TOLL MANUFACTURING: RAPID ASSESSMENT OF REACTOR RELIEF SYSTEMS FOR EXOTHERMIC BATCH REACTIONS

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SYNOPSIS

Relatively straightforward experiments in a state-of-the-art low thermal mass adiabatic calorimeter provide the information necessary for rational vent sizing calculations for batch or semi-batch reactors. The experiments should correspond to carefully analysed worst credible maloperation scenarios. Data from the experiments can be presented in a flexible graphical format and applied to a variety of reactor systems operated with different batch sizes, filling fractions, relief set pressures and allowable overpressures.

Key words : exothermic, runaway, reaction, venting, relief, batch, semi-batch

1. INTRODUCTION

Many international speciality chemical companies use worldwide networks of toll manufacturers to produce their products according to standard recipes. In principle the facilities provided by the toll manufacturer need to be thoroughly assessed for any new process requirements. However, in practice, economic and financial pressures frequently mean that there is only a superficial analysis of the reaction hazard and that even the design of the primary safety feature, that is the relief system, is not properly undertaken.

This paper describes how, in many cases, a single laboratory scale experiment in a suitable adiabatic calorimeter can be used both to quantify the potential explosion hazard and to size the relief device required to protect a batch or semi-batch reactor vessel. This will be possible in situations where there is sufficient experience to enable informed decisions about reaction type and nature of the vented flow to be made. The final relief analysis is presented in terms of design charts which enable the toll manufacturer to evaluate the vent area needed for a given mass of reactant once reactor void fraction, relief set pressure and allowable overpressure have been specified. The results are presented in readily digestible form so that relief sizing can be accomplished with confidence even by the inexperienced design engineer. Simple methods for allowing for the length and complexity of the relief line are provided.

2. THEORY

When the scale of chemical preparations is altered significantly a number of changes in the behaviour of chemical systems can be anticipated. One of the most important of these results from the fact that on the small scale the thermal mass of the reactor vessel is usually a much larger fraction of the total thermal mass of the system than for large scale operations. This is expressed in terms of the phi factor, defined by equation 1:

$$\phi = 1 + \frac{\textit{thermal mass of vessel}}{\textit{thermal mass of reactants}} \tag{1}$$

For industrial scale equipment phi often falls between 1 and 1.05. Except for the most carefully engineered small scale equipment, ϕ is much larger. Unfortunately data obtained in equipment with a large phi factor cannot readily be used for vent sizing calculations relating to large scale reactors with much smaller values of phi.

Most fine chemicals and pharmaceuticals are manufactured in batch or semi-batch reactor systems and many of the chemical process routes involved are inherently exothermic. The potential for these systems to undergo thermal runaway is well known. In the event of such behaviour the system pressure will rise either because of the increase in vapour pressure of the reacting mass as the exotherm develops (a vapour pressure system) or because of the generation of inert gases (a gassy system) or both (a hybrid system). At some designated pressure, relief will probably be required, either by venting to the atmosphere or by relieving into an external catchpot or dump tank. Relief of gassy systems through an appropriately sized line will arrest the pressure build up but can do little to ameliorate the exothermic runaway. Vapour pressure and some hybrid systems behave differently. For reactors operating at above the atmospheric boiling point of the reactor contents, as the system pressure falls following relief a point will be reached at which the reacting mixture boils at the prevailing pressure. When this happens the enthalpy of reaction will provide the latent heat for the flashing off of reactants and/or products. As pressure continues to fall the boiling point of the reactor contents will also fall and so the thermal runaway can be ameliorated or even totally arrested by this sequence of events. Such systems are referred to as "tempered." Relief of gassy, tempered or hybrid systems can be in a single gaseous phase discharge or, more usually, as a two phase mixture of gas and/or vapour and liquid. In this latter case the flow can be in the form of a pseudo-homogeneous two phase discharge, in the bubbly flow regime, of a churn turbulent form or as a two phase droplet flow. These different physical regimes are listed in figure 1. Safe, but not overly conservative, vent sizing requires specification of these reaction characteristics.

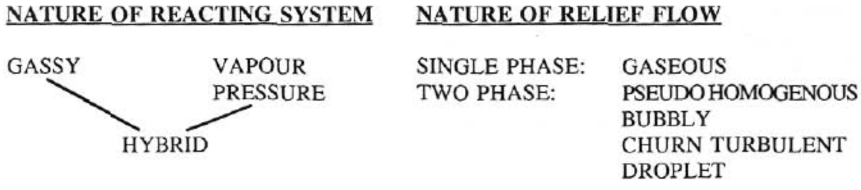

FIGURE 1 : ESTABLISHING THE CHARACTERISTICS OF THE REACTING SYSTEM

To size a reactor relief line rationally several small scale adiabatic calorimetry measurements are required. However, by making realistic "worst case" assumptions in many cases only a single experiment is needed. This should be intended to mimic identifiable worst credible maloperation conditions, i.e. loss of cooling, specified reactant accumulation, mischarging, etc, or an appropriate combination of these scenarios. The relief line size required to achieve a given depressurisation duty is normally largest when the relief discharge is in the form of a "pseudo homogenous" two phase mixture. Unless evidence to the contrary has been gathered, and a less conservative assumption can safely be made, it is a reasonable assumption to design the vent for pseudo homogeneous two phase flow. This is the approach adopted in this paper.

A study of the chemical species present in the reactor will probably give a sound indication of whether the system is likely to be tempered. Systems containing compounds which at atmospheric pressure boil at temperatures well in excess of the normal reactor operating temperature are unlikely to display strong tempering. Evidence of whether the system is vapour pressure dominated can also be derived from small scale experiments: these will be discussed later.

2.1 Vapour pressure and hybrid reactions which temper. Pseudo homogenous two-phase flow

Suppose that a runaway is vented when the temperature is T_s (corresponding to the relief set pressure P_s): at this temperature the rate of temperature rise is $(dT/dt)_s$. If the pressure is allowed to increase beyond the relief opening pressure by say 10% to P_m (corresponding to T_m) then the rate of temperature rise will be higher and equal to $(dT/dt)_m$. For a reactor of volume V containing mass m of reactants the frictionless vent area for pseudo homogenous two-phase flow can be calculated from equation 2, Leung (1).

$$A = \frac{M\bar{q}}{G\left\{\left[\frac{V}{m}\,T_s\,r\left(\frac{dP}{dT}\right)\right]^{1/2} + (Cp\Delta T)^{1/2}\right\}^2} \qquad (2)$$

$\bar{q}$ is the average rate of heat release between the vent opening pressure and the maximum pressure and is defined by equation 3.

$$\bar{q} = [(dT/dt)_s + (dT/dt)_m\ ]\ C_p/2 \qquad (3)$$

dP/dT is the slope of the vapour pressure versus temperature curve at the vent opening conditions, ΔT is equal to $T_m - T_s$ and is the rise in temperature corresponding to the allowable overpressure i.e. $(P_m - P_s)$. Thus $(T_m - T_s)$ is zero for an overpressure of zero and r is equal to 1 for a pure vapour pressure system. Equation 2 can also be used for tempered hybrid systems in which case r is defined as the system vapour pressure divided by the total pressure. Note that the assumption of tempering will often have to be verified experimentally. This may not be necessary when large quantities of a solvent are present at temperatures in excess of its atmospheric boiling temperature. From equation 2 it is clear that, all other things being equal, as the amount of non condensible gas increases, r falls and a larger vent is required.

G is the mass flux of the two phase flashing flow ($kg/(m^2\ s)$) which can be approximated by equation 4.

$$G = (dP/dT)\ (T_s/Cp)^{1/2} \tag{4}$$

Invoking the Clausius Clapeyron approximation results in equation 5.

$$G = \frac{\Delta H_v}{v_{fg}}\ (T_s\ C_p)^{-1/2} \tag{5}$$

Finally, the volume of the reactor and the mass of its contents can be related simply through equation 6.

$$M = V\,(1 - \alpha)\ \rho \tag{6}$$

Combining equations 2, 3, 4 and 6 gives:

$$\frac{A}{M} = \frac{[(dT/dt)_s + (dT/dt)_m]\ C_p/2}{\left[\frac{dP}{dT}\right]\left(\frac{T_s}{C_p}\right)^{1/2}\left[\left(\frac{1}{(1 - \alpha)\rho}\ T_s r\ \frac{dP}{dT}\right)^{1/2} + (C_p \Delta T)^{1/2}\right]^2} \tag{7}$$

2.2 Gassy reactions. Pseudo-homogeneous two-phase flow

If the maximum amount of gas generated during the course of a reaction is $\dot{F}_g$ (m^3/kgs) and if venting produces a two-phase froth of density M/V then the frictionless vent area required is given by equation 8.

$$A = \frac{\dot{F}_g\,M^2}{GV} \tag{8}$$

$\dot{F}_g$ can be evaluated from a small scale experiment in a sealed reactor of volume V_c at temperature T_c. Then,

$$\dot{F}_g = \frac{1}{M_s}\left(\frac{V_c}{P_m}\right)\left(\frac{T_p}{T_c}\right)\left(\frac{dP}{dt}\right) \tag{9}$$

where M_s is the mass of sample tested, P_m is the maximum allowable pressure in the reactor and T_p is the reactant temperature corresponding to the maximum value of dP/dt. Note that since the temperature will continue to rise after the vent device has opened it is important to ensure that the gas generation rate used corresponds to the maximum value which could occur and not simply the value at vent opening conditions. This conservative assumption often leads to larger vent sizes than are actually needed because the two-phase flow will have emptied the reactor before the conditions corresponding to the maximum dP/dt could develop within the reactor.

The two-phase mass flux in equation 8, G, must be calculated from the equation given in Tangren et al (2) in place of equations 4 or 5 which are not valid for gassy reactions.

3. EXPERIMENTAL STUDIES

3.1 The PHI-TEC II Adiabatic Calorimeter

Experimental work was carried out in the PHI-TEC II adiabatic calorimeter, Singh (3). This equipment is illustrated in Figure 2 and is designed to feature all the attributes recommended by the DIERS project, Fisher et al (4). At the heart of the equipment is a low thermal mass test cell of 110 cm^3 volume, 1. Usually this is made of stainless steel with a 0.15 mm wall thickness, but test cells made from a variety of other materials can be used. The contents of the cell are mixed using either a magnetically driven stirring bar or by using a direct drive agitation test cell. The test cell is surrounded by three independent guard heaters, 2, which are controlled to match the sample temperature which is measured within the test cell, 8: these reduce heat losses from the sample down to a very low level, and thus maintain sample adiabaticity. The guard heaters can track the sample temperature at up to 200°C min^{-1}. The test cell and heaters are mounted in a calorimetry assembly, 3, which sits within a high pressure containment vessel, 4. A computer handles the temperature control duty and also activates a pressure compensation system. High pressure nitrogen is admitted to, or bled off from, the pressure vessel so that the pressure therein closely matches the measured sample pressure, 9, within the test cell. This enables the test cell to be used at pressures in excess of 100 bara despite its lack of mechanical strength. The computer is also used for data acquisition and control of the electronics.

3.2 The Experimental Details and Results

The experiments described in this report are for an exothermic polymerisation system for which temperatures are normally controlled in the 45 - 65°C range with a final reaction step at 84°C. For reasons of confidentiality details of the reaction system are not divulged. The data in Figures 3 - 10 are all for this system and result from an experiment conducted in HEL's laboratory.

Figure 3 shows a plot of sample temperature and pressure as a function of time. Thermal runaway develops from 50°C and accelerates continuously through to a maximum temperature of 254°C. This particular test was on 79.10g of material in a directly agitated test cell. Close examination of the test data file reveals that at 39.8 bara (175.1°C) the shaft seals on the test cell started to leak. The temperature continued to rise to 254°C reaching a peak rate in excess of 370°C/min at approximately 218°C. During this period the pressure first fell to approximately 30 bara and then rose to just over 50 bara. At this point the runaway was too fast for the PHI-TEC II equipment to track and the test cell ruptured. Obviously data beyond 175.1°C (when the test cell shaft seals first started to leak) is suspect and should not be used in any design context.

Figure 4 shows the same data with pressure plotted as a function of temperature. At 165°C the pressure rises rapidly, probably due to inert gas generation. Despite pressure compensation, this led to the shaft seal leakage problem referred to above and the eventual rupture of the test cell at approximately 50 bara, and 250°C. The pressure-temperature data is re-plotted as ln (Pressure/Pascals) vs - 1000/(Absolute temperature) in Figure 5. For vapour pressure systems obeying an Antoine type relationship a linear plot would be expected. This is approximately the case from 60 to 140°C (-1000/T from - 3.00 to -2.42), but at higher pressures the very strong deviation from linearity confirms that this is a hybrid system with significant gas generation above a temperature of 140°C.

A measure of the instantaneous rate of reaction is provided by the derivative of the sample temperature with respect to time. This is shown as a function of temperature in Figure 6. This is of the classic form expected for a strongly exothermic runaway reaction.

4. VENTING REQUIREMENTS

In order to size a relief line for this reaction system it is convenient to prepare a number of additional plots. In Figure 7a a detailed graph of pressure vs temperature is shown together with a third order polynomial fit to the data. Figure 7b is analogous data but with temperature as the ordinate. The early portion of figure 6 is expanded in Figure 8 and the data is described by a second order polynomial. Figures 7a and 7b and 8 must span the range of pressures and temperatures which could be experienced during reactor relief conditions.

4.1 Examples of vent sizing calculations

The reaction studied is to be carried out commercially in reactors with volumes between 3 and 20 m^3. The reaction mixture has a density of 1200 kgm^{-3} and a heat capacity of 2000 J kg^{-1} K^{-1}. Reactor void fractions are between 0.5 and 0.7 and the relief set pressure is typically between 1 and 2 barg with an allowable overpressure of up to 1/2 bar. From previous experiences of industrial scale venting of this reaction system it is known that the reaction is tempered: the approximate linearity of figure 5, at least up to temperatures of the order of 140°C, adds weight to the assumption that this is a vapour pressure system and that tempering would be expected. Venting during the exothermic runaway can be used as definite confirmation of this and is a recommended procedure. However this is not illustrated in Figures 3 or 4.

Vent sizing requirements are now calculated using the following methodology:

i) Specify P_s, ΔP, V, α_o, ρ and C_p.

ii) From figure 7b calculate T_s at a specified P_s. Likewise, calculate T_m at $P_m = P_s + \Delta P$. Then find $\Delta T = T_m - T_s$.

iii) Differentiate the polynomial fit found in Figure 7a to give dP/dT. From this expression evaluate dP/dT at T_s.

iv) From the polynomial fit in Figure 8 find dT/dt both at T_s and at T_m.

v) Assume that the reaction system is vapour pressure dominated (not a conservative assumption and only justifiable when there is good evidence that tempering will occur). Use equation 7 with a value of $r = 1$ to find the value of A/M.

vi) Do this repeatedly to produce the necessary data for Figures 9 and 10 or other such diagrams.

Figure 9 is for a reactor void fraction of 0.7 whereas figure 10 is for $\alpha = 0.5$. Charts appropriate to other values of minimum reactor void fraction can also be prepared. For a defined relief set pressure and specified overpressure the frictionless vent area required per unit mass of reactants, i.e. A/M, can be read off from the ordinate directly. The actual vent area needed is then found by multiplying this number by M/Cd where Cd is the discharge coefficient for the relief device: this is seldom less than 0.5 and usually is close to unity.

The ideal vent line downstream of the relief device is straight and short. In practice this may not be possible and account must be taken of the geometric complexity of the relief line. This is achieved by taking the vent line equivalent length and using table 1 (for vapour pressure systems) or table 2 (for gassy systems) to define an additional flow coefficient F. This further increases the diameter required for the vent line as indicated by equation 10.

$$A_{actual} = \left(\frac{A}{M}\,frictionless\right) \times \frac{M}{Cd} \times \frac{1}{F} \tag{10}$$

5. CONCLUSIONS

A reactor relief system should be designed to cope with the venting requirements of the worst credible maloperation conditions. These must be defined with great care. For many batch and semi-batch industrial operations a single runaway experiment in a low thermal capacity adiabatic calorimeter can generate all the data required for rational vent sizing. All data presented in this paper is derived from a single experiment.

Vent line sizing for frictionless flow is accomplished using figures 9 or 10, or equivalent figures prepared for other appropriate values of α. The discharge coefficient of the relief device and the appropriate flow coefficient, defined in tables 1 or 2, are then used to calculate the actual vent area required for safe relief.

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NOMENCLATURE:

		UNITS
A	frictionless vent area	m^2
Cd	discharge coefficient of relief device	-
Cp	specific heat	kJ $(kgK)^{-1}$
D	Vent line diameter	m
F	flow coefficient, tables 1,2	-
$\dot{F}_g$	maximum gas generation rate	m^3 $(kg\ s)^{-1}$
G	mass flux of 2-phase flashing flow	kg $(m^2s)^{-1}$
ΔH_v	latent heat of vaporisation	kJ kg^{-1}
L	equivalent length of vent line	m
M	reactant mass	kg
M_s	mass of sample in small scale test cell	kg
P	pressure	N m^{-2}
$\bar{q}$	average heat release rate between T_s and T_m	kW kg^{-1}
r	factor in equation 2, defined below equation 3	-
T	temperature	K
ΔT	$T_m - T_s$	K
V	Volume	m^3
v_{fg}	difference in specific volume between vapour and liquid	m^3 kg^{-1}

GREEK

α	void fraction	-
ρ	density	kg (m^{-3})
ϕ	phi-factor, defined by equation 1	-

SUBSCRIPTS

c	test cell	-
m	maximum value	-
p	conditions at which dP/dt is maximum	-
s	set value (for pressure relief)	

TABLE 1

FLOW COEFFICIENT vs. VENT LINE EQUIVALENT LENGTH TO DIAMETER RATIO FOR VAPOUR PRESSURE SYSTEMS

L/D	F
0	1.0
50	0.85
100	0.75
200	0.65
300	0.55
400	0.5

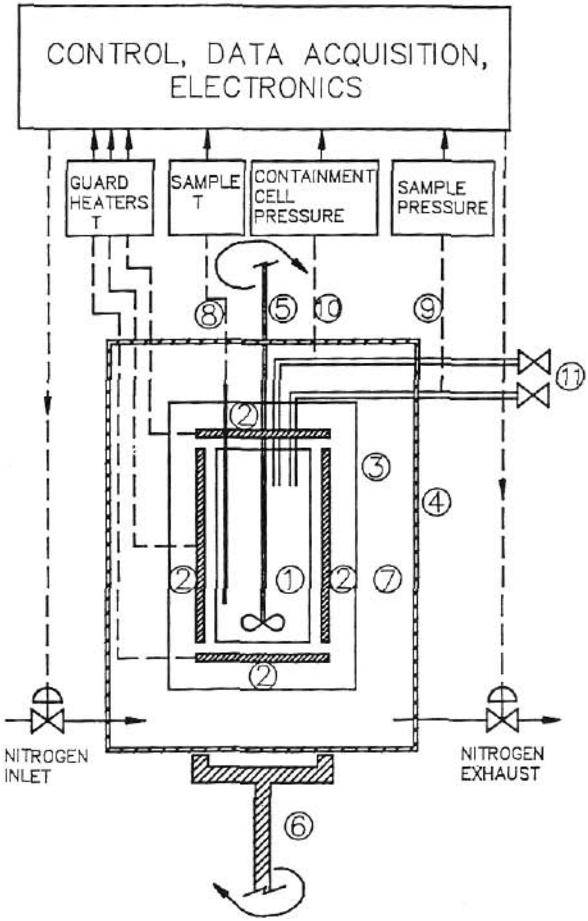
TABLE 2

FLOW COEFFICIENT vs. VENT LINE EQUIVALENT LENGTH TO DIAMETER RATIO FOR GASSY SYSTEMS

L/D	F
0	1.0
50	0.7
100	0.6
200	0.45
300	0.38
400	0.33

FIGURE 2

THE PHI–TEC ADIABATIC CALORIMETER FOR THE ASSESSMENT OF REACTIVE MATERIALS



1. **ADIABATIC TEST CELL, UP TO 120 cm³**
2. **3 RADIANT GUARD HEATERS**
3. **CALORIMETRY ASSEMBLY**
4. ***PRESSURE VESSEL, 4 LITRES***
5. **DIRECT STIRRING (OPTIONAL)**
6. **MAGNETICALLY DRIVEN AGITATOR**
7. **INSULATION**
8. **SAMPLE THERMOCOUPLE**
9. **SAMPLE PRESSURE TRANSDUCER**
10. ***VESSEL PRESSURE TRANSDUCER***
11. **CONNECTIONS FOR INJECTION, VENTING, DISPOSAL SYSTEM (OPTIONAL)**

Figure 3: Temperature and Pressure versus Time
Polymerisation reaction

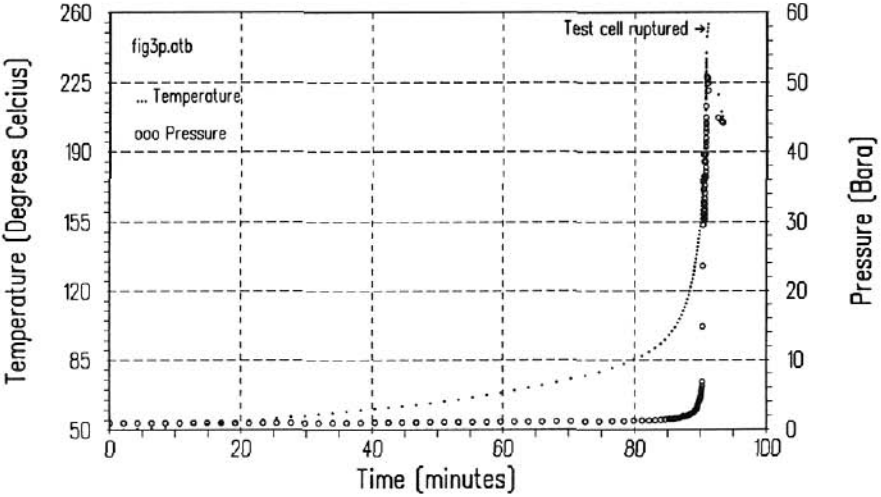


Figure 4: Pressure versus Temperature
Polymerisation reaction

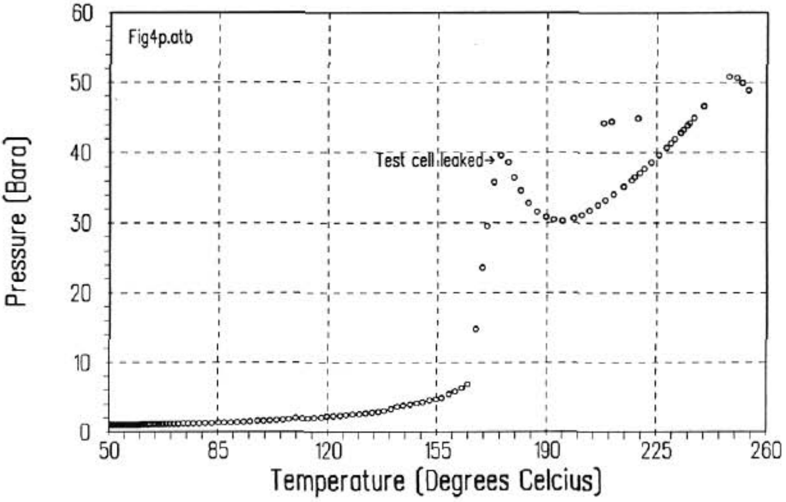


Figure 5. Ln (Pressure/Pascals) versus -1000/Absolute temperature.

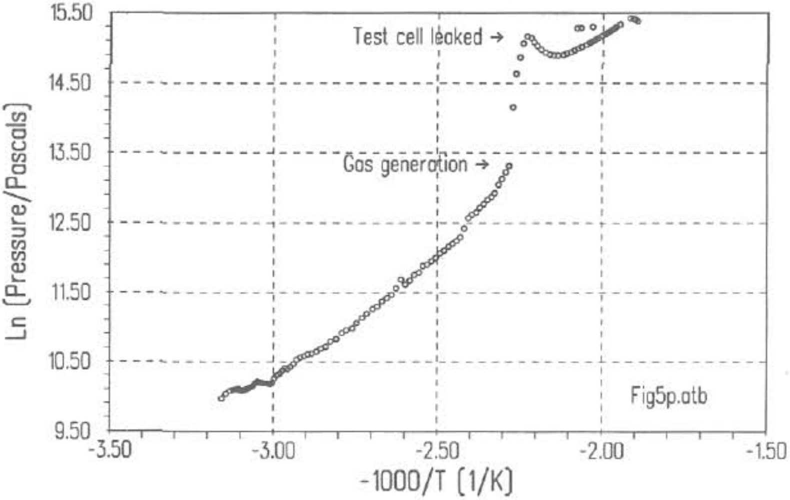


Figure 6: Self-heat rate versus Temperature
Polymerisation reaction

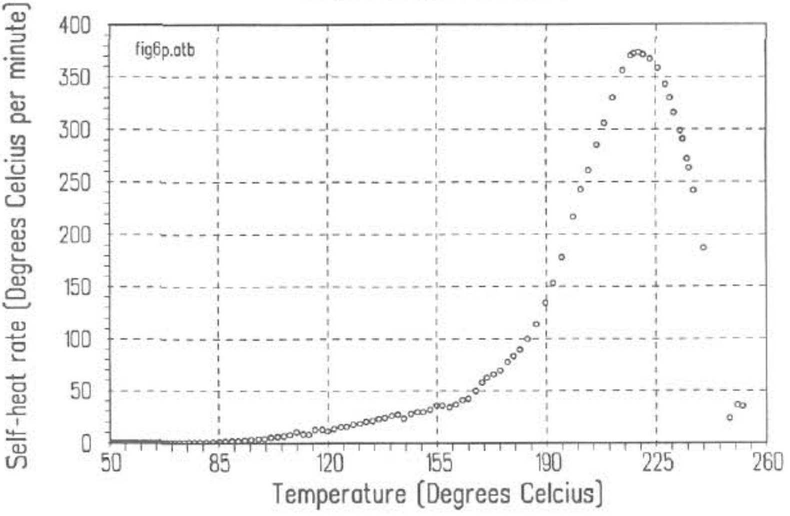


Figure 7a: Pressure versus Temperature. Expanded region of Figure 4. Polymerisation reaction

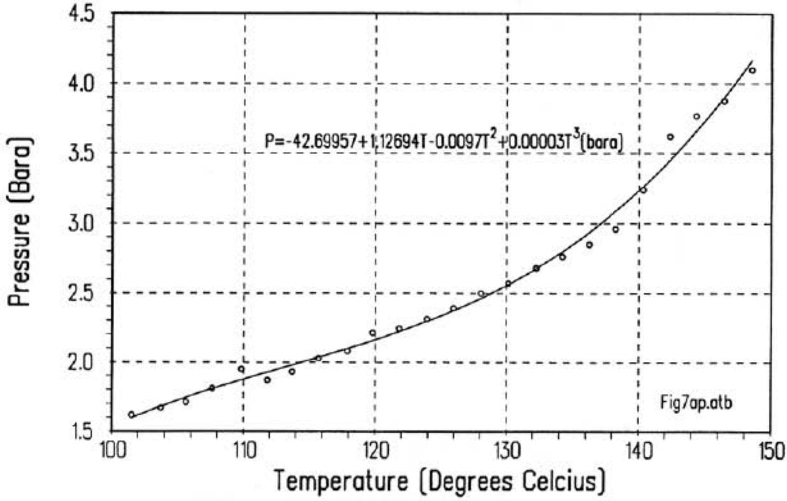


Figure 7b: Temperature versus Pressure. Inverse of Figure 7a. Polymerisation reaction

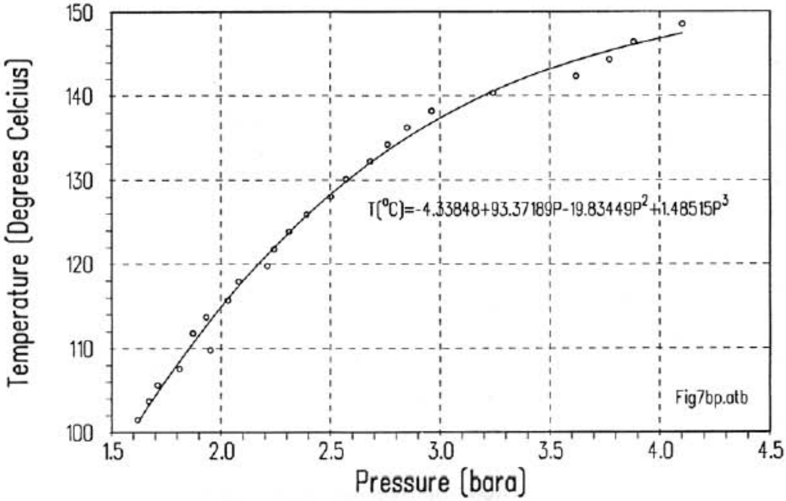


Figure 8: Self-heat rate versus Temperature
Expanded region of Figure 6. Polymerisation reactn

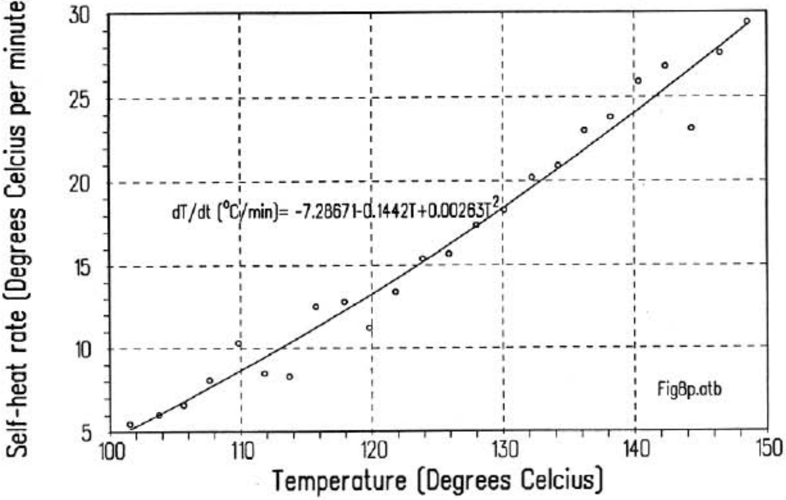


Figure 9: Frictionless vent relief area divided by
reactant mass versus reactor overpressure

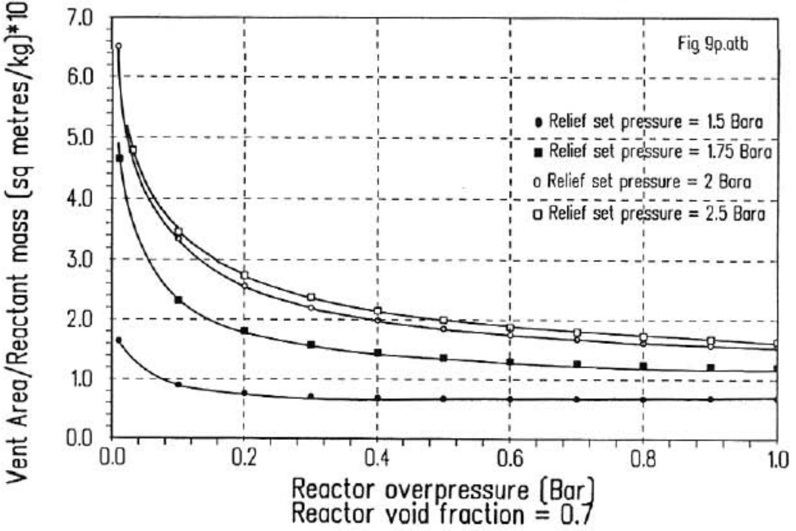


Figure 10: Frictionless vent relief area divided by reactant mass versus reactor overpressure