the position of $R_s$, especially at small values of $\Delta R$, and high pre- and post-rater slopes. Results at two such positions of $R_s$ are displayed in table (10).

Method (A) selects $R_s$ approximately one minute after completion of the reaction period; method (B) positions $R_s$ at the intersection of the reaction period and post-rater lines.

Method (A) shows two effects:

(1) lag time \([t_m-t_2]\) dropping with increased current, and

(2) lag time decreasing with heater positions 1, 2 and 3 (section E3.4.1).

The first trend was due entirely to the position of $R_s$ being slightly in error. For small values of the observed resistance change \((\Delta R = R_1 - R_s)\), this error is accentuated, and reveals itself in $t_m$ current trends. Method (B) eliminates this error as demonstrated by the relative independence of time lag on the calibration current at each particular heater position. Effect (2) — a drop of lag time with positions 1, 2 and 3 of the heater, is real, and still remains. The error in $R_s$ (and hence in $R_m$, $t_m$) introduces a systematic error into the values of $\Delta R$ \((= R_1 - R_f)\) of about 0.001 $\Omega$ which only becomes significant at low current. (e.g. less than 30 mA).
4.5 Variation of Lag-time within Series of Run Experiments: Table (11) shows the effect of the concentration of reacting species and the efficiency of ampoule fracture upon lag-time within a series of run experiments using water, gallium acetylacetonate and tham. The variations in lag-time indicate that, for the most precise work, $t_m$ cannot be assumed to be constant throughout a series.
Table (7)
Different Heater Positions at Constant $\Delta R$: Effect on Lag Time

Calorimetric fluid: water

<table>
<thead>
<tr>
<th>Heater Position</th>
<th>Computer $\Delta R$</th>
<th>Lag Time $[t_m - t_\frac{1}{2}]$ (min)</th>
<th>Error in $\Delta R$ $[\Delta R_{t_m} - \Delta R_{t_\frac{1}{2}}]$</th>
<th>% Error in $\Delta R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.536</td>
<td>.24</td>
<td>+ .007</td>
<td>.23</td>
</tr>
<tr>
<td></td>
<td>3.532</td>
<td>.24</td>
<td>+ .008</td>
<td>.20</td>
</tr>
<tr>
<td>2</td>
<td>3.526</td>
<td>.12</td>
<td>.004</td>
<td>.11</td>
</tr>
<tr>
<td></td>
<td>3.534</td>
<td>.12</td>
<td>.004</td>
<td>.11</td>
</tr>
<tr>
<td>3</td>
<td>3.542</td>
<td>.08</td>
<td>.002</td>
<td>.06</td>
</tr>
<tr>
<td></td>
<td>3.544</td>
<td>.08</td>
<td>.001</td>
<td>.03</td>
</tr>
</tbody>
</table>

Code:

1. suspended in oil in glass heater well
2. same as (1), but heater coils touching sides of glass well
3. sealed directly into calorimeter

Error in $\Delta R$:

Graph plotting used to determine $\Delta R$ values at respective $t_m$ and $t_\frac{1}{2}$ times.
### Table (8)

**Dickinson Areas versus Other Areas at Increasing $\Delta R$ Values**

<table>
<thead>
<tr>
<th>Identification</th>
<th>Computer $\Delta R$</th>
<th>$t$ (min)</th>
<th>Error in $\Delta R$</th>
<th>$t$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dickinson $t$</td>
<td>Other $t^*$</td>
<td>$[\Delta R_{Dick} - \Delta R_{Other}]$</td>
<td>Dickinson $t$</td>
</tr>
<tr>
<td>water c</td>
<td>.290</td>
<td>3.07</td>
<td>3.07</td>
<td>-</td>
</tr>
<tr>
<td>water c</td>
<td>.294</td>
<td>3.09</td>
<td>3.09</td>
<td>-</td>
</tr>
<tr>
<td>water c</td>
<td>3.536</td>
<td>3.24</td>
<td>3.25</td>
<td>-</td>
</tr>
<tr>
<td>water c</td>
<td>5.640</td>
<td>3.09</td>
<td>3.09</td>
<td>-</td>
</tr>
<tr>
<td>water c</td>
<td>10.613</td>
<td>5.26</td>
<td>5.27</td>
<td>-</td>
</tr>
<tr>
<td>TEAM c</td>
<td>13.533</td>
<td>8.29</td>
<td>8.31</td>
<td>0.002</td>
</tr>
<tr>
<td>TEAM r</td>
<td>13.699</td>
<td>4.23</td>
<td>4.23</td>
<td>-</td>
</tr>
<tr>
<td>TEAM r</td>
<td>15.474</td>
<td>3.24</td>
<td>3.24</td>
<td>-</td>
</tr>
</tbody>
</table>

**Code:**
- **r, c** run, calibration respectively.

\[
\Delta R_{Dick} = \text{\textit{Dickinson areas}} \\
\Delta R_{Other} = \text{\textit{Other areas}}
\]

\[
\Delta R_{Dick} = \Delta R \text{ values as calculated using Dickinson area plots.} \\
\Delta R_{Other} = \Delta R \text{ values as calculated using Other area plots.}
\]
### Table (9)

Dickinson \( t_m \) versus Computer \( t_m \) at Various \( f \) values; Runs only

<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>Computer</td>
<td>( [t_m-t_k] )</td>
<td>factor</td>
<td>Error in ( \Delta R )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta R )</td>
<td>( (\text{ohm}) )</td>
<td>( (\text{min}) )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>from Dickinson areas</td>
<td>from 63% ( \Delta R ) calculations</td>
<td>calculated from Dickinson Area plots</td>
</tr>
<tr>
<td>THAM/HCl</td>
<td>15.472</td>
<td>0.24</td>
<td>0.29</td>
<td>0.52</td>
</tr>
<tr>
<td>THAM/HCl</td>
<td>13.699</td>
<td>0.24</td>
<td>0.31</td>
<td>0.50</td>
</tr>
<tr>
<td>GaCl(_3)/HClO(_4)</td>
<td>6.360</td>
<td>0.20</td>
<td>0.25</td>
<td>0.52</td>
</tr>
<tr>
<td>GaCl(_3)/HClO(_4)</td>
<td>19.648</td>
<td>0.75</td>
<td>0.78</td>
<td>0.59</td>
</tr>
<tr>
<td>GaCl(_3)/HClO(_4)</td>
<td>6.750</td>
<td>0.20</td>
<td>0.24</td>
<td>0.51</td>
</tr>
<tr>
<td>H(_2)O/HClO(_4)</td>
<td>3.839</td>
<td>0.16</td>
<td>0.18</td>
<td>0.56</td>
</tr>
<tr>
<td>H(_2)O/HClO(_4)</td>
<td>16.018</td>
<td>0.12</td>
<td>0.14</td>
<td>0.54</td>
</tr>
<tr>
<td>HAcac/HClO(_4)</td>
<td>1.171</td>
<td>0.20</td>
<td>0.22</td>
<td>0.55</td>
</tr>
<tr>
<td>HAcac/HClO(_4)</td>
<td>6.103</td>
<td>0.20</td>
<td>0.24</td>
<td>0.55</td>
</tr>
<tr>
<td>HCl/HClO(_4)</td>
<td>9.918</td>
<td>0.24</td>
<td>0.28</td>
<td>0.52</td>
</tr>
<tr>
<td>GaAcac(_3)/HClO(_4)</td>
<td>0.373</td>
<td>0.29</td>
<td>0.36</td>
<td>0.52</td>
</tr>
<tr>
<td>GaAcac(_3)/HClO(_4)</td>
<td>0.635</td>
<td>0.34</td>
<td>0.37</td>
<td>0.59</td>
</tr>
</tbody>
</table>

**Av.** .55  
**Range** .09

**Code:**  
\( \Delta R = R_1 - R_f \)  
\( \Delta r = R_k - R_s \)  
\( t_k = \text{time at initiation of reaction} \)  
\( f = \text{see sections E.8.3; E.8.4.3} \)  
\( \Delta R_{\text{Dick}} = \text{resistance change calculated from Dickinson area plots.} \)  
\( \Delta R_{f \Delta r} = \text{resistance change calculated from } f \Delta r \text{ calculations.} \)
### Table (10)

Variation of $\Delta R$ with Position of $R_g$; Calibrations at Different Heater Positions

<table>
<thead>
<tr>
<th>Calorimeter</th>
<th>Current $I$ (mA)</th>
<th>Method A $^{**}$</th>
<th></th>
<th>Method B $^{**}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$[t - t_0]$ (min)</td>
<td>$\Delta R$ (min)</td>
<td>$[t - t_0]$</td>
<td>$\Delta R$ (min)</td>
</tr>
<tr>
<td>Heater</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Position*</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>24</td>
<td>.29</td>
<td>.901</td>
<td>.22</td>
<td>.901</td>
</tr>
<tr>
<td></td>
<td>.30</td>
<td>.902</td>
<td>.22</td>
<td>.903</td>
<td></td>
</tr>
<tr>
<td></td>
<td>48</td>
<td>.26</td>
<td>3.531</td>
<td>.24</td>
<td>3.532</td>
</tr>
<tr>
<td></td>
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</table>

Code: * see table (7); ** see section E.8.4.4
Table (11)
Variation of Lag-time within Series of Run Experiments

<table>
<thead>
<tr>
<th>H$_2$O</th>
<th>Ga Acac$_3$</th>
<th>THAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Millimoles Reactant</td>
<td>Computer ([t_n - t_k]) (min)</td>
<td>Millimoles Reactant</td>
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<tr>
<td>6.5</td>
<td>0.187</td>
<td>0.30</td>
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<td>9.8</td>
<td>0.274</td>
<td>0.35</td>
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<td>0.210</td>
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<td>15.3</td>
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<td>0.54</td>
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</table>
1 Ampoule Breaking: Liquid and solid type ampoules (section E.4.4) produced negligible heats of fracture when broken on the calorimeter pin. Because of the more sturdy construction of vacuum line type ampoules a small heat was evolved.

Blank runs with this latter type, sealed off under similar vacuum conditions, indicated a total average heat change of \(0.054\ \Omega\) or \(0.083\) calories for the processes of mechanical fracture and vacuum expansion.

2 Ampoule Fracture in Perchloric Acid (60.4%): Ampoules normally showing no changes in the heat of stirring rate on fracturing in the presence of water or hydrochloric acid (0.1M) altered this rate in the presence of perchloric acid. This was shown not to be due to a heat of reaction between the acid and glass interior of ampoule but rather to the increased density (1.548 g./ml.) of this fluid.

Results were corrected for the above two affects, where appropriate.

3 Other Possible Heats: for example, heat of wetting of ampoule interior, heats of evaporation and condensation \([29]\) etc., were assumed to be negligible.
The accuracy and precision of the equipment was estimated at 25 °C from a series of experiments to determine the heat change during a standard chemical process for reaction calorimeters, that is, the heat of neutralisation of THAM, tris (hydroxymethyl)-aminomethane, at a concentration of 0.5 g per 100 ml. hydrochloric acid (0.10 M) [21].

The data obtained was also used to check the ΔR- calculation method.

The series consisted of five THAM runs, each accompanied by two electrical calibrations. The criterion for rejection of any value was that the difference (Δ = |y - ȳ|) between the mean (ȳ) and expected (y) values was greater than the 3σ = 3ΣΔ²/n level of significance. Statistical tests (Appendix 2) indicated that the grand mean E-value could be used to calculate all the heat of neutralisation values for THAM. Results, using both t₁ and t² values, are shown in table (12). The difference (0.2%) between the two means HT and H̄tC is statistically significant (Appendix 3); thus t₁ cannot be used instead of t² for precise work (see section E.8.2). Temperature corrections for

(1) both thermometer standardisation, and

(2) calorimeter temperature (calibration after a reaction refers to mean temperature before reaction [29]) yield the following:

\[ [\overline{\Delta H_{t2}}]_{25^\circ C} = -7107 \pm 4 \text{ cal. mole}^{-1} \text{THAM} \]

\[ [\overline{\Delta H_{t3}}]_{25^\circ C} = -7121 \pm 4 \text{ cal. mole}^{-1} \text{THAM} \]
Table (12)
Heat of Solution of THAM in 0.1N HCl

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Weight (g)</th>
<th>$\Delta R_T$ (ohm)</th>
<th>$R_{mr}$ (ohm)</th>
<th>T (second)</th>
<th>E (volts)</th>
<th>$\Delta R_{ct}^{1/2}$ (ohm)</th>
<th>$\Delta R_{ct}^{1/2}$ (ohm)</th>
<th>$R_{mc}$ (ohm)</th>
<th>$\Delta t_2^a$ (cal.ohm$^{-1}$)</th>
<th>$\Delta t_m$ (cal.ohm$^{-1}$)</th>
<th>$-\Delta H_{t_2^a}$ (cal.mole$^{-1}$)</th>
<th>$-\Delta H_{t_m}$ (cal.mole$^{-1}$)</th>
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</thead>
<tbody>
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<td>15.4740</td>
<td>1579.50</td>
<td>300.023</td>
<td>640164</td>
<td>15.518</td>
<td>15.406121</td>
<td>1581.07</td>
<td>3009.1</td>
<td>3006.0</td>
<td>7120.5</td>
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<tr>
<td>2</td>
<td>.49240</td>
<td>15.1858</td>
<td>1579.71</td>
<td>300.048</td>
<td>635780</td>
<td>15.211</td>
<td>15.1842</td>
<td>1581.14</td>
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<td>.49564</td>
<td>15.2814</td>
<td>1579.67</td>
<td>300.067</td>
<td>634972</td>
<td>15.291</td>
<td>15.2665</td>
<td>1581.13</td>
<td>3005.0</td>
<td>3013.2</td>
<td>7111.5</td>
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<td>15.0556</td>
<td>1579.67</td>
<td>300.039</td>
<td>631204</td>
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<td>637302</td>
<td>15.379</td>
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</tbody>
</table>

$\Sigma/n$ 3009.7 3015.1 7114.7 7127.5

$\pm 1.5$  $\pm 1.5$  $\pm 3.8$  $\pm 3.8$
R.1 Tables of Experimental Results .. .. .. .. .. 80

R.2 Summary of Experimental Results .. .. .. .. .. 87
The following tables give the experimental results of the reaction scheme shown in section E.3.3. Essential data used in these tables is as follows:

All weighings were corrected to vacuum.

Corrections to $\Delta_k$ values were made where appropriate.

Calibration Constant ($\mathcal{C}$):

$$\mathcal{C} = \frac{(kT_E^2 R_c)}{\Delta R_c} \text{ cal.deg.}^{-1}$$

$$k = \frac{R_H}{J R_S^2} \text{ cal.joule}^{-1}\text{ohm}^{-1}$$

$$R_H = 100.465 \text{ ohm}$$

$$R_S = 9.9980 \text{ ohm}$$

$$J = 4.1840 \text{ joule cal.}^{-1}$$

Heat of Solution ($\Delta H$):

$$\Delta H = \mathcal{C} \Delta R_f / M R_{br} \text{ cal.mole}^{-1}\text{mole}^{-1}$$

For further explanation of symbols, see section E.7.1.
Table (13)

Water M.W. 18.016 d 1.0

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Weight (g.)</th>
<th>$\Delta R_r$ (ohm)</th>
<th>$R_{mr}$ (ohm)</th>
<th>T (seconds)</th>
<th>E (volts)</th>
<th>$\Delta R_c$ (ohm)</th>
<th>$R_{mc}$ (ohm)</th>
<th>$\overline{E}$ (cal.ohm$^{-1}$)</th>
<th>$\overline{E}$ (cal.ohm$^{-1}$)</th>
<th>$-\Delta H$ (cal.mole$^{-1}$)</th>
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<tbody>
<tr>
<td>1</td>
<td>.08636</td>
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<td>90.013</td>
<td>.50741</td>
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<td>2427.2</td>
<td>1226.4</td>
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<tr>
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<td>119.994</td>
<td>.502302</td>
<td>4.750</td>
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<td>.59650</td>
<td>10.003</td>
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<td>2446.7</td>
<td>2446.7</td>
<td>1202.9</td>
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$\Delta H_1 = -1.215 \pm 0.001 \text{ K.cal.mole}^{-1}$ at a concentration of 11.926 mM H$_2$O.
Table (14)

Gallium trichloride M.W. 176.09 d₂₅ 2.47

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Weight (g)</th>
<th>Corrected ΔRᵣ (ohm)</th>
<th>Rₘ₀ (ohm)</th>
<th>T (seconds)</th>
<th>E (volts)</th>
<th>ΔRₐ (ohm)</th>
<th>Rₑ (ohm)</th>
<th>Ɛ (cal.ohm⁻¹)</th>
<th>Ɛₑ (cal.ohm⁻¹)</th>
<th>-ΔH (Kcal/mole⁻¹)</th>
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<td>0.07222</td>
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<td>4.942</td>
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<td>2428.9</td>
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\[ \Delta H₂ = -15.143 \pm 0.058 \text{ K.cal.mole}^{-1} \text{ of GaCl₃}. \]

Ampoule breaking correction applied to \( \Delta R = -0.054 \text{ ohm}. \)
### Table (15)

Acetylacetone M.W. 100.12 d<sub>25</sub> 0.976

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Weight (g.)</th>
<th>$\Delta R_r$ (ohm)</th>
<th>$R_{mr}$ (ohm)</th>
<th>$T$ (seconds)</th>
<th>$E$ (volts)</th>
<th>$\Delta R_c$ (ohm)</th>
<th>$R_{mc}$ (ohm)</th>
<th>$\epsilon$ (cal.ohm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>$\overline{\epsilon}$ (cal.ohm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>$-\Delta H$ (cal.mole&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
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<td>120.253</td>
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$-\Delta H_2 = -1.845 \pm 0.012$ K.cal.mole<sup>-1</sup> of HAcac.
Table (16)

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<tr>
<th>Run No.</th>
<th>Weight (g)</th>
<th>$\Delta R_r$ (ohm)</th>
<th>$R_{mr}$ (ohm)</th>
<th>$T$ (seconds)</th>
<th>$E$ (volts)</th>
<th>$\Delta R_c$ (ohm)</th>
<th>$R_{mc}$ (ohm)</th>
<th>$\mathcal{E}$ (cal.ohm$^{-1}$)</th>
<th>$\overline{\mathcal{E}}$ (cal.ohm$^{-1}$)</th>
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<td>3.7386</td>
<td>1582.81</td>
<td>120.146</td>
<td>120.020</td>
<td>119.950</td>
<td>119.950</td>
<td>3.3884</td>
<td>1583.54</td>
<td>2428.9</td>
</tr>
</tbody>
</table>

$\Delta H_5 = -3.012 \pm 0.002$ K.cal.mole$^{-1}$ of (HCl 7.9504 H$_2$O)
<table>
<thead>
<tr>
<th>Run</th>
<th>Weight Corrected ( R_{\text{mr}} ) (ohm)</th>
<th>( \Delta R_{\text{r}} ) (ohm)</th>
<th>( \Delta H ) (cal.cm(^{-1}))</th>
<th>( T ) (seconds)</th>
<th>E (volts)</th>
<th>( R_{\text{mc}} ) (ohm)</th>
<th>( \Delta \bar{H} ) (cal.cm(^{-1}).mole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.2847</td>
<td>.197</td>
<td>1582.77</td>
<td>119.910</td>
<td>.934</td>
<td>2.89639</td>
<td>1.562</td>
</tr>
<tr>
<td>2</td>
<td>1.2889</td>
<td>.231</td>
<td>1582.65</td>
<td>119.977</td>
<td>.934</td>
<td>1.59995</td>
<td>1.353</td>
</tr>
<tr>
<td>3</td>
<td>1.2624</td>
<td>.251</td>
<td>1582.65</td>
<td>119.975</td>
<td>.930</td>
<td>2.20938</td>
<td>1.943</td>
</tr>
<tr>
<td>4</td>
<td>1.5049</td>
<td>.251</td>
<td>1582.65</td>
<td>119.970</td>
<td>.934</td>
<td>2.59960</td>
<td>1.943</td>
</tr>
<tr>
<td>5</td>
<td>1.6662</td>
<td>.282</td>
<td>1583.42</td>
<td>119.976</td>
<td>.934</td>
<td>.209560</td>
<td>1.943</td>
</tr>
<tr>
<td>6</td>
<td>1.9406</td>
<td>.312</td>
<td>1582.52</td>
<td>120.012</td>
<td>.934</td>
<td>.309700</td>
<td>1.943</td>
</tr>
<tr>
<td>7</td>
<td>2.0418</td>
<td>.317</td>
<td>1582.57</td>
<td>120.013</td>
<td>.934</td>
<td>.320488</td>
<td>1.943</td>
</tr>
<tr>
<td>8</td>
<td>2.1111</td>
<td>.323</td>
<td>1582.57</td>
<td>119.976</td>
<td>.934</td>
<td>.320488</td>
<td>1.943</td>
</tr>
<tr>
<td>9</td>
<td>2.3563</td>
<td>.363</td>
<td>1582.57</td>
<td>120.013</td>
<td>.934</td>
<td>.320488</td>
<td>1.943</td>
</tr>
</tbody>
</table>

\( \Delta H = 0.012 + 0.005 \text{ cal.cm}^{-1}.\text{mole}^{-1} \) at a concentration of 0.5 mM GaAc3.

Stirring correction applied to \( \Delta R. \text{cm}^{-1} \) at \( t = 25-30 \text{ min.} \)

\( \text{stirring correction} = 0.004 \Omega_{\text{cm}} \) at \( t_{1/2} \).
Heat of Solution trend with Concentration of Water

$\Delta H = 1214.9^{+1.0} \text{ cal. mole}^{-1}$ at 11.926 mM $H_2O$.

Heat of Solution trend with Concentration of GaAcac$_3$

$\Delta H = 912^{+15} \text{ cal. mole}^{-1}$ at 0.50 mM GaAcac$_3$. 
### Table (18)

<table>
<thead>
<tr>
<th>Code</th>
<th>$\Delta H$ value $\pm$ 1 K.cal. mole $^{-1}$</th>
<th>2xstandard error of mean ($2\sigma^y$)</th>
<th>$\Delta H$ value taken at</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_1(H_2O)$</td>
<td>$-1.215$</td>
<td>$\pm 0.001$</td>
<td>$11.93$ Moles $H_2O$</td>
</tr>
<tr>
<td>$\Delta H_2(GaCl_3)$</td>
<td>$-15.143$</td>
<td>$0.058$</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_3(HAcac)$</td>
<td>$-1.845$</td>
<td>$0.012$</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_5(HCl)$</td>
<td>$-3.012$</td>
<td>$0.002$</td>
<td>-</td>
</tr>
<tr>
<td>$\Delta H_8(GaAcac_3)$</td>
<td>$0.012$</td>
<td>$0.015$</td>
<td>$0.50$ Moles $GaAcac_3$</td>
</tr>
</tbody>
</table>
D.1 The Solution-Phase Heat of Reaction ($\Delta H_R$) 89

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D.3 The Gas-Phase Enthalpy of Reaction ($\Delta H_{r.g}$) 92

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2. Heterolytic bonding 97

D.6 Conclusions 98
In order to determine the gallium-oxygen bond energy in gallium acetylacetonate, according to equation (16), it is first necessary to determine values for $\Delta H_f[\text{GaAcac}_3(\text{g})]$ and $\Delta H_f^0[\text{GaAcac}_3(\text{c})]$. The latter value can be arrived at via the solution-phase heat of reaction ($\Delta H_R$) of diagram (7). The first problem then, is to determine $\Delta H_R$. The experimental results (table 18) fit the Hess' Law scheme shown in diagram (7), which is set out again for ease of reference:

\[23.85 \text{kJ}^0(\text{1}) + \text{GaCl}_3(\text{c}) + 3\text{HAcac}(\text{1}) \rightarrow 3(\text{HCl}7.95 \text{kJ}^0(\text{aq}) + \text{GaAcac}_3(\text{c})
\]

\[\Delta H_4 = 0\]

\[\Delta H_R = 23.851 \Delta H_1 + \Delta H_2 + 3\Delta H_3 + \Delta H_4 - 3\Delta H_5 - \Delta H_6 \ldots (23)\]

Substituting the results of table (18), the solution-phase heat of reaction is determined as:

\[\Delta H_R = -39.709 \pm 0.074 \text{ KJ.mole}^{-1} \text{ GaAcac}_3\]

For a discussion on conventions and calculations regarding the limits attached to this and forthcoming values, refer to appendix (4).
The reaction defining $\Delta H_R$ in the last section can be simplified for the calculation of the standard enthalpy of formation of gallium acetylacetonate $\Delta H_f^{\circ}[\text{GaAcac}_3(c)]$:

$$\text{GaCl}_3(c) + 3\text{HAcac}(l) \xrightarrow{\Delta H_R} 3\text{HCl}(aq) + \text{GaAcac}_3(c) \ldots \ldots \ldots (49)$$

The heat of reaction ($\Delta H_R$) is given by the equation:

$$\Delta H_R = \sum \Delta H_f^{\circ}[\text{products - reactants}] \ldots \ldots \ldots (50)$$

$$= 3\Delta H_f^{\circ}[\text{HCl}(aq)] + \Delta H_f^{\circ}[\text{GaAcac}_3(c)] - \Delta H_f^{\circ}[\text{GaCl}_3(c)] - 3\Delta H_f^{\circ}[\text{HAcac}(l)]$$

Rearranging:

$$\Delta H_f^{\circ}[\text{GaAcac}_3(c)] = \Delta H_R - \Delta H_f^{\circ}[\text{GaAcac}_3(c)] + 3\Delta H_f^{\circ}[\text{HAcac}(l)] - 3\Delta H_f^{\circ}[\text{HCl}(aq)]$$

Substituting values given in table (19):

$$\Delta H_f^{\circ}[\text{GaAcac}_3(c)] = -354.4 \pm 1.5 \text{ kJ mol}^{-1} \text{ GaAcac}_3(c)$$
Table (19)

Standard Enthalpies of Formation Required for Equation (51)

<table>
<thead>
<tr>
<th>Code</th>
<th>( \Delta H_f^{\circ} ) K.cal.mole(^{-1} )</th>
<th>2xstandard Error of Mean (20(^{\circ})C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaCl(_3)(c)</td>
<td>-125.4</td>
<td>± 1.0</td>
<td>[6]</td>
</tr>
<tr>
<td>HAcac(1)</td>
<td>-101.32</td>
<td>0.37</td>
<td>[17c] liquid tautomeric mixture</td>
</tr>
<tr>
<td>HCl(aq)</td>
<td>-38.23</td>
<td>0.01</td>
<td>[6]</td>
</tr>
</tbody>
</table>

[6] determined by graphical interpolation at a dilution of 7.950 moles H\(_2\)O.
Because of the effects of intermolecular forces, the solution-phase heat of reaction $\Delta H_R$ gives no information on the gallium-oxygen bond energy $E(Ga-O)$ in gallium acetylacetonate. It is first necessary to refer the $\Delta H_R$ defining reaction (section D.1) to the gas state (see section I.4.2) and a suitable scheme is set out in diagram (20).

**Diagram (20)**

**Gas-Phase Reaction Scheme**

\[
\begin{align*}
Ga(g) + 3HA\text{cace} & \overset{k_3=\infty (g)}{\underset{\Delta H_{\text{sub}[Ga(s)]}}{\rightarrow}} \frac{\Delta H_{R,g}}{3} \overset{2H_2(g)}{\rightarrow} + Ga\text{Acac}_3(g) \\
\Delta H_{\text{sub}[Ga]} & \overset{3H_2(g)}{\rightarrow} -3\Delta H^*_{e} \\
Ga(s) & \overset{k_2=1lb(g)}{\rightarrow} 3HA\text{cace} \\
\Delta H^0_{f[GaCl_3(c)]} & \overset{-3\Delta H_{\text{vap}}}{\rightarrow} \Delta H_{\text{sub}[GaAcac]} \\
GaCl_3(c) & \overset{k_1=4.4(1) \Delta H_R}{\rightarrow} 3HC1(aq) + Ga\text{Acac}_3(c) \\
\end{align*}
\]

The value $(-\Delta H_{r,g}/3)$ is not a direct measure of $E(Ga-O)$. It represents the energy expended on rupture of the hydrogen atom from its two cyclic oxygens in the enolic form of acetylacetone plus the energy required to subsequently form two gallium-oxygen
bonds. As the rupture of the hydrogen atom (thought to involve the fracture of one O-H bond and its intermolecular hydrogen bond [171]) is common to other metal acetylacetonates, \( -\Delta H_{r.g}/3 \) will reflect the relative strengths of the metal-oxygen bonds.

In particular, Hill [17] has determined this value for AlAcac_3, and thus a comparison with GaAcac_3 can be made.

The direct measure of \( E(Ga-O) \), as displayed in section D.5 will afford an even better comparison between the metal-oxygen bond energies of Al and Ga; the value of \( -\Delta H_{r.g}/3 \) is only included here for completeness.

From diagram (20), the gas-phase enthalpy of reaction \( \Delta H_{r.g} \) can be defined:

\[
\Delta H_{r.g} = -\Delta H_{sub[Ga(s)]} + \Delta H_f[GaCl_3(c)] - 3\Delta H_e - 3\Delta H_{vap} + \Delta H_R
- 3\Delta H_f[HCl(aq)] + \Delta H_{sub[GaAcac_3]} \]

Substituting values given in table (20):

\[
\Delta H_{r.g} = -125.5 \pm 6.1 \text{ K.cal.mole}^{-1} \text{ GaAcac}_3(g)
\]
Table (20)
Enthalpies Required for Equation (52)

<table>
<thead>
<tr>
<th>Code</th>
<th>Enthalpy ($\Delta H$) (kcal.mole$^{-1}$)</th>
<th>$2\sigma$ Standard error of mean ($\sigma/y$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{sub}}[\text{Ga(s)}]$</td>
<td>66.2</td>
<td>$\pm$ 0.5</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_f^{0}[\text{GaCl}_3(c)]$</td>
<td>-135.4</td>
<td>1.0</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_e^*$</td>
<td>- 0.2</td>
<td>0.01</td>
<td>[17c]</td>
</tr>
<tr>
<td>$\Delta H_{\text{vap}}$</td>
<td>6.5</td>
<td>0.2</td>
<td>[33]</td>
</tr>
<tr>
<td>$\Delta H_R$</td>
<td>- 39.71</td>
<td>0.07</td>
<td>[section D.1]</td>
</tr>
<tr>
<td>$\Delta H_f^{0}[\text{HCl(aq)}]$</td>
<td>-38.23</td>
<td>0.01</td>
<td>[6] see table (19)</td>
</tr>
<tr>
<td>$\Delta H_{\text{sub}}[\text{GaAcac}_3]$</td>
<td>10.</td>
<td>6.</td>
<td>estimated see section D.5</td>
</tr>
</tbody>
</table>
The enthalpy of atomization of GaAcac\textsubscript{3}(g) is defined by the process:

\[ \text{Ga}(\text{C}_5\text{H}_7\text{O}_2)\text{3(g)} \rightarrow \text{Ga}(g) + 15\text{C}(g) + 21\text{H}(g) + 6\text{O}(g) \]  \hspace{1cm} (54)

\[ \Delta H_{\text{atom}} = \Delta H_f[\text{Ga}(g)] + 15\Delta H_f[\text{C}(g)] + 21\Delta H_f[\text{H}(g)] + 6\Delta H_f[\text{O}(g)] \]

\[ - \Delta H_f[\text{Ga}(\text{C}_5\text{H}_7\text{O}_2)\text{3(g)}] \]  \hspace{1cm} (55)

Substituting values from table (21):

\[ \Delta H_{\text{atom}} = +4431 \text{ K.cal.mole}^{-1} \text{ GaAcac}_3(g) \]

**Table (21)**

<table>
<thead>
<tr>
<th>Code</th>
<th>Enthalpy $\Delta H_f$ (K.cal.mole$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f[\text{Ga}(g)]$</td>
<td>66.2</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_f[\text{C}(g)]$</td>
<td>171.291</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_f[\text{H}(g)]$</td>
<td>52.095</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_f[\text{O}(g)]$</td>
<td>59.553</td>
<td>[6]</td>
</tr>
<tr>
<td>$\Delta H_f[\text{Ga}(\text{C}_5\text{H}_7\text{O}_2)\text{3(g)}]$</td>
<td>-344.4</td>
<td>section D.5</td>
</tr>
</tbody>
</table>

**Note:** Re-calculated value of Hill [17g] $\Delta H_{\text{atom}}[\text{GaAcac}_3(g)] = 4523$
1. Homolytic Bonding: The mean gallium-oxygen homolytic bond energy \( E(Ga-O)_{homo} \) in gallium acetylacetonate (see also section 1.4.3) is defined by the following equations:

\[
Ga(g) + 3 C_5H_7O_2(g) \rightarrow Ga(C_5H_7O_2)_3(g) \\
E(Ga-O)_{homo} = -\frac{1}{6} \Delta H_{f.r} \\
\Delta H_{f.r} = \Delta H_f[Ga(C_5H_7O_2)_3(g)] - 3 \Delta H_f[C_5H_7O_2(g)] - \Delta H_f[Ga(g)]
\]

Hill [17f] has calculated the value of \( \Delta H_f[C_5H_7O_2(g)] \) to be \(-42\pm5\) K. cal. mole\(^{-1}\), and \( \Delta H_f[Ga(g)] \) is given in the literature [6] as 68.2 K. cal. \( \text{g. atom}^{-1} \). It only remains to derive a value for \( \Delta H_f[Ga(C_5H_7O_2)_3(g)] \), which is given by the equation:

\[
\Delta H_f[Ga(C_5H_7O_2)_3(g)] = \Delta H_f[Ga(C_5H_7O_2)_3(c)] + \Delta H_{sub}[Ga(C_5H_7O_2)_3(c)]
\]

The heat of sublimation of crystalline gallium acetylacetonate \( (\Delta H_{sub}[Ga(C_5H_7O_2)_3(c)]) \) is unknown. Measured sublimation heats of other acetylacetonates fall mostly within the range 4 - 16 K. cal. mole\(^{-1}\) and the value for \( Al(C_5H_7O_2)_3 \) is 4.58. An estimate for gallium acetylacetonate has been chosen as \( 10^{+6} \) K. cal. mole\(^{-1}\).

This seems reasonable for bond energy purposes since the value \( \Delta H_{f.r} \) is divided by 6 to obtain the average gallium-oxygen bond energy. Furthermore wide discrepancies exist in the literature between heats of sublimation for the same compound [30, 34].
Thus from equation (59):

$$\Delta H_f[ Ga(C_5H_7O_2)_3(g) ] = -344.4 \pm 6.2 \text{ K.cal.mole}^{-1}$$

The gallium-oxygen homolytic bond energy can now be calculated according to equation (58):

$$\Delta H_{fr} = -284.6 \pm 16.2 \text{ K.cal.mole}^{-1}$$

Hence $E(Ga-O)_{homo} = 47.5 \pm 2.7 \text{ K.cal.}$

2 Heterolytic Bonding: The mean gallium-oxygen heterolytic bond energy $E(Ga-O)_{hetero}$, in gallium acetylacetonate (see also section 1.4.3) is defined by the equation:

$$Ga^{2+}(g) + 3 C_5H_7O_2^-(g) \xrightarrow{\Delta H_{f,i}} Ga(C_5H_7O_2)_3(g) \ldots \ldots \ldots \ldots (60)$$

$$E(Ga-O)_{hetero} = -\frac{1}{6} \Delta H_{f,i} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (61)$$

The heterolytic bond energy can be obtained via the homolytic bond energy according to equation (19):

$$6E(M-O)_{hetero} = 6E(M-O)_{homo} + \sum_{i=1}^{3} I_i + 3(5/2 RT) - 3E_L$$

The electron affinity of the ligand $E_L$ (see Appendix 1), has been assumed to be the same as the affinity of the oxygen atom for one electron [37], that is, equal to 1.465 eV or 33.8 K.cal. The ionization potentials were obtained from the literature [38].

$$6E(Ga-O)_{hetero} = -\Delta H_{f,i} \text{ (equation 61)} = 1502 \text{ K.cal.mole}^{-1}$$

hence $E(Ga-O)_{hetero} = 250 \text{ K.cal.}$
A summary of the thermochemical values derived in this thesis for gallium acetylacetonate is shown in table (22), and compared with those for the aluminium complex [17] where appropriate.

### Table 22

**Summary of Thermochemical Values for GaAcac<sub>3</sub>**

<table>
<thead>
<tr>
<th>MAcac&lt;sub&gt;3&lt;/sub&gt;</th>
<th>$\Delta H_R$</th>
<th>$\Delta H^o_f$</th>
<th>$\Delta H_{r.g}$</th>
<th>E(Ga-O)&lt;sub&gt;homo&lt;/sub&gt;</th>
<th>E(Ga-O)&lt;sub&gt;hetero&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga</td>
<td>-39.709 ± 0.074</td>
<td>-354.4 ± 1.5</td>
<td>-125.5 ± 6.1</td>
<td>4431</td>
<td>47.5 ± 250</td>
</tr>
<tr>
<td>Al</td>
<td>-428.8 ± 216.7</td>
<td>4523</td>
<td>63</td>
<td>250</td>
<td></td>
</tr>
</tbody>
</table>

The heterolytic bond energy, $E(M-O)_{hetero}$ in GaAcac<sub>3</sub> as given by equation (19), is dependent upon the sum of the first three ionization potentials. The fact that $E(M-O)_{hetero}$ is the same for the aluminium and gallium complexes implies that the increased electropositive power of the gallium nucleus has just balanced the decreased homolytic binding strength $E(M-O)_{homo}$, brought about by the larger size of the Ga<sup>3+</sup> ion.

The instability constants, see table (2), (measured in solution [39]), show a reversed order of bond strengths from those obtained by direct thermochemical measurement, which seem to indicate that instability constants of similar orders of magnitude can not be used to predict relative orders of bond strengths.

In this thesis, two values for the gallium-oxygen bond energy in gallium acetylacetonate have been calculated, firstly, the
homolytic bond strength (47.5 K.cal), which arises from dissociation into metal atom and ligand radicals, and secondly, the heterolytic bond strength (250 K.cal), which arises from dissociation into metal cation and ligand anions.
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1 Symbols & Abbreviations:

- f.p., m.p., b.p. freezing, melting and boiling points respectively.
- NMR nuclear magnetic resonance
- UV ultra violet
- 6N purity 99.9999%
- ppm parts per million
- M.W. molecular weight
- mM milli Moles
- d25 density in g./ml. measured at 25 °C
- \( \sigma_y \) standard error of the mean (Appendix 4)
- THAM tris (hydroxy-methyl) aminomethane
- H\( \\text{Acac} \) acetylacetone
- M\( \text{Acac}_3 \) trivalent metal acetylacetonate
- C\( _5\text{H}_7\text{O}_2 \) acetylacetone radical

2 Definitions:

Time Constant of Thermistor \( (\tau) \) is defined as the time taken for its resistance, as measured by the wheatstone bridge circuitry (Section E.4.8.2), to fall by \( \frac{e - 1}{e} \) (or 63%) of its value when instantaneously transferred from one medium at a constant temperature, to another. The value includes the time constant of the galvanometer system.

Instability Constant \( (K_n) \) is defined by the equation:

\[
M_n \xrightarrow{K_n} M^{x+} + nY^{-}
\]

where \( K_n = \frac{[M^{x+}][Y^{-}]}{[M_n]} \).

Ionization Potential \( (I) \) is the energy required to remove an electron from a gaseous species leaving each without any kinetic energy. First, second, third, etc., potentials for elements
refer to successive removal of electrons from an originally neutral atom. The algebraic sign of all ionization potentials is positive.

Electron Affinity ($E_L$) is the energy released when a gaseous species captures an electron (of zero kinetic energy). The algebraic sign of electron affinities (where energy is released) is positive. It is to be noted that this is opposite the generally accepted thermochemical sign convention. This has been taken into account and corrected for in the heterolytic bonding expression given in equation (19), where the sign of the electron affinity of the ligand ($E_L$) is shown reversed to the ionization potential summation $\sum_{i=1}^{3} I_i$. Thus positive electron affinities can be substituted directly into equation (19).

In the following definitions unless otherwise stated, a constant pressure of 1 atmosphere and a constant temperature (usually 25 °C) is implied.

The Heat or Enthalpy of Atomization ($\Delta H_{\text{atom}}$) refers to the process of degradation, in the gas phase, of 1 mole of a compound into its constituent atoms in their ground energy states. (see also section 9.4).

Heat or Enthalpy of Enolization ($\Delta H_e$) is the enthalpy change for the conversion of 1 mole of pure keto form of a tautomeric compound into 1 mole of the pure enol form. For Acetylacetone, $\Delta H_e$ is defined by the equation:

$$\Delta H_e = \frac{\Delta H_{C_6H_8O_2(g)}}{\text{keto}} - \frac{\Delta H_{C_6H_8O_2(g)}}{\text{enol}}$$
Heat of Reaction \((\Delta H_R)\) is the enthalpy change for a defined unit chemical reaction.

Heat of Solution is the enthalpy change when a solute is dissolved in an excess of solvent. Its value can depend on the solute concentration, so that there may also be enthalpy changes when a solution is diluted.

Standard Heat or Enthalpy of Formation \((\Delta H_f^0)\) is the enthalpy change when 1 mole of a substance is formed under standard conditions from its elements in their most stable states. Under these conditions, elements are arbitrarily assigned zero enthalpies. By standard conditions is implied a pressure of 1 atmosphere and a temperature usually chosen to be 25 \(^\circ\)C. For example, the standard heat of formation of crystalline gallium acetylacetonate is the enthalpy change for the reaction:

\[
\text{Ga}(c) + 15\text{C}_{\text{graphite}} + 21/2\text{H}_2(g) + 30\text{O}_2(g) \rightarrow \text{Ga(C}_{5}\text{H}_{7}\text{O}_{3})_3(c)
\]

Heat of Sublimation \((\Delta H_{\text{sub}})\) is the enthalpy change accompanying the conversion of 1 mole of a solid into its ideal gaseous state. The value is quoted at 1 atm. pressure and usually at the temperature at which sublimation occurs.

Heat of Vaporization \((\Delta H_{\text{vap}})\) is the enthalpy change accompanying the conversion of 1 mole of a liquid to its ideal gaseous state, quoted at 1 atm. pressure and usually at the temperature at which vaporization occurs.
A.2 Statistical test to determine whether the mean of each pair of $\varepsilon$-values is significantly different from the grand mean of all the $\varepsilon$-values.

Calorimeter calibration series using THAM (see section E.10)

| Run No. | $\varepsilon_{tm}$ | 0  | $|0-\varepsilon|$ | $[0-\varepsilon]^2$ | $\frac{[|0-\varepsilon|^2]}{E}$ |
|---------|---------------------|----|------------------|------------------|---------------------------------|
| THAM 1  |                     |    |                  |                  |                                 |
| Cl      | 3014.1              | 3012.7 | 2.4              | 5.7              | .002                            |
| C2      | 3011.4              |      |                  |                  |                                 |
| 2       |                     |    |                  |                  |                                 |
| Cl      | 3014.5              | 3014.0 | 1.1              | 1.2              | "                               |
| C2      | 3013.6              |      |                  |                  | "                               |
| 3       |                     |    |                  |                  |                                 |
| Cl      | 3009.8              | 3014.0 | 1.1              | 1.2              | "                               |
| C2      | 3018.3              |      |                  |                  | "                               |
| 4       |                     |    |                  |                  |                                 |
| Cl      | 3017.5              | 3017.7 | 2.5              | 6.7              | "                               |
| C2      | 3017.8              |      |                  |                  | "                               |
| 5       |                     |    |                  |                  |                                 |
| Cl      | -                   | 3017.7 | 2.5              | 6.7              | "                               |
| C2      | 3014.6              | 3014.6 | 0.5              | 0.3              | "                               |
| $E = \frac{[\sum \varepsilon]}{n}$ | 3015.1 | |                  |                  |                                 |

$$\chi^2_{\text{calculated}} = \frac{[0-\varepsilon]^2}{E} < 0.02$$

$$\chi^2_{\text{tables}} = 0.207\text{ with 4 degrees of freedom at the}$$

"99.5\% confidence level."

Code: $\varepsilon_{tm}$ = energy content of calorimeter, using $t_m$ values.

0 = observed value, the mean of each $\varepsilon$-pair.

$E$ = expected value, equals $\frac{[\sum \varepsilon]}{n}$, the grand total mean.

The above test shows conclusively that no significant difference
exists between each paired mean and the grand total mean. 
\( \Delta H \) values for THAM can therefore be calculated using a
grand mean \( \Delta \)-value.
A.3 STATISTICAL TEST TO DETERMINE WHETHER THE DIFFERENCE BETWEEN SAMPLE MEANS $\bar{H}_{t_{12}}$ AND $\bar{H}_{tm}$ IS SIGNIFICANT.

Results of a series of THAM calculations (see section E.10)

Hypothesis: There is a significant difference between the two sample means $\bar{H}_{t_{12}}$ and $\bar{H}_{tm}$.

Proof: Criterion: If $|\bar{H}_{t_{12}} - \bar{H}_{tm}|$ is greater than twice the standard error of the difference between sample means $\bar{H}_{t_{12}}$ and $\bar{H}_{tm}$, then this difference is significant.

$$\sigma_{(y-y)} = \text{standard error of the difference} = \left[\left(\frac{(s_1^2)}{n_1}\right) + \left(\frac{(s_2^2)}{n_2}\right)\right]^{\frac{1}{2}}$$

$$= \left[\left(\frac{(4.6)^2}{5}\right) + \left(\frac{(4.6)^2}{5}\right)\right]^{\frac{1}{2}} = 3$$

$$3\sigma_{(y-y)} = 9 \ (99.7\% \text{ level of confidence})$$

$$[\bar{H}_{t_{12}} - \bar{H}_{tm}] = [7115 - 7128] = 13$$

Conclusion: A significant difference exists between the two sample means $\bar{H}_{t_{12}}$ and $\bar{H}_{tm}$ at the 99.7% level of confidence. Therefore $t_{12}$ must not be used to calculate solution heat values.
An experimentally determined value is of little use unless it is accompanied by some indication of the error involved in the measurement. Thermochemical convention [35] requires that these limits should be twice the standard error of the mean \( (\sigma/\bar{y}) \), corresponding to a 95% level of confidence, and given by:

\[
\sigma_{\bar{y}} = \frac{(\sigma/\sqrt{n})}{\sqrt{n(n-1)}} = \frac{1}{n} \left[ \sum \Delta^2 / n(n-1) \right]^{1/2}
\]

where \( \sigma \) is the standard deviation of the set of values and \( \sum \Delta^2 \) is the sum of the squares of the deviations of the \( y \) values from the mean. 'n' is the number of values in the set.

Special cases of limits are shown below:

**1 Error in \( y \) at a particular value of \( x \):** A commonly occurring case is when the \( y \) values (which can be in error) are to be plotted against known \( x \) values, and a suitable curve fitted. The question arises 'what is the error in \( y \) at a particular value of \( x \)?' The answer is given by the following relationship.

\[
\sigma_{\bar{y}} = \frac{(\sigma/\sqrt{n})}{\sqrt{n(n-1)}} = \frac{1}{n} \left[ \sum \Delta^2_{\text{graph}} / n(n-1) \right]^{1/2}
\]

where \( \sum \Delta^2_{\text{graph}} \) is the sum of the squares of the deviations of the plotted \( y \) values (at the known values of \( x \)) about the fitted curve, and other symbols have the same significance as above. If the graph is best represented by a straight line, then it can either be drawn as the line-of-best-fit by eye, or by the method of least squares (appendix A.5).
2 Error in $F$ when $F$ is dependent on other variables $x$, $y$ and $z$.

This case arises when the limit is required of a value which is itself the sum of other values with limits. For example, in the equation:

$$F = a(x + \sigma_x) + b(y + \sigma_y) - c(z + \sigma_z)$$

the limits of $F$ are given by [35a]:

$$
\sigma_F^{-} = \left[ (a \sigma_x)^2 + (b \sigma_y)^2 + (c \sigma_z)^2 \right]^{\frac{1}{2}}
$$
For the equation:

\[ y = mx + b \]

expressing the variation of a set of \( y \) values with given values of \( x \), \( m \) and \( b \), the slope and intercept on the \( y \) axis respectively, are given by:

\[
m = \frac{(n) \sum y_i x_i - \sum x_i \sum y_i}{(n) \sum x_i^2 - (\sum x_i)^2}
\]

\[
b = \frac{\sum x_i^2 \sum y_i - \sum x_i \sum x_i y_i}{(n) \sum x_i^2 - (\sum x_i)^2}
\]

where \( \sum x_i \) denotes the summation of all the \( x \)'s up to the \( n \)th value, and \( n \) is an integer.
REFERENCES


[17a] ibid., p. 20.

[17b] ibid., p. 56.

[17c] ibid., p. 128.

[17d] ibid., p. 139.

[17e] ibid., p. 130.

[17f] ibid., p. 141.

[17g] ibid., p. 138.


[22b] ibid., p. 493.


[29b] ibid., Ch. 4, p. 143.


[35a] ibid., p. 309.


