ANNEX 1

BASIS OF SAFETY

A1.1 INTRODUCTION

The basis of safety for a chemical reaction process is the combination of measures which are relied upon to ensure safety. Defining the basis of safety for a reactor is essential as it highlights those aspects of the design and operation (hardware, protective systems and procedures) which are safety-critical. There are many factors to be considered and further advice is given in references 1 and 2.

The basis of safety can only be selected once all the significant hazards have been identified and evaluated[3,4] (see Chapter 3). There are a number of options for the safe operation of chemical reactions and these are outlined below.

A1.2 INHERENTLY SAFER DESIGN

Where possible, hazards should be eliminated or their effects reduced by inherently safer design, for example:

a) Avoiding hazardous raw materials or intermediates.

b) Changing from batch to semi-batch or continuous processing. This can reduce the hazardous inventory in process. Also, the addition of reactants can be stopped in the event of a process failure.

c) Use of solvents to act as a heat sink. In some cases, the addition of a higher boiling point solvent may prevent the reaction mixture boiling and over-pressurising the reactor. In other cases, lower boiling point solvents can cause the reaction to temper at a lower temperature and control the runaway in this way. However, the possibility of solvent being left out of the batch should be considered.

d) Minimising hazardous inventories.

e) Designing the plant to contain the maximum pressure.

Further information and examples of inherently safer design methods are given in references 3, 5 and 6. It should be noted that the successful incorporation of such measures normally depends on the hazard assessment procedure starting at an early stage in the process development.

In addition, it worth considering inherently less polluting processes at the design stage.

However, in order to maintain a viable process, significant hazards may still remain and further safety measures will be necessary. These can be grouped broadly as "preventive" or "protective" measures.

A1.3 PREVENTIVE MEASURES

Preventive measures either take automatic remedial action or allow for manual intervention to prevent the conditions for uncontrolled reaction being achieved. They include the use of sensors, trips, alarms, control systems, and other safety features. These measures require a thorough understanding of the safe operating envelope within which the process must be maintained.

Where systems incorporating manual intervention are used, they have the advantage that they can be flexible and allow operator judgement to be applied. However, their reliability may be open to question as they are dependent upon a number of factors, including complexity of the task; system design, time available for response and operator training. Further information on this is given in references 7 and 8.

Automatic safety-related control systems have the advantage that high levels of safety integrity can be achieved. However, great care needs to be taken in their design. Such systems can be complex, they may be subject to unforeseen failure modes and it can be difficult to establish their level of safety integrity. Further advice on the design and specification of such systems is given in references 1, 2, 9 and 10.

A1.4 PROTECTIVE MEASURES

Protective measures mitigate the consequences of a runaway reaction. They are rarely used on their own, as some preventive measures are usually present to reduce the demand on the protective system. The main options are:

a) emergency pressure relief;

b) crash cooling;

c) reaction inhibition;

d) drown-out.

A detailed knowledge of the runaway reaction, in particular the rate of runaway, is needed for the specification or design of protective systems. With the exception of (a), these measures are normally reliant upon control systems to operate, and the safety integrity of such systems, including the control system, *is an important factor* in their selection[1].

This Workbook focuses on the design of emergency pressure relief systems.

A1.5 SELECTION OF SAFETY MEASURES

A1.5.1 Factors affecting selection

The selection of safety measures for a particular application will depend upon a number of factors, including:

a) The ease with which runaway can be prevented. For example, in the event of process failure, it is often easier to stop a semi-batch or continuous reaction than an "all-in" batch reaction (see reference 3 for further information).

b) The worst case consequences that could result.

c) The applicability of the various protective measures.

d) The compatibility of safety measures with the plant operation.

A common approach for reactors has been the provision of preventive measures, including control systems and safety trips, backed up by an emergency relief system. The addition of a relief system is seen as having a number of advantages:

a) It has different failure modes to the preventive measures.

b) It provides a relatively passive means of protection.

c) It may still provide adequate protection if all other systems fail.

However, there are instances when companies decide not to incorporate an emergency relief system. The main reasons given are:

a) Cost: In particular, equipment required downstream of vents, such as knock-out pots, scrubbers or flares etc., may be prohibitively expensive.

b) Environmental: Where vented materials are too hazardous to vent directly to atmosphere and there are difficulties in designing effective or reliable downstream treatment or containment systems.

c) Technical: The required relief rates may be so high that it may not be possible to provide a large enough relief system.

In such cases, it may be acceptable to rely on preventive measures, of sufficient integrity, either alone or in combination with alternative protective measures.

A1.5.2 Overall requirements for basis of safety

Whatever the basis of safety selected it is important that:

a) all foreseeable hazards are addressed; and

b) suitable and sufficient safety systems are in place to reduce the overall risk to a level that is as low as reasonably practicable.

In addition, the safety measures should be supported by effective organisational procedures such as rigorous training, instruction and supervision of operators, maintenance and emergency procedures.

REFERENCES FOR ANNEX 1

1. Draft Standard IEC 61508, "Functional Safety of Electrical/ Electronic/ Programmable Electronic Safety-Related Systems", (Contact BSI/IEC for availability)
2. Draft Standard IEC 61511, "Functional Safety: Safety Instrumented Systems for the Process Industries", (Contact BSI/IEC for availability)
3. J A Barton & R L Rogers, (ed.), "Chemical Reaction Hazards", 2nd Edition, IChemE, 1997, ISBN 0 85295 3410
4. T A Kletz, "HAZOP and HAZAN - Identifying and Assessing Process Hazards", 3rd edition, IChemE, Rugby, 1992
5. T A Kletz, "Cheaper Safer Plants or Wealth and Safety at Work", 2nd Edition, IChemE, 1985
6. R L Rogers and S Hallam, "A Chemical Approach to Inherent Safety", IChemE Symposium Series No. 124, 235-241 , 1991
7. "Human Factors in Industrial Safety", HS(G)48, HSE Books, 1989
8. M S Carey, "Safety Management of Process Faults: A Position Paper on Human Factors; Approaches for the Design of Operator Interfaces to Computer Based Control Systems", HSE Contract Research Report No 60/1993, HSE Books, 1993
9. "Programmable Electronic Systems in Safety Related Applications, 2, General Technical Guidelines", HSE Books, 1987

10. "Safety Related Instrument Systems for the Process Industries (Including Programmable Electronic Systems)", Publication No 160, The Engineering Equipment Manufacturers and Users Association (EEMUA), 14/15 Belgrave Square, London SW1X 8PS

ANNEX 2

EXPERIMENTAL METHODS

A2.1 INTRODUCTION

The methods for pressure relief system sizing, described in this Workbook, require certain data that are best measured experimentally. It is recommended that the experiment seeks to simulate the plant-scale runaway reaction. Adiabatic calorimetry is required for this purpose (see A2.2 below). It can be dangerous to attempt to extrapolate data for the normal reaction to the higher temperatures experienced during runaway, particularly as unexpected new reactions may begin at higher temperatures.

This Annex describes the special requirements for adiabatic calorimeters which are suitable for obtaining runaway chemical reaction data for relief system sizing. Methods for obtaining the data required for relief system sizing and for determining the system type for relief sizing (see 4.2) are then described.

Measurement of data for relief system sizing is normally only done once the worst case conditions, or a very small number of worst case candidates, have been identified by small-scale screening tests (see Chapter 3). The calorimetry described in this Annex can be carried out in-house if a suitable calorimeter is available. Alternatively, there are a number of consultancies who will carry out the necessary measurements. Information on these can be obtained from the Institution of Chemical Engineers' list of consultants.

A2.2 SUITABLE ADIABATIC CALORIMETERS

A2.2.1 Requirements of suitable adiabatic calorimeters

The surface to volume ratio of a laboratory-scale reactor is many times greater than that of a plant-scale reactor. This has two effects:

a) The heat losses at plant-scale are much smaller (for example, 0.04-0.08 W/kgK for a 20 m^3 reactor compared with 0.2 W/kgK for a 50 litre reactor[1]).

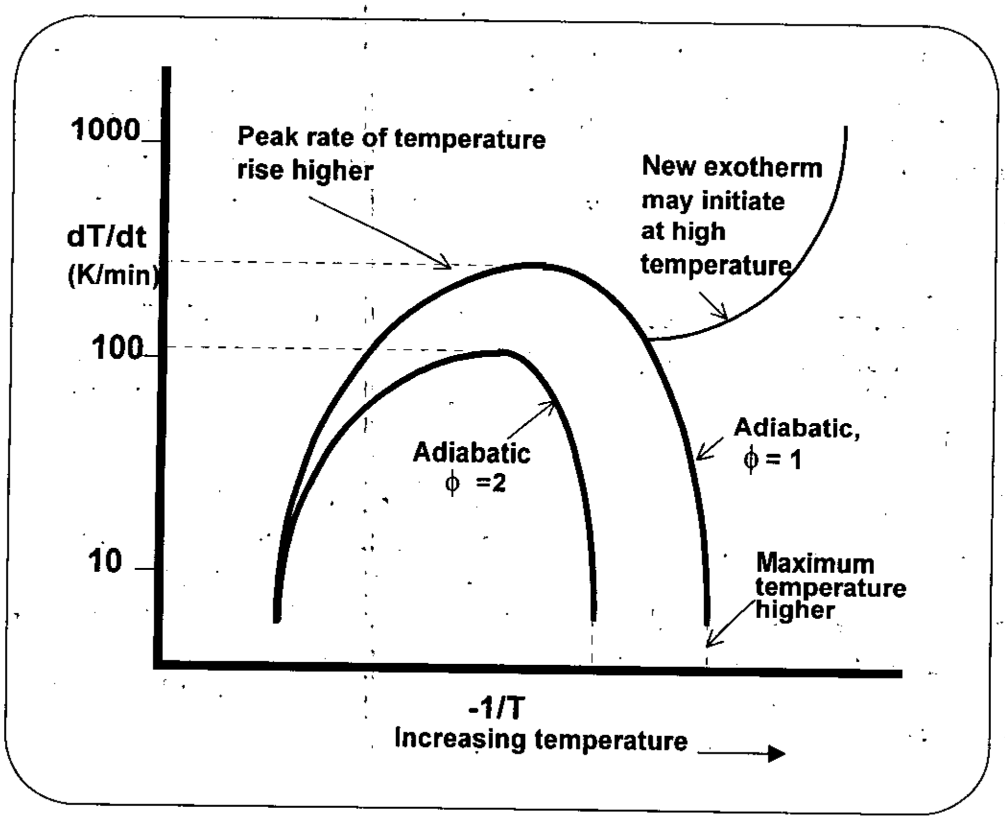
b) The percentage heat transferred into the vessel wall is much smaller at plant-scale than in many laboratory-scale reactors. This is characterised by the thermal inertia or "Phi-factor", ϕ, where:

$$\phi = \frac{\text{Heat capacity of sample plus sample container}}{\text{Heat capacity of sample}} \qquad \text{(A2.1)}$$

For a full-scale reactor, ϕ approaches 1.0.

Any heat losses from the sample, either into the environment or the test vessel wall, act to reduce the sample temperature. This can lead to a serious underestimation of the rate of reaction. The final temperature attained by the runaway will be less in the laboratory-scale reactor than at plant-scale, and this could cause other reactions (such as decompositions) to be missed entirely on the smaller scale. See Figure A2.1.

Figure A2.1 **EFFECT OF THERMAL INERTIA**



To overcome these effects, a suitable adiabatic calorimeter, for measuring runaway reaction relief sizing data, will[1,2] :

a) be adiabatic (very low heat losses to the environment); and

b) have a thermal inertia, ϕ, close to unity, and normally in the range 1.05 to 1.1.

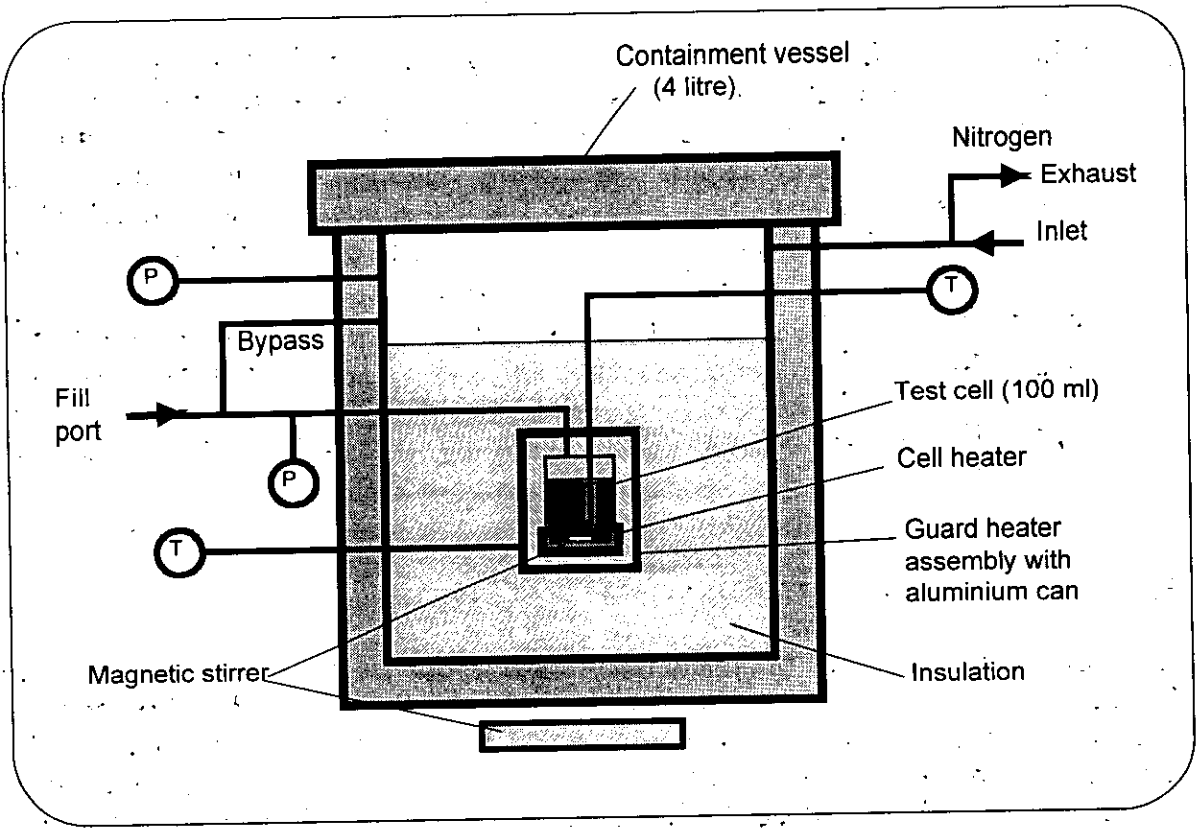
Information on a number of adiabatic calorimeters specifically designed for obtaining relief sizing data is given below.

It is possible, by making certain assumptions about the reaction kinetics, to correct adiabatic data measured in equipment with high thermal inertia. Methods are discussed in A2.7.2. These assumptions introduce uncertainty. Extreme caution must be applied if data are extrapolated to temperatures higher than those measured in the test. In particular, the possibility of side reactions or secondary decompositions at the higher temperatures, and their likely effects, should be considered.

A2.2.2 The DIERS bench-scale apparatus[2] (and derivatives)

This is shown diagramatically in Figure A2.2. The apparatus uses a sample size of approximately 100 ml. Adiabaticity is achieved by insulation and by a "guard heater" which is just outside the sample container (test cell) and automatically controls the temperature to be the same as that within the container. Low thermal inertia is achieved by using a very thin-walled test cell within a larger pressure containment vessel. The test cell is either operated in open mode (using a high superimposed nitrogen pressure in the containment vessel to suppress boiling), or in closed mode. A pressure control system which can either add or vent nitrogen from the containment vessel, is provided to equalise the pressure on either side of the test cell and prevent it from bursting.

Figure A2.2 DIERS BENCH-SCALE APPARATUS



The sample can be stirred using a magnetic stirrer. A heater is provided for rapidly heating the sample to the initial temperature required for the scenario being studied. There are facilities to inject one of the reactants into the calorimeter. Temperatures and pressures in the test cell and containment vessel are measured as a function of time and recorded by a data-logging system. A thermal inertia of about 1.05 can typically be achieved.

Commercially available examples of the DIERS bench-scale apparatus include:

(a) The VSP™ (Vent Sizing Package) calorimeter is produced by Fauske and Associates Inc., who were the main contractors to DIERS and who developed the design for the bench-scale apparatus.

(b) The PHI-TEC™ calorimeter[3], produced by Hazard Evaluation Laboratory Ltd, is another bench-scale apparatus. It allows venting outside of the containment vessel (to reduce clean-up between runs and to facilitate the selection of disposal systems) and heat input to simulate simultaneous external fire and runaway reaction.

(c) The APTAC™ (Automatic Pressure Tracking Adiabatic Calorimeter), marketed by Arthur D Little Inc., was developed by Union Carbide Inc. from the original DIERS bench-scale apparatus. The reaction is carried out in an approximately 130 ml spherical test cell placed in a 4 litre high pressure containment vessel. Further information is given in reference 4.

(d) The RSST™ (Reactive System Screening Tool) calorimeter[5], produced by Fauske & Associates Inc., is a smaller, less expensive calorimeter, intended for screening purposes (see Figure A2.3). It uses a 15 ml sample in an open glass bulb within a containment vessel. Nitrogen pressure in the containment vessel prevents boiling of the sample. The test is non-adiabatic but relies on a constant small heat input to the sample which compensates for the heat losses. Provided the RSST™ is correctly calibrated, so that there is a net rate of heat gain, the results should be safe for relief system sizing purposes but might be expected to overestimate the size of the relief system required. Because RSST™ runs are quicker and cheaper than those of the bench-scale apparatus, is it useful for assessing the worst case runaway for multi-purpose reactors.

A2.2.3 Adiabatic Dewar calorimeters

An alternative method of obtaining very low thermal inertia is the use of Dewar (vacuum) flasks[1,6]. For relief system sizing purposes, the Dewar must be capable of operating under pressure. A calorimeter would typically comprise a 1 litre stainless steel Dewar inside an oven which is programmed to follow the temperature inside the Dewar in order to achieve adiabaticity (see Figure A2.4). The oven should normally be situated inside a blast-resistant container in case the runaway causes failure of the Dewar. A thermal inertia of around 1.1 or better can typically be achieved. A number of designs are available, for example the ADCII™ from Chilworth Technology.

Figure A2.3 RSST™ CALORIMETER

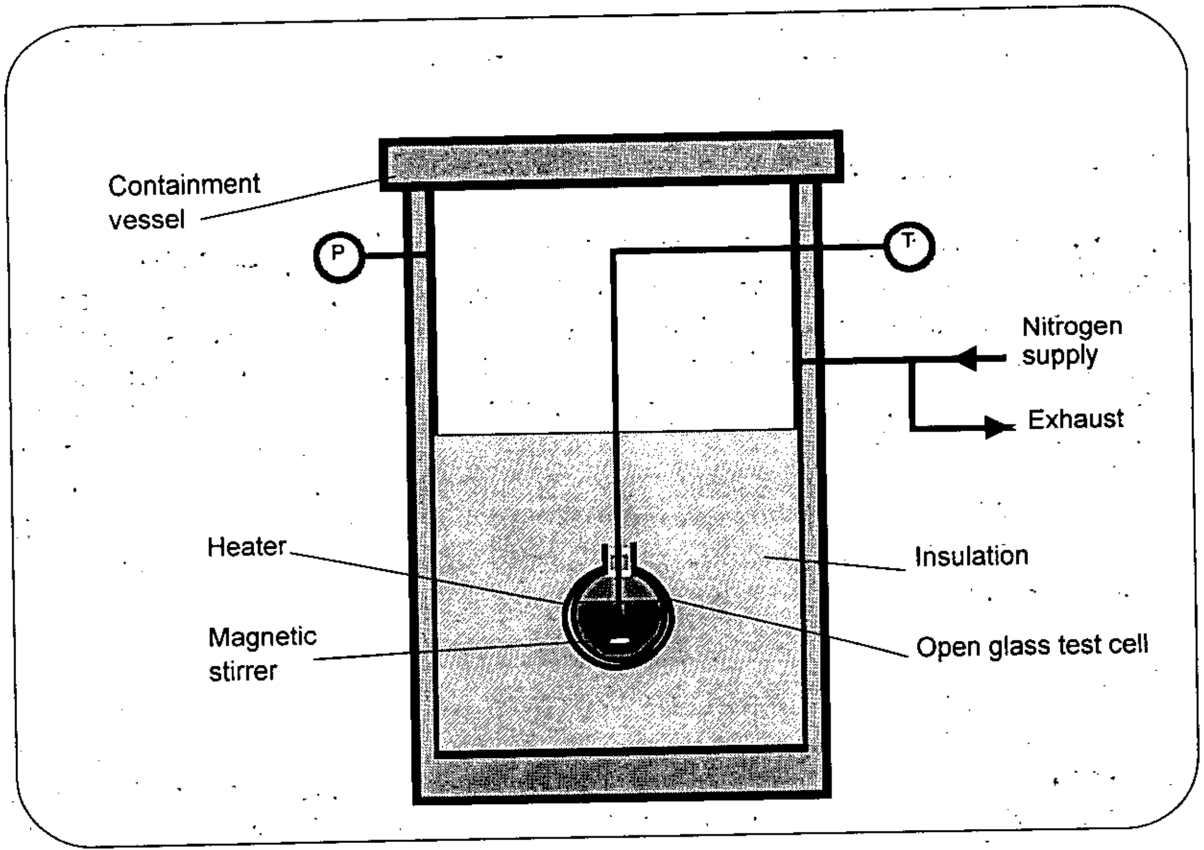
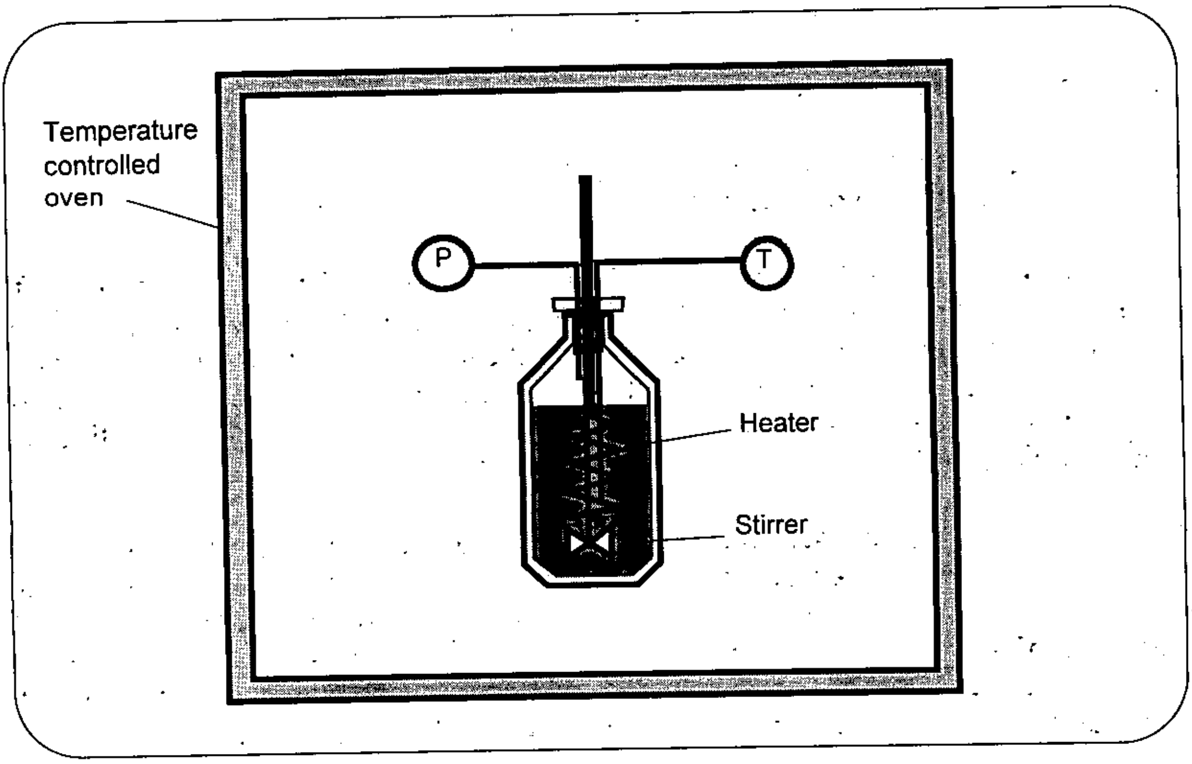


Figure A2.4 ADIABATIC DEWAR CALORIMETER



Adiabatic Dewar calorimeters are usually used in the closed mode. However, it is possible to incorporate a vent line to either an external containment vessel or to a burette for measuring the permanent gas evolution rate. This vent line contains an automatic valve to simulate the operation of the pressure relief system.

A2.2.4 Accelerating Rate Calorimeter (ARC^{TM})

The standard Accelerating Rate Calorimeter (ARC^{TM})[1,7] is adiabatic but has relatively high thermal inertia because it was designed for thermal stability measurements, for which thermal inertia is not critical. The sample is placed in a small bomb (approximately 10 ml), and can be heated to the initial runaway temperature. External heaters then track the sample temperature to ensure adiabaticity. Any data from the standard ARC would need careful correction to a thermal inertia of 1 before use for relief sizing purposes[7]. Recently an add-on "vent sizing unit" (VSUT^{TM}), which has low thermal inertia (typically 1.09 to 1.15), has been developed to allow the same types of relief sizing tests as for the DIERS bench-scale apparatus to be performed.

A2.3 CLASSIFICATION OF RELIEF SYSTEMS

This section is concerned with calorimetry to determine the classification of the reacting system (as described in Chapter 4) so that appropriate relief sizing methods can be used. The measurement of data for relief sizing is described in A2.4 to A2.6 below, depending on the results of the classification of system type for relief sizing.

A2.3.1 System type for relief system sizing

The classification of chemical systems into:

a) vapour pressure, hybrid or gassy, and
b) tempered or untempered

is described in 4.2. As described in A2.2.2 above, the DIERS bench-scale apparatus (and derivatives) can be operated with the test cell either closed or open to the containment vessel (see Figure A2.5). Different information is obtainable from the two types of test. Analogous tests can be done using an adiabatic Dewar calorimeter with an optional vent to an external containment vessel, or by an ARC^{TM} with added vent sizing unit (VSUT^{TM}).

In a closed test, the pressure measured is that due to the reacting system within the test cell. The pressure versus time and temperature versus time data can be used to obtain pressure versus temperature. The pressure can be corrected for the partial pressure of any pad gas to give the vapour pressure (see A2.7.1). This can be plotted on a Cox chart or Antoine plot (log pressure versus -1/ (temperature)). If the data fall on a straight line, the system is a pure vapour pressure system. If they do not, then the system may be either gassy or hybrid (see Figure A2.6). However, note that the Cox chart method is not always reliable. Vapour pressure systems with highly non-ideal physical properties, or with multiple components having a wide range of boiling points, may not give a straight line on the chart.

Figure A2.5 CLOSED AND OPEN TEST CELLS FOR THE DIERS BENCH-SCALE APPARATUS

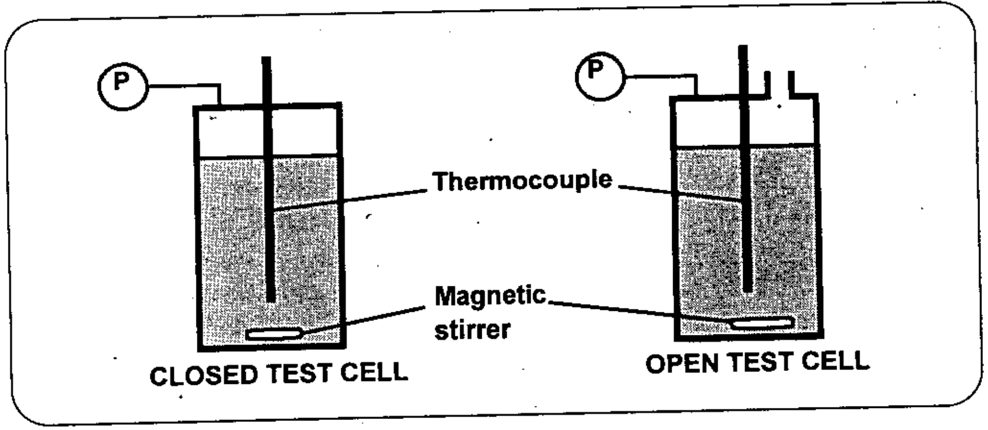
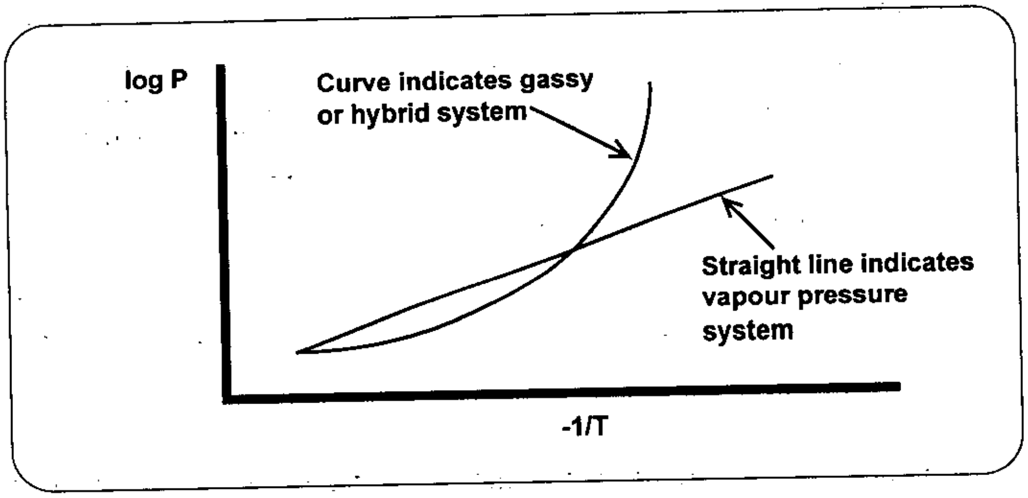


Figure A2.6 USE OF A COX CHART TO DETERMINE SYSTEM TYPE



In an open test, the pressure measured will be the pressure in the containment vessel. If the test is done with the containment vessel closed and the nitrogen pressure control system off, then any permanent gas produced by the reaction will cause the containment vessel pressure to rise. Thus a constant containment vessel pressure indicates a vapour pressure system and a rising containment vessel pressure indicates a gassy or hybrid system.

An open test is required to determine whether tempering will occur. The containment vessel pressure is held at the required relief pressure using the nitrogen pressure control system. The runaway reaction is allowed to heat the mixture from the initial temperature. If the temperature becomes constant, then the system is tempered. If the temperature continues to rise, then the system is untempered (see Figure A2.7). If tempering occurs, it is important to allow the reaction to proceed to completion to check that tempering continues. If tempering is due to the presence of a volatile solvent, then it could all boil off leaving an untempered system. If the temperature becomes nearly constant, but still rises slowly, this could indicate a tempered system in which a more volatile component is vaporising preferentially, so that the boiling point of the mixture is slowly rising. Experience is required to distinguish this behaviour from that of an untempered system.

Figure A2.7 OPEN TEST TO DETERMINE TEMPERING

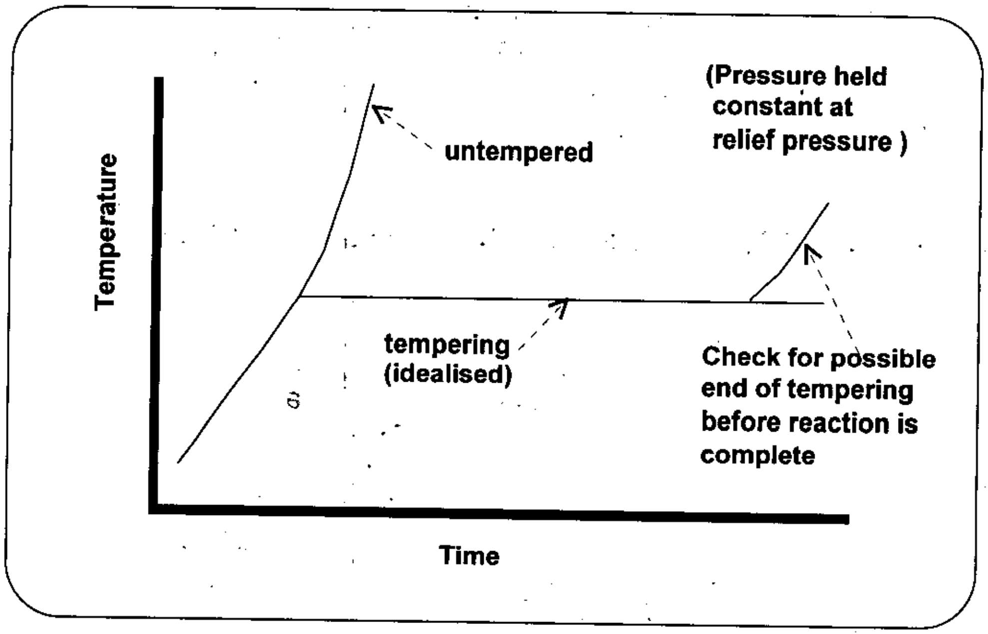


Table A2.1 summarises the information which can be obtained from the experiments described above, and the conclusions which can be made about characterising the system. It can be seen that it is not possible to distinguish experimentally between a gassy system and an untempered hybrid system. Some indication can be obtained from the vapour pressure of the reactants and products. If the mixture might be expected to boil at the temperatures experienced during runaway, then the system may be a hybrid.

Information on the data obtained from the open and closed tests is given in A2.4.

Table A2.1 **RELATIONSHIP BETWEEN EXPERIMENTAL RESULTS AND SYSTEM TYPE FOR RELIEF SYSTEM SIZING**

SYSTEM TYPE	CLOSED TEST	OPEN TEST	
	Log P* vs -1/T a straight line ?	Pressure rise in containment Vessel ?	System tempered ?
Vapour pressure	Yes	No	Yes
Tempered hybrid	No	Yes	Yes
Untempered hybrid	No	Yes	No
Gassy	No	Yes	No

* Pressure which has been corrected for pad gas (see A2.7.1)

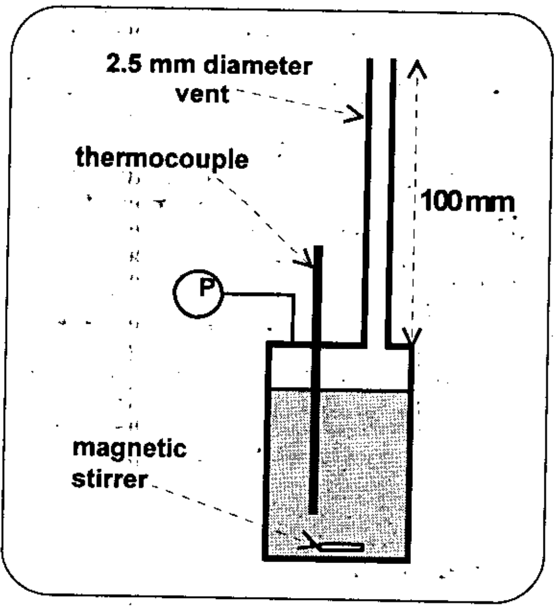
A2.3.2 Level swell characterisation

As described in Annex 3, the amount of level swell increases with gas or vapour superficial velocity. At bench-scale, the superficial velocity due to runaway will be very low compared with that at plant-scale, so that very little level swell occurs in bench-scale tests, even for inherently foamy fluids. However, some level swell at bench-scale is required to determine whether the reacting system is inherently foamy or not. For tempered systems, this can be achieved by rapid depressurisation of the test cell to give flashing and a consequent high superficial velocity, and this is one of the ways in which the DIERS bench-scale apparatus can be used. (Note that the test does not attempt to exactly match the superficial velocity at plant-scale.)

It is recommended by DIERS[2,8] that an open test cell with a 2.5 mm diameter x 100 mm long vent is used (see Figure A2.8). This diameter has been chosen to give the best discrimination between inherently foamy and non-inherently foamy behaviour and relates to the use of a test cell with a diameter of approximately 70 mm. The use of a 100 mm long vent ensures that two-phase flow will flash to equilibrium (see 9.3.1) which simplifies any computer modelling of the test to determine the flow regime.

The test is performed by pressurising the containment vessel with a high nitrogen pressure and allowing the reaction to run away to the temperature at which it tempers at the relief pressure. The containment vessel pressure is then rapidly vented to atmosphere. This causes the test cell to depressurise and a two-phase mixture to be vented. When the pressure stops falling in the test cell (which indicates the end of two-phase venting), the containment vessel is rapidly repressurised with nitrogen to prevent mass loss from the test cell by vaporisation. After cooling, the calorimeter can be opened and the mass remaining in the test cell can be determined.

Figure 2.8 TEST CELL FOR DETERMINING INHERENT FOAMINESS



DIERS[2] suggests that, if virtually all the contents of the test cell vent during depressurisation, then the mixture can be characterised as inherently foamy. (Reference 2 reports 95-98% of the contents vented for inherently foamy fluids.) If a significant quantity remains (typically more than 10% of the initial amount), then the mixture is not inherently foamy. If so, some guidance about the likely vessel flow regime can be obtained by the amount remaining in the test cell, although this would best be done in a test which attempted to obtain the same superficial velocity as in the full-scale reactor. If the flow regime is churn-turbulent, then about one third of the contents might be expected to be left in the test cell (65% vented). If the flow regime is bubbly, then about 80% of the contents might be vented.

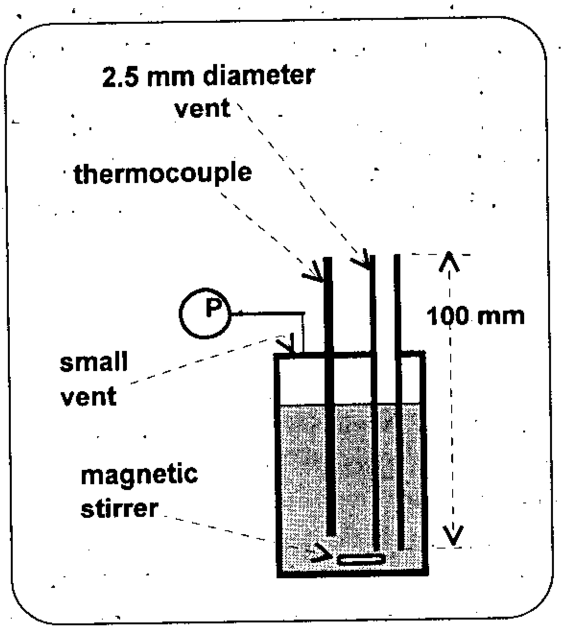
If the reacting system is non-volatile, then depressurisation will not give rise to flashing, and the above test method will not work. DIERS have not described a test for this case. However, whether the system is inherently foamy might be determined by sparging nitrogen into the reacting mixture at a suitably high rate. For level swell characterisation, adiabaticity and low thermal inertia are less important than for the measurement of thermal rate data. Thus, such a sparging test could be carried out in any suitable equipment.

A2.3.3 Viscosity characterisation

Viscosity characterisation[9] involves measuring the flow rate from the test cell in the DIERS bench-scale apparatus and comparing it with the calculated value for turbulent flow (see Chapter 9 for calculation methods). If the measured flow rate is much less than the calculated value, then laminar flow is indicated and should be assumed in relief system sizing calculations (see 10.2). Laminar flow gives rise to larger required relief system sizes than turbulent flow.

For viscosity characterisation, the DIERS bench-scale apparatus is used with a bottom vented open test cell (see Figure A2.9). The vent is 100 mm long to ensure that equilibrium flashing flow occurs. The test is performed by applying a high nitrogen pressure in the containment vessel and allowing the runaway reaction to heat the mixture to the temperature corresponding to the relief pressure at plant-scale. (If viscosity increases greatly with conversion, it may be desirable to do the test at higher conversion than this, as a worst case.) Once the desired temperature/ conversion has been achieved, the containment vessel pressure is rapidly vented. This causes venting of the test cell. The time for the test cell pressure to fall to the containment vessel pressure is measured and then the containment vessel is repressurised. After cool-down, the test cell is removed, and the mass of material vented is determined by weighing.

Figure A2.9 TEST CELL FOR VISCOSITY CHARACTERISATION



The measured value of G (the mass vent capacity per unit area) is obtained from:

$$G = \frac{\text{(mass vented)}}{\text{(venting time).(vent cross-sectional area)}} \qquad \text{(A2.2)}$$

This value of G should be used only for comparison with the calculated turbulent G in order to determine whether flow is laminar or turbulent. If flow is found to be laminar, then the measured G would need correction for scale effects before being used for relief sizing purposes (see 10.2).

A2.4 RELIEF SYSTEM SIZING DATA FOR VAPOUR PRESSURE SYSTEMS

A2.4.1 General

The following data need to be measured for vapour pressure systems:

a) The rate of heat release by the reaction as a function of temperature.

b) The vapour pressure versus temperature for the reacting mixture. (This could be calculated from single component vapour pressure data, but it is often simpler and more accurate to measure it.) Vapour pressure data have a strong influence on relief system sizing because they determine the temperature, and hence reaction rate, at the relief pressure and at the maximum accumulated pressure.

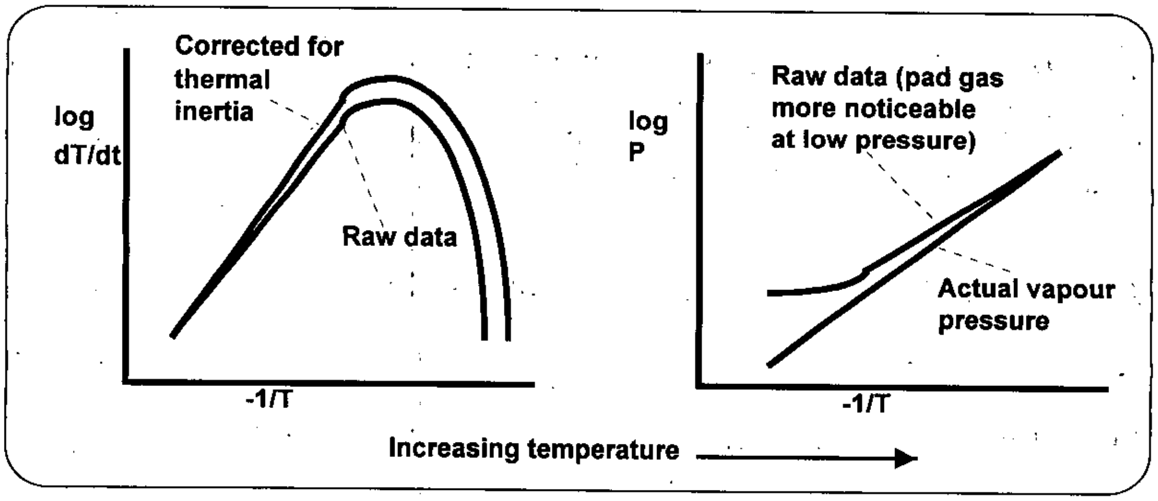
Data on a number of physical properties are also required. This includes vapour and liquid densities, latent heat of vaporisation and liquid specific heat capacity. These can usually be obtained from literature sources. Their measurement is beyond the scope of this Workbook.

If relief sizing is for a continuous or semi-batch reactor, then it may be appropriate to use isothermal calorimetry to determine the amount of reactant accumulation under worst case conditions. The mass of the accumulation, rather than the "all-in" batch mass, can then be used for relief system sizing and this can reduce the required relief system size. It should be noted that it will still be necessary to carry out suitable adiabatic tests, as described below. Further information is given by Singh[10].

A2.4.2 Closed system tests

Closed system tests, using an unvented test cell (see Figure A2.5) or Dewar flask, can be used for vapour pressure systems. The runaway is initiated in the way that best simulates the worst case relief scenario at plant-scale. The closed system pressure and temperature are measured as a function of time. Most commercial calorimeters include a data analysis package which will present the data in terms of rate of temperature rise, dT/dt, versus reciprocal temperature (-1/T), and pressure versus reciprocal temperature (see Figure A2.10). However, it is important to correct the temperature data for the effects of thermal inertia. See 2.7.2.

Figure A2.10 **DATA OBTAINED FROM A CLOSED TEST FOR A VAPOUR PRESSURE SYSTEM (IDEALISED)**



It is also important to correct the raw vapour pressure data for any pad gas which was present in the test cell. This can be done by subtracting the partial pressure of any non-condensible pad gas which was present in the test cell, to obtain the vapour pressure (see A2.7.1). Because pressure transducers may not be very accurate at the bottom end of their range, it is advisable to vent the test cell to atmosphere, once it is filled and before sealing it and heating to the initial runaway temperature, so that a reliable initial pad gas pressure is known. (This may not always be compatible with the desire to simulate the runaway scenario within the test.) An alternative is to evacuate both test cell and containment vessel before the reactants are added so that there is no pad gas and no correction is needed.

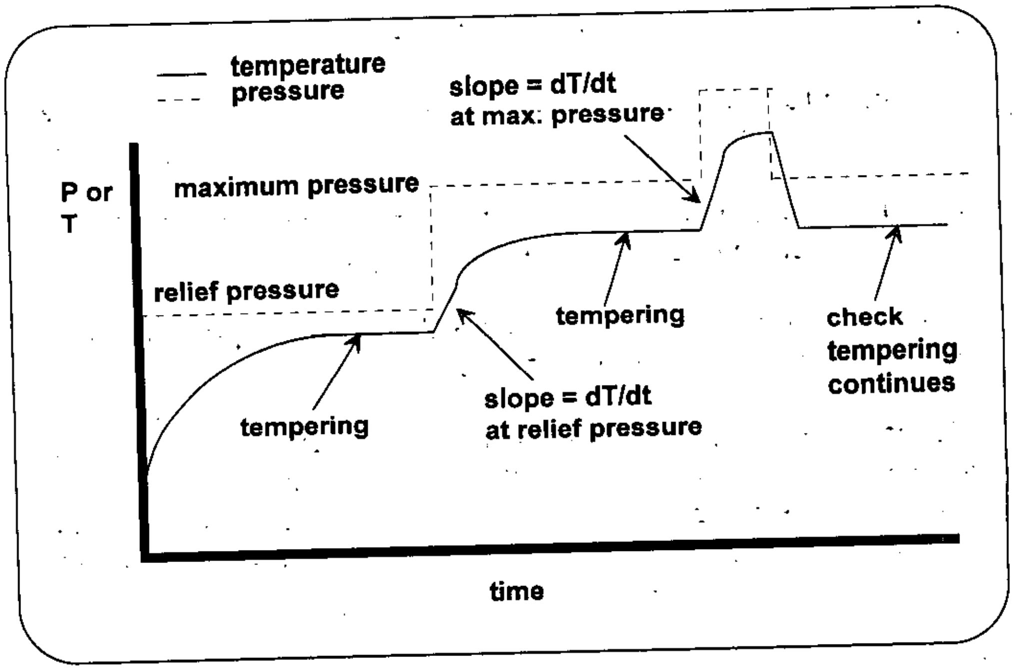
A2.4.3 Open system tests

Similar data can also be obtained for vapour pressure systems from the DIERS bench-scale apparatus operated in the open mode (see Figure A2.5). A high back pressure is superimposed on the containment vessel to suppress boiling of the sample. An adiabatic Dewar calorimeter can also be operated in this mode if it has the facility to vent to an external containment vessel.

If Leung's method is to be used for pressure relief system sizing (see 6.3), then the temperature and rate of heat evolution at the relief pressure and at the maximum accumulated pressure are needed. A possible test protocol to obtain this information from a single test is as follows (see Figure A2.11):

a) Start the runaway with a containment vessel pressure equal to the relief pressure.

Figure A2.11 **IDEALISED PRESSURE AND TEMPERATURE VERSUS TIME FOR OPEN TEST ON A VAPOUR PRESSURE SYSTEM**



b) When tempering occurs (the temperature becomes constant), note the temperature corresponding to the relief pressure, and use nitrogen to raise the containment pressure to the maximum accumulated pressure in the full-scale vessel. This increase in pressure suppresses boiling, so the rate of temperature rise reflects the adiabatic rate of temperature rise at the relief pressure.

c) When tempering occurs at the higher pressure, note the temperature, and raise the containment pressure again to suppress boiling and measure the adiabatic rate of temperature rise at the maximum accumulated pressure.

d) Return the containment vessel pressure to the maximum accumulated pressure and check that tempering continues until the reaction is complete, in case either a solvent evaporates completely or a second reaction begins.

It can be difficult to obtain all this information from a single test and it may be better to use a combination of a closed test (see A2.4.2) to obtain vapour pressure and rate of temperature rise data and an open test to check that tempering continues until the reaction is complete.

The heat release rate per unit mass of reactants, q, can be obtained from the dT/dt data but it is important to correct this for the effects of thermal inertia (see A2.7.2).

A2.5 RELIEF SYSTEM SIZING DATA FOR GASSY SYSTEMS

As with vapour pressure systems, for continuous or semi-batch reactions it may be possible to reduce the relief system size by taking into account the reduced accumulation of reacting mass. See A2.4.1 and reference 10.

For gassy systems, open tests are preferable because:

a) the gas produced pressurises a larger volume than in a closed test (see Figure A2.5) and this allows more accurate recording of the pressure;

b) the pressure will be lower than in a closed test and this will reduce the effect of any dissolved gas (see below);

c) gassy systems can generate very high pressures, particularly in closed tests, and may cause failure of the test cell or Dewar.

The information required for relief sizing for gassy systems is the rate of gas evolution, Q_G, (for the full-scale vessel), as a function of temperature. This can be calculated from the rate of pressure rise in the small-scale test by means of one of the following equations[11,12]. Equation (A2.3) is the more general equation and is best used for data from closed tests:

$$Q_G = \left[\left(\frac{V}{P}\frac{dP}{dt} \right) - \left(\frac{V}{T}\frac{dT}{dt} \right) \right]_e \left[\frac{T_e}{T_c} \frac{m}{m_e} \right] \qquad \text{m}^3\text{/s} \qquad \text{(A2.3)}$$

For data from open tests, the containment vessel gas temperature does not change greatly over time and equation (A2.3) becomes:

$$Q_G = \frac{V_e}{P} \left(\frac{dP}{dt} \right)_e \frac{T_e}{T_c} \frac{m}{m_e} \qquad \text{m}^3\text{/s} \qquad \text{(A2.4)}$$

The data required for the above equation can be obtained by measuring pressure and temperature versus time during a test. Equation (A2.3) assumes that the pressure at which the rates of pressure and temperature rise are measured is the maximum accumulated pressure in the reactor. If the measurement pressure is lower than the maximum accumulated pressure, then Q_G, obtained from equation (A2.3), can be corrected for pressure using the ideal gas law:

$$Q_G = Q_{G(\text{eqn A2.3})} \frac{P_e}{P_m} \qquad \text{m}^3\text{/s} \qquad \text{(A2.5)}$$

It is potentially more of a problem if the measurement pressure is higher than the maximum accumulated pressure. In this case there is the potential for more gas to dissolve in the sample under pressure than would be the case for the reactor and this can lead to the gas evolution rate being underestimated[13]. In such cases, it may be possible to correct for dissolved gas if the kinetics are well-understood. A method for doing this is given in references 14 and 15.

In equations (A2.3) and (A2.4) above:

a) In an open test, V is the containment vessel volume.

b) In a closed test, V is the gas space in the test cell.

c) T_e is the reactant temperature.

d) In an open test, T_c is the gas temperature in the containment vessel. As the containment vessel is initially at ambient temperature and provides a large heat sink, DIERS[11] suggests that the containment vessel temperature is assumed to be the average between ambient and the sample temperature. However, it will be more accurate to use a measured value, if available.

e) In a closed test , the reactant temperature and the gas temperature are the same, so that T_e/T_c is equal to one.

An alternative method of obtaining the gas evolution rate is to use an open test, venting to a constant pressure automated gas burette or to a thermal mass flowmeter[1]. However, these techniques have been developed to characterise the normal chemical reaction by measuring gas flow rates from a heat flow calorimeter and are unlikely to have a sufficiently fast response for many runaway reactions (and they might also cause the system to over-pressurise).

A2.6 RELIEF SYSTEM SIZING DATA FOR HYBRID SYSTEMS

As with vapour pressure and gassy systems, for continuous or semi-batch reactions it may be possible to reduce the relief system size by taking into account the reduced accumulation of reacting mass. See A2.4.1 and reference 10.

A2.6.1 Tempered hybrid systems

The data required for a tempered hybrid system is similar to that for vapour pressure systems. However, because permanent gas is being generated by the reaction, an open test should be used. This is because:

a) An open test is required to determine the tempering temperature at the relief pressure and the maximum accumulated pressure. The generation of permanent gas prevents the measurement of vapour pressure in a closed test.

b) Permanent gas generation causes rapid pressure rise in a closed system and could lead to failure of the test cell and/or excessive gas becoming dissolved during the test.

The open test method for tempered hybrid systems is the same as that given for vapour pressure systems in A2.4.3 above. However, in addition to measuring the test cell temperature, the rate of pressure rise in the closed containment vessel during tempering should also be measured. The rate of heat release per unit mass, q, can be obtained from measured dT/dt data, suitably corrected for thermal inertia (e.g. by using equation (A2.12)). Equation (A2.4) can be used to determine the rate of permanent gas evolution, Q_G. As the containment vessel provides a large heat sink, vapour is likely to condense, so that the rate of pressure rise is due only to the non-condensible gas.

Leung's method for relief system sizing for tempered hybrid systems (see 8.3.1) requires the ratio of the vapour pressure to the total pressure, P_v/P. This is approximately given by:

$$\frac{P_v}{P} = \frac{Q_v}{Q_v + Q_G} \tag{A2.6}$$

where

$$Q_v = m_R \frac{dT}{dt} \frac{c_f}{h_{fg} \rho_v} \tag{A2.7}$$

Q_v and Q_G for use in equation (A2.6) must be calculated at the same temperature, usually the tempering temperature corresponding to the relief pressure.

A2.6.2 Untempered hybrid systems

A similar test to that for gassy systems (see A2.5 above) should be used to determine the permanent gas evolution rate. The rate of temperature rise should also be measured so that the rate of vaporisation can be calculated using equation (A2.7) above.

A2.7 CORRECTION OF CALORIMETRIC DATA

A2.7.1 Correction of vapour pressure data for pad gas

This section presents a method for correcting pressure data measured in closed system tests to remove the partial pressure of pad gas. The method is required for vapour pressure systems. Vapour pressure data obtained during tempering in an open test do not require to be corrected for pad gas.

At the initial conditions, the test cell temperature is T_i (K) and total pressure is P_i (N/m^2 absolute). The initial pad gas pressure, P_{pgi}, can be obtained by subtracting the estimated vapour pressure at T_i, P_{vi}, from the total pressure:

$$P_{pgi} = P_i - P_{vi} \qquad \text{(A2.8)}$$

The pad gas pressure at any temperature can then be estimated assuming an ideal gas. If the gas space volume is assumed constant, then:

$$\frac{P_{pg}}{T} = \frac{P_{pgi}}{T_i} \qquad \text{(A2.9)}$$

If it is calculated that the volume of the gas space in the test cell will decrease significantly during the test, due to liquid thermal expansion, then account needs to be taken of this. Either the test can be performed at a lower fill level (at the cost of increased thermal inertia) or some estimate of the relationship between gas space volume and temperature should be made and the following equation used to find the pad gas pressure at any temperature:

$$\frac{P_{pg}V_G}{T} = \frac{P_{pgi}V_{Gi}}{T_i} \qquad \text{(A2.10)}$$

The vapour pressure at any temperature can then be calculated from:

$$P_v = P - P_{pg} \qquad \text{(A2.11)}$$

Note that, if the reacting system has a wide boiling range, the measured vapour pressure data will be different to that for the relieving reactor. The composition for the relieving reactor will change due to the preferential vaporisation of the most volatile component(s), but this will not be the case for the closed calorimetric test.

A2.7.2 Correction of self-heat rate data for thermal inertia

It may not be necessary to correct self-heat rate data for thermal inertia if the thermal inertia of the calorimeter is less than or equal to that of the full-scale reactor. However, it must be remembered that the effective thermal inertia of a full-scale reactor will be reduced by heat transfer limitations during high rates of temperature rise of the reactor contents. (The high reaction rate period of a runaway is over quite quickly and there is not enough time for much heat transfer during this period.) For this reason, the conservative approach is to always correct calorimetric data to a thermal inertia of 1.

A very simple correction is to multiply by the thermal inertia, as shown in equation (A2.12) below. The heat release rate per unit mass of reactants, q, can be obtained from dT/dt by the following relationship:

$$q = \phi \frac{dT}{dt} C_f \qquad \text{(A2.12)}$$

However, this simple method does not account for the depletion of reactants at any given temperature and can greatly underestimate the heat release rate at temperatures approaching the maximum adiabatic temperature. It is likely to be sufficient if the temperatures of interest for relief system sizing are well within the initial straight-line part of the data (see Figure A2.10). This is often the case for tempered systems, where the relief system is designed to control the temperature to that corresponding to the maximum accumulated pressure of the reactor. It will not be the case for untempered reactions and so more accurate correction methods will be required. Such methods are given by DIERS[16] and by Townsend and Tou[7]. These methods require assumptions to be made about the form of the kinetic expression and this is a potential source of uncertainty.

REFERENCES FOR ANNEX 2

1. J Barton & R Rogers, (ed.), "Chemical Reaction Hazards", Second Edition, IChemE, Rugby, 1997, ISBN 0 85295 3410

2. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter VI, AIChE/DIERS, 1992, ISBN 0-8169-0568-1

3. J Singh, "Phi-Tec: Enhanced Vent Sizing Calorimeter - Application and Comparison with Existing Devices", International Symposium on Runaway Reactions, 313-330, AIChE, 1989, ISBN 0-8169-0460-X

4. M A Young & S Chippett, "Design and Operation of an Automatic Pressure Tracking Adiabatic Calorimeter", International Symposium on Runaway Reactions and Pressure Relief Design, 23-57, AIChE, 1995, ISBN 0-8169-0676-9

5. H K Fauske, G H Clare & M J Creed, "Laboratory Tool for Characterising Chemical Systems", International Symposium on Runaway Reactions, International Symposium on Runaway Reactions, 364-371, AIChE, 1989, ISBN 0-8169-0460-X

6. R L Rogers, "The Advantages and Limitations of Dewar Calorimetry in Chemical Hazard Testing", Plant/Operations Progress, 8, 109-112, 1989

7. D I Townsend & J C Tou, "Thermal Hazard Evaluation by an Accelerating Rate Calorimeter", Thermochimica Acta, 37, 1-30, 1980

8. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A4, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

9. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A5, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

10. J Singh, "Relief Sizing for Semi-batch Exothermic Processes", 1996 Process Plant Safety Symposium, South Texas Section of the AIChE, Volume 2, 140-160, 1996, ISBN 0-8169-9920-1

11. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A7 (Leung Analytical Method III), DIERS/AIChE, 1992, ISBN 0-8169-0568-1

12. J Singh, "Vent Sizing for Gas Generating Runaway Reactions", J Loss Prev Process Ind, 7 (6), 481-491, 1994

13. J C Etchells, T J Snee and A J Wilday, "Relief System Sizing for Exothermic Runaway : The UK HSE Strategy", International Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, 135-162, AIChE, 1998, ISBN 0-8169-0761-7

14. M A Grolmes, G W Boicourt & M J King, "Thermal Kinetics of t-Butyl Peroctoate and Scaling Methods", Process Plant Safety Symposium, Vol 2, 87-116, AIChE, 1996, ISBN 0-8169-9920-1

15. M A Grolmes & M J King, "Simulation of Vented Pressure Tests for Organic Peroxides", J. Haz. Mat., Vol 44, 253-266, 1995

16. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A3, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

ANNEX 3

LEVEL SWELL CALCULATIONS

A3.1 INTRODUCTION

A description of level swell is given in 4.3.1. Level swell calculations do not apply to inherently foamy systems as these always vent a homogeneous two-phase mixture. The calculations can be used to predict the following:

a) The rate of gas or vapour generation by the reaction at which two-phase relief would begin for a given fill level, and hence whether two-phase or single phase relief would occur in a given situation.

b) The amount of liquid remaining in the reactor when two-phase relief ends, and hence the amount of liquid discharged during two-phase relief. This can be used for disposal system design.

c) For tempered systems, the amount of liquid remaining in the reactor when two-phase relief ends. This is used by some sizing methods (see A5.3.4, A5.4 and A5.5), but is inapplicable to relief sizing for untempered systems.

d) The fraction of vapour or gas in the two-phase mixture entering the relief system, during two-phase relief. This is required for a detailed dynamic simulation of a venting reactor.

Calculation methods are given here for cases (a) to (c). In section A3.4 below, references are given to a calculation method for case (d). The level swell calculation methods presented here use the drift flux correlations developed by DIERS[1]. The DIERS correlations apply to a vertical cylindrical vessel, which is most often the case for chemical reactors. Modifications for horizontal cylindrical vessels are given by Sheppard[2,3].

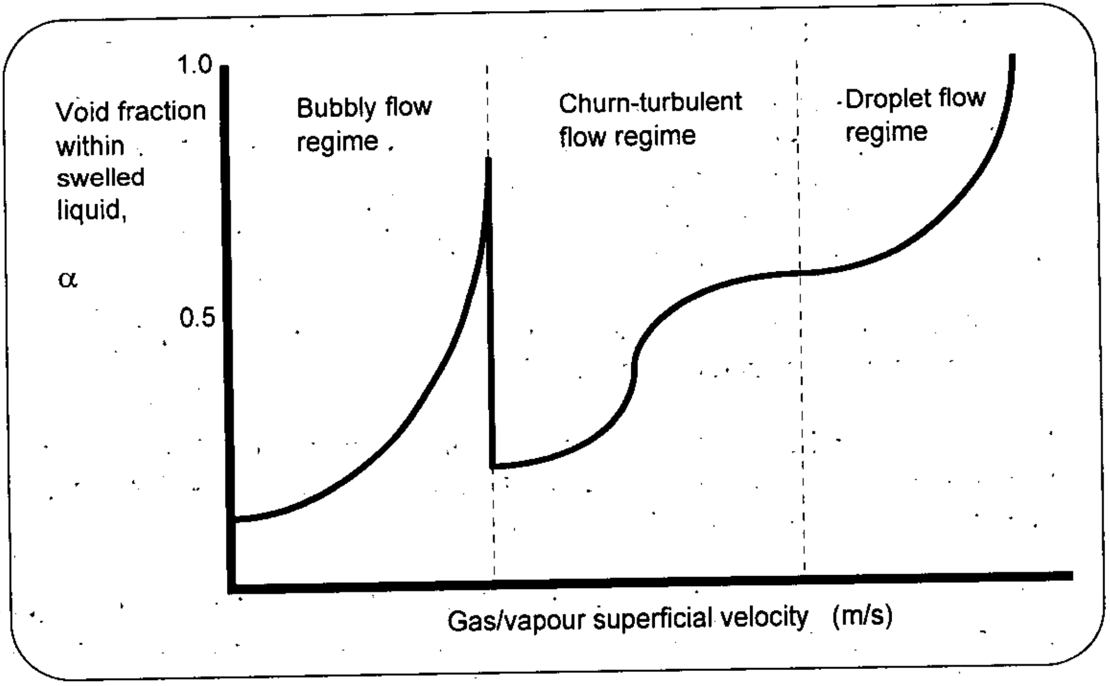
Where it is uncertain whether the system is inherently foamy, it is recommended that the worst case assumption is used (see 4.3.2(1)). For tempered systems, the worst case will be inherent foaminess. Where tempered systems are not inherently foamy, the level swell calculations described in this Annex may lead to a reduction in calculated relief system size. For untempered systems, the worst case is vapour/ liquid disengagement causing reduced mass loss from the reactor during relief. In this case, dynamic simulation (see A3.4) may be needed to take account of level swell in relief sizing.

A3.2 DETERMINATION OF LEVEL SWELL FLOW REGIME

The different flow regimes during level swell (churn-turbulent, bubbly and droplet) were described in 4.3.1. In order to perform a level swell calculation, it is necessary to decide the flow regime.

For a particular mixture, as the gas/ vapour superficial velocity increases, the flow regime moves from bubbly, through churn-turbulent and into droplet (see Figure A3.1). It should be remembered that the picture given by Figure A3.1 is a simplification of quite complex behaviour.

Figure A3.1 FLOW REGIME TRANSITIONS



Moderate viscosity (> 100 cP) will tend to keep the flow regime bubbly at higher superficial velocities. Bubbly flow at high superficial velocity approximates to homogeneous flow. At very high viscosity, completely different flow regimes may occur (see 10.2.3).

For non-viscous (< 100 cP), non-inherently-foamy systems, the churn-turbulent regime is quite likely during a runaway. Bubbly flow may occur at lower superficial velocities. Droplet flow is less important for relief system sizing, because it is usually associated with higher gas/ vapour generation rates than can be accommodated by a practical relief system, but may occur at very high superficial velocities during depressurisation. The transition between churn-turbulent and droplet flow is gradual.

The same small-scale test which distinguishes whether the mixture is inherently foamy (see A2.3.2) may also give some indication of the flow regime. However, careful interpretation is required because the standard test aims to use a higher superficial velocity than in the full-scale runaway. Thus, the test may suggest that the flow regime is churn-turbulent when it will actually be bubbly (see Figure A3.1).

Figure A3.3 (see below) is a plot of the average void fraction in the vessel versus the calculated superficial velocity. This may also be of use in assessing flow regime. If the bubbly flow correlation predicts a void fraction greater than 1, then it is not physically realistic. If, for this case, the small-scale test has indicated that the fluid is not inherently foamy, then the churn-turbulent regime is likely.

A3.3 CALCULATIONS TO PREDICT THE BEGINNING AND END OF TWO-PHASE RELIEF

The prediction of the beginning or end of two-phase relief is carried out as follows:

a) Calculate the superficial velocity of gas or vapour in the reactor. To predict the beginning of two-phase relief (or whether two-phase relief will occur), the calculation is approximated to the rate of gas/ vapour produced by the runaway reaction. To predict the end of two-phase relief, the calculation is based on the relief system capacity. See A3.3.1.

b) Calculate the bubble rise velocity, using a correlation which depends on the flow regime in the reactor. See A3.3.2.

c) Use a level swell correlation (depending on the flow regime) to calculate the void fraction, α, within the swelled liquid in the reactor, as if there was an infinite volume for the liquid to swell into. See A3.3.3.

d) Compare the void fraction, α, from (c) above with the available void fraction in the reactor, α_0, in order to determine whether two-phase relief would result. See A3.3.4.

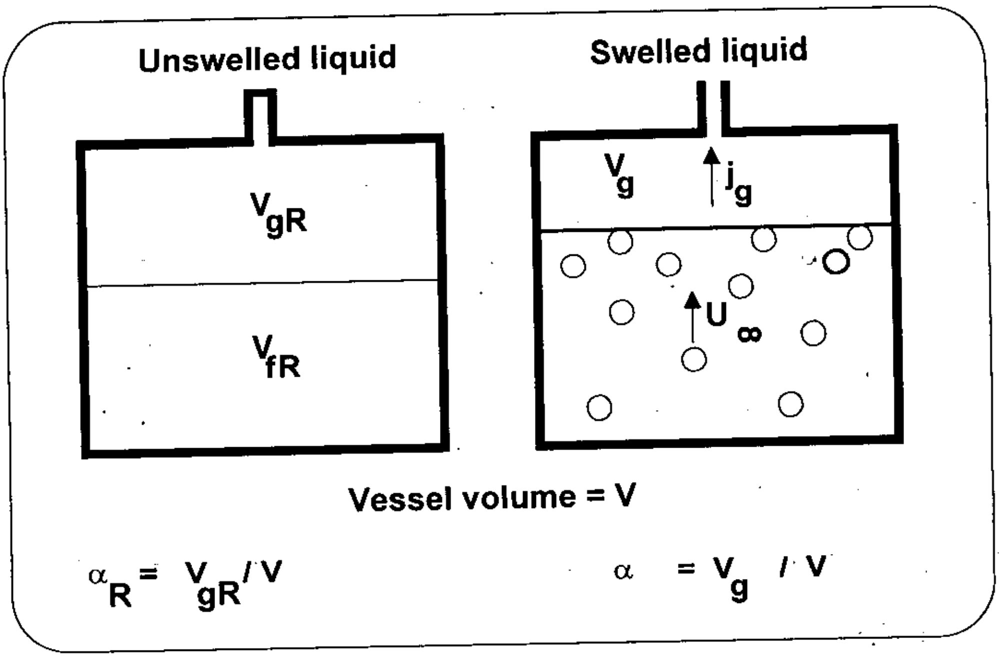
Figure A3.2 illustrates terminology used in level swell calculations. Annex 10 gives the nomenclature.

A3.3.1 Superficial velocity calculations

The amount of level swell is correlated with the superficial velocity, j_g, of gas or vapour at the surface of the liquid. Superficial velocity is the volumetric flow of gas or vapour divided by the vessel cross-sectional area (i.e., with no attempt to account for the fraction of the cross-sectional area occupied by liquid). Within a particular flow regime, level swell increases with increasing superficial velocity.

Accurate prediction of the degree of level swell requires computer simulation[4]. However, conservative estimates can be made to predict superficial velocity for the following cases:

Figure A3.2 DEFINITION OF TERMS IN LEVEL SWELL CALCULATIONS



a) The beginning of two-phase relief.

b) The end of two-phase relief for relief system sizing purposes.

c) The end of two-phase relief for disposal system sizing purposes.

For these approximations, the superficial velocity calculation is different in each case.

Beginning of two-phase relief

In order to predict the beginning of two-phase relief and whether two-phase or single-phase relief should be assumed for relief sizing, the superficial velocity is calculated from the rate at which the chemical reaction generates gas and/or vapour. (The use of this approximation overestimates the superficial velocity.)

The superficial velocity, j_g, is given by:

$$j_g = \frac{Q_G + \frac{q m}{h_{fg} \rho_g}}{A_R} \qquad \text{(A3.1)}$$

The calculation will usually be performed at the relief pressure. If the superficial velocity, calculated above for the gas and vapour generated by the reaction, does not cause two-phase relief, then the relief system can safely be sized for single-phase gas or vapour relief (provided the mixture is not inherently foamy). The above method should not be used to decide whether two-phase relief would actually occur (e.g. for the purpose of sizing a downstream disposal system) as it may predict that single-phase flow would occur when depressurisation would give rise to two-phase flow.

End of two-phase relief for relief system sizing purposes

Some relief sizing methods for vapour pressure systems (e.g. those in A5.3.4, A5.4 and A5.5) require the void fraction at vapour/ liquid disengagement during relief. It is assumed that this occurs at the maximum accumulated pressure. The superficial velocity can be calculated based on the rate at which the chemical reaction generates gas or vapour, using equation (A3.1), but at the maximum accumulated pressure. Again, this approximation is conservative in that it overestimates the superficial velocity. It should not be used to decide whether two-phase relief would actually occur or for carrying out relief sizing calculations for untempered systems which include mass loss (as in 7.4.1).

Actual end of two-phase relief (e.g. for disposal system sizing purposes)

In order to predict the end of two-phase relief, the superficial velocity should be calculated based on the rate of depressurisation by the pressure relief system. (The size of the relief system will have to be known or guessed at this stage).

$$j_g = \frac{A G_g}{\rho_g A_R} \qquad \text{(A3.2)}$$

A3.3.2 Bubble rise velocity

The terminal bubble rise velocity, U_∞, is another correlating parameter for level swell. It can be calculated from the following equations, according to the flow regime.

For the churn-turbulent flow regime:

$$U_\infty = 1.53(\sigma g(\rho_f - \rho_g))^{0.25} \rho_f^{-0.5} \qquad \text{(A3.3)}$$

For the bubbly flow regime:

$$U_\infty = 1.18(\sigma g(\rho_f - \rho_g))^{0.25} \rho_f^{-0.5} \qquad \text{(A3.4)}$$

A3.3.3 Level swell correlations

Level swell is characterised by the void fraction within the swelled liquid, α. This is correlated for each flow regime as a function of Ψ, the dimensionless ratio of the superficial gas/ vapour velocity to the bubble rise velocity, i.e:

$$\Psi = \frac{j_g}{U_\infty} \qquad \text{(A3.5)}$$

The other correlating parameter is C_0. This is intended to take account of channelling of bubbles up the walls, rather than uniform distribution. DIERS[5] recommend the following level swell correlations.

For the churn-turbulent flow regime:

$$\alpha = \frac{\Psi}{2 + C_0\Psi} \qquad \text{(A3.6)}$$

For the bubbly flow regime:

$$\Psi = \frac{\alpha(1-\alpha)^2}{\left(1-\alpha^3\right)(1-C_0\alpha)} \qquad \text{(A3.7)}$$

For the churn turbulent flow regime, the typical range for C_0 is 1.0-1.5, with a value of 1.0 (uniform radial distribution of bubbles) giving the highest predicted level swell. $C_0 = 1.0$ is conservative for relief sizing for tempered systems, whereas $C_0 = 1.5$ is conservative for relief sizing of untempered systems. For the bubbly flow regime, equation (A3.7) gives rise to multiple solutions and it is necessary to check which one is physically realistic. The typical range for C_0 is 1.0-1.2. $C_0 = 1.0$ is conservative for relief sizing for tempered systems, whereas $C_0 = 1.2$ is conservative for relief sizing for untempered systems. If C_0 is 1.0 for the bubbly flow regime, then equation (A3.7) approximates to:

$$\Psi = \alpha(1-\alpha) \qquad \text{(A3.8)}$$

This is a quadratic in α, which can be solved for $\Psi<0.25$ by:

$$\alpha = \frac{1-\sqrt{1-4\Psi}}{2} \qquad \text{(A3.9)}$$

Figure A3.3 is a plot of average void fraction, α, versus the dimensionless superficial velocity, Ψ for the different flow regimes and values of C_0. The correlations presented here may overestimate level swell for pure vapour pressure systems if there is a non-boiling region (in which static head suppresses boiling) at the bottom of the reactor. This is conservative for relief system sizing and is discussed further by DIERS[5].

A3.3.4 Two-phase or single-phase relief ?

The decision about whether relief will be two-phase or single-phase gas or vapour only can be made once an average void fraction in the swelled liquid, α, has been calculated using the methods above, with the gas/ vapour superficial velocity obtained from equation (A3.1). The decision is made by comparing α with the initial void fraction in the vessel, α_R.

$$\alpha_R = \frac{\text{Volume of vapour space in reactor}}{\text{Total reactor volume}} \qquad \text{(A3.10)}$$

If $\alpha > \alpha_R$, then the liquid in the reactor will swell to a volume greater than that of the reactor, the level will reach the top of the reactor, and a two-phase mixture will be relieved.

If $\alpha < \alpha_R$, then the liquid level will remain within the reactor, and single-phase, gas or vapour relief will occur.

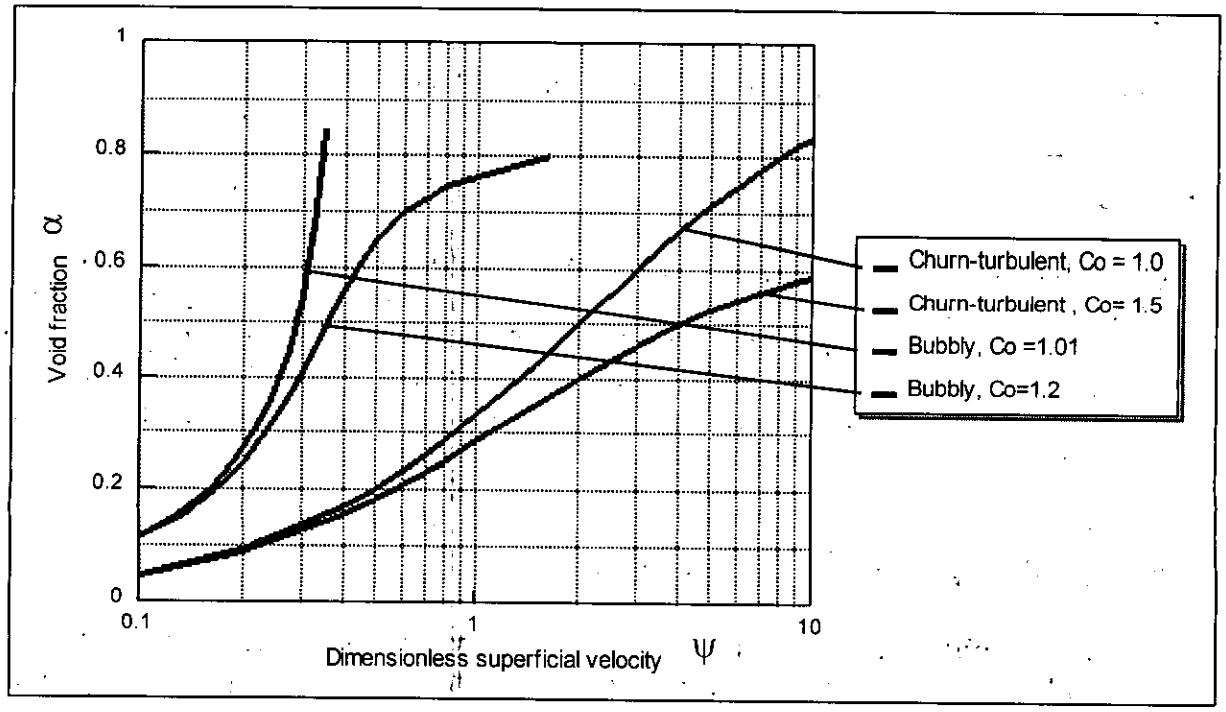
A3.3.5 End of two-phase relief

A void fraction, α, should be calculated using the methods above, and with the superficial velocity, j_g, calculated from equation (A3.2). This void fraction represents the final void fraction in the reactor at the end of two-phase venting. Thus:

$$\text{Mass of liquid remaining} = V\,(1-\alpha)\,\rho_f \qquad \text{(A3.11)}$$

$$\text{Mass of liquid vented} = V\,(\alpha-\alpha_R)\,\rho_f \qquad \text{(A3.12)}$$

Figure A3.3 **AVERAGE VESSEL VOID FRACTION VERSUS DIMENSIONLESS SUPERFICIAL VELOCITY**



A3.3.6 Worked example

This worked example calculates the void fraction at disengagement at the maximum accumulated pressure for the relief sizing worked example given in A5.5.2.

The reactor contains 2610 kg of reactants, has a volume of 3.6 m^3 and a diameter of 1.45 m. The reacting mixture has been shown not to be inherently foamy. It is low viscosity and so the churn-turbulent flow regime is assumed. Data at the maximum accumulated pressure of 7 bara are as follows:

Pressure (bara)	7
Temperature (K)	438
Liquid density (kg/m^3)	902.5
Vapour density (kg/m^3)	3.67
Latent heat (kJ/kg)	2,067
Liquid specific heat (kJ/kg K)	4.367
Surface tension (N/m)	0.046
Self-heat rate (K/minute) (corrected for thermal inertia)	11.2

In this case it is required to find the void fraction at which two-phase relief and pressure rise will no longer result from the heat being generated by the reaction. If this disengagement occurred, the pressure would therefore fall.

Using equation (A3.1) at the maximum accumulated pressure:

$$j_g = \frac{Q_g + \frac{qm}{h_{fg}\,\rho_g}}{A_R}$$

where $q = \frac{dT}{dt} C_f$

$$j_g = \frac{0 + \frac{(11.2/60)\times 4367\times 2610}{2067000\times 3.67}}{(\Pi/4)\times 1.45^2} = 0.170\ m/s$$

The bubble rise velocity for the churn-turbulent flow regime can be found from equation (A3.3):

$$U_\infty = 1.53(\sigma g(\rho_f - \rho_g))^{0.25}\rho_f^{-0.5}$$

$$= 1.53(0.046\times 9.81(902.5 - 3.67))^{0.25}\times 902.5^{-0.5} = 0.2286\ m/s$$

The dimensionless superficial velocity is found from equation (A3.5):

$$\Psi = \frac{j_g}{U_\infty} = \frac{0.17}{0.2286} = 0.7437$$

Equation (A3.6) can now be used to find the level swell. A value is required for the correlating parameter, C_0. As two-phase relief is the worst case for relief system sizing, a value of C_0 of 1.0 will be used, since this gives the highest predicted level swell:

$$\alpha = \frac{\Psi}{2 + C_0\Psi} = \frac{0.7437}{2 + (1.0 \times 0.7437)} = 0.271$$

The void fraction at disengagement is therefore 0.271. Use of this for relief sizing is shown in A5.5.2.

A 3.4 PREDICTION OF GAS/ VAPOUR FRACTION ENTERING VENT

The fraction of gas or vapour in the two-phase mixture entering the pressure relief system is an important parameter if the detailed pressure/ time history for the vented runaway reaction is to be predicted. This type of calculation is performed by a number of computer codes (see Annex 4). In order to predict the gas or vapour fraction in the two-phase flow entering the relief system, the "coupling equation", a material balance for the vessel and relief system, needs to be solved iteratively. This is discussed in detail by DIERS[5] and is beyond the scope of this Workbook.

REFERENCES FOR ANNEX 3

1. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter I, AIChE/DIERS, 1992, ISBN 0-8169-0568-1

2. C M Sheppard, "DIERS Churn-turbulent Disengagement Correlation Extended to Horizontal Cylinders and Spheres", J Loss Prev Process Ind, 6 (3),177-182, 1993

3 C M Sheppard, "DIERS Bubbly Disengagement Correlation Extended to Horizontal Cylinders and Spheres", J Loss Prev Process Ind, 7 (1), 3-5, 1994

4. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Appendix I-A4, AIChE/DIERS, 1992, ISBN 0-8169-0568-1

5. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Appendix I-A2, AIChE/DIERS, 1992, ISBN 0-8169-0568-1

ANNEX 4

COMPUTER CODES

A4.1 INTRODUCTION

A growing number of computer codes are available for relief system sizing or for the evaluation of the flow capacity (and hence the mass relief capacity per unit area, G) for a given relief system. The types of code available are discussed below under the following headings:

a) Dynamic models of a relieving reactor.

b) Models for flow in the pressure relief system.

c) Codes which evaluate simple relief sizing equations.

Kinetics packages also exist which take calorimetric data and fit kinetics correlations to them. These kinetic expressions can then be used within dynamic models of a venting reactor. Care must be taken when using such packages, particularly if the data are extrapolated above the measurement temperature, to ensure that the reaction kinetics still apply at the increased temperature.

The use of any of the above types of code is no substitute for an understanding of the issues involved in relief system sizing. Indeed, many codes offer a range of calculation options, some of which do not make safe assumptions for relief sizing purposes. The use of such codes, without adequate understanding, can result in inadequate relief sizes.

This Workbook discusses the hand calculation methods for relief sizing. In many cases, an adequate relief system size can be obtained in this way, achieving similar accuracy and using fewer resources than those needed for a dynamic computer model[1,2]. Dynamic modelling requires a range of data which are often not readily available, particularly for novel compounds such as in speciality chemicals manufacture. This tends to favour the use of simplified equations which require less data. However, there are situations in which the simple equations are inapplicable or make assumptions which cause them to excessively oversize. In such cases, the use of a dynamic simulation may be the only viable alternative for relief sizing. Dynamic simulation can also be more accurate than the use of simplified equations and can provide quick parametric sensitivity studies. It may also have the advantage that, using standardised assumptions, less experienced engineers may be able to use the computer models. However, care still needs to be taken to ensure that they have sufficient training and supervision to use the models correctly.

A detailed treatment of dynamic models is beyond the scope of this Workbook. It is covered in detail by CCPS[3]. The purpose of this Annex is to give some appreciation of the subject.

A4.2 DYNAMIC MODELS OF A RELIEVING REACTOR

A4.2.1 Model description

Dynamic models solve the differential material and energy balances for the reactor both before and during relief. A relief system size is assumed, and the model calculates the pressure versus time and temperature versus time histories. Examination of these can then determine whether the maximum accumulated pressure for the reactor would be exceeded with the assumed relief size. Multiple runs are required to find the optimum relief size which yields a maximum pressure which just equals the maximum accumulated pressure (see 5.2.1).

Dynamic models contain the following:

a) Chemical kinetics. Provision is made within the code to model the chemical kinetics, usually as a first or second order reaction, but sometimes with provision for inputting more complex reaction schemes. Rate constant, activation energy and heat of reaction must be supplied by the user and should normally be based upon experimental information obtained for the reacting system.

b) Physical properties. Physical properties are calculated by the code at required conditions using correlations. Some codes have databases containing constants for the correlations of property versus temperature for a range of substances. Often the user must obtain and input this data. This may be difficult to obtain for some chemicals, if the data do not already exist on a database. In such cases they may have to be measured or predicted. Vapour pressure data are usually correlated in terms of single component vapour pressure data; this makes it difficult to utilise measured calorimetric data for the reacting system as a whole (see Annex 2) unless the system is modelled as a pseudo-single component system. Codes differ in whether they assume ideal physical properties or can handle non-ideality. Competence in physical property modelling is essential when selecting the best combination of dynamic simulation code and physical property correlations because incorrect choice of vapour/ liquid equilibrium model can lead to considerable sizing errors.

c) Level swell model. A model is required to determine the liquid level in the reactor and whether gas/ vapour or two-phase relief occurs. If two-phase relief occurs, it will be necessary to determine the gas/ vapour fraction in the mixture entering the relief system. This model may be a drift flux model (see Annex 3 which describes the drift flux models recommended by DIERS) or a two-phase slip model, similar to that used for flow in the relief system. Most codes give a number of options, including homogeneous flow in the reactor plus different level swell calculation options. See 4.3 for a discussion of appropriate level swell assumptions for relief sizing.

d) Relief capacity model. A model is required to evaluate the mass flow rate through a specified relief system at the conditions in the reactor. Two-phase flow modelling is discussed in Chapter 9. Most codes give a range of options. The selection of a rigorous two-phase flow method that includes friction will greatly slow down the running of the code, since most codes evaluate the two-phase flow model (which will include considerable iteration) for each time-step.

e) Material and energy balances. It is essential that the differential material and energy balances utilised by the code are correct. DIERS[4] presents equations which were subject to much peer review during the DIERS project.

f) Numerical integration routine. E.g. 4th order Runge Kutta.

g) Other options. E.g. continuing feed or product streams, external heat transfer.

A4.2.2 Code selection

Many companies have developed their own in-house codes. An increasing number of commercially available models are being developed. These typically cost several thousand to tens of thousands of pounds and licence arrangements vary.

Some examples of commercially available dynamic models are:

a) The SAFIRE™ code[4] was written for DIERS and is marketed by AIChE and the DIERS Users Group. SAFIRE™ has been supported, on a voluntary basis, by members of the DIERS Users Group and its use is demonstrated as part of an AIChE short course. SAFIRE™ is a FORTRAN code which implements the DIERS methodology, solving differential material and energy balances using the 4th order Runge Kutta method. The source code is provided to the user, who is at liberty to modify the code if required. The code is not very user friendly, although this has been improved by the SAFIN™ pre-processor and by Windows front-end codes written by Shell and made available to DIERS Users Group members. The DIERS Users Group made a decision in early 1996 to stop further development of SAFIRE™ and replace it with a code based on the Arthur D Little Inc. code SuperChems (see below).

b) The RELIEF™ code[5] was developed by the CEC Joint Research Centre (JRC) at Ispra. RELIEF™ uses a one-dimensional drift flux model that enables the two-phase mixture level to be tracked. This allows the code to determine the beginning of two-phase relief and the local void fraction at the entrance to the relief system. For the relief system flow rate, it has a two-phase flow model developed by JRC Ispra which contains some degree of non-equilibrium, in addition to the homogeneous equilibrium model using the Omega method (see Annex 8). The model is commercially available. An intended update will include the modelling of an effluent handling system and a physical properties database.

c) SuperChems Expert™ [6] is a code developed by Arthur D Little Inc. for risk assessment consequence analysis, which also has a relief system sizing option. The code has a physical properties package that can handle highly non-ideal properties. It can also consider the effect of chemical reaction in the relief system piping. The code uses the DIERS drift flux methods for level swell and has the option of a rigorous two-phase slip model for the relief system capacity.

A version of SuperChems Expert™, to be called SuperChems for DIERS™, and containing the reactor relief options only, is being developed for the DIERS Users Group as a replacement for the SAFIRE™ code. The code will contain both relief and effluent handling options, a comprehensive physical property database and physical property estimating package, extensive vapour/ liquid equilibria parameters, a comprehensive plotting package etc.

d) A version of the AspenPlus™ process flowsheeting package has been developed which allows dynamic simulation of a runaway reaction in order to size the relief system[7].

It is beyond the scope of this workbook to make recommendations between commercially available alternatives. However, it is suggested that the following considerations be addressed when selecting a dynamic simulation code:

i) What quality assurance methods have been used during the development and writing of the code and the documentation?

ii) Has the code has been validated against experimental data for relief of runaway reactions?

iii) Is technical support available from the code suppliers?

iv) Are the assumptions within the code appropriate for the application which is to be modelled?

A4.2.3 Safe assumptions for use in relief system sizing

Most dynamic simulation codes give a number of options for the models used for those aspects listed in A4.2.1. Many of these options are appropriate if a best estimate simulation is required, but this may not be conservative for relief sizing purposes. For relief sizing, it is advisable to use the assumptions given here, unless there is good reason to expect that the actual behaviour during relief will be close to that given by less conservative assumptions. In such cases, it may be worthwhile to check the sensitivity to the less conservative assumption by running the code for both cases.

For tempered systems, the following assumptions are conservative:

a) Two-phase rather than vapour relief.

b) Homogeneous vessel behaviour (inherent foaminess - see 4.3.1).

c) Homogeneous equilibrium model for relief system flow.

d) No heat losses to the environment or the reactor wall.

For untempered systems, the following assumptions are conservative:

a) Two-phase relief at the point of maximum gas generation rate.

b) The type of level swell behaviour in the reactor that minimises early loss of reactants by relief, e.g. churn-turbulent flow regime, rather than bubbly or homogeneous. It may be helpful to look at all possible flow regimes and take the worst case.

c) Homogeneous equilibrium model for relief system flow.

d) No heat losses to the environment or the reactor wall.

A4.2.4 Suggestions for efficient use of dynamic simulation for relief system sizing

Before beginning the series of runs to determine the relief size, the physical property and kinetic data need to be correlated in the form required by the code. In some cases, the code may already have the components required on a database. In all other cases, physical property data must be found, estimated or measured and correlated in the appropriate form. Some codes have a front-end program for curve fitting of data. For tempered systems, the vapour/ liquid equilibrium models are of critical importance since errors will cause the code to open the relief system at the wrong temperature and reaction rate. It is therefore worthwhile to spend time to ensure reasonable behaviour of the vapour pressure predictions. Check that all correlations behave sensibly over the entire temperature range of relevance for relief sizing. A good test for the physical property and kinetic data supplied to the code is to first model the (unrelieved) adiabatic calorimetric test which was used to obtain the kinetic data.

Run times can be significantly reduced by using a (frictionless) nozzle model for flow through the relief system. Most such models incorporate a discharge coefficient, and the value supplied can be used to approximately take account of the friction which will actually occur Alternatively, the discharge coefficient can be set equal to 1 to obtain the required relief flow rate. Once a relief flow rate has been found which yields the maximum accumulated pressure, more accurate relief system flow calculations can be performed to find the relief size required to give the same flow rate (see A4.3).

The use of a dynamic simulation for relief sizing requires multiple runs with different assumed relief sizes in order to determine the optimum relief size. It is likely that a number of additional runs will also be required to check sensitivity to various assumptions. Before embarking on a large number of runs, the input data should be carefully checked for consistency. The output of the first run should also be carefully checked, as far as possible, for correctness. It may be that simple relief sizing equations (see Chapters 6-8) can be used to obtain an indication of the likely relief size, for comparison. Dynamic simulations use a lot of data and it is easy to make mistakes. The output should be treated with extreme caution, rather than being immediately believed. It can be very helpful to plot the data, particularly pressure and temperature versus time, ensuring that any discontinuities have a physical explanation, e.g. the end of two-phase relief. In addition to the pressure and temperature output, it is useful to look at the mass remaining in the reactor, the degree of completeness of the chemical reaction and whether relief is two-phase or not.

When carrying out multiple runs, a systematic way of naming and storing the files should be adopted. A summary table can be produced which indicates the changes from previous runs. It is important to check that all trends between the runs are believable in terms of having a physical explanation.

A4.3 MODELS FOR FLOW IN THE PRESSURE RELIEF SYSTEM

A4.3.1 Two-phase flow models

For simple relief systems and reacting systems for which it is applicable, the Omega method (see Annex 8) can be used to find the mass flow capacity of the relief system. However, if the Omega method is inapplicable, or if the relief system has sections of different diameter, then the use of a suitable computer code to obtain the mass relief capacity may be required.

A discussion of the different types of assumption that can be made in two-phase flow models is given in Chapter 9. DIERS[8] recommended the use of the homogeneous equilibrium model (HEM) for relief sizing, and so, preferably, a code which implements the HEM should be chosen. The model will need to incorporate sufficiently non-ideal modelling of physical properties and provision for multiple line diameters and potential choke points, as required by the application.

Most of the dynamic reactor relief simulation codes, described in A4.2 above, incorporate two-phase flow models. The models vary in their ease-of-use for stand-alone calculation. The use of complex two-phase flow models within a dynamic simulation can lead to very long run-times.

Stand-alone codes for two-phase flow calculations also exist. TPHEM™, a code for evaluating the HEM, is provided with a CCPS publication[3]. Another possible code is INPLANT™ from Simulation Sciences[9].

A4.3.2 Gas/ vapour flow models

A large number of models exist for performing compressible gas flow calculations in pipes. For pressure relief sizing purposes, it is essential to chose a model which is suitable for high velocity calculations and which correctly models choking. Many available models do not do this. A suitable code, COMFLOW™, is to be provided with reference 3.

A4.4 CODES WHICH EVALUATE SIMPLE RELIEF SIZING EQUATIONS

A few codes are available which evaluate the simple relief sizing calculations, as an alternative to evaluation using a pocket calculator. An example is VSSP™ [10] from Fauske and Associates Inc. The VSSP™ code gives an option to calculate the relief size for tempered systems with churn-turbulent or bubbly flow. Another code, VSSPH™ [11], calculates a relief size for hybrid systems.

REFERENCES FOR ANNEX 4

1. H A Duxbury & A J Wilday, "Efficient Design of Reactor Relief Systems", International Symposium on Runaway Reactions, 372-394, AIChE, 1989, ISBN 0-8169-0460-X

2. H A Duxbury & A J Wilday, "The Design of Reactor Relief Systems", IChemE Symposium Series No 115, 125-139, 1989, IChemE, ISBN 0 82595 242 2

3. "Guidelines for Pressure Relief and Effluent Handling Systems", CCPS/AIChE, 1998, ISBN 0-8169-00476-6

4. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter VII, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

5. N Brinkhof, J S Duffield & R Nijsing, "RELIEF User's Manual", European Commission Joint Research Centre, EUR 16267 EN, 1995

6. G A Melhem, "Advanced ERS Design Using Computer Simulation", International Symposium on Runaway Reactions and Pressure Relief Design, 502 566, AIChE, 1995, ISBN 0 8169 0676 9

7. M H Locke, "The ASPEN PLUS Pressure Relief System: Technical Details and Benchmark Results", Attachment 69, Minutes of 17th DIERS Users Group Meeting, Orlando, January 1995

8. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter II, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

9. A A Heiba & C Dean, "ERS Design and Rating with INPLANT - A Pipe Network Flow Simulator", Attachment 11, Minutes of 16th DIERS Users Group Meeting, Boston, September 1994

10. J C Leung, "VSSP (Vent Sizing Software Program), Version 2.1, Windows PC Version", FAI Process Safety News, p9, Spring 1995

11. J C Leung, J A Noronha, A J Torres, J J Sharkey & M H Yue, "A Vent Sizing Program with Particular Reference to Hybrid Runaway Reaction Systems", International Symposium on Runaway Reactions and Pressure Relief Design, 567 - 579, AIChE, 1995, ISBN 0-8169-0676-9

ANNEX 5

ADDITIONAL SIZING METHODS

A5.1 INTRODUCTION

Chapters 6-8 give the sizing methods which are most usually appropriate and efficient for relief system sizing. This Annex details additional methods (see A5.2 to A5.14) which may be appropriate in cases where the usual methods recommended in chapters 6-8 are inapplicable or excessively conservative. In such cases, the user will be directed to this Annex from those chapters. The methods in A5.13 and A5.14 may sometimes be more conservative or take longer to evaluate than the methods in Chapters 6-8, but have been included because they may have been used for existing relief system designs. The methods given in A5.15 and A5.16 are intended for screening purposes, as described in 3.6.

The use of dynamic models for relief system sizing is another possible method, and is covered in Annex 4.

A5.2 HUFF'S METHOD FOR VAPOUR PRESSURE SYSTEMS

Huff's method[1,2] (given in A5.2.2 below) is derived by noting that differential material and energy balances give a simple expression for relief rate at the point where the temperature stops rising and begins to fall:

$$W = GA = \frac{m^2}{\beta} \qquad \text{(A5.1)}$$

No simplifying assumptions are involved to this point in the derivation. Simplifying assumptions are involved to obtain the mass, m, at the point when the temperature begins to fall. The required relief flow rate can then be calculated on the basis that, at the maximum temperature, the heat released by the reaction is balanced by the heat removed by pressure relief. The method makes use of adiabatic experimental data, which can be obtained as described in Annex 2.

There are two versions of Huff's method. The original and more rigorous method is described in reference 1 It requires iteration to find a solution and, therefore, takes longer to evaluate than the simplified method given below[2] for little increase in accuracy

A5.2.1 Conditions of applicability of Huff's method

a) The material vented from the reactor contains the same vapour/ liquid ratio as the average for the reactor at any given time. (For a tempered system, this is a safe assumption for relief sizing, for relief from the top of the reactor.)

b) Vent mass flow rate varies little during the period of overpressure development, and is taken as constant (evaluated at the maximum pressure condition). This assumption breaks down at high overpressures.

c) The pressure will be controlled if the temperature is controlled, i.e. the system is tempered and does not become more volatile as relief proceeds.

d) It is safe to represent all physical properties by values at the maximum pressure.

e) The method, as detailed in A5.2.2, assumes there is no heat gain or heat loss from the reactor contents. It is safe to use the method if the contents of the real reactor are subject to heat loss. The method can include the effect of heat gain from external sources provided that:

    i) external heat is small with respect to reaction heat during the overpressure development period. However, if the external heat rate is proportional to the mass of liquid in the vessel, then there is no restriction on the use of Huff's method; and

    ii) the calorimetric data accounts for the effect of external heat transfer throughout the course of the exotherm (either by appropriate experimental method or by adjusting the raw data as detailed in reference 1).

   (Where the heat input is significant, the methods described in A5.7 and A5.8 can be used).

f) Apart from the relief stream, the reactor is a closed vessel. Thus, the rate of any continuing feed stream is assumed to be negligible.

g) Vapour/ liquid equilibrium is maintained in the reactor during the relief process (although it is recognised that this is unlikely to be true in practice, it is believed to be a safe assumption for relief sizing[3]).

The simplified method which is detailed below makes the following additional assumption:

h) The time, during venting, for the pressure to rise from the relief pressure to the maximum accumulated pressure can be approximated as the Boyle time (See Glossary, Annex 9) plus the time taken to generate the heat of vaporisation to bring the contents to the quality pertaining at the maximum accumulated pressure. This time is estimated using the reaction rate at the maximum accumulated pressure.

A5.2.2 Huff's method

Once it has been checked that the method is applicable (see A5.2.1 above) the relief size can be evaluated as follows:

1. evaluate β at the maximum accumulated pressure:

$$\beta = \frac{V h_{fgm}}{C_{fm}\,(dT/dt)_m\, v_{fgm}} \tag{A5.2}$$

2. evaluate the mass remaining in the reactor at the maximum accumulated pressure:

$$m_m = m_R \frac{\left[\left(\frac{m_R \Delta t_B}{\beta}\right)^{0.5} - 1\right]}{\left[\left(\frac{m_R \Delta t_B}{\beta}\right) - 1\right]} \tag{A5.3}$$

3. evaluate the required relief rate:

$$W = \frac{m_m^2}{\beta} \tag{A5.4}$$

4. estimate the required relief flow area:

$$A = \frac{W}{G} \tag{5.1}$$

A worked example of the use of Huff's method is given below.

A5.2.3 Worked example using Huff's method

This section evaluates the same example problem described in section 6.5. A reactor has a volume of 2 m^3. The worst case runaway reaction has been identified and the data from a suitable adiabatic, low thermal inertia test, with a thermal inertia of 1.05, is given in Figure 6.4. Under these conditions, the reactor would contain 793 kg of reactants. The reacting system is a vapour pressure system. It is desired to relieve the runaway via a safety valve, if possible, with a set pressure of 0.91 barg (relief pressure of 1.0 barg = 2.0 bara). Evaluate the required relief size for an overpressure of 30% of the absolute relief pressure, which gives a maximum accumulated pressure of 1.6 barg = 2.6 bara.

In addition to data already supplied in 6.5 (and repeated here), the Boyle time has been measured as 3.75 seconds. The Table below gives data (see 6.5) at the maximum accumulated pressure of 2 6 bara

Pressure (bara)	2.6
Temperature (K)	411
dT/dt (measured) (K/min)	200
Liquid density (kg/m^3)	937
Liquid specific heat (kJ/kg K)	2.26
Latent heat (kJ/kg)	920
Vapour density (kg/m^3)	2.83
v_{fg} (m^3/kg)	0.3523
G (kg/m^{2}s) (using ERM and C_D of 0.87)	2,633

The parameter β is first evaluated:

$$\beta = \frac{Vh_{fgm}}{C_{fm}\,(dT/dt)_m v_{fgm}} \tag{A5.2}$$

$$\beta = \frac{2\text{x}920000}{2260x(1.05x200/60)x0.3523} = 660.3$$

The mass at maximum accumulated pressure can now be calculated:

$$m_m = m_R\frac{\left[\left(\frac{m_R\,\Delta t_B}{\beta}\right)^{0.5} - 1\right]}{\left[\left(\frac{m_R\,\Delta t_B}{\beta}\right) - 1\right]} \tag{A5.3}$$

$$m_m = 793\frac{\left[\left(\frac{793\text{x}3.75}{660.3}\right)^{0.5} - 1\right]}{\left[\left(\frac{793\text{x}3.75}{660.3}\right) - 1\right]} = 254.0 \text{ kg}$$

The required relief rate is then given by:

$$W = \frac{m_m^2}{\beta} \tag{A5.4}$$

$$W = \frac{254.0^2}{660.3} = 97.7 \text{ kg/s}$$

The required relief area can now be found from:

$$A = \frac{W}{G} = \frac{97.7}{2633} = 0.0371 \text{ m}^2 \tag{5.1}$$

This calculated relief area is very close to the 0.0378 m^2 calculated using Leung's method in 6.5.

A5.3 FAUSKE'S METHOD FOR VAPOUR PRESSURE SYSTEMS

Fauske's method[4,5] (given below) is based on emptying the reactor (or achieving vapour/ liquid disengagement) before the pressure has risen from the relief pressure to the maximum accumulated pressure in a vented system. The method incorporates the simplified equilibrium rate model, ERM, for saturated liquid inlet (see 9.4.2) together with the Clausius-Clapeyron relationship (discussed in 6.3.3). The method makes use of adiabatic experimental rate data for the runaway, whose measurement is described in Annex 2.

The version of Fauske's method given in A5.3.2 below is simplified by assuming that two-phase relief occurs until the reactor is empty (a safe assumption for vapour pressure systems). This makes the results directly comparable with those from Leung's method (in 6.3). The full version of Fauske's method[4,5] allows account to be taken of vapour/ liquid disengagement before the vessel has emptied. This method is given in A5.3.4 below.

A5.3.1 Conditions of applicability of Fauske's method

Fauske's method has the stated condition of applicability that the absolute overpressure (see 6.3.1 or Annex 9 for definition) should be in the range 10-30% of the absolute relief pressure[4,5]. In addition to this, the derivation of the method makes the following assumptions:

a) The vapour phase is an ideal gas.

b) The vapour/ liquid equilibrium is ideal.

c) The mixture behaves like a single pseudo-component (this may not be the case for mixtures with a wide boiling range).

d) The liquid phase is incompressible.

e) Relief is via a frictionless nozzle (a safety valve approximates to this), or via a simple, constant diameter bursting disc system for which the frictional correction factor (supplied below as part of the method) will be adequate. The method may undersize if the relief system has a large upward static head change (static head change greater than about 10% of the relief pressure).

f) Flow is turbulent.

g) There is no heat gain or heat loss. (It is safe to use the method if the contents of the real reactor are subject to heat loss). In the case of heat gain (from process heating or external fire), see A5.7 and A5.8 below.

h) Apart from the relief stream, the reactor is a closed vessel. Thus, the rate of any continuing feed stream is assumed to be negligible.

j) Vapour/ liquid equilibrium is maintained in the reactor during the relief process. (Although it is recognised that this is unlikely to be true in practice, it is believed to be a safe assumption for relief sizing[3].)

A5.3.2 Fauske's method

Once it has been checked that the method is applicable (see above), it can be used for relief system sizing. Fauske's method is[4,5]:

$$A = \frac{1}{2}\frac{m_R(dT/dt)_R}{F\,\Delta P}\sqrt{\frac{C_{fR}}{T_R}} \qquad \text{(A5.5)}$$

where C_{fR} is the liquid specific heat capacity at the relief pressure and ΔP is the difference between the maximum accumulated pressure and the relief pressure. The frictional correction factor, F, can be taken from Table A5.1 below[4], where it is given as a function of the vent line equivalent length to diameter ratio, L_E/D (see also 9.6.1).

Table A5.1 **FRICTIONAL CORRECTION FACTORS FOR USE WITH FAUSKE'S METHOD**

L_E/D	F
0	1
50	0.87
100	0.78
200	0.68
400	0.57
600	0.5

A worked example of the use of Fauske's method for relief sizing is given below.

A5.3.3 Worked example using Fauske's method

This section evaluates the same example problem described in 6.5. A reactor has a volume of 2 m^3. The worst case runaway reaction has been identified and the data from a suitable adiabatic, low thermal inertia test, with a thermal inertia of 1.05, is given in Figure 6.4. Under these conditions, the reactor would contain 793 kg of reactants. The reacting system is a vapour pressure system. It is desired to relieve the runaway via a safety valve, if possible, with a set pressure of 0.91 barg (equivalent to a relief pressure of 1.0 barg = 2.0 bara). Evaluate the required relief size for an overpressure of 30% of the absolute relief pressure, which gives a maximum pressure of 1.6 barg = 2.6 bara.

The Table below gives data (see 6.5) at the relief pressure of 2.0 bara:

Pressure (bara)	2
Temperature (K)	399
dT/dt (measured) (K/min)	140
Liquid specific heat (kJ/kg K)	2.23
Liquid density (kg/m^3)	951

Fauske's method is:

$$A = \frac{1}{2}\frac{m_R (dT/dt)_R}{F\,\Delta P}\sqrt{\frac{C_{fR}}{T_R}} \qquad \text{(A5:5)}$$

Since relief is via a safety valve, F can be taken as 1 because friction is accounted for by the discharge coefficient below.

$$A = \frac{1}{2}\frac{793 \times (1.05 \times 140 / 60)}{1 \times 0.6 \times 10^5}\sqrt{\frac{2230}{399}} = 0.0383\ m^2$$

As the safety valve has a de-rated discharge coefficient of 0.87, then A=0.0383/0.87 = 0.044 m^2. In this case, Fauske's method gives a slightly higher relief area than the 0.0378 m^2 given by Leung's method.

A5.3.4 Fauske's method including disengagement

This method extends Fauske's method[4,5] (see A5.3.2) to cases in which the system is not inherently foamy and so vapour/ liquid disengagement will occur before the reactor is empty.

The method is for vapour pressure systems and the conditions of applicability are as given in A5.3.1, with the addition of (a) and (b) below:

a) The reacting system is not inherently foamy. See 4.3 and Annex 3.

b) The applicability check given by equation (A5.6) below applies. This checks that the disengagement occurs relatively late in the relief process, after two-phase relief has caused the pressure to begin to fall[3]. If the condition in equation (A5.6) is not met, the method for taking account of disengagement given in A5.5 is likely to be applicable. Equation (A5.6) can only be evaluated after the sizing method has been used.

$$q < \frac{G\,A\,h_{fg}\,v_f^2}{V\,v_{fg}\,(1-\alpha_D)^2} \tag{A5.6}$$

In order to use the sizing method, the reactor void fraction, α_D, at which total vapour/liquid disengagement is expected at the maximum accumulated pressure, must first be evaluated. This may be done by level swell calculation (see Annex 3) or by small-scale experiment with the same vapour superficial velocity as will occur at plant-scale (see Annex 2). Equation (A5.7) can then be used to find the relief area:

$$A = \frac{1}{2}\frac{m_R\,(dT/dt)_R}{F\,\Delta P}\sqrt{\frac{C_{fR}}{T_R}}\;\frac{(\alpha_D-\alpha_R)}{(1-\alpha_R)} \tag{A5.7}$$

A value of the correction factor for vent line friction, F, required by equation (A5.7) can be obtained from Table A5.1.

A5.3.5 Worked example of Fauske's method with disengagement

This method will be evaluated for the same example problem detailed in A5.3.3 above. Additional data are that, at the maximum accumulated pressure of 2.6 bara, the latent heat is 920 kJ/kg, v_{fg} is 0.3523, G is 2633 kg/m^{2}s and the liquid density is 937 kg/m^3. Further data required are the void fraction in the reactor at the relief pressure, α_R, and the void fraction at disengagement, α_D.

$$\alpha_R = \frac{V-\frac{m}{\rho_f}}{V} = \frac{2-\frac{793}{951}}{2} = 0.583 \tag{6.8}$$

The void fraction at disengagement has been estimated by level swell calculation (not shown here) as 0.9.

$$A = \frac{1}{2}\frac{m_R\,(dT/dt)_R}{F\,\Delta P}\sqrt{\frac{C_{fR}}{T_R}}\;\frac{(\alpha_D-\alpha_R)}{(1-\alpha_R)} \tag{A5.7}$$

Making use of the relief area calculated in A5.3.3 above:

$$A = 0.0383\,\frac{(0.9-0.583)}{(1-0.583)} = 0.0291\ m^2$$

As the safety valve has a de-rated discharge coefficient of 0.87, then A=0.0291/0.87 = 0.0335 m^2.

This is subject to the applicability check:

$$q < \frac{G\,A\,h_{fg}\,v_f^2}{V\,v_{fg}\,(1-\alpha_D)^2} \tag{A5.6}$$

Evaluating this at the maximum accumulated pressure of 2.6 bara (physical property data for this condition are tabulated in A5.2.3 and in 6.5):

$$q = \phi C_f \frac{dT}{dt} = 1.05x2260x\frac{200}{60} = 7910 \quad \text{W/kg} \qquad \text{(A2.12)}$$

$$\frac{G\,A\,h_{fg}\,v_f^2}{V\,v_{fg}\,(1-\alpha_D)^2} = \frac{2633x0.0335x920000x(1/937)^2}{2.0x0.3523x(1-0.9)^2} = 13079 \quad \text{W/kg}$$

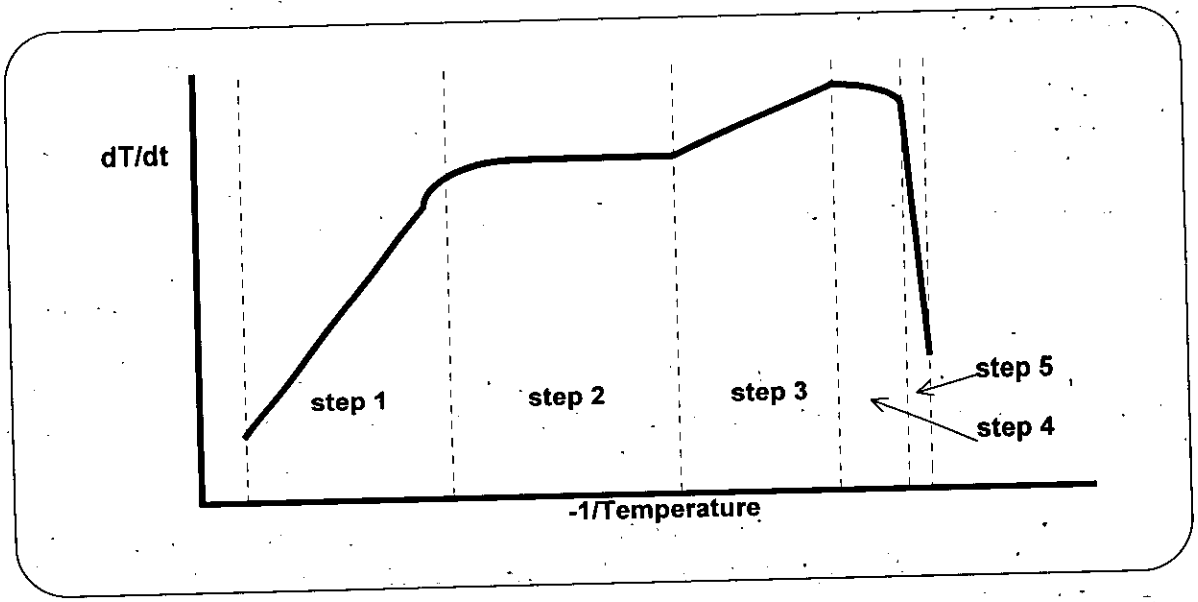
Thus, 7910 < 13079 is true and the method is applicable in this case. Thus, the relief area required is 0.0335 m^2.

A5.4 WILDAY'S STEP-WISE METHOD FOR VAPOUR PRESSURE SYSTEMS

A5.4.1 Method

This method[3] is for vapour pressure systems. It solves the material and energy balance equations, on which Leung's method (see 6.3) is based, in a step-wise manner. The method shares most of the conditions of applicability of Leung's method (see 6.3.1) but does not require values of parameters to be constant over the pressure range from the relief pressure to the maximum pressure. Indeed, systems in which there is a discontinuity in rate of reaction or physical properties can be handled by this method, provided that the step boundaries are chosen such that any discontinuity coincides with a boundary (see, for example, Figure A5.1).

Figure A5.1 **EXAMPLE OF THE CHOICE OF STEPS WHEN THE DATA CONTAINS DISCONTINUITIES**



The available pressure range from the relief pressure to the maximum accumulated pressure is divided into pressure steps (or the corresponding temperature range is divided into temperature steps). Average physical properties, heat release rate per unit mass (q) and relief capacity per unit area (G) need to be evaluated for each step. The method allows calculation of the mass remaining in the reactor at the end of each step, given the mass at the start of the step, and a guess of the relief area. Tests can then be applied at the end of each step to determine whether the pressure has begun to fall due to the emptying effect of homogeneous two-phase relief, or whether total vapour/ liquid disengagement has occurred (in cases where the system is not inherently foamy). The method can be repeated with different guessed relief areas to find the optimum area, for which the pressure reaches a maximum just below the maximum accumulated pressure.

The mass at the end of any step is given by:

$$m_m = \frac{-b_{sw} + \sqrt{b_{sw}^2 - 4a_{sw}c_{sw}}}{2a_{sw}} \qquad \text{(A5.8)}$$

where:

$$a_{sw} = q \qquad \text{(A5.9)}$$

$$b_{sw} = GAC_f\Delta T - \frac{GAVh_{fg}}{m_i v_{fg}} - qm_i \qquad \text{(A5.10)}$$

$$c_{sw} = \frac{GAVh_{fg}}{v_{fg}} \qquad \text{(A5.11)}$$

All parameters in equations (A5.8) to (A5.11) are evaluated at the average conditions for the time-step, except for m_i which is the mass remaining in the reactor at the start of the time-step. The criterion for the pressure to begin to fall during the step due to tempering is:

$$q_m \leq \frac{G_m AVh_{fgm}}{m_m^2 v_{fgm}} \qquad \text{(A5.12)}$$

The criterion for the pressure to begin to fall due to disengagement is:

$$\alpha_{Dm} \leq \frac{V - (m_m v_{fm})}{V} \qquad \text{(A5.13)}$$

where α_{Dm} is the void fraction at total vapour/ liquid disengagement, calculated using the methods given in Annex 3, provided that the system is not inherently foamy (see 4.3).

If the pressure-step is large, then equation (A5.8) may yield an imaginary number (i.e. $4a_{sw}c_{sw} > b^2_{sw}$). When this occurs, it indicates that the pressure has turned over due to homogeneous two-phase relief within the step, so that the relief area chosen is larger than required.

The method is quite laborious to evaluate with a pocket calculator, but is capable of obtaining a relief size in cases where other hand calculation methods are inapplicable. Evaluation using a spreadsheet is less time consuming.

A5.4.2 Worked example using Wilday's step-wise method

Use of the method will be illustrated using the example problem for a vapour pressure system which was described in 6.5. For this example, the relief pressure is 2.0 bara and the maximum accumulated pressure is 2.6 bara. The step-wise method will be demonstrated by using two steps:

step (1) 2.0 - 2.3 bara
step (2) 2.3 - 2.6 bara

The reactor volume is 2.0 m^3 and the charge is 793 kg. The reacting system has been shown not to be inherently foamy (see Annex 2). Total vapour/ liquid disengagement is expected at a void fraction of 0.9. Data which vary with pressure, obtained from physical property correlations, are tabulated below:

				Average for step (1)	Average for step (2)
Pressure (bara)	2	2.3	2.6		
Temperature (K)	399	403	411	401	407
Liquid density (kg/m^3)	951	946	937	948.5	941.5
Liquid specific heat (J/kg K)	2,230	2,240	2,260	2,235	2,250
Latent heat (kJ/kg)	1,050	980	920	1,015	950
Vapour density (kg/m^3)	2.18	2.51	2.83	2.35	2.67
v_{fg} (m^3/kg)	0.458	0.397	0.353	0.428	0.375
dT/dt (K/minute)	140	160	200	150	180
q (W/kg)	5,464	6,272	7,910	5,868	7,091
G (kg/m^2 s) *	2,132	2,409	2,633	2,271	2,521

* This has been taken from 6.5, and corrected for the discharge coefficient of the valve.

Guess an area, A, of 0.03 m^2. (This has been chosen to be lower than was obtained using Leung's method in 6.5).

<u>Step (1)</u>

$$a_{sw} = q = 5868 \qquad \text{(A5.9)}$$

$$b_{sw} = GAC_f\Delta T - \frac{GAVh_{fg}}{m_i v_{fg}} - qm_i \qquad \text{(A5.10)}$$

$$b_{sw} = (2271 \times 0.03 \times 2235 \times 4) - \left(\frac{2271 \times 0.03 \times 2.0 \times 1015000}{793 \times 0.428}\right) - (5868 \times 793)$$

$$= -4451732.3$$

$$c_{sw} = \frac{GA\,V\,h_{fg}}{v_{fg}} = \frac{2271 \times 0.03 \times 2.0 \times 1015000}{0.428} = 323139953 \qquad \text{(A5.11)}$$

$$m_m = \frac{-b_{sw} + \sqrt{b_{sw}^2 - 4a_{sw}c_{sw}}}{2a_{sw}} = \frac{4451732.3 + \sqrt{(-4451732.3)^2 - (4 \times 5868 \times 323139953)}}{2 \times 5868} = 677.3\ kg \qquad \text{(A5.8)}$$

Thus, at the end of step (1), at a pressure of 2.3 bara, the mass remaining in the reactor is 677.3 kg.

Step (2)

$a_{sw} = 7091$

$$b_{sw} = (2521 \times 0.03 \times 2250 \times 8) - \left(\frac{2521 \times 0.03 \times 2.0 \times 950000}{677.3 \times 0.375}\right) - (7091 \times 677.3)$$

$$= -4007158.4$$

$$c_{sw} = \frac{2521 \times 0.03 \times 2.0 \times 950000}{0.375} = 383192000$$

$$m_m = \frac{4007158.4 + \sqrt{(-4007158.4)^2 - (4 \times 7091 \times 383192000)}}{2 \times 7091} = 443.2\ kg$$

Apply criteria

The criteria for the pressure having begun to fall can be applied at the maximum accumulated pressure of 2.6 bara.

For homogenous relief:

$$7910 = q_m \le \frac{G_m\,A\,V\,h_{fgm}}{m_m^2\,vfgm} = \frac{2633 \times 0.03 \times 2.0 \times 920000}{(443.2)^2 \times 0.352} = 2102 \qquad \text{(A5.12)}$$

This criterion has not been met and so a 0.03 m^2 relief size is inadequate if no account is taken of vapour/ liquid disengagement. For this example, in which the system is not inherently foamy, this is done as follows:

$$0.9 = \alpha_{Dm} \le \frac{V - (m_m\,v_{fm})}{V} = \frac{2.0 - (443.2/\,937)}{2.0} = 0.76 \qquad \text{(A5.13)}$$

This criterion has also not been satisfied.

The method must now be repeated using a larger guess of the relief area. The smallest area which will satisfy either of the criteria above is sought.

A5.5 WILDAY'S METHOD INCLUDING DISENGAGEMENT FOR VAPOUR PRESSURE SYSTEMS

A5.5.1 Method

This method[3] is a modification of Leung's method for vapour pressure systems (see 6.3) and shares the same conditions of applicability. It allows some account to be taken of vapour/ liquid disengagement for systems which are not inherently foamy. However, this method assumes that homogeneous two-phase relief from the reactor occurs, whereas actually the two-phase mixture would contain a higher fraction of vapour than this. This assumption should increase the conservatism of the method in that more latent heat than assumed is lost via the relief system. However, this is balanced by considerable uncertainty in estimating the reactor void fraction at which total vapour/ liquid disengagement would occur.

Before using the method, the void fraction at disengagement must be evaluated at conditions corresponding to the maximum accumulated pressure during relief. This can be done by level swell calculation (see A3.3) or possibly by a small-scale experiment that uses depressurisation to achieve the same vapour superficial velocity as in the full-scale reactor during relief (see Annex 2). The required relief rate can then be calculated from[3] :

$$W = \frac{q\,V\,(\alpha_D - \alpha_R)}{v_f\left[\dfrac{h_{fg}\,v_f\left(\alpha_D - \alpha_R\right)}{v_{fg}\left(1-\alpha_R\right)\left(1-\alpha_D\right)} + C_f\,\Delta T\right]} \qquad \text{(A5.14)}$$

The method is only valid if disengagement occurs before the pressure would have turned over due to sufficient emptying during two-phase relief. The following applicability criterion[3] needs to be applied (at conditions corresponding to the maximum accumulated pressure) to the result obtained from equation (A5.14):

$$q_m > \frac{G_m\,A\,h_{fgm}\,v_{fm}^2}{V\,v_{fgm}\,(1-\alpha_{Dm})^2} \qquad \text{(A5.15)}$$

It is also recommended that the method is not used in cases where the peak pressure during relief is limited primarily by the reaction reaching completion.

A5.5.2 Worked example

This example is also used as a worked example for level swell calculations in A3.3.6. A reactor of volume 3.6 m^3 contains 2610 kg of reactants under worst case runaway conditions. The relief pressure is 5.5 bara and the maximum accumulated pressure is 7.0 bara.

The proposed relief system is a bursting disc system with a total equivalent 4fL/D of 3.6.

A level swell calculation (see A3.3.6) indicates that disengagement will occur at the maximum accumulated pressure at a void fraction of 0.271.

Physical properties and other parameters are given in the following Table:

Pressure (bara)	5.5	7	Average
Temperature (K)	432	438	
Liquid density (kg/m^3)	907.4	902.5	905
Liquid specific heat (kJ/kg K)	4.35	4.367	4.359
Latent heat (kJ/kg)	2,087	2,067	2,077
Vapour density (kg/m^3)	3.17	3.67	3.42
V_{fg} (m^3/kg)	0.3145	0.2717	0.2931
Isentropic coefficient	1.1	1.1	1.1
dT/dt (K/minute) (corrected for thermal inertia)	8.6	11.2	
q (W/kg)	623.5	815.2	719.3

Estimate α_R

$$\alpha_R = \frac{\text{volume of vapour space}}{\text{total volume}} = \frac{V - \left(m_R / \rho_f\right)}{V} = \frac{3.6 - (2610 / 907.4)}{3.6} = 0.201 \qquad (6.8)$$

Calculate relief area

$$W = \frac{q\, V\,(\alpha_D - \alpha_R)}{v_f \left[\dfrac{h_{fg}\; v_f\; \left(\alpha_D - \alpha_R\right)}{v_{fg}\left(1 - \alpha_R\right)\left(1 - \alpha_D\right)} + C_f\; \Delta T \right]} \qquad (A5.4)$$

$$W = \frac{719.3 \times 3.6\,(0.271 - 0.201)}{(1/905)\left[\left(\dfrac{2077000 \times (1/905)(0.271 - 0.201)}{0.2931\,(1 - 0.201)(1 - 0.271)} \right) + (4359 \times (438 - 432)) \right]} = 6.05 \text{ kg/s}$$

Estimate G

G can be estimated using the Omega method (see Annex 8).

At the relief pressure:

$$\omega = \frac{\alpha_0}{k} + \frac{C_f T_0 P_{v0}}{v_0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2 = \frac{0.201}{1.1} + \frac{4350 \times 432 \times 5.5 \times 10^5}{(3.6/2610)}\left(\frac{0.3145}{2087000}\right)^2 = 17.2 \qquad (A8.9)$$

where $v_0 = V/m_R$.

Reading from Figure A8.2 gives $G_c^* = 0.21$

Reading from Figure A8.3 with 4fL/D = 3.6 gives a friction correction factor, G/G_c = 0.73.

Reading from Figure A8.7, with ω = 17.2, gives a critical pressure ratio of 0.65.

$$P_c = \eta_c P = 0.65x5.5 = 3.58 \; bara$$

This is well above atmospheric pressure and so the flow will be choked.

$$G = \left(\frac{G}{G_c}\right)_{\text{friction}} G_c^* \sqrt{\frac{P_0}{v_0}} = 0.73x0.21x\sqrt{\frac{5.5x10^5}{(3.6/2610)}} = 3061 \quad \text{kg/m}^2\text{s} \qquad \text{(A8.15) and (A8.16)}$$

The average G can be estimated from:

$$G = G_R\left(1 + 0.5\left(\frac{P_m - P_R}{P_R}\right)\right) = 3061\left(1 + 0.5\left(\frac{7-5.5}{5.5}\right)\right) = 3478 \quad \text{kg/m}^2\text{s} \qquad (6.7)$$

G at the maximum accumulated pressure is therefore = 3478 + (3478 - 3061) = 3895 kg/m^{2}s.

Evaluate required relief area

$$A = \frac{W}{G} = \frac{6.05}{3478} = 0.00174 \quad \text{m}^2$$

Carry out applicability check

The applicability check should be evaluated at the maximum pressure.

$$q_m > \frac{G\,A\,h_{fgm}\,v_{fm}^2}{V\,v_{fg}m\,(1-\alpha_{Dm})^2} \qquad \text{(A5.15)}$$

If this condition is met:

$$815.3 > \frac{3895\,x0.00174\,x\,2067000\,x\,(1/902.5)^2}{3.6\,x\,0.2717\,(1-0.271)^2}$$

i.e. 815.3 > 33.1 which is true. Thus the applicability criterion has been met and the calculation is valid.

A5.6 LEUNG'S ASYMPTOTIC SOLUTIONS FOR VAPOUR PRESSURE SYSTEMS

This method[6] is for vapour pressure systems in cases where the system is not inherently foamy. The method allows for level swell using the churn-turbulent or bubbly drift flux models (see Annex 3) so that, during two-phase relief, the vapour fraction entering the relief system is greater than the average for the vessel. This gives rise to more tempering of the reaction, so that this method will give smaller relief sizes than that in A5.5 which assumes homogeneous vessel behaviour (vapour fraction entering the relief system is the same as the average in the vessel) until disengagement occurs.

Rigorous solution for this case requires a dynamic computer code, such as SAFIRE (see Annex 4). Leung has produced a series of simpler equations by recognising that the rigorous solution approaches an asymptote. Worked examples of the solution is given in references 6 and 7. However, even these simpler equations are laborious to solve without the use of a computer. The VSSP™ code (see A4.4) allows their solution.

A5.7 MODIFIED LEUNG METHOD FOR EXTERNAL HEATING FOR VAPOUR PRESSURE SYSTEMS

A5.7.1 Method

This method[8] is designed for use in cases where there is simultaneous runaway reaction and external heating, such as external fire. It is for vapour pressure systems, and makes use of the same assumptions as in Leung's method (see 6.3) with the same conditions of applicability.

The method uses Leung's method (equation (6.5) or (6.9)), but with a modified value of the heat release rate per unit mass, q, to account for the additional external heat input. This modified value of q is given by:

$$q_{modified} = q + \frac{2Q_{HEAT}}{m_R} \qquad \text{(A5.16)}$$

This modification effectively divides the external heating rate, Q, by the average mass in the reactor during relief, $m_R/2$, in order to get a safe value to add to the value of q from the chemical reaction alone.

The small-scale test (see A2.4) which measures dT/dt, and hence q, for the runaway reaction must be performed in a way which simulates the same external heating rate as for the full-scale reactor. This is to ensure that a safe value of q is obtained. If the small-scale test was not also externally heated, the relief pressure would be reached at a higher reactant conversion, and consequent lower reaction rate, than in the full scale vessel with external heat input. It should also be noted that, as there is no mass loss in the small-scale test, the whole initial mass of reactants, m_R, rather than $m_R/2$ can be used in the calculation of the rate of temperature rise due to external heating which needs to be applied in the small-scale test. (An example of this calculation is given in A5.7.2). The results of such a test can then be analysed as follows:

$$\left(\frac{dT}{dt}\right)_{reaction} = \left(\frac{dT}{dt}\right)_{measured} - \left(\frac{dT}{dt}\right)_{external} \qquad \text{(A5.17)}$$

$$q = C_f \left(\frac{dT}{dt}\right)_{reaction} \qquad \text{(A5.18)}$$

A5.7.2 Worked example of Leung's method modified for external heating

This example uses the same relief sizing problem as has been presented in 6.5.1. A relief system is to be sized for a relief pressure of 2.0 bara and a maximum accumulated pressure of 2.6 bara with a 793 kg charge in a 2 m^3 reactor. However, in this case, the runaway is expected to be caused by external fire. Also, vapour/liquid disengagement is not expected.

The wetted surface area of the 2 m^3 reactor during two-phase relief has been estimated as 8.6 m^2. This is the full surface area of the bottom and the sides of the reactor because, if two-phase relief occurs, this whole area will be wetted inside the reactor with liquid. The heat input rate from the fire is estimated as 252 kW[9]. For a closed reactor containing 793 kg of material, and using the average specific heat capacity of 2.25 kJ/kg K, the effective rate of temperature rise due to the fire is given by:

$$\left(\frac{dT}{dt}\right)_{external} = \frac{Q_{HEAT}}{m\,C_f} = \frac{252}{793 \times 2.25} = 0.141\ K/s$$

Note: the total mass is used in the calculation because the reactor is closed.

A new calorimetric test was performed with this heating rate superimposed. The measured rates of temperature rise in a closed test were 150 K/minute at 2.0 bara and 220 K/minute at 2.6 bara. In each case, the rate of temperature rise due to the reaction can be calculated as:

$$\left(\frac{dT}{dt}\right)_{reaction} = \left(\frac{dT}{dt}\right)_{measured} - \left(\frac{dT}{dt}\right)_{external} \qquad \text{(A5.12)}$$

At 2.0 bara, $\left(\frac{dT}{dt}\right)_{reaction} = \frac{150}{60} - 0.141 = 2.359\ K/s$

At 2.6 bara, $\left(\frac{dT}{dt}\right)_{reaction} = \frac{220}{60} - 0.141 = 3.526\ K/s$

No correction is required for thermal inertia because there is net external heating of the sample (the wall temperature remains hotter than the sample temperature throughout). Since the external heating rate is small compared with the rate of heat generation by the reaction in this example, it can be expected that the method will yield similar results to Leung's standard method. The objective here is to give a worked example of the method which would be more important if the external heating rate is significant compared with the reaction heating rate.

The average value of q for the runaway reaction is:

$$\bar{q} = 0.5C_f\left[\left(\frac{dT}{dt}\right)_R + \left(\frac{dT}{dt}\right)_m\right] = 0.5 \times 2250\,[2.359 + 3.526] = 6621\ W/kg \qquad (6.2)$$

The modified value of q for use in Leung's method can now be evaluated:

$$\bar{q}_{modified} = \bar{q} + \frac{2Q_{HEAT}}{m_R} = 6621 + \left(\frac{2 \times 252000}{793}\right) = 7257\ W/kg \qquad (A5.16)$$

This can then be used in Leung's method. Since the relief area from Leung's method is directly proportional to q, the relief area can be found from that of 0.0378 m^2 calculated in section 6.5.2, using an average q of 6679 W/kg. Thus:

$$A = 0.0378 \times \frac{7257}{6679} = 0.0411\ m^2$$

A5.8 WILDAY'S METHOD FOR EXTERNAL HEATING FOR VAPOUR PRESSURE SYSTEMS

A5.8.1 Method

This method[8] is for vapour pressure systems when there is simultaneous runaway reaction and external heating. It has been derived by using an analogous method to that used to derive Leung's method (see 6.3) and it shares the same conditions of applicability, except that the method is valid when there is an external heat input. The method should be more accurate than that in A5.7 above, but requires an iterative procedure for evaluation.

When using the method, it is essential that the heat release rate per unit mass due to the runaway reaction, q, is measured in an suitable calorimeter (see Annex 2) which simulates the external heat input. If this is not the case, then q can be underestimated since the external heating means that the degree of conversion of the reaction is less (and the reaction rate higher) at any given temperature compared with the adiabatic situation.

The method is evaluated as follows (with all the parameters in the equations being evaluated at average conditions between the relief pressure and maximum accumulated pressure):

a) Estimate the relief area, A.

b) Find the time, t_m, corresponding to the maximum accumulated pressure:

$$t_m = t_{empty} + \left(\frac{Q_{HEAT}}{2\,q\,GA}\right) - \left(\frac{C_f}{2q}\right)\sqrt{\left(\frac{Q_{HEAT}}{GAC_f}\right)^2 + \frac{4\,q\,V\,h_{fg}\,t_{empty}}{C_f^2\,m_R\,v_{fg}}} \qquad \text{(A5.19)}$$

where

$$t_{empty} = \frac{m_R}{GA} \qquad \text{(A5.20)}$$

c) Find the maximum temperature during relief:

$$T_m = T_R + \left(\frac{q\,t_m}{C_f}\right) - \left(\frac{V\,h_{fg}}{m_R\,C_f\,v_{fg}}\right)\left(\frac{t_m}{t_{empty} - t_m}\right) + \left(\frac{Q_{HEAT}}{GAC_f}\right)\ln\left(\frac{t_{empty}}{t_{empty} - t_m}\right) \qquad \text{(A5.21)}$$

d) Compare the calculated value of T_m with the temperature corresponding to the maximum accumulated pressure. If it is higher than the value at the maximum accumulated pressure, then revise the guess of the relief area and return to step (a) above.

A5.8.2 Worked example of Wilday's method for external heating

This example uses the same relief sizing problem as has been presented in 6.5 and A5.7.2. A relief system is to be sized for a relief pressure of 2.0 bara and a maximum accumulated pressure of 2.6 bara with a 793 kg charge in a 2.0 m^3 reactor. However, in this case, the runaway is expected to be caused by external fire. Also, vapour/ liquid disengagement is not expected.

The wetted surface area of the 2 m^3 reactor during two-phase relief has been estimated as 8.6 m^2. This is the full surface area of the bottom and the sides of the reactor because, if two-phase relief occurs, this whole area will be wetted inside the reactor with liquid. Using this value, the heat input rate from the fire is estimated as 252 kW[9].

Physical properties and other data are as follows:

Pressure (bara)	2	2.6	Average
Temperature (K)	399	411	
Liquid density (kg/m^3)	951	937	944
Liquid specific heat (kJ/kg K)	2.23	2.26	2.25
Latent heat (kJ/kg)	1,050	920	985
Vapour density (kg/m^3)	2.18	2.83	2.51
v_{fg} (m^3/kg)	0.4577	0.3523	0.405
q(W/kg)	5,575	8,287	6,931
Q_{HEAT} (kW)			252
G (kg/m^{2}s)			2,382

Estimate relief area

An estimate of 0.04 m^2 has been made since this is close to the result obtained from the worked example in A5.7.2.

Calculate time to maximum pressure during relief

$$t_{empty} = \frac{m_R}{GA} = \frac{793}{2382 \times 0.04} = 8.323\ s \qquad \text{(A5.20)}$$

$$t_m = t_{empty} + \left(\frac{Q_{HEAT}}{2qGA}\right) - \left(\frac{C_f}{2q}\right)\sqrt{\left(\frac{Q_{HEAT}}{GAC_f}\right)^2 + \frac{4\,q\,V\,h_{fg}\,t_{empty}}{C_f^2\,m_R\,v_{fg}}} \qquad \text{(A5.19)}$$

$$t_m = 8.323 + \left(\frac{252000}{2 \times 6931 \times 2382 \times 0.04}\right) - \left(\frac{2250}{2 \times 6931}\right)\sqrt{\left(\frac{252000}{2382 \times 0.04 \times 2250}\right)^2 + \left(\frac{4 \times 6931 \times 2 \times 985000 \times 8.323}{2250^2 \times 793 \times 0.4050}\right)}$$

$$= 5.793\ s$$

Calculate maximum temperature

$$T_m = T_R + \left(\frac{q\,t_m}{C_f}\right) - \left(\frac{V\,h_{fg}}{m_R\,C_f\,v_{fg}}\right)\left(\frac{t_m}{t_{empty} - t_m}\right) + \left(\frac{Q_{HEAT}}{GAC_f}\right)\ln\left(\frac{t_{empty}}{t_{empty} - t_m}\right) \qquad \text{(A5.21)}$$

$$= 399 + \left(\frac{6931 \times 5.793}{2250}\right) - \left(\frac{2.0 \times 985000}{793 \times 2250 \times 0.4101}\right)\left(\frac{5.793}{8.323 - 5.793}\right) + \left(\frac{252000}{2382 \times 0.04 \times 2250}\right)\ln\left(\frac{8.323}{8.323 - 5.793}\right)$$

$$= 412.0\ K$$

This is a little more than the temperature of 411 K at the maximum accumulated pressure of 2.6 bara. Thus the guessed relief size of 0.04 m^2 is slightly too small. The calculation needs to be repeated with a slightly larger estimate of the relief area. For this example, the simplified method provided in A5.7 gives a very similar result to this more rigorous method.

A5.9 SINGH'S METHOD FOR GASSY SYSTEMS

A5.9.1 Method

Singh's method[10] allows some account to be taken of material loss through the relief system as the pressure rises from the relief pressure to the maximum accumulated pressure. An average rate of gas generation is used in the derivation (i.e. between that at the relief pressure and the peak rate for the reaction). This is intended to ensure that the method remains conservative, even though account is taken of material loss. The method allows the relief area calculated by the DIERS equation to be reduced by up to a factor of 3.

The method assumes that the gas is ideal and that homogeneous two-phase relief occurs once the relief system operates. This assumption is potentially non-conservative for untempered systems and the method should only be used where it is known that homogeneous vessel flow occurs (e.g. for inherently foamy systems)[11]. It should not be used if there is external heat input to the reactor, or if the rate of any continuing feed streams is significant.

Singh's method is:

$$W = \frac{1}{K_s} Q_{G_{max}} \frac{m_R}{V} \tag{A5.22}$$

where

$$K_s = 1 + \frac{2\left[1 - \frac{(dP/dt)_R}{(dP/dt)_{max}}\right]}{\left[1 + \frac{(dP/dt)_R}{(dP/dt)_{max}}\right]} \tag{A5.23}$$

$(dP/dt)_R$ is the experimental rate of pressure rise at the temperature at which the relief system is expected to operate and give rise to two-phase relief on the full-scale reactor. Singh suggests that $(dP/dt)_R$ can be obtained at a pressure in the calorimeter given by:

$$P_{Re} = P_R \left(\frac{m_e}{m_R}\right)\left(\frac{\alpha V}{V_e}\right) \tag{A5.24}$$

where αV is the gas space volume in the full-scale reactor and V_e is the gas space volume in the calorimeter. It should also be checked that the rate of gas generation at this condition is sufficient to cause two-phase relief (using the level swell methods in Annex 3, for calculating the beginning of two-phase relief). If two-phase relief would not be predicted at P_R, then the experimental rate of pressure rise, corresponding to the temperature at which two-phase relief would first be predicted in the full-scale reactor, should be used.

A5.9.2 Worked example using Singh's method

The same example problem as used in 7.6 will be used. A reactor of volume 3.5 m^3 has a design pressure of 14 barg (maximum accumulated pressure 16.41 bara). A worst case relief scenario has been identified in which a gassy decomposition reaction occurs. The mass of reactants in the reactor would be 2500 kg. An open cell test has been performed in a DIERS bench-scale apparatus, in which the volume of the gas space in the apparatus was 3800 ml, and the mass of the sample was 44.8 g. The peak rate of pressure rise was 2263 N/m^2s at a temperature of 246°C, and the corresponding rate of temperature rise was 144°C/minute. These have been corrected for thermal inertia. The pressure in the containment vessel corresponding to the peak rate was 20.2 bara. The liquid density at 246°C is estimated as 820 kg/m^3. The gas generated by the runaway has a C_p/C_v value of

1.3. The problem is to evaluate the relief size required. The relief set pressure will be 8 barg.

The calculation performed in 7.6 has given:

Peak gas generation rate, $Q_{G\max} = 0.374$ m^3/s
Void fraction, $\alpha = 0.129$
Two-phase mass flow rate per unit area, G = 19,620 kg/m^{2}s

Firstly, the pressure at calorimetric scale equivalent to the full-scale relief pressure will be estimated. For a set pressure of 8 barg, the relief pressure is (1.1x8) + 1 = 9.8 bara.

$$P_{Re} = P_R\left(\frac{m_e}{m_R}\right)\left(\frac{\alpha V}{V_e}\right) = 9.8\left(\frac{44.8x10^{-3}}{2500}\right)\left(\frac{0.129x3.5}{3800x10^{-6}}\right) = 0.02 \; bara \qquad \text{(A5.24)}$$

This is below the initial pressure in the calorimeter. The initial rate of pressure rise has therefore been taken (from measured data) as that corresponding to the relief pressure. This was 40 N/m^{2}s.

$$K_s = 1 + \frac{2\left[1 - \frac{(dP/dt)_R}{(dP/dt)_{\max}}\right]}{\left[1 + \frac{(dP/dt)_R}{(dP/dt)_{\max}}\right]} = 1 + \frac{2\left[1 - \frac{40}{2263}\right]}{\left[1 + \frac{40}{2263}\right]} = 2.93 \qquad \text{(A5.23)}$$

$$W = \frac{1}{K_s} Q_{G_{\max}} \frac{m_R}{V} = \frac{1}{2.93} x0.374x \frac{2500}{3.5} = 91.2 \text{ kg/s} \qquad \text{(A5.22)}$$

$$A = \frac{W}{G} = \frac{91.2}{19620} = 0.00465 \text{ m}^2 \qquad \text{(5.1)}$$

This suggests that, provided the reactor fills with a homogeneous two-phase mixture (inherently foamy fluid behaviour), the relief system size can be greatly reduced from the area of 0.0136 m^2 calculated using the DIERS method (neglecting mass loss during relief) given in Chapter 7.

A5.10 LEUNG'S METHOD FOR GASSY SYSTEMS

A5.10.1 Method

Leung[12,13] has also derived a simplified method for gassy systems which takes account of the loss of reactant mass from the reactor by pressure relief. The method assumes that the gas is ideal and that homogeneous two-phase relief occurs once the relief system operates. This assumption is potentially non-conservative for untempered systems and so the method should be used with extreme caution unless the reacting system is inherently foamy such that homogeneous vessel conditions can be expected[10]. It should not be used if there is external heat input to the reactor, or if the rate of any continuing feed streams is significant.

The method is as follows:

$$W = Q_{G\max}\,\frac{m_R}{V}\,\frac{1}{(1+\alpha_0)^2} \qquad \text{(A5.25)}$$

The peak gas evolution rate, $Q_{G\max}$, can be obtained from calorimetric measurements (see Annex 2 and equations (A2.3) and (A2.4)). It is important that such calorimetric tests are performed so as to minimise the amount of dissolved gas in the test. "Open" tests are therefore preferred to "closed" tests[14].

A5.10.2 Worked example using Leung's method for gassy systems

The same example problem as used in Chapter 7 and A5.9.2 above will be used. A reactor of volume 3.5 m^3 has a design pressure of 14 barg (maximum accumulated pressure 16.41 bara). A worst case relief scenario has been identified in which a gassy decomposition reaction occurs. The mass of reactants in the reactor would be 2500 kg. An open cell test has been performed in a DIERS bench-scale apparatus, in which the volume of the gas space in the apparatus was 3800 ml, and the mass of the sample was 44.8 g. The peak rate of pressure rise was 2263 N/m^2s at a temperature of 246°C, and the corresponding rate of temperature rise was 144°C/minute. These have been corrected for thermal inertia. The pressure in the containment vessel corresponding to the peak rate was 20.2 bara. The liquid density at 246°C is estimated as 820 kg/m^3. The gas generated by the runaway has a C_p/C_v value of 1.3. The problem is to evaluate the relief size required.

The calculation performed in 7.6 has given:

Peak gas generation rate, $Q_{G\max} = 0.374\ m^3/s$
Void fraction, $\alpha = 0.129$
Two-phase mass flow rate per unit area, $G = 19{,}620\ kg/m^2s$

$$W = Q_{G\max}\,\frac{m_R}{V}\,\frac{1}{(1+\alpha_0)^2} = 0.374 x \frac{2500}{3.5} x \frac{1}{(1+0.129)^2} = 160.5\ kg/s \qquad \text{(A5.25)}$$

$$A = \frac{W}{G} = \frac{160.5}{19620} = 0.00818\ \ m^2 \qquad \text{(5.1)}$$

This shows that the required relief area has been reduced from the value of 0.0136 m^2 calculated, with no account taken for mass loss, in 7.6. This method gives less reduction in relief size than is given by Singh's method (see A5.9.2 above). The two methods give closer agreement when the initial void fraction is higher than in this example.

A5.11 LEUNG'S ALTERNATIVE METHOD FOR TEMPERED HYBRIDS

Leung[15] gives an alternative method for tempered hybrid systems (see 4.2) which is slightly more rigorous than that given in 8.3.1 but takes longer to evaluate. The method assumes:

a) The system remains tempered until the reaction reaches completion.

b) Homogeneous two-phase relief occurs.

c) Two-phase relief begins when the tempering temperature is reached at the relief pressure (this is a conservative assumption as earlier two-phase relief would remove more reactants from the reactor).

d) The sensible heat of the gas/ vapour phase is negligible.

e) The ratio of moles of gas generated to moles of vapour produced is constant.

f) The gas is ideal.

g) The vapour pressure can be correlated by the Antoine equation.

The method is used within the computer code VSSPH[15] (see A4.4).

A5.12 DIRECT SCALE-UP

Direct scale-up from a small-scale experiment can be a valid method of obtaining a relief system size. However, it is imperative that the small-scale experiment is conducted in such a way that scale-up is valid. The following list[16,17] of requirements for valid scale-up should be achieved as far as possible. If any of the list are not satisfied, the designer needs to carefully consider the effects and be convinced that the result will be to overestimate the required relief size.

a) The reaction may be regarded as taking place uniformly throughout the liquid.

b) The reaction recipe is unchanged, except in scale, from that which results in the worst case relief scenario.

c) The operating temperature, pressure and sequence are unchanged from that resulting in the worst case relief scenario.

d) The total rate of reaction changes in proportion to the reactor volume, but retains the same dependence on temperature, pressure and composition. This may not be the case for reactions which are mass transfer controlled, when the agitation efficiency can have a marked effect on the rate of *reaction* and is very difficult to scale.

e) The temperature distribution is unchanged between the small-scale and large-scale reactors. This is best achieved if a uniform temperature distribution exists at both scales.

f) The fill ratio is unchanged.

g) The heat losses (to the vessel wall and to the environment) per unit mass of reactor contents are no higher at small-scale than in the full-scale reactor. (This is discussed further in Annex 2).

h) The relief pressure and maximum accumulated pressure are unchanged with scale.

i) The height of the relief system is unchanged with scale, unless the static head is insignificant in comparison with the relief pressure.

j) The ratios of the masses of gas, liquid and solid (if any) entering the relief system are unchanged. Level swell (see Annex 3) does not scale-up, and the result is that gas or vapour-only relief is more likely from a small-scale test than at full-scale. For tempered systems, this could potentially lead to a considerably undersized full-scale relief system (if the small-scale test relieved vapour whilst the large-scale reactor relieved a two-phase mixture). It is safe to scale-up if the small-scale test relieves a two-phase mixture such that the test reactor is emptied by the relief process.

k) Either the friction in the relief system is negligible at both scales, or it is more at small-scale than at large-scale. An alternative is to do a small-scale test with negligible friction, scale-up to obtain a large-scale relief size with negligible friction, and then use an appropriate two-phase flow model (e.g. the Omega method, if applicable; see Annex 8) to size the real relief system to have the same, or greater, flow capacity than the size for negligible friction.

l) For tempered systems, the length of the relief pipe at small-scale is sufficient to ensure that the two-phase flow flashes to equilibrium. A length of at least 0.1 metres is required.

If all the above are satisfied, then scale-up can be done on the basis of relief area to vessel volume:

$$A = \frac{V}{V_e} A_e \tag{A5.26}$$

If some of the above conditions of applicability are not entirely satisfied (but scale-up is still believed to be safe), it is better to scale-up on the basis of relief area to mass of reactants:

$$A = \frac{m}{m_e} A_e \tag{A5.27}$$

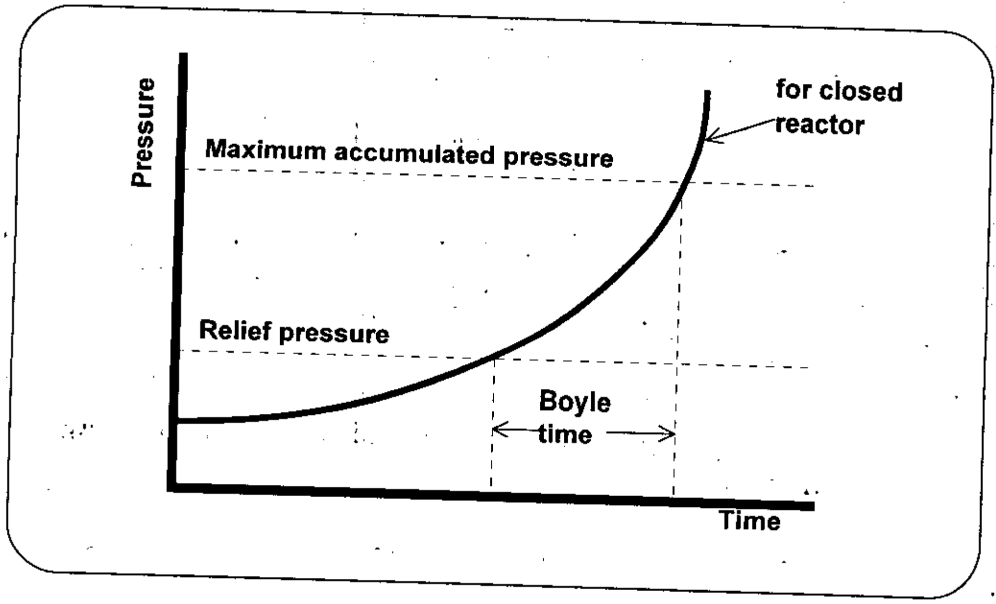
In some cases, direct scale-up may be impracticable, for example because of blockage of the small-scale relief line. The requirement for complete emptying of the small-scale reactor by two-phase relief may also not be met in practice. If this occurs for a tempered system, the problem could be overcome by using a small-scale relief system from the bottom of the test reactor to simulate one at the top of the large-scale reactor. This procedure would not be safe for untempered reactions.

Direct scale-up requires the use of a series of different small-scale tests with different relief sizes in order to find the minimum safe size. This can be costly, so that the use of calorimetry to obtain data to be used in appropriate relief sizing equations may be a better option.

A5.13 MODIFIED BOYLE METHOD

This method[16,18] relies on emptying the reactor by two-phase relief in the time taken for the pressure to rise from the relief pressure to the maximum accumulated pressure in an adiabatic closed reactor. This time is defined as the Boyle time and is illustrated in Figure A5.2.

Figure A5.2 **ILLUSTRATION OF THE BOYLE TIME**



In the original Boyle method[18], it was recommended that the relief system capacity be calculated on the basis of non-flashing liquid flow, and a safety factor of 3 applied to the result. The modified Boyle method[16] uses a relief system capacity calculated on the basis of two-phase flow. The modified Boyle method is therefore:

$$A = \frac{m_R}{G\,\Delta t_B} \qquad \text{(A5.28)}$$

The Boyle time, Δt_B, is best evaluated experimentally using a suitable calorimeter (see Annex 2). Alternatively, it can be calculated if suitable kinetic data are available. However, it can be unwise to extrapolate such data to temperatures above those used to obtain the data.

Duxbury[16] recommends that G should be evaluated at a range of fill levels as the reactor progressively empties due to two-phase relief, and that an appropriate value of G should be used. Duxbury also points out that in certain circumstances, two-phase flow methods can give a relief area which is smaller than that obtained assuming gas or vapour-only relief. In such cases, the installed relief size should be no smaller than for gas/ vapour relief (see Annex 6).

A5.14 TWO-PHASE RELIEF AT CONSTANT PRESSURE

This method[16] is the recommended DIERS method for untempered systems, and is given in detail for that case in 7.3. The method can also be safely used for tempered systems but tends to greatly oversize unless the available overpressure during relief is very small. At zero overpressure, Leung's method for vapour pressure systems (see equation (6.5)) is identical with this method.

The basis of the method is to relieve the same volumetric flow of two-phase mixture as the volumetric rate of gas/ vapour production by the reaction, i.e.

$$W = (Q_G + Q_v)\left(\frac{m_R}{V}\right) \qquad \text{(A5.29)}$$

For a tempered system, this rate can be evaluated at the relief pressure because the relief system will then be designed to limit the pressure (and temperature and reaction rate) to this value. For untempered systems, the peak rate attained during the course of the runaway must be used.

A5.15 FAUSKE'S SIZING EQUATION FOR GASSY SYSTEMS

Fauske[19] has produced an equation that combines the DIERS equation (7.1) with equation (A2.4) from Annex 2, which obtains the value of Q_{Gmax} from experimental measurements. Fauske's equation neglects friction and assumes that the two-phase relief system flow is not choked (this is not a conservative assumption, but he justifies it by the conservatism of the assumptions in the DIERS equation). Fauske's equation is:

$$A = K_G \frac{m_R}{m_t} \frac{(dP/dt)_{max}}{P_m^{3/2}} \qquad \text{(A5.30)}$$

The value of K_G depends on the experimental equipment in which $(dP/dt)_{max}$ is measured (see Annex 2). For an open test in the VSP, $K_G = 3.3 \times 10^{-5}$, if the units in equation (A5.30) are m^2 for A, psi/minute for (dP/dt) and psia for P_m. For the RSST, with the same units, $K_G = 3 \times 10^{-6}$.

A5.16 FAUSKE'S NOMOGRAPHS

Fauske[20,21] has produced nomographs (graphs) for the purpose of relief sizing. That for tempered systems is based on Fauske's sizing method for vapour pressure systems (see A5.3) while that for untempered systems is based on Fauske's method for gassy systems (see A5.15 above). The conditions of applicability of the appropriate sizing methods apply. In addition, the nomographs make assumptions about the values of physical properties and the permitted overpressure. They were produced primarily to allow rapid screening of existing reactor relief systems. For design purposes, it is preferable to use appropriate sizing equations from this Workbook.

REFERENCES FOR ANNEX 5

1. J E Huff, "Emergency Venting Requirements", Plant/Operations Prog, 1 (4), 211-229, 1982
2. J E Huff, Lecture Notes for Session 1 of AIChE Continuing Education Course, "Emergency Relief Design Using DIERS Technology", 1994
3. H A Duxbury & A J Wilday, "Efficient Design of Reactor Relief Systems", International Symposium on Runaway reactions, 373-393, CCPS, 1989, ISBN 0-8169-0460-X
4. H K Fauske, "Emergency Relief System Design for Runaway Chemical Reaction : Extension of the DIERS Methodology", Chem Eng Res Dev, 67, 199-201, March 1989
5. H K Fauske, Plant/Operations Prog, 4, (3), 132-143, 1985
6. J C Leung, "Overpressure During Emergency Relief Venting in Bubbly and Churn-turbulent Flow", AIChE Journal, 33 (6), 952-958, 1987
7. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A7, DIERS/AIChE, 1992, ISBN 0-8169-0568-1
8. A J Wilday & G Daskalakis, "Pressure Relief Design for Chemical Reactors Exposed to External Fire", Paper 53c, AIChE Summer National Meeting, August 1994
9. C F Parry, "Relief Systems Handbook", IChemE, 1994, ISBN 0 85295 267 8
10. J Singh, "Vent Sizing for Gas-generating Runaway Reactions", J Loss Prev Process Ind, 7 (6), 481-491, 1994
11. A J Wilday, J Singh & K R Cliffe, "Development of a Dynamic Model for Pressure Relief of Gas Generating Chemical Reactions", IChemE Symp. Series No 141, 523-536, 1997

12. J C Leung, "Simplified Vent Sizing Methods Incorporating Two-phase Flow" International Symposium on Runaway Reactions and Pressure Relief Design, 200-236, AIChE, 1995, ISBN 0-8169-0676-9

13. J C Leung, "Venting of Runaway Reactions with Gas Generation", AIChE J., 38 (5), 723, 1992

14. J C Etchells, T J Snee and A J Wilday, "Relief System Sizing for Exothermic Runaway : The UK HSE Strategy", International Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, 135-162, AIChE, 1998, ISBN 0-8169-0761-7

15. J C Leung, J A Noronha, A J Torres, J J Sharkey & M H Yue, "A Vent Sizing Program with Particular Reference to Hybrid Runaway Reaction Systems", International Symposium on Runaway Reactions and Pressure Relief Design, 567 - 579, AIChE, 1995, ISBN 0-8169-0676-9

16. H A Duxbury, "The Sizing of Relief Systems for Polymerisation Reactors", The Chemical Engineer, 31-37, January 1980

17. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A8, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

18. J J Boyle, Chem Eng Prog, 63, (8), 61-66, 1967

19. M J Creed & H K Fauske, "An Easy, Inexpensive Approach to the DIERS Procedure", Chem Eng Prog, 86, (3), p 45, 1990

20. H K Fauske, M A Grolmes and G H Clare, "Applying DIERS Methodology to Existing Plant Operations", paper 73F, AIChE Spring National Meeting, March 1988

21 H G Fisher et al, "Emergency Relief System Design Using DIERS Technology", Section VI A6, DIERS/AIChE, 1992, ISBN 0 8169 0568 1

ANNEX 6

SIZING FOR SINGLE-PHASE RELIEF

A6.1 INTRODUCTION

A6.1.1 The assumption of single-phase relief

For tempered systems, the relief system for single-phase relief will be smaller than if two-phase relief occurred, and so is potentially unsafe. For untempered systems, the worst case is initial single-phase gas relief with two-phase relief beginning at the point of maximum reaction rate. In either case, any assumption that relief will be single-phase should be carefully checked using the information in 4.3 and Annex 3. Sometimes, if the reacting system is not inherently foamy, the maximum fill level in the reactor can be controlled to ensure that relief would be single-phase. This Annex covers sizing methods for single-phase relief; sizing methods for two-phase relief are given in Chapters 6 - 8.

A6.1.2 Choice of relief device

For single-phase relief, the required relief system size is not affected by whether relief is via a safety valve or a bursting disc.

However, for tempered systems, relief via a bursting disc may give rise to two-phase relief due to flashing as the reactor depressurises. Although this does not affect the sizing of the relief system, it does increase the mass loss from the reactor and has implications for the disposal system design. Use of a safety valve, rather than a bursting disc, can prevent this.

The relief system can be sized for single-phase vapour flow if:

a) a level swell calculation (see Annex 3), using the vapour production rate due to the runaway reaction (see equation (A3.1)), indicates that single-phase relief would occur; and

b) a level swell calculation, using the relief system capacity (which equals the depressurisation rate) (see equation (A3.2)), indicates that two-phase relief would occur

In such cases, two-phase relief occurs only as a result of depressurisation (i.e. the pressure is falling) and so cannot overpressurise the reactor. Although the relief system can be sized for single-phase vapour flow, the design of any downstream disposal system must take account of the two-phase flow which will actually occur.

A6.1.3 Approach to relief sizing for single-phase relief

Relief sizing for single-phase relief can be done assuming steady-state, i.e. the gas/vapour needs to be removed by the pressure relief system at the rate at which it is generated by the reaction. A required relief rate, W_g, can be specified, and the relief system can be sized to give a capacity which exceeds it. If the capacity is expressed as mass capacity per unit flow area, G_g, then the required relief area can be obtained from:

$$A = \frac{W_g}{G_g} \tag{A6.1}$$

The calculation of the required relief rate, W_g, is described in A6.2 below, and the calculation of the single-phase relief mass flow capacity per unit area, G_g, is described in A6.3 below.

A6.2 REQUIRED RELIEF RATE

Data about the rate of the runaway reaction, (characterised by the adiabatic rate of temperature rise, dT/dt, and the rate of permanent gas generation, Q_G, as appropriate), is best obtained experimentally. Methods are given in Annex 2. The relief system sizing method will depend on whether the system is tempered or untempered (see 4.2 and Annex 2).

A6.2.1 Tempered systems

For tempered systems, the required relief rate depends on the reaction rate, usually expressed as the adiabatic rate of temperature rise, dT/dt, at the tempering temperature at the relevant pressure. (The relevant pressure may be the relief pressure or the maximum accumulated pressure, whichever yields the smaller relief size.) Because the system is tempered (see 4.2), the relief system will prevent the temperature (and reaction rate) from rising higher than this. It is likely that the relief system size will be minimised by carrying out the calculation of required relief rate at the lowest possible relief pressure. However, if the equipment design pressure is sufficiently high so that the reaction is almost complete before the design pressure is reached, then a smaller relief system might be obtained by carrying out the calculation at the maximum accumulated pressure.

The required relief rate for tempered systems is given by:

$$W_g = \frac{dT}{dt}\frac{m\,C_f}{h_{fg}} + Q_G\,\rho_g \tag{A6.2}$$

The first term is the vaporisation rate and the second term is the rate of production of permanent gas by the reaction The second term is only required for tempered hybrids

A6.2.2 Untempered systems

For untempered systems, pressure relief cannot control the temperature rise caused by the runaway. The reacting mixture will therefore increase in temperature and reaction rate during relief. The steady-state relief sizing calculation needs to be performed at the peak reaction rate, which is normally close to the end of the reaction. The minimum relief system size will be obtained if the calculation is performed at the maximum accumulated pressure.

The required relief rate for untempered systems is given by:

$$W_g = Q_{G\max}\,\rho_g + \frac{m\,C_f}{h_{fg}}\left(\frac{dT}{dt}\right)_{\max} \qquad \text{(A6.3)}$$

Here the first term is the peak rate of permanent gas generation and the second term is the corresponding rate of vaporisation. The second term is only required for untempered hybrids (see 4.2).

A6.3 RELIEF SYSTEM CAPACITY

The relief system capacity should be calculated at the same pressure as was the required relief rate in A6.2 above, so that they can be compared.

Gases are compressible, so their density decreases and velocity increases with pressure drop through a relief system. The increasing velocity leads to choking when the velocity reaches the speed of sound in the gas. This is discussed in more detail in 9.2.

Figure A6.1 is a decision tree to aid selection of a calculation method for relief system capacity.

A6.3.1 Relief via a safety valve

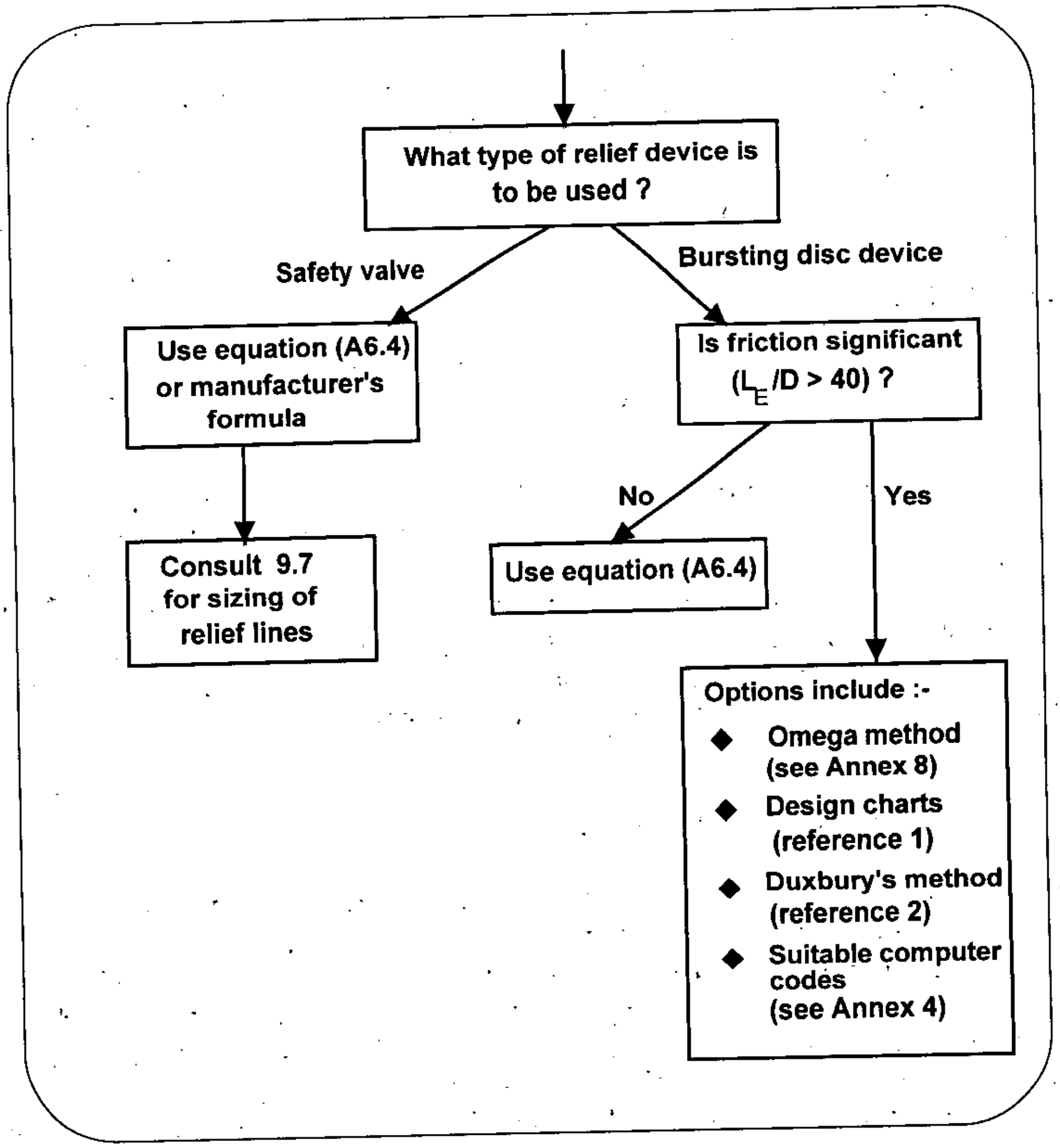
The formula for semi-ideal gas flow through a nozzle is commonly used to obtain the flow capacity of a safety valve[3]:

$$G_g = C_D\,P_0\,C_{sv}\sqrt{\frac{M_W}{Z_0 T_0}}\;F_B \qquad \text{(A6.4)}$$

The value of F_B in equation (A6.4) depends on whether or not flow is choked in the safety valve nozzle. Choking occurs if:

$$\eta_c \geq \frac{P_B}{P_0} \qquad \text{(A6.5)}$$

Figure A6.1 **DECISION TREE FOR SELECTION OF METHOD FOR SINGLE-PHASE GAS FLOW CAPACITY**



where P_B is the back pressure on the safety valve. This will depend on any constant back pressure and pressure drop (built-up back pressure) in the downstream piping. For a conventional safety valve, the built-up back pressure should be limited to 10% of the gauge set pressure. Higher back pressures can be tolerated by balanced valves (see 9.7.3). Values of the parameter C_{sv} and of the critical pressure ratio, η_c, are given in Table A6.1 as a function of the isentropic coefficient, k, (which is equal to the specific heat ratio C_p/C_v if the gas is ideal). The compressibility factor, Z, can be obtained from a generalised chart[1] as a function of the reduced temperature and pressure (temperature divided by thermodynamic critical temperature and pressure divided by thermodynamic critical pressure)

Table A6.1 **CHOKED FLOW DATA FOR GASES AS A FUNCTION OF ISENTROPIC COEFFICIENT**

k	1	1.1	1.2	1.3	1.4
C_{sv}	6.67×10^{-3}	6.90×10^{-3}	7.09×10^{-3}	7.30×10^{-3}	7.52×10^{-3}
η_c	0.606	0.585	0.565	0.546	0.529

If choking occurs (see equation A6.5), then F_B is equal to 1.0. For unchoked (subsonic) flow, F_B is given by[3]:

$$F_B = \left(\frac{P_B}{P_0}\right)^{1/k} \sqrt{\frac{2}{k-1}\left(1-\left(\frac{P_B}{P_0}\right)^{(k-1)/k}\right)\left(\frac{k+1}{2}\right)^{(k+1)/(k-1)}} \qquad \text{(A6.6)}$$

Sizing formulae based on equations (A6.4) to (A6.6) are given in many safety valve manufacturers' catalogues. Where possible, the method given by the manufacturer of the particular safety valve should be used to find its capacity because this will contain the correct values of flow area and discharge coefficient for the valve. (This is not usually true in the USA where National Board certification information should be used.) The relief lines upstream and downstream of the safety valve also need sizing. Further information is given in 9.7 and references 2 and 4.

A6.3.2 Relief via a bursting disc

If relief is via a bursting disc, the flow capacity of the relief system will normally depend on friction and choke points in the relief system. The only exception is where friction is not important (L_E/D less than about 40), where equation (A6.4) can be used.) Where friction is significant, an isometric sketch of the route of the relief system will be required to determine the capacity. If the system is to be of constant diameter, then using the sketch, the total equivalent length, L_E, of the route, including the frictional resistance of bends and fittings can be determined[1]. This can also be expressed in terms of total frictional velocity head loss, K:

$$K = \frac{4fL_E}{D} \qquad \text{(A6.7)}$$

For a system of constant diameter (giving a single potential choke point at the end of the pipe), and if the gas is ideal, then the Design Charts for adiabatic flow of gases, given in Perry[1] or the Omega method with $\omega = 1$ (see Annex 8) can be used to determine the flow capacity. K is a parameter within these charts.

For multi-diameter systems, approximate analogous hand calculations can be made for ideal gas by converting the equivalent lengths or K values for each section (and the friction losses at enlargements and contractions) to corresponding equivalent lengths of pipe of just one chosen diameter and adding them up. If there are any choke points, then the smallest estimate of flow will be obtained by choosing the smallest diameter in the system. Duxbury[2] discusses this, and gives examples. If it is desired to know the conditions at a particular point (e.g. identifying where any choke occurs), or if the gas is significantly non-ideal, more elaborate calculations will be necessary.

A number of proprietary computer codes for gas flow exist (see Annex 4). Many of these are intended for low velocity flow and do not handle choking. Before using such a code to evaluate relief system capacity, it should be checked that it is valid for high velocity choked flow (unless the use of equation (A6.5) indicates that flow will not be choked).

A6.4 WORKED EXAMPLE : RELIEF SYSTEM SIZING FOR SINGLE-PHASE RELIEF

A6.4.1 Description of problem

A reaction has been characterised as a tempered hybrid system and it has been determined that the system will relieve single-phase gas/vapour. Relief sizes for both a safety valve and a bursting disc system are required. The reactor contains a charge of 3000 kg. Data for relief sizing have been compiled in Table A6.2. The type of safety valve selected has a de-rated discharge coefficient under BS 6759[3] of 0.87.

Table A6.2 **DATA FOR WORKED EXAMPLE : SINGLE-PHASE RELIEF SIZING**

	Relief pressure	Maximum permitted pressure
Pressure (barg)	4.4	6.05
Tempering temperature (K)	380	392
dT/dt (K/min) (corrected for thermal inertia)	8	17
Q_G (m^3/s) (corrected for thermal inertia)	0.06	0.13
Liquid specific heat (kJ/kg K)	1.98	2.11
Latent heat (kJ/kg)	301	289
Gas molecular weight	44	44
Gas compressibility	1	1
Gas isentropic coeff.	1.4	1.4
Vapour molecular weight	82	82
Vapour compressibility	0.9	0.8
Vapour isentropic coefficient	1 05	1 05

The total number of velocity heads for the proposed relief routes are as follows:

Safety valve	
upstream of valve	K = 0.9
downstream of valve	K = 1.6
Bursting disc and all relief pipework	K = 1.9

A6.4.2 Required relief rate

The required relief rate will first be calculated using equation (A6.2). It can be seen from Table A6.2, that both dT/dt and Q_G are considerably lower at the relief pressure than at the maximum accumulated pressure. The calculation will therefore be performed at the relief pressure since this should give the smallest relief size. Operation of the relief system will then prevent the pressure rising to the maximum accumulated pressure, for which a larger relief system would be needed.

Required relief rate is given by:

$$W_g = \frac{dT}{dt}\,\frac{m\,C_{pf}}{h_{fg}} + Q_G\,\rho_g \qquad \text{(A6.2)}$$

The gas density can be approximated for an ideal gas:

$$\rho_g = \frac{M_W}{22.4} \times \frac{P}{1.01\times10^5} \times \frac{273}{T} = \frac{44}{22.4} \times \frac{(4.4+1.01)\times10^5}{1.01\times10^5} \times \frac{273}{380} = 7.56\ kg/m^3$$

Inserting the data from Table A6.2 into equation (A6.2), modifying units as required, gives:

$$W_g = \left(\frac{8}{60} \times \frac{3000\times1980}{301000}\right) + (0.06 \times 7.56) = 2.63 + 0.4536 = 3.08\ kg/s$$

A6.4.3 Safety valve sizing

The above calculation indicates that the vapour flow rate is 2.63 kg/s and the gas flow rate is 0.4536 kg/s. This can be used to obtain weighted average values of physical properties required for calculating the relief system capacity.

$$M_W = \frac{(2.63\times82)+(0.4536\times44)}{(2.63+0.4536)} = 76.4$$

$$Z = \frac{(2.63\times0.9)+(0.4536\times1.0)}{(2.63+0.4536)} = 0.915$$

$$k = \frac{(2.63x1.05)+(0.4536x1.4)}{(2.63+0.4536)} = 1.10$$

Equation (A6.5) shows that choking occurs if :

$$\eta_c \geq \frac{P_B}{P_0} \qquad \text{(A6.5)}$$

Table A6.1 indicates that for k=1.1, $\eta_c = 0.585$.

Assume that the back pressure on the safety valve will be limited to 10% of the gauge set pressure. (The back pressure required is the sum of the constant and built-up back pressure. If the relief system discharges direct to the atmosphere, then the constant back pressure will be zero.) If the relief pressure is 4.4 barg, the set pressure is 4.4/1.1 = 4.0 barg, and the maximum back pressure is 0.1 x 4.0 = 0.4 barg. Thus:

$$\frac{P_B}{P_0} = \frac{0.4+1.01}{4.0+1.01} = 0.281 \ < \ 0.585$$

This is true, and so flow through the safety valve will be choked. Equation (A6.4) can then be used to obtain the mass flow capacity per unit area of the safety valve, setting F_B equal to 1.0 because the flow is choked. From Table A6.1, for k = 1.1, C_{sv} is $6.90x10^{-3}$.

$$G_g = C_D P_0 C_{sv} \sqrt{\frac{M_W}{ZT}}\, F_B \qquad \text{(A6.4)}$$

$$= 0.87 \times (4.4 + 1.01)x10^5x6.9x10^{-3}\sqrt{\frac{76.4}{0.915x380}}\, x1.0 = 1522\ kg/m^2s$$

The required flow area of the safety valve can now be found using equation (A6.1):

$$A = \frac{W_g}{G_g} = \frac{3.08}{1522} = 2.02x10^{-3}\ m^2 \qquad \text{(A6.1)}$$

This can be used to select the required size of safety valve. For the type of safety valve chosen, the next largest valve size has an actual area of $2.36x10^{-3}$ m^2. The inlet and outlet pipe sizes for this valve are 0.075 m inlet and 0.1 m outlet.

Upstream pressure drop

The objective is to calculate the non-recoverable (frictional) pressure loss rather than the total pressure drop (which will also contain recoverable pressure drop due to change in momentum)

The flow capacity for checking the upstream pressure drop and back pressure for the valve is obtained by using the actual flow area and multiplying by 1.1 to remove the 0.9 de-rating factor in the discharge coefficient[4]:

$$W_{g,actual} = 1.1A_{actual}G_g = 1.1x1522x2.36x10^{-3} = 3.951\ kg/s$$

The upstream pressure drop can be estimated using non-compressible flow equations together with the (conservative) gas density at the downstream pressure i.e. at the set pressure of 4.0 barg = 5.0 bara. (Alternatively the upstream pressure drop could be estimated using the Design Charts for adiabatic flow of gases given in Perry[1], but use of the Design Charts is not demonstrated here.) For an ideal gas:

$$\rho_g = \frac{M_W}{22.4}x\frac{P}{10^5}x\frac{273}{T} = \frac{76.3}{22.4}x\frac{5x10^5}{10^5}x\frac{273}{380} = 12.24\ kg/m^3$$

The velocity in a 0.075 m diameter pipe is given by :

$$u = \frac{W_g}{\rho_g A_p} = \frac{3.951}{12.24x\frac{\pi}{4}x(0.075)^2} = 73.1\ m/s$$

The upstream pressure drop is given by :

$$\Delta P = K\tfrac{1}{2}\rho_g u^2 = 0.9x\tfrac{1}{2}x12.24x73.1^2 = 29433\ N/m^2$$

$$\text{Percentage pressure drop} = \frac{29433}{4x10^5}x100\% = 7.36\%$$

This exceeds 3% and is therefore too high. Increasing the inlet pipe diameter to 0.1 m will reduce the upstream pressure drop to approximately 7.36 x $(0.075/0.1)^4$ = 2.33% which would be acceptable.

Back pressure on safety valve

The Omega method (see Annex 8) can be used to check whether or not the back pressure would exceed 10%. This calculation is performed with an upstream pressure of 10% of set pressure (i.e. 0.4 barg = 1.4 bara) and a downstream pressure of atmospheric. For single-phase gas flow, ω = 1. Figure A8.2 indicates that G_c^* = 0.6. Figure A8.3 for ω = 1 and K = 4fL/D = 1.6 gives G/G_c = 0.75.

Reading from Figure A8.7 with G/G_c = 0.75 and ω = 1 gives a critical pressure ratio, η_c = 0.45.

10% of set pressure is 0.4 barg = 1.4 bara. Thus the back pressure ratio, η, = 1/1.4 = 0.714. The dimensionless back pressure, $(1-\eta)/(1-\eta_c)$ = (1-0.714)/(1-0.45) = 0.52. Reading from Figure A8.6 gives a back pressure correction factor, G/G_c=0.88.

$$G_c = G_c^* \sqrt{P_0 \rho_0} \qquad \text{(A8.14)}$$

$$\rho_{g0} = \frac{M_W}{22.4} x \frac{P}{10^5} x \frac{273}{T} \approx \frac{76.3}{22.4} x \frac{1.4x10^5}{10^5} x \frac{273}{380} = 3.43\ kg/m^3$$

Thus

$$G_g = \left(\frac{G}{G_c}\right)_{friction} \left(\frac{G}{G_c}\right)_{backpressure} G_c^* \sqrt{P_0 \rho_0}$$

$$= 0.75x0.88x0.6\sqrt{1.4x10^5 x3.43} = 274\ \text{kg/m}^2\text{s}$$

The actual G in the 0.1 m diameter line is:

$$G_{g,actual} = \frac{W_{g,actual}}{A_p} = \frac{3.951}{\frac{\Pi}{4}(0.1)^2} = 503.1\ \text{kg/m}^2\text{s}$$

This exceeds the 274 kg/m^{2}s, which can be achieved with a back pressure of 10%. The back pressure will therefore be greater than 10%. If the downstream pipe diameter were increased to 0.15 m (the next largest standard pipe size), then

$$G_{g,actual} = \frac{3.951}{\frac{\Pi}{4}(0.15)^2} = 223.6\ \text{kg/m}^2\text{s}$$

This is less than that which can be achieved with a 10% back pressure, and so the actual back pressure, with a 0.15 m diameter pipe will be less than 10%. This method could be used iteratively with different guesses of the back pressure in order to find the actual back pressure. Alternatively, the Design Charts for adiabatic flow of gases given in Perry[1] could be used instead of the Omega method as they are more rigorous for the gas-only relief case. However, their use has not been demonstrated here.

A6.4.4 Bursting disc sizing

The vent mass flow capacity per unit area, G_g, can be obtained using the Omega method (see Annex 8). For gas flow, $\omega = 1$, and reading from Figure A8.2, the dimensionless mass flow per unit area of a choked nozzle is 0.6.

$$G_c = G_c^* \sqrt{P_0 \rho_0} \qquad \text{(A8.13)}$$

The gas density at 4.4 barg is given by:

$$\rho_{g0} \approx \frac{M_W}{22.4} x \frac{P}{10^5} x \frac{273}{T} = \frac{76.4}{22.4} x \frac{5.4x10^5}{10^5} x \frac{273}{380} = 13.2\ \text{kg/m}^3$$

$$G_c = 0.6\sqrt{5.4x10^5 x13.2} = 1602\ \text{kg/m}^2\text{s}$$

This must now be corrected for friction and non choked flow

Reading from Figure A8.3 for K =4fL/D =1.9 and ω = 1, gives a friction correction factor of 0.7) Figure A8.7 indicates that the critical pressure ratio is 0.4. This exceeds the available pressure ratio (venting to atmospheric pressure) of 1/5.4 = 0.185, and so flow is choked. Therefore no correction is needed for non-choked flow.

$G_g = 0.7 \times 1602 = 1121 \text{ kg/m}^2\text{s}$

The relief area can now be found:

$$A = \frac{W_g}{G_g} = \frac{3.10}{1121} = 2.77x10^{-3} \text{ m}^2$$

The corresponding relief diameter is 0.059 m, and the next largest pipe size of 0.075 m would be chosen.

REFERENCES FOR ANNEX 6

1. R H Perry & D W Green (ed.), "Perry's Chemical Engineer's Handbook", Chapter 5, 7th Edn., McGraw Hill, 1997

2. H A Duxbury, "Relief Line Sizing for Gases", The Chemical Engineer, 783 and 851, 1979

3. BS6759: part 3: 1984, "Specification for Safety Valves for Process Fluids", BSI, 1984

4. L Friedel & J Schmidt, "Design of Long Safety Valve Vent Line Systems for Gas Relief", J Loss Prev Process Ind, 6, 293-301, 1993

ANNEX 7

SAFETY FACTORS

A7.1 THE USE OF SAFETY FACTORS

Uncertainty is introduced at many stages in the sizing of pressure relief systems for runaway chemical reactions, and the application of a safety factor to offset this uncertainty may be appropriate. This Annex gives some guidance on the selection of an appropriate value for any safety factor.

The following procedure is suggested:

a) Consider the value of safety factor required to cover expected uncertainties in data used in the relief sizing method (see A7.2 below).

b) Consider the likely conservatism of the relief sizing method which has been chosen (see A7.3 below).

c) Make a judgement on the basis of (a) and (b) about the value of any safety factor to be applied.

The chosen safety factor may be applied to increase the calculated relief area. Alternatively, the value of the required mass relief rate from the reactor may be multiplied by the safety factor before calculation of the relief area required to pass this flowrate.

A7.2 UNCERTAINTY IN THE SIZING CALCULATION

The general approach to uncertainty followed here is that of Duxbury[1,2]. The overall safety factor, F_o, may be represented as the product of a number of sub-factors each taking account of particular features:

$$F_o = F_1 . F_2 . F_3 . F_4 .... F_N \qquad \text{(A7.1)}$$

It is up to the designer to determine what sub-factors need to be included for any particular application. Possible sub-factors include:

a) Uncertainty in the data. The magnitude and direction of any errors arising from data assumptions should be assessed. Particular attention should be paid to any errors affecting the rate of reaction or its dependence on temperature. See Annex 2 for advice on the use of suitable calorimeters for the measurement of reaction rate data. Calorimetric data (suitably corrected for thermal inertia as described in A2 7 2) can be used directly in many of the relief sizing equations given in this Workbook. The main sources of uncertainty are then the extent to which the calorimeter reproduced full-scale, worst case reaction conditions and the reproducibility of the calorimetric data. For tempered systems, the accuracy of the vapour pressure data, by which the temperatures at the relief pressure and maximum accumulated pressure are estimated, can greatly affect the values of self-heat rate used in the relief sizing calculation.

For computer simulation (see Annex 4), it will be necessary to correlate the kinetics of the reaction. The results of the relief sizing calculation will be sensitive to the chosen value of the activation energy.

b) Inaccuracy in the fluid flow calculation. It is assumed that the largest realistic pipe roughness will have been used in the calculations. The most accurate, computerised two-phase flow calculations may be accurate only to a factor of 2[1,2] or 1.7[3] ($=\sqrt{3}$) although for systems with negligible friction and static head change, this may be reduced to somewhere in the range 1.2 to 1.5[2]. However, the HEM (see Chapter 9 and Annex 8) was always conservative when compared with the results of DIERS tests for non-viscous systems[4], but the scope of such tests was limited.

If an applicable version of the HEM has been used, then a safety factor may not be required for relief sizing, but one may be needed for sizing of any downstream disposal system (since for disposal system sizing, underestimation of the flow is unsafe).

c) Neglect of gas/ vapour phase non-ideality. Detailed comments on appropriate safety factors for this case are given in reference 1.

d) Assumption of constant liquid properties. The effect of assuming constant liquid properties should be estimated (if this assumption has been made, such as in the Omega method) and a sub-factor applied if necessary[1]. Safe values, giving a low value of flow, are low density, high specific heat and low latent heat.

e) Any other factors which could cause undersizing in the particular application.

It is difficult to treat the following causes of uncertainty by means of a safety factor:

i) Uncertainty in the choice of the worst case relief scenario. If the worst case scenario has not been chosen, the required factor is unknown and could be extremely large (several orders of magnitude). It is therefore recommended to pay great attention to selecting the correct worst case (see Chapter 3).

ii) Cases where the chosen sizing method is invalid for the application. It is important to check that all conditions of applicability for sizing methods have been met.

A7.3 CONSERVATISM OF SIZING METHODS

The likely conservatism of different sizing methods cannot be quantified without extensive large-scale experimental validation. (Some such validation at pilot-scale is currently being carried out by the Health and Safety Executive and as part of a collaborative EC project[5].) However, some qualitative guidance can be given.

It is recommended that the chosen sizing method be evaluated for a range of overpressures. This will give an indication of the likely consequence of undersizing, in terms of how far the pressure may be expected to rise above the maximum permitted for the vessel. For moderate overpressures (typically 10-30% of the absolute relief pressure), the consequence of undersizing may sometimes be small.

For tempered systems, if significant vapour/ liquid disengagement is to be expected, then a method which assumes homogeneous two-phase relief is likely to be conservative. The extent of this conservatism can be estimated by comparison with the use of a method which allows for disengagement. Sizing methods which take account of vapour/ liquid disengagement, particularly those computer simulations which use level swell calculations to estimate the vapour fraction entering the relief system, should be regarded as best estimate rather than conservative calculations.

For untempered systems, the DIERS sizing equation (see 7.3) can be conservative, unless relief is of gas alone until close to the peak reaction rate. However, it is important to correctly account for any dissolved gas in the experimental test[5]. Methods which account for early loss of reactants from the reactor, by two-phase relief, should be regarded as best estimate methods rather than conservative calculations.

REFERENCES FOR ANNEX 7

1. H A Duxbury, "Comments on Safety Factors to be Applied When Sizing a Simple Relief System", Notes of Short Course on "Pressure Relief : The Design of Pressure Relief Systems", Session 9, Loughborough University, 1996 (This was also published with same title as Appendix 13 in F P Lees, "Loss Prevention in the Process Industries", 2nd Edn., Butterworth-Heinemann, 1996, ISBN 0 7506 1547 8. However, note misprinted power in Equation A13.2: the last term should be $Z_{max}^{1/2}$.)

2. H A Duxbury & A J Wilday, "The Design of Reactor Relief Systems", IChemE Symposium Series No 115, 125-140, IChemE, 1989

3. L L Simpson, "Navigating the Two-phase Maze", International Symposium on Runaway Reactions and Pressure Relief Design, 394-417, AIChE, 1995, ISBN 0-8169-0676-9

4 H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Chapter II, DIERS/AIChE, 1992, ISBN 0 8169 0568 1

5. J C Etchells, T J Snee and A J Wilday, "Relief System Sizing for Exothermic Runaway : The UK HSE Strategy", International Symposium on Runaway Reactions, Pressure Relief Design and Effluent Handling, 135-162, AIChE, 1998, ISBN 0-8169-0761-7

ANNEX 8

THE OMEGA METHOD

A8.1 INTRODUCTION

The Omega method calculates the two-phase flow capacity per unit area, G, of a nozzle or pipe of constant diameter. It evaluates the homogeneous equilibrium model (see 9.4.1) for two-phase flow. The Omega method is particularly convenient, when applicable, because it does not require the use of a computer. All properties can often be evaluated at the conditions in the upstream vessel, (which are known). Most other methods to evaluate G for two-phase flow require the use of appropriate computer codes (see Annex 4). Exceptions are given in 9.4.

The Omega method can be used for any system type: vapour pressure, gassy or hybrid. A8.3 below discusses the selection of the appropriate Omega method calculation in any particular case.

Omega is a correlating parameter in an "equation of state" (EOS) which links the specific volume of a two-phase mixture flowing in a relief system with the pressure at any point. Such an EOS is required to evaluate the HEM without performing repeated flash calculations. The EOS used by the Omega method is:

$$\left(\frac{v}{v_0}-1\right)=\omega\left(\frac{P_0}{P}-1\right) \qquad \text{(A8.1)}$$

This EOS has the advantage that it is simple enough to facilitate analytical solution of the HEM equations. Its limitations are discussed in A8.2 below. Simpson[1] reviews alternative possible EOSs for numerical solution of the HEM. A computer code which evaluates a selection of these methods is provided with the CCPS Guide[2].

Omega is a dimensionless number which characterises the compressibility of the two-phase mixture. In order of increasing compressibility:

gassy two-phase systems ($\omega < 1$)
gas-only single-phase flow ($\omega = 1$)
flashing two-phase systems (vapour pressure and hybrid systems) ($\omega > 1$)

A8.2 APPLICABILITY OF THE OMEGA METHOD

The Omega method makes the following assumptions[3]:

a) Flow is turbulent.

b) Homogeneous two phase flow (no phase slip) occurs (see 9 3 1)

c) If the two-phase mixture flashes (vapour pressure and hybrid systems) then:

   i) vapour/ liquid equilibrium is maintained;
   ii) the expansion process for the flashing mixture is isenthalpic.

d) If the two-phase mixture is non-flashing (gassy systems) then:

   i) thermal equilibrium is maintained between the phases;
   ii) the expansion process is isentropic.

e) The friction factor is constant.

f) The method is inapplicable close to the thermodynamic critical point[3] and conditions of applicability are:

$$\frac{T}{T_{Tc}} < 0.9 \qquad (A8.2)$$

and

$$\frac{P}{P_{Tc}} < 0.5 \qquad (A8.3)$$

An improved nozzle correlation close to the thermodynamic critical temperature is given by Leung in reference 4.

g) If the Omega parameter is evaluated at the stagnation conditions in the upstream vessel, the method can be inaccurate for wide boiling multi-component mixtures[5] and systems with a high pressure drop[6]. This is less of a problem when equation (A8.4), rather than the simplified equations, is used to evaluate the Omega parameter. Alternatively, the charts proposed by First and Huff[7] can be used to calculate G for wide boiling multi-component mixtures (see condition (h) below). For both equation (A8.4) and First and Huff's method, a physical properties package is needed to evaluate the behaviour of the mixture on flashing. First and Huff's charts are based on correlation of the results of a computer code for the HEM, rather than on use of the Omega method to evaluate the HEM.

The above conditions of applicability apply even when the Omega parameter is evaluated by the most accurate method, i.e. using equation (A8.4) and making use of computerised physical property calculations. Alternatively, simplified equations for evaluating Omega can also be used (equations (A8.5) to (A8.10)). These introduce a further condition of applicability:

h) The most common forms of the definition of Omega for flashing two-phase mixtures (equations (A8.5) to (A8.10)) make use of the Clausius-Clapeyron thermodynamic relationship. This holds for ideal single component systems[4] and will be approximately true for ideal mixtures which do not have too wide a boiling range. Leung[5] suggests that if the range of atmospheric boiling temperatures between the heaviest and lightest components in the mixture is less than 80°C, then the error in using the Omega method will be less than 15%. If this is not the case, Omega can be calculated using equations (A8.4) or (A8.11).

A8.3 STRATEGY FOR THE USE OF THE OMEGA METHOD

A flow chart for selecting the appropriate elements of the Omega method is given in Figure A8.1. Different versions of the Omega method calculation are provided for the following types of reacting system:

i) Vapour pressure systems or gassy systems: these systems are covered in A8.4.

ii) Hybrid systems: these systems are covered in A8.5.

Leung[5] also gives an Omega method calculation procedure for vapour pressure systems in which the liquid is subcooled at the inlet to the relief system. This could be due either to the presence of pad gas or to a significant static head of liquid above the point of relief. This is very unusual for the design of relief systems, unless the relief system is from the bottom of the reactor. For relief from the top of the reactor, any pad gas will be vented as soon as the relief system operates, and before the reactor contents begin to boil and give rise to two-phase relief. Thus, the methods given in A8.4 are appropriate for two-phase relief of a vapour pressure system from the top of the reactor.

Each calculation to obtain the two-phase mass discharge capacity per unit cross-sectional area, G, consists of the following stages:

a) Calculate Omega using the most appropriate equation.

b) Find the dimensionless two-phase mass flow per unit area for choked nozzle flow, and hence the actual G for choked nozzle flow.

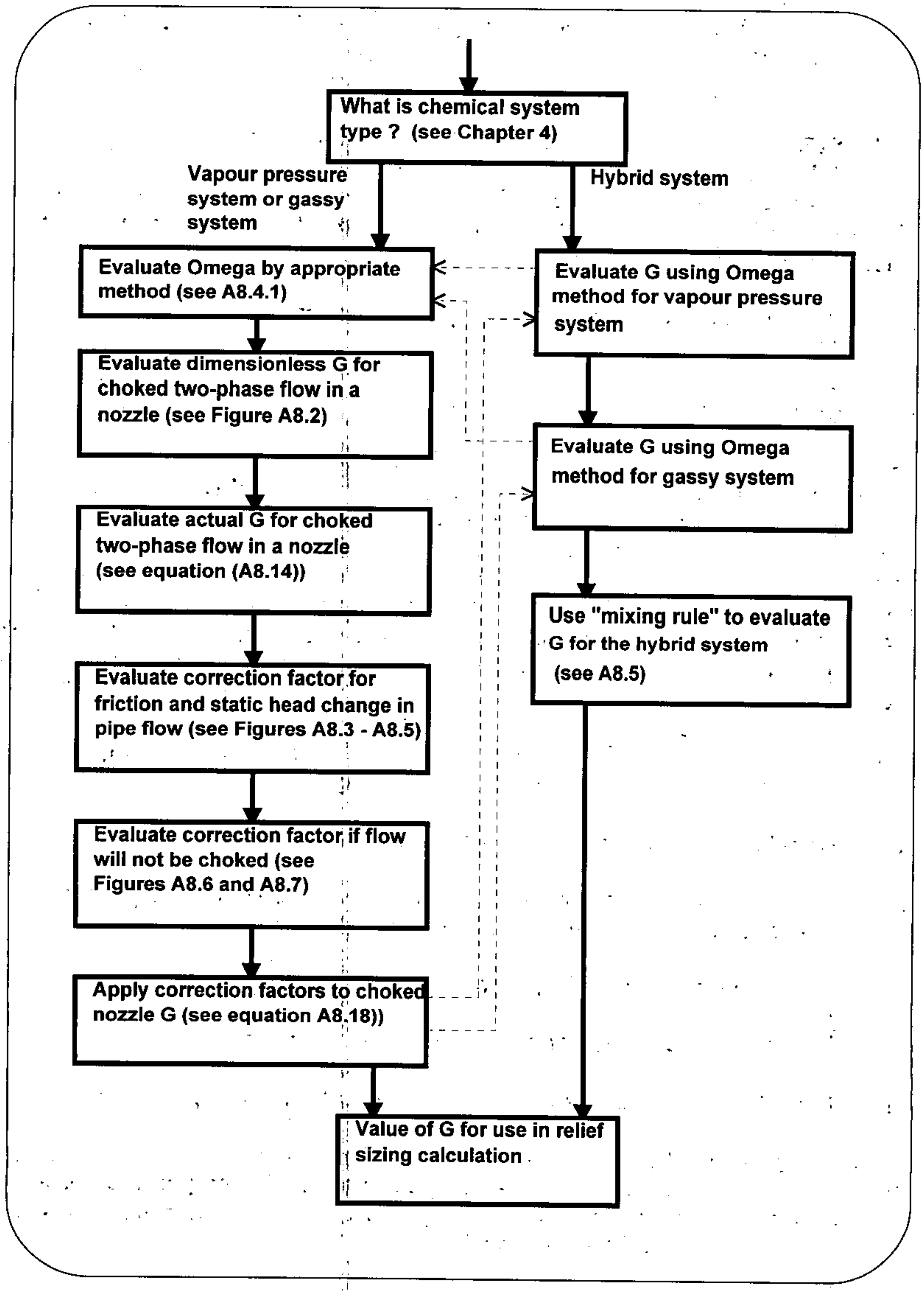
c) Find a correction factor for pipe friction and static head change.

d) Find a correction factor for non-choked flow (if appropriate).

e) Apply these correction factors to find the actual G for the application.

In the Omega method as given here, a series of dimensionless groups are calculated and then these are used to read values from graphs. The graphs are convenient because many of the equations underlying the graphs require a time-consuming trial and error procedure for evaluation

Figure A8.1 **FLOW CHART FOR OMEGA METHOD CALCULATION FOR ANY GIVEN APPLICATION**



A8.4 OMEGA METHOD FOR VAPOUR PRESSURE SYSTEMS AND GASSY SYSTEMS

A8.4.1 Calculation of Omega

Most accurate definition of Omega

Omega can be evaluated directly from the EOS for the Omega method (see equation (A8.1)[5,8]:

$$\omega = \frac{\frac{v_t}{v_0}-1}{\frac{P_0}{P_t}-1} \qquad \text{(A8.4)}$$

This relationship makes use of properties at a pressure, P_t, which is lower than that in the upstream vessel. It is suggested[5] that P_t is taken to be 80 or 90% of P_0 (90% if there is little friction) and that an isenthalpic flash routine (within a computerised package for evaluating multi-component physical properties) is used to find the two-phase specific volume v_t at P_t. Woodward[6] gives examples of the use of this approach.

Approximate simplified definitions

It will not always be possible to use the more accurate definition given in equation (A8.4) above, for example in cases where the required physical property data would be difficult to generate. In such cases, the following alternative approximate definitions of Omega have been proposed[3,4,5]. However, the additional condition of applicability (h) in A8.2 needs to be considered before their use. Omega can be calculated by any of equations (A8.5) to (A8.10) below, which are essentially equivalent. In these equations, Omega is evaluated entirely at the conditions in the upstream reactor.

$$\omega = \frac{x_0 v_{fg0}}{k\, v_0} + \frac{C_f\, T_0 P_{v0}}{v_0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2 \qquad \text{(A8.5)}$$

$$\omega = \frac{x_0 v_{g0}}{k\, v_0} + \frac{C_f\, T_0 P_{v0}}{v_0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2 \qquad \text{(A8.6)}$$

$$\omega = \frac{\alpha_0}{k} + (1-\alpha_0)\rho_{f0} C_f T_0 P_{v0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2 \qquad \text{(A8.7)}$$

$$\omega = \frac{\alpha_0}{k}\left(1 - 2\frac{P_{v0}\, v_{fg0}}{h_{fg0}}\right) + \frac{C_f\, T_0 P_{v0}}{v_0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2 \qquad \text{(A8.8)}$$

$$\omega \quad \begin{matrix}\alpha_0\\ k\end{matrix} + \frac{C_f\, T_0 P_{v0}}{v_0}\begin{pmatrix}v_{fg0}\\ h_{fg0}\end{pmatrix}^2 \qquad \text{(A8 9)}$$

Note that for gassy systems, a number of terms in the above equations disappear and leaves:

$$\omega = \frac{\alpha_0}{k} \tag{A8.10}$$

Earlier descriptions of the Omega method[3,4] defined Omega such that the first term in equations (A8.5)-(A8.10) was equivalent to α_0 rather than to $\frac{\alpha_0}{k}$. This led to discrepancies for $\omega < 4$ in calculating G for choked nozzle flow, compared with experimental results. The definitions of Omega given above[5] overcome this problem.

For wide boiling multi-component mixtures, the Clausius-Clapeyron relationship, used in deriving equations (A8.5)-(A8.10), is invalid. The definitions of Omega can be rewritten without the use of the Clausius-Clapeyron relationship. For example, equation (A8.5) becomes:

$$\omega = \frac{x_0 v_{fg0}}{k\, v_0} + \frac{C_{f0} P_0 v_{fg0}}{v_0 h_{fg0}} \frac{1}{(dP/dT)_0} \tag{A8.11}$$

Equations such as (A8.11) have wider applicability because they do not require the Clausius-Clapeyron relationship to hold and they should, therefore, be applicable for wider boiling mixtures. However, all of the approximate equations given in this section are evaluated only at the conditions in the upstream reactor. This reduces their accuracy if the pressure drop is high (e.g. if there is a piping system with substantial pressure drop). In such cases, equation (A8.4) is to be preferred. Alternatively, different calculation methods to the Omega method can be used.

A8.4.2 Calculation for choked nozzle flow

The Omega method can be used to obtain both the dimensionless mass flux, G_c^*, and the critical pressure ratio, η_c. Analytical solutions for these are as follows[5]:

$$G_c^* = \frac{\eta_c}{\sqrt{\omega}} \tag{A8.12}$$

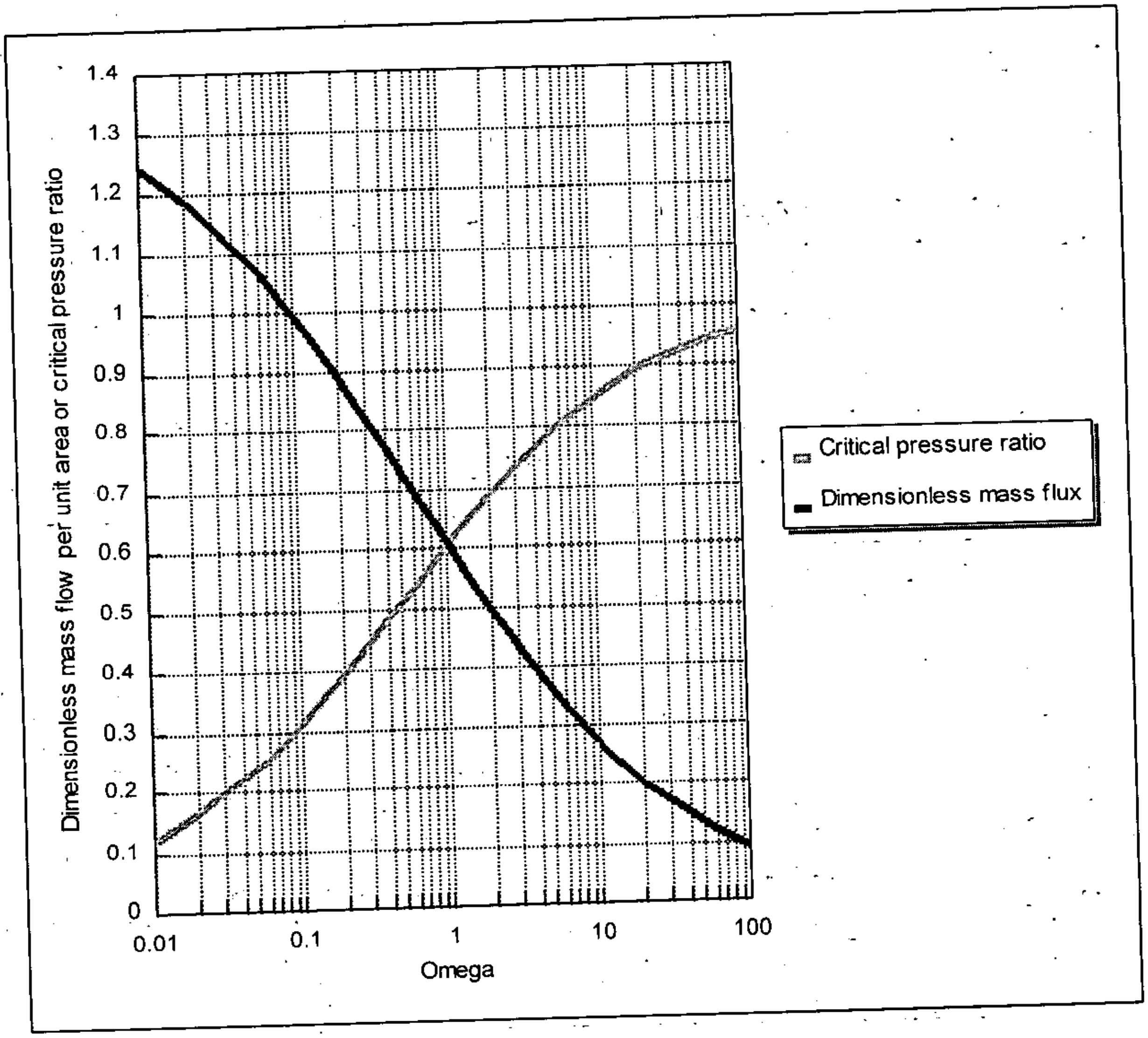
$$\eta_c^2 + (\omega^2 - 2\omega)(1 - \eta_c)^2 + 2\omega^2 \ln \eta_c + 2\omega^2(1 - \eta_c) = 0 \tag{A8.13}$$

However, equation (A8.13) must be solved by trial and error and it is therefore more convenient to use the plot of the solutions to the above equations, given in Figure A8.2, of G_c^* and η_c versus ω. η_c can be used to check whether the flow through a frictionless nozzle would be choked. Leung[3,4] has also published some equations which are numerical solutions for G_c^* and η_c for vapour pressure systems, but these make use of a slightly different definition of Omega (see A8.4.1).

Having obtained G_c^*, the value of G for choked nozzle flow, G_c can be obtained from the following equation[3,4,5]:

$$G_c = G_c^* \sqrt{\frac{P_0}{v_0}} \tag{A8.14}$$

Figure A8.2 PLOT OF DIMENSIONLESS MASS FLUX, G_c^*, AND CRITICAL PRESSURE RATIO, η_c, VERSUS OMEGA FOR A CHOKED NOZZLE



A8.4.3 Correction for friction and static head change

The equivalent length of the proposed relief line, including the contribution of bends, the relief device and any fittings, needs to be evaluated (see Chapter 9). Within the Omega method, the value of G for a long vent line is correlated with the dimensionless group 4fL/D, where f is the Fanning friction factor. For fully turbulent flow, f is a function only of the pipe roughness to diameter ratio and is given by friction factor plots, for example by Perry[9]. Flow in relief systems is frequently fully turbulent. However, when G has finally been calculated, the Reynolds number could be evaluated to check the assumption of fully turbulent flow and, if necessary, the value of the friction factor can be revised. The Omega method, as detailed in this Annex, applies only to turbulent flow, for laminar flow see 10 2

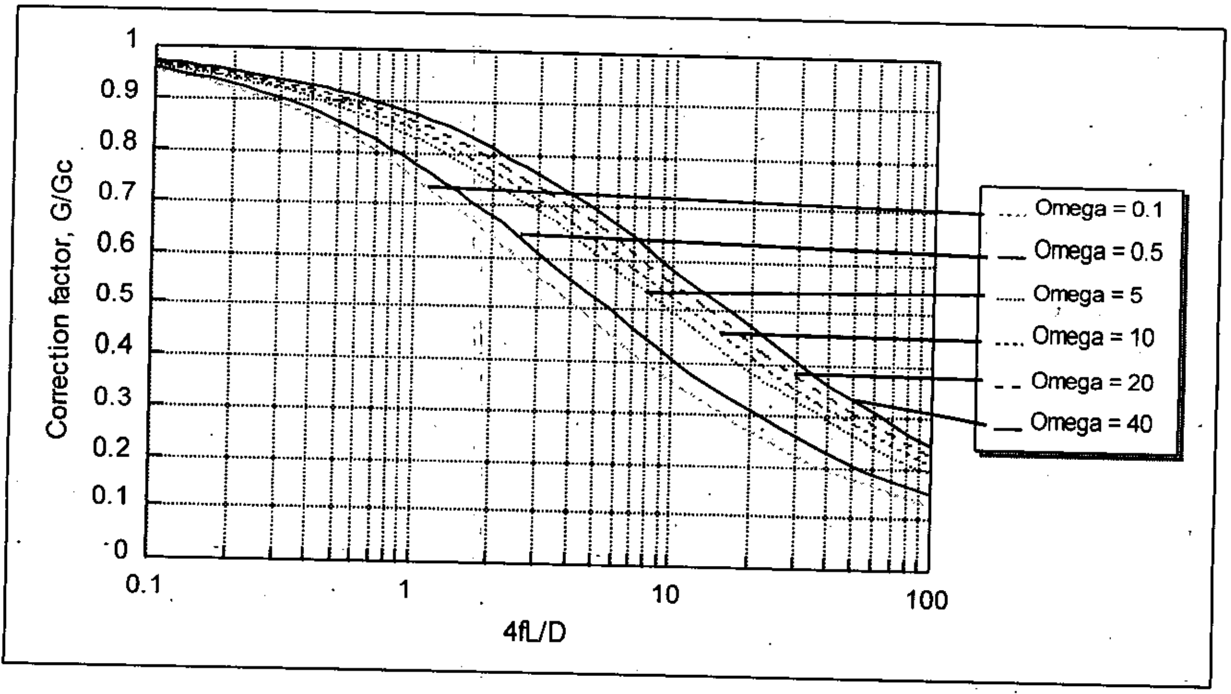
If there is a significant upwards static head change, then account should be taken of this. Within the Omega method, the dimensionless group used to characterise static head change is the flow inclination number[10], Fi, where:

$$Fi = \frac{\rho_0 \, g \, H}{P_0 \, (4fL/D)} \qquad \text{(A8.15)}$$

The flow inclination number is zero for horizontal flow.

A correction factor to be applied to the value of G for a nozzle, G_c, can be evaluated using Figures A8.3, A8.4 or A8.5, depending on the flow inclination number (see above). These Figures have been produced by evaluating the formulae given by Leung in Appendix 1 of reference 5. A composite graph is also given by DIERS[11]

Figure A8.3 **CORRECTION FACTOR FOR RELIEF LINE FRICTION FOR HORIZONTAL FLOW (Fi = 0)**



The flow inclination number should be evaluated from equation (A8.15) above, and the Figure to be used to obtain the correction factor (from Figures A8.3 to A8.5) is selected on the basis of the flow inclination number. If the static head change is small in comparison with the total upstream pressure, then the flow inclination number may be close to zero and Figure A8.3 can be used. In other cases, values of the correction factor may be read from the two graphs which bound the actual value of the flow inclination number, and the correction factor found by linear interpolation between the values. Flow inclination numbers higher than about 0.2 (as in Figure A8.5) are unlikely in practical relief systems.

Figure A8.4 CORRECTION FACTOR FOR RELIEF LINE FRICTION FOR UPWARDS INCLINED FLOW WITH Fi = 0.1

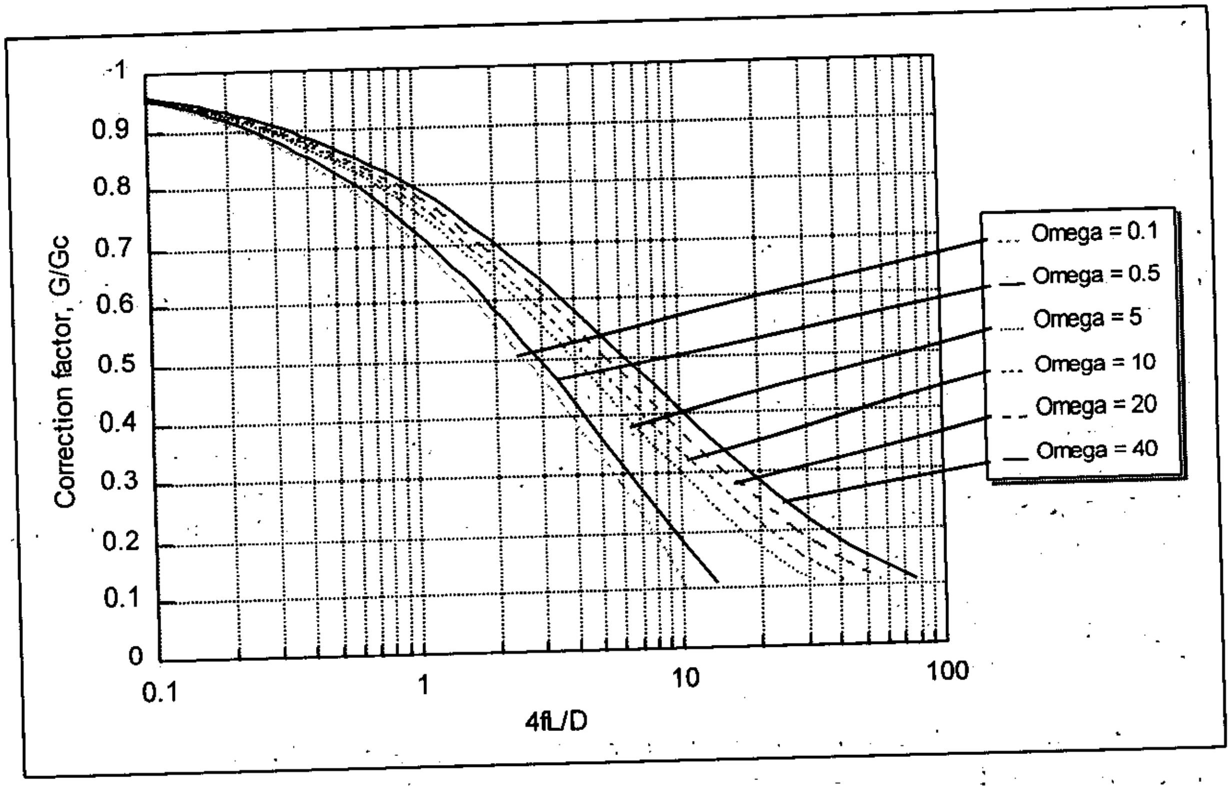
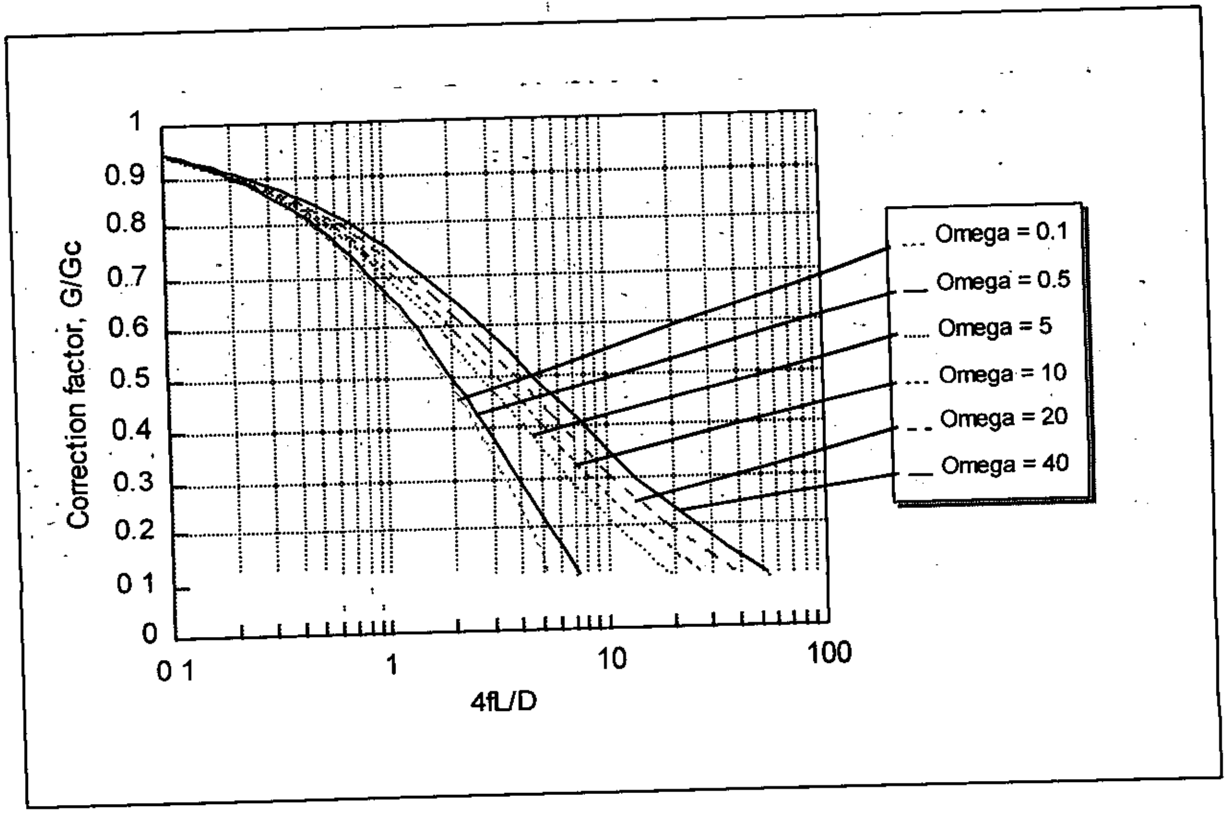


Figure A8.5 CORRECTION FACTOR FOR RELIEF LINE FRICTION FOR UPWARDS INCLINED FLOW WITH Fi = 0.2



If correction for non-choked flow is not required (see A8.4.4 below), the value of G, taking account of friction and static head, can then be found from:

$$G = G_c(G/G_c)_{friction} \qquad \text{(A8.16)}$$

A8.4.4 Correction for non-choked flow

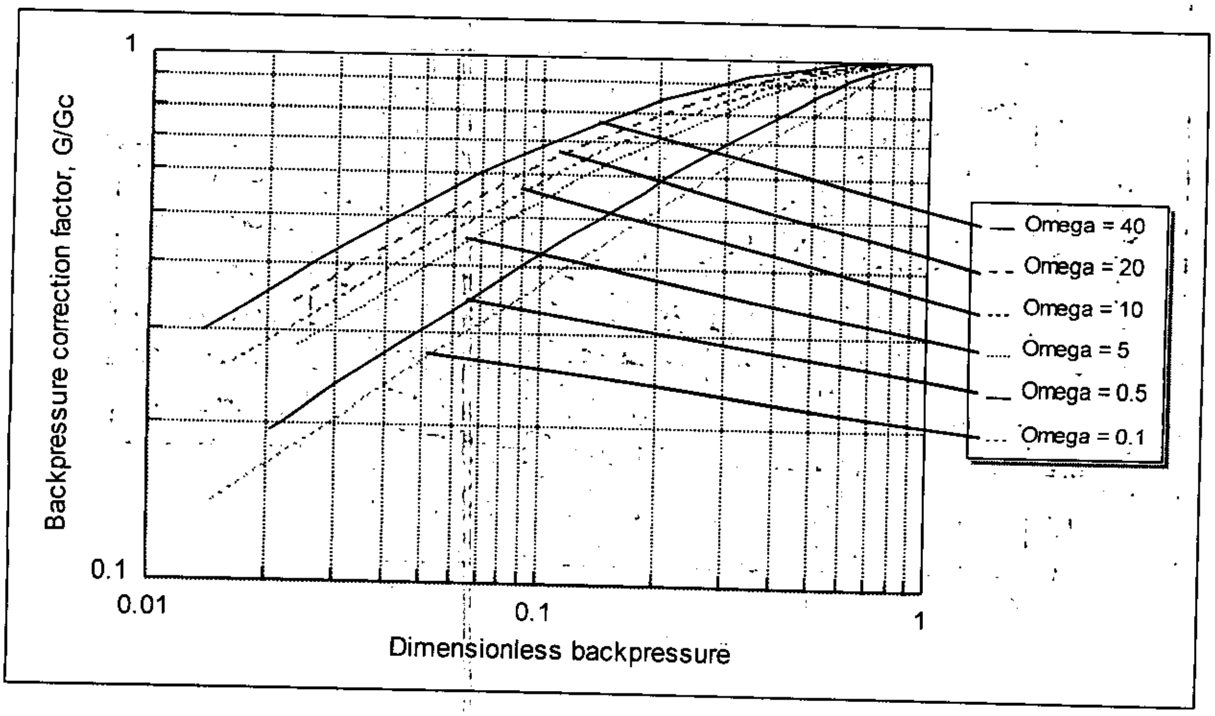
The evaluation of G in a rigorous way using the Omega method for non-choked flow in the presence of friction and static head change requires the solution of an integral equation (equation (21) of reference 5). This can be time-consuming.

An alternative approach, which allows an approximate correction to be made, was suggested by Leung and Fisher[12] and given by DIERS[11]. This involves the use of the correction factor which applies for frictionless flow, even in cases where there is friction. Figure A8.6 gives values of such a correction factor, calculated for frictionless flow using the following equation[5]:

$$G\sqrt{\frac{v_0}{P_0}} = \frac{\sqrt{-2[\omega \ln \eta + (\omega-1)(1-\eta)]}}{\omega\left(\frac{1}{\eta}-1\right)+1} \qquad \text{(A8.17)}$$

In the above equation, η is the actual available pressure ratio (back pressure, e.g. atmospheric, divided by pressure in the upstream reactor).

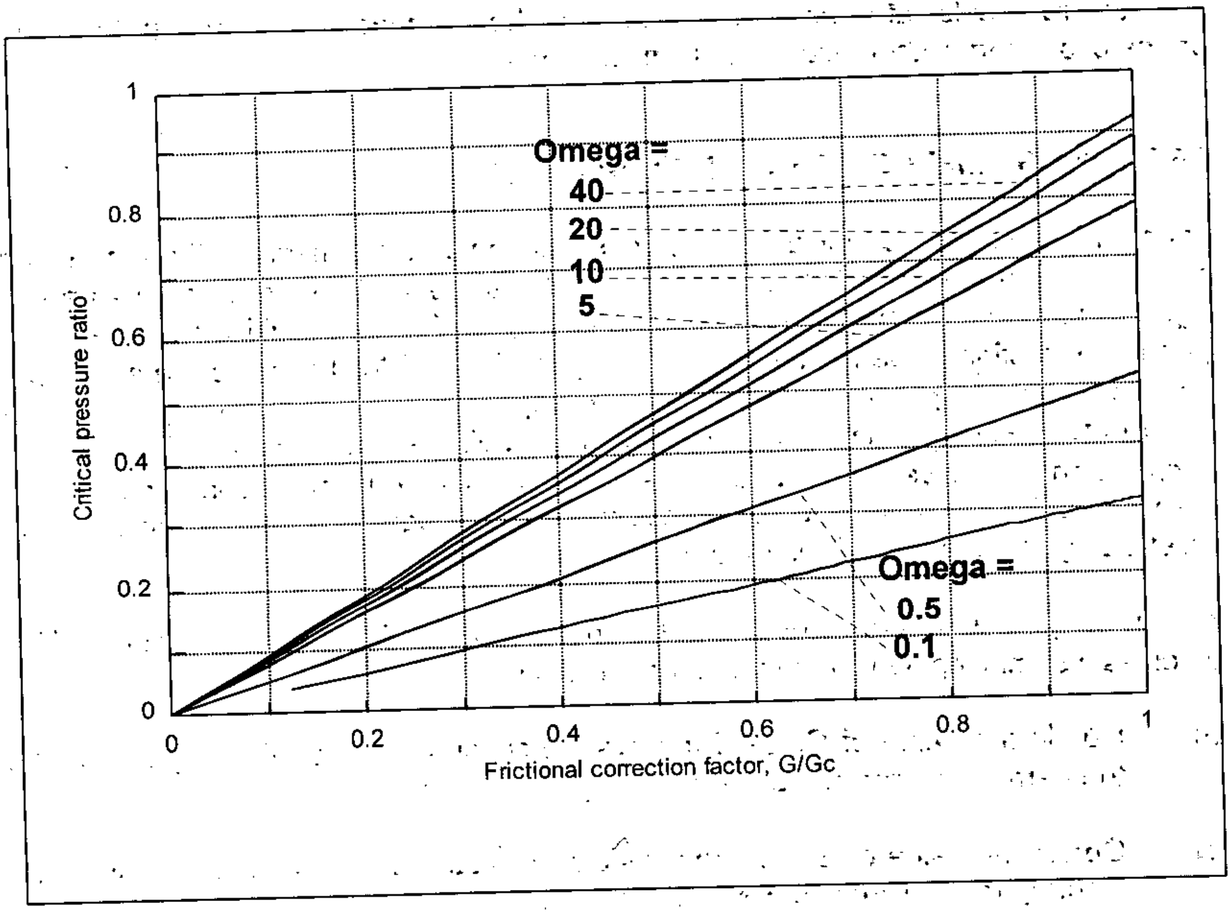
Figure A8.6 BACK PRESSURE CORRECTION FACTOR (FOR NON-CHOKED FLOW)



In Figure A8.6, the correction factor for non-choked flow is plotted against the dimensionless back pressure $(1-\eta)/(1-\eta_c)$, where η is the actual available pressure ratio (see above) and η_c is the critical pressure ratio. For flow in which friction is not significant, η_c can be read from Figure A8.2.

For flow in long pipes, the correction factor for non-choked flow given in Figure A8.6 can still be used although it is an approximation. In this case, the critical pressure ratio, η_c, can be obtained from Figure A8.7 where it is plotted as a function of Omega and of the correction factor due to friction (see A8.4.3 above). Figure A8.7 has been generated by evaluating equations given in Appendix 1 of reference 5.

Figure A8.7 **CRITICAL PRESSURE RATIO FOR FLOW THROUGH RELIEF LINES WITH FRICTION**



Finally, the value of G, taking account of both friction and back pressure, can be evaluated from:

$$G = G_c\left(\frac{G}{G_c}\right)_{friction}\left(\frac{G}{G_c}\right)_{back\ pressure} \qquad \text{(A8.18)}$$

A worked example is given in A8 6 below

A8.4.5 Use of Omega method for bursting disc systems with multiple pipe diameters

If the relief line contains changes in diameter, then each expansion is a potential choke point (see 9.2). DIERS[13] and Simpson[1] suggest calculation procedures which can be used in such cases. A suggested procedure for using the Omega method to find the capacity of a bursting disc line with two sections having different pipe diameters is given in Figure A8.8. This method could be extended for use with more than two sections of different diameter. If flow is into a header, then the header may contain flows from other sources as well as from the bursting disc. This can be dealt with by adding the flows from other sources to the guessed flow from the bursting disc when using the method. (Note that the mass flow capacity per unit area, G, evaluated by the Omega method, is the mass flow rate divided by the cross-sectional area of the relevant pipe section.) This method assumes that the critical pressure ratio calculated using the Omega method is correct. This may not actually be the case, and further discussion is given in 9.4.1.

A8.5 OMEGA METHOD FOR HYBRID SYSTEMS

Leung has presented equations for rigorous solution of the Omega method for hybrid systems[3,5]. However, for hybrid systems, solutions are in terms of three parameters: ω_{sat} (the value of Omega if no gas was present), α_0 (the inlet void fraction) and y_{g0} (the mole fraction of permanent gas in the gas phase). Solutions are therefore less easy to present in graphical form as multiple graphs would be required, e.g. graphs of G_c^* versus α_0 and y_{g0}, with each graph being for a different value of ω_{sat}. Examples of such graphs are given by Leung[3,5]. Leung has also produced a computer code[14] (see Annex 4), VSSPH, which evaluates both the Omega method for hybrids and a relief sizing method for hybrids (see A5.11).

Alternatively, Leung has presented an approximate "mixing rule" method[5]. This involves first making two Omega method calculations:

a) Obtain the value of G_G as if the system consisted of non-flashing liquid plus the permanent gas component.

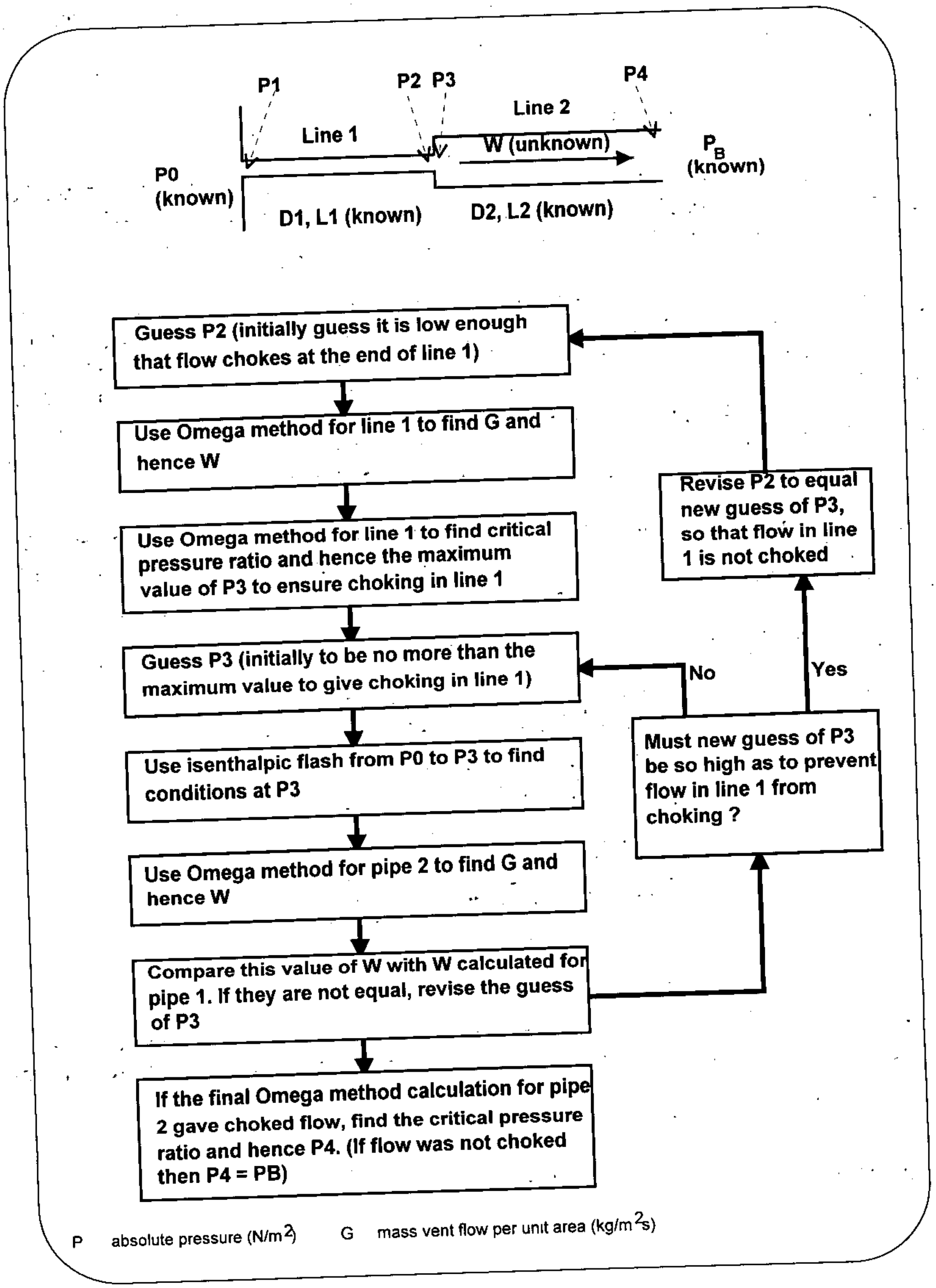
b) Obtain the value of G_v as if the system consisted only of a flashing liquid (i.e. ignoring the presence of permanent gas).

These calculations can be done for nozzle flow or flow through a vent line as appropriate.

The "mixing rule" can then be used to estimate G for a hybrid system:

$$G = \sqrt{y_{g0} G_G^2 + (1 - y_{g0}) G_v^2} \qquad \text{(A8.19)}$$

Figure A8.8 PROCEDURE FOR CALCULATION OF RELIEF CAPACITY FOR A LINE WITH TWO SECTIONS OF DIFFERENT DIAMETER



P absolute pressure (N/m^2) G mass vent flow per unit area (kg/m^2s)

where y_{g0} is the mole fraction of permanent gas (rather than vapour) in the gas/ vapour phase.

Leung[5] states that this mixing rule is "only an empirical correlation". No limits of applicability are given.

A8.6 WORKED EXAMPLE

This worked example calculates G for the tempered hybrid relief sizing worked example given in Chapter 8. It uses the mixing rule for hybrids and therefore shows example Omega calculations for vapour pressure, gassy and hybrid systems.

It is required to size a bursting disc system with a maximum bursting pressure of 2.2 barg (3.2 bara) for a reactor of volume 1.5 m^3 and design pressure 3 barg (maximum accumulated pressure = 4.3 bara). The frictional resistance of the bursting disc system in this case is equivalent to 4fL/D = 5. The worst case reaction has been identified as a tempered hybrid, and an open system calorimetric test has demonstrated that it will continue to temper until the reaction is complete. For the worst case reaction, the mass in the reactor would be 860 kg.

Calorimetry has shown that the tempering temperature at the relief pressure of 3.2 barg is 353 K. The ratio of vapour pressure to total pressure, P_v/P, has been estimated as 0.8 (see 8.5).

The following physical property data have been compiled:

Pressure (bara)	3.2
Temperature (K)	353
Liquid density (kg/m^3)	820
Vapour density (kg/m^3)	8.18
v_{fg} (m^3/kg)	0.12
Latent heat (kJ/kg)	621
Liquid specific heat (kJ/kgK)	1.98

In addition, isentropic coefficients, k, are estimated as 1.05 for the vapour and 1.2 for the gas. The problem is to evaluate G for the hybrid mixture at the relief pressure of 3.2 bara.

Evaluate G for a vapour pressure system

This should be evaluated at the pressure corresponding to the tempering temperature.

$$P_v = \left(\frac{P_v}{P}\right) P = 0.8x3.2 = 2.56\ bara$$

Omega can now be calculated using equation (A8.9):

$$\omega_{sat} = \frac{\alpha_0}{k} + \frac{C_f T_0 P_{v0}}{v_0}\left(\frac{v_{fg0}}{h_{fg0}}\right)^2$$

The relief sizing equation for tempered hybrids, in which the calculated value of G is to be used (see Chapter 8) assumes that the reactor fills with a homogeneous two-phase mixture during relief. Thus:

$$v_0 = \frac{V}{m} = \frac{1.5}{860} = 0.00174\ m^3/kg$$

$$\alpha_0 = \frac{V - \left(\frac{m}{\rho_f}\right)}{V} = \frac{1.5 - \left(\frac{860}{820}\right)}{1.5} = 0.301$$

$$\omega_{sat} = \frac{0.301}{1.05} + \frac{1980x353x2.56x10^5}{0.00174}\left(\frac{0.12}{621000}\right)^2 = 4.13 \qquad \text{(A8.9)}$$

G_c^* is now read from Figure A8.2 with ω=4.13, giving a value of 0.38.

Figure A8.3 is read for 4fL/D = 5 and ω=4.13, giving a value of the friction correction factor, G/G_c of 0.6.

It should now be checked whether or not the flow is choked. Reading from Figure A8.7, with G/G_c=0.6 and ω=4.13 gives value of the critical pressure ratio, η_c, of 0.45.

$$P_c = P\eta_c = 2.56x0.45 = 1.152$$

Thus, the critical pressure for choking, P_c, is just above atmospheric, so the flow is just choked and no further correction factor needs to be applied.

G for a vapour pressure system can now be evaluated:

$$G_v = \left(\frac{G}{G_c}\right)_{\text{friction}} G^* \sqrt{\frac{P_0}{v_0}} = 0.6x0.38x\sqrt{\frac{2.56x10^5}{0.00174}} = 2766\ kg/m^2 s$$

Evaluate G for a gassy system

$$\omega = \frac{\alpha_0}{k} = \frac{0.301}{1.2} = 0.251$$

Reading from Figure A8.2 with ω=0.251, gives G_c^* = 0.85

Reading from Figure A8.3 with ω=0.251 and 4fL/D = 5, gives the frictional correction factor, G/G_c 0 52

It should now be checked whether or not the flow has choked. Reading from Figure A8.7 with ω=0.251 and G/G_C = 0.52, gives the critical pressure ratio, η_c=0.2.

$$P_c = P\eta_c = 3.2x0.2 = 0.64\ bara$$

This is below atmospheric pressure and therefore the flow is not choked. A further correction factor for unchoked flow is therefore required.

The dimensionless back pressure, for a back pressure of atmospheric (1 bara) on the relief system, is:

$$\frac{(1-\eta)}{(1-\eta_c)} = \frac{\left(1-\left(\frac{1}{3.2}\right)\right)}{(1-0.2)} = 0.86$$

Reading from Figure A8.6 with ω=0.251 and a dimensionless back pressure of 0.86 gives a non-choked flow correction factor, G/G_c, of 0.98.

G for gassy flow can now be evaluated:

$$G_G = \left(\frac{G}{G_c}\right)_{\text{friction}} \left(\frac{G}{G_c}\right)_{\text{back pressure}} G^* \sqrt{\frac{P_0}{v_0}} = 0.52x0.98x0.85x\sqrt{\frac{3.2x10^5}{0.00714}} = 5874\ kg/m^2s$$

<u>Evaluate G for a hybrid system</u>

G for the hybrid mixture can now be evaluated using the mixing rule:

$$G = \sqrt{y_{g0}G_G^2 + (1-y_{g0})G_V^2} \qquad \text{(A8.19)}$$

y_{g0} is the gas mole fraction in the gas/ vapour phase. For an ideal gas, y equals the ratio of partial pressure to total pressure. Thus:

$$y_{v0} = \frac{P_v}{P} = 0.8$$

$$y_{go} = 1 - y_{v0} = 1 - 0.8 = 0.2$$

$$G = \sqrt{0.2(5874)^2 + (1-0.2)(2766)^2} = 3609\ kg/m^2s$$

REFERENCES FOR ANNEX 8

1. L L Simpson, "Navigating the Two-Phase Maze", International Symposium on Runaway Reactions and Pressure Relief Design, 394-417, AIChE, 1995, ISBN 0-8169-0676-9

2. "Guidelines for Pressure Relief and Effluent Handling Systems", CCPS/AIChE, 1998, ISBN 0-8169-00476-6

3. J C Leung, "Two-Phase Flow Discharge in Nozzles and Pipes - A Unified Approach", J Loss Prev. Process Ind., 3 (1), 27-32, January 1990

4. J C Leung, "A Generalised Correlation for One-component Homogeneous Equilibrium Flashing Choked Flow", AIChE Journal, 32 (10), 1743-1746, 1986

5. J C Leung, "The Omega Method for Discharge Rate Evaluation", International Symposium on Runaway Reactions and Pressure Relief Design, 367-393, AIChE, 1995, ISBN 0-8169-0676-9

6. J L Woodward, "An Amended Method for Calculating Omega for a Homogenous Equilibrium Model of Predicting Discharge Rates", J Loss Prev Process Ind, 8 (5), 253-259, 1995

7. K E First & J E Huff, "Design Charts for Two-Phase Flashing Flow in Emergency Pressure Relief Systems", Plant/Operations Prog, 8 (1), 40-54, 1989

8. F N Nazario & J C Leung, "Sizing Pressure Relief Valves In Flashing And Two-Phase Service: An Alternative Procedure", J Loss Prev Process Ind, 5 (5), 263, 1992

9. R H Perry & C H Chilton, "Perry's Chemical Engineers' Handbook", 7th Edition, McGraw Hill, 1997

10. J C Leung & M Epstein, Trans ASME J of Heat Transfer, 112 (2), 524, 1990

11. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section VI-A5-5, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

12. J C Leung and H G Fisher, "Two-Phase Flow Venting from Reactor Vessels", J Loss Prev Process Ind, 778-86, April 1989

13. H G Fisher et al., "Emergency Relief System Design Using DIERS Technology", Section 3.5.6, DIERS/AIChE, 1992, ISBN 0-8169-0568-1

14. J C Leung, J A Noronha, A J Torres, J J Sharkey & M H Yue, "A Vent Sizing Program with Particular Reference to Hybrid Runaway Reaction Systems", International Symposium on Runaway Reactions and Pressure Relief Design, 567 579, AIChE, 1995, ISBN 0 8169 0676 9

ANNEX 9

GLOSSARY

absolute pressure	A pressure measured from absolute zero pressure, rather than from atmospheric pressure.
accumulation	i) A build-up of reactants in a semi-batch or continuous reactor. ii) Accumulated pressure. Any increase in pressure above the design pressure of a pressure vessel during discharge through its pressure relief system.
adiabatic	No heat transfer occurs to or from the environment surrounding the sample, including the sample container.
adiabaticity	A measure of the heat loss from a calorimeter.
adiabatic temperature rise	The increase in temperature of a reacting mixture as a result of exothermic chemical reaction, when there is no heat transfer to or from the environment.
Antoine plot	A plot of vapour pressure data on log pressure versus 1/temperature axes. This gives a straight line for vapour pressure systems.
ARC™	The Accelerating Rate Calorimeter (a type of adiabatic calorimeter). See A2.2.4.
back pressure	The pressure of the environment downstream of a relief pipe or relief device, into which the pipe or device discharges. Back pressure can be "constant" or "built-up". A constant back pressure always exists, irrespective or the relief process, e.g. atmospheric pressure. A built-up back pressure exists due to the frictional pressure drop caused by flow through the relief system.
blowdown	The difference between the set pressure and the reseating pressure of a safety valve.

Boyle time	The time for the pressure to rise in a closed adiabatic system from the relief pressure to the maximum accumulated pressure.
bubbly	A flow regime in which small discrete bubbles exist within a liquid. See 4.3.1.
bursting disc	The pressure containing and pressure sensitive component of a bursting disc device. A bursting disc device is a non-reclosing pressure relief device actuated by differential pressure and designed to function by the bursting or venting of the bursting disc(s). There are many different designs of bursting disc and manufacturers should be consulted for details.
bursting pressure	The value of the pressure differential across a bursting disc at which it will nominally burst or open. (See also "specified bursting pressure")
calorimeter	A laboratory test apparatus for measuring thermal effects of chemical reactions.
choked flow	The maximum flow rate of a compressible fluid (gas or two-phase) for a given upstream pressure. Choking is described in 9.2.
churn-turbulent	A flow regime in which large bubbles exist within a liquid. See section 4.3.1.
closed test	An adiabatic calorimetric test in which the sample is held within a sealed container. See A2.3.1.
compressible	A property of a fluid such that its density is a function of pressure.
compressible flow	Flow in which a drop in pressure causes a decrease in fluid density. This is true of two-phase flow and of single-phase gas/ vapour flow. See section 9.2.
containment vessel	i) The outer casing of the DIERS bench-scale calorimeter (see A2.2.2). ii) An enclosed vessel downstream of the pressure relief system, with the purpose of containing the material without release to atmosphere (see section 11 2)

conversion	The fractional progress of a chemical reaction towards completion.
coupling equation	A material balance of the flow from the reactor and the flow into the relief system, taking account of the vapour fraction at inlet to the relief system as calculated using level swell methodology. See A3.4.
Cox chart	A plot of log vapour pressure versus the inverse of temperature, which provides a straight line for a system with ideal vapour pressure. See A2.3.1.
critical pressure	The highest back pressure which still results in choked flow for a given upstream pressure. See 9.2.
de-rated discharge coefficient	The discharge coefficient measured in a type test for a particular design of safety valve, reduced by 10% according to BS 6759.
design pressure	The pressure for which a pressure vessel has been designed, according to a recognised pressure vessel code such as BS 5500. This is the "maximum allowable pressure" in the Pressure Equipment Directive (see Chapter 5).
Dewar	A vacuum flask that can be used in calorimetry (see A2.2.3).
DIERS	The Design Institute for Emergency Relief Systems of the American Institute of Chemical Engineers. A collaborative group of companies and organisations.
DIERS bench-scale apparatus	A type of adiabatic calorimeter designed for DIERS. (See A2.2.2).
discharge capacity	The flow rate through a safety valve for a specified set pressure and overpressure.
discharge coefficient	The ratio of the actual flow rate (which is reduced by friction etc.) to the calculated flow rate through an ideal frictionless nozzle.
drift flux	A model for bubble rise rate within a liquid, used by DIERS as the basis for their level swell methodology. See Annex 3.

dynamic simulation	A mathematical model in which the pressure, temperature, mass, conversion etc. within a relieving reactor are calculated, as a variable with time. See A4.2.
equilibrium	The state reached by a system given infinite time. In this Workbook, it usually refers to vaporisation or condensation having taken place to bring the system into vapour/ liquid equilibrium. See 9.3.1.
equivalent length	The length of straight pipe of given roughness which is equivalent in frictional resistance to the actual piping which contains bends and fittings.
flow area	The minimum cross-sectional area available for flow.
flow rating pressure	The pressure at which the flow capacity of a safety valve is calculated. It is usually 10% above the set pressure to ensure the valve is fully open.
flow regime	An idealised model of the behaviour of a two-phase system which best describes the actual behaviour. See 4.3.1 for vessel flow regime and 9.3.1 for relief system flow regime.
foamy	A flow regime in which the vapour and liquid phases are uniformly mixed as a foam.
frozen flow	Two-phase flow in which no flashing of the liquid phase occurs. This may be due to the liquid being non-volatile or due to insufficient time for flashing to occur (non-equilibrium flow).
gassy	A system type for relief sizing. See 4.2.1.
gauge pressure	A pressure measured relative to atmospheric pressure.
hand calculation methods	Methods which are suitable for evaluation using a pocket calculator or spreadsheet
homogeneous	A system in which the liquid and gas/ vapour phases are uniformly mixed. In pipe flow, "homogeneous" also implies no slip between the phases and complete vapour/ liquid equilibrium (see 9 3 1)

homogeneous equilibrium flow	A model for two-phase flow which assumes vapour/ liquid equilibrium, thermal equilibrium and no slip between the phases. See 9.4.1.
hybrid	A system type for relief sizing. See 4.2.1.
inherently foamy	A property of a system which causes it to give rise to uniform mixing of the gas/ vapour and liquid phases. See 4.3.1.
isenthalpic	No enthalpy change occurs. An isenthalpic depressurisation is irreversible. It is common to assume that the pressure drop across the pressure discontinuity at a choke is isenthalpic.
isentropic	No entropy change occurs. This usually requires that the process is adiabatic and reversible.
laminar flow	A type of flow at low Reynolds number in which streamlines exist across the pipe with no radial mixing.
latent specific volume change	The difference between the vapour specific volume and the liquid specific volume at the same conditions.
level swell	The increase in liquid level due to the presence of gas/ vapour bubbles within the liquid. See 4.3.1 and Annex 3.
lift	The distance that the disc in a safety valve rises off the seat when it opens.
maximum accumulated pressure	The maximum pressure that can be allowed transiently in the pressure vessel system by the vessel design code or by a competent stress engineer (see 5.2.1). Under BS 5500 this will be 10% above the design pressure of the vessel with the lowest design pressure.
Newtonian	An ideal fluid for which the shear rate is proportional to the shear stress and the viscosity is approximately constant.
non-boiling region	A region at the bottom of a vessel containing a boiling liquid in which boiling is prevented by the static head of liquid above it. See A3.3.3.

non-equilibrium flow	Flow in which the residence time is too short to allow flashing to cause the system to restore vapour/ liquid equilibrium within the piping. See 9.3.1.
overpressure	This is normally the gauge pressure increase above the set pressure of a safety valve (see 5.2). The absolute overpressure is the pressure increase above the relief pressure of any relief device (see equation (6.1))
open test	An adiabatic calorimetric test in which the sample is held within a container which is vented to an outer pressurised containment vessel. See A2.3.1.
Pad gas	Permanent gas (usually air) which is present in a calorimeter or reactor above the reacting liquid.
pad gas correction	Correction of pressure measurements from a calorimetric test to remove the pad gas pressure and leave the vapour pressure. See A2.7.1.
performance tolerance	A measure of the range of possible bursting pressures of a bursting disc. See 5.2.2.
permanent gas	A gas which cannot be condensed (or solidified) under the range of conditions of interest in relief system sizing. Usually a gas which is above its thermodynamic critical temperature.
Phi-factor	A measure of the thermal inertia of a system. See A2.2.1.
PHI-TEC™	A type of adiabatic calorimeter. See A2.2.2.
quality	The mass fraction of gas/ vapour in a two-phase mixture.
relief pressure	The pressure at which the relief system is first certain to be fully open. See 5.2.2.
relief system	All parts of the pressure relief flow path from the protected vessel to atmosphere or containment within a disposal system. This includes relief device(s), piping and any containment/ disposal system.

relief system capacity	The flow rate through the pressure relief system under specified conditions.
relief valve	i) A type of safety valve (usually designed specifically for liquid duty). ii) A term sometimes used as synonymous with "safety valve".
required relief rate	The flow rate, or average flow rate, which must be removed from the protected vessel in order to prevent overpressurisation.
reseating pressure	The pressure at which a safety valve recloses when the pressure falls.
runaway	A reaction which has become out of control because the rate of heat generation by an exothermic reaction exceeds the rate of cooling.
rupture disc	A term which is often used to be synonymous with "bursting disc".
RSST™	A type of semi-adiabatic calorimeter. See A2.2.2.
safety valve	A valve which automatically, without the assistance of any energy other than that of the fluid concerned, discharges a certified quantity of the fluid so as to prevent a predetermined safe pressure being exceeded, and which is designed to re-close and prevent further flow of fluid after normal pressure conditions of service have been restored. See 5.2.2. In this Workbook, "safety valve" is used to mean any type of safety or relief valve (following the definition in BS 6759). The term is sometimes used to denote relief valves designed for gas/ vapour service only.
safety relief valve	A term which is often used to be synonymous with "safety valve". It is sometimes used to denote a valve which can be used for either vapour or liquid service depending on the position of the blowdown ring.
saturated liquid	A liquid at its boiling point at the particular pressure.

sensitivity	The minimum heat rate onset (e.g. 0.02 °C/min) which can be detected by a particular type of calorimeter.
set pressure	The pressure at which a safety valve first starts to open (see 5.2.2).
slip flow	Two-phase flow in which the gas/ vapour phase moves at higher velocity than the liquid phase. See 9.3.1.
sonic flow	Choked flow of gas/vapour.
specified bursting pressure	The bursting pressure (taking account of tolerances) quoted with a coincident temperature when defining bursting disc requirements.
specified maximum bursting pressure	The maximum pressure at which a bursting disc will burst or open, quoted with a coincident temperature.
specified minimum bursting pressure	The minimum pressure at which a bursting disc will burst or open, quoted with a coincident temperature.
stagnation pressure	The pressure if the flow were to be stopped in an (imaginary) reversible process. For a relief system, the upstream stagnation pressure is the pressure in the vessel being relieved.
steady-state	A continuous process in which the flows out balance the flows in.
superficial velocity	The velocity of one phase, calculated as if the other phase were not present.
tempering	A situation in which the temperature of a runaway reaction is brought under control by the removal of latent heat. See 4.2.1.
terminal bubble rise velocity	The average terminal velocity at which bubbles, of size typical of a particular level swell flow regime, will rise through the liquid. See Annex 3.
turbulent flow	Flow at Reynolds numbers above about 2000 in which turbulent mixing occurs radially across the pipe.

turnover	The point at which the pressure in a relieving system stops rising and begins to fall. This is also sometimes called "turnaround".
two-phase	Any system in which two phases exist. In the context of relief system sizing, a two-phase system usually comprises a gas/ vapour phase and a liquid phase.
untempered	A reacting system in which the temperature cannot be held constant at constant pressure, because there is insufficient vapour pressure to cause sufficient cooling by removal of latent heat.
vapour pressure system	A system type for relief sizing. See 4.2.1.
velocity head	The quantity $\frac{1}{2}\rho u^2$ (N/m^2) where ρ is density (kg/m^3) and u is velocity (m/s).
venting	i) Process flow from the gas/ vapour space of a reactor. ii) Term sometimes used synonymously with "pressure relief".
viscosity characterisation	Process of determining whether relief system flow will be laminar or turbulent. See 4.4.
void fraction	The volume fraction of gas/ vapour bubbles held up within the liquid phase.
VSP™	"Vent Sizing Package". A type of adiabatic calorimeter. See A2.2.2.
wide boiling	A mixture of components with differing volatility so that the mixture exhibits a significant difference between the initial and final boiling points.
worst case scenario	For the purposes of the Workbook, the worst case scenario is the credible combination of equipment failures and maloperations that gives rise to the largest calculated relief size compared with other credible scenarios. See Chapter 3. The worst case scenario is the basis for the relief system design.

ANNEX 10

NOMENCLATURE

A	cross-sectional flow area of relief system (m^2)
A_{actual}	actual cross-sectional area of safety valve nozzle (m^2)
A_{approx}	approximate cross-sectional flow area of relief system obtained from screening technique (m^2)
A_e	cross-sectional area of relief system in calorimeter used for direct scaling test (m^2)
A_n	cross-sectional area of nozzle in safety valve (m^2)
A_p	cross-sectional flow area of relief pipe (m^2)
A_R	cross-sectional area of reactor (m^2)
a	constant in Antoine equation (ln N/m^2)
a_{sw}	parameter defined by equation (A5.9)
b	constant in Antoine equation (K ln N/m^2)
b_{sw}	parameter defined by equation (A5.10)
C	specific heat capacity (J/kgK)
C_f	liquid specific heat capacity (J/kgK)
$\overline{C_f}$	average "liquid" specific heat capacity, taking account of the presence of solids (J/kgK)
C_{fe}	liquid specific heat capacity in small-scale calorimetric test (J/kgK)
C_{fR}	liquid specific heat capacity at relief pressure conditions (J/kgK)
C_D	discharge coefficient
C_0	correlating parameter in level swell correlations
C_p	specific heat capacity at constant pressure (J/kg K)
C_v	specific heat capacity at constant volume (J/kg K)
C_s	specific heat capacity of solid (J/kgK)
C_{sv}	parameter defined by Table A6.1
c_{sw}	parameter defined by equation (A5.11)
D	relief system diameter (m)
D_e	relief system diameter in small-scale experimental test (m)
dP/dt	rate of pressure rise (N/m^2 s)
$(dP/dt)_{max}$	maximum rate of pressure rise (N/m^2 s)
$(dP/dt)_R$	rate of pressure rise at relief pressure or at start of two-phase relief, whichever is higher (N/m^2 s)
dP_G/dt	rate of rise of gas partial pressure (N/m^2 s)
dP_v/dt	rate of rise of vapour pressure (N/m^2 s)
dP_v/dT	slope of vapour pressure curve (N/m^2K)
dT/dt	adiabatic rate of temperature rise due to the runaway reaction (K/s)
$(dT/dt)_e$	adiabatic rate of temperature rise due to the runaway reaction as measured in calorimeter (K/s)
$(dT/dt)_{external}$	rate of temperature rise due to external heating (K/s)
$(dT/dt)_R$	adiabatic rate of temperature rise due to the runaway reaction at relief pressure (K/s)
$(dT/dt)_{reaction}$	adiabatic rate of temperature rise due to the runaway reaction alone (K/s)

$(dT/dt)_m$	adiabatic rate of temperature rise due to the runaway reaction at maximum accumulated pressure (K/s)
$(dT/dt)_{max}$	maximum adiabatic rate of temperature rise (K/s)
$(dT/dt)_{measured}$	total measured rate of temperature rise (K/s)
$(dT/dt)_{max}$	adiabatic rate of temperature rise due to the runaway reaction at point of maximum reaction rate (K/s)
E_A	activation energy (J/kmol)
F_B	back pressure correction factor
F_D	dynamic load factor
F	frictional correction factor in Fauske's method (see A5.3)
Fi	flow inclination number
F_0	safety factor for uncertainty in relief sizing
f	Fanning friction factor
G	two-phase mass flow rate per unit flow area (kg/m^2 s)
G_c	choked two-phase mass flow rate per unit flow area (kg/m^2 s)
G_c^*	dimensionless choked two-phase mass flow rate per unit flow area
G_g	gas or vapour-only mass flow rate per unit flow area (kg/m^{2}s)
G_G	two-phase mass flow rate per unit flow area for gassy two-phase flow (neglecting vapour pressure in a hybrid system) (kg/m^2 s)
G_L	laminar two-phase mass flow rate per unit flow area (kg/m^2 s)
G_{Le}	laminar two-phase mass flow rate per unit flow area obtained in experimental test (kg/m^2 s)
G_{nozzle}	two-phase mass flow rate per unit flow area for a frictionless nozzle (kg/m^2 s)
G_R	two-phase mass flow rate per unit flow area at relief pressure (kg/m^2 s)
G_v	two-phase mass flow rate per unit flow area for flashing two-phase flow (neglecting permanent gas in a hybrid system) (kg/m^2 s)
G_T	turbulent two-phase mass flow rate per unit flow area (kg/m^2 s)
G^*	dimensionless G
$(G/G_c)_{friction}$	correction factor in Omega method for friction
$(G/G_c)_{backpressure}$	correction factor in Omega method for non-choked flow
g	acceleration due to gravity (m/s^2)
h_{fg}	latent heat of vaporisation (J/kg)
H	static head change (m)
j_g	superficial gas/ vapour velocity in reactor (m/s)
k	isentropic coefficient
K	number of velocity heads lost
$K_{fittings}$	number of velocity heads lost in pipe fittings
K_G	constant in equation (A5.30)
K_S	parameter in equation (A5.22)
L	equivalent length of vent line (m)
L_E	equivalent length (m)
m	mass in reactor (kg)
m_e	mass in calorimetric test (kg)
m_f	mass of liquid in reactor (kg)
m_m	mass remaining in reactor at maximum accumulated pressure (kg)
m_R	mass in reactor at relief pressure (kg)
m_s	mass of solid in reactor (kg)
M_W	molecular weight (relative molecular mass)
P	pressure (N/m^2 abs.)

P_a	atmospheric pressure (N/m^2 abs.)
P_B	back pressure (N/m^2 abs.)
P_e	measurement pressure in calorimeter (N/m^2 abs.)
P_E	pressure at the exit of the relief pipe (N/m^2 abs.)
P_G	partial pressure of gas (N/m^2 abs.)
P_i	initial total pressure (at start of calorimetric test) (N/m^2 abs.)
P_m	maximum accumulated pressure (N/m^2 abs.)
P_{pg}	partial pressure of pad gas (N/m^2 abs.)
P_{pgi}	initial partial pressure of pad gas (N/m^2 abs.)
P_R	relief pressure (N/m^2 abs.)
P_{Re}	pressure in calorimeter corresponding to full-scale relief pressure (N/m^2 abs.)
P_t	estimated downstream pressure for calculation of Omega (see equation (A8.4) (N/m^2 abs.)
P_{Tc}	thermodynamic critical pressure (N/m^2 abs.)
P_v	vapour pressure (N/m^2 abs.)
P_{vi}	initial vapour pressure (N/m^2 abs.)
P_0	stagnation pressure (in upstream equipment) (N/m^2 abs.)
ΔP	difference between maximum pressure and relief pressure (N/m^2)
$\Delta P/\Delta T$	approximate slope of pressure versus temperature curve (N/m^{2}K)
q	heat release rate per unit mass of reacting mixture (W/kg)
$q_{modified}$	heat release rate per unit mass of reacting mixture modified for presence of external heating (W/kg)
$\bar{q}$	average heat release rate per unit mass of reacting mixture (W/kg)
Q_G	volumetric rate of permanent gas evolution in the reactor (m^3/s)
Q_{Gmax}	peak volumetric rate of permanent gas evolution in the reactor (m^3/s)
Q_{HEAT}	external heating rate (W)
Q_v	volumetric rate of vapour generation in reactor (m^3/s)
Q_{vmax}	peak volumetric rate of vapour generation in reactor (m^3/s)
R	universal gas constant (J/kmol K)
Re	Reynolds number
ref	reference number
R_F	reaction force at a bend (N)
T	temperature (K)
T_c	temperature in containment vessel of bench-scale calorimeter (K)
T_e	temperature in calorimetric test cell (K)
T_i	initial temperature (at start of calorimetric test (K)
T_R	temperature at relief pressure (K)
T_0	temperature at stagnation condition at inlet to relief system (K)
T_F	thrust (N)
T_{Tc}	thermodynamic critical temperature (K)
ΔT	temperature difference between the temperatures at the relief pressure and maximum accumulated pressure (K)
ΔT_H	temperature change in a closed vessel as the pressure of a hybrid system rises from the relief pressure to the maximum accumulated pressure (K)
t	time (s)
t_{empty}	time from start of venting until reactor is empty (s)
t_m	time from start of venting corresponding to maximum accumulated pressure (s)

Δt_B	Boyle time: time for pressure to rise from relief pressure to maximum pressure in an adiabatic closed vessel test (s)
Δt_{empty}	time to empty reactor by homogeneous two-phase relief (s)
U_∞	characteristic bubble rise velocity (m/s)
u	velocity (m/s)
v	specific volume (m^3/kg)
v_0	specific volume at stagnation conditions at inlet to relief system (m^3/kg)
v_f	liquid specific volume (m^3/kg)
v_{fg}	difference between vapour and liquid specific volumes (m^3/kg)
v_t	specific volume at estimated downstream pressure for calculation of Omega (see equation (A8.4)) (m^3/kg)
V	volume of reactor (m^3)
V_e	volume of gas-space within calorimeter, including the containment vessel volume for an open test (m^3)
V_f	volume of liquid space in reactor (m^3)
V_{fR}	volume of liquid space in reactor at relief pressure (just before operation of relief system) (m^3)
V_g	volume of gas space in reactor (m^3)
V_{gR}	volume of gas space in reactor at relief pressure (just before operation of relief system) (m^3)
V_G	volume of gas space (m^3)
V_{Ge}	volume of gas space in test cell (m^3)
V_{Gi}	initial volume of gas space in test cell (m^3)
W	mass flow rate (kg/s)
W_{approx}	approximate required relief rate estimated using screening method (kg/s)
W_g	mass flow rate of single-phase gas or vapour (kg/s)
x	mass fraction of gas/vapour in a two-phase mixture
y_g	mole fraction of gas in the gas/vapour phase
y_{g0}	mole fraction of gas in the gas/vapour phase at stagnation condition at inlet to the relief line
y_v	mole fraction of vapour in the gas/vapour phase
y_{v0}	mole fraction of vapour in the gas/vapour phase at stagnation condition at inlet to the relief line
Z	compressibility factor
Z_0	compressibility factor at stagnation condition at inlet to relief system

α	void fraction
α_D	void fraction at disengagement
α_R	void fraction in reactor when relief system first operates (at relief pressure)
α_0	void fraction in reactor at inlet to relief line
β	parameter in Huff's relief sizing method (see A5.2)
ϕ	thermal inertia
η	pressure ratio
η_c	critical pressure ratio
μ	dynamic viscosity (Ns/m^2)
μ_ϕ	liquid dynamic viscosity (Ns/m^2)

$\mu_{\phi\varepsilon}$	liquid dynamic viscosity in small-scale experimental test (Ns/m^2)
ρ	density (kg/m^3)
ρ_f	liquid density (kg/m^3)
ρ_v	vapour density (kg/m^3)
ρ_g	gas density (kg/m^3)
σ	surface tension (N/m)
Ψ	dimensionless gas/vapour superficial velocity in reactor
θ	angle of a bend (^{o})
ω	the Omega dimensionless number
ω_{sat}	the Omega dimensionless number, calculated for the vapour pressure component of a hybrid system, as if the permanent gas was not present

Subscripts

a	at atmospheric pressure
B	refers to environment downstream of pressure relief system
c	in containment vessel within calorimeter
calculated	obtained by calculation rather than experiment
closed	in a closed (unvented) reactor or calorimeter
D	at point of vapour/liquid disengagement
e	in experimental test equipment
E	at exit of relief system piping
f	liquid
F	force
g	gas or vapour
G	gas
H	hybrid
i	initial , or at the beginning of a step for method A5.5
L	laminar flow
m	at the maximum pressure during a vented runaway (or at the end of a step for method A5.5)
max	at the maximum rate
pg	pad gas
p	refers to relief pipe
R	at the relieving pressure
s	solid
sat	saturated (i.e. the value for saturated liquid with no permanent gas present)
T	total
Tc	evaluated at the thermodynamic critical point
t	at an intermediate pressure between the upstream reactor and the choking condition
v	vapour
0	refers to stagnation conditions in upstream reactor

Superscripts

TM	trade mark
*	dimensionless (as in G^*)

ANNEX 11

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