NON-ISOTHERMAL HEAT-FLOW CALORIMETRY FOR BATCH AND SEMI-BATCH PROCESS DEVELOPMENT

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Non-isothermal heat flow calorimetry, Enthalpy of Reaction, Baseline construction, Experimental errors.

INTRODUCTION

Heat flow calorimetry has been used extensively to measure isothermal heats and energies of commercially important synthesis reactions. In common with other calorimetry techniques, some measurement principle is calibrated against a known heat flow. The unknown heat flow due to the reaction of interest is compared with the calibration heat flow, and so can be evaluated. If the calibration and measurement experiments are as identical as possible, then the (unknown) errors will cancel, being common to both experiments.

The technique has not been widely applied to non-isothermal reactions, presumably due to the difficulties arising as a result of the changing reactor temperature. Recent advances in computing technology have now made accurate temperature control possible, and so non-isothermal operation has become a practical proposition. In this paper we describe how a modern isothermal calorimeter (SIMULAR) [1] has been used to measure the heat of reaction of both a well-documented test reaction (methanolysis of acetic anhydride) and of a commercially useful synthesis reaction.

PRINCIPLE OF OPERATION

ISOTHERMAL OPERATION.
A sophisticated control system is used to keep the calorimeter at a set temperature. In isothermal calorimetry this is a constant value, and in non-isothermal calorimetry the reactor temperature is a function of time. The controlling effect in isothermal calorimetry as implemented in the commercially available calorimeter, SIMULAR [1] is the temperature of the oil circulated through the reactor jacket:

Heat flow to and from the calorimeter is described by the relationship

$$(1) \quad q_f = U.A.(T_R - T_J)$$

where q_f is the heat flow from reactor to jacket, T_R and T_J are the temperatures of the reactor and jacket respectively, A is the effective heat transfer area and U is the heat transfer coefficient. The equation describes differential heat flow – i.e. the heat flow over unit time. Integration of q_f over the period of the reaction is necessary to determine the total heat (or energy) of the reaction.

Typical experiments using this technique involve one or more electrical calibration steps. The reactor contents are heated electrically and the power to the heater is measured directly. The heat flow from the reactor at equilibrium is equal to the heat input to the heater, and so the U.A term in equation (1) above can be found. The heat flow from the calorimeter at any time can be calculated from the observed temperatures of the reactor contents and jacket. The U.A term depends on a number of variables, such as the fill level in the reactor, the thermal conductivity of the reactor contents and so on. Carrying out a number of electrical

calibrations during a measurement may be necessary to determine the changing values of U.A as the reaction or process simulation proceeds.

NON-ISOTHERMAL OPERATION

In the real world, at least some useful synthetic reactions are carried out over a range of temperatures. To study these reactions isothermally is to deviate from normal plant operating conditions and may lead to erroneous conclusions. The question then arises as to whether the calorimeter can be operated non-isothermally.

In isothermal operation, the baseline or zero heat flow condition is easily established. However, in non-isothermal operation, the control system is actively changing the temperature in the calorimeter. In this case a baseline can only be established if the control action is reasonably reproducible. Figure 1 below shows how the time temperature data for two separate temperature ramps can be superimposed.

Figure 1 here.

It can be seen that the control action for each ramp is virtually identical. This means that if a thermal event occurs during the ramp then there will be a detectable effect in the control system response (See Figure 2).

Figure 2 here.

In non-isothermal experiments, it is also necessary to estimate the amount of heat (or energy) which is used to change the temperature of the reactor contents:

$$(2) \qquad q_{Acc} = C.\frac{dT}{dt}$$

where C is the overall heat capacity of the calorimeter and contents, dT/dt is the change in temperature per unit time and q_{Acc} is the amount of power needed to bring about the temperature change.

Determination of the heat capacity of the reactor (i.e. calorimeter) is not easily possible for a number of reasons. For instance, it is not possible to define how much of the glass in the reactor walls is to be included in a conventional heat capacity determination. Similarly, the contribution of any reactor fittings, such as the thermometer probe, cannot be easily defined.

Two approaches have been used for the present paper. The first approach has been to define a calorimeter "constant" (E_{cal}) which includes the effective part of the calorimeter and its contents (Accumulation Heat Methodology). The software supplied with the calorimeter (WinCalc ™) was used. The calorimeter constant is measured in separate calibration steps, done before and after the reaction. The drawback with this approach is definition of the baseline for the heat flow integration. Under isothermal conditions the baseline heat flow is easily defined. The question of baselines for the non-isothermal experiment is not so clear.

As far as we are aware, equation 2 has never been used to determine the heat flow, and subsequently, after integration, the energy released for a system which has been deliberately perturbed from isothermal conditions – i.e. the temperature of the system is deliberately ramped up between two set temperatures.

The second approach takes as its baseline the temperature data from the calibration steps. No attempt is made to calculate a separate calibration constant. The assumption is that systematic errors are common to both measurement and calibration experiments and therefore cancel out.

EXPERIMENTAL.

REACTION OF ACETIC ANHYDRIDE AND METHANOL – UNCATALYSED REACTION.

The reaction was carried out by addition of acetic anhydride to methanol at 20°C followed by ramping the reactor temperature up to 50°C over 1 hour followed by a stir out at 50°C. Calibrations for both UA and the heat capacity of the reactor and contents were carried out before and after the reaction. The experiment is depicted graphically in Figure 3.

Figure 3 here.

Accumulation Heat Methodology.

The measured value of E_{cal} pre-reaction is an underestimate since at this point no acetic anhydride has been added to the vessel. It has been corrected by addition of the heat capacity of the acetic anhydride. E_{cal} used in the calculation is the mean of the two values.

Inspection of the graph (Figure 3) indicates that the feed of acetic anhydride to methanol at 20°C is slightly endothermic (+0.9kJ/mol) as calculated by normal methods. Clearly, during the final stir out stage at 50°C reaction is still taking place since the oil inlet temperature is still rising. Reaction is therefore occurring over the heat up and stir out periods.

Interpolation of both the baseline and the change in UA were not straight forward. These parameters were interpolated following the reactor temperature. In any event, the total change in UA was less than 3% over the reaction and is probably not significant. The final result for the molar heat of reaction was –59.3 kJ/mol of acetic anhydride for the heat up ramp and final stir out. This figure breaks down as +23.4 kJ as total heat flow and -82.8kJ/mol accumulated in the reactor contents. The overall heat of reaction is therefore –58.4kJ/mol of acetic anhydride. This compares reasonably well with the generally accepted value of about -66kJ/mol [2] for an uncatalysed reaction.

Residual Differences Methodology.

This method relies on the fact that two separate temperature ramps can be almost perfectly superimposed (Figure 1). Subtraction of the mean reactor - jacket temperature differences of the two calibration ramps from those for the reaction ramp yields the temperature differences due to the chemical reaction alone. Integration of these residual differences affords the enthalpy of reaction. A consistent method has been employed to calculate the enthalpy of reaction in the stir out step. The total enthalpy measured was –59kJ/mol of acetic anhydride charged. This is in fair agreement with both the heat accumulation methodology and the literature value.

Figure 4 here

REACTION OF ACETIC ANHYDRIDE AND METHANOL – CATALYSED REACTION.

The experiment was repeated but a trace of sulphuric acid catalyst was added part way into the heat up stage. The same quantities of raw materials were used in this experiment and the calibration data from the first experiment were applied. The time temperature details are depicted in Figure 5.

Figure 5 here.

Accumulation Heat Methodology.

The results were calculated in an identical manner to the previous case using identical values for UA and the specific heat capacities. The result of -76.1kJ/mol compares very well with the generally accepted value of -74.8kJ/mol [3] for the catalysed reaction. In principle, using calibration data from previous experiments is probably unsound. In this case however, careful attention to detail was taken in assembling the experiment and the data plotted with the calibration data from the previous experiment justifies this strategy.

Residual Differences Methodology.
The residual differences gives an enthalpy of reaction of -65kJ/mol of acetic anhydride. This is a little low compared with the literature value and the value calculated by the accumulation heat methodology.

Figure 6 here.

A REACTION OF INDUSTRIAL IMPORTANCE.
For reasons of commercial sensitivity, the chemistry of this real example can only be represented in general terms. A solid raw material (A) is suspended in a solvent with stirring. The second reagent is added over a period of time. This addition is exothermic and converts the starting material into a new insoluble intermediate (B). The reaction mixture is then slowly heated at a constant rate to an elevated temperature to convert the intermediate (B) into the product (C). During this stage a gas is evolved. The heat of reaction of this stage had never been measured previously although adiabatic reaction calorimetry had indicated that the reaction may be endothermic. Again appropriate calibration and specific heat determination stages were included in the experimental plan. The experimental time temperature data are depicted in Figure 7.

Figure 7 here.

Accumulation Heat Methodology.

The feed of the raw material was exothermic while the heat up stage was strongly endothermic (Figure 6). The enthalpy of reaction for the heat up stage only (not on a molar basis) was calculated as $+97$kJ. It is interesting to note that the energy released curve is almost an exact mirror image of the gas evolved curve. This is expected as the amount of gas released is proportional to the extent of the reaction, in turn proportional to the heat of reaction. Furthermore, during the initial part of the reaction some energy is absorbed and no gas is evolved, indicating a minimum two stage mechanism.

Figure 8 here.

Residual Differences Methodology.
The residual differences are plotted in Figure 7 and Figure 8 shows the integrated enthalpy curve. The enthalpy of reaction quoted on the same basis as above is $+90$kJ. The agreement between the two results is fair although, again, the residual differences method has given a lower result than the accumulation heat methodology.

Figure 9 here.

Figure 10 here.

DISCUSSION.

The three experiments reported above show that reasonable results can be achieved using a modern heat flow calorimeter in non-isothermal mode. Unfortunately, because of the calibration problems the experiments are necessarily time consuming. The industrially important reaction took 42 hours to complete.

The results calculated for the two reference reactions agree well with the accepted best values. This shows that the general calculation methods used for isothermal calorimetry are also valid for non-isothermal work. Of the two calculation methods used, the residual differences method appears to give slightly lower results than the heat accumulation methodology. It is not immediately clear why this is so.

Experimental errors in isothermal heat flow calorimetry are normally minimised by allowing the calorimeter to reach equilibrium. Under non-isothermal conditions the equilibria are much more dynamic and it is likely that systematic errors are larger as a result. Traditionally, calorimetrists design experiments so that the measurement and the calibration are as near identical as practically possible. This allows the systematic errors to cancel completely in the calculation. The reproducibility of the temperature ramps which is possible using a modern computer controlled calorimeter will contribute to reduced errors.

It is interesting to note that in the industrially important example, the order in the experiment of UA determination followed by the ramp stage is probably not the best. This is almost certainly linked to the fact that the raw material (A) dissolved on heating. On cooling back, the material crystallised in a different form and crystallised on the walls of the calorimeter. This undoubtedly introduced a significant error in UA. A better arrangement would have been to carry out the ramp stage first, followed by the UA determination.

In the industrially important example, the measured enthalpy relates to an overall effect which includes a variety of physical state changes as well as the reaction. Of course, this information is exactly that which a Process Design Engineer requires.

CONCLUSION.

* Heat flow calorimetry is a viable practical means of determining the enthalpy of reactions carried out under non-isothermal conditions.
* There are a number of sources of error in addition to those normally present in isothermal heat flow calorimetry.
* Errors associated with the temperature ramps can be significantly reduced by keeping the calibration and measurement experiments practically identical.
* Modern computer controlled instrument helps significantly in the reduction of the errors between experiments.

References:

1.   J. Singh, 1997, *"Reaction Calorimetry for Process Development: Recent Advances", Process Safety Progress, Volume 16, No1, Spring, AIchE (New York),* 43-49.
2.   T. K. Wright & C. W. Butterworth, 1987, *IChemE Symp. Series No: 102, UMIST*: 85.
3.   Barton & Rogers, 1997, *Chemical Reaction Hazards*: 22.
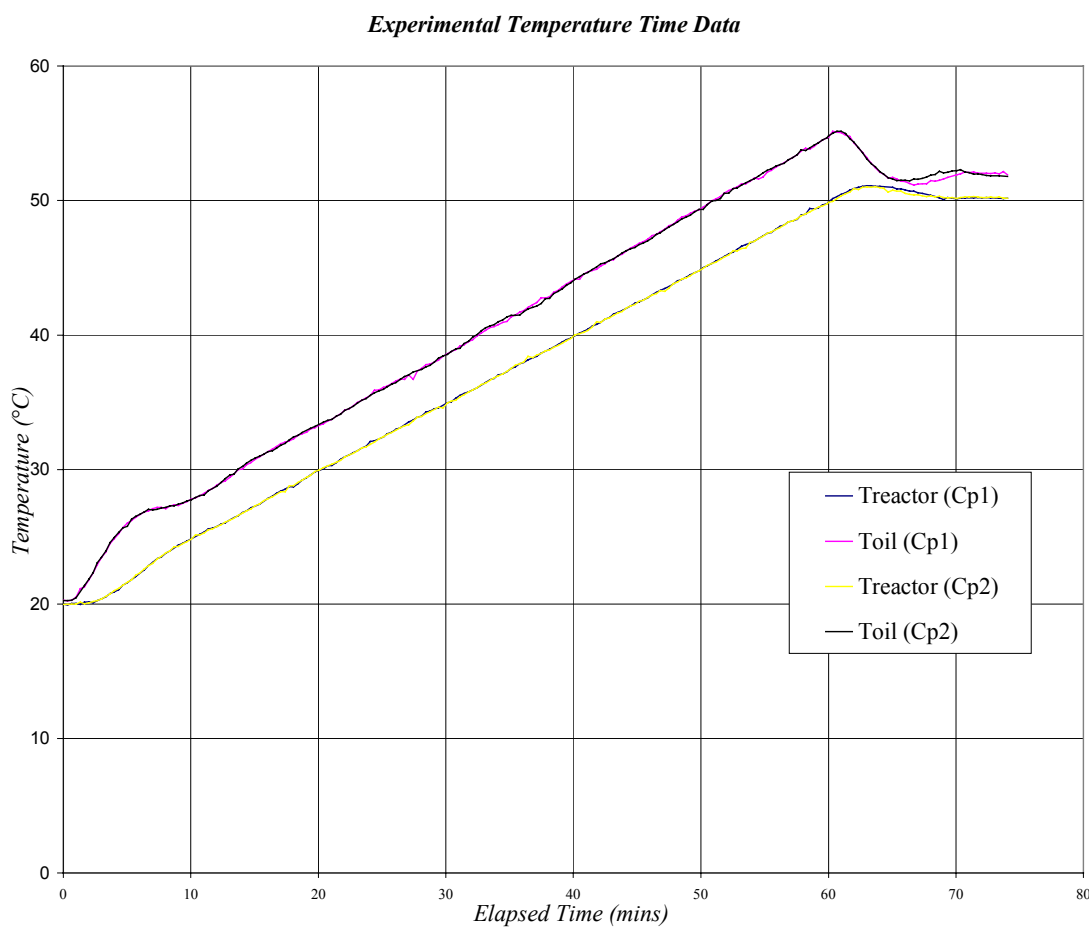
Experimental Temperature Time Data

Figure 1: Time Temperature Data from two Separate Temperature Ramps Superimposed.
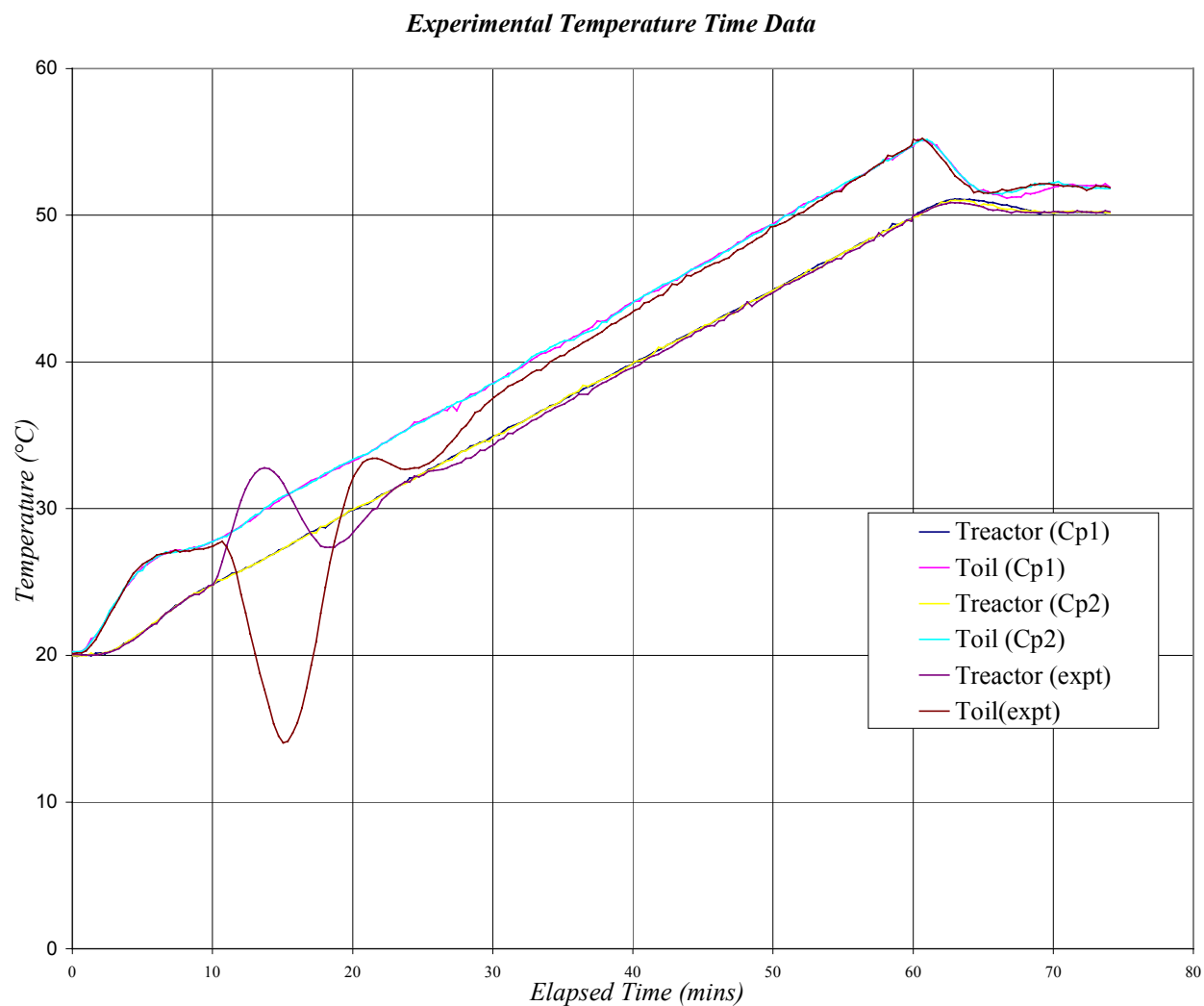
Figure 2: Experimental Data for Catalysed Reaction Superimposed on data from two calibrations.
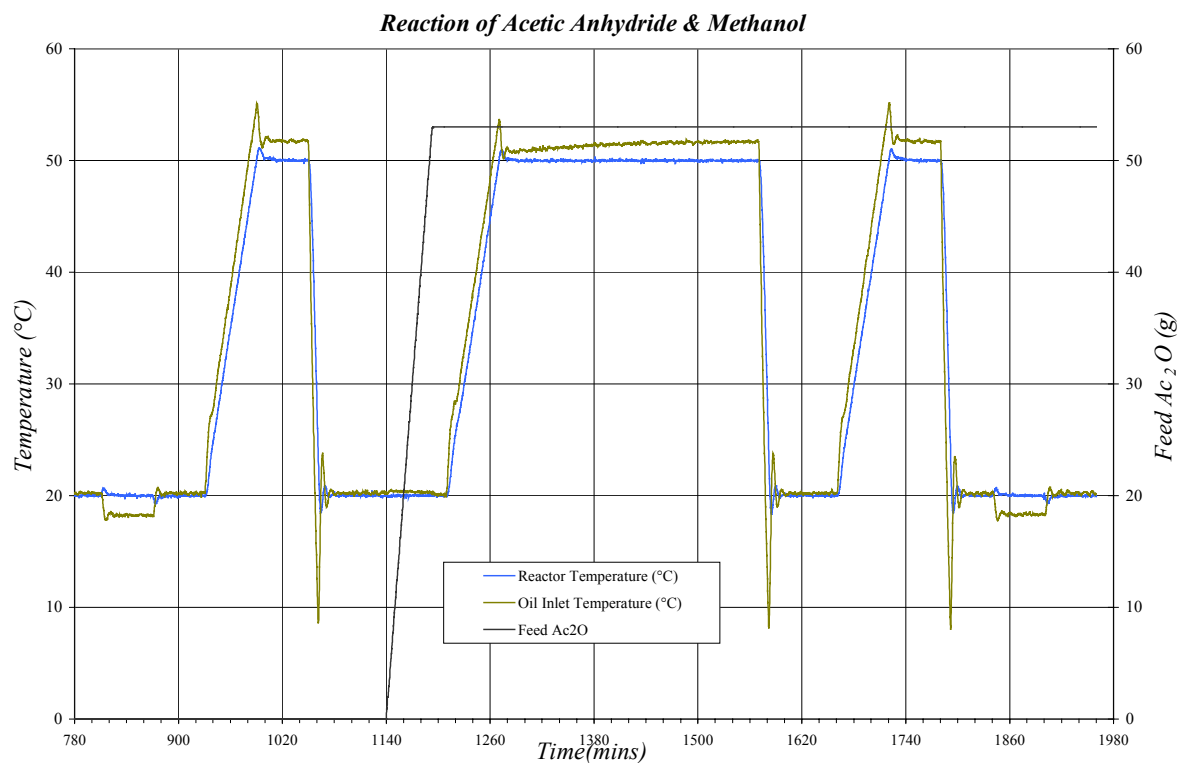
Figure 3: Time Temperature Data from Reaction of Acetic Anhydride and Methanol.
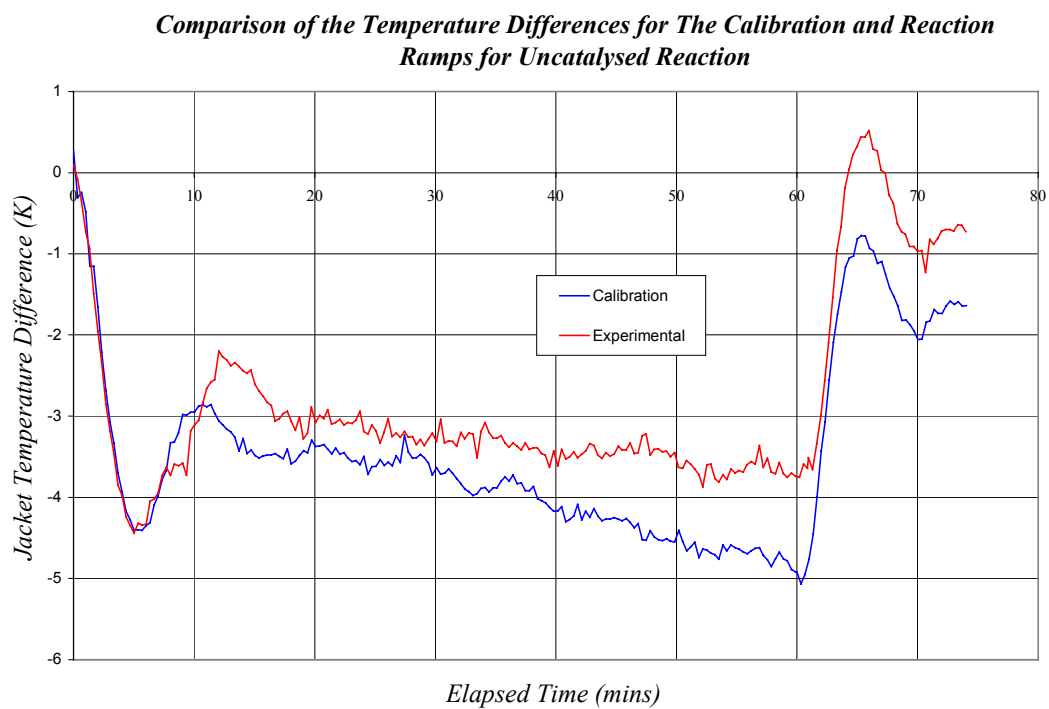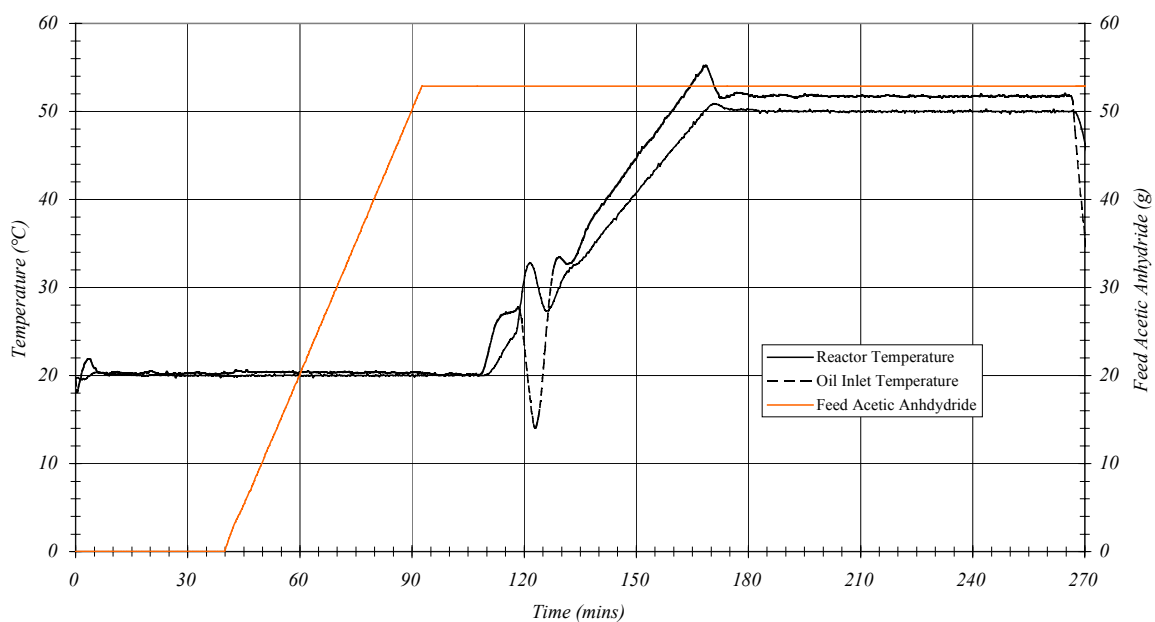
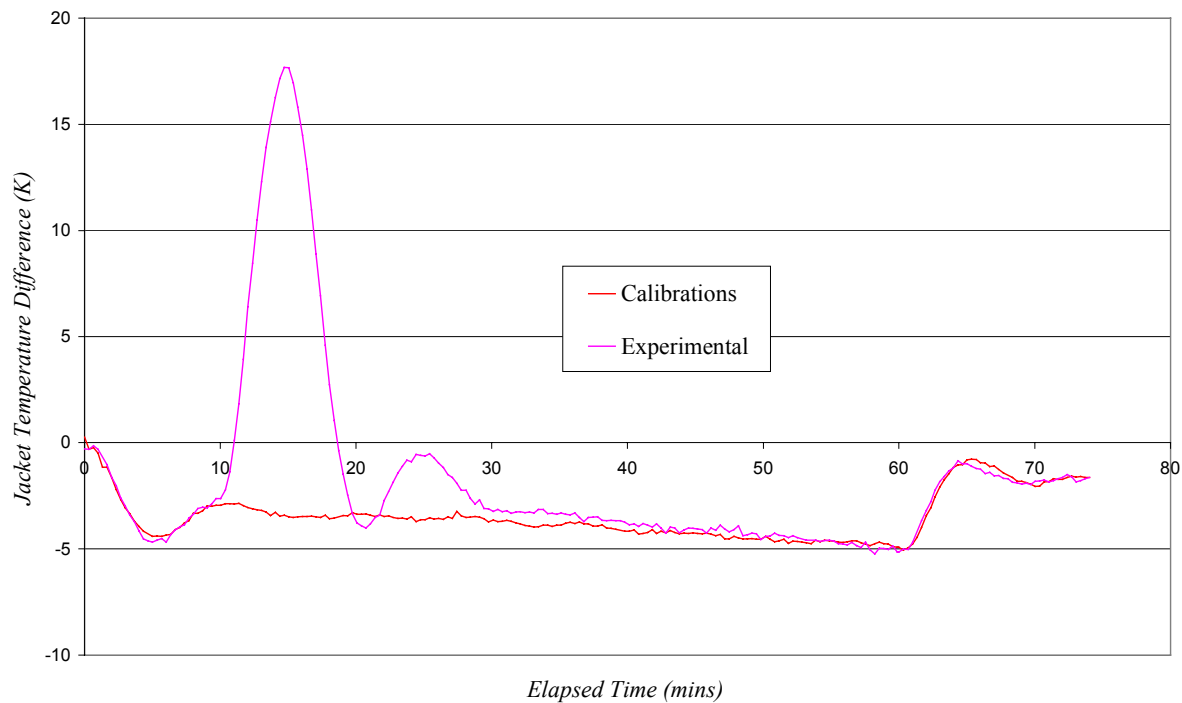**Comparison of the Temperature Differences for The Calibration and Reaction Ramps for Uncatalysed Reaction**

Figure 4: Jacket Temperature Differences for Calibration Ramp and Experiment for Uncatalysed Reaction.

Acid Catalysed Reaction of Acetic Anhydride and Methanol

Figure 5: Time Temperature Data from Acid Catalysed Reaction of Acetic Anhydride and Methanol.

Comparison of the Temperature Differences for The Calibration and Reaction Ramps for Catalysed Reaction

Figure 6: Jacket Temperature Differences for Calibration Ramp and Experiment for Catalysed Reaction.

Non-Isothermal Industrially Important Reaction
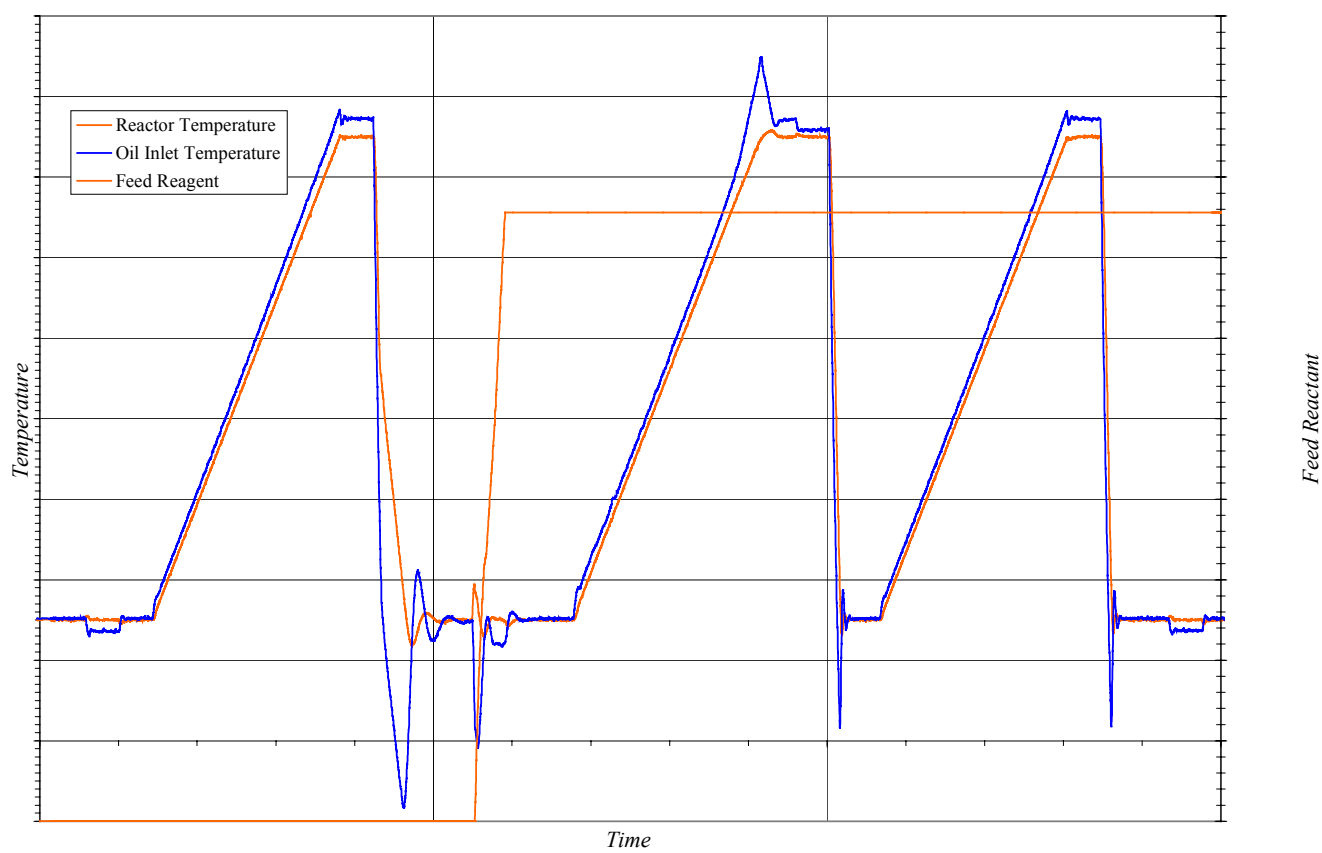
Figure 7: Time Temperature Data from an Industrially Important Example.

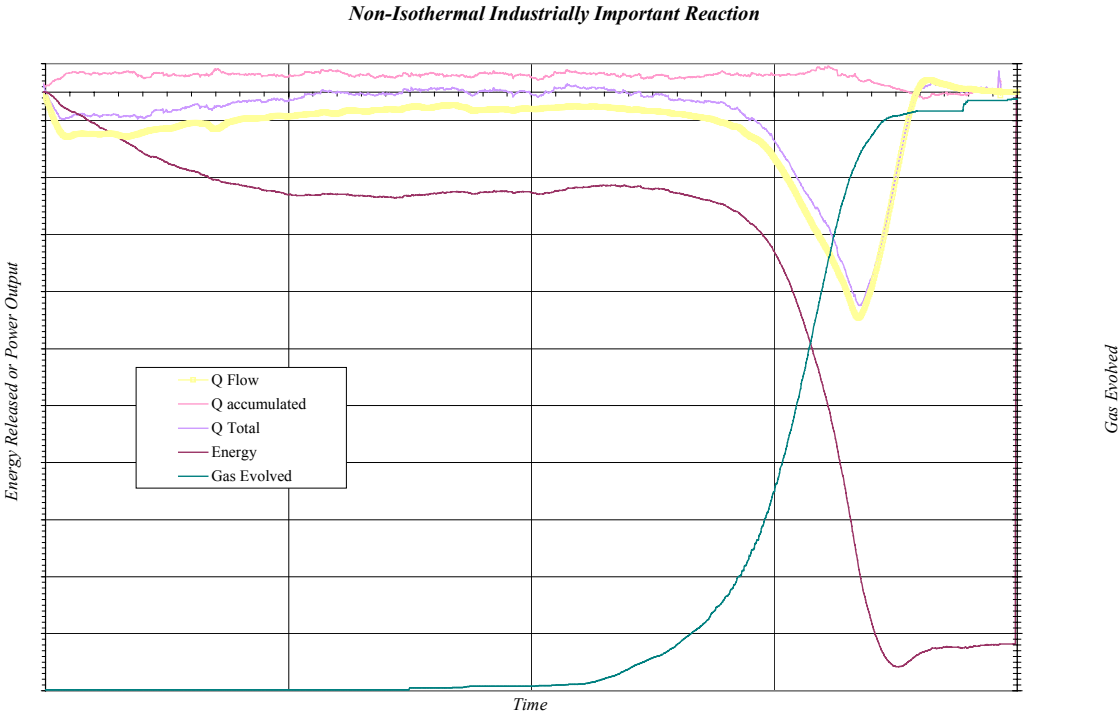**Non-Isothermal Industrially Important Reaction**

Figure 8: Energy Released for Industrially Important Example.

**_Temperature Differences for the Calibration and Measurement Ramps from the
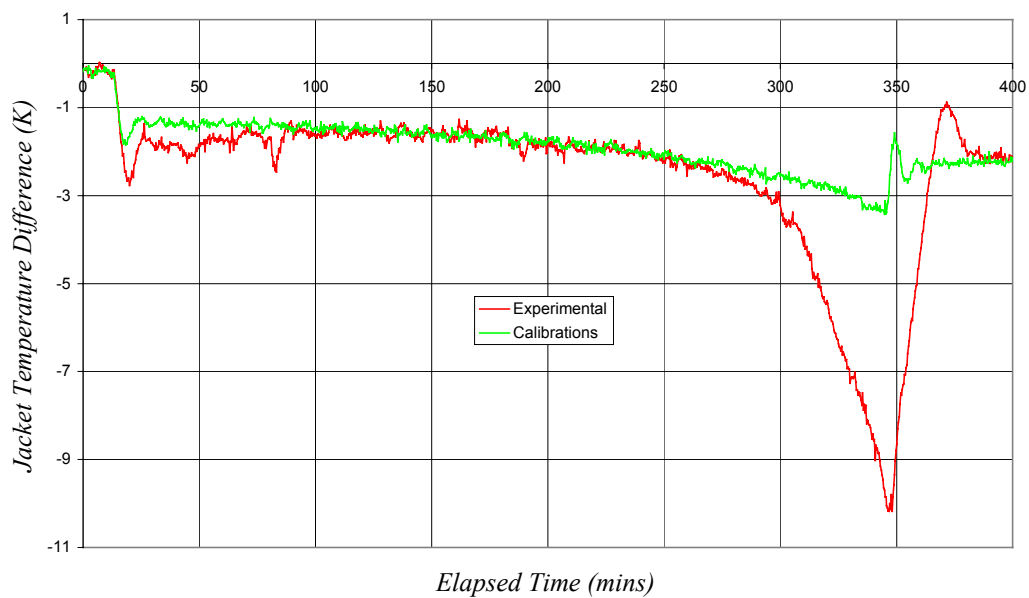Industrially Important Reaction._**

Figure 9: Jacket Temperature Differences for Calibration Ramp and Experiment for Industrially Important Reaction.

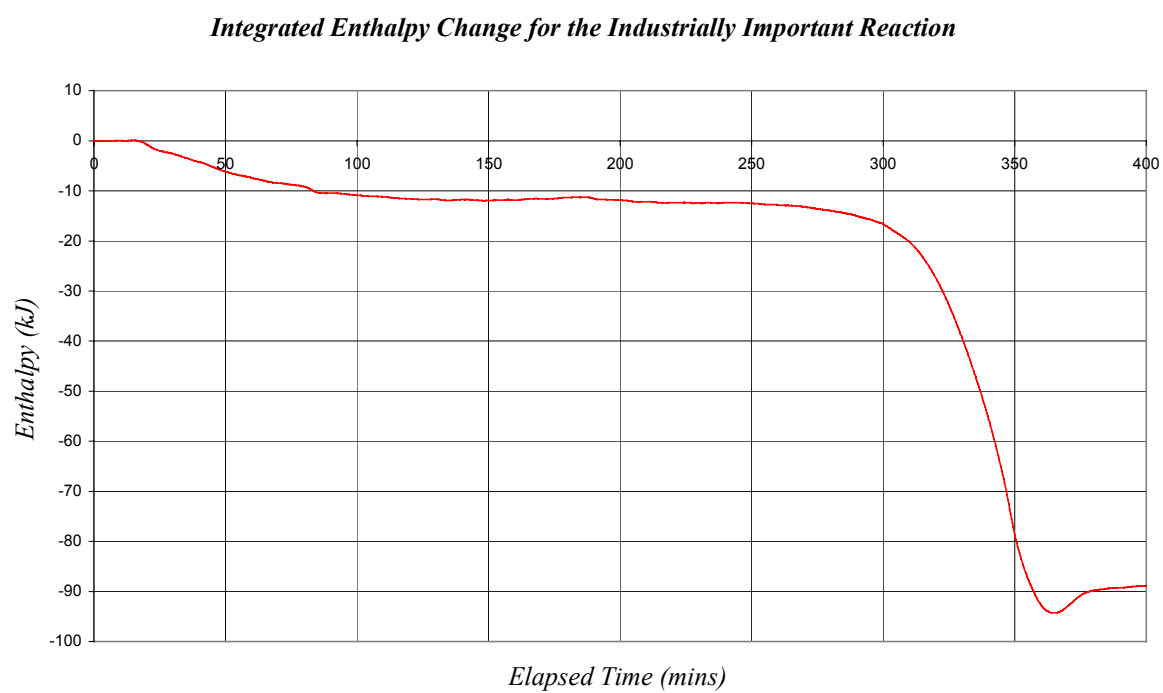**Integrated Enthalpy Change for the Industrially Important Reaction**

Figure 10:Integrated Enthalpy Change for the Industrially Important Reaction.