The calculation procedures required to convert calorimetric data to the desired heat change is similar to that given by Eatough et al [29]. It involves the following basic steps.

- Experimental determination of the gross heat liberated in the reaction vessel, \( Q_0 \), as a function of titrant added.

- Calculation of all correction terms for heat effects occurring in the reaction vessel other than those due to chemical reaction.

For simplicity the procedure given applies to measurements obtained using the model 1250 Tronac Calorimeter as a continuous titration, constant temperature environment apparatus.

The determination of the amount of heat produced as titrant is added to reaction vessel, involves the following two steps i.e. calibration of calorimeter and analysis of the thermogram.
5.1 CALIBRATION OF THE CALORIMETER

Calorimeter calibration involves calibration of buret and thermistor. The buret is calibrated by gravimetric procedure. Weighed amounts of distilled water delivered by the buret over several time intervals give the buret delivery rate (BDR) in gms. per unit time. From this the delivery rate in volume units (ml/minute) can be calculated. This calibration is made using a stop watch to measure the time of titrant delivery. The computer programme for calibration of buret is given in Appendix C.

The most common means of measuring temperature changes in the reaction vessel is by means of a thermistor incorporated into a Wheatstone bridge circuit. This is the technique used in this calorimeter. The change in the output voltage of the bridge may be related to temperature change by calibration against a temperature standard. The calibration procedure consists of placing the thermistor and the thermometer in close proximity in a constant temperature water bath and measuring changes in the voltage $E$ (RT temperature), as a function of the bath temperature $\theta$ over a narrow range of temperature change (± 1.0 °C). The following equation can be used to correlate $E$ and $\theta$

$$E = a + b\theta$$  \hspace{1cm} (74)
The thermistor constant \( b \) is given by the equation:

\[
b = \frac{\sum_{i=1}^{m} E_i B_i - \sum_{i=1}^{m} B_i \sum_{i=1}^{m} E_i}{\sum_{i=1}^{m} B_i^2 - (\sum_{i=1}^{m} B_i)^2}
\] 

\( \ldots(75) \)

Where \( m \) is the number of data points taken. When the constant \( b \) has been determined the experimentally measured \( E \) values may be related to temperature changes during calibration as,

\[
\theta - \theta = b(E - E)
\]

\( \ldots(76) \)

5.2 TOTAL HEAT GENERATED IN THE REACTION VESSEL

The total heat \( Q_p \), generated in the reaction vessel from point \( x \) to any point \( p \), as shown in Figure 5.1 in given by

\[
Q_p = C_{PT} (\theta - \theta)
\]

\( \ldots(77) \)

The total heat capacity \( C_{PT} \), of the reaction vessel and its contents can be determined by either

- measuring the heat capacity for various additions of titrant and obtaining heat capacity as a function of amount of titrant added or
- measuring or evaluating heat capacity of empty reaction vessel, its contents, and the titrant and combining them to give the total heat capacity of the system as a function of the amount of titrant added.

First method is the more accurate of the two methods in that the heat capacity of the system is directly measured for each system but at the same time it is also the most time consuming and laborious method.
Figure 5-1 Chemical Calibration Titration Thermogram
Second method depends on the total heat capacity being equal to the sum of heat capacities of the parts which, for dilute solutions, is a very good assumption. This method has the advantage that once the heat capacity of the empty reaction vessel has been determined no further calibrations are necessary as long as the heat capacities of the solutions used in reaction vessel and as titrants can be evaluated from other sources.

Because of its simplicity, second method has been used in this work to evaluate total heat capacity as a function of titrant added.

The heat capacity of the reaction vessel and its contents is most accurately measured electrically by introducing a constant current through a resistance heater over a measured period of time. Distilled water is used for reaction vessel solution as its heat capacity is known as a function of temperature. The heat capacity of the reaction vessel plus contents, \( C_p \), is given by the equation:

\[
C_p = \frac{Q}{\left\{ \sum_{i} S_i - (S_i + S_f) t/2 \right\}} \text{ ....(78)}
\]

\( S_i \) and \( S_f \) are the initial and final rates of temperature rise due to non-electrical heat contributions (stirring, radiation, conduction, etc.). The derivation of the correction terms \( S_i \) and \( S_f \) are given, in the
following paragraphs. The heat capacity of the empty reaction vessel, $C$, is found from equation:

$$ C_{pr} = C - V \rho C $$  \hspace{1cm} (79) 

The corrected temperature rise in mVis given as

$$ \Delta \theta_C = \Delta \theta_T - (S + S_i) t/2 $$ \hspace{1cm} (80) 

The experimental $Q$ and $\Delta \theta$ values are related to $C$ and $b$ by equation

$$ Q = (C_{pr} + V \rho C) \Delta \theta_C b $$ \hspace{1cm} (81) 

Experiments on two liquids for which the heat capacity values, $c$, are known will result in two equations which may be solved for the unknown $C$ and $b$. Two liquids with significant difference in $C$ values should be used. Distilled water and CCl₄ or benzene are suitable liquids.

$C$ is constant for a given volume of liquid in the reaction vessel but varies as the liquid volume changes when titrant is added. This change in $C$ is due primarily to more of reaction vessel wall coming into contact with liquid as the liquid volume increases. For the calorimeter used in this work, which is similar to that described by Christensen et al \[19,20\] the changes in $C$ are about 0.1% or less of the value of $C$, the total heat capacity. This change can be evaluated by measuring $C$ as a function of the volume of liquid in the reaction vessel. For a given amount of titrant
added, the total heat capacity of the reaction vessel and contents, \( C \), is given by the equation:

\[
C = C_{\text{pt}} + C_{\text{ps}} + \left( \frac{\partial C}{\partial t} \right)_{\text{pt}} + \left( \frac{\partial C}{\partial t} \right)_{\text{ps}} \ldots \ldots \text{(82)}
\]

\( \frac{\partial C}{\partial t} \) is the increase in heat capacity due to the increase in the liquid wall contact area in the reaction vessel. The quantities \( C \) and \( \left( \frac{\partial C}{\partial t} \right) \) are independent of liquids used in the reaction vessel. By combining Equations 76, 77 and 82, \( Q \) becomes:

\[
Q = \left\{ C_{\text{pt}} + C_{\text{ps}} + \left( \frac{\partial C}{\partial t} \right)_{\text{pt}} + \left( \frac{\partial C}{\partial t} \right)_{\text{ps}} \right\} - E
\]

A thermogram, measure of temperature change with time is shown in Figure 5.1. The lead (A to B) and trail periods (D to E) are a measure of the nonchemical heat effects due to stirring, heating at the thermistor and heat losses to the surroundings during these periods. Titrant is added in the region B to C with the resulting temperature rise due to nonchemical heat effects, dilution of titrant and titrate. The following data can be evaluated from the thermogram the slopes of the LEAD period \( (5 \text{ C/Sec}) \) and after TRAIL period \( (5 \text{ C/Sec}) \), the temperature of titrate at the beginning of titration \( B \), and the temperature of the titrate at different time intervals \( (B, B, \ldots B, \ldots B) \). A
set of Q values can be calculated using Equations 77 or 83. These Q values represent the total heat produced in reaction vessel from point x to p and must be corrected for all heat effects before they can be used to calculate enthalpy changes. These corrections are detailed in the following section.

5.3 CORRECTION TERMS

Contributions to the total energy change measured in the reaction vessel from non-chemical contributions include those energy quantities associated with the solution, heat losses between reaction vessel and its surroundings and heating of thermistor. The initial and final equilibration slopes, S and S

are used to calculate the rates of heat loss at x and y. Assumptions are made that the energy input from the thermistor and stirrer (w) is constant during the run and that the rate of heat loss is proportional to the temperature difference between reaction vessel, 8

and its surroundings 8. Based on these assumptions following equations are obtained:

\[
\frac{dq}{dt} = \frac{H_L}{x} - S (C_{pT,x}) = w + k (\Theta - \Theta_x) \ldots (84)
\]

\[
\frac{dq}{dt} = \frac{H_L}{y} - S (C_{pT,y}) = w + k (\Theta - \Theta_y) \ldots (85)
\]

Where both w and k are positive constants. Both the above equations can be solved for w and k using the
experimental values for $S_i$, $S_j$, $S_x$, $S_y$, and $S_z$. These can then be used to calculate the value of $q_H$ at any point $p$.

$$q_H = u + k \left( \Theta - \Theta \right)$$ \hspace{1cm} \ldots (86)$$

Above equations can be combined to give

$$q_H = q_x + (q_y - q_Y) - \frac{\Theta - \Theta}{x}$$ \hspace{1cm} \ldots (87)$$

The total contribution of the non-chemical heat effects from the start of the titration (point $x$) to any time during run (point $p$) is given by equation,

$$Q_{p,H} = \int_0^t Q_{p,H} \, dt$$ \hspace{1cm} \ldots (88)$$

The Equation 88 may be solved by fitting the $q_H$ value calculated from Equation 87 for each data point to some analytical equation to give $q_H$ as a function of $t$, then integrating the resulting function.

A more simple method is to assume for the time interval $\Delta t$ between data points that $q_H$ is a linear, first order equation in time. Then Equation 88 can be simplified as:

$$Q_{p,H} = \sum_{i=0}^{p-1} \frac{\Delta t}{2} (q_{H,i} - q_{H,i+1})$$ \hspace{1cm} \ldots (89)$$

$Q_{p,H}$ values calculated from the above equation are used to correct $Q_p$ values for energy contributed by non-chemical terms.
The temperature of the titrant $\theta$ and titrate, $t$, at point $x$ should be same ideally. In practice this identity is difficult to achieve. If $(\theta - t)_x$ is positive there will be endothermic heat effect. Conversely there will be exothermic heat effect if quantity $(\theta - t)_x$ is negative. The correction that must be made to $Q$ value is:

$$Q_{T,C,p} = (V C_p)_t,p (\theta_x - t_x)$$  \hspace{1cm} \text{..(90)}$$

Where $(V C_p)_t,p$ is the volume and heat capacity of titrant, $t$, at point $p$.

The above correction is to be applied only if the titrant introduced is at a different temperature than titrate.

Usually the concentrations and changes in concentration of chemical species in the titrate are small enough that their contribution to the net correction for heat of dilution is negligible. This effect occurs due to changes as hydrolysis and solvation. In enthalpies of mixing of pure components, this type of effect is not present.

A correction can be made to measured enthalpy of mixing for the change in enthalpy of the vapour space during the mixing of two liquids, $\Delta H_{v,max}$. The assumptions made in deriving the simple equation are:
- The binary pairs obey Raoult's Law
- The mixing process is isothermal
- Equilibrium between liquid and vapour is rapidly attained after mixing.

Because of the uncertainty experienced in estimating the errors caused by vapourization effects, an attempt was made to place reasonable limits upon them by using the following equation [44].

$$\Delta H^V_{\max} = \frac{V}{RT} \left[ \lambda_1^D + \lambda_2^D \right]$$ .....(91)

The correction is usually small and further minimised or eliminated by keeping the vapour space negligible.

If reaction other than the one of interest occur in the calorimeter, the energy contributions must be corrected. Such type of effect occur while measuring the heats of reactions.

5.4 CORRECTED TOTAL ENTHALPY OF MIXING

The total enthalpy of mixing is given as

$$Q_{(\text{Total})} = Q_p + Q_{\text{HL}} + Q_{\text{TC}} + \Delta H^V_{\max} + \text{(heat loss due to other effects)}.$$ (92)

The enthalpy of mixing $h^E$, is given as

$$h^E = \frac{Q_{\text{Total}}}{\text{moles of mixture}} \text{ (Joules/mol).}$$ (93)

The computer programme to calculate total enthalpy of mixing is given in Appendix C. Also the programme documentation for the estimation of enthalpy of mixing is given in Appendix A.