SCALE UP

Safe Process

H·E·L

better chemistry - faster

and Hazard Assessment

Safe Process Scale-Up

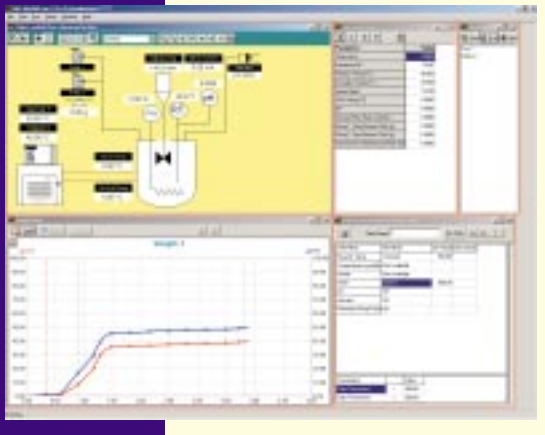
HEL produces three main devices to assist in the evaluation of thermal hazards: (TS^u, PHI-TEC and SIMULAR). These are complementary instruments that are useful at different stages of the process development. In the well equipped laboratories of large corporations, all three are used. The devices use the same software platform (winISO) and produce similar data files, etc. making it simple for users to move between the different systems.

Thermal Screening: TS^u

Thermal Screening is used to determine conditions of temperature, pressure and concentration, at which chemicals can safely be handled. It is necessary to consider all feeds, products and isolated intermediates, as well as the main reactions.

Many companies have historically used DSC/DTA type devices for this purpose. However, these have limitations that can compromise the results.

The screening methods must be inexpensive and fast, and the TS^u is just that. Moreover, the results are easy to understand even by non-specialists.



SIMULAR winISO interface

TS^u winISO interface

Reaction Calorimetry: SIMULAR

Depending on the results of the thermal screening tests, it is possible to study the reaction on the larger scale (~1 litre) with the SIMULAR. Here the objective is to study the desired reaction and confirm the safety and operability of the process.

SIMULAR is a computer controlled reaction calorimeter with features that allow all key reaction parameters to be reliably scaled, minimising the cost of pilot trials. Reactions are run exactly as they will be on the large scale and conditions are accurately reproduced. Power output released under these conditions is measured as the reaction is performed and the data can be put to a variety of uses.

Adiabatic Calorimetry: PHI-TEC II

When the intended process has been suitably demonstrated, it is necessary to consider deviations from the desired process. Typical examples are loss of cooling, failure of electrical power, agitation failure, or operator error (e.g. incorrect addition).

PHI-TEC allows 'what if' failure scenarios to be evaluated experimentally, generating data that can be applied directly to a large-scale plant. The information - pressure and temperature as a function of time, is simple to understand and easy to apply, for example for relief sizing.

Software

Running experiments

All of HEL's applications are based around the same software platform - winISO. It has been developed in-house to provide a logical and simple interface for describing multiple step processes. The user interface is common throughout except for a mimic representation, which is specific to each application.

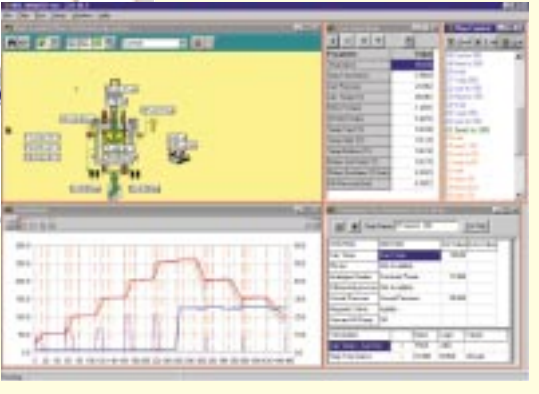
Using input screens, arranged in a series of "recipe cards", the operator simply indicates the required set point for each peripheral. Each step is then terminated on any selected conditions, (e.g. temperature, time, feeds completed), or by a series of logic statements.

During operation, all conditions are displayed on a mimic, numerically and on a trend graph. All steps can also be modified during operation. Changes are fully documented in the output file.

Data files produced by winISO can either be imported directly into standard packages such as Excel or into HEL's proprietary iQ software. It allows data to be printed, posted into other applications and has built-in calculation procedures.

The winISO interface for SIMULAR is configured according to the system specification. Unlike TS^u and PHI-TEC, the recipes are created entirely by the user based on the precise needs of the chemistry. Each recipe can be saved and later re-run; with modification if necessary.

The recipes are predefined and the user has only to complete a table of run parameters (e.g. start, temperature, maximum temperature, etc.).



PHI-TEC winISO interface

General features

- Real - time graphical, tabular and mimic display of data
- Real-time editing: change virtually anything as you run the experiment. All modifications are noted
- Alarms and shutdowns are based on any measured variable
- Recipe loops/jumps are incorporated into TS^u and PHI-TEC recipes, and are available on SIMULAR

TS^u

Simple, Rapid and Reliable Hazard Assessment

The Thermal Screening Unit (TS^u) has been developed for the first step in reaction hazards assessment, a more comprehensive solution than traditional screening by DSC/DTA. For effective reaction hazards screening, two critical pieces of data need to be determined: the 'onset' temperature for the reaction and the pressure generated by the runaway. The TS^u offers you the simplicity of operation associated with DSC and DTA, whilst providing pressure data. In addition, by utilising sample cells from 1 to 8ml, representative samples and reaction mixtures can be tested.

Operating Modes

The standard procedure involves heating of the sample at a user defined rate (typically between 0.5 and 10°C/minute) whilst both the temperature and pressure are recorded. Deviation from linearity (e.g. a sharp rise) indicates the 'onset' of an exotherm. The subsequent rise shows the severity of the hazard directly, without the need for any calculation. Additional operating modes include isothermal, dual scan and soak-and-scan.

Operating Range

Temperature from ambient to 400°C, resolution of 0.01°C. Pressure transducers are available in several ranges, typically up to 200 bar.

Test Cells

Spherical test cells of approximately 8ml in stainless steel, hastelloy, and other alloys are available as well as in glass. The large volume allows for truly representative samples, and the study of liquids, solids and reaction mixtures.

Features

- Alternative to DSC/DTA as a primary thermal hazard screening method
- Wide temperature range
- Wide pressure range
- Simultaneous pressure and temperature data
- High pressure mid-test injections possible
- Rapid sample turn around
- Representative sample size
- Low running costs

Key Data Produced

- 'Onset' temperature of exotherm
- Indication of rate of temperature rise
- Indication of rate of pressure rise
- Indication of likely maximum temperature and pressure
- Indication of non-condensable gas generation
- Indication of energy released

TS^u Applications

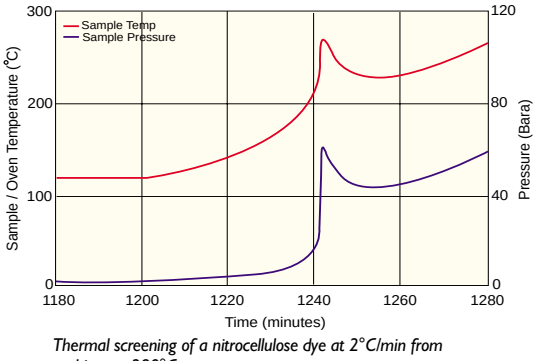
Thermal screening of a series of nitrocellulose dyes

A series of nitrocellulose dyes (0.5 g) were heated from ambient temperature to 280°C at a rate of 2°C/min to assess their thermal stability. A typical trace for the thermal screening of a yellow nitrocellulose dye is shown in the graph.

The results obtained from a series of such tests are shown in the table. From these results the violet pigment can be identified as having the lowest thermal stability with an onset temperature (as determined from a dT/dt against temperature graph) of 127.4°C.

Pigment	Onset Temp (°C)	T_{Max} (°C)	dT/dt_{Max} (°C/min)	dP/dt_{Max} (Bar/min)
Violet	127.4	338.8	318.4	497
Yellow	139.5	302.5	269.5	550
Red	149.3	392.8	422.8	630

Thermal screening of a series of nitrocellulose dyes



Thermal screening of a nitrocellulose dye at 2°C/min from ambient to 280°C

Metal test cells

Glass test cells

SIMULAR

Reaction Calorimetry

A reaction calorimeter is a tool that allows for the precise simulation and thermal study of chemistry, typically at the one litre scale.

Subsequently, important safety, viability and optimisation data can be obtained prior to scale-up.

Turn-key systems

For safe and efficient scale up, it is essential that your tools simulate your plant as closely as possible. In addition, it is important that as much information and insight about the process is obtained. As such the options, upgrades and flexibility offered by the SIMULAR are almost limitless, and are put together in a dedicated turn-key solution.

Reactors

The standard reactor is a 1 litre atmospheric pressure system. Optional volumes range from 0.2 to 20 litres in glass, stainless steel or resistant alloy, with pressure ratings of up to 200 bar. Specialist geometries and custom designed vessels are available to simulate real plant conditions.

Operating Range

Pressure - HEL offer a range of options for the study of reactions under pressure including 6 and 12 bar glass and 60 bar stainless steel reactors. There are other alloys and specialist material options. We even produce systems that operate at up to 200 bar reactor pressure.

Temperature - By using commercially available heater/chiller systems, we can offer you the temperature range you need, between -80 and over 350°C, with precision of better than +/-0.1°C. These systems also offer a small foot print and emergency cooling is available when required.

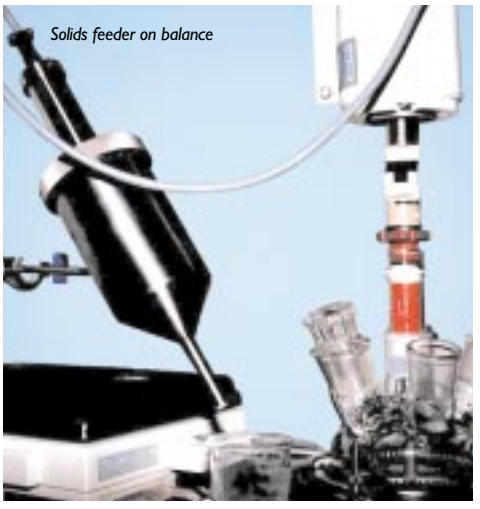
Feeds

Reagent feeds - gas, liquid and solid feeds are all available using a variety of application dependent techniques. Standard liquid feeds are pump and balance combinations, but options include syringe pumps for low flow rate feeds and pressurised vessels for faster rates and/or highly volatile reagents.

Gas feeds can be controlled via constant reactor pressure, bottle/balance combinations or even mass flow control. Finally automated solids addition is also made possible using a screw feed system developed exclusively by HEL.

Controls & Sensors

Software and electronics allow a variety of inputs to be logged and if necessary, used for feedback control. These include pH, turbidity, conductivity, FTIR, particle size etc.



Solids feeder on balance

Sampling

HEL have developed tools for automatic sampling and dilution during chemical reactions. A portable sampler, software driven, is available as an option.

Multiple Calorimetric Methods

Unlike most leading reaction calorimeters, SIMULAR is designed to be used by research chemists and safety specialists alike. Only SIMULAR offers you three different methods of reaction calorimetry:

HEAT FLOW is the most widely used method, and is standard on all SIMULAR systems. Heat generated by the reaction is removed by the oil jacket, and by using precise calibration heaters, pre and post reaction, the energy evolved can be determined.

REFLUX CALORIMETRY allows for the determination of heat flow even during large changes in reflux temperature and reactant volume.

POWER COMPENSATION is a method that allows accurate determination of heat release without the need for the time-consuming calibrations or complex calculation procedures involved in heat flow.

BENEFITS OF POWER COMPENSATION

- ▲ Reduced experiment time
- ▲ Intuitive 'live' results
- ▲ Improved temperature control

Key Data Produced

- ▲ Reaction entalphy (△Hr)
- ▲ Heat accumulation
- ▲ Heat release rate (Q)
- ▲ Heat transfer rate (UA)
- ▲ Batch cycle times
- ▲ Scale-up data

Four Feed Pumps

Process Optimisation

Yield, batch time

Optimisation of chemical reactions, to maximise yield, minimise side product formation etc., sometimes need complex combinations of measurements and control. SIMULAR is uniquely flexible in being able to take inputs from a range of sensors – FTIR, turbidity, particle sizing devices – and then using the data to gain a better understanding of the process.

The diagram shows the simultaneous use of FTIR and calorimetry – the appearance of product and disappearance of reactants, seen in the IR spectra, is supplemented by heat flow data.

SIMULAR is unique in being able to combine different sensor inputs and allow adjustment of control parameters to influence the reaction. Control based on model predictions is also possible – the model can run in parallel with the SIMULAR software.

Process Safety

Reagent accumulation

Most reactions are now run in a semi-batch manner: one or more reagents are held back and then dosed at a controlled rate. If the reaction rate is slow at the selected operating temperature, the dosed component can accumulate in the reactor – the amount of accumulation being a function of the feed rate.

The example shows a reaction where over 70% of the dosed chemical has accumulated. By introducing a catalyst, this is immediately reduced to 30%.

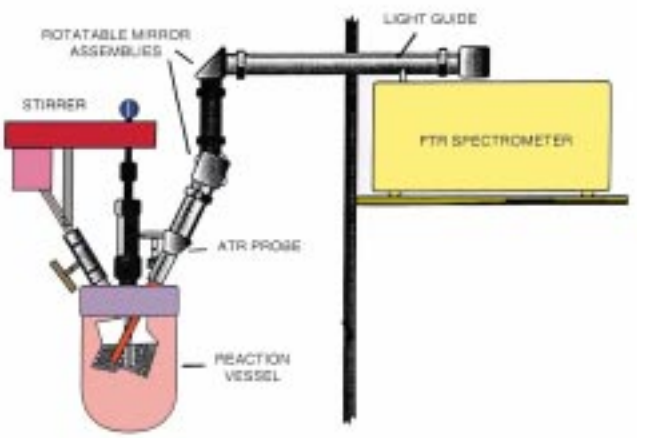
SIMULAR data can be used to estimate the accumulation and evaluate the different ways in which it can be reduced. The influence of a catalyst on the reaction is illustrated below.

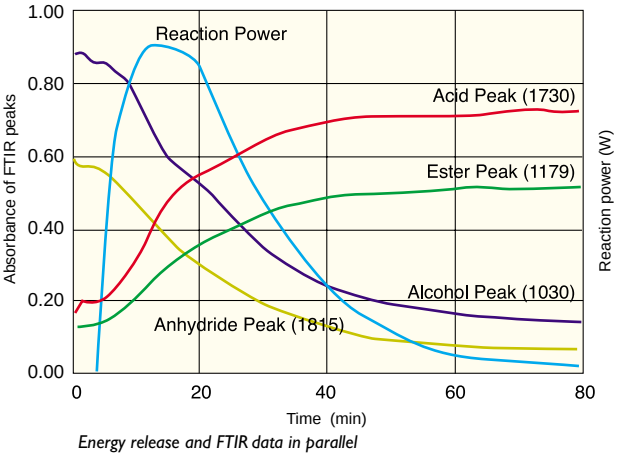
Scale-up Data

Heat transfer, cooling duty

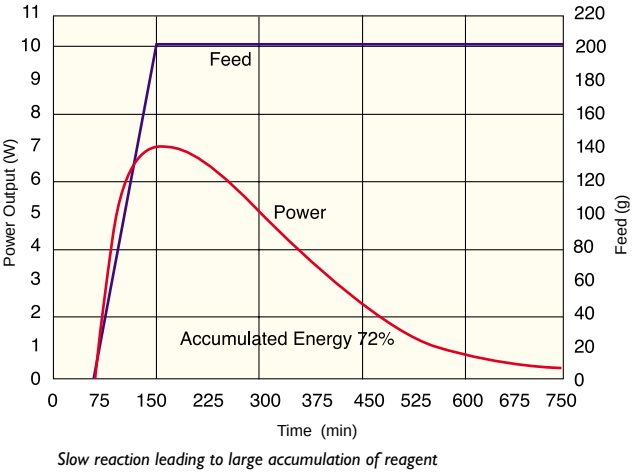
Chemical engineering information necessary for the scale-up of reactions is readily obtained from the SIMULAR. This includes the cooling duty (Q) for either jacketed reactors or reflux condensers and heat transfer rate (UA).

For multi-phase reactions where mixing is crucial, aspects of agitation can also be studied.

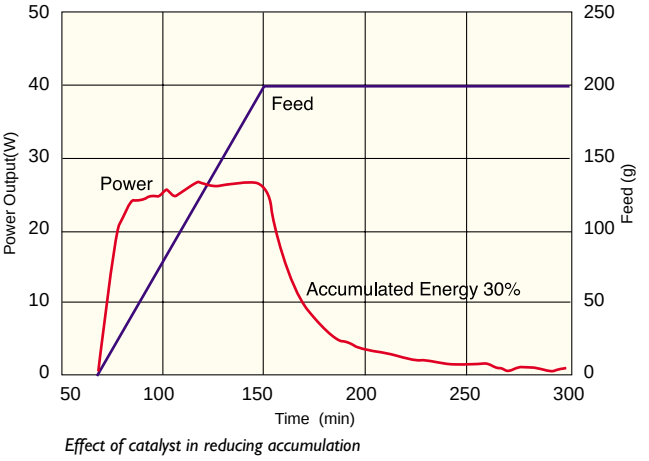




Energy release and FTIR data in parallel



Slow reaction leading to large accumulation of reagent



Effect of catalyst in reducing accumulation

PHI-TEC II

Adiabatic Calorimetry

PHI -TEC II is a computer controlled adiabatic calorimeter, small enough to be placed in a normal chemistry laboratory and yet with the capability of simulating the behaviour of a large-scale chemical reactor under conditions virtually identical to a large scale plant using only 10-100ml of sample. This is due to the low phi-factor data obtained from the PHI -TEC II.

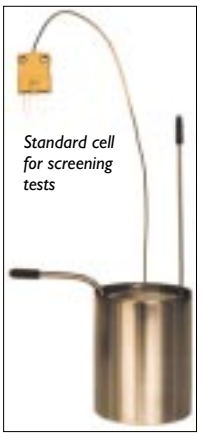
Information on reaction hazards, kinetics and thermodynamics can be obtained. Since reactions are allowed to proceed at rates identical to large-scale plant, no extrapolation or complex modelling is needed.

DESIGN SPECIFICATION

Sample cells

Test cells can be made of glass or a range of metals. For screening tests, metal or glass cells (~10ml) may be used, but for detailed studies of reactions, larger (100 to 120ml) cells are appropriate.

Mechanically stirred test cell



Standard cell for screening tests

Standard low phi-factor glass test cell

Sample agitation

Agitation of viscous liquids or multi-phase samples can be performed by use of mechanical agitation driven by a conventional electric motor. This design can be used on thin-walled test cells and is often essential if reliable design data is to be generated.

Sample addition

The sample can be loaded into the test cell at any stage: prior to placement in the containment vessel, whilst in situ, or during the experiment.

Temperature/pressure measurement

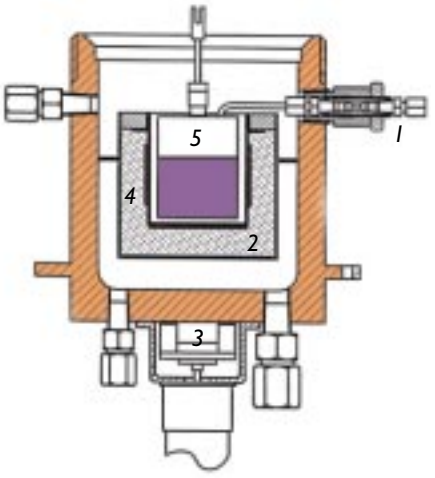
A fast-response, type k thermocouple is placed inside the test cell directly in contact with the sample, range 0 to 500°C. Maximum pressure is typically 138 bar (2000psi).

Exotherm detection-sensitivity

In general, exotherm detection down to 0.02°C/min. Heaters can track rates of over 200°C/min.

Key data produced

- ▲ Accurate 'onset' temperature of exotherm
- ▲ Runaway data suitable for DIERS RELIEF LINE SIZING
- ▲ Determination of venting behaviour (Gassy, tempered, hybrid)
- ▲ Determination of flow regime (two-phase or single phase)
- ▲ Kinetic data (eg for t_{MR} or T_{NR} calculations)



1. Feed pipe Connection
2. Bottom Guard Heater
3. Magnetic Drive
4. Side Guard Heater
5. Test Cell

PHI-TEC Applications

HAZARD SCREENING can be done in a simple but rapid test, where the sample temperature is linearly ramped until an effect is observed, or else more precisely by performing a heat-wait-search test. The latter procedure, though slower, produces a more accurate determination of the 'onset' temperature and yields more useful thermal data.

THE CONSEQUENCE OF A RUNAWAY in a large-scale reactor can be explored under a variety of situations. In this way hazards can be truly quantified without the need for reaction modelling, extrapolation or expensive pilot plant trials.

RELIEF SIZING to prevent equipment damage following an unwanted reaction is another application of PHI-TEC II. The equipment allows investigation of gas generating reactions, vapour pressure dominated systems, checking for two-phase flow and design of external dump tanks.

Adiabatic Runaway Reaction Data

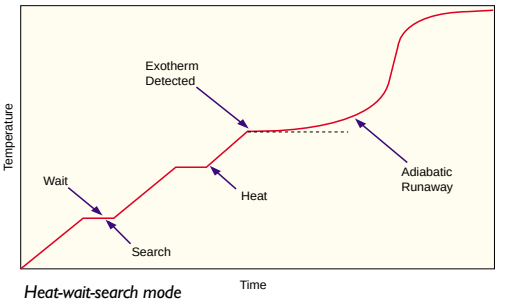
The classical data from the PHI-TEC is shown below, temperature and pressure as a function of time, after onset of the reaction. PHI-TEC II has unique design characteristics that compensate for small heat losses (in addition to excellent mechanical design aspects).

25% DTBP Decomposition

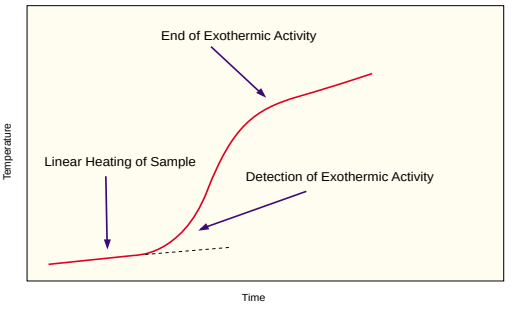
This graph shows why phi-factor data is so important. Small changes in phi-factor can lead to huge differences in reaction rate. PHI-TEC II emulates conditions essentially the same as in a large scale plant (i.e. a low phi-factor). The data is produced from tests with di-tertiary butyl peroxide in test cells which have a different mass and hence produce different phi-factors.

Sample mixing

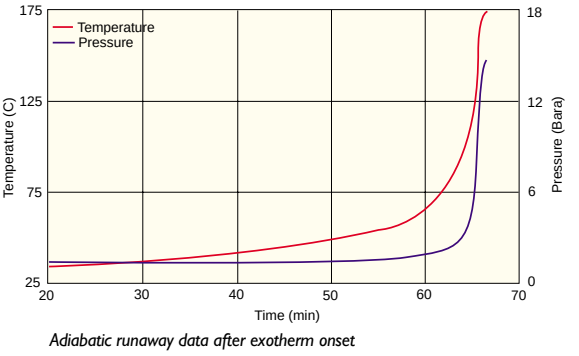
For viscous and heterogeneous systems where mixing is critical, the PHI-TEC can be equipped with mechanically stirred sample cells to give realistic plant conditions.



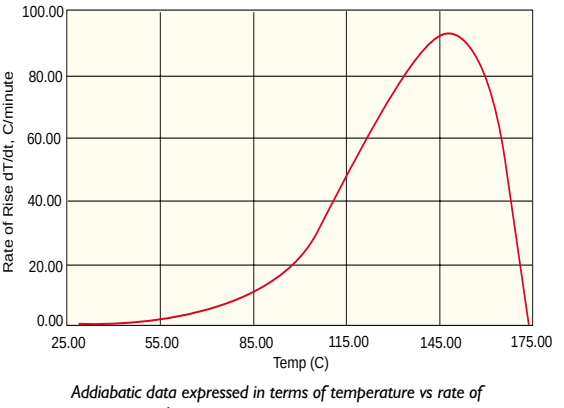
Heat-wait-search mode



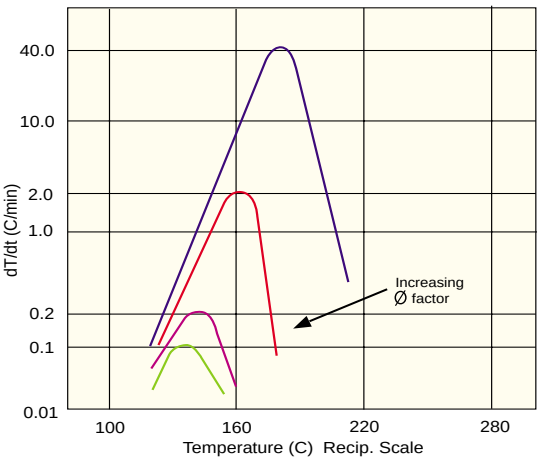
Linear ramp of sample – deviation from linearity indicates exotherm



Adiabatic runaway data after exotherm onset



Addiabatic data expressed in terms of temperature vs rate of temperature rise



Rate of temperature rise using different test cells

HEL Limited

HEL is an international company offering leading edge technology solutions to the process development chemist. We offer you the tools for safe and efficient scale up of chemical processes. HEL specialises in producing research equipment that can address a wide range of chemistry applications with a common theme: improvements in the quality of a process being developed, but obtained more quickly.

These devices include Process Screening, Parallel Synthesis, Calorimetry (Adiabatic and Reaction) as well as Automated Reactors for the pre-pilot plant stage. We have built our name, and product range, on the basis of aggressive research and development and therefore we know that we currently have the most comprehensive and powerful solutions to allow you, the user, to develop... better chemistry - faster.

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