THERMOCHEMISTRY OF SOME TRIVALENT METAL

ACETYLACETONATES

by

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'The heart of the prudent getteth knowledge;
and the ear of the wise seeketh knowledge.'

Proverbs: 18, 15.
ACKNOWLEDGMENTS

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Previous determinations of the standard heats of formation of trivalent, first row, transition metal acetylacetonates are based upon inaccurate heat of combustion data. In this thesis, new values are reported for the standard heats of formation, at 25°, of four trivalent metal acetylacetonates, \( M(C_5H_7O_2)_3 \) (\( M = \text{Al III, Cr III, Mn III and Fe III} \)); the maximum associated uncertainty interval is 0.2% respectively. All heat measurements (± 0.01 cals.) involved the use of an electrically calibrated solution calorimeter. Previously, solution calorimetry has been exclusively confined to the thermochemical study of simple chemical processes of well-authenticated stoichiometry. Although the reactions inherent in the present work failed to conform to such simplicity, apparent thermodynamic inexactitudes were conveniently eliminated by introducing a non-volatile solvent, in which all the components in the theoretical heterogeneous complex formation reaction were soluble. The prearranged thermodynamic equivalence of two homogeneous systems simplified the thermochemical cycle, from which the standard heat of formation of the complex was derived directly by successive applications of Hess's law.
The formation reaction was finally referred to the ideal gas state in order to eliminate the effect of intermolecular forces.

Subsequent to the estimation of the O-H bond dissociation energy in acetylacetone (enol isomer), and the electron affinity of the acetylacetonate radical, the homolytic and heterolytic bond energy parameters were calculated for each complex by presuming the equivalence of the six metal-oxygen bonds. By convention, the ground energy state was adopted as the thermodynamic reference state for all components in the hypothetical dissociation process.

The characteristic 'twin-peaked' curve, obtained from a plot of the empirical heat of formation of the gaseous transition metal acetylacetonate versus the corresponding metal atomic number, has been inadequately interpreted by specific reference to the crystal field theory. Some preliminary inferences have been drawn pertaining to the 'nature' of the metal-oxygen coordinate bond.
SECTION 1

INTRODUCTION
1.1. Chemical bonds and bond properties

A molecule is generally defined as a discrete group of atoms linked together by a chemical bond. Such a definition is valueless without a supplementary definition of the term 'chemical bond'. Pauling [1] has offered a rigorous and precise definition of this vague concept: 'there is a chemical bond between two atoms or groups of atoms in the case that the forces acting between them are such as to lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent molecular species'. Within this definition, Pauling recognises three distinct types of chemical bond, the electrostatic (or ionic) bond, the covalent bond and the metallic bond; weak van der Waals forces between molecules are not considered as leading to chemical bond formation. Each pure bond type has well defined properties, but in most molecules, transition from one extreme bond type to another occurs, resulting in bonds of intermediate type and unpredictable properties. Of particular current interest are the coordination compounds, for in these both covalent and ionic bonds are present, e.g. [Co(NH₃)₆]⁺Cl⁻. Werner's coordination theory [2], with its fundamental concept of primary and directed secondary valence, provides an adequate explanation for the existence, general
properties, thermodynamic stability and stereochemistry of such complexes. Lewis [3] (1914) proposed the term 'coordinate or dative bond' to represent Werner's secondary valence bond. Although indistinguishable from a 'normal' covalent bond, the coordinate bond is reserved to describe the unique situation in which a ligand donates a pair of electrons to the restricted electronic environment of a metal atom or ion. Paramount interest is therefore focused upon the complex ion and on the nature of the metal-ligand coordinate bond. Of primary importance are the variable factors which govern the ionic/covalent characteristics and hence the strength of such a bond. In this thesis, special reference is made to four trivalent metal acetylacetonates, \(\text{M(C}_5\text{H}_7\text{O}_2\text{)}_3\) \((\text{M} = \text{Al III, Cr III, Mn III and Fe III})\); these are 'inner complexes', a term first introduced by Ley [4] to describe neutral, non-electrolyte complexes. The standard heat of formation at 25° and the metal-ligand coordinate bond energy are reported for each complex and an attempt is made to correlate the empirically derived bond strength with current theories pertaining to the nature of the metal-ligand coordinate bond.
1.2. **The nature of bonding in coordination complexes**

The mathematical difficulties in solving the Schrödinger wave equation for any except the simplest molecules have compelled the introduction of certain approximations in describing the 'nature' of the metal-ligand coordinate bond in transition metal complexes. The electrostatic (or crystal field theory), the valence bond (or ligand field theory) and the molecular orbital theory are three alternative approaches to this intricate problem. All three theories are based upon the concept of heterogeneous splitting of the inner d or f orbitals on the central metal cation under the perturbing influence of the circumambient ligands; e.g. in the case of octahedral symmetry, the five degenerate d orbitals on the metal are split into two groups of different energy, a lower energy triply degenerate set \( t_{2g} \) and a higher, doubly degenerate set \( e_g \). However, each theory begins with a different premise; the electrostatic theory tacitly assumes that the chemical bond between the metal and ligand is totally ionic, whereas the valence bond theory hypothesises that the same coordinate bond is purely covalent; the more versatile molecular orbital theory postulates the possibility of both ionic and covalent bonding although it does not specifically mention either.

The principal features of the orbital energy level
diagram (Figure 1.2A), evolved from all three theories, are the same, but accumulative evidence has clearly shown that if any one theory is accepted with the exclusion of the other two then it is impossible to provide a unified explanation of the properties of a particular coordination complex.

\[ \begin{align*}
\text{Figure 1.2A} & \quad \text{Stabilisation due to metal-ligand bonding} \\
E & \quad \text{eg} \\
\text{metal ion in octahedral ligand environment} & \quad \text{t}^2_g \\
5 \text{ degenerate d orbitals on the metal} & \\
\end{align*} \]

\( \begin{align*}
\Delta & \quad \text{E}_0 \\
\text{eg} & \\
\text{t}^2_g & \\
\end{align*} \)

\textbf{Energy level diagram for octahedral coordination}

\( \Delta \) is the total energy increment between the eg and t^2_g orbitals; it is a mutual property of the metal and ligand and varies when either is changed. E_0 is the 'energy zero' for the coordinated system, and is arbitrarily taken as the weighted mean energy of the five d orbitals; thus an electron in a t^2_g orbital is
stabilised to the extent of $2/5 \Delta$ while an electron in an $e_g$ orbital is destabilised by $3/5 \Delta$. The absolute energy of an electron in a $d$ orbital need not be known.

The energy of all five $d$ orbitals on the central metal cation is increased due to the ligand 'atmosphere'; this suggests that the resulting complex is less stable than the free metal ion. However, the initial increase in orbital energy is over-compensated for by chemical bonding between the metal and ligand, and thus the coordination process is thermodynamically favoured due to a net decrease in free energy of the system.

For a given metal cation, the magnitude of $\Delta$ is largely predetermined by the 'nature' of the ligand: $\Delta$ increases as the electronegativity and size of the ligand decreases and its polarisability increases. The relative 'splitting power' of a ligand may be inferred from its position in the Shimura-Tsuchida spectrochemical series [5]. For a given ligand, $\Delta$ increases as the oxidation state of the metal increases, i.e. as the ionic radius of the metal cation decreases and its electronegativity increases. $\Delta$ increases markedly if secondary $\pi$ bonding between metal and ligand is possible.

The defects of the crystal field theory become apparent when the latter is employed to interpret the 'twin peaked'
curves obtained when many physical properties of transition metals, within one transition series, are plotted versus atomic number. Figure 1.4B shows a pair of such curves obtained from a plot of the heat of hydration of di- and trivalent first series transition metal cations versus the corresponding metal atomic number. Similar curves showing trends in ionic radii, lattice energies, dissociation energies of gaseous complexes and stability constants of complex ions have been rationalised but not completely explained by the crystal field theory.

According to the basic concepts of the theory, the thermodynamic properties of equivalent transition metal ions within the same transition series vary as a linear function of atomic number, after correction for crystal field effects, due to the progressive decrease in the cationic radius and concomitant increase in metal electronegativity with increasing atomic number. The observed discontinuities are due to enhanced stability of the complex resulting from the presence of a crystal field. However, when the calculated crystal field stabilisation energy is subtracted from the corresponding experimentally derived thermodynamic property (expressed as an energy function), the resulting corrected values do not vary linearly with atomic number; generally a smooth ascending curve is obtained (the interpolation curve). The precise
interpolation curve cannot be derived theoretically as it is currently impossible to calculate the exact stabilisation energy inflicted upon the central metal ion by the presence of the electronic ligand environment. The crystal field theory gives an over-simplified metal-ligand bonding picture: the metal-ligand coordinate bond is not purely ionic, as the theory presupposes, but possesses some covalent character probably enhanced by secondary $\pi$ bonding, both of which are not accounted for in the crystal field theory. Thus, for complexes where $\sigma$ bonding only appears important, e.g. ammino and halo complexes, the crystal field theory can be successfully applied, but for systems stabilised by $\pi$ bonding, the crystal field theory leads to erroneous results and the molecular orbital theory has proved to be most successful in defining unambiguously the 'nature' of the metal-ligand coordinate bond.

1.3. **The bond energy parameter**

There are many diverse interpretations of the term 'bond strength'. For a diatomic molecule, it is simply the resonance energy of a pair of electrons between two atoms and the maximum bond strength is represented by the depth of the 'energy well' in the ground state potential energy function for the molecule. Similarly, for a polyatomic molecule, the maximum
bond strength of a particular chemical bond is theoretically given by the minimum in the corresponding ground state, potential energy hypersurface. According to the principal concepts of wave mechanics, the covalent bond strength is a function of the related orbital overlap integral; in polyatomic molecules it is possible to judge qualitatively the relative strengths of chemical bonds from the character of the bonding orbitals. The theory of wave mechanics depicts a molecule as a complete electronic unit and associates chemical bond formation with the transfer of electrons from localised atomic orbitals to delocalised molecular orbitals enveloping the entire molecule. On this broad basis, therefore, the bond strength is a measure of the electronic forces which bind a component atom, not only to an adjacent atom, but to the molecule as a whole. The bond strength is also identified as the energy required to break a chemical bond, i.e. the bond dissociation energy, or, alternatively, it is regarded as a parameter which, when summed over all the bonds in a molecule, yields the heat of atomisation of the latter. For a diatomic molecule, the covalent bond strength is numerically equal to the heat of formation of the gaseous molecule, and similarly for a polyatomic molecule, the strength of a specified chemical bond is closely related to the heat energy evolved upon the intimate
union of two radicals, i.e. to the 'heat of formation' of the bond. The bond strength is also related to the bond length, as measured by X-ray diffraction techniques, and to the bond force constant, as derived from infrared data.

The 'nature' of the covalent bond in a simple diatomic molecule can, in principle, be determined from a complete solution of the relevant Schrödinger wave equations and the bond strength can be calculated from the related planar potential energy function or by solving the orbital overlap integral. For polyatomic molecules, immense mathematical complexities prevent the theoretical evaluation of bond strengths and in such cases the experimental determination of bond dissociation energy remains as the only method of deriving the corresponding bond strength. The various methods of determining bond dissociation energies have been reviewed in detail by Cottrell [6]. From the viewpoint of the present work, the thermochemical method is the most relevant, i.e. either the heat of formation of the bond, or the energy required to break it, is measured directly.

It is appreciated that an approximation has been introduced, for fracture of a chemical bond in a polyatomic molecule is either facilitated or hindered by its immediate electronic environment, so that the bond dissociation energy is not a true measure of the bond strength. Also, the measured bond
dissociation energy is intimately associated with the reorganisational energy of the molecular fragments produced by the dissociation process.

In the present work, certain conventions are adopted in defining the metal-ligand bond energy parameter $E_{ML}$ in order to avoid ambiguity. Following the general definition of Evans and Szwarc [7], $E_{ML}$ is specified as the average metal-ligand bond dissociation energy and is equivalent to the endothermicity of a hypothetical dissociation process in which all the bonds in the complex are stretched independently and simultaneously with the metal-ligand bond, such that the molecule swells infinitely without losing its original shape. The quoted value of $E_{ML}$ is the maximum possible, i.e. each component in the dissociation reaction is considered to assume its lowest, most stable energy state at the reference temperature, 25°. Thus the reorganisational energy associated with the ligand is ignored and the exact 'reacting state' of the metal and ligand is not specified.

$E_{ML}$, in the general case, is the resultant of three interrelated and inseparable components, the covalent, ionic and $\pi$ bond energies. The mono-ligand complex $ML$ may be considered as being formed from gaseous metal cations and gaseous ligand anions in their respective ground state configurations: -
\[ M^{m+}(g) + L^{l-}(g) = ML^{(m-l)+} \quad \Delta H_f' \]

\( \Delta H_f' \) is a direct measure of the metal-ligand heterolytic coordinate bond energy \( (E'_{\text{ML}}) \). In the special case when the integers \( m \) and \( l \) are equal and a neutral complex results, the latter may also be considered as being formed from gaseous metal atoms and gaseous ligand molecules (or radicals), all in their respective ground energy states:

\[ M(g) + L(g) = ML(g) \quad \Delta H_f'' \]

\( \Delta H_f'' \) is numerically equal to the metal-ligand homolytic coordinate bond energy \( (E''_{\text{ML}}) \). \( \Delta H_f' \) and \( \Delta H_f'' \) are generally referred to as 'heats of ligation'; neither is equal to the standard heat of formation of the complex, since the latter has not been formed from its elements. The two bond energy parameters for the neutral complex are related by the general equation [8]:

\[ E'_{\text{ML}} = E''_{\text{ML}} + \sum_{i=1}^{i=m} I_i + m(5/2 \text{ RT}) - E_L \quad (1.3.1) \]

where \( I_i \) is the ionisation potential for removal of the \( i \)th electron from the metal. The term \( m \ (5/2 \text{ RT}) \) corrects the ionisation potential summation to the reference temperature \( (25^\circ) \).
$E_L$ is the electron affinity of the ligand and $m$ is the oxidation number of the metal.

In the present work the standard heat of formation of the inner complex was determined experimentally and the two metal-ligand bond energy parameters, $E'_{MO}$ and $E''_{MO}$, were evaluated from the calculated enthalpy change for the corresponding gaseous formation process at 25°C.

Although diverging from the simplest bond energy interpretation, a more realistic estimate of the metal-ligand bond strength is derived by subtracting the total promotion energy from the $E_{ML}$ term. The promotion energy associated with a given reacting species is the energy difference between the 'reacting state' and the ground energy state. The total promotion energy forms a major contribution to the activation energy of the gaseous formation reaction. The reacting state of a metal atom (or ion) depends upon the nature of the complex to be formed. The promotion energy for the ligand is generally small compared to that for the metal atom (or ion) and is usually neglected. The 'reacting state' for a metal atom (or ion) in a specified ligand environment may not be a definite spectroscopic state and thus its identification is associated with considerable speculation. However, a general guiding principle is usually adopted, in which it is tentatively assumed that the number of d electrons on the metal atom (or
ion) in the 'reacting state' is equal to the number of non-bonding d electrons in the d shell of the coordinated metal ion. Pritchard and Skinner [9] have reported promotion energies for a few transition metal ions (in specified complexes) each estimated from spectroscopic data.

A 'reacting state' is proposed (4.5) for the central metal ion in the trivalent transition metal acetylacetonates but no subsequent attempt was made to calculate the corresponding promotion energy.

The metal-ligand coordinate bond energy is currently a parameter of immense theoretical significance, yet in spite of this, the heats of formation of remarkably few coordination compounds have been reported and, of these, even fewer have been measured directly.

Cotton [10] has calculated the heat of formation at 25° of several bipoitive hexammine cations [$M(NH_3)_6^{2+}$] in the gas phase ($M$ = Ca, Mn, Fe, Co, Ni, and Zn). The standard heat of formation at 25° of the corresponding solid halide $M(NH_3)_6X_2$ ($X$ = Cl, Br or I) was calculated directly from known experimental data and conversion to the gas phase was possible after accurate calculation of the lattice energy of the complex. One sixth the heat of the formation reaction:

$$M^{2+}(g) + 6NH_3(g) = [M(NH_3)_6]^{2+}(g)$$
gave the average metal-nitrogen coordinate bond energy:

\[
\begin{align*}
\text{Ca} - \text{N} & : 47, \quad \text{Mn} - \text{N} : 60, \quad \text{Fe} - \text{N} : 63 \\
\text{Co} - \text{N} & : 68, \quad \text{Ni} - \text{N} : 69, \quad \text{Zn} - \text{N} : 67 \text{ Kcals. respectively.}
\end{align*}
\]

Paoletti and Sabatini [11] derived the metal-chlorine and metal-bromine coordinate bond energies in the tetrahedral anionic complexes \([\text{MX}_4]^2^-\), \((\text{M} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}; \ X = \text{Cl} \ or \ \text{Br})\). The heat of formation of the solid complex \([\text{(C}_2\text{H}_5)_4\text{N}]_2\text{MX}_4\) was measured and its lattice energy calculated.

\[
\begin{array}{cccc}
\text{M} & \text{M - Cl Kcals.} & \text{M - Br Kcals.} & \text{M} & \text{M - Cl Kcals.} & \text{M - Br Kcals.} \\
\text{Mn} & 136.9 & 128.5 & \text{Ni} & 145.9 & 141.1 \\
\text{Fe} & 139.7 & 134.0 & \text{Cu} & 149.2 & 144.3 \\
\text{Co} & 144.6 & 138.9 & \text{Zn} & 148.0 & 142.6 \\
\end{array}
\]

The metal-ligand bond energies were plotted versus atomic number and, when corrected for the corresponding crystal field stabilisation energy, a smooth variation of the parameter throughout the series was observed.

Cotton, Fischer and Wilkinson [12] measured the heat of combustion of chromium, molybdenum and tungsten hexacarbonyls, iron pentacarbonyl and nickel tetracarbonyl and calculated the respective standard heat of formation and mean metal-carbon
coordinate bond energy at 25° :

\[
\text{Cr - C : 27.1; Mo - C: 35.9, W - C: 42.1, Fe - C: 27.7; Ni - C: 35.2 Kcals. respectively.}
\]

Pauson [13] has calculated the ring to metal thermochemical bond energy in ferrocene and nickel dicyclopentadiene to be 147 and 123 Kcals. respectively, derived from heat of combustion data given by Cotton and Wilkinson [14,15].

Jones and co-workers [16,17,18,19], using a Parr adiabatic static bomb calorimeter, have measured the heats of combustion of a large variety of inner complexes, including some trivalent metal acetylacetonates. The standard heat of formation at 25° of the complex was calculated together with the mean metal-ligand homolytic coordinate bond energy. The thermochemical data for Cr III, Mn III and Fe III trisacetylacetonates is compared with the corresponding data derived from the present work (4,4).

1.4. The effect of Inner Orbital Splitting on the thermochemical properties of coordination complexes

Crystal field theory predicts that the coordination complexes of transition metal ions, except those with \(d^0\), \(d^5\) and \(d^{10}\) electronic configurations, are thermodynamically stabilised as a direct consequence of inner d orbital splitting. Differentiation of the degenerate d orbital system results in a
lowering of energy of the inner non-bonding d electrons on the metal cation. The perturbing crystal field may be considered to arise either from the electrostatic charge distribution of the ligands or from the 'chemical bonding' between the central metal cation and the ligand (1,2). The parameter $\Delta$ is a measure of the total intensity or 'strength' of the crystal field. A simplified energy level diagram for an octahedral ligand environment is given in Figure 1.4A.

**Figure 1.4A**

Splitting of the degenerate d shell under the influence of an octahedral crystal field
Under isothermal conditions, the total crystal field stabilisation energy is manifested as exothermic energy $\delta H$ in the gaseous formation process and forms a small but significant contribution to the overall heat of formation of the complex ($\Delta H_f$) defined by:

$$M(g) + nL(g) = ML_n(g) \quad \Delta H_f$$

The extent of raising or lowering the energy of a set of $d$ orbitals is inversely proportional to their degeneracy. The net heat increment $\delta H$ tending to stabilise the complex is given by:

$$\delta H = -(2/5n_t - 3/5n_e) \Delta$$  \hspace{1cm} (1.4.1)

where $n_t$ and $n_e$ are the number of electrons in the $t_{2g}$ and $e_g$ orbitals respectively. Table 1.4a lists the $\delta H$ values (as fractions of $\Delta$) for high spin and low spin octahedral complexes.
TABLE 1.4a

<table>
<thead>
<tr>
<th>High Spin</th>
<th>Low Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>configuration</td>
<td>$\delta H$</td>
</tr>
<tr>
<td>$d^1, d^6$</td>
<td>$-2/5 \Delta$</td>
</tr>
<tr>
<td>$d^2, d^7$</td>
<td>$-4/5 \Delta$</td>
</tr>
<tr>
<td>$d^3, d^8$</td>
<td>$-6/5 \Delta$</td>
</tr>
<tr>
<td>$d^4, d^9$</td>
<td>$-3/5 \Delta$</td>
</tr>
<tr>
<td>$d^0, d^5, d^{10}$</td>
<td>0</td>
</tr>
</tbody>
</table>

This simple derivation of $\delta H$ has neglected the effect of inter-electronic repulsion. The largest energies of this type occur when two electrons occupy the same orbital. The first three non-bonding d electrons on the metal may be placed singly in each of the three equivalent $t_{2g}$ orbitals, the fourth however must either be raised in energy by $3/5 \Delta$ and placed in one of the $e_g$ orbitals, or be spin-paired with an electron in a lower energy $t_{2g}$ orbital at the expense of gaining pairing (or exchange) energy $P$. Similarly the complexes of metals with the d electronic configuration $d^5, d^6$ and $d^7$ may be of the high spin or low spin type. The net crystal field stabilisation energy $\delta H$ for a low spin complex is given by :-
\[ \Delta H = - \left( \frac{2}{5n_t} - \frac{3}{5n_e} \right) \Delta + P \]  

(1.4.2)

P is the total pairing energy and is evaluated from spectral data for the metal cation. For one electron, P is the mean electrostatic energy required to spin pair an electron initially in an e_g orbital with an electron already in a t_2g orbital. It is a specific property of the metal and is independent of the ligand environment. P is zero, except for the d electronic configurations d^4, d^5, d^6 and d^7. Thus, whether the high-spin or low-spin configuration is assumed by a given complex depends upon the relative magnitudes of \( \delta H \) and P, i.e. \( \delta H > P \): low-spin; \( \delta H < P \): high-spin.

In addition to stabilising inner d electrons, the presence of a crystal field reduces the radius of the central metal cation - the net energy contribution to the heat of formation of gaseous complex is small and, to a first approximation, may be neglected.

Orgel [19] has shown that the heats of hydration of the di- and trivalent first series transition metal ions fall on irregular curves showing a distinct minimum at Mn^{2+} and Fe^{3+} respectively. If the calculated crystal field stabilisations \( \delta H \), obtained from spectroscopic \( \Delta \) values, are subtracted from the empirical hydration energies, the corrected heats of
hydration fall on a smooth ascending curve which reflects the progressive decrease in ionic radius and the concomitant increase in the electronegativity of the metal. The heats of hydration of di- and trivalent first series transition metal ions have recently been calculated by George and McClure [20], who define the heat of hydration, \( \Delta H_H \) as the enthalpy change for the reaction:

\[
M^{m+}(g) + me^{-}(g) + m\,H^+(aq) = \frac{m}{2}H_2(g) + M^{m+}(aq) \quad \Delta H_H
\]

\( \Delta H_H \) is calculated from the heat changes of the reactions:

\[
M(c) = M^{m+}(g) + me^{-}(g) \quad \Delta H_i
\]

\[
M(c) + m\,H^+(aq) = M^{m+}(aq) + \frac{m}{2}H_2(g) \quad \Delta H_F
\]

\[
\Delta H_H = \Delta H_F - \Delta H_i \quad (1.4.3)
\]

\( \Delta H_F \) is the heat of formation of the metal cation in solution and is equal to the heat of solution of the metal in infinitely dilute acid. The N.B.S. 'selected' values [21] for \( \Delta H_F \) at 25° were taken. The heat of formation of hydrogen ions in aqueous solution was taken to be zero.

According to George and McClure, the heat of formation \( \Delta H_i \) of a gaseous metal cation \( M^{m+} \) at 25° is given by:

\[
\Delta H_i = \Delta H_{sub} + \sum_{i=1}^{i=m} I_i + m(5/2RT) + F^{m+} - N \quad (1.4.4)
\]
where $\Delta H_{\text{sub}}$ is the heat of sublimation of the metal at 25°;
$I_i$ is the ionisation potential for the removal of the $i$th electron from the outermost shell;
$m(5/2RT)$ corrects the ionisation potential term to 25°;
$p^{m+}$ is the valence state preparation energy;
$N$ is the electronic heat content of the metal atoms at 25°.

Thus for divalent ions at 25°:

$$\Delta H_{\text{II}}^1 = \Delta H_{\text{sub}} + I_1 + I_2 + 2(5/2RT) + P^{2+} - N \quad (1.4.5)$$

and for trivalent ions at 25°:

$$\Delta H_{\text{III}}^1 = \Delta H_{\text{sub}} + I_1 + I_2 + I_3 + 3(5/2RT) + P^{3+} - N \quad (1.4.6)$$

Tables 1.4b and 1.4c give $\Delta H_1$ values calculated by George and McClure for di- and trivalent first series transition metal ions. The ionisation potentials were obtained from Moore's tables [22] and the heats of sublimation of the metals were taken from the new compilation by Sinke and Stull [23]. The ionic radii according to Goldschmidt [24] are listed for comparison purposes.
TABLE 1.4b

Heat of formation of gaseous first row divalent transition metal ions at 25°

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H_{\text{sub}}$</th>
<th>$I_1 + I_2$</th>
<th>N</th>
<th>$p^{2+}$</th>
<th>$\Delta H_{\text{II}}^{11}$ (Kcals./mole)</th>
<th>Ionic radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>42.2</td>
<td>414.5</td>
<td>0.0</td>
<td>0.0</td>
<td>459.7</td>
<td>0.99</td>
</tr>
<tr>
<td>Ti</td>
<td>112.6</td>
<td>471.7</td>
<td>0.3</td>
<td>0.9</td>
<td>587.9</td>
<td>0.85</td>
</tr>
<tr>
<td>V</td>
<td>122.75</td>
<td>482.7</td>
<td>0.7</td>
<td>0.9</td>
<td>608.8</td>
<td>0.82</td>
</tr>
<tr>
<td>Cr</td>
<td>95.0</td>
<td>536.1</td>
<td>0.0</td>
<td>1.0</td>
<td>635.1</td>
<td>0.80</td>
</tr>
<tr>
<td>Mn</td>
<td>66.73</td>
<td>531.9</td>
<td>0.0</td>
<td>0.0</td>
<td>601.6</td>
<td>0.91</td>
</tr>
<tr>
<td>Fe</td>
<td>99.83</td>
<td>555.1</td>
<td>0.2</td>
<td>1.2</td>
<td>658.9</td>
<td>0.83</td>
</tr>
<tr>
<td>Co</td>
<td>101.6</td>
<td>574.3</td>
<td>&lt;0.1</td>
<td>2.3</td>
<td>681.2</td>
<td>0.82</td>
</tr>
<tr>
<td>Ni</td>
<td>101.26</td>
<td>594.4</td>
<td>&lt;0.1</td>
<td>2.8</td>
<td>701.4</td>
<td>0.78</td>
</tr>
<tr>
<td>Cu</td>
<td>81.1</td>
<td>645.8</td>
<td>0.0</td>
<td>2.4</td>
<td>732.3</td>
<td>0.72</td>
</tr>
<tr>
<td>Zn</td>
<td>31.18</td>
<td>630.5</td>
<td>0.0</td>
<td>0.0</td>
<td>664.7</td>
<td>0.83</td>
</tr>
</tbody>
</table>
### TABLE 1.4c

Heat of formation of gaseous first row trivalent transition metal ions at 25°

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H_{\text{sub}}$</th>
<th>$I^+I^2I^3$</th>
<th>$N$</th>
<th>$P^{3+}$</th>
<th>$\Delta H^{\text{III}}_1$ Kcals/mole</th>
<th>Ionic radius(A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc</td>
<td>82.0</td>
<td>1019.0</td>
<td>0.2</td>
<td>0.0</td>
<td>1105.1</td>
<td>0.83</td>
</tr>
<tr>
<td>Ti</td>
<td>112.6</td>
<td>1120.4</td>
<td>0.3</td>
<td>0.6</td>
<td>1237.6</td>
<td>0.64</td>
</tr>
<tr>
<td>V</td>
<td>122.75</td>
<td>1167.5</td>
<td>0.7</td>
<td>1.2</td>
<td>1295.1</td>
<td>0.69</td>
</tr>
<tr>
<td>Cr</td>
<td>95.0</td>
<td>1249.6</td>
<td>0.0</td>
<td>1.7</td>
<td>1350.6</td>
<td>0.65</td>
</tr>
<tr>
<td>Mn</td>
<td>66.73</td>
<td>1308.6</td>
<td>0.0</td>
<td>1.5</td>
<td>1381.1</td>
<td>0.66</td>
</tr>
<tr>
<td>Fe</td>
<td>99.83</td>
<td>1261.5</td>
<td>0.2</td>
<td>0.0</td>
<td>1365.5</td>
<td>0.67</td>
</tr>
<tr>
<td>Co</td>
<td>101.6</td>
<td>1346.4</td>
<td>&lt;0.1</td>
<td>1.5</td>
<td>1453.8</td>
<td>0.65</td>
</tr>
<tr>
<td>Ga</td>
<td>65.0</td>
<td>1318.9</td>
<td>0.1</td>
<td>0.0</td>
<td>1388.1</td>
<td>0.62</td>
</tr>
</tbody>
</table>
The method of deriving the crystal field splitting parameter $\Delta$ from spectral data has been fully explained by Orgel [25]. It is assumed that the metal cations are six coordinate in aqueous solution and that the hydrate complexes are of the high spin type. The former assumption is supported by the identity of the spectra in solution with those of the crystalline hydrates [26]. For the metal ions for which spectral data was not available, $\Delta$ values were obtained indirectly by extrapolation of a plot of $\Delta$ versus atomic number, such as the one given by Holmes and McClure [26] and by using the approximate relationship:

$$\frac{\Delta_{M^{3+}}}{\Delta_{M^{2+}}} = 1.5 \quad (1.4.7)$$

Tables 1.4d and 1.4e list the empirical and corrected heats of hydration ( $\Delta H_H$ and $\Delta H^*_H$, respectively) for the di- and trivalent first series transition metal ions; the spectroscopic $\Delta$ values were taken from data by Orgel [25] and Jørgensen [27] $\Delta H_H$ and $\Delta H^*_H$, are plotted versus atomic number in Figure 1.4B.
TABLE 1.4d

Heat of hydration of divalent, first series, transition metal ions at 25°.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H_{III}^{H}$ Kcals./mole</th>
<th>$\Delta H_{F}$ Kcals./mole</th>
<th>$\Delta H_{III}^{H'}$ Kcals./mole</th>
<th>$\Delta$ Kcals./mole</th>
<th>$\delta H$ Kcals./mole</th>
<th>$\Delta H_{III}^{H'}$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>+459.7</td>
<td>-129.8</td>
<td>-589.5</td>
<td>-</td>
<td>-</td>
<td>-589.5</td>
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<tr>
<td>Ti</td>
<td>+587.9</td>
<td>-65.0</td>
<td>-653.0</td>
<td>35</td>
<td>28.0</td>
<td>-625.0</td>
</tr>
<tr>
<td>V</td>
<td>+608.8</td>
<td>-55.0</td>
<td>-664.0</td>
<td>34</td>
<td>40.8</td>
<td>-623.2</td>
</tr>
<tr>
<td>Cr</td>
<td>+635.1</td>
<td>-33.0</td>
<td>-668.0</td>
<td>40</td>
<td>24.0</td>
<td>-644.0</td>
</tr>
<tr>
<td>Mn</td>
<td>+601.6</td>
<td>-52.0</td>
<td>-654.0</td>
<td>40.0</td>
<td>0.0</td>
<td>-654.0</td>
</tr>
<tr>
<td>Fe</td>
<td>+658.9</td>
<td>-21.0</td>
<td>-680.0</td>
<td>28.4</td>
<td>11.4</td>
<td>-668.6</td>
</tr>
<tr>
<td>Co</td>
<td>+681.2</td>
<td>-16.0</td>
<td>-697.0</td>
<td>28.4</td>
<td>22.8</td>
<td>-674.2</td>
</tr>
<tr>
<td>Ni</td>
<td>+701.4</td>
<td>-15.0</td>
<td>-716.0</td>
<td>24.4</td>
<td>29.4</td>
<td>-686.6</td>
</tr>
<tr>
<td>Cu</td>
<td>+732.3</td>
<td>+15.4</td>
<td>-716.9</td>
<td>37.0</td>
<td>22.2</td>
<td>-694.7</td>
</tr>
<tr>
<td>Zn</td>
<td>+664.7</td>
<td>-36.4</td>
<td>-701.1</td>
<td>-</td>
<td>-</td>
<td>-701.1</td>
</tr>
</tbody>
</table>
Heat of hydration of trivalent, first series, transition metal ions at 25°.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\Delta H_{\text{III}}$</th>
<th>$\Delta H_{\text{F}}$</th>
<th>$\Delta H_{\text{H}}$</th>
<th>$\Delta$</th>
<th>$\delta H$</th>
<th>$\Delta H_{\text{III}}^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kcals./mole</td>
<td>Kcals./mole</td>
<td>Kcals./mole</td>
<td>Kcals./mole</td>
<td>Kcals./mole</td>
<td>Kcals./mole</td>
</tr>
<tr>
<td>Sc</td>
<td>+1105.1</td>
<td>-148.8</td>
<td>-1254</td>
<td>-</td>
<td>0</td>
<td>-1254</td>
</tr>
<tr>
<td>Ti</td>
<td>+1237.6</td>
<td>-96.0</td>
<td>-1334</td>
<td>58</td>
<td>23</td>
<td>-1311</td>
</tr>
<tr>
<td>V</td>
<td>+1295.1</td>
<td>-65.0</td>
<td>-1360</td>
<td>51</td>
<td>40</td>
<td>-1320</td>
</tr>
<tr>
<td>Cr</td>
<td>+1350.6</td>
<td>-61.0</td>
<td>-1412</td>
<td>50</td>
<td>60</td>
<td>-1352</td>
</tr>
<tr>
<td>Mn</td>
<td>+1381.1</td>
<td>-24.0</td>
<td>-1405</td>
<td>60</td>
<td>36</td>
<td>-1369</td>
</tr>
<tr>
<td>Fe</td>
<td>+1365.5</td>
<td>-11.0</td>
<td>-1377</td>
<td>0</td>
<td>0</td>
<td>-1377</td>
</tr>
<tr>
<td>Co</td>
<td>+1453.8</td>
<td>+21.0</td>
<td>-1433</td>
<td>55</td>
<td>22</td>
<td>-1411</td>
</tr>
<tr>
<td>Ga</td>
<td>+1388.1</td>
<td>-50.0</td>
<td>-1439</td>
<td>-</td>
<td>-</td>
<td>-1439</td>
</tr>
</tbody>
</table>

The thermodynamic stabilisation energy $\delta H^*$, as predicted by the crystal field theory, is represented by the displacement of the corresponding empirical heat of hydration from the interpolation curve, i.e. the straight line joining the heats of hydration of the $d^0$, $d^5$ and $d^{10}$ cations (Figure 1.4B).
Table 1.4f compares the theoretical $\delta H'$ with the experimentally derived $\delta H$. The poor agreement reflects the oversimplifications inherent in the crystal field theory ($\delta H'-\delta H$) is a measure of the covalent character of the metal-oxygen coordinate bond.

**TABLE 1.4f**

<table>
<thead>
<tr>
<th>Divalent cation</th>
<th>$\delta H'$ Kcals./mole</th>
<th>$\delta H$ Kcals./mole</th>
<th>Trivalent cations</th>
<th>$\delta H'$ Kcals./mole</th>
<th>$\delta H$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>47</td>
<td>28</td>
<td>Ti</td>
<td>54</td>
<td>23</td>
</tr>
<tr>
<td>V</td>
<td>42</td>
<td>41</td>
<td>V</td>
<td>56</td>
<td>40</td>
</tr>
<tr>
<td>Cr</td>
<td>30</td>
<td>24</td>
<td>Cr</td>
<td>84</td>
<td>60</td>
</tr>
<tr>
<td>Mn</td>
<td>0</td>
<td>0</td>
<td>Mn</td>
<td>53</td>
<td>36</td>
</tr>
<tr>
<td>Fe</td>
<td>16</td>
<td>11</td>
<td>Fe</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>23</td>
<td>23</td>
<td>Co</td>
<td>40</td>
<td>22</td>
</tr>
<tr>
<td>Ni</td>
<td>32</td>
<td>29</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>25</td>
<td>22</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The evaluation of the metal oxygen coordinate bond energy requires precalculation of the lattice energy by the Born method [28]. For the hydrated cations $\text{Fe(H}_2\text{O)}_6^{2+}$ and
Fe(H₂O)₃⁺, Basolo and Pearson [29] have calculated the lattice energy as -186 and -437 Kcals./mole respectively and the corresponding metal-oxygen bond energy as 56 and 116 Kcals.

In the case of the metal acetylacetonates, the lattice energy is equal to the heat of sublimation, which may be measured directly and therefore a direct route to the metal-oxygen coordinate bond energy is possible (4.3), (4.4).

1.5. **General properties and crystal structure of trivalent metal acetylacetonates**

The metal β diketonates are non electrolytes, practically insoluble in water but readily soluble in the common organic solvents, e.g. benzene, acetone, dioxane; many have low melting points (< 200°) and possess volatile characteristics, e.g. tris(acetylacetonato)chromium III may be sublimed in a vacuum and the corresponding aluminium III complex can be distilled without decomposition at temperatures above 300° [30]. Cryoscopic measurements in such solvents as benzene [31] show that the trivalent metal acetylacetonates are monomolecular in solution, and vapour density measurements at elevated temperatures [32] confirm monomolecularity in the gas phase. The complexes are stable in alkaline solution but are spontaneously decomposed by strong acids.
The first crystal structure determinations for trivalent metal acetylacetonates are due to Astbury [33]. The aluminium III, chromium III and manganese III complexes were found to be isomorphous and monoclinic (four molecules per unit cell). The crystal structures of chromium, manganese and iron tris-acetylacetonates have recently been redetermined by Shkolnikova and Shugam [34], Brathovde and Moresin [35] and Roof [36] respectively, each employing X-ray diffraction techniques. Bond lengths and interbond angles pertaining to the chelate ring are given in Table 1.5a, together with the unit cell dimensions of the crystal lattice.
<table>
<thead>
<tr>
<th>$\text{M}(\text{C}_5\text{H}_7\text{O}_2)_3$</th>
<th>unit cell dimensions (Å)</th>
<th>Bond lengths (Å)</th>
<th>Bond Angles</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a</td>
<td>b</td>
<td>c</td>
<td>$\text{C}_1\text{O}_1$</td>
</tr>
<tr>
<td>Al III</td>
<td>14.1</td>
<td>7.42</td>
<td>16.5</td>
<td>-</td>
</tr>
<tr>
<td>Cr III</td>
<td>14.2</td>
<td>7.62</td>
<td>16.5</td>
<td>1.28</td>
</tr>
<tr>
<td>Mn III</td>
<td>13.87</td>
<td>7.467</td>
<td>16.20</td>
<td>1.29</td>
</tr>
<tr>
<td>Fe III</td>
<td>15.471</td>
<td>13.577</td>
<td>16.565</td>
<td>1.28</td>
</tr>
</tbody>
</table>

**Figure 1.5A**

Labeling scheme for one chelate ring in $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_3$. 
The assumed octahedral structure [37] was confirmed for each complex and the existence of three planar chelate groups arranged symmetrically around the central metal ion was conclusively proved. All six metal-oxygen bond lengths were equivalent to within experimental error. The crystal lattice consists of discrete molecules linked together in layers by van de Waals forces; in the case of the orthorhombic ferric complex (eight molecules per unit cell) the closest approach of terminal carbon atoms of molecules in adjacent layers is 3.78Å - such a relatively large separation accounts for the volatility of the complex. Roof concluded that extensive delocalisation of π electrons occurred within each chelate ring as the observed iron-oxygen bond length (1.95Å) was two-thirds between a pure ionic bond (2.05Å) and a pure covalent bond (1.90Å), and the ring carbon-carbon and carbon-oxygen bond lengths on Pauling's scale [1] corresponded to approximately 50% covalent character and thus each six-membered ring was resonance stabilised.

1.6. **The metal-oxygen bond characteristics.**

The 'nature' of the metal-oxygen coordinate bond in the metallic derivatives of acetylacetone has been the subject of much speculation since the cyclic chelated structure for
these complexes became generally accepted in 1937 [38]. The 'benzenoid' structure, proposed by Calvin and Wilson [39], is invalidated by modern theories on π bonding. Double bonds between metals and donor systems may be of the dπ - pπ or dπ - dπ type, the first being exemplified by the complex cyanides, and the second by the complex phosphine halides. The mechanism of π bonding is such that it tends to relieve the charge accumulation on the metal and ligand, established by the primary σ bonding. The crystal field stabilisation energy Δ is increased, resulting in an enhanced overall stability of the complex. Such a σ-π synergic interaction may be represented as M≡L. In the metal acetylacetonates a converse π mechanism probably operates, in which electrons are transferred from the ligand to the metal, both by primary σ bonding and secondary π bonding, represented as M←L. The formal charges on the metal and ligand are increased; the crystal field parameter Δ is decreased leading to an overall destabilisation of the complex. Using the terminology of the molecular orbital theory, both the triply degenerate t_{2g} non-bonding orbitals on the metal and the t_{1u} triply degenerate bonding orbitals on the ligand are occupied, the latter being employed for primary σ bonding. Thus π bonding is only made possible by the overlap of t_{2g} bonding orbitals on the
metal with \( t_{1u} \) antibonding orbitals on the ligand (\( d_{x^2} - p_x \)). The Pauling valence bond theory explains this unfavourable type of secondary bonding as partial donation of electrons from the \( p_z \) unhybridised orbital on the oxygen to the \( d_{xz} \) orbital on the metal. Thus, there is no parallel between \( \pi \) bonding in the metal acetylacetonates and that believed to occur in, e.g., the complex cyanides or carbonyls.

Cotton and Holm [40] have given nuclear magnetic resonance and ultra-violet spectroscopic data to support the existence of weak \( \pi \) bonding in the metal acetylacetonates, which they regard as arising from inextensive mixing of oxygen \( p\pi \) and metal \( p\pi \) and/or \( d\pi \) orbitals where symmetry permits. Paramagnetic resonance experiments by Jarrett [41], confirmed the presence of a six-membered ring and the hyperfine structure, superimposed on the primary spectra, could only be rationalised if metal-oxygen \( \pi \) bonding was postulated. The Raman spectra of Al III, Ga III and In III trisacetylacetonates, obtained by Hester and Plane [42], gave some evidence for the existence of weak \( d\pi-d\pi \) bonding in these complexes.

The infrared spectra of metal acetylacetonates have been studied extensively by many investigators, notably Duval, Freyman and Lecomte [43,44], who found that the spectra of all such complexes were closely inter-related, variation of the
metal producing only small deviations in the overall spectrum. A cyclic chelate structure was concluded but no evidence for metal-oxygen π bonding was found. Martell, McCarthy, Nakamoto and Ruby [45] investigated the infrared spectra of Al III, Co III, Cr III and Fe III trisacetylacetonates and, from the assigned metal-oxygen vibration frequencies, calculated the metal-oxygen bond force constant as 2.6, 2.4, 2.3, 1.65 × 10^6 dynes cm.⁻¹ respectively. The large value for the aluminium-oxygen bond suggested that the latter was strongly covalent, whereas the smaller iron-oxygen bond force constant was consistent with an ionic metal-ligand bond; the spectrum of the aluminium complex gave no evidence for π bonding. Bellamy [44] postulated that the metal-oxygen bond force constant was directly related to the thermodynamic stability of the complex. Fernelius and co-workers [47] have given the stability constants (pK_D) for Al III and Fe III trisacetylacetonates as 22.3 and 26.2 respectively (30°); thus the decreasing order of metal-oxygen force constants, given above, is also the order of decreasing stability. (The bond force constant is directly related to the bond energy parameter, but for the metal acetylacetonates, no relationship between the two constants has yet been formulated.) Bailar, Dismukes and Jones [48] stated that such force constants were inaccurate, as the metal-oxygen
vibrational modes were strongly coupled with three low frequency vibrational modes of the acetylacetonate anion; thus the pure metal-oxygen stretching frequency, and hence the related bond force constant, could not be evaluated. Forman and Orgel [49] found their infrared data for the Cr III, Mn III and Fe III complexes consistent with a Jahn-Teller distortion in the Mn III complex, in agreement with the original, earlier prediction of Dunitz and Orgel [50].

One of the most important single methods of inferring semiquantitatively the extent of electron delocalisation in complexes is from an analysis of their optical spectra. Barnum [51] has given an extensive theoretical interpretation of the electronic absorption spectra of acetylacetonate complexes and has shown that certain specific electronic transitions can only be accounted for if very weak metal-ligand \( \pi \) bonding occurs. Barnum postulates that such \( \pi \) bonding results from the overlap of metal \( t_{2g} \) orbitals with \( \pi \) delocalised molecular orbitals of the acetylacetonate anion, and not specifically with a \( t_{1u} \) antibonding orbital on either oxygen. However, as the three \( t_{2g} \) orbitals on the metal are mutually orthogonal, delocalised \( \pi \) electrons cannot move freely in a circular path around the six-membered ring due to the potential barrier sited at the metal. Resonance is hindered and therefore
the system is not analogous to benzene. The higher energy $4p$ orbitals on the metal, which offer no such potential barrier, may participate in metal-ligand $\pi$ bonding. Barnum has placed the acetylacetonate anion adjacent to water in the Shimura-Tsuchida spectrochemical series [5], and concludes that $\pi$ bonding in metal acetylacetonates is either very weak or non existent, for ligands which are known to form strong $\pi$ bonds occupy a higher relative position in the series.

It is tentatively suggested that secondary bonding in the metal acetylacetonates is a combination of two opposing $\pi$ bonding mechanisms, (i) $d\pi-p\pi$ bonding, effected by inextensive orbital mixing and resulting in an increased $\Delta$ value, and (ii) $d\pi^*-p\pi^*$ bonding which decreases the $\Delta$ value. It is apparent that if these two interactions counterbalance, either exactly or approximately, then the $\pi$ bonding component is effectively zero.

1.7. **Thermodynamic and thermochemical functions**

The total intrinsic energy of a molecule in its various quantised states is the sum of the associated potential and kinetic energies. The former depends upon the position of the molecule in space, whilst the latter is the algebraic sum of the quantised vibrational, rotational and translational energies.
The intrinsic energy of a molecule is temperature dependent and varies from one molecular type to another; chemical reactions therefore usually proceed with the liberation or absorption of energy, which may be manifested as heat energy.

The first law of thermodynamics states that 'the intrinsic energy $E$ of an isolated system remains constant irrespective of any interconversions between the various energy forms'.

$$E_B - E_A = \Delta E = q - w$$  \hspace{1cm} (1.7.1)

where $\Delta E$ is the increase in energy effected by transfer of the system from a defined thermodynamic state $A$ to a second defined state $B$.

$q$ is the total heat absorbed by the system during transition;

$w$ is the total work done by the system during transition;

$$w = - \int PdV$$  \hspace{1cm} (1.7.2)

$p = \text{pressure}$ ; $V = \text{volume}$

For a condensed system, i.e. one confined to a constant volume, $w$ is zero.

$$\therefore q = \Delta E$$  \hspace{1cm} (1.7.3)

i.e. the heat absorbed by a system at constant volume is equal to the total increase in intrinsic energy.
If the system is subjected to a constant confining pressure $P$,

$$w = -P \int dV = -P \Delta V $$  \hspace{1cm} (1.7.4)

From (1.7.1) $\Delta E = q - P \Delta V$ \hspace{1cm} $q = \Delta E + P \Delta V$ \hspace{1cm} (1.7.5)

The total heat content or enthalpy $H$ of a system is defined by:

$$H = E + PV$$  \hspace{1cm} (1.7.6)

Both $H$ and $E$ are functions of state: at constant pressure the enthalpy change $\Delta H$ is given by:

$$\Delta H = \Delta E + P \Delta V$$  \hspace{1cm} (1.7.7)

From (1.7.5) $\Delta H = q$  \hspace{1cm} (1.7.8)

The heat absorbed by a system at constant pressure is equal to the increase in its total heat content. Thus the absorbed heat energy associated with any chemical reaction, proceeding in an isothermal calorimeter at constant pressure, is equal to the corresponding enthalpy change $\Delta H$, usually expressed as Kcals. per unit reaction. $\Delta H$ is equal to $\Delta E$ for reactions in which all the reactants and products are either liquids or solids and for ideal gaseous reactions in which the total volume change is zero. For other ideal gaseous reactions involving a net volume change $\Delta V$, ($\Delta n$ moles) :-
\[ P \Delta V = \Delta nRT \quad (1.7.9) \]

\[ \therefore \Delta H = \Delta E + \Delta nRT \quad (1.7.10) \]

Since a system is generally stabilised by a decrease in heat content, a chemical process should proceed to completion if the total heat content of the products is less than the total heat content of the reactants, i.e. the reaction is exothermic (\( \Delta H_R \) negative). However, many endothermic reactions occur spontaneously and proceed to completion; thus the enthalpy parameter is not necessarily that which influences the reaction path. The second law of thermodynamics defines reaction affinity in terms of the free energy state function \( G \), defined by:

\[ G = H - TS \quad (1.7.11) \]

where \( T \) is the absolute temperature and \( S \) the total entropy of a system, which may be envisaged as a quantitative measure of its degree of disorder. At constant temperature the free energy change \( \Delta G \) is given by:

\[ \Delta G = \Delta H - T \Delta S \quad (1.7.12) \]

For all real systems \( \Delta S \) is positive, i.e. the degree of disorder of a system progressively increases. It is the free energy term which directly influences the reaction path; a thermodynamically favoured reaction is that which is associated
with a decrease in total free energy. The free energy change for a reversible chemical process may be calculated from the condensed reaction isotherm relationship:-

\[ \Delta G = -RT\ln K \]  

(1.7.13)

where \( K \) is the thermodynamic equilibrium constant at absolute temperature \( T \).

The empirical thermochemical law of Hess [52] (1840), is a direct consequence of the first law of thermodynamics and states that 'the heat change associated with a unit chemical process at constant temperature is independent of the reaction path'. An important corollary of Hess's law is that stoichiometric thermochemical equations may be summed algebraically yielding heats of reaction which are not directly accessible. In expressing a heat of reaction generally it is vital to define the physical state of each component.

1.8. Definitions

[A constant pressure (one atmosphere) and a constant temperature (25°) is assumed.]

Heat of reaction \( \Delta H_R \) is the enthalpy change for a defined unit chemical process.
Heat of solution $\Delta H_{\text{sol}}$ is the enthalpy change for the process of physically dissolving a solute (1 mole) in a large excess of solvent such that the resulting solution is infinitely dilute. The degree of association or dissociation of solute and solvent is assumed to be negligible. $\Delta H_{\text{sol}}$ is a direct measure of the solvation energy of the solute.

Standard heat of formation $\Delta H_f^0$ is the enthalpy change for the formation of a compound (1 mole) from its elements in their defined stable thermodynamic states:

- **Solid**: the pure crystalline solid or the most stable crystalline allotrope thereof at the reference temperature and pressure.
- **Liquid**: the pure liquid at the reference temperature and pressure.
- **Gas**: the ideal gas at the reference temperature and pressure.
- **Compound**: the pure compound in its accepted thermodynamic stable state at the reference temperature and pressure.

The standard heat of formation, and hence the heat content of an element in its standard state, is arbitrarily taken to be zero at all temperatures and pressures.

The standard heat of formation of a trivalent metal
acetylacetonate, \( M(C_5H_7O_2)_3 \), is the enthalpy change for the reaction:

\[
M(c) + 15C + 21/2H_2(g) + 3O_2(g) = M(C_5H_7O_2)_3(c) \quad \text{(graphite)}
\]

**Heat of decomposition** \( \Delta H_D \). From the first law of thermodynamics, \( \Delta H_D \) is numerically equal to \( \Delta H_f^O \) but opposite in sign.

**Heat of combustion** \( \Delta H_c \) is the enthalpy change for the complete combustion of a compound (1 mole) in excess pure gaseous oxygen. \( \Delta H_c \) is most useful for the indirect evaluation of the corresponding \( \Delta H_f^O \) (4.1), (4.2).

**Heat of sublimation** \( \Delta H_s \) is the enthalpy change for the conversion of a crystalline compound (1 mole) into the corresponding ideal gaseous modification.

**Heat of vaporisation** \( \Delta H_v \) is analogous to the heat of sublimation but specifically applicable to liquids. Since molecules of a vapour possess on average more potential energy than those in the liquid, the process of evaporation is endothermic.

**Heat of atomisation** \( \Delta H_{\text{Atom}} \) is the enthalpy change for the degradation of a molecule (1 mole) into its constituent gaseous atoms in their ground energy states.
It is generally calculated from the corresponding standard heat of formation of the compound.

\[ A_aB_b \rightarrow (g) = aA(g) + bB(g) + \Delta H_{\text{Atom}} \]

\[ \Delta H_{\text{Atom}} = a \Delta H_A + b \Delta H_B + \ldots - \Delta H_{A_aB_b} \]  

(1.8.1)

\( \Delta H_{A_aB_b} \) is the heat formation of the parent gaseous molecule;
\( \Delta H_A \) is the heat of formation of gaseous atom A, etc.

**Heat of enolisation** \( \Delta H_E \) applies specifically to a tautomeric compound, e.g. acetylacetone. It is the enthalpy change for the conversion of the pure keto form (1 mole) into the pure enol form (1 mole) in a defined homogeneous reaction medium, e.g.

\[ C_5H_8O_2(g) = C_5H_8O_2(g) \quad \Delta H_E \]

keto enol

**Heat of neutralisation** \( \Delta H_N \) is the enthalpy change for the total neutralisation of one equivalent of a base in an infinitely dilute acid solution.

The heat of neutralisation of all 'strong' bases by strong acids is constant and numerically equal to the heat of ionisation of water \( \Delta H_1 \).
\[ \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) = \text{H}_2\text{O}(l) \quad \Delta H_i = -\Delta H_n \]

A recent selected value for \( \Delta H_n \) at 25° is -13.335 Kcals./mole [53].

**Units** [54]
- Universal Gas Constant \( R = 1.98719 \) cals./deg./mole
- Wave number \( Z (\text{cm}^{-1}) = 2.8589(17) \) cals.cm./mole
- Thermochemical calorie = 4.1840 absolute joules
- Electron volt \( eV = 23.063 \) Kcals.
SECTION 2

EXPERIMENTAL
2.1. The Calorimeter

The isothermal homogeneous reaction calorimeter used throughout the present work was that originally designed by Sunner and Wadsö [55] and is shown schematically in Fig. 2.1A. It consisted of a thin uniform glass reaction vessel C of approximately 100 ml capacity suspended from the lid of a surrounding chromium-plated brass jacket J by a wide uniform glass tube. A hard glass pin B protruded symmetrically upwards from the base of the vessel and acted as the ampoule breaker. The stirrer shaft S passed symmetrically through the lid of the can and was so constructed that, without interrupting the stirring, the claw stirrer S' could be depressed sufficiently to fracture a thin glass ampoule attached to it. The combined ampoule holder/stirrer was made of stainless steel, except for work in strong acid solution, when an all gold stirrer was employed and connected to the stirrer shaft by means of a solid 'teflon' joint. The reaction vessel was fitted with two thin glass re-entrant tubes which acted respectively as retainers for the calibration heater H and the temperature sensor T, both of which were immersed in transformer oil to achieve rapid thermal equilibrium within the reaction vessel. The temperature sensor was a thermistor, (2.2) and the 50 ohm calibration heater was constructed from lacquered
nylon spun manganin wire (diameter 0.15 mm; resistivity 25.2 ohms per metre), wound uniformly and non-inductively on a cylindrical glass former and coated with epoxy resin. In a more recent version, the heater resistance was increased to 100 ohms and constructed from enamelled 'Karma' wire (diameter 0.18 mm; resistivity 46.04 ohms per metre), no former was necessary. Both re-entrant tubes were vacuum tightly sealed with a film of 'Araldite'. The stirrer assembly was connected, by means of a flexible rubber junction, to the spindle of a 600 r.p.m. synchronous motor, the speed being checked periodically using a stroboscope. The stirring was efficient enough to effect good thermal equilibrium within one minute. The calorimeter assembly was submerged in a well-lagged thermostat (25° ± 0.001°), controlled by a mercury-toluene regulator, designed so as to have a low thermal lag. The regulator was fitted with a Gouy-type proportionating head (Sunvic Controls Ltd.), coupled to a relay circuit. Bath temperature control was therefore fully automatic. The bath temperature was recorded by a mercury-in-glass thermometer, previously calibrated using an N.P.L. standardised platinum resistance thermometer (Tinsley: Type 5187H: No. 177744). The room temperature was maintained at 23° ± 0.5°. All metal parts of the calorimeter were maintained highly polished to ensure rapid thermal
equilibrium, which generally occurred within two minutes. Once submerged, the only free space between the solution in the calorimeter vessel and the atmosphere was a 0.5 mm. air gap around the stirrer shaft. Thick uniform copper leads joined the extremities of the heater and thermistor to their respective junctions h and t on the inside of the lid. These junctions were further connected by shielded copper leads to the respective gold sockets within a Cannon precision plug P (I.T.T. Cannon Electric Inc.: Type D.A.M.7.W.2), rigidly mounted at the top of the metal tube M. The counterpart, female section of the plug served to link the heater to the electrical calibration unit (Fig.2.3A), and the thermistor to the Wheatstone bridge (Fig.2.2A).

Ampoules were blown in a brass mould [55] from selected thin walled glass tubing, so that the bulbs generated were of uniform and predetermined size and the end walls microscopically thin, thus facilitating fracture and minimizing possible heat effects. For liquid samples, the ampoule shaft was drawn to a fine capillary as near to the bulb as possible, but for solid samples, the shaft was only slightly narrowed. The bulb capacity was 1 ml. for liquids and 0.5 g. for solids. After the sample had been introduced, the bulb was mounted vertically in a small copper tray, cooled by dry ice, and the shaft sealed
very close to the bulb wall with a microflame. As the shaft near to the bulb was extremely narrow, decomposition of solids or evaporation of liquids was reduced to negligible proportions. The sample weight was the difference between the sum of the weights of the filled bulb and detached glass stem, and the empty complete unit. The sealed ampoule was inserted centrally in the claw stirrer S' which, during rotation, gave the solution a vigorous upward swirling motion.

Several miscellaneous sources of heat, and hence sources of error, were investigated, but as the quantities of heat involved were calculated to be less than the total experimental error, no allowance was made for them in the final results. McKerrell [56], by direct measurement, has found the heat of stirring to be between 0.02 and 0.05 small calories per minute, or a maximum of 3 small calories per hour. It was assumed that the heat generated by friction between the solution and the unbroken ampoule was the same as that generated between the solution and the shattered ampoule, i.e. the 'heat of stirring' was constant throughout the calorimetric experiment. Such an assumption was justified as the stirring speed was constant. Bartell and Suggitt [57] have pointed out that the breaking of an ampoule may give rise to one or more small heat effects. The heat of fracture of an ampoule depends upon the mechanical
properties of the glass; it was assumed to be negligible as the end walls were thin and fractured readily. The heat of wetting the inner surface of the bulb was also assumed to be negligible [55]. Fracture of an ampoule, partly filled by a volatile liquid, is accompanied by a condensation process [55]. As the ampoule capacity was so small, this heat effect was neglected. The total heat lost from the calorimeter via the glass neck, the heater and thermistor leads was determined from approximate thermal conductivity calculations to be of the order of $10^{-3}$ cals./sec. The maximum total heat change which could be measured in this type of calorimeter was 50 small calories.

2.2. Temperature measurement

Temperature was measured indirectly by a thermistor ('Stantel': Type F.2311/300), in a conventional D.C. Wheatstone bridge network shown schematically in Fig. 2.2.A. Several fundamental precautions were taken in its construction so as to ensure the highest possible sensitivity. Resistors $R_1$ and $R_2$ were 1000 ohms (Croydon substandards); $R_3$ was the thermistor, and $R_4$ was a standard decade resistance box (Croydon: Type R.B.6), consisting of precision manganin resistors wound non-inductively (six dials, complete range, 10,000 ohms decreasing to 0.01 ohms). The junctions A, B, C and D were solid copper
FIGURE (2.2.A)

THERMISTOR BRIDGE CIRCUIT

FIGURE (2.3.A)

ELECTRICAL CALIBRATION CIRCUIT
rivets mounted rigidly on an insulating thick perspex block, and the four leads a, b, c, and d were shielded untinned copper wires. The bridge current was supplied from a 2 volt accumulator and was adjusted to 250 microamps by an external 10K.ohm variable series resistance R_s. The bridge junctions were surrounded by polystyrene foam to maintain them at constant temperature, and the network was encased by an earthed aluminium box to protect the circuitry from external stray magnetic fields. The galvanometer G was connected across the junctions B and D via the 50K.ohm variable series resistance R_5. Initially a Tinsley (Type 4500L) moving coil galvanometer with lamp and scale attachment was used; internal resistance 54 ohms, period 5 secs, and sensitivity 1000 mm. per microamp. This was later replaced by a Tinsley photocell galvanometer amplifier unit (Type 5214), provided with a thermal compensator, the function of which was to counter-balance the total thermal e.m.f. in the bridge network, thus equilibrating the electrical zero of the galvanometer with the mechanical zero. The compensator was powered by a Mallory cell. The galvanometer (Type M.52.45E) had an internal resistance of 450 ohms, period 2.5 secs, and maximum sensitivity 1000 mm./microamp. Both galvanometers were extremely sensitive to external vibrations and were therefore mounted on an iron plate over foam rubber; they were
also shielded from draughts. At the null point, the thermistor resistance \( R_3 \) was recorded to the nearest 0.01 ohms; the resulting error in the temperature difference was calculated to be not greater than \( 2.10^{-4} \)° [58]; it was known that a temperature change of 1° was equivalent to a resistance span of approximately 50 ohms. The most precise relationship between the resistance \( R \) and temperature \( \Theta \) of a thermistor is given by Bosson, Gutmann and Simmons [59] as:

\[
\log R = A + \frac{B}{(\Theta + \phi)}
\]  (2.2.1)

where \( A, B \) and \( \phi \) are constants. Thus, over a limited temperature range, the thermistor resistance is directly proportional to the inverse of temperature. For a resistance change from \( R_i \) to \( R_f \), the corresponding temperature change is:

\[
\Theta_i - \Theta_f = B \left( \log R_i - A \right)^{-1} - \left( \log R_f - A \right)^{-1}
\]  (2.2.2)

\[\therefore \delta \Theta = -B \log R_i/R_f \left( \log R_i - A \right)^{-1}(\log R_f - A)^{-1}
\]  (2.2.3)

If \( R_i - R_f \) is less than 75 ohms, (2.2.3) approximates to

\[
\Delta \Theta = -C \log \frac{R_i}{R_f}
\]  (2.2.4)

where \( C \) is a constant. This equation was used in all subsequent calculations. The absolute calibration heater resistance was measured at 25° by comparing the potential drop across it (taken between the mid-points of the heater leads), to that
across an N.P.L. calibrated 10 ohm resistor (Croydon: No.10762; 9.9991 ohms at 25°). The heater resistance was redetermined periodically; it was found to remain constant to 1 part in $10^5$; changes in resistance of the heater due to a current of 20 to 100 mA passing through it were neglected.

2.3. Electrical Calibration: Heat Capacity measurement

The calorimeter was calibrated by passing a measured current through the calibration heater for a known period of time and determining the corresponding temperature change. It was assumed that none of the electrical energy dissipated in the heater cavity was lost from the calorimeter vessel by conduction along the lead wires, or through dissipation in that section of the lead wires between the calorimeter and jacket. Both these sources of error were eliminated by using a high resistance heater (100 ohms), and thick copper leads (S.W.G.30), i.e. all the heat generated by the heater was absorbed by the calorimeter and contents. The electrical calibration circuit diagram is shown in Fig.2.3.A. A stabilised 20 volt D.C. power supply (Ether AA0500), supplied a steady current (1 in $2.10^4$) through a dummy heater equal in resistance to that of the calibration heater - the current was adjusted to the desired value using the external variable series resistance $R_v$. Currents
from 20mA. up to 60mA. were used in most cases. After stabilisation for a period of at least one hour, the current was diverted through the heater by closing the three way/two pole switch S, thus initiating a tenth second stopwatch A (Jaquet), and simultaneously an electronic millisecond timer B (Venner: Type T.S.A. 1014/ABC). The precise current flowing through the calibration heater was determined by measuring the potential drop across a 1 ohm, or in later cases, a 10 ohm standard resistance in series with the heater. Both resistances had been previously calibrated using the N.P.L. calibrated 10 ohm standard resistance as comparator. The potential drop across the standard resistant \( R_s \) was measured on a precision vernier potentiometer (Croydon: Type P.10), capable of an accuracy of 1 part in 10^5 of its range, previously standardised using a precision double Weston Cadmium standard cell (Croydon: Type S.C.2.: 1.01859 volts at 20°). The current source for the potentiometer was a 2 volt, mains operated, stabilised power supply (Croydon: Type P.10.S. stability 1 in 2.10^4). The measured potential drop across \( R_s \) remained constant to within 5 parts in 10^5 over the total heating period, which usually varied between 100 and 300 secs., depending upon the amount of heat dissipated by the chemical reaction preceding calibration. The full procedure for calibration is now given, reference being
made to Fig. 2.3.B which represents a typical case. The calorimeter temperature was increased to 25° by means of the calibration heater. A sufficient number of points along the resistance/time pre-rating curve, from \( t = 0 \) to \( t = t_1 \) were taken, time \( t \) being measured to one hundredth of a minute using a 'split-second' stopwatch. At the pre-selected time \( t_1 \), the calibration current was passed and the potential drop \( E_s \) across the standard resistance \( R_s \) was measured at half minute intervals during the heating period. At the pre-selected time \( t_r \), the calibration current was discontinued and a sufficient number of points along the resistance time post-rating curve were taken. The heating period was recorded to 0.01 sec. The characteristics of a thermistor are such that resistance/time curves are directly proportional to temperature/time curves but have opposite slopes. For the purposes of determining temperature differences, it is therefore possible to treat resistance/time plots in the same manner as temperature/time plots. The method of determining the corrected temperature rise was that first described by Dickenson [60]; a time \( t_m \) was found to which both pre- and post-rating curves were extrapolated. As electrical energy was supplied to the calorimeter system at a constant rate, \( t_m = \frac{1}{2}(t_1 + t_r) \); \( \log R_i / R_f \) was then proportional to the corrected temperature rise and
THERMISTOR RESISTANCE (ohms)

FIGURE (2.3.B)

TYPICAL RESISTANCE/TIME PLOT

FOR AN ELECTRICAL CALIBRATION

area 1 = area 2

\[ t_m = \frac{(t_i + t_f)}{2} \]
Dickinson's criterion, that the shaded areas 1 and 2 should be equal, was fulfilled. In every case a linear variation of resistance with time was obtained for both pre- and post-rating periods, thus showing conclusively that a steady rate of change of temperature with time had been attained. The rate of exchange of heat by radiation between the calorimeter and jacket is given by Newton's Law:

\[
\frac{dT}{dt} = \beta (T_J - T_C)
\]

(2.3.1)

where \( T_J \) is the jacket temperature and \( T_C \) the average calorimeter temperature; \( \beta \) is the leakage modulus for the system and is defined by:

\[
\beta = \frac{g_i - g_f}{T_f - T_i}
\]

(2.3.2)

where \( g_i \) = rate of temperature change over the pre-rating period

\( g_f \) = rate of temperature change over the post-rating period

\( T_i \) = mean temperature during pre-rating period

\( T_f \) = mean temperature during post-rating period

For this type of reaction calorimeter, Sunner and Wadsö have determined \( \beta \) as \( 2.10^{-3} \text{min}^{-1} \). [55]

The total heat capacity \( E \) of the calorimeter is defined as the quantity of heat required to raise the temperature of
the complete calorimeter system by 1°: $\epsilon$ is temperature dependent.

At $25^\circ$, $\epsilon^{25} = \frac{i^2 R_H t_h}{J \Delta T} = \frac{E_S^2 H_h}{J R_S^2 \Delta T}$ (2.3.3)

where $i$ is the calibration current (amps.): $R_H$ the heater resistance at $25^\circ$: $E_S$ is the mean potential drop across the series standard resistance $R_s$, (volts): $t_h$ is the heating period (secs.) and $\Delta T$ the corrected temperature rise ($^\circ$C): $J$ is the mechanical equivalent of heat (4.1840 absolute joules per calorie [54]). Substituting for $\Delta T$ from (2.2.4):

$$\epsilon^{25} = \frac{E_S^2 R_H t_h}{J R_S^2 C \log R_i/R_f} = \frac{kt_h E_S^2}{C \log R_i/R_f}$$ (2.3.4)

The constant $k$ is measured directly but the thermistor constant $C$ is never determined. Therefore the constant actually measured $\epsilon'$ is directly proportional to the absolute heat capacity $\epsilon'$. Careful consideration of all accumulative errors indicates that the total uncertainty in the value of $\epsilon'$ is not greater than 2 in $10^4$.

2.4. The Water Equivalent of the calorimeter

If the calorimetric solution is pure water than the resulting value of $\epsilon'$ is directly proportional to the total water
equivalent of the calorimetric system and is designated $\epsilon_{H_2O}^{25}$. This constant is in itself a direct measure of the overall precision of measurement, and periodical redetermination of its value gives a quantitative estimate of the reproducibility and working performance of the equipment. Water equivalents for all the various calorimeters used in the present work are recorded in Table 2.4a. The associated uncertainty interval (2.7) is given as twice the standard deviation from the mean and includes all systematic errors.
<table>
<thead>
<tr>
<th>Calorimeter ref. no.</th>
<th>Mean capacity ml.</th>
<th>( k = \frac{R_H}{\sqrt{R_S}} )</th>
<th>( R_i ) (ohms)</th>
<th>( R_f ) (ohms)</th>
<th>( \log R_i/R_f \cdot 10^4 )</th>
<th>Mean ( E_s ) (volts)</th>
<th>( t_n ) (secs.)</th>
<th>( \varepsilon_{25}^{H_2O} ) Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>98.59</td>
<td>12.098</td>
<td>1718.946</td>
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<td>40.670</td>
<td>0.117270</td>
<td>180.00</td>
<td>7364</td>
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<td></td>
<td></td>
<td>( R_H = 50.532 ) ohms</td>
<td>1719.668</td>
<td>1708.939</td>
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<td>0.117317</td>
<td>120.20</td>
<td>7364</td>
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<td></td>
<td></td>
<td>( R_S = 0.99915 ) ''</td>
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<td>1708.292</td>
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<td>0.117414</td>
<td>120.00</td>
<td>7372</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( i = 117 ) mA</td>
<td>1719.330</td>
<td>1708.596</td>
<td>27.200</td>
<td>0.117486</td>
<td>120.00</td>
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<td></td>
<td></td>
<td></td>
<td>1719.070</td>
<td>1703.056</td>
<td>40.647</td>
<td>0.117501</td>
<td>119.50</td>
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<td>1428.510</td>
<td>21.880</td>
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<td>1428.510</td>
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<td>0.754920</td>
<td>240.03</td>
<td>7371</td>
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<td></td>
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<td>0.754920</td>
<td>240.18</td>
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<td>( i = 75 ) mA</td>
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<td>2171.480</td>
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<td>0.19531</td>
<td>180.08</td>
<td>9450</td>
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<td>2167.445</td>
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<td>4.322</td>
<td>0.30687</td>
<td>180.00</td>
<td>9441</td>
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<td></td>
<td>( R_H = 100.674 ) ohms</td>
<td>2174.570</td>
<td>2172.405</td>
<td>4.326</td>
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<td>9442</td>
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<td>( R_S = 9.9979 ) ''</td>
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<td>0.30687</td>
<td>180.05</td>
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<td>( i = 30 ) mA</td>
<td>2174.548</td>
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<td>2171.363</td>
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<td></td>
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<td></td>
<td>2173.485</td>
<td>2171.325</td>
<td>4.319</td>
<td>0.30682</td>
<td>180.00</td>
<td>9444</td>
</tr>
</tbody>
</table>

Calorimeter II: Capacity 98.88 ml.: \( \varepsilon_{25} = 7525 \pm 6 \)

" III: " 98.59 ml.: \( \varepsilon = 7877 \pm 4 \)

" V: " 99.70 ml.: \( \varepsilon_{H_2O} = 6912 \pm 6 \)

\( \varepsilon_{25}^{H_2O} \) is expressed as cal/unit log \( R_i/R_f \)
2.5. Measurement of enthalpy change $\Delta H$

The modern calorimetric method has been conveniently described as a 'substitution method' [61], in which the amount of electrical energy, needed to duplicate the chemical energy, generated by the chemical reaction under investigation is measured. A calorimetric investigation of a chemical reaction may therefore be divided into two separate parts in which, (a) a measured amount of chemical reaction proceeds in the calorimeter, and (b) a measured amount of electrical energy is dissipated as heat within the calorimeter. In order to rigidly conform to the requirements of the substitution method, it is necessary to exactly equilibrate the amount of electrical energy dissipated during the calibration to that generated in the preceding chemical reaction, thus eliminating certain errors common to both experiments. In such an ideal case, the exothermic reaction heat is equal to the electrical energy input but opposite in sign, the fixed calorimeter system being the absorber and comparator of the two forms of energy. Even for the most favourable of chemical reactions, such precise equilibration of chemical and electrical energy is impossible to achieve and therefore, in practice, only a close similarity between the two experiments is feasible (Fig. 2.5A). For a chemical process to be amenable to an accurate calorimetric
FIGURE (2.5.A)

TYPICAL RESISTANCE/TIME PLOT FOR A CALORIMETRIC EXPERIMENT

area 1' = area 2
area 1 = area 2'

\[ t = \left( t_m + t_f \right) / 2 \]

THERMISTOR RESISTANCE (ohms)

TIME (mins.)
investigation, it must follow a single path, involve only stoichiometric compounds and proceed to completion rapidly.

In the general case, the calorimetric solution, which may also have been one of the reactants, was prepared and analysed. As required, it was run into a graduated delivery pipette (100 ml.) and was then allowed to flow into the calorimeter vessel. The weight of solution delivered to the calorimeter was reproduced to 1 in $10^4$. The ampoule, containing one of the reactants previously weighed to the nearest 0.05 mg., was inserted centrally between the prongs of the claw stirrer and the latter inserted into the calorimeter. The brass jacket was fitted and the whole submerged in the thermostat. External connections having been made and the stirrer started, the calorimeter and contents were brought to 25° using the calibration heater. Resistance/time readings were taken on the pre-rating curve from $t = 0$ to $t = t_1$ (Fig.2.5A); at the pre-selected time $t_1$ the stirrer shaft was lowered and the ampoule fractured on the pin provided within the calorimeter vessel. If the ensuing chemical reaction was exothermic, the thermistor resistance dropped sharply but, after equilibration, reached a constant value at time $t_1^\prime$, thereafter resistance/time readings were taken on the post-rating curve from $t = t_1^\prime$ to $t = \infty$. The equilibration time varied from 0.5 mins. up to 3 mins. for
the reactions investigated, but all reactions were classed as 'fast' reactions so that corrections for heat leakage of the type described by Dickenson [60] were valid. Thus a time $t_m$ was found such that the shaded areas $1'$ and $2'$ (Fig. 2.5A) were equal; the corrected temperature rise was then proportional to $\log \frac{R_1'}{R_f'}$. In view of the rapidity of the chemical reactions studied, points on the curve during the reaction period (about 20 secs.) could not be determined. For an exothermic process, the products of the reaction were cooled to the initial temperature and the system calibrated electrically: the resulting $\mathcal{E}'$ value obtained being directly proportional to the total thermal capacity of the system. For an endothermic process, the post-rating curve for the reaction was duplicated as the pre-rating curve for calibration so that, at the end of which, the system reverted to the initial reaction temperature, i.e. a measured quantity of electrical energy was dissipated in the calorimeter in an amount approximately equal to the energy removed from the system by the preceding chemical reaction. In most cases it was possible to dissipate the electrical energy over a similar time interval to the chemical reaction equilibration period (3 mins.). Both for exo- and endothermic reactions, electrical calibrations were always performed on the products of the chemical reaction and therefore the
corresponding heat increment was referred to the initial temperature, equal to the water bath temperature.

[All sample weights were corrected to vacuum, and molecular weights calculated on the basis of the 1961 Atomic Weights Table].

The enthalpy change $\Delta H_R$ at 25° for a defined chemical process $R$ is given by:

$$\Delta H_R^{25} = \frac{\varepsilon \Delta T'}{n_R} \text{Kcals/unit reaction (2.5.1)}$$

$\varepsilon$ is the absolute heat capacity of the calorimetric system at 25° (cals./C°).

$\Delta T'$ is the corrected temperature rise.

$n_R$ is the mole number of the component defining unit reaction.

But $\Delta T' = C \log \frac{R_1'}{R_f'}$ (2.5.2) and $\varepsilon = \varepsilon'/C$ (2.5.3)

$\therefore \Delta H_R^{25} = \frac{\varepsilon' \log \frac{R_1'}{R_f'}}{1000 n_R} \text{Kcals/unit reaction (2.5.4)}$

2.6. Chemical Standard for reaction calorimeters

Up to 1964 there was no one generally accepted standard chemical process for the intercomparison of solution calorimeters. Such a process is desirable so that systematic errors, such as evaporation or condensation effects, heat leakage from
the calibration heater and slow thermal equilibrium, can be discovered. However, as reaction calorimetry embraces such a wide range of chemical reactions and very diverse calorimetric equipment, a large number of test reactions of well authenticated heat changes are required. This is in contrast to the field of combustion calorimetry where the one universally accepted calibrating standard reaction is the combustion of pure benzoic acid. In reaction calorimetry, standardisation of the calorimeter by direct electrical calibration is the most accurate method. In his paper 'Comparison Standards for Solution Calorimetry', Gunn [62] has listed eighteen desirable characteristics for a standard thermochemical process.

Irving and Wadso" [63] have recently proposed the reaction of tris(hydroxymethyl)aminomethane(2-amino-2-hydroxymethyl-1,3-propanediol), designated 'THAM', with aqueous hydrochloric acid as a standard thermochemical process:

\[ \text{H}_2\text{N.C.} (\text{CH}_2\text{OH})_3 + \text{H}_3\text{O}^+ \xrightarrow{\Delta H^{25}_{\text{THAM}}} \text{H}_3\text{N.C.} (\text{CH}_2\text{OH})_3 + \text{H}_2\text{O}. \]

\[ \Delta H^{25}_{\text{THAM}} = -7104 \pm 3 \text{ cals./mole THAM}. \]

'THAM' is a well defined crystalline compound m.p. 171.1°[54], it is a weak monoacid base, pK_b = 5.92 [65]; it has a low hygroscopicity, does not absorb carbon dioxide, is readily
soluble in water and has therefore found use as a primary acidimetric standard [64]; it can easily be recrystallised from methanol and several such recrystallisations yield a purity of greater than 99.95%. From their results, Irving and Wadsø concluded that 'THAM' has well defined thermochemical properties. The 'THAM' reaction is highly exothermic and has a very low differential heat of dilution [63]. Other laboratories have recently reported values for the enthalpy change of the 'THAM' reaction. Gunn [62] obtained \(-7107 \pm 1\) cals./mole at 25°, THAM concentration: 0.5 g./litre 0.100M HCl. Kilday and Prosen (N.B.S.) [58] obtained \(-7114 \pm 1\) cals./mole and Beezer and Mortimer [58] \(-7104 \pm 4\) cals./mole. Irving and Wadsø have recently recalculated their original results and now propose a reliable value of \(-7112 \pm 2\) cals./mole. The 'THAM' reaction was used to check the reproducibility and accuracy of the present calorimetric equipment. The results are given in Table 2.6a.
TABLE 2.6a

M.wt. THAM 121.136: Density 1.15 g.cm.\(^{-3}\): Vac. wt. correction const. \(K = \pm 0.90\), conc. aq. HCl 0.10M: 'THAM' Lund sample 'D'.

<table>
<thead>
<tr>
<th>Calr. ref.no.</th>
<th>wt. 'THAM' (mg.)</th>
<th>wt. 'THAM' m.moles</th>
<th>(R'_i) (ohms)</th>
<th>(R'_f) (ohms)</th>
<th>(\log R'_i/R'_f) (10^4)</th>
<th>(\varepsilon')</th>
<th>Heat change Q cals.</th>
<th>(\Delta H_{25}^{THAM}) Kcals/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>500.54</td>
<td>4.1321</td>
<td>1723.115</td>
<td>1707.370</td>
<td>39.867</td>
<td>7375</td>
<td>29.40</td>
<td>-7115</td>
</tr>
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<td></td>
<td>501.01</td>
<td>4.1359</td>
<td>1722.900</td>
<td>1707.140</td>
<td>39.909</td>
<td>7374</td>
<td>29.42</td>
<td>-7115</td>
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<tr>
<td></td>
<td>479.65</td>
<td>3.9596</td>
<td>1723.120</td>
<td>1708.020</td>
<td>38.226</td>
<td>7374</td>
<td>28.19</td>
<td>-7119</td>
</tr>
<tr>
<td>II</td>
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<td>3.5822</td>
<td>1478.320</td>
<td>1466.880</td>
<td>33.828</td>
<td>7519</td>
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<td>434.77</td>
<td>3.5891</td>
<td>1477.850</td>
<td>1466.315</td>
<td>33.929</td>
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<td>1706.565</td>
<td>41.423</td>
<td>7519</td>
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<td>-7111</td>
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<td>1442.790</td>
<td>1430.455</td>
<td>37.289</td>
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<td>502.76</td>
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<td></td>
<td>309.83</td>
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<td>2167.900</td>
<td>2158.330</td>
<td>19.213</td>
<td>9469</td>
<td>18.19</td>
<td>-7113</td>
</tr>
</tbody>
</table>

'Selected' \(\Delta H_{25}^{THAM} = -7110 \pm 4\) cals./mole
2.7. The Uncertainty Interval

The magnitude of systematic errors inherent in thermochemical measurements depends upon several independent factors, e.g. (a) the nature, purity and velocity of the specified chemical reaction, (b) the accuracy in measurement of the 'amount' of chemical reaction (represented by the mole number of the component defining unit reaction), (c) the sensitivity of the auxiliary measuring equipment, (d) the purity of the individual components, (e) the precision of maintaining true isothermal conditions.

Consideration of all accumulative errors in the present work indicated that any single thermal measurement was subject to a maximum variation of ± 0.01 small calories. The 'selected' value for the enthalpy change \( \Delta H^\circ_{R} \) of a specified chemical reaction \( R \), was taken as the mean of a minimum of five independent determinations and the associated standard deviation \( S_R \) calculated from the relationship:

\[
S_R = \left[ \frac{\sum \delta^2}{p(p-1)} \right]^{\frac{1}{2}}
\]

(2.7.1)

where \( \sum \delta^2 \) is the sum of the squares of the deviations \( \delta \) from the mean and \( p \) is the total number of determinations.

Rossini [54] has suggested that each thermochemical measurement be quoted together with an uncertainty interval,
which is taken by convention [66] to be twice the standard deviation from the mean; accordingly all results (Section 3) are expressed in the form:

\[ \Delta H_{25}^R \pm 2S_R. \]

The first law of thermodynamics permits thermochemical equations to be added algebraically (1.7.); the standard deviation \( S_T \) associated with the total enthalpy change \( \Delta H_T \) is given by:

\[
S_T = \left[ \sum_{n=1}^{n=t} S_n^2 \right]^{\frac{1}{2}}
\]

(2.7.2)

where \( S_n \) is the standard deviation associated with \( \Delta H_n \) and \( t \) is the total number of reactions.

The total uncertainty associated with the empirical standard heat of formation of Al III, Cr III, Mn III and Fe III trisacetylacetonates (Section 3) is 0.7 Kcals./mole, i.e. approximately 0.2%.
SECTION 3

RESULTS
3.1. The General reaction scheme

The heat increment \( Q_R \) at 25° for the general reversible heterogeneous reaction \( R \):

\[
\begin{align*}
\text{n}_A + \text{n}_B + & \cdots \text{n}_M \rightleftharpoons \text{n}_A' + \text{n}_B' + \cdots \text{n}_M'
\end{align*}
\]

is measured indirectly in an isothermal solution calorimeter by introducing a non-volatile solvent \( S \), in which all the components are soluble. The general thermochemical cycle is given in Scheme 3.1.A.

**Scheme 3.1.A**

\[
\begin{align*}
\text{n}_A + \text{n}_B = & \cdots \text{n}_M \xrightarrow{Q_R} \text{n}_A' + \text{n}_B' + \cdots \text{n}_M'
\end{align*}
\]

\[
\begin{align*}
\Delta H_a \quad \Delta H_b \quad \Delta H_m \quad \Delta H_a' \quad \Delta H_b' \quad \Delta H_m'
\end{align*}
\]

Solution \( S' \) \( \xrightarrow{\Delta H_R'} \) Solution \( S'' \)
(Solvent \( S \)) (Solvent \( S \))

The pure reactants \( A, B, \cdots M \), (mole ratio \( \text{n}_A, \text{n}_B \cdots \text{n}_M \)) are dissolved consecutively in a measured volume \( V \) of the pure solvent \( S \) at 25° and the corresponding heats of reaction \( \Delta H_a, \Delta H_b \cdots \Delta H_m \) are measured. Similarly the pure products \( A', B', \cdots M' \), (mole ratio \( \text{n}_A', \text{n}_B' \cdots \text{n}_N' \)) are added in succession to an equal volume \( V \) of the pure solvent \( S \) at 25°.
and the corresponding enthalpy change for each process measured, 
\( (\Delta H_a', \Delta H_b', \ldots, \Delta H_m') \). A thermodynamic equilibrium state is established in both solutions and the concentration of any one component is predetermined by the equilibrium constant, either \( K_R (S') \) or \( K_R (S'') \). However, since the solutions \( S' \) and \( S'' \) are at the same constant temperature, \( K_R (S') \) and \( K_R (S'') \) are equal; the systems are thermodynamically equivalent and thus \( \Delta H_R \), is equal to zero. The heat of reaction \( Q_R \) is calculated from the Hess law relationship :

\[
Q_R = [n_A \Delta H_a + n_B \Delta H_b + \ldots + n_M \Delta H_m] - [n_A' \Delta H_a' + n_B' \Delta H_b' + \ldots + n_M' \Delta H_m'] \quad (3.1.1)
\]

and \( \Delta H_R = Q_R / n_R \quad (3.1.2) \)

where \( n_R \) is the mole number of the component defining unit reaction.

\( \Delta H_R \), the enthalpy change per unit reaction, is independent of the following indeterminant factors: the equilibrium constant \( K_R \); the activity coefficient of each component; the kinetic order of reaction \( R \); the 'nature' and molecularity of side reactions; the structure of each species in solution. All these factors are common to both systems and are thus conveniently elminated from the theory.
The standard heat of formation of any one component may be calculated at 25° if the corresponding constant is known for all the other components, as:

$$\Delta H_R = [n_A \Delta H_A^o + n_B \Delta H_B^o + \ldots + n_M \Delta H_M^o]$$

$$- [n_A \Delta H_A^o, + n_B, \Delta H_B^o, + \ldots + n_M, \Delta H_M^o] \quad (3.1.3)$$

where $\Delta H_A^o$ is the standard heat of formation of component A, etc. The availability of an accurate value for the standard heat of formation of a compound is thus a prerequisite for its inclusion in the reaction scheme.

3.2. Solution thermochemistry of tris(acetylacetonato)aluminium III [67]

The heterogeneous stoichiometric reaction (R1):

$$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}(c) + 3\text{C}_5\text{H}_7\text{O}_2(1) + 6\text{H}_2\text{O}(1) \rightarrow \text{Al(C}_5\text{H}_7\text{O}_2)_3(c) + 3\text{HCl} \cdot 8\text{H}_2\text{O}(aq)$$

was used as the basis for calculation of the standard heat of formation of tris(acetylacetonato)aluminium III.

All four components dissolved instantaneously at 25° in 50% (volume) water/dioxane (mole fraction of dioxane 0.174). The mixed aqueous/organic solvent is known to function essentially as pure water [68], i.e. ions or molecules are solvated to approximately the same extent in both solvents. Dioxane
and water have similar physical properties, e.g. the corresponding m.p.'s are +11.5° and 0°, and the b.p.'s are 101.5° and 100° respectively [69]. The heat of mixing equal volumes of water and dioxane is low, $\Delta H_M = -0.130$ k.cals/mole dioxane [70], and therefore precise volume measurements are unnecessary. The ability of dioxane to hydrogen-bond to water but not to itself result in it being infinitely soluble in the latter - a near ideal solution results. The thermochemical cycle is given in Scheme 3.2.A.

**Scheme 3.2.A**

$$\begin{align*}
\text{AlCl}_3 \cdot 6\text{H}_2\text{O}(c) + 3\text{C}_5\text{H}_8\text{O}_2(1) + \text{CH}_2\text{O}(aq) & \rightarrow \text{Al(}3\text{C}_5\text{H}_7\text{O}_2\text{)}(c) + 3\text{HCl} + \text{H}_2\text{O}(aq) \\
\Delta H_1 & \rightarrow \text{NaOH (Solv)} \quad 3\Delta H_2 \\
\Delta H_3 & \rightarrow \text{NaOH (Solv)} \quad 3\Delta H_4 \\
\text{50% (volume) Dioxane/water} & \rightarrow \text{50% (volume) dioxane/water} \\
\text{Solution S}_1' & \rightarrow \text{Solution S}_1'' \\
\Delta H_{R1} & = \Delta H_1 + 3\Delta H_2 - \Delta H_3 - 3\Delta H_4 \quad (3.2.1)
\end{align*}$$

The concentration of each component was within the range $10^{-3}$ to $10^{-4}$ molar, and therefore all measured heats of reaction corresponded to the infinite dilution values $\Delta H_1$, $\Delta H_2$, $\Delta H_3$ and $\Delta H_4$ were measured experimentally.
Reagents

p-Dioxane. 'AnalaR' grade dioxane (1 l.) was dried over potassium hydroxide pellets for 24 hours and was then refluxed for 6 hours with sodium, nitrogen being passed continuously through the mixture, which was fractionally distilled and the fraction of b.p. 101-102° collected (refractive index 1.4232, 25°). The dioxane was passed down a column of finely divided chromatographic alumina to remove traces of organic peroxides, and was stored under nitrogen over potassium hydroxide pellets. As required, 50% (volume) water/dioxane solution was prepared ('conductivity water') and stored under nitrogen.

Acetylacetone. Reagent grade acetylacetone was dried over anhydrous sodium sulphate (12 hours), and then fractionally distilled - the fraction of b.p. 134-136° was collected (refractive index 1.4518, 25°). It was necessary to redistil the reagent immediately before use.

Aluminium chloride hexahydrate. The 'AnalaR' grade reagent was dissolved in the minimum quantity at concentrated hydrochloric acid and hydrogen chloride gas passed continuously through the saturated solution to reprecipitate the pure salt. The white crystalline solid was dried over sodium hydroxide and analysed gravimetrically for aluminium by conversion to the oxide Al₂O₃ (platinum crucibles). Theoretical Al. 11.17%.
Experimental : 11.19, 11.18% - corresponds to AlCl₃·6H₂O.

**Tris(acetylacetonate)aluminium III.** The compound was prepared according to the method of Biltz [71]. The white complex was recrystallised twice from dry benzene - reprecipitation being effected by adding ligroin, (b.p. 100° to 120°). The product was air dried, m.p. 194-195° (reported 194.6 [72]); it was analysed gravimetrically for aluminium by conversion to the oxide Al₂O₃ (platinium crucibles). Theoretical Al. 8.32% : Experimental : 8.31, 8.31%.

**Determination of ΔH°{25/4.** Ampoules were loaded with pure crystalline aluminium chloride hexahydrate (1.9-2.1 m.moles) in a dry box, the salt hydrate being hygroscopic. Sodium acetylacetonate solution (0.1% mole excess), (5.7 - 6.3 m.moles) was prepared in situ in the calorimeter vessel from equimolar proportions of pure acetylacetone (added from a calibrated microsyringe) and sodium hydroxide, 0.940M (added from a micro-burette); equal volumes of water and dioxane were added from grade 'A' burettes to just fill the calorimeter vessel (98.46 ml.). The reaction product mixture gave negative qualitative tests for the Al³⁺ cation, thus showing complete formation of tris(acetylacetonate)aluminium III in solution. The reaction was exothermic.
TABLE 3.2a

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>k</th>
<th>R_1 (ohms)</th>
<th>R_f (ohms)</th>
<th>log R_1/R_f</th>
<th>Mean E_5 (volts)</th>
<th>t_h (secs.)</th>
<th>E' (Mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (1)</td>
<td>0.11790</td>
<td>1439.770</td>
<td>1418.400</td>
<td>64.946</td>
<td>1.15372</td>
<td>239.80</td>
<td>5794</td>
</tr>
<tr>
<td>1 (2)</td>
<td>R_f=49.367 ohms</td>
<td>1439.900</td>
<td>1418.840</td>
<td>63.989</td>
<td>1.15375</td>
<td>236.30</td>
<td>5796</td>
</tr>
<tr>
<td>(3)</td>
<td>R =10.004 ohms</td>
<td>1439.660</td>
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<td>64.945</td>
<td>1.15368</td>
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<td>5798</td>
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<td>i=115mA</td>
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<td>1414.555</td>
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<td>(5)</td>
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<td>64.957</td>
<td>1.15369</td>
<td>239.98</td>
<td>5798</td>
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</tbody>
</table>

Heat change Q_1 (cal.s.)

- 42.08
- 39.42
- 39.76
- 38.12
- 40.96

\[ \Delta H_1 = -19.840 \pm 0.006 \text{ Kcals./mole for the reaction} \]

\[ \text{AlCl}_3 \cdot 6\text{H}_2\text{O}(c) + 3\text{C}_{5}\text{H}_7\text{O}_2^- \rightarrow \text{Al(C}_{5}\text{H}_7\text{O}_2^-)\text{3(solv.)} + 3\text{Cl}^- \text{(solv.)} + 6\text{H}_2\text{O(solv.)} \]

The heat of solution \( \Delta H_8 \) at 25° of aluminium chloride hexahydrate (1.6 - 2.8 m.moles) in the mixed solvent was also measured.
TABLE 3.2b

<table>
<thead>
<tr>
<th>Calr. ref. No.</th>
<th>Run no.</th>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log R_i/R_f$ $10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\mathcal{E}'$ (mean)</th>
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</thead>
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<td>0.11790</td>
<td>1435.360</td>
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<td>240.05</td>
<td>5986</td>
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<tr>
<td></td>
<td>(2)</td>
<td></td>
<td>1435.560</td>
<td>1419.190</td>
<td>49.808</td>
<td>1.18565</td>
<td>180.00</td>
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<td>1435.095</td>
<td>1418.735</td>
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<td>1435.220</td>
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<td>(6)</td>
<td></td>
<td>1435.565</td>
<td>1419.190</td>
<td>49.823</td>
<td>1.18534</td>
<td>180.05</td>
<td>5986</td>
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</table>

<table>
<thead>
<tr>
<th>Run No.</th>
<th>$\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ (mg.)</th>
<th>$\text{AlCl}_3\cdot 6\text{H}_2\text{O}$ (m. moles)</th>
<th>$R_i'$ (ohms)</th>
<th>$R_f'$ (ohms)</th>
<th>$\log R_i'/R_f'$ $10^4$</th>
<th>$\mathcal{E}'$</th>
<th>Heat change $Q_{\text{cal}}$ (Kcals./mole)</th>
<th>$\Delta H_s$ (Kcals./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>591.94</td>
<td>2.4516</td>
<td>1435.550</td>
<td>1414.070</td>
<td>65.475</td>
<td>5986</td>
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<td>-15.986</td>
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<td>1.6479</td>
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<td>1421.220</td>
<td>43.947</td>
<td>5990</td>
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<td>5989</td>
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<td>5989</td>
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<td>-15.940</td>
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<td>73.606</td>
<td>5986</td>
<td>44.06</td>
<td>-15.940</td>
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</table>

\[ \Delta H_s = -15.948 \pm 0.024 \text{ Kcals./mole} \] for the reaction:

\[ \text{AlCl}_3\cdot 6\text{H}_2\text{O}(c) \rightarrow \text{Al}^{3+}_{\text{solv.}} + 3\text{Cl}^-_{\text{solv.}} + 6\text{H}_2\text{O}(\text{solv.}) \]
The enthalpy change $\Delta H_D$ for the dissociation process:

$$\text{Al(C}_5\text{H}_7\text{O}_2\text{)}_3\text{(solv.)} = \text{Al}^{3+}\text{(solv.)} + 3\text{C}_5\text{H}_7\text{O}_2^-(\text{solv.})$$

is given by:

$$\Delta H_D = \Delta H_S - \Delta H_L = +3.892 \pm 0.025 \text{ Kcals./mole}$$

The stability constant $pK_D$ for tris(acetylacetonate)aluminium III in aqueous solution is 22.3 at 30° [47]. As the mixed solvent functions essentially as pure water, it is most probable that the $pK_D$ value in 50% (volume) water/dioxane is of the same order. The free energy change $\Delta G_D$ of the dissociation process is given by:

$$\Delta G_D = -RT\ln K_D = 2.303RT \cdot pK_D = 1.364pK_D = +30.0\text{Kcals./mole}$$

and $\Delta G_D = \Delta H_D - T \Delta S_D$

The entropy of ionisation, $\Delta S_D = -88$ cals./deg./mole.

The large negative value for $\Delta S_D$ reflects the high stability of the complex: it is virtually undissociated in solution.

**Determination of $\Delta H_2^{25}$**

Ampoules were loaded with pure acetylacetone (1.9-2.0 m. moles), delivered from a calibrated microsyringe; the reactant was added to sodium hydroxide (2.46 m.moles: 27.5 mole excess) dissolved in 50% (volume) water/dioxane solvent (98.46 ml.). The reaction was exothermic.
### TABLE 3.2c

<table>
<thead>
<tr>
<th>Calr. ref.no. and run.no.</th>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log\frac{R_i}{R_f} \cdot 10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\mathcal{E}'$</th>
<th>$\mathcal{E}'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I (1)</td>
<td>0.11790</td>
<td>1435.260</td>
<td>1425.930</td>
<td>28.323</td>
<td>0.75495</td>
<td>240.13</td>
<td>5697</td>
<td></td>
</tr>
<tr>
<td>(2) $R_H = 49.367$ ohms</td>
<td></td>
<td>1435.315</td>
<td>1425.880</td>
<td>28.340</td>
<td>0.75495</td>
<td>240.08</td>
<td>5693</td>
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<td>(3) $R_s = 10,004$ ohms</td>
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<td>0.75497</td>
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<td>240.14</td>
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</tbody>
</table>

$m.wt. \ C_5H_8O_2 = 100.118$: Density $0.9721 \ g.cm^{-3}$: $K = +1.05$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$C_5H_8O_2$ (mg.)</th>
<th>$C_5H_8O_2$ (m.moles)</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log\frac{R_i}{R_f} \cdot 10^4$</th>
<th>Heat change $Q_2$ (cals.)</th>
<th>$\Delta H_2$ Kcals./mole</th>
</tr>
</thead>
<tbody>
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<td>(1)</td>
<td>187.19</td>
<td>1.8697</td>
<td>1437.065</td>
<td>1427.395</td>
<td>29.322</td>
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<td>(2)</td>
<td>187.76</td>
<td>1.8754</td>
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<td>1425.865</td>
<td>29.430</td>
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<td>1.9936</td>
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<td>1424.980</td>
<td>31.263</td>
<td>5704</td>
<td>17.05</td>
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<tr>
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<td>1.9832</td>
<td>1435.307</td>
<td>1425.135</td>
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<tr>
<td>(5)</td>
<td>191.11</td>
<td>1.9088</td>
<td>1435.340</td>
<td>1425.490</td>
<td>29.906</td>
<td>5700</td>
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</tr>
</tbody>
</table>

$\Delta H_2 = -8.936 \pm 0.005$ Kcals./mole for the reaction:

$$\text{C}_5\text{H}_8\text{O}_2(1) + \text{OH}^-(\text{solv.}) = \text{C}_5\text{H}_7\text{O}_2^-\text{solv.} + \text{H}_2\text{O}(\text{solv.})$$

The heat of solution $\Delta H_s$ of acetylacetone, (2.8 - 3.0 m.moles) in the mixed solvent at 25° was also measured. The reaction was endothermic.
TABLE 3.2d

<table>
<thead>
<tr>
<th>Calr. ref.no. and run.no.</th>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log R_i/R_f$ $\cdot 10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\epsilon'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (1) 0.11790</td>
<td>1434.910</td>
<td>1432.570</td>
<td>7.087</td>
<td>0.73492</td>
<td>60.18</td>
<td>5706</td>
<td></td>
</tr>
<tr>
<td>2 (2) $R_s=49.367$ ohms</td>
<td>1434.790</td>
<td>1432.450</td>
<td>7.089</td>
<td>0.73492</td>
<td>60.17</td>
<td>5703</td>
<td></td>
</tr>
<tr>
<td>3 (3) $R_s=10.004$ ohms</td>
<td>1434.780</td>
<td>1432.440</td>
<td>7.089</td>
<td>0.73488</td>
<td>60.17</td>
<td>5702</td>
<td></td>
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<tr>
<td>4 (4) $i=75mA$</td>
<td>1434.730</td>
<td>1432.385</td>
<td>7.104</td>
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<td>60.33</td>
<td>5706</td>
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</tr>
<tr>
<td>5 (5)</td>
<td>1434.700</td>
<td>1432.365</td>
<td>7.074</td>
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<table>
<thead>
<tr>
<th>Run no.</th>
<th>$C_{5H8O2}$ (mg.)</th>
<th>$C_{5H8O2}$ (m. moles)</th>
<th>$R_f$ (ohms)</th>
<th>$R_f'$ (ohms)</th>
<th>$\log R_f'/R_f$ $\cdot 10^4$</th>
<th>$\epsilon'$ (cals.)</th>
<th>$\Delta H_S'$ (Kcals./mole)</th>
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<tbody>
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<td>1434.980</td>
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<td>2 (2)</td>
<td>286.02</td>
<td>2.8568</td>
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<td>1434.870</td>
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<td>7.757</td>
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<td>1437.645</td>
<td>1434.930</td>
<td>8.210</td>
<td>5705</td>
<td>4.68</td>
</tr>
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</table>

$\Delta H_S' = +1.584 \pm 0.005$ Kcals./mole for the reaction

$C_{5H8O2}(1) = C_{5H8O2}(solv.)$
The heat of ionisation of water, $\Delta H_1$ at 25° has been measured by Christensen, Hale and Izatt [53] and independently by Swanson and Vanderzee [53], the same value being obtained (+13.334 ± 0.015 Kcals./mole, and +13.332 ± 0.016 Kcals./mole respectively).

Fernelius and Kido [68] obtained $\Delta H_1 = +13.57 \pm 0.02$ Kcals./mole and in 50% (volume) water/dioxane, $\Delta H_1 = +13.70 \pm 0.02$ Kcals./mole. Assuming that the systematic error in $\Delta H_1$, is the same as that in $\Delta H_1$, i.e. 0.23 Kcals./mole, the true $\Delta H_1$ in the mixed solvent was taken to be $+13.47 \pm 0.04$ Kcals./mole ($\Delta H_1 = -\Delta H_10$). The heat of ionisation $\Delta H_{1''}$ of acetylacetone in the mixed solvent is defined by the equation:

$$C_5H_8O_2(\text{solv.}) = H^+ (\text{solv.}) + C_5H_7O_2(\text{solv.}) \quad \Delta H_{1''}$$

which is the algebraic sum of the following three equations:

1. $C_5H_8O_2(1) + OH^- (\text{solv.}) = C_5H_7O_2(\text{solv.}) + H_2O(\text{solv.})$:

$$\Delta H_2 = -8.936 \pm 0.005$$

2. $C_5H_8O_2(\text{solv.}) = C_5H_8O_2(1) : - \Delta H_{3''} = -1.584 \pm 0.005$

3. $H_2O(\text{solv.}) = H^+(\text{solv.}) + OH^- (\text{solv.}) : \Delta H_{1''} = +13.47 \pm 0.04$
By Hess's law: \[ \Delta H_{2}'' = \Delta H_{2} - \Delta H_{3}'' + \Delta H_{1}' \]

\[ \therefore \Delta H_{2}'' = +2.95 \pm 0.04 \text{ Kcals./mole.} \]

The dissociation constant \( pK_{1}'' \) for acetylacetone is given by:

\[ pK_{1}'' = 8.35 + 11.6 n_{D} \text{ [73]} \]

where \( n_{D} \) is the mole fraction of dioxane = 0.174.

\[ \therefore pK_{1}'' = 10.37 \text{ and } \Delta G_{1}'' = 1.364 \text{ Kcals./mole.} \]

\[ \Delta G_{1}'' = \Delta H_{1}'' - T \Delta S_{1}'' \]

Thus the entropy of ionisation \( \Delta S_{1}'' = -38 \text{ cals./deg./mole.} \)

Gentile, Cefola and Celiano [74] deduced empirically that \( pK_{1}'' \) for acetylacetone was directly proportional to the reciprocal of the dielectric constant of the solvent. For the mixed solvent water/dioxane (\( n_{D} = 0.053 \)) \( pK_{1}'' = 9.25 \) at 25°, and the heat and entropy of ionisation were calculated to be +2.3 Kcals./mole and -34.9 cals./deg./mole respectively. These values compare favourably with those given above, allowing for the deviation in solvent composition.

Determination of \( \Delta H_{3}^{25} \). Ampoules were loaded with pure finely divided tris(acetylacetonato)aluminium III (0.5 - 0.7 m.moles). Pure sodium chloride (1.8 - 2.2 m.moles) was added to the calorimetric solution to exactly balance stoichiometry. The reaction was endothermic.
### TABLE 3.2e

<table>
<thead>
<tr>
<th>Calr. ref.no. and run.no.</th>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log \frac{R_i}{R_f}$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\varepsilon'$</th>
<th>$\varepsilon'$ (mean)</th>
</tr>
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<tbody>
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</tr>
<tr>
<td>I (1)</td>
<td>0.11790</td>
<td>1439.990</td>
<td>1437.550</td>
<td>7.365</td>
<td>0.75417</td>
<td>60.22</td>
<td>54.83</td>
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<td></td>
</tr>
<tr>
<td>(2) $R_h = 49.367$ ohms</td>
<td></td>
<td>1439.920</td>
<td>1437.485</td>
<td>7.350</td>
<td>0.75416</td>
<td>60.10</td>
<td>54.83</td>
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<tr>
<td>(3) $R_s = 10.004$ ohms</td>
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<td>1439.945</td>
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<tr>
<td>i = 75mA</td>
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<td>1440.085</td>
<td>1437.655</td>
<td>7.335</td>
<td>0.75417</td>
<td>59.96</td>
<td>54.82</td>
<td></td>
</tr>
</tbody>
</table>

m.wt. $\text{Al(C}_{5}\text{H}_{7}\text{O}_{3})_3 = 324.314$: Density = 1.27 [33]: $K = +0.77$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$\text{NaCl in solution}$ (m.moles)</th>
<th>Complex (mg.)</th>
<th>Complex (m.moles)</th>
<th>$R_1^\prime$ (ohms)</th>
<th>$R_f^\prime$ (ohms)</th>
<th>$\log \frac{R_1^\prime}{R_f^\prime} \times 10^4$</th>
<th>$\varepsilon'$</th>
<th>Heat change of $\text{Al} (\text{mole})$</th>
<th>$\Delta H_3$ (Kcals./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>1.86</td>
<td>198.78</td>
<td>0.61293</td>
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<td>1440.230</td>
<td>5.365</td>
<td>54.83</td>
<td>2.94</td>
<td>+4.799</td>
</tr>
<tr>
<td>(2)</td>
<td>2.07</td>
<td>219.57</td>
<td>0.67703</td>
<td>1442.020</td>
<td>1440.050</td>
<td>5.938</td>
<td>54.83</td>
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<td>54.82</td>
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<td>+4.803</td>
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<td>(4)</td>
<td>2.16</td>
<td>229.57</td>
<td>0.70786</td>
<td>1442.100</td>
<td>1440.045</td>
<td>6.194</td>
<td>54.89</td>
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<td>+4.803</td>
</tr>
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<td>1.83</td>
<td>194.90</td>
<td>0.60096</td>
<td>1441.810</td>
<td>1440.065</td>
<td>5.259</td>
<td>54.82</td>
<td>2.88</td>
<td>+4.797</td>
</tr>
</tbody>
</table>

$\Delta H_3 = +4.802 \pm 0.004$ Kcals./mole for the reaction:

$$\text{Al(C}_5\text{H}_7\text{O}_3)_3 (c) = \text{Al(C}_5\text{H}_7\text{O}_2)_3 (\text{solv.})$$.
Substituting $\Delta H_4$, $\Delta H_5$, $\Delta H_9$ and $\Delta H_{10}$ in (3.2.1), $\Delta H_{R_1} = -11.04 \pm 0.07$ Kcals./mole complex. The following standard heats of formation (Kcals./mole) were taken from the literature:

$\text{HCl} \rightleftharpoons \text{H}_2\text{O(aq)} : -39.96 \pm 0.05$ [21] ; $\text{C}_5\text{H}_8\text{O}_2(1) : -101.32 \pm 0.36$ (4.2) ; $\text{H}_2\text{O}(1) : -68.314 \pm 0.010$ [21].

Coughlin's recent value [75] for the standard heat of formation of aluminium chloride hexahydrate : $-643.60 \pm 0.21$ Kcals./mole was taken in preference to the N.B.S. 'selected' value, $-641.1$ Kcals./mole [21], based on the original determination by Sabatier in 1889 [76].

The standard heat of formation of tris(acetylacetonato)-aluminium III at $25^\circ$ was calculated from the relationship :

$$\Delta H^\circ_{f}(\text{complex}) = \Delta H^\circ_{R_1} - 3 \Delta H^\circ_{f} \text{HCl} \rightleftharpoons \text{H}_2\text{O} - 6 \Delta H^\circ_{f} \text{H}_2\text{O} +$$

$$\Delta H^\circ_{f} \text{AlCl}_3\cdot6\text{H}_2\text{O} + 3 \Delta H^\circ_{f} \text{C}_5\text{H}_8\text{O}_2 \quad (3.2.3)$$

$$\Delta H^\circ_{f} \text{Al} (\text{C}_5\text{H}_7\text{O}_2)_3(c) = -428.84 \pm 0.66 \text{ Kcals./mole}$$

3.3. Solution thermochemistry of tris(acetylacetonato)chromium III

A reaction scheme similar to the one given for tris(acetylacetonato)aluminium III (Fig.3.2.A) could not be used for
the corresponding chromium complex as the reaction between chromic ions and acetylacetone (or sodium acetylacetonate) in the mixed solvent was too slow to permit the precise measurement of the total heat change. However, the reverse process, decomposition of the complex in strong acid solution, was found to be rapid and quantitative at 25°. The complex was insoluble in the dilute mineral acids and in constant boiling hydrochloric acid, but it was soluble in concentrated hydrochloric and perchloric acids. 60% perchloric acid (HClO₄·3.57 H₂O) was used as the universal solvent, concentrated hydrochloric acid being unsuitable due to its extreme volatility and hence varying composition. The empirical thermochemical cycle is given in Scheme 3.3.A.

Scheme 3.3.A

\[
\begin{align*}
\text{Perchloric acid} & \quad \Delta H_{R2} = 0 \\
\text{Solution } S_2' & \quad \text{Perchloric acid} \\
\text{HClO}_4\cdot3.57\text{H}_2\text{O} & \quad \text{HClO}_4\cdot3.57\text{H}_2\text{O} \\
\text{Cr(C}_5\text{H}_7\text{O}_2)_3(\text{aq}) + 3\text{HClO}_4\cdot3.57\text{H}_2\text{O}(\text{aq}) & \rightarrow \text{CrCl}_3\cdot6\text{H}_2\text{O}(\text{aq}) + 3\text{C}_5\text{H}_8\text{O}_2(\text{l}) + 8\text{H}_2\text{O}(\text{aq}) \\
\Delta H_5 & \quad \Delta H_8 \\
3\Delta H_6 & \quad 3\Delta H_9 \\
3\Delta H_7
\end{align*}
\]
\[ \Delta H_{R2} = 3 \Delta H_7 + 3 \Delta H_6 + \Delta H_5 - \Delta H_8 - 3 \Delta H_9 \] 

(3.3.1)

\( \Delta H_{R2} \) is independent of the extent of protonation [77] of free acetylacetone in solution.

**Reagents.** Analytical grade hydrochloric and perchloric acids were used; the former was diluted to the required strength and analysed for chloride ion gravimetrically by conversion to silver chloride; the density of perchloric acid was determined at 20° and its composition subsequently obtained from Tables [78].

HCl: density 1.173 g.cm\(^{-3}\). %Cl: 33.89; 33.93, HCl.3.78H\(_2\)O.

HClO\(_4\): " 1.543 g.cm\(^{-3}\). %HClO\(_4\): 61.0, HClO\(_4\).3.57H\(_2\)O.

Chromic chloride hexahydrate. The 'AnalaR' grade reagent was dissolved in the minimum quantity of concentrated hydrochloric acid and hydrogen chloride gas passed through the saturated solution to reprecipitate the pure hexahydrate. The dark green crystalline solid was dried over potassium hydroxide pellets and the chromium estimated gravimetrically by conversion to the oxide Cr\(_2\)O\(_3\) (platinum crucibles).

Cr. (theoretical) 19.51% : Experimental: 19.49, 19.53% - corresponds to the molecular formula CrCl\(_3\).6.00H\(_2\)O.
Tris(acetylacetonato)chromium III was prepared by Cooperstein's urea hydrolysis method [79]. The deep maroon complex was recrystallised twice from benzene, reprecipitation being effected by adding ligroin (b.p. 100-120°), m.p. 215-216°; reported m.p. 216° [31].

Determination of \( \Delta H^\circ \). Ampoules were loaded with hydrochloric acid, HCl.3.78H_2O (1.3 - 2.0 m.moles); the required volume of acid being delivered from a calibrated microsyringe. The reactant was added to perchloric acid, HClO_4.3.5H_2O (100.13 ml.) containing the stoichiometric weight of excess water, added to the calorimetric solution from a calibrated microsyringe. The reaction was endothermic.
TABLE 3.3a

<table>
<thead>
<tr>
<th>Calr. ref. no. and run no.</th>
<th>k</th>
<th>R₁ (ohms)</th>
<th>R₂ (ohms)</th>
<th>logR₁/R₂</th>
<th>Mean Eₛ (volts)</th>
<th>tₕ (secs.)</th>
<th>ε' (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11968</td>
<td>2163.7325</td>
<td>2163.6200</td>
<td>0.225</td>
<td>0.20320</td>
<td>30.18</td>
<td>6628</td>
</tr>
<tr>
<td>(2)</td>
<td>R₉=5.056 (ohms)</td>
<td>2166.2125</td>
<td>2166.1000</td>
<td>0.225</td>
<td>0.20314</td>
<td>30.17</td>
<td>6622</td>
</tr>
<tr>
<td>(3)</td>
<td>R₉=9.983 (ohms)</td>
<td>2166.2850</td>
<td>2166.3975</td>
<td>0.225</td>
<td>0.20311</td>
<td>30.17</td>
<td>6620</td>
</tr>
<tr>
<td>(4)</td>
<td>i=20mA</td>
<td>2166.1425</td>
<td>2166.0301</td>
<td>0.223</td>
<td>0.20306</td>
<td>29.97</td>
<td>6632</td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td>2166.9675</td>
<td>2166.8550</td>
<td>0.225</td>
<td>0.20325</td>
<td>30.17</td>
<td>6629</td>
</tr>
</tbody>
</table>

m.wt. HCl₃.78H₂O = 104.562: Density = 1.173 g.cm⁻³: K = 0.88

<table>
<thead>
<tr>
<th>Run</th>
<th>Excess H₂O (m.moles)</th>
<th>HCl₃.78 H₂O (mg.)</th>
<th>HCl₃.78 H₂O (m.moles)</th>
<th>R₂ (ohms)</th>
<th>R₂ (ohms)</th>
<th>logR₁/R₂</th>
<th>Mean Eₛ (volts)</th>
<th>tₕ (secs.)</th>
<th>ε' (mean)</th>
<th>Heat change (mole)</th>
<th>ΔH₇ (Kcals./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>3.1</td>
<td>149.19</td>
<td>1.4268</td>
<td>2164.9475</td>
<td>2164.7275</td>
<td>0.431</td>
<td>6628</td>
<td>0.29</td>
<td>+0.200</td>
<td>-0.001</td>
<td>+0.200</td>
</tr>
<tr>
<td>(2)</td>
<td>2.3</td>
<td>149.67</td>
<td>1.4314</td>
<td>2166.7350</td>
<td>2166.5175</td>
<td>0.436</td>
<td>6622</td>
<td>0.29</td>
<td>+0.202</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>2.9</td>
<td>151.89</td>
<td>1.4526</td>
<td>2166.4105</td>
<td>2166.1900</td>
<td>0.441</td>
<td>6620</td>
<td>0.29</td>
<td>+0.201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>3.1</td>
<td>163.60</td>
<td>1.5646</td>
<td>2166.5350</td>
<td>2166.3000</td>
<td>0.471</td>
<td>6632</td>
<td>0.31</td>
<td>+0.200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>2.6</td>
<td>135.79</td>
<td>1.2987</td>
<td>2166.3500</td>
<td>2166.1550</td>
<td>0.391</td>
<td>6629</td>
<td>0.26</td>
<td>+0.200</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

ΔH₂⁵ = +0.200 ± 0.001 Kcals./mole for the reaction:

3HCl₃.78H₂O (aq) = 3H⁺ (solv.) + 3Cl⁻ (solv.) + 11.34H₂O (solv.)

Determination of ΔH₂⁵. The solution obtained after dissolution of hydrocholoric acid was employed as 'solvent' for tris(acetylacetonato)chromium III (0.4 - 0.5 m.moles), the weight (g.moles) of complex added to HCl₃.78H₂O already present in solution being in the ratio 1 : 3 respectively. The reaction was endothermic.
\[ \Delta H^\circ_{25} = +2.764 \pm 0.007\ \text{Kcal./mole for the reaction:} \]

\[ \text{Cr(C}_5\text{H}_7\text{O}_2\text{)}_3(c) + 3\text{H}^+(\text{solv.}) = \text{Cr}^{3+}\text{(solv.)} + 3\text{C}_5\text{H}_8\text{O}_2\text{(solv.)} \]

### TABLE 3.3b

<table>
<thead>
<tr>
<th>Calc. ref.no.</th>
<th>( k )</th>
<th>( R_i ) (ohms)</th>
<th>( R_f ) (ohms)</th>
<th>( \log R_i/R_f ) ( \cdot 10^4 )</th>
<th>Mean ( E_s ) (volts)</th>
<th>( t_h ) (secs.)</th>
<th>( E' ) (volts)</th>
<th>( E'' ) (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11968</td>
<td>2166.1975</td>
<td>2165.7500</td>
<td>0.446</td>
<td>0.20314</td>
<td>60.16</td>
<td>6662</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>( R_s = 50.056 ) (ohms)</td>
<td>2166.9300</td>
<td>2166.8200</td>
<td>0.222</td>
<td>0.20321</td>
<td>30.02</td>
<td>6683</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>( R_s = 9.9983 ) (ohms)</td>
<td>2165.6900</td>
<td>2165.4675</td>
<td>0.447</td>
<td>0.20311</td>
<td>60.45</td>
<td>6677</td>
<td>6665 + 12</td>
</tr>
<tr>
<td>(4)</td>
<td>( i = 20\text{mA} )</td>
<td>2167.7825</td>
<td>2167.5600</td>
<td>0.446</td>
<td>0.20319</td>
<td>60.03</td>
<td>6651</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>( i = 20\text{mA} )</td>
<td>2166.3400</td>
<td>2166.1175</td>
<td>0.446</td>
<td>0.20314</td>
<td>60.09</td>
<td>6654</td>
<td></td>
</tr>
</tbody>
</table>

m.wt. \( \text{Cr(C}_5\text{H}_7\text{O}_2\text{)}_3 = 349.323; \) Density = \( 1.266\ \text{g} \cdot \text{cm}^{-3} \) [80]; \( \Delta H = +0.77 \)

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Complex (mg.)</th>
<th>Complex ( \text{(m.moles)} )</th>
<th>( R'_f ) (ohms)</th>
<th>( R'_i ) (ohms)</th>
<th>( \log R'_i/R'_f ) ( \cdot 10^4 )</th>
<th>( \epsilon' )</th>
<th>Heat change ( Q^0 ) (cals.)</th>
<th>( \Delta H^\circ_{25} ) (Kcal./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>182.43</td>
<td>0.52224</td>
<td>2167.3475</td>
<td>2166.2625</td>
<td>2.174</td>
<td>6662</td>
<td>1.45</td>
<td>+2.773</td>
</tr>
<tr>
<td>(2)</td>
<td>131.80</td>
<td>0.37730</td>
<td>2167.8100</td>
<td>2167.0275</td>
<td>1.560</td>
<td>6683</td>
<td>1.04</td>
<td>+2.763</td>
</tr>
<tr>
<td>(3)</td>
<td>170.37</td>
<td>0.48771</td>
<td>2167.4050</td>
<td>2166.4025</td>
<td>2.010</td>
<td>6677</td>
<td>1.34</td>
<td>+2.752</td>
</tr>
<tr>
<td>(4)</td>
<td>179.62</td>
<td>0.51149</td>
<td>2167.3900</td>
<td>2166.3250</td>
<td>2.135</td>
<td>6651</td>
<td>1.42</td>
<td>+2.762</td>
</tr>
<tr>
<td>(5)</td>
<td>151.38</td>
<td>0.43335</td>
<td>2.67.1800</td>
<td>2166.2800</td>
<td>1.804</td>
<td>6654</td>
<td>1.20</td>
<td>+2.770</td>
</tr>
</tbody>
</table>

\[ \Delta H^\circ_{25} = +2.764 \pm 0.007\ \text{Kcal./mole for the reaction:} \]

\[ \text{Cr(C}_5\text{H}_7\text{O}_2\text{)}_3(c) + 3\text{H}^+(\text{solv.}) = \text{Cr}^{3+}\text{(solv.)} + 3\text{C}_5\text{H}_8\text{O}_2\text{(solv.)} \]

Determination of \( \Delta H^\circ_{25} \). Ampoules were loaded with pure chromic chloride hexahydrate (0.4 - 0.5 m.moles) under nitrogen. The reactant was added to perchloric acid, \( \text{HClO}_4 \cdot 3.57\text{H}_2\text{O} \), (100.13 ml.) in the calorimeter. The reaction was endothermic.
TABLE 3.3c

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>k</th>
<th>$R_I$</th>
<th>$R_f$</th>
<th>$R_f$/$R_i$ $^{10^4}$</th>
<th>Mean $E_s$</th>
<th>$t_h$</th>
<th>$E'$</th>
<th>$E'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11968</td>
<td>2163.43</td>
<td>2162.38</td>
<td>2.108</td>
<td>0.20721</td>
<td>300.04</td>
<td>7314</td>
<td>7327.210</td>
</tr>
<tr>
<td>(2) $R_H$=50.056 (ohms)</td>
<td></td>
<td>2163.17</td>
<td>2162.22</td>
<td>1.898</td>
<td>0.20725</td>
<td>270.09</td>
<td>7315</td>
<td></td>
</tr>
<tr>
<td>(3) $R_f$=9.9983 (ohms)</td>
<td></td>
<td>2163.81</td>
<td>2162.77</td>
<td>2.102</td>
<td>0.20721</td>
<td>300.14</td>
<td>7337</td>
<td></td>
</tr>
<tr>
<td>(4) $s$=$i=20mA$</td>
<td></td>
<td>2163.04</td>
<td>2162.10</td>
<td>1.892</td>
<td>0.20719</td>
<td>270.20</td>
<td>7337</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td>2162.98</td>
<td>2161.94</td>
<td>2.104</td>
<td>0.20721</td>
<td>300.18</td>
<td>7331</td>
<td></td>
</tr>
</tbody>
</table>

m.wt. CrCl$_3$.6H$_2$O = 266.457; Density = 1.76 $^{169}$; $K = +0.54$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>CrCl$_3$.6H$_2$O</th>
<th>CrCl$_3$.6H$_2$O</th>
<th>$R_f$</th>
<th>$R_f$</th>
<th>log $R_f$/$R_i$ $^{10^4}$</th>
<th>$E'$</th>
<th>Heat change $q_8$ (cals.)</th>
<th>$\Delta H_8$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>140.11</td>
<td>0.52583</td>
<td>2166.13</td>
<td>2163.2050</td>
<td>5.878</td>
<td>7314</td>
<td>4.30</td>
<td>+8.176</td>
</tr>
<tr>
<td>(2)</td>
<td>100.81</td>
<td>0.37834</td>
<td>2164.84</td>
<td>2162.6350</td>
<td>4.235</td>
<td>7315</td>
<td>3.10</td>
<td>+8.188</td>
</tr>
<tr>
<td>(3)</td>
<td>130.40</td>
<td>0.48938</td>
<td>2165.72</td>
<td>2163.0000</td>
<td>5.466</td>
<td>7337</td>
<td>4.01</td>
<td>+8.198</td>
</tr>
<tr>
<td>(4)</td>
<td>129.65</td>
<td>0.48657</td>
<td>2165.77</td>
<td>2163.0625</td>
<td>5.442</td>
<td>7337</td>
<td>3.99</td>
<td>+8.206</td>
</tr>
<tr>
<td>(5)</td>
<td>118.29</td>
<td>0.44394</td>
<td>2165.58</td>
<td>2163.1100</td>
<td>4.957</td>
<td>7331</td>
<td>3.63</td>
<td>+8.186</td>
</tr>
</tbody>
</table>

$\Delta H_8 = +8.191 \pm 0.010$ Kcals./mole for the reaction:

CrCl$_3$.6H$_2$O = Cr$^{3+}$ (solv.) + 3Cl$^-$ (solv.) + 6H$_2$O (solv.)

Determination of $\Delta H_8^{25}$. The solution obtained after dissolution of chromic chloride hexahydrate was employed as 'solvent' for acetylacetone (1.2 - 1.6 m.moles), the weight (g.moles) of ligand added to the Cr$^{3+}$ ion already present in solution being in the ratio of 3 : 1 respectively. The reaction was exothermic.
TABLE 3.3a

Calr. ref.no.
and run no.

<table>
<thead>
<tr>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log R_i / R_f \cdot 10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\mathcal{E}$ (mean)</th>
<th>$\mathcal{E}'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11968</td>
<td>2161.1175</td>
<td>2.499</td>
<td>0.20722</td>
<td>360.06</td>
<td>74.04</td>
<td>74.02±9</td>
</tr>
<tr>
<td>(2)</td>
<td>0.20722</td>
<td>2161.6600</td>
<td>2.080</td>
<td>0.20722</td>
<td>300.18</td>
<td>74.17</td>
<td>74.00</td>
</tr>
<tr>
<td>(3)</td>
<td>0.20724</td>
<td>2162.4650</td>
<td>2.501</td>
<td>0.20720</td>
<td>360.18</td>
<td>74.00</td>
<td>73.96</td>
</tr>
<tr>
<td>(4)</td>
<td>0.20722</td>
<td>2161.9200</td>
<td>2.084</td>
<td>0.20721</td>
<td>299.97</td>
<td>74.00</td>
<td>73.96</td>
</tr>
<tr>
<td>(5)</td>
<td>0.20721</td>
<td>2161.6600</td>
<td>2.080</td>
<td>0.20722</td>
<td>300.18</td>
<td>74.17</td>
<td>74.00</td>
</tr>
</tbody>
</table>

m.wt. $C_5H_8O_2 = 100.118; \text{ Density } = 0.9721 \text{ g.cm.}^{-3}; K = +1.05$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$C_5H_8O_2$ (mg.)</th>
<th>$C_5H_8O_2$ (m.moles)</th>
<th>$R_i^1$ (ohms)</th>
<th>$R_f^1$ (ohms)</th>
<th>$\log R_i^1 / R_f^1 \cdot 10^4$</th>
<th>$\mathcal{E}$ (cals.)</th>
<th>$\mathcal{E}'$ (cals.)</th>
<th>$\Delta H_g$ (Kcals./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>157.32</td>
<td>1.5713</td>
<td>2162.0850</td>
<td>2160.1000</td>
<td>3.989</td>
<td>7404</td>
<td>2.95</td>
<td>-1.880</td>
</tr>
<tr>
<td>(2)</td>
<td>115.27</td>
<td>1.1513</td>
<td>2162.5100</td>
<td>2161.0500</td>
<td>2.932</td>
<td>7392</td>
<td>2.17</td>
<td>-1.883</td>
</tr>
<tr>
<td>(3)</td>
<td>146.19</td>
<td>1.4612</td>
<td>2161.8100</td>
<td>2159.9600</td>
<td>3.718</td>
<td>7417</td>
<td>2.76</td>
<td>-1.889</td>
</tr>
<tr>
<td>(4)</td>
<td>131.53</td>
<td>1.3137</td>
<td>2150.2500</td>
<td>2148.5900</td>
<td>3.354</td>
<td>7400</td>
<td>2.48</td>
<td>-1.889</td>
</tr>
<tr>
<td>(5)</td>
<td>129.52</td>
<td>1.2937</td>
<td>2162.2015</td>
<td>2160.5700</td>
<td>3.290</td>
<td>7396</td>
<td>2.43</td>
<td>-1.881</td>
</tr>
</tbody>
</table>

$\Delta H_g = -1.884 \pm 0.004$ Kcals./mole for the reaction:

\[
C_5H_8O_2(1) = C_5H_8O_2(solv.)
\]

As a check on the accuracy of the thermodynamic system at 25°, the reactants were added to the perchloric acid solution in the reverse order, i.e. acetylacetone dissolved prior to chromic chloride hexahydrate; the total enthalpy change for the combined process was constant to within the experimental error, as theory predicts.
The heat of formation of HCl·3.78H₂O was determined graphically as \(-36.55 \pm 0.05\) Kcals./mole and therefore \(\Delta H_6 = +3.41 \pm 0.06\) Kcals./mole. Substituting for \(\Delta H_5\), \(\Delta H_6\), \(\Delta H_7\), \(\Delta H_8\), \(\Delta H_9\) in (3.3.1), \(\Delta H_{R2} = +11.06 \pm 0.08\) Kcals./mole complex.

The N.B.S. 'selected' value for the standard heat of formation of chromic chloride hexahydrate is \(-581.1 \pm\) Kcals./mole [21].
based on the original determination by Recoura in 1909 [81].
The standard heat of formation of tris(acetylacetonato)chromium III was calculated at 25° from the relationship:

$$
\Delta H^o_{f}(\text{complex}) = - \Delta H^o_{f} \text{CrCl}_3 \cdot 6\text{H}_2\text{O} + 3 \Delta H^o_{f} \text{C}_9\text{H}_6\text{O}_2
$$

$$
+ \Delta H^o_{f} \text{CrCl}_3 \cdot 6\text{H}_2\text{O} + 3 \Delta H^o_{f} \text{C}_9\text{H}_6\text{O}_2
$$

$$
\Delta H^o_{f} \text{Cr(C}_9\text{H}_7\text{O}_2)_3 = -366.48 \pm 0.67 \text{ Kcals/mole.}
$$

3.4. Solution thermochemistry of tris(acetylacetonato)iron III

The heterogeneous reaction (R3) :

$$
\text{Fe(C}_9\text{H}_7\text{O}_2)_3(c) + 3\text{HCl} \cdot \text{H}_2\text{O(aq)} = \text{FeCl}_3(c) + 3\text{C}_9\text{H}_6\text{O}_2(1) + 6\text{H}_2\text{O(aq)}
$$

was used as a basis for the calculation of the standard heat of formation of tris(acetylacetonato)iron III. 4.358 Molal hydrochloric acid was used as the universal solvent; dissolution of both liquid acetylacetone and the crystalline complex was instantaneous at 25°. The thermochemical cycle is given in Scheme 3.4.A.
\[
\text{Scheme 3.4-A}
\]

\[
\begin{align*}
\text{Fe}(C_5H_7O_2)_3(c) + 3\text{HCl} + \text{H}_2\text{O}(aq) & \rightarrow \text{FeCl}_3(c) + 3\text{C}_5\text{H}_8\text{O}_2\text{H} + \text{H}_2\text{O}(aq) \\
\Delta H_{R3} & \rightarrow \\
\Delta H_{10} + 3\Delta H_{11} & \rightarrow \\
3\Delta H_{12} = 0 & \rightarrow \\
3\Delta H_{R3} = 0 & \rightarrow \\
4.358 \text{ m. Hydrochloric acid} & \rightarrow \\
\text{(HCl.12.73H}_2\text{O)} & \rightarrow \\
\text{Solution S'} & \rightarrow \\
\text{Solution S'')[39]}
\end{align*}
\]

\[
\Delta H_{R3} = \Delta H_{10} + 3\Delta H_{11} - \Delta H_{13} - 3\Delta H_{14} \quad (3.4.1)
\]

Concentrations of reagents employed were:

- Fe : 0.014 g.moles per 1936.2 g. solvent.
- C$_5$H$_8$O$_2$ : 0.056 g.moles per 1936.2 g. solvent.

Coughlin [82] has determined the heat of solution of rigorously purified crystalline ferric chloride in 4.360 m. hydrochloric acid at 30°: (conc. Fe : 0.03 g.moles per 1936.2 g. solvent).

\[
\text{FeCl}_3(c) = \text{Fe}_3^+(\text{solv.}) + 3\text{Cl}^-\text{(solv.)} : \Delta H_{13'} = 24.460 \pm 0.020 \text{ Kcals/mole}
\]

Correcting $\Delta H_{13'}$ to 25° using heat capacity data of Kelly [83].
Rossini and Giguere [85], \( \Delta H_{13}^{25} = -24.560 \pm 0.020 \) Kcals./mole. Assuming that the concentration effect may be neglected, \( \Delta H_{13} \) (Scheme 3.x.A) is equal to \( \Delta H_{13}^{25} \). \( \Delta H_{10} \) and \( \Delta H_{14} \) were measured experimentally.

**Reagents.** 'AnalaR' grade hydrochloric acid (specific gravity 1.18 : 34.9% pure HCl at 20°)(768 g.) was diluted with distilled water (1236.7 g.) and the solution analysed gravimetrically for chloride ion by conversion to silver chloride. The mean molality, derived from six determinations, was 4.358, i.e. 158.92 g. pure HCl per 1000 g. water: measured density : 1.066 g.cm.\(^{-3}\). The bulk solution was divided into two volumes, 1000 ml. and 880 ml. and stored under nitrogen.

'Resorcinol solution'. Pure iron wire (Koch Light Laboratories Ltd.) (432.37 mg., 7.745 m.moles) was dissolved in 4.358 m. hydrochloric acid solution (1000 ml.) under reflux (8 hours). The pale green ferrous chloride solution was quantitatively oxidised by hydrogen peroxide solution, \( \text{H}_2\text{O}_2\cdot12.58\text{H}_2\text{O} \) (3.87 m.moles), prepared by dilution of the '100 vol.' reagent (29.99% \( \text{H}_2\text{O}_2 \) at 25° [78], density 1.1078 g.cm.\(^{-3}\); \( \text{H}_2\text{O}_2 \cdot5.09\text{H}_2\text{O} \) (496.60 mg.) with water (531.63 mg.). The bulk solution was stored under nitrogen.
Tris(acetylacetonato)iron III was prepared by the method of Dehierne and Urbain [86]; the deep red crystalline complex was recrystallised twice from benzene, reprecipitation being effected by adding ligroin (b.p. 100–120°): m.p. 178–179°; reported 179° [87]. The complex was analysed gravimetrically for iron by decomposing with excess concentrated sulphuric acid and igniting the ferric sulphate residue at red heat to the oxide, Fe₂O₃ (platinum crucibles).

%Fe. Theoretical, 15.81%; Experimental, 15.90; 15.84%.

Determination of ΔHᵢ₀. Pure crystalline tris(acetylacetonato)iron III (0.5 – 0.8 m.moles) was dissolved in 4.358m hydrochloric acid solution (100.13 ml.) in the calorimeter. The subsequent reaction, in which the complex was completely decomposed to ferric ions, proceeded in two stages, an endothermic dissolution followed by an exothermic decomposition: ΔHᵢ₀, the algebraic sum of two components, was positive. A typical resistance/time plot (Run 3) is given in Fig. 3.4B.
At time $t_{m'} = 3.3\text{ mins.}$

$\text{area } 1' = \text{area } 3' - \text{area } 2'$

$R_{t'} = 2169.3450$

$R_{i'} = 2167.5575$

$\log_{10} \frac{R_{t'}}{R_{i'}} = 3.579 \times 10^{-4}$
TABLE 3.4

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>k</th>
<th>$R_s$ (ohms)</th>
<th>$R_i$ (ohms)</th>
<th>$\log_{10}(R_i/R_f)$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\mathcal{E}$ (mean)</th>
<th>$\mathcal{E}'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11973</td>
<td>2168.7875</td>
<td>2167.2900</td>
<td>3.000</td>
<td>0.40930</td>
<td>120.05</td>
<td>8027</td>
<td></td>
</tr>
<tr>
<td>(2) $R_f = 50.074$ (ohms)</td>
<td></td>
<td>2168.2150</td>
<td>2166.7150</td>
<td>3.005</td>
<td>0.40973</td>
<td>119.98</td>
<td>8025</td>
<td></td>
</tr>
<tr>
<td>(3) $R_i = 9.9979$ (ohms)</td>
<td></td>
<td>2168.5200</td>
<td>2167.0200</td>
<td>3.005</td>
<td>0.40965</td>
<td>120.09</td>
<td>8030</td>
<td>8029±3</td>
</tr>
<tr>
<td>(4) $i = 40mA$</td>
<td></td>
<td>2168.9600</td>
<td>2167.4600</td>
<td>3.004</td>
<td>0.40963</td>
<td>120.10</td>
<td>8032</td>
<td></td>
</tr>
<tr>
<td>(5) $i = 40mA$</td>
<td></td>
<td>2169.4650</td>
<td>2167.9650</td>
<td>3.004</td>
<td>0.40964</td>
<td>120.09</td>
<td>8032</td>
<td></td>
</tr>
</tbody>
</table>

m.wt. $\text{Fe(C}_5\text{H}_7\text{O}_2\text{)}_3 = 353.174$: density = 1.343 g.cm.$^{-3}$ [80]; $k = +0.77$

<table>
<thead>
<tr>
<th>Run no.</th>
<th>Complex (mg.)</th>
<th>Complex (m.moles)</th>
<th>$R_i'$ (ohms)</th>
<th>$R_f'$ (ohms)</th>
<th>$\log_{10}(R_i'/R_f')$</th>
<th>$\mathcal{E}'$ (mean)</th>
<th>Heat change $Q_{10}$ (cals.)</th>
<th>$\Delta H_{10}$ (Kcals./mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>179.07</td>
<td>0.50703</td>
<td>2168.6150</td>
<td>2167.2050</td>
<td>2.825</td>
<td>8027</td>
<td>2.27</td>
<td>+4.473 ± 0.002</td>
</tr>
<tr>
<td>(2)</td>
<td>220.08</td>
<td>0.62315</td>
<td>2168.7675</td>
<td>2167.0350</td>
<td>3.472</td>
<td>8025</td>
<td>2.79</td>
<td>+4.471</td>
</tr>
<tr>
<td>(3)</td>
<td>226.75</td>
<td>0.64203</td>
<td>2169.3450</td>
<td>2167.5575</td>
<td>3.579</td>
<td>8030</td>
<td>2.87</td>
<td>+4.476</td>
</tr>
<tr>
<td>(4)</td>
<td>253.14</td>
<td>0.73091</td>
<td>2169.8650</td>
<td>2167.8325</td>
<td>4.071</td>
<td>8032</td>
<td>3.27</td>
<td>+4.474</td>
</tr>
<tr>
<td>(5)</td>
<td>269.76</td>
<td>0.76382</td>
<td>2169.5600</td>
<td>2167.4375</td>
<td>4.252</td>
<td>8032</td>
<td>3.42</td>
<td>+4.471</td>
</tr>
</tbody>
</table>

$\Delta H_{10} = +4.473 \pm 0.002 \text{ Kcals./mole}$ for the reaction:

$$\text{Fe(C}_5\text{H}_7\text{O}_2\text{)}_3(\text{c}) + 3\text{H}^+ (\text{solv.}) = \text{Fe}^{2+} (\text{solv.}) + 3\text{C}_5\text{H}_8\text{O}_2 (\text{solv.})$$

Determination of $\Delta H_{25}^{29}$. Ampoules were loaded with pure liquid acetylacetone (2.32 m.moles), the required volume of the reagent being delivered from a calibrated microsyringe (glass needle). The reactant was added to the 'ferric chloride solution' (100.13 ml.) in the calorimeter. The reaction was exothermic.
TABLE 3.4b

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>k</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log\frac{R_i}{R_f} \times 10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\varepsilon'$ (mean)</th>
<th>$\varepsilon'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.11968</td>
<td>2164.3500</td>
<td>2166.3000</td>
<td>1.023</td>
<td>0.19361</td>
<td>180.89</td>
<td>7949</td>
<td>7954</td>
</tr>
<tr>
<td>(2) $R_H=50.056$ (ohms)</td>
<td></td>
<td>2166.2425</td>
<td>2165.7550</td>
<td>1.018</td>
<td>0.19364</td>
<td>180.13</td>
<td>7957</td>
<td>7952±7</td>
</tr>
<tr>
<td>(3) $R_S=9.9983$ (ohms)</td>
<td></td>
<td>2166.0775</td>
<td>2165.5650</td>
<td>1.028</td>
<td>0.19392</td>
<td>181.67</td>
<td>7954</td>
<td>7952±7</td>
</tr>
<tr>
<td>(4) $i=20mA$</td>
<td></td>
<td>2166.7850</td>
<td>2166.2775</td>
<td>1.017</td>
<td>0.19393</td>
<td>179.85</td>
<td>7960</td>
<td>7939</td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td>2166.6150</td>
<td>2166.1050</td>
<td>1.022</td>
<td>0.19392</td>
<td>180.28</td>
<td>7939</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Run no.</th>
<th>$C_5H_8O_2$ (mg.)</th>
<th>$C_5H_8O_2$ (m.moles)</th>
<th>$R'_i$ (ohms)</th>
<th>$R'_f$ (ohms)</th>
<th>$\log\frac{R'_i}{R'_f} \times 10^4$</th>
<th>$\varepsilon'$</th>
<th>Heat change $Q_{14}$ (cals.)</th>
<th>$\Delta H_{14}$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>233.16</td>
<td>2.3289</td>
<td>2164.7600</td>
<td>2164.2375</td>
<td>1.049</td>
<td>7949</td>
<td>0.82</td>
<td>-0.358</td>
</tr>
<tr>
<td>(2)</td>
<td>232.62</td>
<td>2.3235</td>
<td>2166.2550</td>
<td>2165.7400</td>
<td>1.034</td>
<td>7957</td>
<td>0.82</td>
<td>-0.354</td>
</tr>
<tr>
<td>(3)</td>
<td>233.17</td>
<td>2.3290</td>
<td>2166.2050</td>
<td>2165.6125</td>
<td>1.068</td>
<td>7954</td>
<td>0.85</td>
<td>-0.365</td>
</tr>
<tr>
<td>(4)</td>
<td>232.42</td>
<td>2.3215</td>
<td>2166.8225</td>
<td>2166.2875</td>
<td>1.071</td>
<td>7960</td>
<td>0.85</td>
<td>-0.367</td>
</tr>
<tr>
<td>(5)</td>
<td>232.66</td>
<td>2.3239</td>
<td>2166.7150</td>
<td>2166.1850</td>
<td>1.062</td>
<td>7939</td>
<td>0.64</td>
<td>-0.363</td>
</tr>
</tbody>
</table>

$\Delta H_{14} = -0.361 \pm 0.005$ Kcals./mole for the reaction:

$$C_5H_8O_2(1) = C_5H_8O_2(solv.).$$
Coughlin [82] calculated the heat of formation of 4.36 m. hydrochloric acid as $-38.900 \pm 0.050$ Kcals./mole and therefore $\Delta H_{11} = +1.06 \pm 0.07$ Kcals./mole. Substituting for $\Delta H_{10}$, $\Delta H_{11}$, $\Delta H_{13}$ and $\Delta H_{14}$ in (3.4.1), $\Delta H_{R3} = +33.30 \pm 0.12$ Kcals./mole.

Coughlin [82] determined the standard heat of formation of ferric chloride as $-95.700 \pm 0.200$ Kcals/mole. This value is identical with that selected by Evans and Kubaschewski [88] but is 1.1 Kcals./mole more positive than the N.B.S. 'selected' value ($-96.800$ Kcals./mole [21]). The standard heat of formation of tris(acetylacetonato)iron III at 25° was calculated from the relationship:

$$\Delta H_f^o(\text{complex}) = - \Delta H_{R3} - 3 \Delta H_f^o \text{HClO}_2\text{H}_2\text{O} - \Delta H_f^o \text{FeCl}_3 + 3 \Delta H_f^o \text{C}_5\text{H}_7\text{O}_2$$

(3.4.2)

$$\Delta H_f^o \text{Fe(C}_5\text{H}_7\text{O}_2)_3 = -313.20 \pm 0.67 \text{ Kcals./mole.}$$

3.5. **Solution thermochemistry of tris(acetylacetonato)manganese III**

Crystalline tris(acetylacetonato)manganese III is instantaneously decomposed by 4.36 m. hydrochloric acid solution, but the intervening manganic ion immediately disproportionates.
to MnIV and MnII, the 'solvent' being oxidised to chlorine gas.

\[
2\text{Mn}^{3+} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + \text{Mn}^{2+}
\]

\[
\text{MnO}_2 + 4\text{H}^+ + 2\text{Cl}^- = \text{Mn}^{2+} + 2\text{H}_2\text{O} + \text{Cl}_2.
\]

To avoid gas liberation in the calorimeter and concurrent variation of solvent composition, an internal redox system \((\text{Fe}^{2+} - e \rightarrow \text{Fe}^{3+})\) was incorporated in solution; the redox potentials [69] :-

\[
2\text{Cl}^- - 2e = \text{Cl}_2 : -1.358\text{v} \quad \text{and} \quad \text{Fe}^{2+} - e = \text{Fe}^{3+} : 0.700\text{v}
\]
are such that ferrous ion is oxidised preferentially by the liberated manganic ion. The thermochemical cycle is given in Scheme 3.5.A).

**Scheme 3.5.A**

\[
\Delta H_{\text{R4}} = \Delta H_{15} + 3\Delta H_{16} + \Delta H_{18} - \Delta H_{19} - \Delta H_{20} - 3\Delta H_{21} + \Delta H_{\text{R4}}, \quad (3.5.1)
\]
The concentration of reagents employed was:

\[ \begin{align*}
\text{Mn} & : 9.4 \text{ m.moles per 1936.2 g. solvent} \\
\text{Fe} & : 10.3 \text{ m.moles per 1936.2 g. solvent (10\% mole excess)} \\
\text{C}_5\text{H}_8\text{O}_2 & : 28.2 \text{ m.moles per 1936.2 g. solvent}
\end{align*} \]

Coughlin [82] has determined the heat of solution of pure crystalline ferrous chloride in 4.360 m. hydrochloric acid solution at 30° (conc. Fe : 0.03 g. moles per 1936.2 g. solvent).

\[ \text{FeCl}_2(c) = \text{Fe}^{2+}_{(\text{solv.})} + 2\text{Cl}^-(\text{solv.}) \cdot \Delta H_{18}^0 = -15.000 \pm 0.020 \text{Kcals./mole} \]

Correcting \( \Delta H_{18}^0 \) to 25° using heat capacity data of Kelly [83] and Rossini [84], \( \Delta H_{18}^{25} = -15.080 \pm 0.020 \text{ Kcals./mole} \).

Assuming that the concentration effect may be neglected, \( \Delta H_{18} \) (Scheme 3.5A) is equal to \( \Delta H_{18}^{25} \) and \( \Delta H_{20} = \Delta H_{13}^{25} = -24.560 \pm 0.020 \text{ Kcals./mole} \) (3.4). Also \( \Delta H_{21} = \Delta H_{14} = -0.361 \pm 0.005 \text{ Kcals./mole} \) (3.4) and \( \Delta H_{16} = \Delta H_{11} = +1.06 \pm 0.07 \text{ Kcals./mole} \) (3.4). \( \Delta H_{15} \) and \( \Delta H_{19} \) were measured experimentally.

Pure crystalline tris(acetylacetonato)manganese III (0.517 m.moles, 182 mg.) was 'dissolved' in 4.340 m. hydrochloric acid (100.13 ml.), containing 10% mole excess ferrous ion (0.569 m.moles, 31.8 mg.) plus the stoichiometric weight of water (2.068 m.moles : 37.3 mg.) added from a calibrated
microsyringe. The heat of reaction $\Delta H_{15}$ was measured (exo-
thermic). To complete the thermochemical cycle, pure crystall-
ine manganese chloride tetrahydrate (0.517 m.moles, 102.3 mg.)
was added to 4.340 m. hydrochloric acid solution (100.13 ml.),
containing 10% mole excess of ferrous ion (0.569 m.moles,
31.8 mg.) plus the stoichiometric weight of acetylacetone
(1.551 m.moles, 155.3 mg.) added to the calorimetric solution
from a calibrated microsyringe. The corresponding heat of
reaction $\Delta H_{19}$ was measured (endothermic).

Reagents. Preparation and analysis of the solvent has been
given previously (3.4). The mean molality, derived from two
determinations, was 4.340, i.e. 158.35 g. pure HCl per 1000 g,
water: measured density 1.066 g.cm.$^{-3}$. The bulk solution was
divided into two volumes, 1005.2 ml. and 974.4 ml. and stored
under nitrogen.

'Ferrous chloride solution'. Pure iron wire (5.73 m.moles,
319.86 mg.) was dissolved in 4.340 m. hydrochloric acid solution
(1005.2 ml.) under reflux (8 hours), hydrogen being passed con-
tinuously through the solution to displace air, which left the
system via a bunsen valve. The pale green solution was 'blown
over' into a storage vessel, previously flushed out with
hydrogen, and stored in the dark under a positive hydrogen
pressure. Prepared under these conditions, the concentration of ferric iron in the solution was in the p.p.m. range (qualitative tests with potassium thiocyanate gave a pale orange tint). The ferrous ion content remained substantially constant over a period of seven days. [Mean concentration Fe$^{2+}$ ion per 100.13 ml. solution = 0.569 m.moles, 31.8 mg.].

'Ferric chloride solution'. Pure iron wire (5.55 m.moles, 309.82 mg.) was dissolved in 4.340 m. hydrochloric acid solution (974.4 ml.) under reflux (8 hours), hydrogen being passed continuously through the mixture. 90% of the ferrous ion content was quantitatively oxidised to ferric ion by hydrogen peroxide solution (H$_2$O$_2$, 12.58 H$_2$O) (2.50 m.moles, 116.7 mg.), prepared by diluting the '100 vol.' reagent (314.20 mg.) with water (337.65 mg.). The bulk solution was stored under nitrogen. [Mean concentration Fe$^{2+}$ ion per 100.13 ml. solution, 0.570 m.moles, 31.8 mg.].

The ferrous ion content of solutions $S'_4$ and $S''_4$ was determined after each calorimetric 'run' by direct titration with standardised potassium dichromate solution (0.86 m.moles/litre), in the presence of phosphate ion and using 10% sodium diphenylamine sulphonate as indicator.
Manganese chloride tetrahydrate. The 'analAr' reagent was analysed for manganese potentiometrically [89] by titrating manganese chloride solution (0.06M) (25 ml.) at pH 6 - 7 with standardised potassium permanganate solution (0.0200M) in the presence of excess pyrophosphate ion.

$$4\text{Mn}^{2+} + \text{MnO}_4^- + 8\text{H}^+ + 15\text{H}_2\text{P}_2\text{O}_7^{2-} = 5\text{Mn(H}_2\text{P}_2\text{O}_7)^3^- + 4\text{H}_2\text{O}.$$ 

The mean end-point derived from three determinations was 18.77 ml. 0.02M KMnO$_4$, corresponding to 27.75%. Mn (theoretical, 27.76%). Derived molecular formula : MnCl$_2$.4.00 H$_2$O.

Tris(acetylacetonato)manganese III was prepared by the method of Debierne and Urbain [86]; the black crystalline complex was recrystallised twice from benzene, reprecipitation being effected by adding ligroin (b.p. 100°-120°). The complex was analysed gravimetrically for manganese by decomposing with excess concentrated sulphuric acid followed by addition of diammonium hydrogen phosphate solution to precipitate MnNH$_4$PO$_4$.H$_2$O which was ignited to the pyrophosphate Mn$_2$P$_2$O$_7$ [89].

Theoretical Mn : 13.16%  Experimental : 13.09, 13.07%.
Determination of $\Delta H_{15}^{25}$

### TABLE 3.5a

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>$k$</th>
<th>$R_i$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log \frac{R_i}{R_f} \cdot 10^4$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (secs.)</th>
<th>$\epsilon'$ (mean)</th>
<th>$\epsilon'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV (1)</td>
<td>0.24072</td>
<td>2174.2750</td>
<td>2169.7675</td>
<td>9.003</td>
<td>0.40882</td>
<td>180.10</td>
<td>804.9</td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>R$^H = 100.674$ (ohms)</td>
<td>2174.3850</td>
<td>2169.8850</td>
<td>8.998</td>
<td>0.40871</td>
<td>180.16</td>
<td>8051</td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>R$^s = 9.9979$ (ohms)</td>
<td>2174.3400</td>
<td>2169.8400</td>
<td>8.998</td>
<td>0.40887</td>
<td>180.12</td>
<td>8056</td>
<td>8051$\pm3$</td>
</tr>
<tr>
<td>(4)</td>
<td>i=4.0mA</td>
<td>2174.2625</td>
<td>2169.7600</td>
<td>9.003</td>
<td>0.40888</td>
<td>180.10</td>
<td>8050</td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td></td>
<td>2174.2825</td>
<td>2169.7800</td>
<td>9.003</td>
<td>0.40884</td>
<td>180.08</td>
<td>8048</td>
<td></td>
</tr>
</tbody>
</table>

m.wt. Mn(C$_5$H$_7$O$_2$)$_3 = 352.265$: Density = 1.3 g.cm.$^{-3}$: $K = +0.74$.

### Run No. Complex Complex $R_i'$ (mg.) $R_f'$ (ohms) $\log \frac{R_i'}{R_f'} \cdot 10^4$ $\epsilon'$ Heat change $Q_{15}$ (cals.) %Fe$^{2+}$ solution $S_4'$ $\Delta H_{15}$ (Kcals./mole)
<table>
<thead>
<tr>
<th>No.</th>
<th>(mg.)</th>
<th>(m.moles)</th>
<th>(ohms)</th>
<th>(ohms)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>181.45</td>
<td>0.51510</td>
<td>2174.2800</td>
<td>2170.6700</td>
<td>7.217</td>
<td>804.9</td>
<td>5.80</td>
<td>9.2</td>
<td>-11.277</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2)</td>
<td>182.72</td>
<td>0.51870</td>
<td>2174.1200</td>
<td>2170.5350</td>
<td>7.167</td>
<td>8051</td>
<td>5.77</td>
<td>8.9</td>
<td>-11.124</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(3)</td>
<td>181.19</td>
<td>0.51436</td>
<td>2174.3000</td>
<td>2170.7075</td>
<td>7.182</td>
<td>8056</td>
<td>5.79</td>
<td>9.2</td>
<td>-11.249</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4)</td>
<td>181.95</td>
<td>0.51646</td>
<td>2174.3175</td>
<td>2170.7250</td>
<td>7.182</td>
<td>8056</td>
<td>5.78</td>
<td>9.0</td>
<td>-11.194</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(5)</td>
<td>183.27</td>
<td>0.52026</td>
<td>2174.2000</td>
<td>2170.6200</td>
<td>7.157</td>
<td>804.8</td>
<td>5.76</td>
<td>8.8</td>
<td>-11.071</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta H_{15} = -11.183 \pm 0.077 \text{ Kcals./mole for the reaction:} \]

\[ \text{Mn(C}_5\text{H}_7\text{O}_2\text{)}_3(\text{solv.}) + 3\text{H}^+ (\text{solv.}) + \text{Fe}^{2+} (\text{solv.}) = \text{Mn}^{2+} (\text{solv.}) + \text{Fe}^{3+} (\text{solv.}) + 3\text{C}_5\text{H}_8\text{O}_2 (\text{solv.}) \]
Determination of $\Delta H^{25}_{\text{19}}$

**TABLE 3.5b**

<table>
<thead>
<tr>
<th>Calr. ref.no. and run no.</th>
<th>$k$</th>
<th>$R_1$ (ohms)</th>
<th>$R_f$ (ohms)</th>
<th>$\log R_1/R_f$</th>
<th>Mean $E_s$ (volts)</th>
<th>$t_h$ (sec.)</th>
<th>$E'$ (mean)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>1</td>
<td>0.23769</td>
<td>1713.7150</td>
<td>1713.1300</td>
<td>1.483</td>
<td>0.20110</td>
<td>90.15</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>99.406</td>
<td>1712.3350</td>
<td>1711.7100</td>
<td>1.586</td>
<td>0.20796</td>
<td>90.26</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9.9978</td>
<td>1712.9925</td>
<td>1712.5400</td>
<td>1.403</td>
<td>0.19537</td>
<td>90.19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>i=20mA</td>
<td>1712.7750</td>
<td>1711.1900</td>
<td>1.485</td>
<td>0.20110</td>
<td>90.20</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td></td>
<td>1712.9250</td>
<td>1712.3000</td>
<td>1.585</td>
<td>0.20799</td>
<td>90.05</td>
</tr>
</tbody>
</table>

$m$-wt. MnCl$_2$·4.00H$_2$O = 197.904; Density = 2.01 [69]; $K = +0.45$.

<table>
<thead>
<tr>
<th>Run no.</th>
<th>C$_5$H$_8$O$_2$ in soln. (mg.)</th>
<th>C$_5$H$_8$O$_2$ in soln. (m.moles)</th>
<th>MnCl$_2$ $4H_2$O in soln. (m.moles)</th>
<th>MnCl$_2$ $4H_2$O (ohms)</th>
<th>$R'_1$ (ohms)</th>
<th>$R'_f$ (ohms)</th>
<th>$\log R'_1/R'_f$</th>
<th>$E'$</th>
<th>Heat change $Q_{19}$ (cals.)</th>
<th>$\Delta H_{19}$ Kcals/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>153.5</td>
<td>1.533</td>
<td>101.15</td>
<td>0.51111</td>
<td>1713.8000</td>
<td>1713.0200</td>
<td>1.976</td>
<td>5843</td>
<td>1.15</td>
<td>+2.299</td>
</tr>
<tr>
<td>(2)</td>
<td>155.5</td>
<td>1.553</td>
<td>102.40</td>
<td>0.51743</td>
<td>1713.4850</td>
<td>1712.6950</td>
<td>2.002</td>
<td>5850</td>
<td>1.17</td>
<td>+2.263</td>
</tr>
<tr>
<td>(3)</td>
<td>154.2</td>
<td>1.540</td>
<td>101.61</td>
<td>0.51343</td>
<td>1713.7800</td>
<td>1713.0000</td>
<td>1.976</td>
<td>5836</td>
<td>1.15</td>
<td>+2.246</td>
</tr>
<tr>
<td>(4)</td>
<td>155.1</td>
<td>1.549</td>
<td>102.17</td>
<td>0.51626</td>
<td>1712.9250</td>
<td>1712.1400</td>
<td>1.991</td>
<td>5838</td>
<td>1.16</td>
<td>+2.251</td>
</tr>
<tr>
<td>(5)</td>
<td>156.2</td>
<td>1.560</td>
<td>102.90</td>
<td>0.51994</td>
<td>1714.0500</td>
<td>1713.2600</td>
<td>2.002</td>
<td>5842</td>
<td>1.17</td>
<td>+2.249</td>
</tr>
</tbody>
</table>

$\Delta H_{19} = +2.254 ± 0.005$ Kcals/mole for the reaction:

$$\text{MnCl}_2\cdot 4\text{H}_2\text{O} = \text{Mn}^{2+} \text{(solv.)} + 2\text{Cl}^- \text{(solv.)} + 4\text{H}_2\text{O} \text{(solv.)}.$$
The systems $S'_4$ and $S''_4$ were not thermodynamically equivalent due to a small, significant difference in the concentration of ferrous ion ($\delta c$) and thus $\Delta H_{R4}^\prime$ was finite.

$$\Delta H_{R4}^\prime = \delta c \cdot \Delta H_{ox}^{25} \text{ Kcals./unit reaction (3.5.2)}$$

where $\delta c = [\text{Fe}^{2+}]_{S''_4} - [\text{Fe}^{2+}]_{S'_4}$ (3.5.3)

$\Delta H_{ox}^{25}$ is the heat of oxidation of ferrous ion at 25° in 4.340 m. hydrochloric acid solution and was evaluated from the thermochemical cycle (3.5.B).

**Scheme 3.5.B**

\[
\begin{align*}
\text{FeCl}_2(c) + \frac{1}{2}\text{Cl}_2(g) & \underset{\Delta H_k}{\longrightarrow} \text{FeCl}_3(c) \\
\Delta H_{18'}^{25} & \\
\text{Fe}^{2+} \text{(solv.)} + 2\text{Cl}^- \text{(solv.)} + \text{Cl}^- \text{(solv.)} & \underset{\Delta H_{ox}^{25}}{\longrightarrow} \text{Fe}^{3+} \text{(solv.)} + 3\text{Cl}^- \text{(solv.)} \\
\Delta H_{ox}^{25} & = \Delta H_{13'}^{25} + \Delta H_k - \Delta H_g - \Delta H_{18'}^{25} \quad (3.5.4)
\end{align*}
\]

$\Delta H_k = -13.84 \text{ Kcals./mole [82]}$; $\Delta H_g = -40.023 \text{ Kcals./mole [21]}$.

$\therefore \Delta H_{ox}^{25} = +16.70 \text{ Kcals./g.ion.}$
TABLE 3.5c

<table>
<thead>
<tr>
<th>Run no.</th>
<th>%Fe(^{2+}) ion solution (S'_4)</th>
<th>%Fe(^{2+}) ion solution (S''_4)</th>
<th>(\delta N \times 10^{-7}) g. ions</th>
<th>(\Delta H_{R4}' \times 10^3) Cals/unit R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>9.2</td>
<td>9.1</td>
<td>-5.7</td>
<td>+9.5</td>
</tr>
<tr>
<td>(2)</td>
<td>8.9</td>
<td>9.1</td>
<td>+11.4</td>
<td>-19.0</td>
</tr>
<tr>
<td>(3)</td>
<td>9.2</td>
<td>9.1</td>
<td>-5.7</td>
<td>+9.5</td>
</tr>
<tr>
<td>(4)</td>
<td>9.0</td>
<td>9.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(5)</td>
<td>8.8</td>
<td>9.0</td>
<td>+11.4</td>
<td>-19.0</td>
</tr>
</tbody>
</table>

Each absolute value of \(\Delta H_{R4}'\) is negligible compared with all other enthalpy terms in (3.5.1) and thus, to a first approximation, \(\Delta H_{R4}'\) is independent of \(\Delta H_{R4}\).

Substituting for \(\Delta H_{15}'\), \(\Delta H_{16}'\), \(\Delta H_{18}'\), \(\Delta H_{19}'\), \(\Delta H_{20}'\) and \(\Delta H_{21}'\) in (3.5.1): \(\Delta H_{R4}' = +0.31 \pm 0.15\) Kcals./mole complex.

Coughlin [82] determined the standard heat of formation of ferrous chloride as \(-81.860 \pm 0.120\) Kcals./mole at 25°. This value is 360 cals./mole more negative than the N.B.S. 'selected' value, \(-81.500\) Kcals./mole [21], but agrees with the value \(-81.900\) Kcals./mole selected by Humphrey, Kelly and King [90]
in connection with thermochemical measurements of ferrous oxide. The N.B.S. 'selected' value for the standard heat of formation of manganous chloride tetrahydrate at 25° is 

\[ 407.0 \pm 0.2 \text{ Kcals./mole} \]  

[21]. The standard heat of formation at 25° of tris(acetylacetonato)manganese III was calculated from the relationship:

\[
\Delta H_f^\circ(\text{complex}) = - \Delta H_{\text{R4}} - 3 \Delta H_f^\circ\text{MnCl}_2\text{Cl}_2 - \Delta H_f^\circ\text{FeCl}_2 - 4 \Delta H_f^\circ\text{H}_2\text{O} + \Delta H_f^\circ\text{MnCl}_2\text{Cl}_2\text{Cl}_2 + \Delta H_f^\circ\text{FeCl}_2 + 3 \Delta H_f^\circ\text{C}_5\text{H}_7\text{O}_2 \quad (3.5.5)
\]

\[
\Delta H_f^\circ\text{Mn(C}_5\text{H}_7\text{O}_2)_3 = -332.09 \pm 0.72 \text{ Kcals./mole.}
\]

**TABLE 3.5a**

**Summary**

<table>
<thead>
<tr>
<th>Metal Acetylacetonate</th>
<th>Standard Heat of formation at 25° Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(C₅H₇O₂)₃</td>
<td>-428.84 ± 0.66</td>
</tr>
<tr>
<td>Cr(C₅H₇O₂)₃</td>
<td>-366.48 ± 0.67</td>
</tr>
<tr>
<td>Mn(C₅H₇O₂)₃</td>
<td>-332.09 ± 0.72</td>
</tr>
<tr>
<td>Fe(C₅H₇O₂)₃</td>
<td>-313.20 ± 0.67</td>
</tr>
</tbody>
</table>
SECTION 4

DISCUSSION
4.1. **Heat of combustion data for trivalent metal acetylacetonates.**

Kawasaki, Okawara and Tanaka [91] measured the heat of combustion at 25° of tris(acetylacetonato)aluminium III, \((\Delta H_{c.1} = -1910 \text{ Kcals./mole})\). From the equation:

\[
\text{Al(C}_5\text{H}_7\text{O}_2)_3(c) + 18\text{O}_2(g) = \frac{1}{2}\text{Al}_2\text{O}_3(c) + 15\text{CO}_2(g) + 21/2\text{H}_2\text{O}(g)
\]

\(\Delta H_{c.1}\)

and taking the N.B.S. 'selected' values [21] for the standard heat of formation of carbon dioxide, water and \(\alpha\) alumina, \((-94.052 \pm 0.01, -68.314 \pm 0.01\) and \(-399.09 \pm 0.01\) Kcals./mole respectively), the standard heat of formation of the complex was calculated to be \(-417.6\) Kcals./mole. A large uncertainty interval is associated with the latter as it was assumed that the solid combustion product was pure \(\alpha\) alumina and that combustion of the complex was complete under the conditions imposed.

The heats of combustion of the trivalent first row transition metal acetylacetonates (ScIII to CoIII) have been measured in a Parr adiabatic calibrated oxygen bomb calorimeter to a low degree of accuracy by Jones and Wood [8]; their results are given in Table 4.1a. The calculated standard heats of formation are also tabulated.
The oxide residues were subject to X-ray crystallographic analysis and were characterised as: Sc₂O₃, V₂O₅, Cr₂O₃, MnO, MnO₂, Fe₂O₃, Fe₃O₄, H₂O and CoO, Co₃O₄ respectively; the appropriate heat of formation of the 'oxide' was calculated. The derived standard heats of formation of the Cr III, Mn III and Fe III complexes agree favourably with the values given in Table 3.5d if an allowance is made for the large uncertainty interval associated with the combustion data.
4.2. **Thermochemical properties of Acetylacetone.**

Acetylacetone exhibits tautomerism; the molecular proportions of the open chain, keto form I and the intramolecularly, hydrogen bonded, acidic enol form II in the pure liquid and in the gas phase are 18.6%, 81.4% (k_1 = [enol]/[keto] = 4.4) [92], and 8.3%, 91.7% (k_2 = 11.0) [93] respectively.

Nicholson [94] has measured the heat of combustion of acetylacetone; \( \Delta H_{c.2} = -642.20 \pm 0.36 \text{ Kcals./mole} \) at 25°.

\[
C_5H_8O_2(1) + 6O_2(g) = 5CO_2(g) + 4H_2O(1) \quad \Delta H_{c.2}
\]

The standard heat of formation \( \Delta H_{f.1} \) of the liquid tautomeric mixture at 25° was calculated as \(-101.32 \pm 0.36 \text{ Kcals./mole}\).

The heat of formation of the gaseous enol isomer, \( \Delta H_{f.1} \) at 25° was derived directly from the thermochemical cycle given in Scheme 4.2.A.
ΔH

is the heat of vaporisation of liquid acetylacetone at 25°,
ΔH

e', is the 'effective' heat of enolisation at 25° (1.8).

The most accurate evaluation of ΔH

appears to be that of Farrer and Jones [18], ΔH

= +6.5 ± 0.2 Kcals./mole which includes the energy change for the tautomeric shift.

Bernstein and Powling [95] derived the heat of enolisation ΔH

at 25° of acetylacetone in various non-polar solvents (decalin, tetrachloroethylene and bromoform) and also in the gas phase by an infrared analytical method. The empirical gas phase value, -2.4 ± 0.2 Kcals./mole, was also evaluated independently by extrapolation (to P = 0) of the linear plot of

ΔH

ev versus the solvent property P (P = \( \frac{e - 1}{2e + 1} \)), M is the
molecular weight, \( \rho \) the density and \( \varepsilon \) the dielectric constant of the solvent.

\[ \Delta H_e', \] (Scheme 4.2.A) is the enthalpy change for the gaseous reaction:

\[
C_5H_8O_2(g) = C_5H_8O_2(g) \quad \Delta H_e',
\]

\[ k_2 = 11.0 \quad k_3 = +\infty \]

\[ \therefore \Delta H_e' = 0.083 \Delta H_e = -0.20 \pm 0.01 \text{ Kcals.} \]

From (4.2.1)

\[
\Delta H_{f,e} = -95.02 \pm 0.42 \text{ Kcals./mole}
\]

\[
\Delta H_{f,k} = -92.62 \pm 0.46 \text{ Kcals./mole}
\]

(gaseous keto)

Bond dissociation energies, \( D(RO-H) \) for the six aliphatic alcohols \( C_1 \) to \( C_4 \) are all within the range 100 to 106 Kcals. [96], the corresponding value for acetic acid is 110 Kcals.[96] and for water, 110.6 Kcals. [96]. In the dissociation process, the \( O-H \) bond and the adjacent weak intermolecular hydrogen bond are fractured simultaneously and therefore the measured dissociation energy includes the energy of the hydrogen bond. Hydrogen bond energies generally fall within the range 2 to 10 Kcals., e.g. water, 5 Kcals., Methanol 6 Kcals. and acetic acid 7.6 Kcals. [1].

In the absence of empirical bond strength data for enolic
Acetylacetone, two bond energy terms for this molecule were estimated by close analogy to the corresponding parameters in structurally similar molecules; the hydrogen bond strength in the enol was assumed to be equal to that in acetic acid, 7.6 Kcals. and the one enolic O - H bond dissociation energy, D(C₅H₇O₂-H), was taken as 105 ± 5 Kcals. by comparison with the hydroxyl bond strength in the aliphatic alcohols. The heats of atomisation, ∆H_{Atom} at 25° of the keto and enol isomers were calculated from the thermochemical cycle given in Scheme 4.2.B.

\[ \begin{align*}
\text{Scheme 4.2.B} \\
5\text{C(g)} + 4\text{H}_2(g) + \text{O}_2(g) & \xrightarrow[\Delta H_{\text{Sub}}]{\Delta H_0^0} \text{C}_5\text{H}_8\text{O}_2(1) \\
5\text{C(g)} + 8\text{H}(g) + 2\text{O}(g) & \xleftarrow[\Delta H_{\text{Atom}}]{\Delta H_0^0} \text{C}_5\text{H}_8\text{O}_2(g) \\
k_1 = 4.4 \\
k_3 = +\infty
\end{align*} \]

\[ \Delta H_{\text{Atom}} = 4\Delta D(\text{H-H}) + \Delta D(\text{O-O}) + 5\Delta H_{\text{Sub}} - \Delta H_0^0 - \Delta H_v^- - \Delta H_e^- \quad (4.2.2) \]

\[ \Delta H_{\text{Sub}} = +171.7 \text{Kcals./g.} \text{atom} \quad \Delta D(\text{H-H}) = 104.2 \text{Kcals.} \quad \Delta D(\text{O-O}) = 118.4 \text{Kcals.} \quad [21] \]

\[ \Delta H_{\text{Atom}}(\text{enol}) = 14.89 \text{Kcals./mole} \quad \Delta H_{\text{Atom}}(\text{keto}) = 14.86 \text{Kcals./mole} \]
The heat of atomisation is equal to the sum of the individual average bond energy terms and the associated resonance energy R:

\[ \Delta H_{\text{Atom}} = \sum_{i=1}^{i=n} E_i + R \]  

(Eq. 4.2.3)

\( E_i \) is the bond energy of the \( i \)th bond and \( n \) is the total number of chemical bonds in the molecule.

The required average bond energy parameters were taken from Pauling's most recent compilation [1]: (C-H: 98.8, C-C: 83.1, C=C: 147.0, C-O: 84.0 and C=O: 174.0 Kcals. respectively) and the approximate resonance energy for each isomer was calculated.

\[ \sum_{i=1}^{i=14} E_i \text{ (keto)} = 1471 \text{ Kcals.}; \quad R(\text{keto}) = 16 \text{ Kcals./mole.} \]

\[ \sum_{i=1}^{i=15} E_i \text{ (enol)} = 1459 \text{ Kcals.}; \quad R(\text{enol}) = 27 \text{ Kcals./mole.} \]

The keto and enol isomers have approximately equal intrinsic energy; the higher resonance energy of the enol is a direct consequence of internal chelation, which promotes delocalisation of \( \pi \) electrons in the pseudo six-membered ring system.
4.3. **The gas phase replacement reaction**

The enthalpy change $\Delta H_{r,g}$ at 25° for the gas phase replacement reaction:

$$M(g) + 3C_5H_8O_2(g) = M(C_5H_7O_2)_3(g) + \frac{3}{2}H_2(g) \quad \Delta H_{r,g}$$

$k_3 = + \infty$

$(M = Al, Cr, Fe, Mn)$ was calculated respectively from the empirical thermochemical cycles given in Schemes 4.3.A, 4.3.B, 4.3.C and 4.3.D.

**Scheme 4.3.A**

\[
\begin{align*}
\text{Al}(g) + 3C_5H_8O_2(g) & \xrightarrow{\Delta H_{r,g,l}} \text{Al}(C_5H_7O_2)_3(g) + \frac{3}{2}H_2(g) \\
\text{Al}(c) & \xrightarrow{\Delta H_{1.1}} \text{AlCl}_3(c) \\
\text{AlCl}_3(c) & \xrightarrow{\Delta H_{3.1}} \text{AlCl}_3(6H_2O(c) + 3C_5H_6O_2(l) + 3H_2O(aq) \quad k_1 = 4.4} \\
- \Delta H_{r,g,l} &= - \Delta H_{R.1} + \Delta H_{1.1} + \Delta H_{3.1} + 3 \Delta H_e' + 3 \Delta H_v + \Delta H_{4.1} \\
&\quad + \Delta H_{2.1} + 3 \Delta H_{f.h} + 3 \Delta H_{f.h.s} \quad (4.3.1)
\end{align*}
\]
Scheme 4.3.B

\[
\begin{align*}
\text{Cr(C}_5\text{H}_7\text{O}_2)\text{Cl}_3(g) + 3\text{H}_2(g) & \xrightarrow{\Delta H_{r.g.2}} \text{Cr}(g) + 3\text{C}_5\text{H}_8\text{O}_2(g) \\
3\Delta H_{f.h} & \\
\text{CrCl}_3(c) & \\
3\Delta H_{f.h.s} & \\
\text{Cr(C}_5\text{H}_7\text{O}_2)\text{Cl}_3(c) + 3\text{HCl} & \xrightarrow{\Delta H_{r.g.2}} \text{Cr}(c) + 3\text{C}_5\text{H}_8\text{O}_2(c) + 3\text{H}_2\text{O}(l)
\end{align*}
\]

- \( \Delta H_{r.g.2} = \Delta H_{r.2} + \Delta H_{1.2} + \Delta H_{2.2} + \Delta H_{3.2} + 3\Delta H_{e.1} + 3\Delta H_{v} + 3\Delta H_{f.h} + 3\Delta H_{f.h.s} \) (4.3.2)
Scheme 4.3.C

\[
\begin{align*}
\text{Fe(C}_5\text{H}_7\text{O}_2)^3\text{(g)} + \frac{3}{2} \text{H}_2\text{(g)} & \xrightarrow{\Delta H_{r.g.3}} \text{Fe}\text{(g)} + 3\text{C}_5\text{H}_8\text{O}_2\text{(g)} \\
\Delta H_{4.3} & \downarrow \Delta H_{f.h} \downarrow \Delta H_{1.3} \downarrow \Delta H_{2.3} \\
\text{Fe(C}_5\text{H}_7\text{O}_2)^3\text{(c)} + 3\text{HCl} & \xrightarrow{\Delta H_{r.g.3}} 3\text{H}_2\text{O}\text{(aq)} + \text{FeCl}_3\text{(c)} + 3\text{C}_5\text{H}_8\text{O}_2\text{(g)} \\
\kappa_2 &= 11.0 \\
\kappa_1 &= 4.4
\end{align*}
\]

\[ - \Delta H_{r.g.3} = \Delta H_{r.3} + \Delta H_{1.3} + \Delta H_{2.3} + 3 \Delta H_{e.1} + 3 \Delta H_{v.1} + \Delta H_{4.3} + 3 \Delta H_{f.h} + 3 \Delta H_{f.h.s} \quad (4.3.3) \]
Scheme 4.3.4

\[
\begin{align*}
\text{Mn(C}_5\text{H}_7\text{O}_2)_3(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) & \quad \xrightarrow{\Delta H_{R.4.4}} \quad \text{Mn(g)} + 3\text{C}_5\text{H}_8\text{O}_2(\text{g}) \\
3\Delta H_{f.h} & \quad \xrightarrow{3\Delta H_e} \quad 3\Delta H_v \\
3\text{HCl}(\text{g}) & \quad \xrightarrow{3\Delta H_{f.h.s}} \quad \text{FeCl}_2(\text{c}) \\
\Delta H_{f.h} & \quad \xrightarrow{\Delta H_{5.4}} \quad \text{FeCl}_3(\text{c}) + \text{MnCl}_2 \quad \xrightarrow{\Delta H_{R.4}} \quad \Delta H_{R.4} \\
\text{Mn(C}_5\text{H}_7\text{O}_2)_3(\text{c}) + 3\text{HCl\text{H}_2O}(\text{aq}) + \text{FeCl}_2(\text{c}) & \quad \xrightarrow{+\infty\text{H}_2O(\text{aq})} \quad \text{FeCl}_3(\text{c}) + \text{MnCl}_2 \quad \xrightarrow{\Delta H_{4.4} + 3\text{C}_5\text{H}_8\text{O}_2(\text{g})} \\
\end{align*}
\]

\[
\begin{align*}
- \Delta H_{R.4.4} & = \Delta H_{R.4} + \Delta H_{1.4} + \Delta H_{2.4} + \Delta H_{3.4} + 3 \Delta H_e + \\
3 \Delta H_v + \Delta H_{4.4} + \Delta H_{5.4} + \Delta H_{2.3} + 3 \Delta H_{f.h} + 3 \Delta H_{f.h.s}. \\
\quad (4.3.4)
\end{align*}
\]
TABLE 4.3a

<table>
<thead>
<tr>
<th>( \Delta H^\ddagger ) ± 2s R Kcals./mole</th>
<th>Ref.</th>
<th>( \Delta H^\ddagger ) ± 2s R Kcals./mole</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_{R.1} ) = -11.04 ± 0.07</td>
<td>(3.2)</td>
<td>( \Delta H_{1.1} ) = +77.5 ± 0.2</td>
<td>[97]</td>
</tr>
<tr>
<td>( \Delta H_{2.1} ) = +168.570 ± 0.200</td>
<td>[75]</td>
<td>( \Delta H_{2.1} ) = +65.130±0.080</td>
<td>[75]</td>
</tr>
<tr>
<td>( \Delta H_{e.1} ) = -0.20 ± 0.01</td>
<td>(4.2)</td>
<td>( \Delta H_{v} ) = +6.5 ± 0.2</td>
<td>[18]</td>
</tr>
<tr>
<td>( \Delta H_{4.1} ) = -4.58 ± 0.50</td>
<td>[98]</td>
<td>( \Delta H_{f.h} ) = -22.06 ± 0.05</td>
<td>[21]</td>
</tr>
<tr>
<td>( \Delta H_{f.h.2} ) = -17.90 ± 0.07</td>
<td>[21]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta H_{R.2} ) = +11.06 ± 0.08</td>
<td>(3.3)</td>
<td>( \Delta H_{1.2} ) = +95.0 ± 0.2</td>
<td>[97]</td>
</tr>
<tr>
<td>( \Delta H_{2.2} ) = +134.6 ± 0.50</td>
<td>[21]</td>
<td>( \Delta H_{3.2} ) = +36.02 ± 0.54</td>
<td>[21]</td>
</tr>
<tr>
<td>( \Delta H_{4.2} ) = -6.64 ± 0.7</td>
<td>[8]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta H_{R.3} ) = +33.30 ± 0.12</td>
<td>(3.4)</td>
<td>( \Delta H_{1.3} ) = +99.8 ± 0.2</td>
<td>[97]</td>
</tr>
<tr>
<td>( \Delta H_{2.3} ) = +95.700 ± 0.200</td>
<td>[82]</td>
<td>( \Delta H_{4.3} ) = -15.6 ± 0.4</td>
<td>[8]</td>
</tr>
<tr>
<td>( \Delta H_{R.4} ) = +0.31 ± 0.15</td>
<td>(3.5)</td>
<td>( \Delta H_{1.4} ) = +66.7 ± 0.2</td>
<td>[97]</td>
</tr>
<tr>
<td>( \Delta H_{2.4} ) = +115.190 ± 0.120</td>
<td>[82]</td>
<td>( \Delta H_{3.4} ) = +18.55 ± 0.24</td>
<td>[82]</td>
</tr>
<tr>
<td>( \Delta H_{4.4} ) = -18.6 ± 0.2</td>
<td>[8]</td>
<td>( \Delta H_{5.4} ) = -81.860±0.120</td>
<td>[82]</td>
</tr>
</tbody>
</table>

The \( \Delta H_{R.g} \) values, together with the heat of formation of the gaseous complex \( \Delta H_{f.g} \) and the corresponding heat of atomisation are listed in Table 4.3a. The heat of atomisation is the enthalpy change of the process:

\[
M(C_5H_7O_2)_3(g) = M(g) + 15C(g) + 21H(g) + 6O(g) \quad \Delta H_{\text{Atom}}
\]
The relatively large uncertainty interval associated with the $\Delta H_{r.g}$ term is a direct consequence of imprecise enthalpy data currently available for the individual reactions from which the corresponding thermochemical cycle is composed.

### TABLE 4.3b

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta H_{r.g}^{\pm 2s}$ Kcals./mole complex</th>
<th>$\Delta H_{f,g}^{\pm 2s}$ Kcals./mole</th>
<th>$\Delta H_{\text{Atom}}$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al(C}_5\text{H}_7\text{O}_2)_3$</td>
<td>-216.7 $\pm$ 0.7</td>
<td>-424.3 $\pm$ 0.8</td>
<td>+4576</td>
</tr>
<tr>
<td>$\text{Cr(C}_5\text{H}_7\text{O}_2)_3$</td>
<td>-169.1 $\pm$ 1.1</td>
<td>-359.8 $\pm$ 1.0</td>
<td>+4529</td>
</tr>
<tr>
<td>$\text{Fe(C}_5\text{H}_7\text{O}_2)_3$</td>
<td>-112.2 $\pm$ 0.6</td>
<td>-297.6 $\pm$ 0.8</td>
<td>+4472</td>
</tr>
<tr>
<td>$\text{Mn(C}_5\text{H}_7\text{O}_2)_3$</td>
<td>-95.0 $\pm$ 0.6</td>
<td>-313.5 $\pm$ 0.8</td>
<td>+4455</td>
</tr>
</tbody>
</table>

$\Delta H_{r.g}/3$ is a measure of the energy required to replace the enolic hydrogen atom in the cyclic ligand molecule III by M/3 leading to structure IV.

\[
\text{CH}_3 - \text{CH} - \text{CH}_3
\]

(III)

\[
\text{CH}_3 - \text{CH} - \text{CH}_3
\]

(M/3)

(IV)
In such a replacement process, one O-H bond and the intramolecular hydrogen bond (Structure III) are fractured and simultaneously two equivalent metal-oxygen coordinate bonds are formed (Structure IV). The fraction $-\Delta H_{r,g}/3$ represents the energy difference between two metal-oxygen coordinate bonds in the complex and the sum of O-H bond strength and hydrogen bond strength in the ligand molecule. Hence the $\Delta H_{r,g}$ value is not a direct measure of the metal-oxygen coordinate bond energy, but as the formation of 1.5 moles of gaseous hydrogen is common to each replacement reaction, the $\Delta H_{r,g}$ values taken as a series reflect the relative metal-oxygen bond strengths in the complexes.

4.4. The metal-oxygen bond energy parameter

In order to derive the metal-oxygen homolytic bond energy parameter $E_{M0}^\alpha$ a prior calculation of the heat of the reaction

$$\text{M}(g) + 3 \text{C}_5\text{H}_7\text{O}_2(g) \xrightarrow{25^\circ} \text{M}(\text{C}_5\text{H}_7\text{O}_2)\text{3}(g)$$

is necessary.

$$\Delta H_{f,r} = \Delta H_{f,g} - 3 \Delta H_{f,R} - 3 \Delta H_{f,M} \quad (4.4.1)$$

$$\Delta H_{f,g} = \Delta H_f^0 + \Delta H_{s.c} \quad (4.4.2)$$
\[ \Delta H_{f,r} = \Delta H_f^0 + \Delta H_{s,c} - 3 \Delta H_{f,R} - 3 \Delta H_{f,M} \] (4.4.3)

\[ \Delta H_{f,g} \] is the heat of formation of the gaseous complex at 25°;

\[ \Delta H_{f,R} \] acetylacetonate radical at 25°;

\[ \Delta H_{f,M} \] gaseous metal atom at 25° (Table 4.3a);

\[ \Delta H_f^0 \] is the standard heat of formation of the complex at 25° (Table 3.5d);

\[ \Delta H_{s,c} \] heat of sublimation of the complex at 25° (Table 4.3a);

[Each component is assumed to be in the lowest, most stable energy state].

As the reorganisational energy for the ligand radical is neglected and since all six metal-oxygen coordinate bonds are equivalent (1.5) :-

\[ \Delta H_{f,r} = -6E_{MO} \] (4.4.4)

The acetylacetonate radical is resonance stabilised and may be represented unambiguously as :-
There is no heat of formation data currently available for this radical, which is formed upon the removal of the enolic hydrogen atom from the gaseous parent enol molecule.

\[ C_5H_8O_2(g) = C_5H_7O_2(g) + H(g) \quad D(C_5H_7O_2-H) \]

\[ D(C_5H_7O_2-H) = \Delta H_{f.R} + \Delta H_{f.H} - \Delta H_{f.e} \quad (4.4.5) \]

The heat of formation of the gaseous hydrogen atom \( \Delta H_{f.H} \) at 25° is 52.1 Kcals./g atom [21]. It is assumed that the dissociation process at 25° leads to the formation of the gaseous radical and hydrogen atom in their ground energy states. As the O-H bond dissociation energies of the comparable molecules fall within such a narrow range (10 Kcals.), the estimated value of \( D(C_5H_7O_2-H) \) as 105 ± 5 Kcals., given in (4.2), is justified. Any discrepancy between the estimated and 'true'
values is a constant applied equally to all subsequent calculations. Thus, the standard heat of formation of the acetylacetone radical \( \Delta H_{f,R} \) as derived from (4.4.5), is \(-42 \pm 5 \) Kcals/mole.

The \( \Delta H_{f,r} \) value, and hence \( E_{M_0}'' \), may also be calculated indirectly from the \( \Delta H_{r,g} \) value:

\[
M(g) + 3C_5H_8O_2(g) = M(C_5H_7O_2)^3(g) + 3/2H_2(g); \quad \Delta H_{r,g}
\]
\[
3\Delta H(g) + 3C_5H_7O_2(g) = 3C_5H_8O_2(g); \quad -3D(C_5H_7O_2-H)
\]
\[
3/2 H_2(g) = 3\Delta H(g) \quad ; \quad +3/2 D(H-H)
\]

Summation gives:

\[
M(g) + 3C_5H_7O_2(g) = M(C_5H_7O_2)^3(g); \quad \Delta H_{f,r}
\]

\[
\Delta H_{f,r} = \Delta H_{r,g} + 3/2 D(H-H) - 3D(C_5H_7O_2-H) \quad (4.4.6)
\]

The \( \Delta H_{f,r} \) values calculated from (4.4.3) and (4.4.6) are identical and are given in Table 4.4a together with the corresponding metal-oxygen homolytic bond energy, calculated from (4.4.4).
The uncertainty interval associated with the homolytic bond energy parameter is one sixth of that associated with $\Delta H_{\text{f.r.}}$. For comparison purposes, Table 4.4b lists the $\Delta H_{\text{r.g}}$ and $E_{\text{MO}}$ values at 25° for the first row, trivalent, transition metal acetylacetonate complexes, as derived from the corresponding heats of combustion, measured at 25° by Jones and Wood (Table 4.1a). The heat of formation of the gaseous complex and the corresponding heat of atomisation at 25° are also given.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta H_{\text{f.r.}} \pm 2\sigma$ Kcals./mole</th>
<th>$E''_{\text{MO}} \pm 2\sigma$ Kcals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(C₅H₇O₂)₃</td>
<td>-375.4 ± 8.7</td>
<td>63 ± 1.4</td>
</tr>
<tr>
<td>Cr(C₅H₇O₂)₃</td>
<td>-327.8 ± 8.7</td>
<td>55 ± 1.5</td>
</tr>
<tr>
<td>Fe(C₅H₇O₂)₃</td>
<td>-270.9 ± 8.7</td>
<td>45 ± 1.4</td>
</tr>
<tr>
<td>Mn(C₅H₇O₂)₃</td>
<td>-253.7 ± 8.7</td>
<td>42 ± 1.4</td>
</tr>
</tbody>
</table>
### TABLE 4.4b

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta H_{f,r}^\dagger$ Kcals./mole</th>
<th>$\Delta H_{r,g}^\dagger$ Kcals./mole</th>
<th>$\Delta H_{f,r}^\dagger$ Kcals./mole</th>
<th>$E'' +2s_{MO}$ Kcals.</th>
<th>$\Delta H_{Atom}^\dagger$ Kcals./mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(C$_5$H$_7$O$_2$)$_3$</td>
<td>-412.6$^{\pm}$3.6</td>
<td>-209.6$^{\pm}$3.8</td>
<td>-368.3$^{\pm}$9.4</td>
<td>61$^{\pm}$1.6</td>
<td>+4569</td>
</tr>
<tr>
<td>V(C$_5$H$_7$O$_2$)$_3$</td>
<td>-383.5$^{\pm}$7.3</td>
<td>-221.3$^{\pm}$7.4</td>
<td>-380.0$^{\pm}$11.4</td>
<td>63$^{\pm}$1.9</td>
<td>+4581</td>
</tr>
<tr>
<td>Cr(C$_5$H$_7$O$_2$)$_3$</td>
<td>-347.2$^{\pm}$3.5</td>
<td>-157.2$^{\pm}$3.6</td>
<td>-315.9$^{\pm}$9.2</td>
<td>53$^{\pm}$1.5</td>
<td>+4517</td>
</tr>
<tr>
<td>Mn(C$_5$H$_7$O$_2$)$_3$</td>
<td>-306.4$^{\pm}$2.8</td>
<td>-88.1$^{\pm}$2.9</td>
<td>-247.8$^{\pm}$9.1</td>
<td>41$^{\pm}$1.5</td>
<td>+4448</td>
</tr>
<tr>
<td>Fe(C$_5$H$_7$O$_2$)$_3$</td>
<td>-339.5$^{\pm}$3.5</td>
<td>-154.3$^{\pm}$3.6</td>
<td>-313.0$^{\pm}$9.2</td>
<td>52$^{\pm}$1.5</td>
<td>+4514</td>
</tr>
<tr>
<td>Co(C$_5$H$_7$O$_2$)$_3$</td>
<td>-308.2$^{\pm}$4.4</td>
<td>-124.8$^{\pm}$4.5</td>
<td>-283.5$^{\pm}$9.8</td>
<td>47$^{\pm}$1.6</td>
<td>+4484</td>
</tr>
</tbody>
</table>

Reasonable agreement is given between corresponding values in Tables 4.3b, 4.4a and 4.4b, except in the case of the iron complex.

The $\Delta H_{f,r}$ value and corresponding $E'' +2s_{MO}$ value is plotted versus the metal atomic number in Figure 4.4A.

The metal-oxygen heterolytic bond energy $E''_{MO}$ is related to the homolytic bond energy parameter by: c.f. (1.3.1)

$$6E''_{MO} = 6E''_{MO} + I_1 + I_2 + I_3 + 15/2 RT - 3E_L$$  \hspace{1cm} (4.4.7)

The electron affinity of the ligand $E_L$ is the energy change for the process:--
FIGURE (4.4.A)

\[ \Delta H_{f.r} \text{ Kcals./mole.} \]

- Ref. [8]
- Present work

ATOMIC NUMBER

21 Sc 22 Ti 23 V 24 Cr 25 Mn 26 Fe 27 Co

E'' Kcals.

HOMOLYTIC BOND ENERGY

250 300 350 400

- Present work

- Ref. [8]
and was estimated to be approximately equal to the electron affinity of the oxygen atom for one electron, i.e. 1.465eV = 33.8 Kcals. [99].

Also

\[ -6E_{\text{MO}} = \Delta H_{f.'i} \]  \( (4.4.8) \)

\( \Delta H_{f.'i} \) is the enthalpy change for the process at 25°:

\[ M^{3+}(g) + 3C_5H_7O_2(g) = M(C_5H_7O_2)_3(g) \Delta H_{f.'i} \]

[Each component is assumed to be in its lowest most stable energy state].

Table 4.4c lists the \( \Delta H_{f.'i} \) values and the corresponding heterolytic bond energy parameters for tris(acetylacetonato) aluminium III and for the first row, trivalent, transition metal acetylacetonates, calculated directly from (4.4.7). The sum of the first three ionisation potentials in each case was taken from Table 1.4c. The \( \Delta H_{f.'i} \) value is plotted versus the metal atomic number in Figure 4.4B.

\( \Delta H_{f.'i} \) contains the full crystal field stabilisation energy \( \delta H \) (1.4). All the complexes are of the high spin type [100] except tris(acetylacetonato)cobalt III which is of the low spin type. The empirical parameter \( \delta H \) was evaluated for each complex (except the cobalt complex) by substitution of
$\Delta H_{f,i}$, Kcals./mole.

ATOMIC NUMBER

$\Delta H'_{f,i}$

Ref. [8]

Present work

INTERPOLATION CURVE
the appropriate spectroscopic $\Delta$ value, as given by Carlin and Piper [101], into (1.4.1).

In order to derive the corresponding $\delta H$ value for the cobalt complex, prior calculation of the exchange or pairing energy $P$, required to spin pair two nonbonding $d$ electrons, is necessary. $P$ has been estimated at 42,000 cm.$^{-1}$ ≈ 120 Kcals. [102]. Hence the net energy increment $\delta H$ tending to stabilise the complex was calculated from (1.4.2).

The sixth column of Table 4.4c lists the $\Delta H_{f,i}$ values corrected for 'crystal field effects':

$$\Delta H'_{f,i} = \Delta H_{f,i} - \delta H$$ (4.4.9)

and the seventh column gives the corresponding $\delta H'$ value as derived from the displacement of the empirical $\Delta H_{f,i}$ value from the interpolation curve.
TABLE 4.4c

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta H_{f,i}$</th>
<th>$E'_{\text{MO}}$</th>
<th>$\Delta$</th>
<th>$\delta H$</th>
<th>$\Delta H'_{f,i}$</th>
<th>$\delta H'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Al}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1501*</td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Sc}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1290</td>
<td>215</td>
<td>0</td>
<td>0</td>
<td>-1290</td>
<td>0</td>
</tr>
<tr>
<td>$\text{V}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1450</td>
<td>242</td>
<td>52</td>
<td>42</td>
<td>-1408</td>
<td>102</td>
</tr>
<tr>
<td>$\text{Cr}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1480*</td>
<td>247</td>
<td>52</td>
<td>62</td>
<td>-1418</td>
<td>103</td>
</tr>
<tr>
<td>$\text{Mn}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1465*</td>
<td>244</td>
<td>49</td>
<td>29</td>
<td>-1436</td>
<td>59</td>
</tr>
<tr>
<td>$\text{Mn}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1458</td>
<td>243</td>
<td>49</td>
<td>29</td>
<td>-1429</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Fe}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1435*</td>
<td>239</td>
<td>47</td>
<td>0</td>
<td>-1435</td>
<td>0</td>
</tr>
<tr>
<td>$\text{Co}(C_5\text{H}_7\text{O}_2)_3$</td>
<td>-1533</td>
<td>256</td>
<td>60</td>
<td>24</td>
<td>-1509</td>
<td>69</td>
</tr>
</tbody>
</table>

[* Calculated from the corresponding $E'_{\text{MO}}$ value given in Table 4.4a].

$(\delta H' - \delta H)$ is an approximation to the covalent character of the metal-oxygen bond. Although the absolute metal-oxygen covalent bond strength cannot be calculated, it is apparent from Table 4.4c that the relative proportion of covalent character in the coordinate bond is in the order :-
\[ V - 0 > Cr - 0 > Mn - 0 > Fe - 0 < Co - 0 \]
i.e. the cobalt-oxygen bond is strongly covalent.

4.5. **General conclusions**

The first row trivalent transition metal acetylacetonates (Sc III to Fe III) are of the outer orbital, high spin type \[103\] and the metal-oxygen coordinate bond is predominantly ionic. In sharp contrast, the Co III complex is of the inner orbital, low spin type, and the metal-oxygen bond is predominantly covalent. It therefore transpires that within a selected transition series, and with metals assuming a common oxidation state, the cation with the \(d^6\) electronic configuration is spin paired by ligands producing only a relatively small crystal field intensity, e.g. acetylacetonate anion, while metal ions lower in the series transform to the spin-paired state only in the presence of ligands higher in the Shimura-Tsuchida spectrochemical series. Griffith \[102\] has estimated the pairing energies (for one electron) for the \(\text{Mn}^{3+}\), \(\text{Fe}^{3+}\) and \(\text{Co}^{3+}\) cations from spectroscopic data, and these are listed in the second column of Table 4.5a. The third column gives the total pairing energy associated with the spin-paired state (Kcals.) and the forth column shows the corresponding
crystal field stabilisation energy $\delta H$ for the low spin trivalent metal acetylacetonate complex.

**Table 4.5a**

<table>
<thead>
<tr>
<th>Cation $\text{M}^{3+}$</th>
<th>$P \text{ cm}^{-1}$</th>
<th>Total $P \text{ Kcals.}$</th>
<th>$\delta H$ (low spin) $\text{Kcals.}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}^{3+} (d^4)$</td>
<td>28,000</td>
<td>81</td>
<td>83</td>
</tr>
<tr>
<td>$\text{Fe}^{3+} (d^5)$</td>
<td>60,000</td>
<td>172</td>
<td>94</td>
</tr>
<tr>
<td>$\text{Co}^{3+} (d^6)$</td>
<td>42,000</td>
<td>120</td>
<td>144</td>
</tr>
</tbody>
</table>

In the case of the ferric complex, the pairing energy required to spin pair two d electrons in the $t_{2g}$ triplet far exceeds the corresponding crystal field stabilisation energy, and hence the high spin configuration is assumed, but in the case of the cobaltic complex, the reverse situation arises and the low spin configuration is thermodynamically stabilised.

Selected individually, the homolytic and heterolytic bond energy parameters (Tables 4.4a, 4.4b and 4.4c) provide no estimate of the percentage covalent (or ionic) character of the metal-oxygen coordinate bond. However, when each parameter is reviewed as a series, definite trends are revealed. The
homolytic and heterolytic bond energy parameters for the aluminium complex are both relatively high, indicating that the aluminium-oxygen coordinate bond is predominantly covalent, as is clearly predicted from the relatively small metal ionic radius (0.57 Å) and its enhanced polarising power. In contrast, the relatively low $E^i_\text{MO}$ and $E^\text{ii}_\text{MO}$ values for the ferric complex, signify that the iron-oxygen bond is associated with a high percentage ionic character. The homolytic parameter $E^\text{ii}_\text{MO}$ decreases progressively as the metal atomic number increases (Figure 4.4A) and becomes an insignificant minimum at atomic number 25. Thus the ionic character of the metal-oxygen coordinate bond increases steadily along the series (Sc to Mn). Such a specific trend in the homolytic bond energies parallels the decreasing sequence of the metal-oxygen force constants and the increasing sequence of stability constants and metal-oxygen bond lengths given previously (1.5)(1.6). The heats of formation, $\Delta H_{f,i}$ of the first row, trivalent, transition metal acetylacetonates (derived from the gaseous component ions) ascend gradually after correction for crystal field effects (Figure 4.4B). This effect is predominantly due to the successive decrease in cationic radius and concomitant increase in electronegativity as the transition series progresses.

The 'twin peaked' curve, Figure 4.4B, is favourably
interpreted without the specific application of any one of the three theories concerned with metal-ligand bonding characteristics. The curve obtained from a plot of $\Delta H_{f.i}$ versus the metal atomic number shows a distinct minimum at atomic number 26, corresponding to the ferric complex. The ferric ion, in the coordinated state, contains a half filled inner 3d shell and is thus not thermodynamically stabilised by the 'perturbing effect' of the surrounding ligand electronic environment. The discontinuities in the empirical heat of formation curve are thus a direct consequence of thermodynamic stabilisation, effected by the presence of the electronic ligand atmosphere. There is no direct route to the 'true' thermodynamic stabilisation energy for a specific metal acetylacetonate, for although the heat of formation of the gaseous complex $\Delta H_{f.i}$ may be derived experimentally, the corresponding heat of formation in the absence of 'ligand perturbing effects' is a hypothetical quantity.

In order to show qualitatively that the heats of formation of the gaseous complexes, after correction for 'ligand perturbing effects', vary as a smooth function of the metal atomic number, the approximate thermodynamic stabilisation energy $\delta H$, as predicted by the crystal field theory, was calculated for each complex from the corresponding spectroscopic
Δ value. $\delta H$ is, at best, only a near approximation to the true thermodynamic stabilisation energy, for its derivation has assumed a semistatic state, in which integral numbers of electrons are assigned to the $t_{2g}$ and $e_g$ nonbonding orbitals on the metal. The real situation is a dynamic one, in which orbital mixing and extensive electron delocalisation occurs. Also the 'effect' of the ligand environment on the cationic radius has been neglected and refinements, such as the extra stabilisation of the manganic complex due to a Jahn-Teller mechanism, have not been allowed for and, as a consequence, the corrected $\Delta H_{f,i}$ value for this complex lies slightly above the otherwise smooth interpolation curve.

It has become customary to compare the $\delta H$ value with the corresponding parameter $\delta H'$, calculated from the displacement of the empirical heat of formation from the linear interpolation function, obtained by joining the heats of formation of the 'd°, d⁵ and d¹⁰ complexes'. Such a comparison has proved to be successful in the case of the octahedral, divalent, first row, transition metal cations (Figure 1.4B) and for the tetrahedral halide complexes $[M^{II}X_4]^{2-}$ [11]. In these selected cases, the crystal field theory successfully characterises the predominantly ionic metal-ligand coordinate bond. For the trivalent metal acetylacetonates, agreement between the two
stabilisation energy parameters is poor, signifying that the crystal field theory inadequately describes the nature of the metal-oxygen coordinate bond. The difference between $\delta H'$ and $\delta H$ is an approximate measure of the increased stabilisation of the complex due to the covalent and $\pi$ bonding. On this basis, therefore, the cobalt-oxygen bond is associated with a high degree of covalent character, whereas the iron-oxygen coordinate bond is predominantly ionic.

All the quantitative and semiquantitative evidence collected so far indicates some degree of covalent character in the metal-oxygen bond, and it is probable that a more realistic interpolation curve could be derived if it were possible to calculate the $\delta H$ value from a molecular orbital treatment, for although certain approximations are again introduced, the actual metal-ligand bond is not specified as either ionic or covalent and the possibility of secondary $\pi$ bonding is considered.

Although departing from convention, a fairer estimate of the metal-oxygen bond energy can in principle be attained if the metal atom (or ion), participating in the formation reaction, is considered in its 'reacting state', the energy of which exceeds that of the ground state by the total 'promotion energy'. The metal atom (or ion) in its 'reacting state' is
normally considered to possess the same basic d electron configuration as that of the coordinated metal ion; any surplus d electrons on the free metal are redistributed in higher energy orbitals prior to coordination.

In the 'neutral' formation process, the 'reacting state' for the gaseous metal atom is the hypothetical state in which one 3d and one 4s electron has been promoted to a set of six sp^3d^2 hybrid orbitals (valence bond interpretation). As this is not a definite spectroscopic state, the total inherent promotion energy cannot be evaluated.

In the 'ionic' formation process, the total promotion energy appears to be zero, for the free gaseous metal cation already contains the requisite number of d electrons, and thus it seems that the heterolytic parameter E'_{MO} closely approaches the 'true' metal-oxygen coordinate bond energy.

The 'true' 'reacting states', however, are not so clearly defined; it is unlikely that the coordinated metal exists in the trivalent state for, as a consequence of the Pauling electroneutrality principle [104], the formal positive charge on the metal approximates to zero. On this basis, therefore, the homolytic parameter E''_{MO} is a more realistic measure of the coordinate bond strength. The homolytic cleavage process is undoubtedly thermodynamically favoured, for the corresponding heterolytic cleavage process is hindered by a high
activation energy, the greater part of which is manifested in overcoming the strong interionic attractive forces which tend to encourage gaseous 'ion-pair' formation.

The aim of this thesis has been to present empirical bond energies, and therefore the problem of 'reacting states' and 'promotion energies' has not been pursued further. The oversimplification of choosing the ground state as the energy reference state for all components has inevitably led to bond energies which are only approximations to the theoretical absolute parameters, obtainable from a detailed wave mechanical interpretation of the metal-oxygen coordinate bond.
P. Paoletti, A. Sabatini and A. Vacca, ibid., 61, 2417.
1952, 74, 5764.
[31] F. Gach, Monatsh., 1900, 21, 98.
[34] L. M. Shkolnikova and E. A. Shugam, Kristallografiya, 1960, 5, 32.


