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## The protection of batch chemical reactors against overpressure

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**The Protection of Batch  
Chemical Reactors Against Overpressure**

by

**Graham Paul Somerville-Marrs**

**A Doctoral Thesis  
Submitted in Partial Fulfilment of the Requirements  
for the Award of  
Doctor of Philosophy  
of the Loughborough University of Technology**

**September 1987**

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I would also like to thank the Health and Safety Executive for their co-operation and assistance during this project.

It happens, like as not,  
There's an explosion and good-bye the pot!  
These metals are so violent when they split  
Our very walls can scarce stand up to it.  
Unless well-built and made of stone and lime,  
Bang go the metals through them every time  
And some are driven down into the ground  
- That way we used to lose them by the pound -  
And some are scattered all about the floor;  
Some even jump into the roof, what's more

Some said the way the fire was made was wrong;  
Others said, "No - the bellows. Blown too strong."  
That frightened me, I blew them as a rule.  
"Stuff!", said a third. "You're nothing but a fool,  
It was not tempered as it ought to be!"  
"No!", said a fourth. "Shut up and listen to me;  
I say it should have been a beech wood fire  
And that's the real cause, or I'm a liar."  
I've no idea why the thing went wrong;  
Recriminations, though, were hot and strong.  
"Well", said my lord, "there's nothing more to do.  
I'll note these dangers for another brew;  
I'm pretty certain that the pot was cracked,  
Be that as it may, don't gape! We've got to act.  
Don't be alarmed, help to sweep up the floor  
Just as we always do, and try once more!"

Extract from "The Canon Yeoman's Tale" from  
"The Canterbury Tales" by Geoffrey Chaucer, 1386.  
(translation by Neville Coghill)



"Experience is the name everyone gives to their mistakes"

- Oscar Wilde

"The errors of a wise man make your rule,  
Rather than the perfections of a fool"

- William Blake

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## 1. INTRODUCTION

A study was required of the methods of protecting chemical reactors against overpressure. At present the use of bursting discs, or pressure relief valves is not only normal but virtually mandatory. There are, however, some uncertainties and difficulties in the design of venting systems based on bursting discs and pressure relief valves and some evidence of failures of such systems. There is also some pressure to permit alternative means of protection based on control systems, including trip and interlock systems.

### 1.1 Background

Traditionally chemical reactors are provided with bursting discs, or pressure relief valves, as overpressure protection and it has been the policy of the Health and Safety Executive (HSE) to require the use of these devices on such reactors.

The reactors of interest are exothermic chemical reactors, primarily but not exclusively, batch reactors.

There are, however, certain problems associated with the use of venting systems. There have been accidents in which a reactor has exploded even though it has been fitted with a bursting disc.

There are a number of problems in the design of venting systems. One is that it is not always easy to specify all the



fault conditions which may occur and for which therefore pressure relief may be required. Another is that methods for the design of relief systems have not been fully developed, although the work done by the Design Institute for Emergency Relief Systems (DIERS) has resulted in progress in vent design. Another is that it may be difficult to dispose of the material vented.

In addition to these design problems there is the separate problem of the reliability of the system elements. There appears to be very little information available on this aspect. What is known is that reliability engineers tend to assume lower reliability for bursting discs than for pressure relief valves and that the failure rate of the latter is not negligible. It is also necessary to consider factors such as plugging of entry pipes, back pressure in vent lines, etc.

As a consequence of these problems there is some pressure to permit an alternative approach based on control systems, including trip and interlock systems. There has been insufficient information to determine the relative dependability of this approach compared with the conventional one.

The use of a control system, including trips and interlocks, deals with the problems by eliminating the causes, rather than by mitigating the effect of overpressure and is thus perhaps a more modern approach. On the other hand it may not be easy to design instrument systems to handle all the fault modes and they may be more vulnerable to management system deficiencies, particularly in maintenance, than are venting systems based on devices such as bursting discs, which are a relatively passive device.

This project was supported as part of a continuing programme of work by the HSE on the safety of batch chemical reactors. Previous and current work includes studies of

incidents (e.g. Townsend and Pantony, 1979 [1]; Nolan, 1983 [2]; Barton and Nolan, 1984 [3]) and of reaction screening.

## 1.2 Objectives

The objectives were:

"To define more precisely the problem of overpressure protection of chemical reactors and to compare the methods of protection available, notably bursting discs and pressure relief valves versus control systems, including trips and interlocks."

This involved the following program of work:

- (1) Review of failure data.
- (2) Probabilistic approach to vessel/system failures:
  - (a) Failure modes of reactions/reactors and emergency relief systems.
  - (b) Qualitative identification of failure mode parameters.
  - (c) Quantification of failure rates as far as possible.
- (3) Preliminary consideration of control systems for comparison with emergency relief systems.

The second stage objectives of the work took the following form:

- (1) Information on the failure modes and failure frequencies of bursting discs/vent systems.

- (2) Information on the modes of overpressure and paths to overpressure with special reference to the estimation of the frequency of overpressure and to protection against overpressure by control/trip systems.
- (3) And finally to make recommendations on choice of venting versus control/trip systems as means of protection against overpressure.

Thus the programme of work for the second stage was:

- (1) Development of taxonomy of modes of overpressure.
- (2) Development of generalized fault trees for overpressure.
- (3) Estimation of failure frequency:
  - (a) Estimation of number of reactors at risk.
  - (b) Estimation of proportion of failures in each modeusing:
  - (i) Historical data
  - (ii) Expert judgement
- (4) Comparison of vent systems versus control and trip systems.
- (5) Study of typical reactor designs with alternative protective systems.
- (6) Overview of regulatory implications for both large and small firm environments.
- (7) Results and recommendations.

Estimates of the failure frequency have been sought from historical data, but these have been supplemented by expert judgement, using methods analogous to those used to obtain human error estimates.

The development of the generalized fault tree is seen as the core of the project, since this will form the basis for judging whether venting is an option in particular cases and for assessing the effectiveness of control/trip system alternative.

In developing the recommendations the regulatory background has been borne very much in mind, and in particular the situations of both large and small firms.

## 2. CHEMICAL REACTOR DESIGN AND OPERATION

In general batch reactors may be classified in several different ways, according to: the type of equipment (tank, tube, tower); the reaction system (homogeneous or heterogeneous, liquid, gas or solid phase); the means of temperature control (isothermal or adiabatic); and as to the mode of operation (batchwise, semi-batch or continuous).

With this later classification in mind, a summary of the different types is presented below, the emphasis being on liquid phase reactions. The agitation and heating/cooling requirements for these reactors are then presented to give an indication of the potential hazards associated with the system.

### 2.1 Batch Reactors

Batch reactors usually employ a single tank which accommodates a charge of reactants and processes them according to a predetermined course of reaction during which no material is fed into or removed from the vessel. The tank itself can be fitted with either a loose cover to exclude dust and other contaminants (reaction kettle) or, for reactions which are processed at pressures greater or less than atmospheric, a rigid cover securely bolted to the reactor body (autoclave). In most instances batch reactors are equipped with some means of agitation (stirring, rocking, shaking) as well as provisions for heat transfer (jacket, external and internal heat exchangers - tubes, coils, etc. - the choice

depending on whether the reaction is exothermic or endothermic).

Batch reactors are used primarily for liquid phase (homogeneous) reactions but may also involve heterogeneous reactions between a liquid and suspended solid or the dispersion of an immiscible liquid or gas in another liquid. They can be operated over wide ranges of temperature and pressure either under isothermal (low reaction rate) or non-isothermal (high reaction rate) conditions.

As with most batch operated processes, batch reactors have certain inherent disadvantages including: relatively high labour (manual operation and supervision) costs, control problems (automation being not only difficult but costly) and loss of production whilst changing from one batch to another. Batch reactors are therefore confined to the production of expensive, fine chemicals, dyestuffs, pharmaceuticals, etc., which do not warrant large scale manufacture. The big advantage therefore of batch reactors in small scale production is their versatility and flexibility.

Typical examples of batch reactions are the ammonolysis of nitrochlorobenzenes, hydrolysis of esters and polymerization of butadiene and styrene in aqueous suspension.

In some processes such as polymerization and fermentation, batch reactors are traditionally preferred because the downtime between batches provides an opportunity to clean the system out in order to prevent fouling or contamination of the product.

Another advantage is that (small scale) batch reactors generally require less auxiliary equipment and less elaborate control systems than continuous processes and are therefore lower in capital costs.

## 2.2 Semi-Batch Reactors

This type of reactor is generally the same in construction as that described above, employing a single stirred tank with heat exchange facilities. The difference, however, is in the method of operation, in that some of the reactants are loaded into the reactor as a single charge and the remaining ones are then fed in gradually as the reaction progresses.

This method of operation is especially favoured when large heat effects occur, since exothermic reactions may be slowed down or endothermic rates maintained by limiting the concentration of one of the reactants, and the reaction may therefore be kept within controllable limits. Other situations in which this sort of operation is desirable occur when high concentrations may result in the promotion of undesirable side reactions, or where one of the reactants has a limited solubility and is charged at the dissolution rate. Examples are the production of high molecular weight polyglycols or detergents by the reaction of ethylene oxide glycol in the first case and alkylated phenols in the second. Ethylene oxide is added gradually to the second reactant, thereby avoiding large hazardous concentrations being present at any one time.

## 2.3 Continuous Reactors

In this type of reactor reactants are introduced and products withdrawn simultaneously in a continuous manner. It may assume the shape of a tank, a tubular structure, or a tower, and finds extensive applications in medium and large scale plants for the purpose of reducing the operating cost and facilitating control of product quality.

The continuous stirred tank reactor (CSTR) in the form of either a single tank, or more often a series of tanks, is particularly useful for liquid phase reactions. Continuous

stirred tank reactors are currently used in the liquid phase nitration of hydrocarbons or polyhydric alcohols. The construction as regards provision for agitation and heat exchange is generally the same as described previously for batch and semi-batch reactors. The main difference is in the provision of overflow pipes or weirs to facilitate the transfer of reactants/products from one reactor to the next.

In a CSTR the reactants are diluted immediately on entering the tank. In many cases this favours the desired reaction and suppresses the formation of byproducts. With the exception of very viscous liquids, a close approximation to perfect mixing (back mixing) can be achieved. Because fresh reactants are rapidly mixed into a large volume, the temperature of the tank is readily controlled, and hot spots are less likely to occur than in batch reactors. Moreover, if a series of stirred tanks are used, it is relatively easy to hold each tank at a different temperature so that an optimum temperature sequence can be obtained. The flow of the process stream from one tank to the next results in a stepwise change in composition between successive tanks.

The use of several tanks in series also reduces the bypassing of unreacted reagents between the reactor inlet and outlet. Although this loss is, in a sense, the result of stirring itself, bypassing would be even greater in the absence of stirring, due to bulk streaming of reactants between inlet and outlet.

Other advantages of CSTR's include consistent product quality, ease of automatic control, lower manpower requirements and openness of construction giving rise to ease of cleaning.

For these various reasons the typical fields of application of the CSTR are the continuous processes of sulphonation, nitration, polymerization, etc. It is used very



extensively in the organic chemical industry and particularly in the production of plastics, explosives, synthetic rubber and so on.

The CSTR is also used whenever there is a special necessity for stirring; for example in order to maintain gas bubbles or solid particles in suspension in a liquid phase, or to maintain droplets of one liquid in suspension in another as in the nitration of benzene or toluene.

Instead of using a series of vessels, the several stages of a CSTR may be incorporated into a single reaction vessel (either vertical or horizontal) by means of a number of compartments, each equivalent to a stirred tank reactor, over which the reacting mixture cascades.

In addition to stirred tank reactors there are a number of other types of continuous reaction equipment, but these are of little concern here and will not be considered further.

#### 2.4 Agitation in Batch Reactors

Agitation in stirred reactors is a necessity to achieve the satisfactory reaction and heat transfer duty. The following discussion is concerned primarily with the agitation requirements for batch reactors although the principles still apply for other types of reactor.

Impellers of many types are used to produce agitation and mixing in the liquid phase. To produce mixing it is necessary to supply energy and it is usually accomplished by the rotation of an impeller. The rate at which energy is supplied, or the power, is not only dependent upon the type of impeller used and how rapidly it is rotated but also on the physical properties and characteristics of the fluid, shape of the container, and relative location of all component parts of the system such as baffles, coils and supports. Hence to

characterize the behaviour of any impeller or specify an agitator requirement, it is necessary to take into consideration the complete environment in which it operates.

#### 2.4.1 Factors Influencing Agitation

In all applications of agitation the primary effects are concerned with one or more of the following:

- (a) Mass transfer at an interface,
- (b) Heat transfer at an interface,
- (c) Dispersion of solids, liquids or gases.

Agitation does not directly affect chemical reaction; the rate of a chemical reaction taking place can be influenced by the agitation only if the reaction itself is controlled by one or more of the above primary effects. In batch reactors where the reaction process operates on a cyclic basis there are points where the potential for an exothermic runaway reaction is greater than at others, e.g. at the changeover from heating to cooling when the concentration of reactants is greatest, and at these moments mass and heat transfer may be critical.

In some instances the reaction system may be able to absorb micro-scale mixing and heating effects and show no obvious deviation from the normal behaviour. In others, however, the micro effects of a small deviation from the intended cycle could cause an escalation to macro effects if mass and/or heat transfer are insufficient. In these instances it is important to have a clear understanding of the mass and heat transfer characteristics of the system so the potential constraints of a reactor design can be appreciated and where necessary the design can be changed or operation/emergency procedures modified.

The factors which influence the rate and degree of mixing as well as the efficiency may, however, be classified as

follows:

- (a) Characteristics concerned with the rotating impeller, e.g. its shape, speed, dimensions and position in the vessel.
- (b) Physical properties of the materials concerned, e.g. their densities, viscosities and physical states.
- (c) Shape and dimensions of the containing vessel and of any fittings which may be immersed in the fluid.

Although agitation is concerned with obtaining the primary effects mentioned above, it is not easy to specify the exact circumstances needed to achieve them efficiently. This is because the physical properties of the materials being processed are themselves the main factors which determine the choice of impeller and because these properties vary widely.

The application of any of the common types of impeller to a given problem will provide a partial solution. For equipment of low cost and power consumption, efficiency is often of secondary importance provided the required effect is produced. In this case, choice of impeller is not critical. Thus a particular impeller is chosen because of the type of reactor contents rather than to achieve a specific mixing efficiency.

#### 2.4.2 Impeller Type and Speed

All agitators impart kinetic energy to the fluid in the form of either general mass flow or of turbulence. Different mixing problems require different proportions of these two forms of kinetic energy as well as different levels of intensity. The question of power input per unit volume has also to be considered.

Various sources of information on these points exist (EEUA, 1963 [4]; Oldshue, 1983 [5]) to help select the blade geometry. Typically these compare types of blade to produce

certain mixing effects per 1000 gal volume. The speed of the impeller selected is then found from tables which recommend values for a standard vessel, e.g. 6 ft in diameter, for a given level of mass flow and turbulence. The speed required for the volume of reactor actually to be used can then be found by scaling up or down.

Some typical agitator tip speeds are given below:

Table 2.1 Agitator Tip Speeds for Various Duties

Duty	Tip Speed (m/s)
Normal Mixing	2.5 - 3.3
Heat Transfer Duty	3.5 - 5.0
High Shear (Two-Phase Dispersion Duty)	5.0 - 6.0

2.4.3 Scale-Up

Scale-up is necessary when bringing a process up to the full scale plant operation and strives to attain the identical conditions on the full scale as were found to be optimum on the pilot plant. This is generally not possible, because areas per unit volume must change with scale and mixing conditions also change. It is therefore necessary to decide which criteria are most significant for the reaction under consideration and then to choose a scale-up method which holds these critical conditions constant on the two scales, and lets the inevitable differences occur in the less significant conditions.

For example, if heat removal was a problem, then one would ensure that agitation on the two scales produced similar heat transfer characteristics; if the gas dispersion was important, scale-up based upon equal shear rates would be more appropriate.

The problems in scaling up complex single phase reactions are that:

- (a) Changes in temperature can effect selectivity of the yield.
- (b) Changes in heat transfer coefficient can effect film temperatures and degradation when heat sensitive materials are used.
- (c) Changes in heat transfer area/unit volume alter the heat removal potential and thus can lead to hazardous situations.

It is therefore understandable that when the scale-up approach is being used and the reactor mechanism is not fully understood, a very conservative attitude must be taken.

The various scale-up criteria are discussed below.

#### 2.4.3.1 Constant Stirring/Unit Volume

This is a suitable criterion when the main duty of the agitator is liquid mixing. The reactor volume is scaled up proportionally to the larger output required and the power is scaled up by the same factor. The stirrer speed required to input this power can then be calculated as follows; the relation between power and dimensions for a fixed physical system can be defined as:

$$P_w = Kd_i^5 N^3 \quad (2.1)$$

For a full definition of the terms used refer to the list of symbols.

Since we are scaling up at constant power/unit volume:

$$\frac{P_{w1}}{V_1} = \frac{P_{w2}}{V_2} \quad (2.2)$$

and since scale up is based on geometrical similarity:

$$\frac{D_2}{D_1} = \frac{d_{i2}}{d_{i1}} = \left( \frac{V_2}{V_1} \right)^{1/3} \quad (2.3)$$

Hence for constant power per unit volume we can write:

$$N_2 = N_1 \left( \frac{V_2}{V_1} \right)^{-2/9} \quad (2.4)$$

Notice that the stirrer speed,  $N$  must reduce on the larger scale.

#### 2.4.3.2 Constant Heat Transfer Coefficient

This criterion is suitable when heat removal from the reactor is the main problem. By dimensional analysis the Nusselt number,  $Nu$ , which contains the process fluid side heat transfer coefficient  $h_o$ , can be represented as a function of the Reynolds number,  $Re$ , and the Prandtl number,  $Pr$ .

$$Nu = f(Re, Pr) \quad (2.5)$$

This gives the equation:

$$h_o = K_T D^{-1} . d_i^{1.3} . N^{0.65} \quad (2.6)$$

$K_T$  is a constant. Scaling up a reactor from volume  $V_1$  to volume  $V_2$ , maintaining geometric similarity, to give the same heat transfer coefficient and using equation (2.3) the following equation can be produced:

$$N_2 = N_1 \left( \frac{V_2}{V_1} \right)^{-0.15} \quad (2.7)$$

Having achieved the same heat transfer coefficient on the larger scale, the heat removal facilities must be increased because the heat generation is proportional to  $V_2/V_1$  but the surface area of the vessel has increased by only  $(V_2/V_1)^{2/3}$ . This can usually be done by adding additional area in the form of coils in the reactor itself. In extreme cases, larger areas can be added by using external heat exchangers and a pump around system (until the volume of the exchanger is significant compared to the volume of the reactor).

In some cases it may be possible to lower the coolant temperature and so increase the heat flow through the existing surface, but this is usually fixed by stability considerations which normally require the coolant temperature to be within a few degrees of the reactant temperature.

Thus, if the heat transfer area is not sufficient, if a reaction runaway situation were to occur within the reactor the cooling system would be unable to cope and could easily cause an explosive situation. Thus it is most important to ensure the correct transfer area in a scale-up involving constant heat transfer coefficients.

#### 2.4.3.3 Constant Tip Speed

This criterion maintains constant shear in the liquid and this would be expected to maintain the same gas distribution

qualities in the pilot and full scale plant.

To achieve this and maintain geometric similarity of the vessels, equation (2.3) holds and, defining the tip speed as:

$$s = N\pi d_i \quad (2.8)$$

For constant tip speed we have:

$$N_2 = N_1 \left( \frac{v_2}{v_1} \right)^{-1/3} \quad (2.9)$$

#### 2.4.3.4 Constant Pumping Rate/Unit Volume

This can be taken as a criterion when the mixing time is thought to be a significant factor in the system. The pumping rates for impeller type pumps are given by the relationship:

$$Q = K_D N d_i^3 \quad (2.10)$$

$K_D$  is the discharge coefficient and  $Q$  is the pumping rate ( $m^3/s$ ). Hence using equation (2.3):

$$N_1 = N_2 \quad (2.11)$$

#### 2.4.3.5 General Relationships

The four scale-up criteria mentioned above produce different relationships between the full-scale plant stirrer



speed and the pilot stirrer speed. They all have the general form:

$$N_2 = N_1 \left( \frac{V_2}{V_1} \right)^n \quad (2.12)$$

where  $n$  varies between 0 and  $-1/3$  depending on the criterion. Although this range suggests that the different criteria are in fairly good agreement, because scale-up ratios are necessarily high, full scale stirrer speed predictions can be significantly different. For example, take a 40 litre pilot plant operating satisfactorily with a stirrer speed of 2 revs. A 40 m<sup>3</sup> full scale reactor (scale-up of 1000) would have a stirrer speed of either 2 or 0.2 revs depending upon the criterion chosen.

The engineer scaling up must therefore use his judgement to decide which criterion to employ and must then check that the resulting power consumption at tip speed is reasonable. When this is not the case, various manipulations in dimensions must be made to produce a viable design that reproduces as well as possible the conditions used in the pilot plant.

## 2.5 Heating and Cooling in Batch Reactors

Heat transfer coefficients are important parameters in the design of stirred batch reactors. The heat transfer process in batch reactors is an unsteady-state process: heat input and/or temperature vary over a fixed processing time.

The factors which can effect the rate of heat transfer within a reactor are:

- (a) The type and speed of agitation;
- (b) The type of heat transfer surface;
- (c) The nature of the fluid (Newtonian, etc.);
- (d) The geometry of the vessel.

Some information on the design of the heat transfer systems is gathered here. The heating and cooling of stirred batch reactors is one of the most common operations in the chemical industry. However, the ways in which the various factors involved in batch reactor design can affect the heat transfer characteristics is not clearly understood. The rule-of-thumb approach adopted by engineers when tackling these problems often results in over-designed plant; such plant, whilst operable, inevitably has high capital and operating costs. A better approach is for the engineer to have an appreciation of how the different variables involved in batch reactor design relate to each other. Then using sensible design data and correlations which relate to the specific system under design, it will be possible to achieve an optimal compromise between system design and engineering cost.

### 2.5.1 Heat Transfer Systems

Heating systems for stirred tanks can be classified as either direct or indirect. Direct firing is nowadays seldom used due to the fact that the heating tends to be uneven and the temperature difficult to control.

Indirect systems use carrier fluids to take heat to and from the process. The closer the temperature of the heating or cooling medium to the reaction mass, i.e. the smaller the thermal inertia, the quicker the response to the temperature changes and hence the safer the system. The main heat transfer fluids are water and steam. The principal disadvantage is the high pressure involved in high temperature systems. Water in its natural state is never pure. It frequently contains dissolved materials which decrease in solubility with

increasing temperature. This may result in the formation of scale over heat transfer surfaces and the reduction of the heat transfer coefficient. Water may also contain corrosive or foam-producing substances and may freeze in cold weather when the system is not in use. Other fluids commonly used to transfer heat are mineral oils and a number of organic compounds having a variety of trade names. These organic materials are high boiling materials so that the heat transfer system can be operated at low pressures. Both liquid and vapour phase heat transfer systems are used.

In liquid systems, the heat transferred is from sensible heat. The faster the liquid is pumped through the system, the less is its change in temperature over the heat transfer surface and the more uniform is the heating or cooling.

In vapour systems, the heat transferred is from latent heat. Since all the heat transfer takes place at the saturation temperature, the entire heat transfer surface is at a uniform temperature.

Indirect heating and cooling is the most common method of adding and removing heat from a stirred tank reactor and are discussed further below.

The removal of heat from a stirred tank can be done in a number of ways. One is the refluxing of boiling solvent, whereby the heat of vaporization of the boiling solvent is removed from the system by the reflux condenser. The condensed solvent is then returned to the reactor. This method has the advantage that it reduces thermal inertia and ensures a quick response to any temperature fluctuations. To supply heating as well the technique must be applied in conjunction with one of the methods described below.

The next method involves the use of a jacket around the reactor. This can be used to circulate a heating or cooling

medium and is frequently used on its own or with the above technique.

A third method is the insertion of cooling heat transfer area, usually in the form of coils. This also has the advantage that it can be used to provide heating as well as cooling. However, it does have the disadvantage in that it may become fouled easily and significantly affect heat transfer. They are also difficult to maintain and clean.

If still further heat transfer is required, then external heat exchange can be provided and a pump-around system installed. This is not a very attractive proposition when highly exothermic, or endothermic, reactions are involved because this introduces a significant time lag in any control response and could cause considerable thermal inertia during which a reaction runaway may be caused. A diagrammatical presentation of the methods available for heating and cooling batch reactors is given in Figure 2.1.

### 2.5.2 Heat Transfer Surfaces

The two most common means of providing a heat transfer surface to batch reactors are jackets and internal cooling coils. Other types, like vertical baffles and plates, exist but only find use in speciality applications.

Coils are usually preferred to jackets as they are cheaper and give higher overall film coefficients. Jacketed reactors are usually more expensive than those equipped with coils; they are normally used when other factors outweigh the cost as, for example, when processing highly viscous fluids with paddle type impellers. The agitator operates close to the vessel wall in this case and so precludes the use of coils. Other examples include the processing of batches which demand minimal cross-contamination between batches. Jacketed vessels, particularly glass-lined ones, are easier to clean.

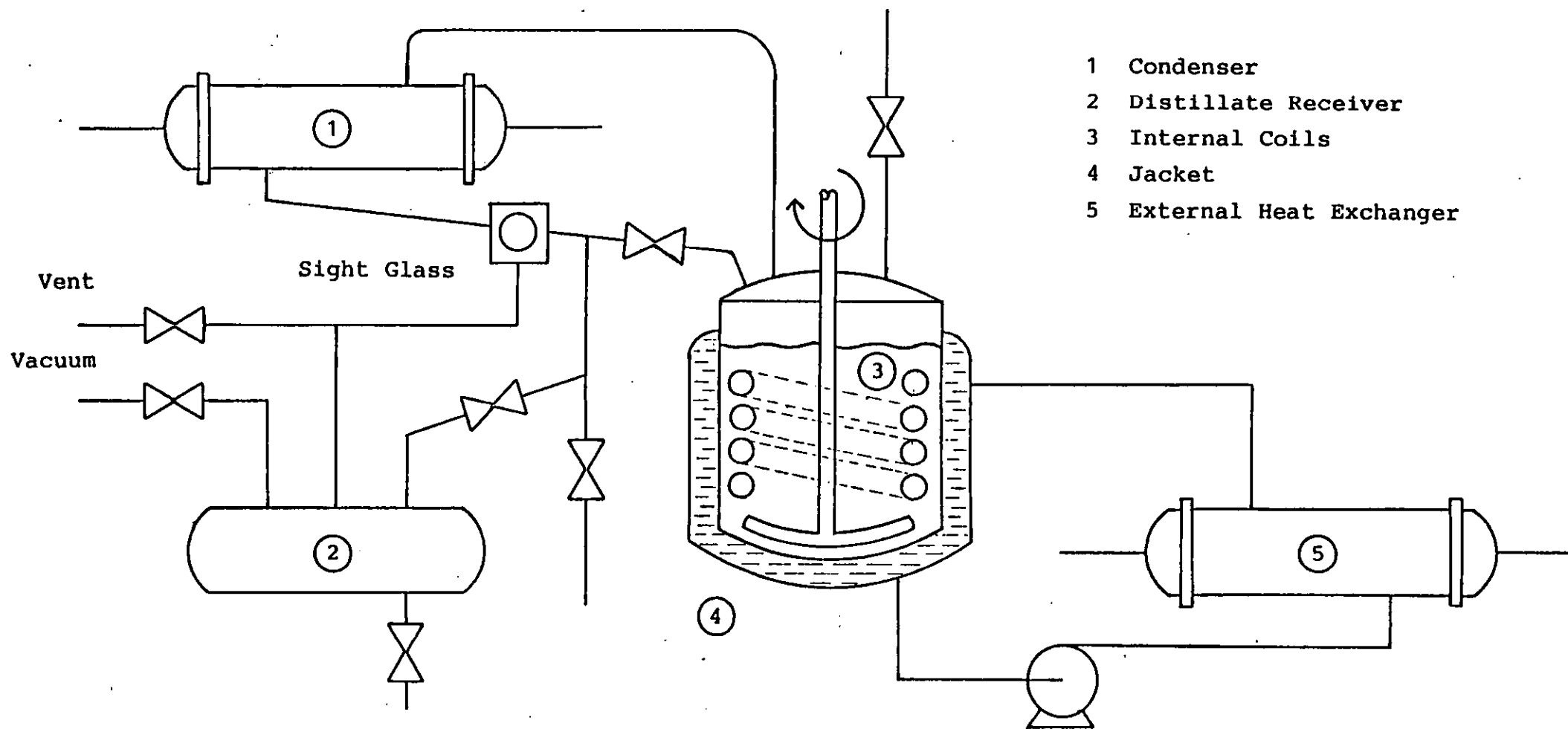


Figure 2.1 Heating and Cooling Methods in Batch Reactors

Jackets come in various shapes and forms including:

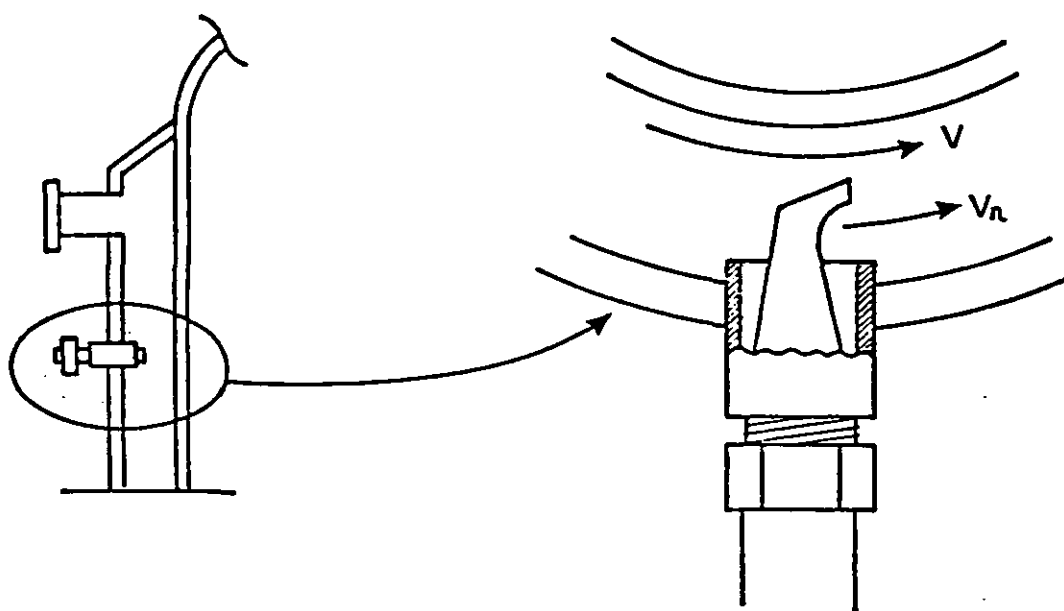
- (a) Simple jacket,
- (b) Jacket with agitation nozzles,
- (c) Spirally baffled jacket,
- (d) Dimple jacket and
- (e) Half-pipe coil jacket (limpet coil).

Figure 2.2 shows some of these. The most common type of jacketed reactor is the glass lined mild steel reactor. It is resistant to most corrosive liquids and has a smooth internal finish making it easy to clean. It usually has a simple jacket fitted with agitation nozzles.

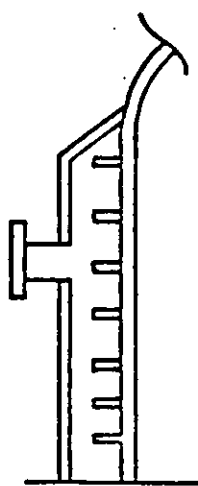
The selection of a jacket type is ruled by the process requirements and service conditions. If the heating and cooling demands of the process are low, and only steam or water are used, then a simple jacket will be adequate. More arduous duties requiring brine coolants or high temperature heat transfer media may need a jacket designed to encourage higher outside film heat transfer coefficients.

A key factor in jacket selection is the pressure differential between the service and process sides of the vessel wall. This will determine the vessel wall thickness and in turn influence the overall cost. Care must be taken in selecting sensible design pressure figures, so as to get an optimum wall thickness.

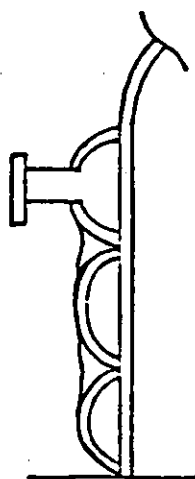
Further optimization may be achieved by selecting jackets which do not exert pressure over the whole surface of the vessel. Vessels with simple jackets are structurally the weakest compared with other types, because the jacket pressure is applied over a large area of unsupported metal. If half pipe coil or dimple jackets are used, they exert pressure over a lesser area and this will lead to a reduction in the required vessel wall thickness. Such jackets are more



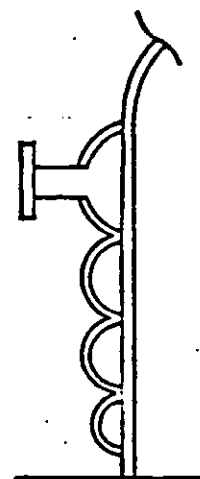
SIMPLE JACKET WITH OPTIONAL AGITATION NOZZLE



SPIRALLY BAFFLED JACKET



DIMPLE JACKET



HALF-PIPE OR LIMPET COIL JACKET

Figure 2.2 Means of Providing Heat Transfer Surface in Batch Reactors

expensive to fabricate, and a careful analysis is required not only to establish the most cost effective route but to ensure that the heat transfer requirements are met.

As a rule when using carbon steel vessels with a jacket pressure greater than 11 bar, half-pipe coil or dimple jackets may have economic advantages over simple jackets. For vessels manufactured from more expensive alloy steels the economic advantages become more apparent at much lower jacket pressures.

### 2.5.3 Heat Transfer Coefficients

The heat transferred in an agitated vessel can be expressed by the standard equation:

$$q = UA_H \Delta \theta_{LM} \quad (2.13)$$

When determining the required heat transfer area for a reactor it is important that  $U$  is calculated accurately. In doing so it is essential to use accurate physical property data, at the specific operating conditions.

To calculate values for  $U$  the following generalized expressions are used:

$$\frac{1}{U} = \frac{1}{h_i} + \frac{x}{k} + \frac{1}{h_j} + r_d \quad (2.14)$$

for jackets

$$\frac{1}{U} = \frac{1}{h_j} + \left( \frac{x}{k} \right) \left( \frac{D_{c,o}}{D_{c,LM}} \right) + \left( \frac{1}{h_{c,i}} \right) \left( \frac{D_{c,o}}{D_{c,i}} \right) + r_d \quad (2.15)$$

for coils



Normally the resistance provided by the wall or coil wall is so small that the term  $X/k$  can be ignored.

Values for the individual film coefficients are determined using correlations developed from the Seider-Tate equation. Correct selection of design correlations will enable accurate evaluation of heat transfer performance. Summarized below are various correlations which can be used to obtain values for  $h_i$ ,  $h_j$  and  $h_{c,i}$ .

#### 2.5.4 Heat Transfer Film Coefficient: Jacket Process Side

The correlation for prediction of the film coefficient of jacketed reactors is dependent on the type and speed of agitation. The basic correlation is:

$$\frac{h_i d_i}{k} = f(Re)^a (Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right) \quad (2.16)$$

where  $Re = D^2 N \rho / \mu$  and  $Pr = \mu C_p / k$ .

The values of the constants  $f$  and  $a$  can be found for standard agitators such as turbines, propellers, paddles and anchor types from the literature (Chapman and Holland, 1965 [6]; Ackley, 1960 [7]; Kapustin, 1963 [8]; Chilton and Drew, 1944 [9]; Uhl and Grey, 1966 [10]). The value of  $f$  varies from 0.33 to 1.00 and  $b$  is typically 0.67. a

#### 2.5.5 Heat Transfer Film Coefficient: Jacket Service Side

The outside coefficient will be influenced by the type of jacket. The fluid flow in a simple annular unbaffled jacket will be low due to the large cross-sectional flow area. Thus heat transfer will be mainly due to natural convection. When using this form of simple jacket, the equation recommended by

Uhl and Gray (1966) [10] should be used for determining the service side film coefficient:

$$\frac{h_j}{k} = 0.8K_H \left( \frac{C_p \mu}{k} \right)^{0.33} \left( \frac{\rho^2 g \beta \Delta \theta}{\mu^2} \right)^{0.33} \quad (2.17)$$

As a guide, expected heat transfer coefficient values for condensing steam are around 5700 W/m<sup>2</sup> K, for brines and organic fluids 170-570 W/m<sup>2</sup> K and for cooling water 1400-2300 W/m<sup>2</sup> K.

Jackets with agitation nozzles are predominantly used to improve the jacket heat transfer performance of glass-lined steel reactors. The nozzles produce a spiral flow pattern tangential to the jacket wall which sets the entire contents of the jacket in rotation. The increase in velocity is sufficient to cause turbulent flow and thus increase the heat transfer performance. The velocity of rotation is normally in the range of 0.6-1.0 m/s. The heat transfer coefficient can be calculated using the following equations for forced convection developed from the Seider-Tate equation, depending on the type of fluid in the jacket (Bollinger, 1982 [11]):

$$h_j = \frac{91(1 + 0.011\theta)V^{0.8}}{D_e^{0.2}} \quad \text{for water} \quad (2.18)$$

$$\frac{h_j D_e}{k} = 0.027(Re)^{0.8}(Pr)^{0.33}$$

for brines and organics (2.19)

where  $Re = D_e V \rho / \mu$

The value of  $V$ , the velocity of rotation, can be determined on a trial and error basis from the equation below:

$$W_p(V_n - V) = \left( \frac{4fL}{D_e} \right) \left( \frac{V^2}{2} \right) \rho A_f \quad (2.20)$$

where a value for  $f$ , the friction factor, is assumed and used to calculate  $V$ . This value of  $V$  is then used to calculate  $Re$  which is in turn used to determine the new value of  $f$ .

For a spiral baffled and half-pipe coiled jacket at Reynolds number greater than 10,000 a modified form of the Seider-Tate equation for a straight pipe can be used to calculate the outside coefficient.

A correction factor is used to take account of the turbulent flow in the coil (Perry and Chilton, 1973 [12]):

$$\frac{h_j D_e}{k} = 0.027 (Re)^{0.8} (Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \left( 1 + 3.5 \frac{D_e}{D_c} \right) \quad (2.21)$$

For  $Re < 2100$  the following equation can be used:

$$\frac{h_j D_e}{k} = 1.86 \left( \frac{Re \cdot Pr \cdot D_e}{L} \right)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (2.22)$$

These equations can also be applied when determining film coefficients for dimple jackets.

### 2.5.6 Heat Transfer Film Coefficient: Coils Process Side

The approach to calculating the heat transfer coefficient in reactors containing coils is similar to that used for jacketed vessels. All the following correlations assume a vessel containing a single helical coil.

For a vessel containing a flat blade turbine (Oldshue and Gretton, 1954 [13]) with six flat blades and with values of Reynolds number between 400 and 1,500,000:

$$\frac{h_i D_{C,o}}{k} = 0.17(Re)^{0.67}(Pr)^{0.37} \left( \frac{D}{d_i} \right)^{0.1} \left( \frac{D_{C,o}}{d_i} \right)^{0.5} \left( \frac{\mu}{\mu_w} \right)^Z \quad (2.23)$$

Z is a function of bulk viscosity and can be obtained from charts. Typical values are Z=0.97 at 0.3 cP and Z=0.18 at 1000 cP.

For a six blade retreating turbine (Ackley, 1960 [7]) with a single internal helical coil:

$$\frac{h_i d_i}{k} = 1.4(Re)^{0.62}(Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (2.24)$$

For a propeller:

$$\frac{h_i D_{C,o}}{k} = 0.078(Re)^{0.62}(Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (2.25)$$

For a paddle type impeller:

$$\frac{h_i d_i}{k} = 0.87 (Re)^{0.62} (Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (2.26)$$

### 2.5.7 Heat Transfer Film Coefficient: Coils Service Side

Determination of the outside film coefficient for a coil should assume turbulent flow. Values can be calculated using modified versions of equations (2.26) and (2.27) as used for spiral baffled jackets:

$$\frac{h_{c,i} D_e}{k} = 0.027 (Re)^{0.8} (Pr)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \left( 1 + 3.5 \frac{D_e}{D_c} \right) \quad (2.27)$$

$$\frac{h_{c,i} D_e}{k} = 1.86 \left( \frac{Re \cdot Pr \cdot D_e}{L} \right)^{0.33} \left( \frac{\mu}{\mu_w} \right)^{0.14} \quad (2.28)$$

### 2.5.8 Fouling Factors

Selection of fouling factor ( $r_d$ ), where possible, should be based on previous operating experience. When information is not available texts such as Kern (1950) [14] can be used for guidance. Table 2.2 lists typical values for a variety of duties.

Table 2.2 Fouling Factors

Duty	Fouling Factor (W/m <sup>2</sup> K) <sup>-1</sup>
Water	0.0005
Organics	0.0005
Brine	0.0005
Caustic Solutions	0.001
Hydrocarbons	0.001

### 2.5.9 Overall Heat Transfer Coefficients

It is difficult to give values of the overall heat transfer coefficients. The type of agitation, the nature of the fluid and the type of heat transfer surface can all affect the heat transfer coefficient. The unsteady nature of batch operations, whereby the physical properties of the reactants change during the course of processing, means that there may be a wide range of U values for any one batch operation. These factors should be borne in mind when using the typical values of U which are listed in Table 2.3:

Table 2.3 Typical Overall Heat Transfer Coefficient

Equipment	Heat Transfer Coefficient	
	Heating	Cooling
	U (W/m <sup>2</sup> K)	U (W/m <sup>2</sup> K)
Simple Jacket (mild steel vessel)	400-900	150-600
Simple Jacket (glass-lined vessel)	200-700	100-350
Limpet Coil	600-1100	200-700
Dimple Jacket	500-1000	300-550
Internal Coil	600-1500	250-800

The calculation of an accurate agitation and heat transfer system is a necessary requirement in the design of a batch reactor where an exothermic reaction is taking place.

In using the above equations a certain level of inaccuracy is bound to occur. Thus it is a prerequisite that the reaction being used is sufficiently well known so the demands upon the reactor are covered to an acceptable level.

### 2.6 Control Systems

The conduct of a typical batch operation involves the following steps:

- (1) Charge the reactor with reactants and catalyst.
- (2) Heat the charge to operating temperature.
- (3) Maintain charge temperature as reaction proceeds.
- (4) Cool at the reaction end point.
- (5) Discharge the reactor.

#### 2.6.1 Control of Charging

Control of charging may be carried out manually or under automatic control, typically by a computer.

With manual charging the operator adds reactant from drums or sacks through a fixed pipe or through a manhole. Addition through a fixed pipe may be by gravity or by pulling a vacuum on the reactor.

Addition by this method is only considered satisfactory for reactions of low or moderate heat release and is prone to various hazards. These include the addition of the wrong chemical, addition of too much or too little chemical, the wrong order of chemical addition, or too fast addition relative to the temperature.

With automatic control the reactants are generally all charged to header tanks with level measurement and alarm. The tanks may also be provided with weighing facilities. The required dosage can be added based either on change of level or weight in the tanks.

An important distinction is between true batch operation, in which all the reactants are added initially, and semi-batch operation, in which all but one of the reactants are added initially and the remaining reactant is added continuously. This latter method has the advantage that if the charge overheats, the feed of this second reactant can be cut off at once, reducing the heat production by chemical reaction and giving the reactor cooling system the opportunity to regain

equilibrium.

A further account of some common methods of reactant addition is given by Rose (1981) [16].

### 2.6.2 Control of Temperature

In general it is necessary first to heat the batch to bring it up to the reaction temperature, then cool it as the reaction proceeds, and finally to cool it prior to discharge. It may also be necessary to heat the reaction towards the end of the batch to bring it up to its end point.

These requirements mean that it is necessary to provide heating as well as cooling. Two methods which are used are:

- (1) Use of a two-way heat transfer system, capable of both cooling and heating.
- (2) Preheating of the reactants.

The typical two-way system utilizes water for cooling and steam for heating.

Temperature control of a batch reactor can be difficult. There is a tendency for the temperature to overshoot or undershoot and exhibit instability.

The aim of the temperature control system is to prevent instability and to maintain the charge temperature within limits sufficiently close to obtain the desired products.

One common temperature control system is illustrated in Figure 2.3. In this single loop system the temperature in the reactor is controlled by manipulating the flow of coolant.

Another common system for temperature control is shown in Figure 2.4. In this cascade system the temperature in the



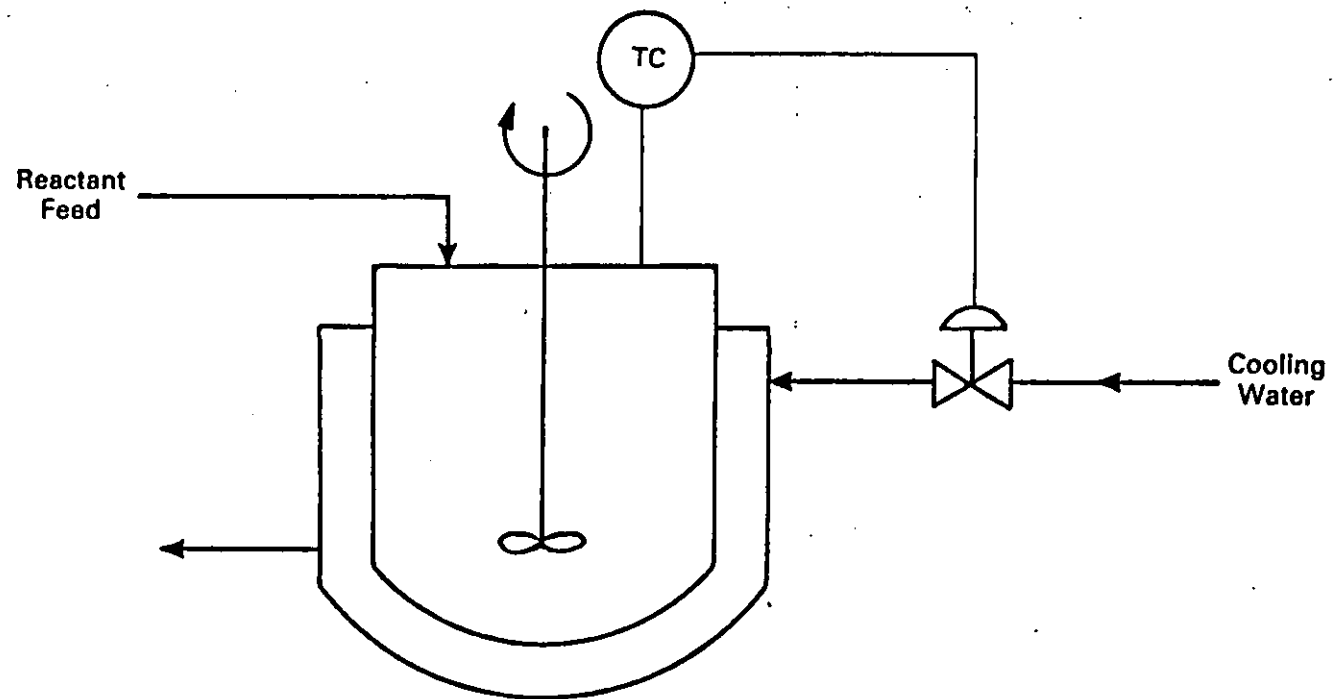


Figure 2.3 Control of Temperature in a Batch Reactor using a Single Loop

reactor is controlled by the master loop via the setpoint of the slave loop controller which controls the coolant outlet temperature by regulating the flow of coolant.

The use of a cascade system can create problems in the transfer from manual to automatic control during startup. Thus although cascade control has certain benefits, the simple single loop system may be preferred.

For any control system the measurement of the reactor temperature is critical. There have been numerous incidents due either to outright failure or to slow dynamic response of the measuring device.

Temperature control of the reactor is not necessarily carried out exclusively by cooling and heating. In some reactions periodic addition of catalyst plays an important part.

Accounts of reactor temperature control are given by Shinskey (1967) [15], Buckley (1970) [17] and Anon. (1984) [18] and further accounts in the list of references.

## 2.7 Protective Systems

Two distinct types of protective systems are used on batch reactors. These are:

- (1) Instruments
- (2) Relief devices

The first level of instrument protection is the provision of alarms. Important variables for alarm includes reactor pressure and temperature, agitator rotation, reactant feed flow (if any), coolant flow and temperature.

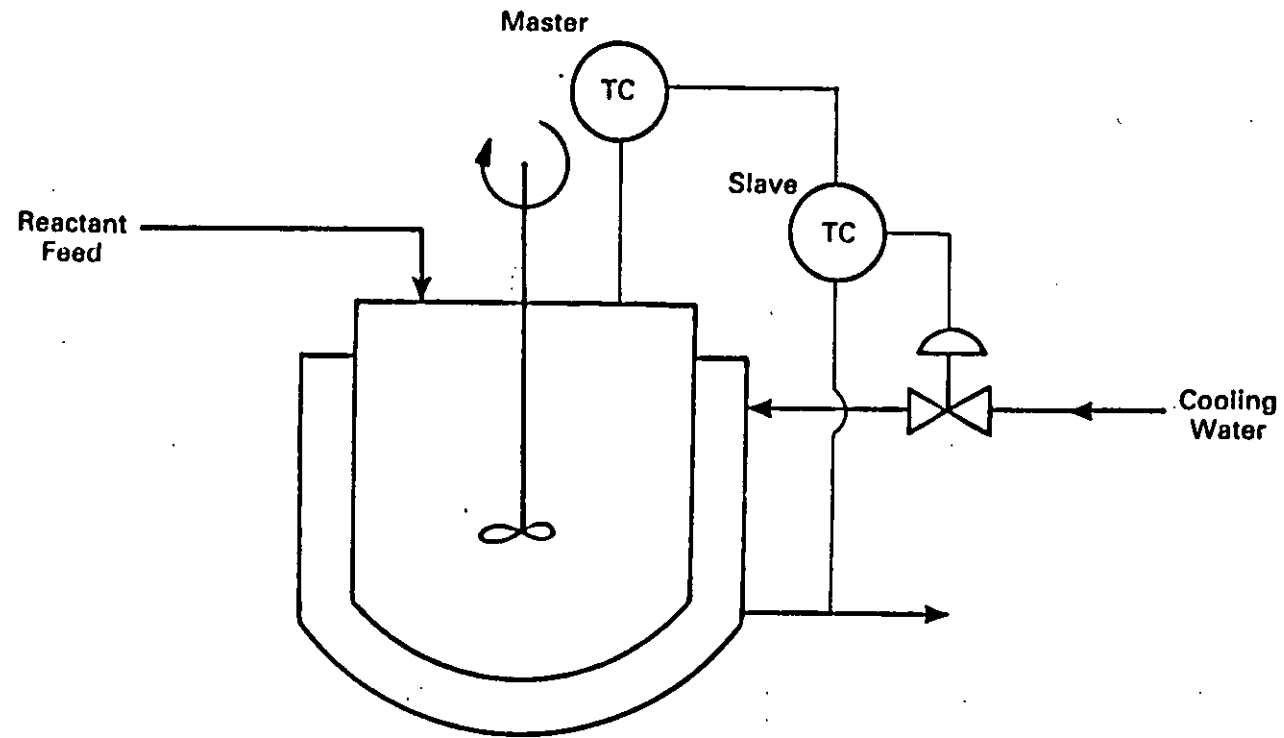


Figure 2.4 Control of Temperature in a Batch Reactor using a Cascade System

It is desirable that the alarm on a critical variable such as reactor temperature should be taken from a measuring device separate from that used for temperature control, otherwise failure of the single temperature measurement may cause hazardous action by the control loop to go undetected.

The provision of an alarm on agitator rotation is important. Loss of agitation can cause unreacted material to build up and then to react violently. An alarm may also be provided on motor power to indicate loss of the paddle.

In order to ensure that there is agitation use is made of interlocks. Typically an interlock is used to prevent the addition of reactants if the agitator is not operating.

The use of a trip requires the selection not only of the parameter the deviation of which will initiate trip action but also of a parameter to be manipulated. In a semi-batch reactor this latter parameter is usually the flow of the second reactant.

Thus Roy et al. (1984) [19] describe a protective system for a semi-batch reactor with external circulation cooling in which such a trip action is taken on deviation of the following variables:

- (1) High reactor pressure,
- (2) High reactor temperature,
- (3) Low reactor temperature,
- (4) Low reactor circulation flow and
- (5) Low coolant flow.

In a batch reactor the choice of parameter to manipulate is less easy. Actions which may be taken include use of additional emergency cooling or quenching and addition of reactant shortstop.

The second line of defence is the use of pressure relief devices such as bursting discs and pressure relief valves.

Some form of pressure relief device is normally provided on a reactor in order to meet the requirements of pressure vessel codes. Supplies of utilities such as air and nitrogen may be possible sources of overpressure.

For protection against reaction runaway the usual protective device is a bursting disc. A bursting disc is simple and has no moving parts and should be reliable and it has a very rapid response. It does, however, discharge material until the pressure falls to atmospheric. For this reason a pressure relief valve which will discharge material only as long as the reactor pressure is above the set pressure may be preferred despite the dangers of blockage and jamming and the slower response.

Further discussion of relief systems is given below.

### 3. REACTIONS AND REACTION HAZARDS

The following presentation is aimed to give a brief description of some of the more typical chemical reaction hazards that occur in batch reactors by describing some common reaction types i.e. nitration, sulphonation and polymerization. Groggins (1958) [20] gives a more detailed account of these reactions and other processes used in industry together with some suggestions for the operation of the process.

It is the aim of this section to summarize, for the reactions mentioned, the background information obtained by the author useful for the control of reactor hazards. It does not purport to be an expert account.

#### 3.1 Nitration

The nitration reaction introduces one or more nitro groups ( $\text{NO}_2$ ) into a reacting molecule. The nitro group may become attached to carbon to form a nitro-aromatic or nitro-paraffinic compound. If it becomes attached to oxygen a nitro-ester is formed, while attachment to nitrogen produces a nitramine. In the nitration process the entering nitro group may replace a number of different monovalent atoms.

##### 3.1.1 The Nitrating Reagents

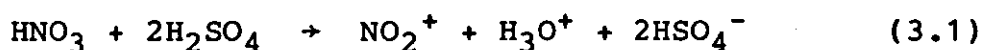
A variety of reagents effect nitration. These can include nitric acid, mixtures of nitric acid with sulphuric acid,

acetic acid, acetic anhydride, phosphoric acid, and chloroform. Occasionally nitrogen pentoxide and nitrogen tetroxide have been used. Nitration is one of the most important reactions in industrial synthetic organic chemistry. Nitration products are used as solvents, dyestuffs, pharmaceuticals and explosives, as well as being intermediates in other processes, e.g. preparation of amines.

All nitration reactions are potentially hazardous, not only due to the frequently explosive characteristics of the end products but also due to the fact that most nitrating agents are also strong oxidizing agents. Both nitration and oxidation reactions are usually highly exothermic. Temperature control is absolutely vital and a knowledge of the temperature sensitivities of the final products is essential.

### 3.1.2 The Nitronium Ion, $\text{NO}_2^+$

The system nitric acid - sulphuric acid, commonly known as mixed acid, is the most important nitrating medium from a practical standpoint and produces the nitronium ion for nitration by the following equation:

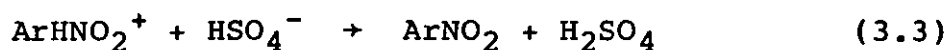
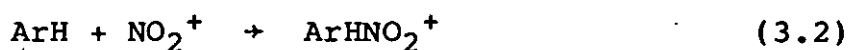


In solutions weaker than 86% sulphuric acid, the ionization of nitric acid is very slight but rapidly rises as the sulphuric acid becomes more concentrated. In 94% sulphuric acid, the nitric acid is practically completely ionized to nitronium ion. Thus addition of nitric acid alone will not ensure nitration. The combination with sulphuric acid is important. The mixed acid is usually made up elsewhere on the plant so inconsistencies in its composition may not be considered when operating the reaction cycle.

### 3.1.3 Kinetics and Mechanism of Aromatic Nitration

This is by far the most common nitration type carried out in industry today. The kinetics of the nitration reaction depend upon the reaction medium. The rate of nitration is proportional to the concentration of added nitric acid and of the organic substrate.

The widely accepted mechanism for the nitration of an aromatic compound (denoted Ar-) by the nitronium ion is shown below:



### 3.1.4 The Composition and Use of Mixed Acid

The materials used to form the acid are 65% oleum, 56-60% nitric acid, and spent acid from the nitration operation. The mixed acid composition required will have been determined from a pilot plant or some means of process research and development.

When using mixed acid there are two primary conditions that must be met:

- (1) The amount of 100% nitric acid present must be enough to satisfy the stoichiometric requirements of the nitration reaction.
- (2) The amount of 100% sulphuric acid, with its associated dissolved sulphur trioxide (oleum), must be sufficient to promote the desired reaction regardless of the mechanism which is involved.



Two values which are calculated from the reaction stoichiometry in one case and determined in the process development in the other are used to fulfil these requirements. These are the dehydrating value of sulphuric acid (DVS) and the nitric ratio (R).

DVS is the ratio of sulphuric acid to water present at the end of the reaction. The R value is the ratio of the weights of 100% nitric acid to weight of material being nitrated.

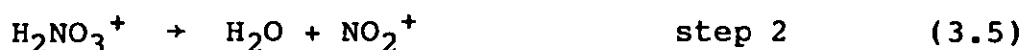
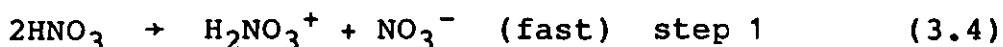
The ratio R is set by the specifications of the process and any safety consideration which will affect production. The presence of water is not required to effect a smooth nitration so a high DVS value is needed. It is common practice for the DVS value, along with the mixed acid composition, to be reported prior to the execution of a particular batch nitration. This is despite the fact that the DVS value applies to the situation at the end of the nitration when the acid has been used under specified conditions.

An important consideration in nitration reactions is the stability of the nitrator charge or product when in contact with its own spent acid. Increasing the DVS value favours high stability, while decreasing it results in the lowering of stability. This is as expected, since increasing DVS tends to drive nitration to completion, whereas lowering DVS allows accumulation of partially nitrated material, along with increased dilution, which would favour oxidation reactions. The instantaneous DVS can give an indication of the most hazardous point in the nitration reaction. At the start of the reaction there is no water present, and the amount of sulphuric acid remains constant throughout the reaction. Thus at the start DVS is infinity, as the reaction proceeds sulphuric acid can mop up any water produced and the DVS decreases. The sulphuric acid then reaches the stage where it can deal with no more water and the DVS decreases rapidly at

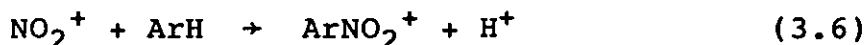
first and then at a slower rate as the reaction comes to a gradual halt and the water inhibits nitration. The point when the sulphuric acid is balanced by the water produced occurs typically after approximately 18% of the batch has been nitrated. The DVS then approaches the specified value for the end of the reaction. It is after 18% of the batch has been nitrated that the greatest risk is likely to occur. This risk decreases on approaching the end of the batch.

### 3.1.5 Aromatic Nitration in Organic Solvents

In order to remove the hazards of using mixed acid as the nitrating agent some reactions are carried out in solvents such as nitromethane or acetic acid with nitric acid in large excess when nitration occurs by the following path:



In strongly acidic, highly polar solvents like sulphuric acid, this takes place very quickly. However, in less strongly acidic media such as acetic acid or nitromethane, this step can be relatively slow. The nitrating step is shown below:



All the highly reactive compounds are nitrated at the same rate, which is the rate of formation of the nitronium ion. In most cases it is the nitration step which is the rate determining stage.

In order to maintain a high rate of reaction, anhydrides such as acetic anhydride are also included in the reaction. Anhydrides react with any water produced during the nitration process forming acetic acid hence preventing the dilution of the sulphuric acid and hence a decrease in the production of the nitronium ion as commented above. Thus the constituents required to maintain a safe, maximum rate of nitration can be calculated and this rate will stay approximately constant throughout the cycle.

### 3.1.6 Kinetics and Mechanism of Aliphatic Nitration

Unlike aromatic hydrocarbons aliphatic hydrocarbons are not susceptible to attack by electrophilic reagents like the nitryl ion, the aliphatic hydrocarbons are quite inert to such reagents. In order to effect nitration of these compounds the reaction must be carried out in the vapour phase and at temperatures of 350-450 °C by free radical reaction. A characteristic feature of reactions involving alkyl radicals is the great variety of products formed. The variation is in the length of the aliphatic chain, but only mononitro-compounds are formed. Due to this fact this reaction does not find significant use; however, aliphatic nitration can also be carried out in the liquid phase. This reaction is of less importance than the vapour phase nitration because of lower yields, lower conversions, and the occurrence of unwanted side reactions.

### 3.1.7 Batch Nitration

Nitration reactions have traditionally been carried out in batch reactors, but in order to reduce the amount of hazardous, and often explosive, material being processed at any one time, continuous processes have been used. However, due to the flexibility of batch processes they still find a significant use.

Nitration is usually done in a closed cast-iron or mild steel vessel. When nitrating with mixed acid, the life of such reactors is satisfactory, and any short life failures can usually be traced to excessive water or to low actual nitric acid content in the waste acid.

A common accessory is a suction line in the vapour space above the liquid to remove the acid fumes and oxides of nitrogen which may be liberated. The reactor is also continually purged with carbon dioxide. A common safety device is a dump tank partially filled with water into which the reactor contents can be dumped if the reaction gets out of hand.

### 3.1.8 Continuous Nitration

Continuous operation is considered to be the first solution to the problem of dealing with a troublesome and hazard ridden batch nitration process. New processes which may be producing a new product usually use continuous nitration methods. The actual nitration process is carried out in equipment similar to that for batch processes, with the exception that an overflow pipe or weir arrangement is provided for the continuous withdrawal of the products and continuous addition of the reactants. There are usually slight modifications to enhance mass transfer and contact time, thus increasing the conversion and hence efficiency of the process. The basic safety measures taken are the same as in those for batch reactors.

### 3.1.9 Typical Industrial Nitration Process

A typical nitration process is that used for the manufacture of nitrobenzene. The reactor is charged with a quantity of spent acid from a previous cycle in which some nitrobenzene and acid are present. Cooling water is circulated and the temperature is maintained at 50 °C or lower while the

benzene is charged to the reactor. It must be fed under the liquid layer, or onto it with heavy agitation forcing the reactants downwards.

The temperature can vary between moderate limits but if no cycle acid is used it must not rise above 50 °C. When fortified spent acid is used it must be maintained between 50 and 55 °C.

Upon completion of the reaction the batch is allowed to settle for 4-12 hours in order to separate. Spent acid is drawn off at the bottom and returned to acid tanks for further settling or for treatment with more benzene. The nitrobenzene is then delivered to a neutralizing vessel.

The neutralizing vessel is prepared with a heel of warm water which is delivered to an adjacent vat and the nitrobenzene blown into it. The charge is thoroughly agitated and warmed with live steam for about 30 minutes or until neutral. It is then allowed to settle for a similar period. The acid/water is then run out and nearly all the nitrobenzene is settled out.

The charge is then given a neutralizing wash at 40-50 °C. with warm sodium carbonate, until alkaline. The nitrobenzene is then delivered to storage tanks where it is again settled to remove final traces of water.

#### 3.1.10 Nitration Reaction Hazards

The types of hazard most likely to occur can be grouped and sub-grouped as follows:

(1) Charging of the basic chemicals:

- (a) Deficiency of a reactant.
- (b) Addition of wrong reactant.
- (c) Too fast addition of reactants.

(2) Maintenance of the correct temperature:

(a) Inadequate coolant circulation.

(b) Inadequate agitation.

(3) Adequate batch control:

(a) The use of the correct batch temperature cycle.

(4) Impurities effecting reaction:

(a) Water, air, steam deposits, etc.

The two factors of prime importance in the design of nitrators are the degree of agitation and the control of temperature.

Agitation generally must be very efficient, even violent, in order to obtain smooth reactions and to avoid local overheating which could occur if stagnant spots were to exist in the nitrator. This also means that the material fed to the nitrator is quickly and thoroughly mixed with the contents of the nitrator, and so local concentrations of reactants which could lead to local overheating do not occur.

Temperature control in nitrators is usually achieved by the use of coils of tubes through which cold water or brine is circulated. A wall jacket is not efficient enough except in the case of small vessels. Due to the fact that a large surface area, a high coolant circulation velocity and a high flow rate of medium past the surfaces are required only coiled internal heating and cooling is adequate for nitrators. The thermal effects which are encountered and the heat transfer characteristics of the various materials involved are generally well known so that an efficient cooling system can be designed.

### 3.2 Sulphonation

Sulphonation may be defined as any chemical process by which the sulphonic acid group  $\text{-SO}_2\text{OH}$ , or the corresponding salt or sulphonyl halide group (e.g.  $\text{SO}_2\text{Cl}$ ) is introduced into an organic compound.

There is also the process of sulphation which is similar to the sulphonation process but which involves the placement of the  $\text{-OSO}_2\text{OH}$  group on a carbon, yielding an acid sulphate ( $\text{ROSO}_2\text{OH}$ ), or the  $\text{-SO}_4\text{-}$  group between two carbons forming the sulphate ( $\text{ROSO}_2\text{OR}$ ).

The reactions require strong concentrations to give a good driving force and usually need high temperatures. The reactions are mildly exothermic, but usually relatively easy to control.

Sulphonates and sulphates are used as detergents, emulsifying, de-emulsifying, penetrating, wetting and solubilizing agents, lubricant additives, and rust inhibitors. Polymeric sulphonates include dispersing agents, elastomers, water-soluble synthetic gums and thickening agents, ion-exchange resins which function as strong acids with complete water insolubility, an unusual combination of properties leading to many important applications.

#### 3.2.1 The Sulphonating Reagents

Most commercial sulphonations use direct treatment with sulphuric acid or sulphur trioxide compounds such as oleum. However, sulphur trioxide is theoretically the most efficient possible sulphonating and sulphating agent, since in the overall sense only direct addition is involved.

Sulphur trioxide polymerizes easily at room temperature, as a trimer, and if this form is exposed to even a trace of

moisture, for which it has a very strong affinity, it is converted to a chain type polymer which is solid at room temperature, and which is not practical for use as a sulphonating agent. This transformation is accompanied by a great evolution of heat. Trimer-SO<sub>3</sub> can be satisfactorily stabilized against further polymerization by the addition of a small quantity (as little as 0.1%) of various compounds, especially derivatives of boron, phosphorus, or sulphur.

The major problem with sulphonating with sulphur trioxide hydrates is finding practical procedures for overcoming this affinity for water so that the SO<sub>3</sub> becomes free to react with the organic compound. The sulphur trioxide solution must not contain too much water or its presence will prevent SO<sub>3</sub> from reacting with the chemical to be sulphonated.

The advantages for sulphur trioxide (and correspondingly for oleums) namely, rapid and complete reaction, minimum reactor capacity, and no requirement for heat to complete sulphonation, have become increasingly attractive industrially because of lower labour and fixed capital costs and the desire to obviate waste-acid disposal.

The disadvantages of high heat of reaction and consequent decomposition or side reactions, high viscosity of the reaction mixture can often be overcome by engineering design, choice of conditions, or use of a solvent.

Sulphuric acid and oleum are often used in excess, thereby advantageously functioning as cheap, low viscosity solvents for the product sulphonic acids which are often quite viscous in pure form. They are always used in liquid form, while sulphur trioxide, on the other hand, is usually employed as a vapour since it is easily vaporized and the vapour form is considerably milder than the liquid. Liquid sulphur dioxide is an excellent sulphonation solvent for use with sulphur trioxide and with oleums.



### 3.2.2 Chemical and Physical Factors in Sulphonation and Sulphation

When employing sulphur trioxide or its compounds for sulphonation or sulphation, important variables determining the rate and course of the reaction are:

- (1) Concentration of sulphur trioxide in the sulphonating agent.
- (2) Time in relation to temperature and reagent strength.
- (3) Catalysts.
- (4) Solvents.

### 3.2.3 The Concentration of Sulphur Trioxide

To carry out sulphonation or sulphation to completion, it is necessary to maintain the sulphur trioxide concentration in the sulphonating agent at a certain minimum level.

There is a level of sulphur trioxide concentration below which sulphonation will not take place. This level has been defined as the  $p_i$  value. The  $p_i$  value is specific for every organic compound and the easier a compound is to sulphonate, the lower this  $p_i$  value (i.e. the lower is the concentration of sulphur trioxide required to carry out sulphonation). This level is unchanged by temperature, agitation or catalysis. The level of sulphur trioxide required for any particular reaction also depends on many other factors, including the excess of starting compound, the reaction time, and the concentration of the starting acid.

The minimum concentration of sulphur trioxide can be maintained, and the reaction completed, in a number of ways. These include the use of excess acid, and the physical and/or chemical removal of water.

In the use of excess acid the organic compound will be completely sulphonated if sufficient excess acid is employed to stay above the  $p_i$  value even when diluted by the water formed during the reaction. In practice, the excess quantity should be sufficient to effect complete sulphonation at a point above the  $p_i$  value, since the reaction rate becomes impractically slow as the  $p_i$  value is closely approached.

The spent acid approach is fairly simple, but requires excess acid which must be separated and discarded. It can be made more efficient by employing acid (oleum) of maximum strength compatible with yield and product quality and by operating at the maximum permissible temperature. Neither of these expedients will give complete utilization of acid, however.

The excess acid method is used in sulphation as well, although maximum strength oleum cannot always be used since it causes decomposition of the reactants.

The removal of water can be effected by either physical or chemical means. The physical removal of water and the theoretical utilization of both acid and organic compound can be achieved by partial pressure distillation of the water from the reaction mixture by repeatedly distilling an excess of the material to be sulphonated through the reactor. In this manner the acid is maintained above the  $p_i$  concentration until completely consumed. This is the prevalent industrial approach to the sulphonation of low-boiling stable aromatic hydrocarbons such as benzene and xylenes, etc. Slight modifications, such as sulphonating agents and operating temperatures, are required for other processes but the method is essentially the same for most sulphonations.

The chemical removal of water is achieved by adding a chemical which reacts with the water to produce a substance which can be easily removed, hence allowing the sulphonation

to go to completion. Boron trifluoride and thionyl chloride can be used to accomplish this, however, due to the expense this is rarely used except in the laboratory.

#### 3.2.4 Catalysts and Sulphonation Aids

The addition of other chemicals, usually in small amounts, can have a marked effect on some sulphonations in a variety of ways. The presence of only 1% mercury, relative to the compound being sulphonated, can cause an isomer of the required sulphonated compound to be produced. Mercury, only, has this catalytic effect when used with oleum or sulphur trioxide as the sulphonating compound. Mercury also allows the use of lower reaction temperatures, improves yields and accelerates the reaction. Unwanted oxidation and the resultant release of heat can occur at elevated temperatures in the presence of small quantities of catalytic materials such as mercury.

The addition of acetic acid (approximately 5% by weight of the hydrocarbon) hinders the unwanted side reaction which produces sulphones during the sulphonation of aromatic hydrocarbons such as benzene, toluene and xylenes with sulphur trioxide or oleum. Variations in reaction temperature and time can also cause sulphone formation but can be used to limit and eradicate this unwanted side reaction.

#### 3.2.5 Sulphonation Solvents

Many sulphonates are viscous liquids or solids. The use of solvents is therefore either essential or preferable to obtain efficient mixing and eliminating side reactions, thereby ensuring the wanted uniform reaction. In many cases they function as suspending media, rather than as true solvents, since either or both of the reagents as well as the sulphonate product may be only slightly soluble.

Excess acid can be used as an inexpensive, low viscosity solvent for most sulphonic acids but is often not used because of the difficulty of recovering a product dissolved in it, or because of the disposal problem often encountered.

Chlorinated solvents such as ortho-dichlorobenzene are used because they are high boiling, relatively inert, inexpensive, and are immiscible with water, thereby facilitating the removal of the latter by partial pressure distillation.

Liquid sulphur dioxide can also be used as an excellent solvent. It is inexpensive, widely available, inert, non-flammable, miscible with sulphonating and sulphating agents as well as with many organic compounds and product sulphonates. It can also function as its own refrigerant to remove heat of reaction because of its boiling point ( $-10^{\circ}\text{C}$ ). Objections to its use are its strong odour, a tendency to corrode the equipment used for its recovery, and the necessity of operating under pressure at temperatures above  $-10^{\circ}\text{C}$ .

The addition of acetic acid increases the solubility of the organic compounds.

It is not always essential that a prospective solvent, well suited to a particular sulphonation reaction in one or more respects, be completely inert toward the pure sulphonating agent. Several of the above solvents will react with sulphur trioxide or its derivatives either by sulphonation or oxidation and in some cases quite easily. Reactive solvents can be employed with little loss if:

- (1) The organic compound is much more easily sulphonated than the solvent.
- (2) The sulphonating agent is added to a mixture of the solvent and the compound being sulphonated.

- (3) The temperature of the sulphonation can be maintained below the point at which attack of the solvent becomes extensive.

### 3.2.6 Side Reactions During Sulphonation

In the sulphonation of certain aromatic compounds undesired side reactions can occur for any number of reasons. These include the nature of the chemical to be sulphonated, the sulphonating agent, and the physical conditions being used. Typical side reactions include the production of sulphones which are favoured by the use of strong reagents and operation in the vapour phase rather than the liquid phase and polysulphonation. Sulphone formation is reduced by the use of a solvent, addition of the organic compound to the sulphonating agent (rather than vice versa), the use of chemical inhibitors such as ethanoic acid or sodium sulphate, and conducting the reaction in a comparatively large volume of the reaction product.

### 3.2.7 Typical Industrial Sulphonation Process

Dodecylbenzene (detergent alkylate) is reacted with 20% oleum. The hydrocarbon (11,000 lb - 1,500 gals) is pumped into the glass-lined sulphonation kettle, 2,500 gals capacity with a 10 hp turbo-type mixer, and external heat exchanger of about 1,000 ft<sup>2</sup> of cooling capacity. Circulation of the alkylate through the exchanger is begun. The mixer is turned on, and 20% oleum (13,750 lb) is added as fast as possible, not exceeding a temperature of 30 °C, which usually requires one and a half to two hours. Following addition, the batch is digested for about two hours at about 30 °C to complete the reaction. At this point the spent acid has a strength of about 98.2% and is mixed with the sulphonic acid. To effect layer separation, water (2,600 lb) is added with full agitation and cooling at not over 60 °C to yield a spent acid of approximately 78%. Layer separation occurs upon standing for

about 4 hours at 60 °C; the lower layer, comprising of 10,800 lb of 78% acid is removed. The upper sulphonic acid layer is neutralized by addition to aqueous caustic soda (3,000 lb as 20% solution) at not over 55 °C at a final pH of 7.5-8.0 to yield a sodium salt slurry which can be processed further as appropriate, depending upon the final formulation required. Approximately 99% of the hydrocarbon charged is sulphonated and product loss by solution is small. The overall batch cycle lies between ten and thirteen hours.

### 3.2.8 Sulphonation Reaction Hazards

From the above it can be seen that there are a number of potential hazardous areas with sulphonation and sulphation reactions which can be broadly listed as below:

These are essentially basic chemistry problems which should be picked up at the laboratory and/or scaling up stages at the pilot plant.

(1) Regular reaction inadequate information:

- (a) Polymerization of sulphur trioxide with water.
- (b) Unusual variation in batch cycle time and temperature causing side reactions.

(2) Excessive heating:

- (a) Due to oxidative side reactions.
- (b) High viscosity batch and insufficient agitation.

(3) Inadequate agitation:

- (a) Insufficient solvent or a higher batch viscosity than usual.

(4) Impurity reaction exotherm:

- (a) Catalysis by small quantities of material.

(5) Regular reactant unknown decomposition:

(a) Using a strong sulphonating agent or insufficient solvent.

(b) Solvent decomposition or reaction with batch.

### 3.3 Polymerization Reactions

Polymerization can be classified as either condensation or addition reactions involving basic  $\text{-CH}_2\text{-}$  building blocks and a variety of functional groups.

Condensation polymerization reactions proceed in a step-wise manner through various intermediates such as dimers and trimers, etc. These exist as stable molecules until the next step. Small molecules, usually water, are split off at each step of the reaction.

Polymerization reactions usually proceed in four steps:

- (a) Activation,
- (b) Chain propagation,
- (c) Termination,
- (d) Chain transfer.

Addition polymerization is characterized by the fact that the reaction from monomer to polymer occurs without elimination of by-products. During the addition reaction, no stable compounds are formed because the intermediates are comparatively short-lived radicals or ions. The formation of the polymer chain is usually accomplished in a fraction of a second and in one single sweep. Polymerization at the double bond is a typical addition reaction of this type. Certain addition reactions, which proceed by first opening the ring of a cyclic compound, take a step-wise procedure. Thus they occupy a position between the two reaction types, showing similarities to each.

### 3.3.1 Heat Effects During Polymerization Reactions

Heat effects can be extremely sudden, making temperature control difficult. The quantity of heat released depends on the stage of polymerization reached.

Due to the fact that polymerization is specifically involved with making large molecules from comparatively small ones, as reaction proceeds viscosity effects of the reacting mix become very important. This problem is of particular interest when designing effective temperature control for the entire reaction cycle. Some means, therefore, of using a solvent to reduce the viscosity of the mixture and also provide a means of removing heat by reflux is most advantageous in the control of polymerization reactions.

Reactor heating is usually applied to speed up the reaction early on and cooling used to slow it down later, thus evening out the rate of heat release and preventing any tendency to speed up at the end when the reaction is nearly run out and when effective heat transfer is more difficult. The fact that the reaction in many cases is a pure batch operation makes the process even more hazardous in that any over-charging can increase the potential reaction energy available for release. The scaling of the process must therefore take this into consideration at the equipment design or the laboratory analysis stages.

### 3.3.2 Typical Industrial Polymerization Process

Typical polymerization processes include the production of PVC, and the manufacture of phenolic and alkyd resins.

PVC is the polymer of vinyl chloride and in the strict sense vinyl polymers are those made from the vinyl type monomer,  $\text{CH}_2\text{CHX}$  where X can be any substituent, although in industry this also means those made from vinyl ethanoate and



vinyl ethers, etc.

The monomer, vinyl chloride, can be made by direct addition of hydrogen chloride to ethylene or by controlled chlorination of ethylene and the subsequent removal of hydrogen chloride. The polymerization of the gaseous monomer can be achieved by the charging of the monomer and the catalyst or initiator into a reactor and controlling the product formation by manipulation of the batch temperature and pressure. In order to achieve better solubility in a wide variety of solvents the polymers are treated with acids or subject to extra chlorination.

The polymer produced can be of either high or low density which determines its end use, varying from containers to car parts, etc.

Phenolic resins are similarly made by the addition of phenol, formaldehyde, a catalyst and solvent together with various product modifiers to a reactor. The reaction is controlled by the application of cooling and manipulated by controlling catalyst, ratio of reactants, degree of reaction, and type of phenol to give the product the desired properties. The reaction can be halted at any point if the temperature is reduced and, in some cases, if the basic catalyst is neutralized.

The good physical and electrical properties of phenolic resins contribute to the development of a large number of end uses.

Alkyd resins are fatty-acid modified polyesters used primarily in the surface-coating field. A variation in the resin produced can be achieved by varying the amount, and type, of acid used, which can include phthalic and maleic anhydrides and benzoic acid.

There are three methods by which alkyd resins can be processed: the fatty acid process, the monoglyceride process and the solvent process. In the fatty acid process the glycerine, phthalic anhydride, and fatty acid are placed in the reactor and heated to 200-232 °C in about two hours until the required viscosity is obtained.

The monoglyceride process requires the initial reaction of a triglyceride and glycerine at 232 °C to form monoglyceride by transesterification. The phthalic anhydride is then added and the process continued until the end point.

The solvent process uses about 10% of water immiscible solvent in the reaction mixture. The solvent promotes better control by reducing the viscosity and provides a good means of water removal by azeotropic distillation.

It is important that inert gas blanketing is used so as to improve agitation and help remove water, thereby speeding up the final stages of esterification. Sufficient precaution should be taken to prevent the sublimation of phthalic anhydride in vents, etc., where it can cause blockages.

### 3.3.3 Polymerization Reaction Hazards

The reaction hazards of polymerization processes include the following:

- (1) Regular reactant inadequate information:
  - (a) consequences of excessive heat release unknown.
  - (b) "En masse" reactions producing a large heat release.

- (2) Incorrect charging:
  - (a) Pure batch operation allowing a greater quantity of heat release during the reaction if the wrong reactant ratio is used.
- (3) Inadequate cooling or excessive heating:
  - (a) Underdesign by scale-up.
- (4) Inadequate agitation:
  - (a) High viscosity or large viscosity changes during the reaction.
- (5) Inadequate batch control:
  - (a) Moderation of the reaction cycle.
- (6) Undesired catalysis:
  - (a) Too rapid addition of catalyst.
  - (b) Excess of catalyst.

### 3.4 General Considerations

From the above descriptions of some typical reactions carried out in batch-wise processes it can be seen that there are some basic considerations to be made when analyzing a reaction. These are:

- (1) Standard laboratory investigation of the reaction cycle.
- (2) Laboratory investigation of the scenarios which can occur on the full scale plant using the reaction cycle.
- (3) Adequate scale-up of the reaction and the hazards associated with it from the laboratory to the plant using the above information.

A laboratory investigation procedure considered necessary is suggested by the ABPI (1981) [21]. This covers all the

laboratory screening considered practical to detect hazardous points in a reaction cycle ranging from the collection of basic physical and reaction data to the determination of thermodynamic properties such as the combustibility characteristics, explosion and detonation potential etc.

This helps identify the conditions which must be avoided during the process cycle and form a set of rules for the operator to follow to carry out the reaction safely.

#### 4. RUNAWAY REACTIONS AND THEIR DETECTION

##### 4.1 Types of Reaction Runaway

One of the most potentially hazardous situations present in the chemical industries today is that due to the considerable chemical energy which may be partly or wholly released during an exothermic chemical reaction or physical change.

Such reactions are normally controlled by the removal of the heat energy released. A situation can arise, however, where the rate at which heat is generated by the reaction exceeds that at which it is removed from the system, thereby subjecting the reaction mass to some elevated temperature. Overheating subsequently causes the desired chemical reaction to proceed at an accelerated rate with a consequential increase in the heat released.

A good indication of just how much the rate of reaction is increased can be found from the Arrhenius equation:

$$K = A \exp(-E/RT) \quad (4.1)$$

where: K = rate constant for the reaction,  
A = a constant,  
E = energy of activation of reaction,  
R = gas constant,

T = absolute temperature.

In general the rate of heat release is exponential with respect to temperature whilst the ability to remove heat varies linearly with temperature across the heat transfer surface. The problem of temperature control therefore becomes compounded. This situation is commonly referred to as a runaway reaction condition and usually results in an excessive rate of gas and/or vapour evolution due to the reactor contents boiling. Matters are compounded if at elevated temperatures, above normal process conditions, any of the starting materials, intermediates or products are prone to thermal (exothermic) decomposition, causing further heat liberation and increased rate of reaction in addition to formation of gaseous byproducts. Even slightly exothermic reactions may become dangerous if they can initiate exothermic decomposition at some higher temperature.

Although runaway reactions and thermal decompositions are similar, i.e. both give rise to self-heating, they are in fact very different processes, the former being a production process which becomes unstable and the latter an unwanted reaction which goes out of control.

The net effect of either/both of these conditions is overpressurisation of the reactor vessel and the common outcome, if the pressure generated exceeds the vessel's strength, or if a fitted vent is inadequately sized, etc., is a potential explosion hazard with resultant loss of containment.

#### 4.2 Causes of Reaction Runaway

The two main types of reaction runaway have been identified as that of:

- (a) an exothermic desired reaction which becomes unstable

and (b) an unwanted exothermic decomposition which goes out of control.

In order to avoid conditions for a runaway arising it is necessary to have a knowledge of the causing factors. The most common causes of reaction runaway in chemical reactors are summarized below:

#### 4.2.1 Unidentified Reaction Exotherm

Despite even the most comprehensive of thermal hazard studies (including heat stability tests on reactants, intermediates and products) for a particular reaction system, there remains the possibility that a reaction exotherm, which may only be realized under certain process conditions (i.e. over a specific temperature range), will go undetected. The existence of such an exotherm may give rise to an undesired but "safe" i.e. controllable side reaction, or, in the worst possible case, it may initiate a serious uncontrollable exothermic runaway reaction generating sufficient overpressure to cause a potentially hazardous situation, e.g. vessel rupture.

#### 4.2.2 Unintended Reaction

There are many possible (related) factors which can result in an undesired exothermic reaction occurring. Amongst these are the existence of an unidentified reaction exotherm (discussed above), loss of cooling capacity or excessive heating, excess addition of one or more reactants (including catalyst), incorrect sequence of reactant addition, contamination of one or more of the reactants (i.e. inclusion of catalytically acting impurities), an external fire around the reactor, leakage of heat transfer media into reaction the vessel, etc. These are discussed in further sections. Extraneous reactions may also be possible between the reaction mass and materials of construction of the reactor itself, e.g.

vessel lining, stirrer, etc.

#### 4.2.3 Autodecomposition

Autocatalytic decomposition or self-heating of reactants, intermediates or products may be possible when stored or held (e.g. due to process difficulties, shut-down periods, etc.) under certain process conditions. These conditions are invariably specific to a particular reaction system.

Other factors such as steam leakage and contamination should also be taken into consideration as potential initiators of autocatalytic decomposition.

#### 4.2.4 Excess Catalyst

It is the general function of a catalyst to enable a reaction to proceed at a faster rate than would normally be possible. Overcharging of the catalyst may therefore result in an unexpectedly rapid rate of the desired reaction, causing a corresponding increase in the reaction temperature sufficient to overwhelm the available cooling capacity of the system. Similarly, such a situation may promote an undesired exothermic reaction which may subsequently go out of control.

#### 4.2.5 Impurities

Contamination of the reaction mass with catalytically acting impurities from whatever source, e.g. reactants, catalyst, reactor materials of construction, etc. may propagate an undesired reaction or, alternatively, cause the intended reaction to proceed at a more vigorous rate than usual, exceeding the cooling capacity available. The leakage or ingress of heat transfer media into the reactor may not only cause an untoward reaction, but a significant increase in pressure since the coolant/steam vapour pressure is likely to be much more than that of the vessel contents.



#### 4.2.6 Overheating

Excessive heating due to variations in process operation or conditions, including instrumentation failure and/or operator error (e.g. loss of cooling, delays in initiating agitation or transferring from heating to cooling, feed flow or temperature deviations, errors in charging sequence or ratio of reactants, etc.), may cause a desired exothermic reaction to go out of control, or an undesired (side or decomposition) reaction to occur, which may subsequently develop into a runaway condition if the situation cannot be contained.

Overheating of reactor contents is also possible due to an external fire hazard in the vicinity of the vessel which, in addition to the above, can cause the vapour pressure of the reaction mass to increase due to the fire heat input contributing further to the overpressure condition.

#### 4.2.7 Loss of Cooling

In most reaction systems cooling water is essentially used as the main control medium i.e. to remove excess heat from the process. Loss of cooling capacity is therefore similar to overheating, in that it may cause a desired exothermic reaction to go out of control or it may propagate an undesired (decomposition) reaction, both giving rise to overpressurisation of the reactor vessel.

#### 4.2.8 Loss of Agitation

The major consequences of agitator failure are two-fold: one is the possibility of phase separation which may allow large quantities of unreacted material (reactants and intermediates) to accumulate in the reactor vessel, resulting in a sudden and violent reaction when agitation is finally resumed; the second is the problem of poor heat transfer

(local overheating, etc.) the effects of which can be compared to that of loss of cooling.

Loss of agitation can occur in a number of ways: temporary power failure, electrical or mechanical component failure, e.g. agitator paddle falling off, operator error, etc.

#### 4.2.9 Reactant Charging Problems

This can be taken to include such factors as high flow, wrong ratio, wrong sequence, no agitation, etc.

The manipulation of fluid flows is one of the principal means by which control is exercised in chemical reactors. Flow deviations (too high, too low, zero, etc.) can therefore cause deviations of temperature (over heating), pressure and level which may lead to loss of control. This is also taken to include cases where manual charging of reactants is employed.

Imbalance in one or more reactant feeds and/or incorrect sequence of addition of reactants essentially results in the same outcome; a significant increase in the reaction rate of the desired reaction which may generate sufficient heat energy to exceed the cooling capacity available; or the promotion of an undesired exothermic side reaction, both of which may give rise to an overpressure situation.

Loss of agitation while charging can also present a serious hazard in that reactive material will concentrate in the reactor, with the possibility of local overheating causing a sudden and violent reaction to occur.

#### 4.2.10 Operator Error

This is not so much a direct cause of reaction runaway but more of a contributing or related factor. By this it is

meant that operator error can be traced back to many of the potential causes discussed above, including those of overheating, loss of cooling, loss of agitation, addition of excess reactants, incorrect sequence of reactant addition, too high reactant feed rate and so on.

#### 4.2.11 Instrument Error

As with operator error, this can be considered as more of an indirect cause of reaction runaway. For example, overheating of reactor contents due to a failed thermocouple, overcharging of reactants due to a faulty weigh balance, flow meter or level indicator, etc.

The simple scheme shown in Figure 4.1 (Regenass, 1984, [22]) relates the above mentioned most frequent causes of reactor incidents. Many other more elaborate schemes have been presented. Figure 4.2 is another attempt of this kind, mainly devoted to the causes of reactant accumulation and unexpected temperature increases.

A fuller reactor overpressure taxonomy is developed further in sections below.

#### 4.3 Identification of Potential Runaway

An all important aspect of chemical reactor protection is the hazard assessment of potential runaway reactions. This requires a thorough knowledge of and understanding of the chemistry and associated thermochemistry of the desired reaction and possible (unintended) side reactions, (including, for both types of reaction, information on the relative kinetics, starting temperature, enthalpy/heat of reaction, and adiabatic temperatures, etc.) and also of the thermal stability and physical properties of reactants, intermediates and products. A program for testing the thermal safety of chemical processes is described by Eigenman (1977) [23] and

Desired Reaction

Exothermic Decomposition

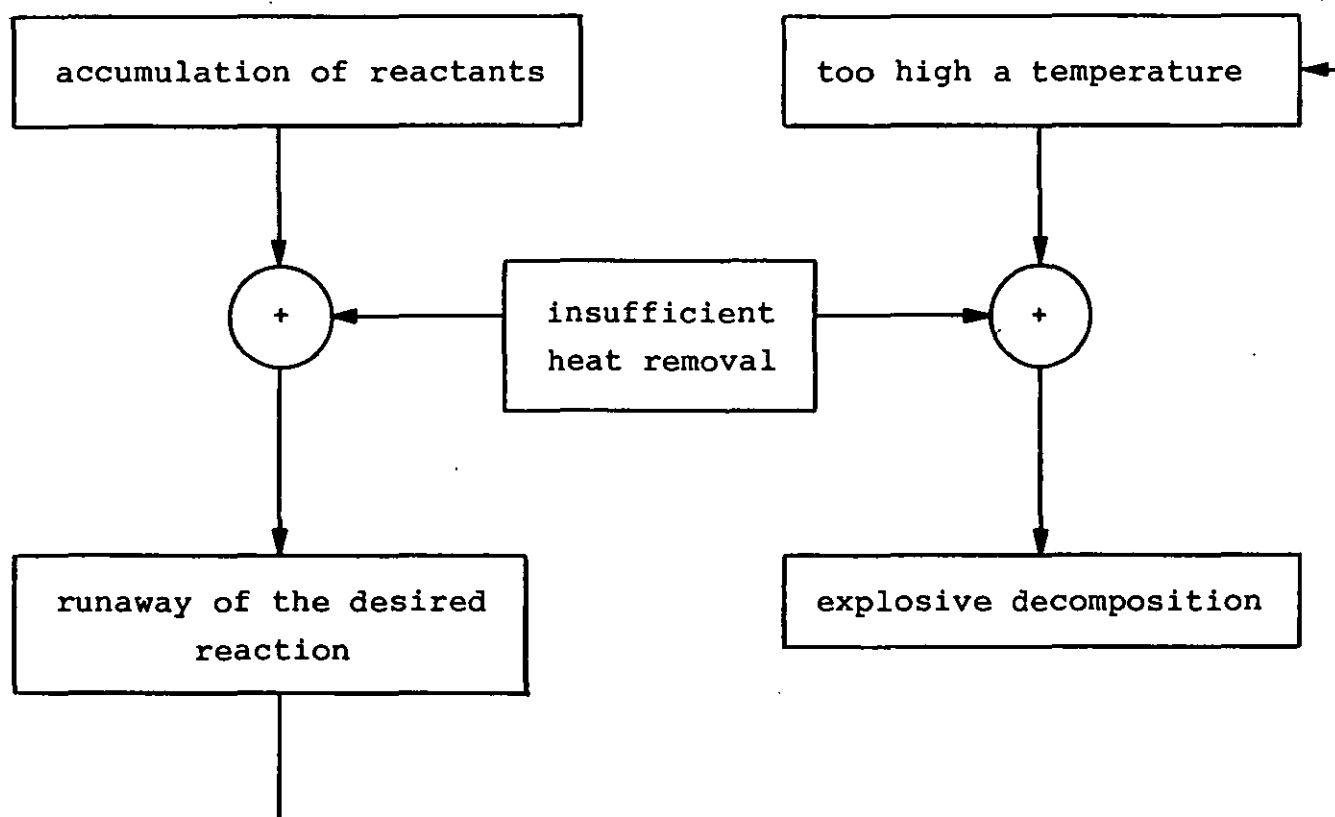


Figure 4.1 Common Causes of Reaction Runaway  
(simplified scheme)

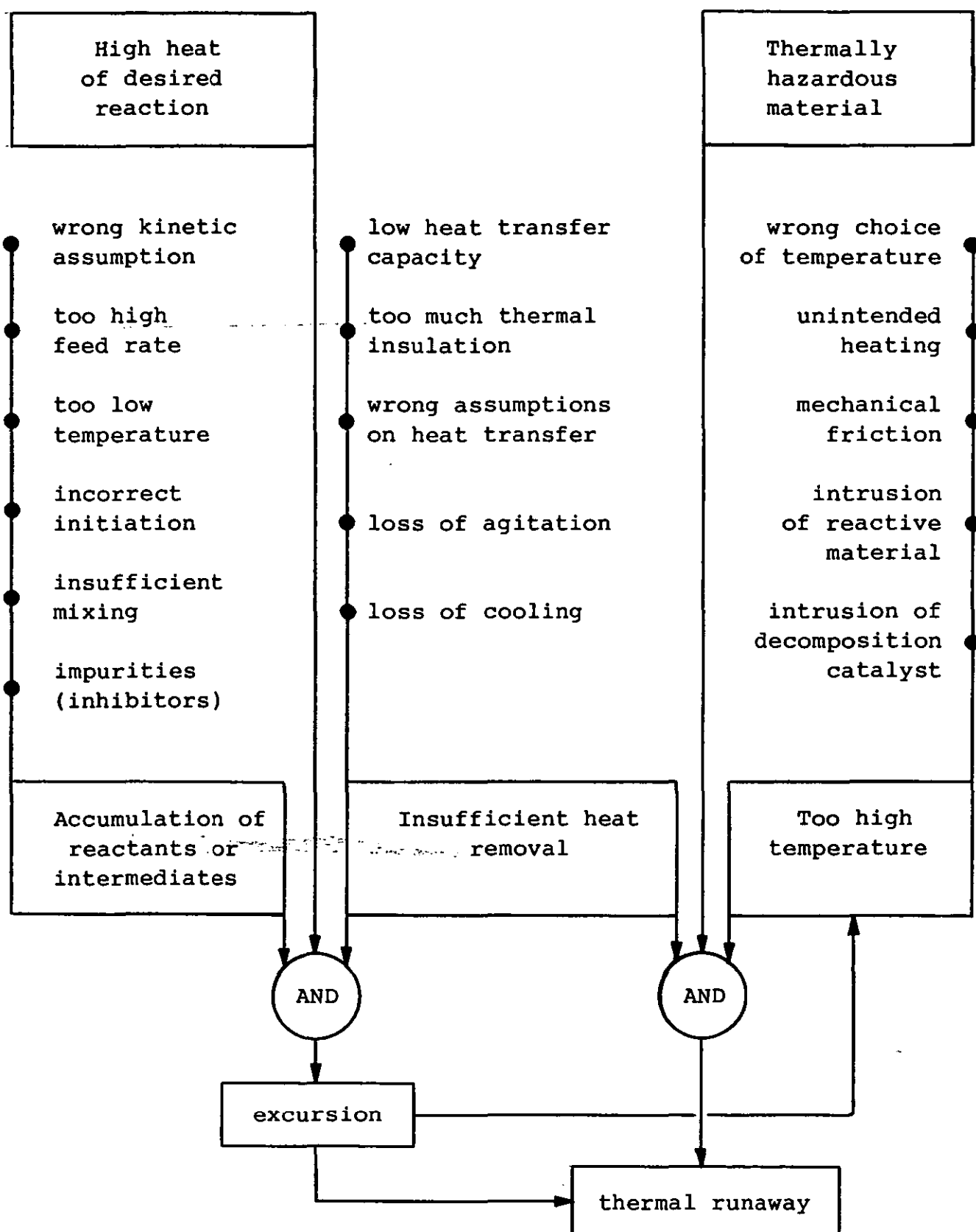


Figure 4.2 Common Causes of Reaction Runaway  
(detailed scheme)

Snyder (1982) [24].

The overall approach to assessing the hazard of chemical reactions generally involves; a literature survey, reaction screening and experimental testing. Information on the hazardous features of chemical reactions is not as readily available as that for individual chemicals. There are, however, a number of sources which can be referred to, these include Kirk and Othmer [25] and Bretherick [26]. In most instances it is necessary to conduct some sort of chemical reaction analysis on the intended reaction cycle to determine the reactivity and thermal instability of the chemical reaction. Many of the experimental test methods are described by authors such as Grever [27] and Hub [28].

One of the most useful tests for detecting reaction exotherms is Differential Thermal Analysis (DTA). In principle, this involves holding a sample of the reaction mixture in a vessel surrounded by a heat transfer medium and heating it at a constant rate. A plot is made of the temperature difference between the sample and the heat transfer medium versus the temperature of the heat transfer medium. There are peaks in the plot at points where reaction, or some kind of heat release such as thermal decomposition, occur.

Another method of detecting exotherms is Differential Scanning Calorimetry (DSC). A sample of the reaction mixture and a reference material are placed in separate containers and heated at a steady rate. The heating is carried out by a control system which maintains the sample and the reference material at the same temperature. A quantitative measure of the existence of an exotherm in the reaction mixture is given by the variation in heat which has to be supplied to the reference material to keep it at the same temperature as the sample. A plot is made of the rate change of heat input to the sample with time versus the temperature of the reference

sample.

A further technique for detecting the onset of exothermicity is Accelerating Rate Calorimetry (ARC), as described by Townsend [29]. A sample is placed in a container under adiabatic conditions and then heated stepwise, a typical increment being 10 °C. After each step the sample is held for a period at that temperature and the adiabatic system is checked for self-heating. If after a temperature increment is made, the sample temperature continues to rise, i.e. self-heating is observed, this indicates the existence of an exotherm and the sample is allowed to run away under its own inertia. Time-temperature and rate data are collected as the runaway proceeds and are presented as both a time-temperature plot and log rate reaction profile plot. The adiabatic temperature rise and maximum rate conditions are noted and the time to maximum rate (TMR) of the reaction determined. ARC is particularly useful in that it provides predictions of heat generation and reaction response time under simulated plant conditions of loss of cooling or loss of agitation.

A multipurpose safety calorimeter (SIKAREX) has been developed which can not only detect the existence of an exotherm but also gives a quantitative measure of the heat released by the exotherm. This is described, with examples of its use, by Hub [30,31]. The safety calorimeter consists of a test tube which fits into a cylindrical jacket, through which air is circulated by means of a blower, and the temperature of which is controlled by a heater. The temperature of the test sample is measured and controlled by a second heating element mounted on the test tube wall and a sensor inside the tube. This arrangement enables three different tests to be made.

In quasi-isothermal calorimetry the jacket temperature is held constant. Equilibrium temperature differences between the sample and the jacket are measured for corresponding sample temperatures to identify the onset of exothermicity, i.e. the

start of the reaction.

In adiabatic calorimetry the jacket temperature is controlled at that of the sample, thereby establishing a constant temperature differential between the two. The temperature rise of the sample is measured to follow the progress of a self-heating reaction.

In isothermal calorimetry the sample temperature is controlled at a constant value by holding the jacket at a lower temperature (usually 50-100 °C) and manipulating the test tube heat control. Any change in the heat input of the heater is measured and the corresponding heat released by the sample obtained.

Whereas a process running under adiabatic conditions is generally accepted as a standard measurement in investigating the hazard of self-heating reactions, it is sometimes known that the real process in question deviates from these conditions, e.g. dissipation of the heat of stirring in highly viscous reaction mixtures. In such cases it is better to simulate the actual process conditions in the laboratory test as far as possible. The SEDEX (SEnsitive Detector of EXothermic Process) device described by Hakl [32] can investigate the thermal sensitivity of reaction mixtures under industrial operating conditions.

There are other types of apparatus available, providing a range of data, but some have limitations regarding accuracy and sensitivity in detecting the onset of an exotherm, interpretation of measurements, continuous assessment of certain reaction types (e.g.  $A + B \rightarrow \text{products}$ ) etc. For instance, in some types of apparatus it is not possible to stir the reaction mixture and relatively small (unrepresentative) amounts of sample are investigated. Further, in the case of decomposition reactions Grever and Duch [33] have pointed out that reaction energies measured by



methods such as DTA and DSC can be inaccurate, since they have been determined isothermally, whereas decomposition for practical purposes corresponds more closely to an adiabatic situation.

Having detected the onset of an exothermic reaction, the tests described above can be followed up by a range of tests based on isothermal and/or adiabatic storage. Many of these tests can incorporate process variables and deviations from process conditions, e.g. addition of samples of materials of construction of the reactor vessel to determine any catalytic or side reactions. One such technique, the adiabatic storage test, involves placing the sample in a constant temperature environment adjusting this to the sample temperature if the latter changes due to reaction heat effects. A suitable starting temperature is about 50 °C below the exotherm shown in the DTA test. Another similar test is the adiabatic reaction test where the process is started at the reaction temperature.

Possibly the best method of studying chemical reaction mixtures on a continuous basis is the heat flow calorimeter [34]. A number of variants are available, incorporating a stirrer, reflux facilities and heating/cooling jackets, etc. to simulate actual process conditions as far as possible. The information obtained in such tests has, however, to be interpreted and applied to the process reactions (i.e. scale-up).

## 5. REACTOR OVERPRESSURE

### 5.1 Taxonomies

A taxonomy has been developed for analysis of whole incidents. This is given in Table 5.1.

Table 5.1 Taxonomy for Reactor Overpressure Analysis:  
Overall Taxonomy

#### A - System Description

Chemical Reaction

Reactants, Intermediates, Products

Heat of Reaction

Known Exotherms

Reactor Pressure

Reactor Temperature

Charging

Cooling

Heating

Agitation

Control System

Trip/Interlock System

Batch Cycle/Control

Operating Vents

Relief System

## B - Reaction Type

- B1 Alcoholysis
- B2 Amination
- B3 Condensation
- B4 Cyclisation
- B5 Diazotisation
- B6 Esterification
- B7 Halogenation
- B8 Hydrogenation
- B9 Hydrolysis
- B10 Isomerisation
- B11 Methylation
- B12 Nitration
- B13 Oxidation
- B14 Polymerization
- B15 Sulphonation

## C - Pressuring Fluid

- C1 Vaporized Liquid
- C2 Decomposition Gas
- C3 Water Vapour
- C4 Flammable Gas
- C5 Other Gas/Vapour

## D - Pressurising Event

- D1 Regular Reaction Exotherm
- D2 Impurity Reaction Exotherm
- D3 Heat of Mixing or Dilution
- D4 Regular Reaction Decomposition
- D5 Impurity Decomposition
- D6 Water Ingress and Vaporization
- D7 Air Ingress and Combustion
- D8 High Pressure Gas Ingress

## E - Process Deviation

- E1 Regular Reaction Inadequate Information
- E2 Regular Reaction Unknown Decomposition
- E3 Impurity Reaction Exotherm
- E4 Impurity Decomposition
- E5 Incorrect Charging
- E6 Inadequate Cooling
- E7 Excessive Heating
- E8 Incorrect Agitation
- E9 Inadequate Batch Control
- E10 Undesired Catalysis
- E11 High Pressure Gas Connection

## F - Initiating Fault

- F1 Inadequate Reaction Screening
- F2 Incorrect Design
- F3 Mechanical Failure
- F4 Utilities Failure
- F5 Control System Failure
- F6 Operator Error

## G - Overpressure Effect

- G1 Open Vessel
- G2 Excursion Only
- G3 Bursting Disc Operated
- G4 Vessel Ruptured
- G5 Bursting Disc Operated but Inadequate, Vessel Ruptured

## H - Bursting Disc Failure Cause

- H1 Undersize for Design Conditions
- H2 Demand Greater than Design Conditions
- H3 Installation Error
- H4 Modification Error
- H5 Maintenance Error
- H6 Disc Failure
- H7 Vent Piping Failure

## I - Release Effects

- I1 Flammable Release
  - I1.1 No Ignition
  - I1.2 Fire
  - I1.3 Explosion
- I2 Toxic Release

Most of the items in this taxonomy are straight forward but a few require explanation.

No distinction is made between the main, intended reaction and side reactions, but these two are distinguished from impurity reactions. The main and side reactions are referred to as the regular reactions. In this context, materials left over from a previous batch are treated as impurities.

Distinctions are made between reactions which are known and those which are unknown and between reactions which occur inside the regular operating envelope of pressure, temperature and time etc., and those which occur outside this envelope.

The Process Deviations in section E are defined such that a given incident can be uniquely classified under one of these deviations. Thus a regular reaction unknown exotherm is sufficient in itself to cause the overpressure, whether or not

it is in fact combined with an excursion outside the operating envelope. In this sense the Process Deviations in this section may be regarded as the cause of the incident.

These causes themselves, however, have further causes. These are given as the Initiating Faults. This section gives a very broad classification of the initiating event which must occur for the process deviation to occur.

In some cases the situation is such that one or more further enabling faults must occur for the initiating fault to lead to the process deviation or for the process deviation to lead to overpressure. It is a main subject of design to ensure that these protective features exist.

No classification of these protective features is included in the taxonomy. The function of the taxonomy is to create a framework for the construction of the demand tree.

The taxonomy just given can be developed in greater detail. This development is given in Table 5.2 in a form which has been found to fit well the incident data analyzed. Separate treatment is given for all the different Pressurising Fluids listed in section C. Each case refers to a scenario.

Table 5.2 Taxonomy for Reactor Overpressure Analysis:  
Pressurizing Fluids

Case 1: C1 Overpressure by Vaporized Liquid

D1 Regular Reaction Exotherm

- E1 Regular Reaction Unknown Exotherm
- E5 Incorrect Charging
- E6 Inadequate Cooling
- E7 Excessive Heating
- E8 Incorrect Agitation
- E9 Inadequate Batch Control
- E10 Undesired Catalyst

#### E1 Regular Reaction Inadequate Information

- E1.1 Unknown Exotherm
- E1.2 Inadequate Definition of Operation

#### E5 Incorrect Charging

- E5.1 Excess of Reactant
- E5.2 Deficiency of Reactant
- E5.3 Too Fast Addition of Reactant
- E5.4 Too Slow Addition of Reactant
- E5.5 Addition of Wrong Reactant
- E5.6 Modification of Reactant
- E5.7 Incorrect Order of Reactant Addition
- E5.8 Too Slow Reaction of Solid (coarse particles)
- E5.9 Too Fast Reaction of Solid (fine particles)

#### E5.3 Too Fast Addition of Reactant

- E5.3.1 Automatic Control Failure
- E5.3.2 Manual Control Failure
  - Measurement/Alarm
  - Operator Error

#### E6 Inadequate Cooling

- E6.1 Underdesign (especially scale-up)
- E6.2 Coolant Circulation Fault - see below
- E6.3 Inadequate Agitation (for heat transfer)
- E6.4 Internal Fouling
- E6.5 External Fouling
- E6.6 Evaporative Coolant Fault
- E6.7 Condenser Fault
- E6.8 Moderating Solvent Fault
- E6.9 Steam Jacket Coolant Inadequate
- E6.10 Other Causes

#### E6.2 Coolant Circulation Fault

- E6.2.1 Coolant Source Failure
- E6.2.2 Power Failure
- E6.2.3 Pump Failure
- E6.2.4 Coolant Turned Off
- E6.2.5 Coolant Leak/Loss
- E6.2.6 Blockage
- E6.2.7 Freezing
- E6.2.8 Automatic Control Failure
- E6.2.9 Manual Control Failure
  - Measurement/Alarm
  - Operator Error

#### E6.7 Condenser Fault

- E6.7.1 Condenser Blocked Off
- E6.7.2 Condenser Flooding
- E6.7.3 Condenser Frozen

#### E7 Excessive Heating



- E7.1 Initial Overheating
- E7.2 Heating/Cooling Changeover Fault
- E7.3 Heating Instead of Cooling
- E7.4 Pump Energy
- E7.5 Agitator Energy
- E7.6 Steam Leak
- E7.7 Live Steam
- E7.8 Automatic Control Failure
- E7.9 Manual Control Failure
  - Measurement/Alarm
  - Operator Error

E8 Incorrect Agitation

E9 Incorrect Batch Control

- E9.1 Initial Temperature Low
- E9.2 Initial Temperature High
- E9.3 Too Fast Reactant Addition Relative to Initial Temperature
- E9.4 Incorrect Cycle
- E9.5 Inadequate Chemical Moderation
- E9.6 Stewing
- E9.7 Other Causes

E10 Undesired Catalyst

- E10.1 Excess of Catalyst
- E10.2 More Active Catalyst
- E10.3 Catalyst Maldistribution
- E10.4 Catalyst Impurity
- E10.5 Catalyst Left Over from Previous Batch

D2 Impurity Reaction Exotherm

- D2.1 Water
- D2.2 Air
- D2.3 Materials Left in Reactor
- D2.4 Heat Transfer Fluid
- D2.5 Other Impurities

Case 2: C2 Overpressure by Decomposition Gas

D4 Regular Reactant Decomposition

E2 Regular Reactant Unknown Decomposition

D5 Impurity Reaction Decomposition

E4 Impurity Decomposition

Case 3: C3 Overpressure by Water Vapour

D6 Water Ingress and Vaporization

Case 4: C4 Overpressure by Flammable Gas  
(Ignition of Explosive Mixture)

D7 Air Ingress and Combustion

There are, in addition, some other cases:

- X1 Overpressure following operator attempts to recover from fault conditions
- X2 Overpressure following an unknown exotherm, where it is unclear if an exotherm is a decomposition

## Z1 Causes Unknown

### 5.2 Fault Trees

The taxonomy just given can be applied directly to the construction of the "demand" fault tree, i.e. that part of the overall fault tree which shows the propagation of the fault in the absence of any protective action from protective devices, the instrumentation and/or the process operator.

## 6. RELIEF AND VENT SYSTEMS

### 6.1 Bursting Discs

Bursting or rupture discs are thin membranes designed to burst at some pre-determined pressure which are widely used as relatively cheap means of protecting against overpressure in the chemical process industries. Bursting discs may be used to relieve inexpensive and inert material where loss of pressure can be tolerated, or, alternatively, to vent highly toxic, poisonous or corrosive materials into a vent header or blowdown system.

The relevant standards to be consulted in their use are B.S. 2915: 1984 (Specification for Bursting Discs and Bursting Disc Devices) and B.S. 5500: 1982 (Unfired Fusion Welded Pressure Vessels).

#### 6.1.1 Bursting Discs Design

The simplest form of bursting disc comprises a solid sheet of metal, either flat or pre-bulged (conventional) in the bursting direction, of the correct thickness and other mechanical properties to rupture at the desired temperature and pressure.

Conventional discs can be less than 0.05 mm thick and are normally made of metal, but graphite discs are also available. Composite slotted discs are a variation on the conventional disc and consist of the main disc which is grooved to burst at

the rated pressure, and a protective membrane, in plastic or metal. The groove is usually a cross or circular mechanical score. The use of grooving allows the disc to be made of thicker material so that it is less liable to fatigue, while the use of the membrane gives protection against corrosion by the process fluid.

These basic discs are generally specified where operating pressures are steady and do not exceed 66% of burst pressure. Grooving offers an improved operation to burst pressure ratio in the range of 75 to 85%. A third type of disc, the reverse buckling design, features a metal plate pre-bulged towards the upstream pressure. Once burst pressure is obtained, the disc buckles very rapidly with a snap action and complete reversal. As the bulge passes from the up to downstream side it is pierced and then cut into segments by knife blades positioned against the disc, so as to provide full opening for pressure relief.

The reverse buckling disc can have an operating to burst pressure ratio as high as 90%. The use of reverse buckling discs allows the disc to be made thicker, generally some 3-5 times as thick as conventional discs, and less liable to fatigue failure and also eliminates fragmentation. A reverse buckling disc is thicker than a conventional disc for the same duty; for 50 mm diameter discs rated at a burst pressure of 20 bar at 20 °C, Watton and Brodie [35] quote thicknesses of 0.04 mm and 0.3 mm for conventional and reverse buckling discs respectively. Reversal times of reverse buckling discs are very short; Watton and Brodie [35]; quote reversal times of 40 ms at 0.035 bar and 5 s at 10 bar for a 450 mm diameter disc.

The different types, general performance and specific problems of reverse buckling discs are discussed by Watton et al [35] who claim that, in certain cases, such discs do not give venting relief as quickly as do conventional simple domed discs.

In addition to metal discs, both impervious graphite and other brittle material discs, such as glass, have come into use. These tend to shatter into many parts when ruptured and have an operating to burst pressure ratio in the range 75-85%. Additional advantages include excellent corrosion resistance and burst ratings which are not affected by temperature variation.

There are also various special purpose discs available, designed to do a specific job. One such speciality disc is the shear disc in which the complete centre of the disc is blown out downstream. These discs are extremely accurate, but can present problems in that the shear head can cause plugging in a vent header, or can be dangerous if shot into the air.

Another disc construction relies on an external device to burst the disc rather than the process pressure. This external device can be a temperature or pressure actuated explosive charge [36], or a downstream pressure backloading device [37]. The advantage of these constructions is that the disc can be operated at high operating to burst pressure ratios. The main drawback, however, is that there are added components in the system that must function properly for the disc to rupture at the desired burst pressure.

All discs are supplied with flange holders (specified as part of the complete assembly) and vacuum supports (except for the reverse buckling type which is reported to be capable of withstanding a back pressure differential of 15 psi [37]). The latter are assemblies placed on the upstream face of the disc to prevent flexing or collapse should vacuum be created during startup, shutdown, mal-operation, etc.

Because of the simplicity of bursting discs, they are available in many materials of construction, 300 series stainless steel, inconel, monel, nickel, copper, aluminium and carbon being commonly used. In many cases it is necessary to

provide the disc with additional upstream corrosion protection. Materials used as linings or coatings include vinyls, lead, teflon, epoxy resins, etc. Many of these materials (metals and non-metals) are also used in combinations to form composite or veneered bursting discs.

#### 6.1.2 Bursting Disc Arrangement

One of the first factors to be decided when selecting a bursting disc for pressure relief is whether it is to be used alone or in conjunction with pressure relief valve(s). There are, as might be expected, advantages and disadvantages either way.

Where a bursting disc is used as a primary or sole-relieving device (Figure 6.1) the obvious advantages are (i) lower capital, installation and maintenance costs, (ii) fast action and full unrestricted flow upon rupture, and (iii) no valve to clean or maintain. However, once the disc has ruptured the system is open to atmosphere (i.e. complete blowdown) and operations will have to be shut down until the disc can be replaced. The circumstances under which a bursting disc is preferred for primary relief are given by B.S. 5500 as those where the pressure rise may be so rapid as virtually to constitute an explosion, where even minute leakage cannot be tolerated or where blockage might render a valve ineffective.

Alternatively, a bursting disc may be used as a supplementary relieving device where a relief valve is fitted as the primary means of protection (Figure 6.2), the disc being set to relieve at the higher pressure. With this arrangement the relief valve will open on mild overpressures, relieve the pressure build-up and then reclose the system. Thus the bursting disc will only function when a more extreme condition arises where the primary relief device fails. When such a system does arise it is most probable that the whole process will have to be shut down, hence complete system

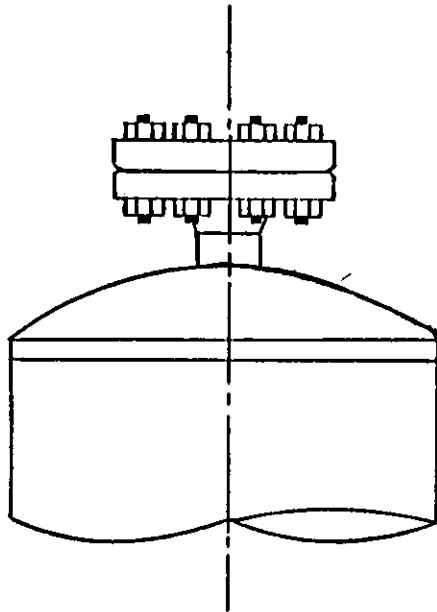


Figure 6.1

Bursting Disc Used as Primary Relief

RELIEF VALVE (Primary)

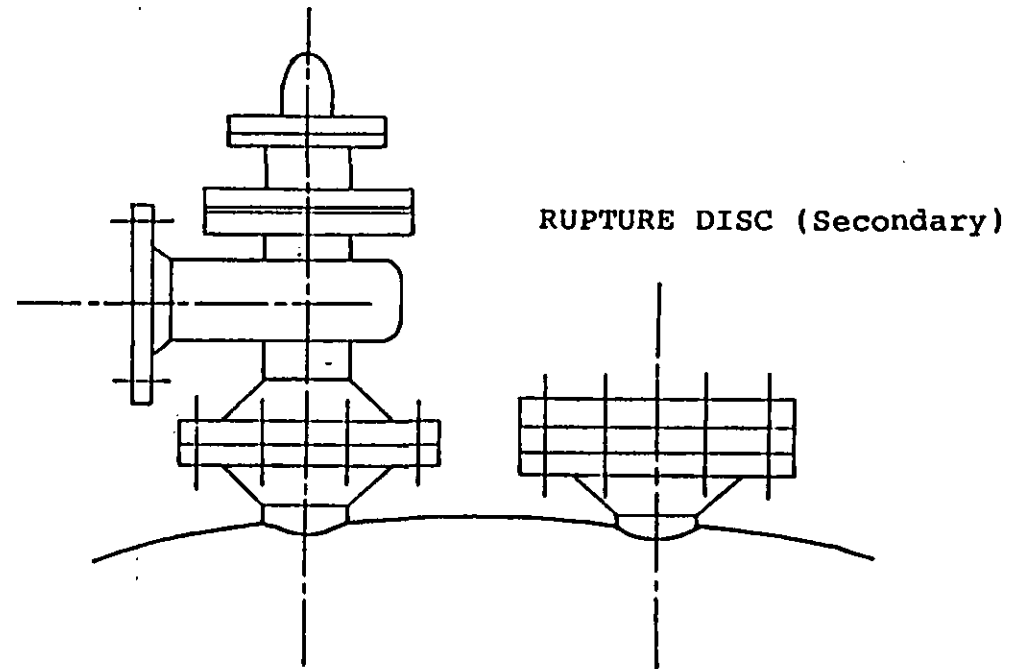


Figure 6.2

Relief Valve as Primary and a Bursting  
Disc as a Secondary Relief



pressure loss due to disc rupture is not so critical as in the previous case.

A common arrangement nowadays (Figure 6.3) is to install a bursting disc upstream of a relief valve [38]. The main advantages of this application being that (i) once the disc ruptures the relief valve will shut, thereby saving the balance of the product in the system, (ii) production can continue while operating with the relief valve until the disc can be replaced and, (iii) under normal conditions the disc will provide a tight seal, isolating/protecting the relief valve against corrosion, plugging, etc. In this way the best characteristics of both devices are utilized. The main drawbacks to be considered, however, are the additional capital cost and the cost of cleaning/maintaining the valve before putting it back into operation. In addition the space between the bursting disc and the relief valve seat must be monitored or vented to detect or eliminate any build-up of pressure in this line, thus adding extra cost. This is because a bursting disc is a differential pressure device and any downstream back pressure (due to leaking disc, say) would give rise to a much higher relieving pressure than the intended design value. Figure 6.4 shows an excess flow valve for this purpose. This is a device which permits limited flow. When this flow is exceeded, the valve closes, sealing the system and in this case causing material to pass through the vent system and not the excess flow valve.

Bursting discs may also be used downstream of a relief valve. This is becoming a more common installation on plants where all relieving devices are connected to a common header system. The downstream disc protects the relief valve from corrosive or plugging materials that may be in the header in addition to preventing header pressure variations appearing on the downstream side of the relief valve seat. This arrangement is only effective as long as there are no pinhole leaks in the disc. A pressure gauge is usually mounted on the space between

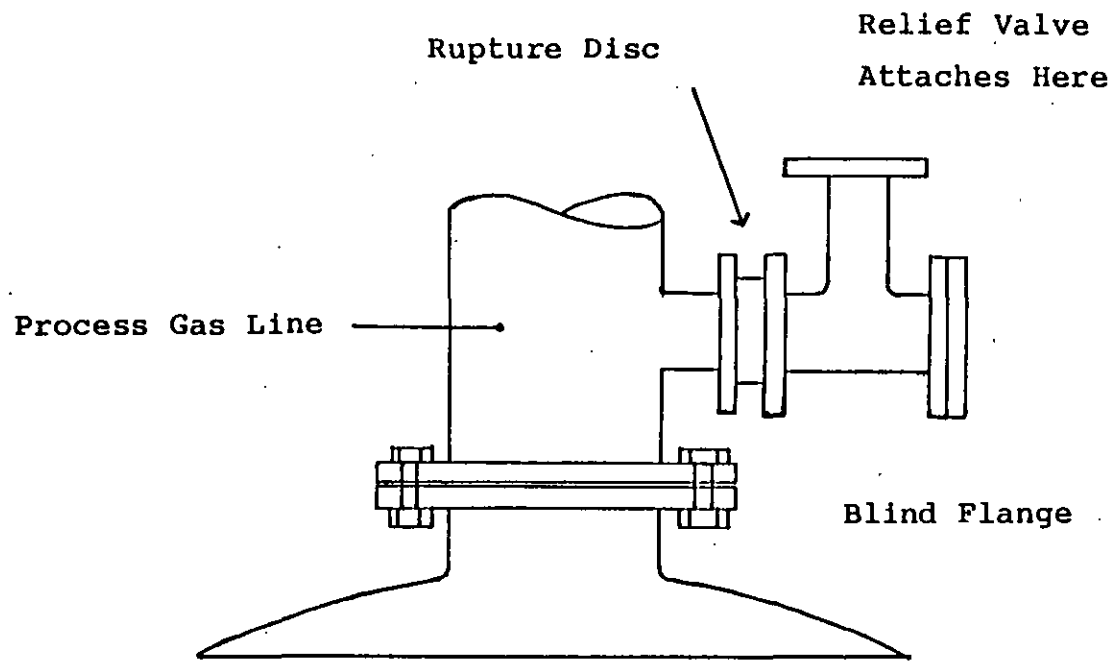


Figure 6.3

Bursting Disc Upstream of a Relief Valve

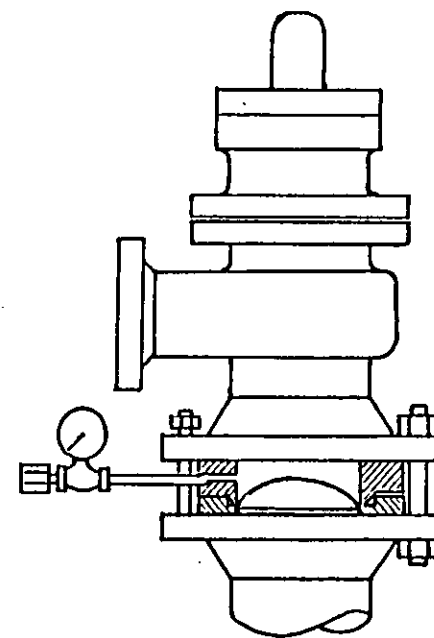


Figure 6.4

Excess Flow Valve Fitted in Space  
Between Bursting Disc and Relief Valve

the valve and the disc to detect any rise of pressure due to leakage. In this arrangement the bursting of the disc must not cause an obstruction to the relief valve.

Added safety can be provided where extreme process conditions are anticipated, by using a double disc assembly (two discs in series) as shown in Figure 6.5. The advantage of this type of arrangement is that the downstream disc will hold the pressure once the upstream disc bursts due to effects of corrosion, metal fatigue or other unforeseen operating conditions. The upstream disc can then be replaced at the next convenient shut down.

Figure 6.6 shows another interesting innovation. It is possible with this arrangement to get back into operation in a short space of time in addition to saving part of the batch if the pressure has lowered to a safe level.

### 6.1.3 Sizing of Bursting Discs

B.S. 2915 (1984) gives the following general equation for sizing a bursting disc for gas or vapour service:

$$Q_{mg} = APF\alpha \sqrt{\frac{M}{TZ}} \quad (6.1)$$

Where:  $Q_{mg}$  = discharge capacity of gas (kg/hr)

$A$  = actual orifice area ( $\text{mm}^2$ )

$\alpha$  = discharge coefficient (0.62)

$F$  = function of isentropic coefficient,  $k$ , and ratio of back absolute pressure to inlet absolute pressure (-)

$k$  = isentropic coefficient at the inlet conditions

$M$  = molecular weight (kg/kmol)

$P$  = absolute vessel pressure (bar)

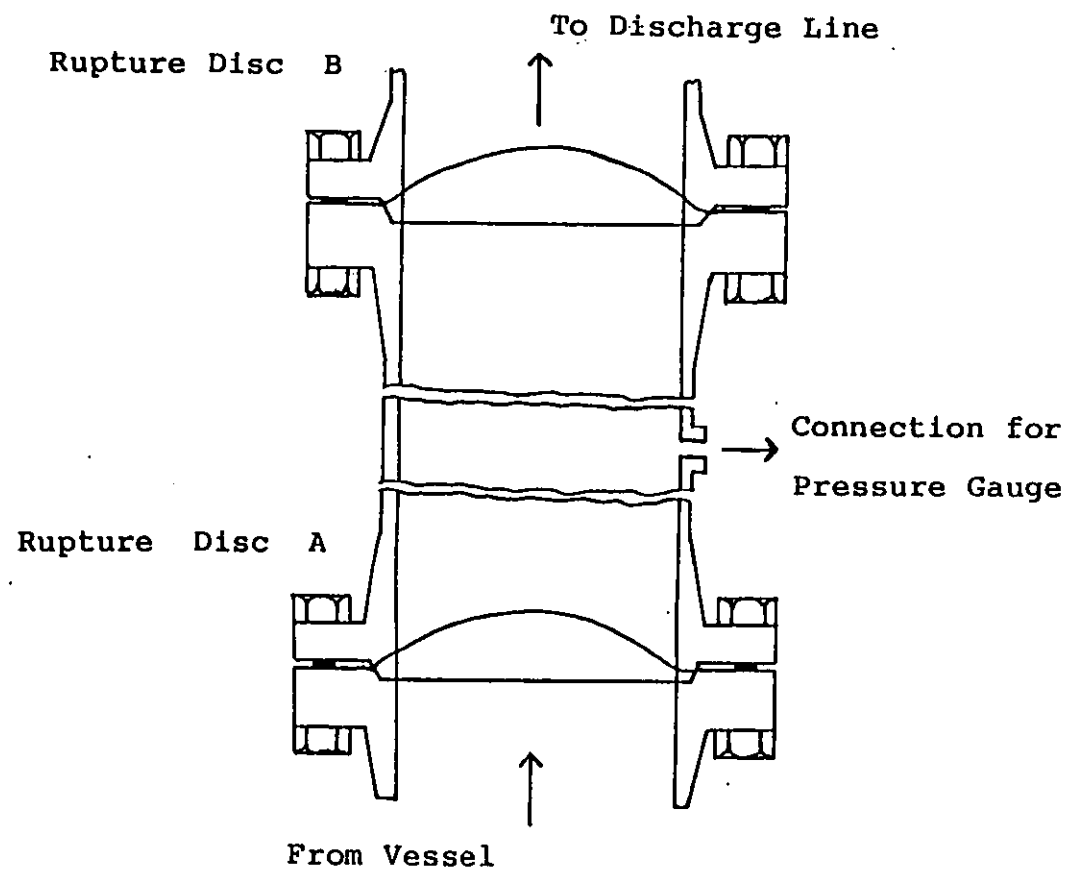


Figure 6.5

Double Disc Assembly

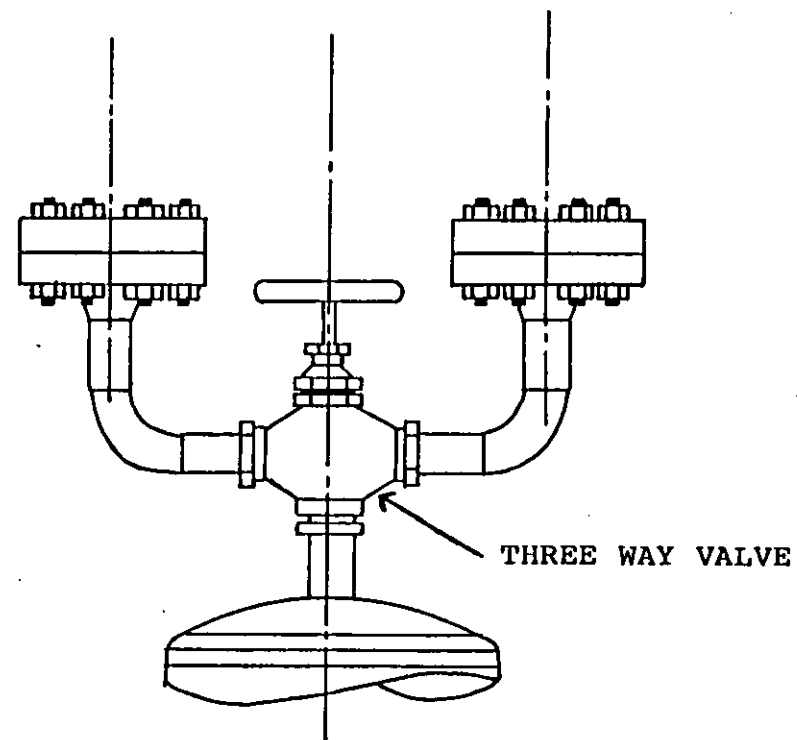


Figure 6.6

Switching Valve with Bursting Discs

T = inlet temperature (K)

Z = compressibility factor (-)

The value of F also contains the numeric constants arising as a result of the system units being used. Appropriate values of F can be found from BS 2915 Table 2.

If values of k, the isentropic coefficient at the inlet conditions, are not available then the value at 1.013 bar, absolute, and 15 °C should be used. These are given in BS 2915 Table 3.

For saturated or superheated steam:

$$Q_{ms} = 0.2883AF\alpha \sqrt{\frac{P}{V}} \quad (6.2)$$

Where:  $Q_{ms}$  = discharge capacity of steam (kg/hr)

V = specific volume at the inlet conditions ( $m^3/kg$ )

A,  $\alpha$ , F and P are as defined above

The theoretical flowing (discharge) capacity for a liquid is given as:

$$Q_{ml} = \frac{\sqrt{\rho \Delta P}}{0.6211} A\alpha f_{\mu} \quad (6.3)$$

Where:  $Q_{ml}$  = discharge capacity of liquid (kg/hr)

$\Delta P$  = (p -  $p_b$ ), pressure drop (bar)

p = pressure at the inlet to bursting disc (bar abs)

$p_b$  = back pressure (bar abs)

$\rho$  = volumetric mass ( $kg/m^3$ )

$f_{\mu}$  = correction factor for liquid viscosity

A and  $\alpha$  are as defined above

Where the liquid has a dynamic (absolute) viscosity less than or equal to that of water (1.0 cP at 20 °C) then the factor  $f_\mu$  may be taken as 1.0. For greater dynamic (absolute) viscosities, the discharge through a given orifice will be reduced. The coefficient,  $f_\mu$ , is related to the Reynolds number and can be found from charts (BS 2915 Figure 14).

In comparison, the corresponding equations are given by API RP 520 (1963) for the following flow conditions.

For gas or vapour service (using a discharge coefficient of 0.62 and  $C_p/C_v$  ratio of 1)

$$d = \sqrt{\frac{W}{146P}} \quad 4 \sqrt{\frac{T}{M_w}} \quad (6.4)$$

For liquid service:

$$d = 0.236 \sqrt{Q} \quad 4 \sqrt{\frac{S.G.}{P_1}} \quad (6.5)$$

Where:  $d$  = minimum rupture disc diameter (inches)

$M_w$  = molecular weight

$P$  = relieving pressure (lb/in<sup>2</sup> abs) including allowable accumulation

$P_1$  = relieving pressure (lb/in<sup>2</sup> gauge) including allowable accumulation

$Q$  = relieving rate (gal/min)

S.G. = liquid specific gravity

$T$  = relieving temperature (°R, i.e. 460 + °F)

$W$  = relieving rate (lb/hr)

It should be emphasized that these are general sizing formulae and that manufacturers' advice should be sought when sizing a disc for a particular application, as well as the relevant standards and codes.

#### 6.1.4 Bursting Disc Operation and Modes of Failure

In general bursting discs are relatively accurate after being manufactured. Most discs will rupture within a range of  $\pm 2-5\%$  of their design rating [39], high pressure discs being inherently more accurate than low pressure discs.

For a bursting disc it is usual to specify a range of pressures within which it will burst. Therefore a disc has a minimum, mean and maximum bursting pressure. This is often referred to as the manufacturing range and is expressed as a  $\pm\%$  applied to the design rupture pressure.

A recent investigation by Prickett [40] has shown that the rate of pressurisation can have a significant effect upon the deformation and bursting characteristics of bursting discs. Experimental work using aluminium discs suggests that at extreme rates of pressurisation (dynamic as opposed to quasi-static testing) there is an increase in the final burst pressure by as much as 5%. This could well lead to a dangerous delay in the venting of an out of control pressurized system.

Prickett's work also confirms the findings of an earlier investigation undertaken by Davies and Magee [41] which indicated an increase of up to 12% in the strength of stainless steel discs under dynamic pressure conditions.

This phenomenon can be explained in terms of the rate of strain and its effects on the ultimate tensile strength and total elongation of the bursting disc material. In general these properties increase with strain as discussed by Harvey [42].

In the case of most bursting discs it is not considered feasible to operate at pressures higher than 65-85% of the design pressure. The difference between disc rupture pressure and operating pressure is referred to as the operating margin and this takes into account the fact that bursting discs themselves are a designed weak spot in any pressure system. There are several reasons why such a conservative rating is necessary, in addition to the manufacturing range discussed above. One is that pressure fluctuations, even though they may be below the design pressure, tend to decrease the life of the disc through gradual metal fatigue. This varies, of course, with the metal and actual operating conditions. Fatigue has the effect of eventually causing rupture below the design pressure rating.

Another reason is the effect of temperature, which must be taken into account when using bursting discs. In general all materials and all types of discs reduce in rupture pressure with an increase in temperature and, consequently, increase in rupture pressure with a decrease in temperature. Most manufacturers place relative temperature limits on their discs; these may be exceeded or lowered depending on the conditions of operation. The effect of elevated temperature on metal discs is to cause creep of the metal at operating conditions leading to eventual failure. It can be very difficult to predict the operating temperature of a bursting disc, i.e. the actual temperature of the disc at the time of bursting. Not only can it prove expensive if the disc operates hotter than expected, and therefore, relieves too soon but, more significantly, extremely dangerous if the disc operates too cool and subsequently relieves too late. Operating and design temperatures therefore play an important part in disc selection as regards material(s) of construction and type.

A further reason for specifying an operating margin is due to adverse operating conditions or type of service. The effect of corrosion, for example, can be a serious problem



drastically reducing the life of a disc through premature failure either by pinholing or actual rupture. Materials for bursting disc applications should be chosen to give zero or minimum corrosion rates. Hence the use of corrosion resistant linings and coatings.

Work carried out by Kneale and Binns [43] using bursting discs in some 50 instances recorded failures in many of these. The most common cause of failure (often only a pinhole) was identified as corrosion, particularly of nickel discs due to atmospheric sulphides.

Like any protective device, a bursting disc may suffer functional or operational failures. In other words it may fail to burst at the set burst pressure and thus fail to danger or it may burst below that pressure and thus fail prematurely, but generally, safe. Damaged discs, whatever their form, will generally burst at a lower pressure than the specified burst pressure and therefore fail safe.

Another problem sometimes run into with bursting disc installations is that the disc itself may plug or cake over. This can occur especially in polymerization/crystallization reactors or where foam or subliming vapours are produced. Depending on the severity and type of plug formed, a problem of this kind can change the burst pressure rating of the disc or, more probably, reduce the venting area when the disc ruptures.

As highly stressed components, bursting discs have a limited life and as such require inspection and/or replacement at regular intervals. The frequency of replacement generally depends on the disc type and material, the corrosive nature of the environment, operating temperature, resistance to creep and fatigue, etc. Manufacturer's advice should be sought in all cases. Correct (re)assembly of bursting discs after maintenance/cleaning or replacement should be ensured at all

times; this in itself being a fundamental factor as regards disc performance. An example of mal-installation is putting more than one disc in the the holder. Discs are sometimes supplied in stacks and in this case duplication may be a simple error. In other cases the use of more than one disc is done deliberately to avoid frequent bursting, particularly during the plant commissioning stages. The burst pressure may be altered and the dome shape changed if the disc slips sideways in its holder.

A disc should always be carefully installed and securely mounted. There are some standard foolproofing features added to the discs by the manufacturers to ensure that this is the case. The disc is preassembled in the holder and pre-torqued. The holder is provided with a pin to ensure that it is mounted the right way up. The screws in the holder are of special type which require the use of a special tool to be turned. Another device to ensure that the disc is installed the right way up is a J-bolt. Only when the bolt is in can the holder be centred and the flange bolts tightened. This arrangement is particularly useful where frequent cleaning of the discs is necessary.

Reverse buckling discs are thicker than conventional discs and are less prone to fatigue, creep and corrosion, but they have their own characteristic failures. One of these is "roll through". The dome of the disc becomes dented, perhaps through handling, and it rolls through onto the knife but with insufficient energy to cause bursting. Insufficient energy to cause cutting of the disc is a particular problem when venting liquids. A disc in this condition can have a burst pressure some 3-5 times that intended. The condition of the knife in a reverse buckling disc is also critical. It may suffer corrosion, cracking, or blunting so that it is no longer capable of cutting. Installing the disc upside down is a typical problem with reverse buckling discs where the fitter is used to installing conventional discs.

From the literature and consultation with industry the failure modes of bursting discs can be summarized as the following:

- (a) Undersizing of the disc.
- (b) Blanking off the disc.
- (c) Blockage of the fitting by polymer, solids etc.
- (d) Material failure of the disc e.g. corrosion, creep, and general fatigue.
- (e) Bad installation of the disc e.g. wrong disc installed, two or more discs installed, vacuum support installed downstream, disc installed upside down (reverse buckling disc).

For reverse buckling discs especially:

- (f) Roll through of the disc.
- (g) Knife defective e.g. cracks, corrosion, or off centre.
- (h) Disc holder failure and release to atmosphere.

Also for discs in series there is the risk of pinhole leak and pressure build-up between the discs and effectively increasing the burst pressure.

For a pressure relief valve protected by a bursting disc failure modes include:

- (a) Blockage of the pressure relief valve by disc fragments.
- (b) Pinhole leak and pressure build-up between the disc and the pressure relief valve.

#### 6.1.5 Bursting Disc Failure Study

A study has been carried out to obtain quantitative data on bursting disc failure. This is described in Appendix 4.

Bursting disc failure, discussed qualitatively above, was limited to the listings of some of the failure modes of bursting discs. In the present section an attempt is made to provide quantitative data on the failure of bursting discs.

For this purpose the entity considered is the complete bursting disc system, which may include more than one bursting disc assembly, but not the subsequent vent piping, which is considered separately. A separate vent system failure study is given in the following sections.

A study has been made of bursting disc failure. This study is described in Appendix 3. The estimate made for the probability of failure on demand, fractional dead time (fdt), of a bursting disc assembly with a one year inspection interval is:

Predicted Dead Time = 0.012

There was no observed failure on demand. Adopting the common statistical device of assuming that such a failure was just about to occur (see Appendix 4) gives:

Observed Dead Time = 0.083

with 95% confidence limits of 0 - 0.32. The latter estimate is recognized as very pessimistic; essentially it is a function of the relatively small number of trials. The predicted dead time is regarded as the better estimate in this case.

There is also another mode in which a bursting disc may fail. This is failure due to undersizing. It is more difficult to estimate the probability of this failure. In the HSE case

histories it appears to be the dominant mode, although these may be regarded as a biased set. An estimate is required for this failure mode and that made is the probability of failure by undersizing is three times that of failure by not rupturing.

The estimate used for bursting disc failure is therefore:

Probability of Failure to Rupture = 0.01

Probability of Failure by Undersizing = 0.03

Total Probability of Failure = 0.04

These estimates assume disc sizing by reasonably good practice. Thus where such practice cannot be assumed it is estimated that the probability should be increased by a factor of up to three to give a total probability of failure of approximately 0.1.

## 6.2 Vent Systems

A vent system is basically a pipe fitted to a reactor, and separated from the reaction by a bursting disc and/or a relief valve. It may lead to another catchment vessel or simply go to atmosphere. If the pressure in the reactor rises above a specific value then the bursting disc will rupture or the relief valve lift and material will enter the vent. The design of the vent size will depend on the physical properties of the vented material. The problems associated with this are discussed below.

Other considerations when designing the system include allowance for the forces of the vented material. The discharge rates can be quite high and exert significant forces on the vent structure. Thus the pipe work must have a minimum of bends and restrictions. If the vent leads to a catchment vessel, which is usually the case when dealing with hazardous and potential dangerous material, it must be designed so as

not to produce a back pressure and thus hinder the discharge of material from the reactor.

#### 6.2.1 Types/Arrangements

Three typical vent arrangements are shown in the Figures 6.7 to 6.9. These show a reactor connected to three different types of catchment vessel. They illustrate some typical methods of containment and examples of general arrangement.

Due to the expense of the vessels required, in some instances when it is thought that the process is relatively safe, a manifold system may be incorporated whereby several reactors are connected to the same catchpot by a common vent.

It is important that the vent is correctly sized in these cases to allow for any back pressure to other reactors which may rupture bursting discs and cause contamination of other reactions. The use of common vents is usually restricted to reactors carrying out the same reaction.

#### 6.2.2 Failure Modes

There appears to be less information on the failure modes of vent systems, but some information has been obtained, both from the literature and from company visits.

Vent system failure modes include:

(1) Blockage by:

- (a) Test blank left in
- (b) Corrosion and polymerization products
- (c) Disc fragments
- (d) Slow moving polymer

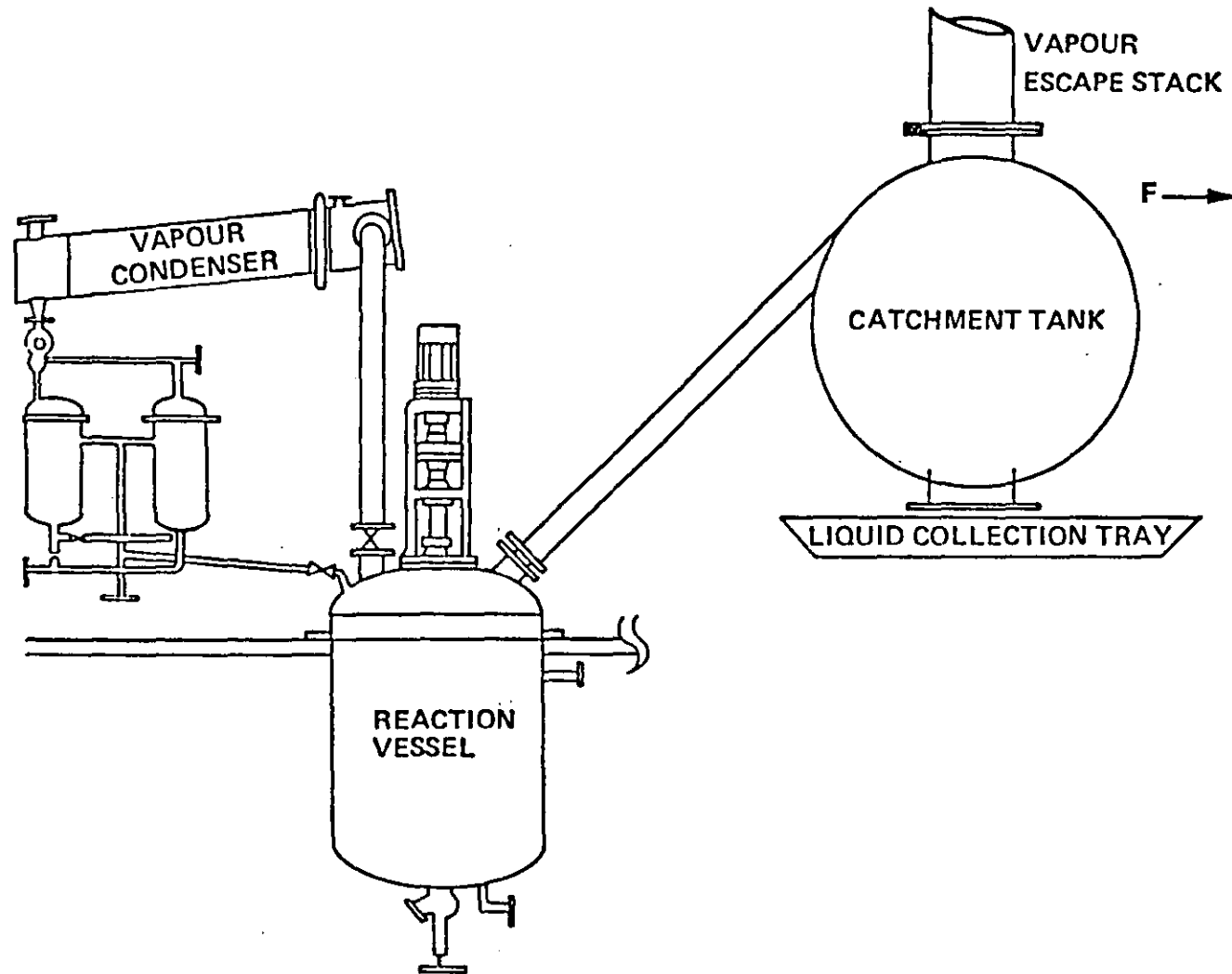


Figure 6.7 Example of Catchment System - Horizontal Tank

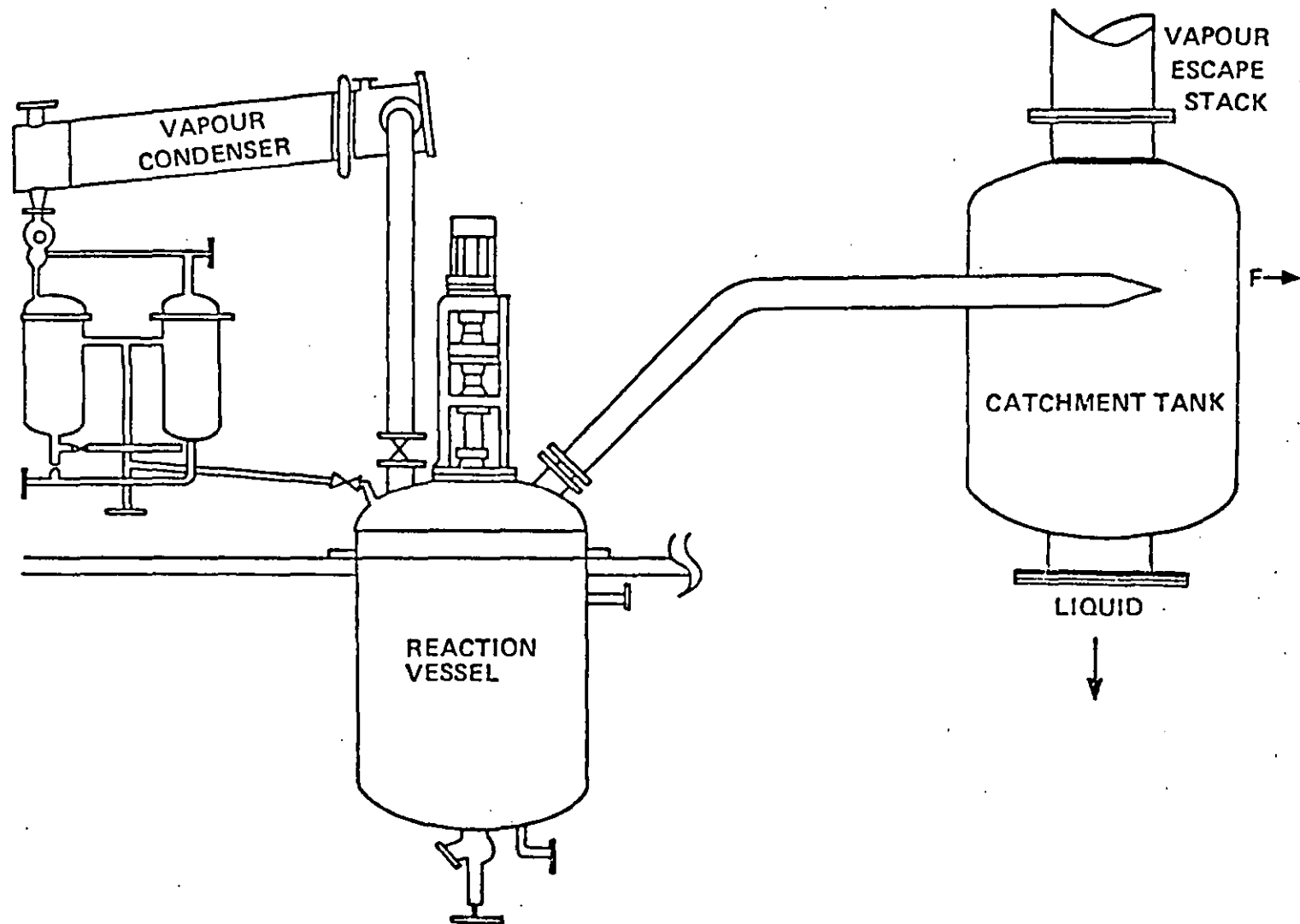


Figure 6.8 Example of Catchment System - Vertical Tank



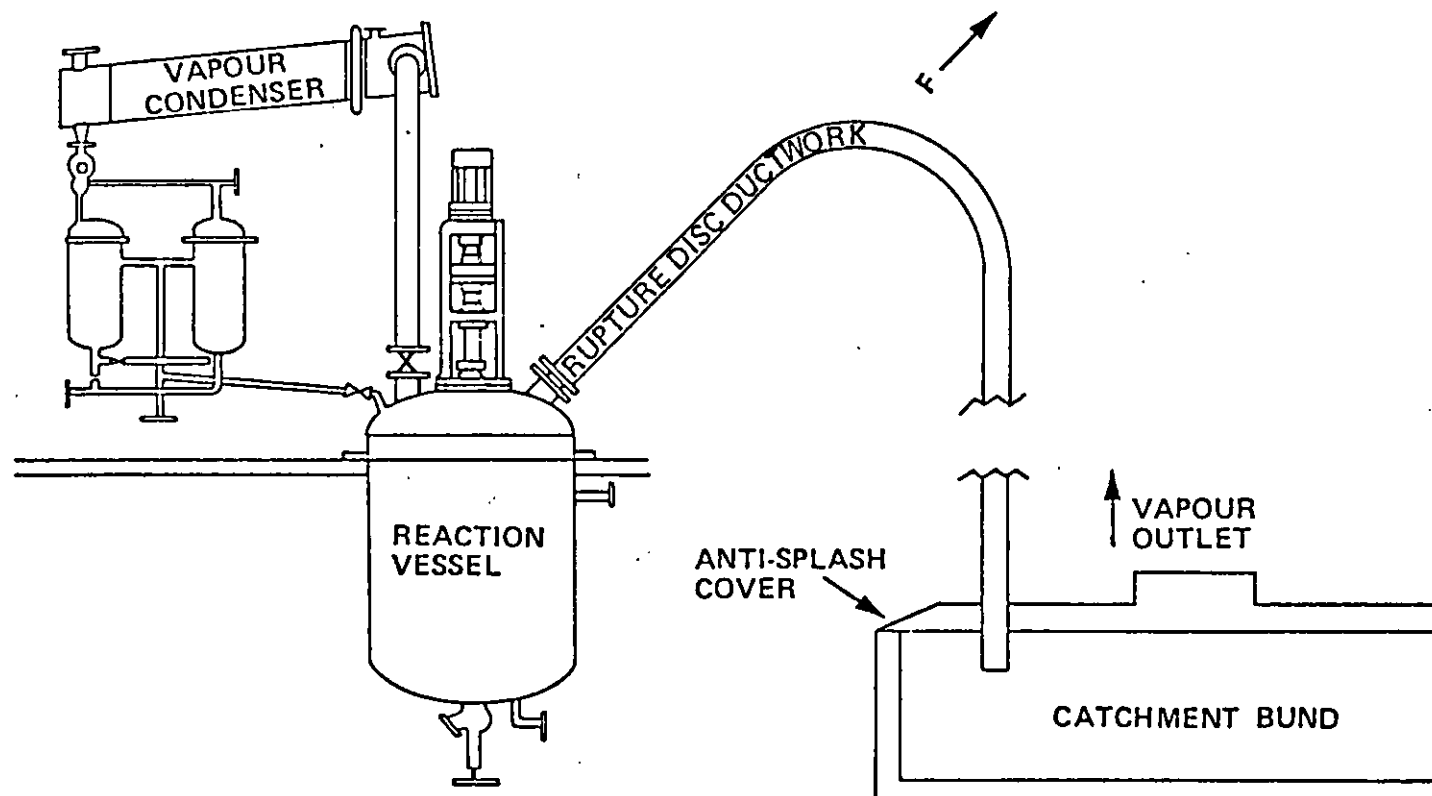


Figure 6.9 Example of Catchment System - Bund Type

(2) Leakage/rupture due to:

- (a) Vent flange leak
- (b) Piercing by disc fragments
- (c) Damage by pipe whip
- (d) Bursting disc flange leak (as above)

An attempt is made below to determine the failure rate of vent systems.

### 6.2.3 Failure Study

A study has been carried out to obtain quantitative data on vent system failure. This is described in Chapter 12 and in Appendix 4.

In the present section an attempt is made to provide quantitative data on the failure of vent systems.

No data has been found in the literature for failure rates of vent systems as opposed to those of bursting discs.

A study has been made of vent system failure. This study is described in Appendix 4. The study was part of the bursting disc failure study. The estimate made for the probability of failure on demand, or fractional dead time (fdt), of a vent system (excluding the bursting disc assembly itself) with a one year inspection interval is:

$$\text{Predicted Fractional Dead Time} = 0.0019$$

There was no observed failure on demand. But adopting the same approach as used in the bursting disc study of assuming that such failure was just about to occur gives the observed value:

Observed Fractional Dead Time = 0.034

with 95% confidence limits 0 - 0.15. Again the latter estimate is a very pessimistic one.

Another source of information on vent system failure is available in the form of the BPF survey, [44], but it is concluded in Appendix 5 that the information in that survey is not such as to allow improvement to be made on the above estimate.

There is also another mode in which a vent system may fail. This is failure due to incorrect design. It is more difficult to estimate the probability of this failure. In the HSE case histories undersizing or otherwise incorrect design of the whole relief system, relief device and vent system, appears to be the dominant mode, although these may be regarded as a biased set. An estimate is required for this failure mode and that made is that the probability of failure by undersizing or incorrect design is three times that of failure by blockage. The estimate used for vent system failure is therefore:

Probability of Failure by Blockage	= 0.002
Probability of Failure by Undersizing	= 0.006
or Incorrect Design	
Total Probability of Failure	= 0.008

These estimates assume vent sizing by reasonably good practice. Where such practice cannot be assumed, it is estimated that the probability should be increased by a factor of up to three to approximately 0.02.

Obtaining the estimates for bursting discs and vent systems to obtain an estimate for the relief system gives:

$$\begin{aligned}\text{Probability of Failure of Relief} &= 0.04 + 0.008 = 0.048 \\ &= 0.05, \text{ say}\end{aligned}$$

### 6.3 Vent System Design

Although vent system design is explicitly excluded from the project, some work has been done to obtain a feel for current vent system design methods, including the method of the British Plastics Federation (1979) [44] and that of DIERS (Fisher, 1985 [45]). The objective was to understand better how the vent design can go wrong.

It is intended in the following discussion to give a broad overview of the various vent sizing techniques, ranging from simple to complex, which are currently available for designing emergency relief systems (ERS). In the main this will be directed towards the venting of runaway exothermic reactions in liquid phase reactors. This subject has received much attention in the literature [46,47,48,49,50], with special reference to polymerization reactions. An excellent review of the various venting methods available and their respective limitations is given by Duxbury [51], whilst a discussion of more recent design developments is presented by Swift [52].

An empirical approach to reactor vent sizing prepared by the former Factory Insurance Association (FIA) is described by Sestak [46], in which the required vent area is given as a function of reaction classification or reactivity (defined as the heat release per unit volume of reaction mass) and reactor volume. The vent area is approximately proportional to reactor capacity to the power 0.92. This method, being relatively quick and simple, has been widely used in the past as a means of preliminary assessment. There are, however, a number of inherent difficulties [51] in its use which may lead to marked over/under sizing of the vent area. This method is no longer

recognized by the Industrial Risk Insurers (IRI), successors to the FIA, who recommend that vent sizing calculations should normally be based on theoretical considerations, particularly for reactions involving novel recipes, conditions, and properties, etc.

In general the vent area for liquid phase reactors is established by determining, first, the relief flow to be vented to prevent overpressure, and then the vent area required to effect this discharge./

Difficulties arise, however, in predicting the nature of the relief flow. A number of possible physical situations can arise. Immediately after the vent opens vapour flow will normally ensue. As pressure falls, given sufficient nucleation sites, vapour bubbles will appear in the liquid and cause it to expand ("swell"). Depending on the system properties, the contents may expand to fill the vessel with foam or froth, and a two-phase vapour-liquid mixture will enter the vent line. This state may be maintained throughout venting, resulting in the vessel being emptied of practically all its contents, a well known phenomenon. Under some conditions, vapour could disengage completely from the liquid inside the vessel, so that the expanded liquid level remains below the level of the vent and all vapour flow ensues. This may happen as soon as the vent opens, or after a period of two-phase flow (known as partial disengagement). Finally, in cases of extremely rapid vapour generation, slug flow (similar to water hammer effect) could occur.

In order to take account of these different situations, vent sizing models have been developed based on the following assumptions:

- (i) flow of vapour only
- (ii) flow of single phase (non-flashing) liquid only
- (iii) homogeneous two-phase (vapour-liquid) flow
- (iv) partial vapour-liquid disengagement.

Of these, (i) and (ii) yield a simpler treatment, but assumption (iii) is probably the most realistic situation. Observations of the relief of various polymerization reactions by Boyle [47], Harmon and Martin [48], Huff [49] and Duxbury [51], have reported that in practice the discharge is more likely to be a liquid or homogeneous two-phase mixture. Work is continuing on the fourth assumption by the Design Institute for Emergency Relief Systems (DIERS). The DIERS analysis uses several mathematical models to consider the problems of:

- (a) Flashing; at what stage along the vent pipe does this occur?
- (b) Velocity; do the gas and liquid flow along the pipe at the same speed or do they "slip"?
- (c) Radial variations; do different effects take place at the centre of the pipe and at the wall of the pipe?
- (d) Equilibrium; to what extent are the properties of the liquid and its vapour in equilibrium with each other at various stages along the pipe?
- (e) Gas pressure; is the system pressure determined by the vapour of a liquid or by a chemically generated gas?

The models used have been verified by experimental work on several vent arrangements. A qualitative assessment of the progress made so far is given by Swift [52]. One particular aspect being studied is the liquid and vapour motion inside the reactor vessel during pressure relief in terms of

expansion and vapour-liquid disengagement, previously considered by Fauske [55].

### 6.3.1 Vapour Flow Method

A once common approach to reactor vent sizing is based on the rate of release of single phase vapour, from the boiling liquid reaction mass, at an intermediate value of pressure between activation of the relief device and the maximum allowable for the reactor, so that the pressure remains constant. Known as the "steady state" vapour venting method, this involves calculating the maximum allowable liquid temperature, related by vapour phase considerations to the maximum allowable pressure, and then determine the rate of reaction and heat of generation at this temperature, the rate of vapour evolution and hence the flow of vapour to be vented.

Thus the vapour flow can be calculated from:

$$G = \frac{r(\Delta H_r)V}{\Delta H_v} \quad (6.6)$$

where  $G$  = mass flow of vapour (kg/s)

$r$  = reaction rate (kg/m<sup>3</sup>s)

$\Delta H_r$  = heat of reaction (kJ/kg)

$\Delta H_v$  = latent heat of vaporization (kJ/kg)

$V$  = volume of reaction mass (m<sup>3</sup>)

The vent area can then be calculated from equations for vapour discharge, this being typically multiplied by a factor of two or three, as recommended by Boyle [47].

Sizing on the basis of total vapour flow can only be regarded as accurate if the assumption of no liquid carryover

can be justified, since the inclusion of liquid usually results in a larger diameter vent being required [47,49].

### 6.3.2 Liquid Flow Method

An alternative approach to that described above, put forward originally by Boyle [47], is based on the assumption of single phase (non-flashing) liquid flow. This defines the required vent size as that which would pass vapour-free liquid at a rate sufficient to empty the reactor before the pressure could rise above some allowable level. Effectively this technique separates the calculation of vent flow (for conditions prevailing of initial release) and reactor conditions (determined from a hypothetical pressure/time curve for the reactor) and as such is much quicker to apply than a detailed unsteady state model.

The required flow is calculated from the rate of reaction and heat of generation at the maximum liquid temperature and the time required to heat the liquid reaction mass to this temperature. Thus the liquid flow can be calculated from:

$$G = \frac{W}{\Delta t} \quad (6.7)$$

$$\Delta t = \frac{W c_p \Delta T}{r (-\Delta H_r) V} \quad (6.8)$$

Where:  $G$  = mass flow of liquid (kg/s)

$W$  = reaction mass (kg)

$t$  = time interval to maximum allowable pressure (s)

$c_p$  = specific heat of reaction mass (kJ/kg K)

$\Delta T$  = temperature difference at equilibrium between initial and maximum allowable pressure ( $^{\circ}\text{C}$ )

$r, \Delta H_r, V$  as defined previously.



Boyle concludes from his experiments on styrene polymerization reactors that the liquid flow method incorporates a reasonable factor of safety. He nevertheless recommends that the vent area be checked using the steady state single phase vapour venting method, and that a further safety factor of between two and three be applied to the larger of the two calculated areas.

In practice Boyle's method usually leads to a larger (i.e. "safer") vent area than the steady state vapour venting approach, but this is not always the case. Experiments by Harmon and Martin [48], Huff [49] and others have provided evidence that this approach may significantly underestimate vent areas for larger reaction vessels compared to those calculated by the FIA method.

#### 6.3.3 Two-Phase Flow Method

As mentioned previously, the two-phase flow assumption is probably a more realistic situation, with liquid (whether foam or froth) entering the relief system and subsequently some or all of it flashing to vapour in the vent line.

A number of approaches have been developed using two-phase flow models. These are summarized by Leung [51]. The most comprehensive of the techniques described is by Huff [49] and involves a detailed computer simulation to solve simultaneously the unsteady state mass and energy balance equations relating to the reactor conditions and flow through the relief system (assuming vapour-liquid equilibrium). A refined and generalized version of this computer approach is described by Huff [53]. The principal equations, programming approach, and example simulation results are presented. A more recent paper by Huff [54] summarizes the basic theory and equations and further demonstrates the versatility of the program for three example reaction systems of varying degrees of complexity. An extension of the method to take account of

non-uniform vapour distribution is also presented.

Huff reports that for the cases considered, this model is more conservative (i.e. "safer") than the FIA method, or the approach based on the assumption of "steady state" single phase vapour venting, or the Boyle (non-flashing liquid flow) model.

The major disadvantage, however, with this approach is that the model requires modification for each application and is thus expensive and time consuming. A quicker and easier, but more approximate, approach is based on a modification of the model as proposed by Boyle for non-flashing liquid flow. This first part of Boyle's method is used to determine the required relief flow i.e. the mean mass flowrate which will empty the reaction vessel in the time between the relief valve operating and pressure attainment of some maximum allowable pressure, as before. The vent is then sized assuming flashing two-phase flow, rather than non-flashing liquid flow, with an allowance for entrained solids. As with the original Boyle approach, this method conveniently separates the reactor condition and fluid flow calculations and is more readily accessible.

A further treatment of vent sizing of liquid phase reactors is given by Kneale and Binns [43].

Although the vent size calculated assuming two-phase flow is usually the largest, this is not always the case [51]. A check should also be made on the basis of single phase steady state vapour venting and a safety factor of between two and three (as recommended by Boyle) applied to the larger of the areas.

An alternative approach to vent sizing of emergency relief systems for liquid phase reactors is scaling from experimental tests and small scale trials. The cost, or

difficulty, of developing a system model and the lack of appropriate kinetic and physical property data to use such an approach proves too prohibitive in many cases.

Before scaling can be justified, similarity between the test and full-scale systems must be established. Conditions whereby similarity can be assumed to exist are detailed by Duxbury [51]. These include ensuring that the reaction takes place uniformly throughout the liquid phase and only in the liquid phase; that the reactor recipe is unchanged (except in scale); that the normal operating temperature, pressure and operating sequence are unchanged; that the total rate of reaction changes in proportion to the reactor volume; that the temperature distribution is unchanged in any way, etc.

One scaling rule frequently applied is that of scaling-up on the basis of a fixed ratio of vent area to reactor volume. This would appear from the limited experimental data [48] available, to be "safe" provided the original vent area to be scaled from is itself "safe" and the conditions listed above for assuming similarities are satisfied. Confirmation is also given to a certain extent by the former FIA method (fixed ratio of vent area to heat release) in which vent area increases with reactor volume to the power 0.92. Scaling-down on the above basis is not considered "safe", however.

The safe application of this simple area to volume scale-up rule does, however, require that the vessel size remains insensitive to the liquid-to-vapour phase ratio entering the vent line. Recent work by Swift et al [50] and Fauske et al [55] has shown that this assumption may not be valid in practice and that application of small scale test vessel data (indicating all vapour venting) to full-size vessels (warranting two-phase mixture venting) by scaling on the above basis may lead to unsafe design practices. Swift et al [50] go on to suggest an alternative approach whereby a practical and safe, but not overly conservative, sizing method can still be

provided by the simple scale-up rule by replacing top venting with bottom venting data.

Scaling, therefore, should be treated with caution and restricted to small ranges of scale unless experimentally determined or calculated vent areas have shown the scaling rule to be safe. In addition test equipment has been developed which will allow the direct experimental determination of vent size without the need for kinetic or thermo-physical properties of the system being studied.

#### 6.3.4 DIERS Design Strategy

The program initiated in 1976 had as its principal objective the development of methods for the design of emergency relief systems (ERS) to handle runaway reactions and, in particular, methods for dealing with the possibility of two-phase flow.

The program was divided into three phases. Phase I was directed at predicting the likelihood and magnitude of batch swell when the relief device activates, leading to an ability to quantify the phase ratio entering the ERS. Phase II was intended to evaluate the adequacy of existing flow predictions when applied to multicomponent flashing flows. If existing techniques were found to be insufficient new methods were to be developed. Phase III was to bring together the work of phases I and II by large-scale testing of real runaway reactions.

As the program progressed, additional activities under phase IV were added. These included the development of test equipment that would allow the direct, experimental determination of vent size without the need for kinetic or thermophysical properties of the system under study. The test equipment was also to allow the heat generation rate to be determined under runaway conditions that simulate reality more

closely than existing techniques (including ARC, DTA or reaction calorimeters) and to characterize systems in terms of their flow behaviour. This latter activity was felt necessary in order to identify systems that have a foamy character under runaway conditions.

Other phase IV activities included a project to investigate the behaviour of safety relief valves and the preparation of a computer program incorporating the technologies derived in phases I and II.

#### 6.3.4.1 Phase I - Vapour Disengagement Dynamics

The approach taken was to utilize one-dimensional drift flux formulations to establish vapour hold up correlations for the churn turbulent and bubbly flow regimes in terms of the average vessel void fraction and the superficial vapour velocity. Using these relationships for mass flow rate and system energy, an integral model was developed that defines the flow entering the ERS.

Using the analysis scheme developed allows the effects of partial disengagement to be utilized in design, usually leading to a smaller vent size. However, viscous effects and the propensity to form foams limits the use of this technique in many practical systems. The presence of small amounts of impurity can cause the formation of a stable foam which effectively eliminates vapour disengagement and leads to homogeneous two-phase venting.

The outcome of phase I appears to confirm the widely held feeling that a conservative design should always assume that a homogeneous two-phase mixture enters the relief device throughout the venting sequence. Of course, if direct experimental data, obtained under runaway conditions, are available to indicate the absence of foaming or viscous effects, then advantage can be taken of partial disengagement.

There can occur, however, situations in which the homogeneous assumption may not be conservative. For example, when homogeneous venting is assumed at a low energy release (or gas generation) rate, a vent could be sized smaller than actually needed if phase separation occurs, and the system is able to reach a higher energy release or gas generation rate. Care should be taken to check the vent size for both vapour as well as homogeneous venting.

#### 6.3.4.2 Phase II - Vent Flow Dynamics

Vent flow models for flashing and critical flows range from the homogeneous equilibrium model to the two-fluid approach which is capable of representing most of the recognized non-equilibrium phenomena.

The greatest obstacle to the widespread use of the two-fluid approach is the dearth of information on the interfacial coefficients that are needed to characterize the heat, mass and momentum transfer. Simple models are thus to be preferred, particularly since other uncertainties of greater magnitude are often the concomitant of "worst case" design.

Some of the simple models evaluated were homogeneous equilibrium, Henry-Fauske non-equilibrium model, equilibrium rate model (a derivative of the Henry-Fauske model) and Moody and Fauske slip equilibrium models. Comparisons were made with literature data on a variety of single component systems, and additional data from multicomponent, chemically reacting systems under different geometries. Detailed recommendations for flow models applicable to nozzles and long pipes were given for two-phase and single-phase flows, and for both sonic and subsonic conditions with the inclusion of flashing for multicomponent systems.

#### 6.3.4.3 Phase III - Large Scale Tests

This program, initially conceived as a limited, overall test of the validity of the tools produced from phases I and II, evolved into 70 tests with vessels of different size, vent configuration, and different fluids. All tests were analyzed using the integral model developed, which in turn contributed to the model refinement. The disengagement model was verified for water and ethylbenzene, although important scale effects relating to the vessel and vent size and hydrostatic head, accounting for a vapour lean or non-boiling region, had to be introduced. The viscous and foaming fluids showed much reduced vapour disengagement. While the models could be used to explain the experimental data, a priori prediction of the vessel flow behaviour proved impossible. The tests confirmed that a homogeneous assumption of vessel flow behaviour should be retained for ERS design.

In testing vent flow models, the data showed the homogeneous equilibrium model to be the best choice for ERS design. In the case of long vent lines especially, it was shown not to be overly conservative.

#### 6.3.4.4 Phase IV - Additional Activities

A significant accomplishment of the DIERS project may well have been the development of a small-scale test apparatus that will allow direct scaling of vent requirements.

With the scheme nothing needs to be known about the system to be tested, not even the identities of the chemicals involved. A description of the test apparatus and the tests undertaken on the various systems is given by Swift [52]. The styrene and di-tertiary-butyl peroxide (DTBP) data show excellent agreement with established kinetic models.

Flow characterization to distinguish between bubbly or foaming and churn turbulent behaviour has also been carried out on a number of systems. The flow regimes were clearly distinguishable and in agreement with the large scale data obtain in phase III. As a result of the phase IV activities, a more quantified version of the FIA chart has been presented in which the four sets of lines (A, B, C and D) are given in terms of heat generation rate at the relief condition.

#### 6.3.4.5 Elements of ERS Design Strategy

The emergency relief system method of design generally follows the steps outlined in Figure 6.10.

The first step is particularly critical to the eventual design and some form of hazard analysis should be conducted to ensure consideration of all the possible upset pathways to arrive at a credible worst case.

The amount and type of data needed will depend on the particular design strategy used. Data generated as part of the normal process development or optimization are not usually suitable since they seldom cover the extreme conditions of interest and are often derived in equipment that may not reveal the full extent of the hazard.

The least conservative, yet correct, approach to ERS design is to formulate a system model from a consideration of the mass and energy balance of the vessel. Kinetic models will be required to determine instantaneous gas and liquid phase composition, for the upset condition, along with appropriate state equations. However, this type of approach does have drawbacks, the most serious being the need for lots of data characterizing the system and the considerable computing power to effect a solution in a reasonable time. In most cases of practical interest the data may not be available and often impossible to obtain.



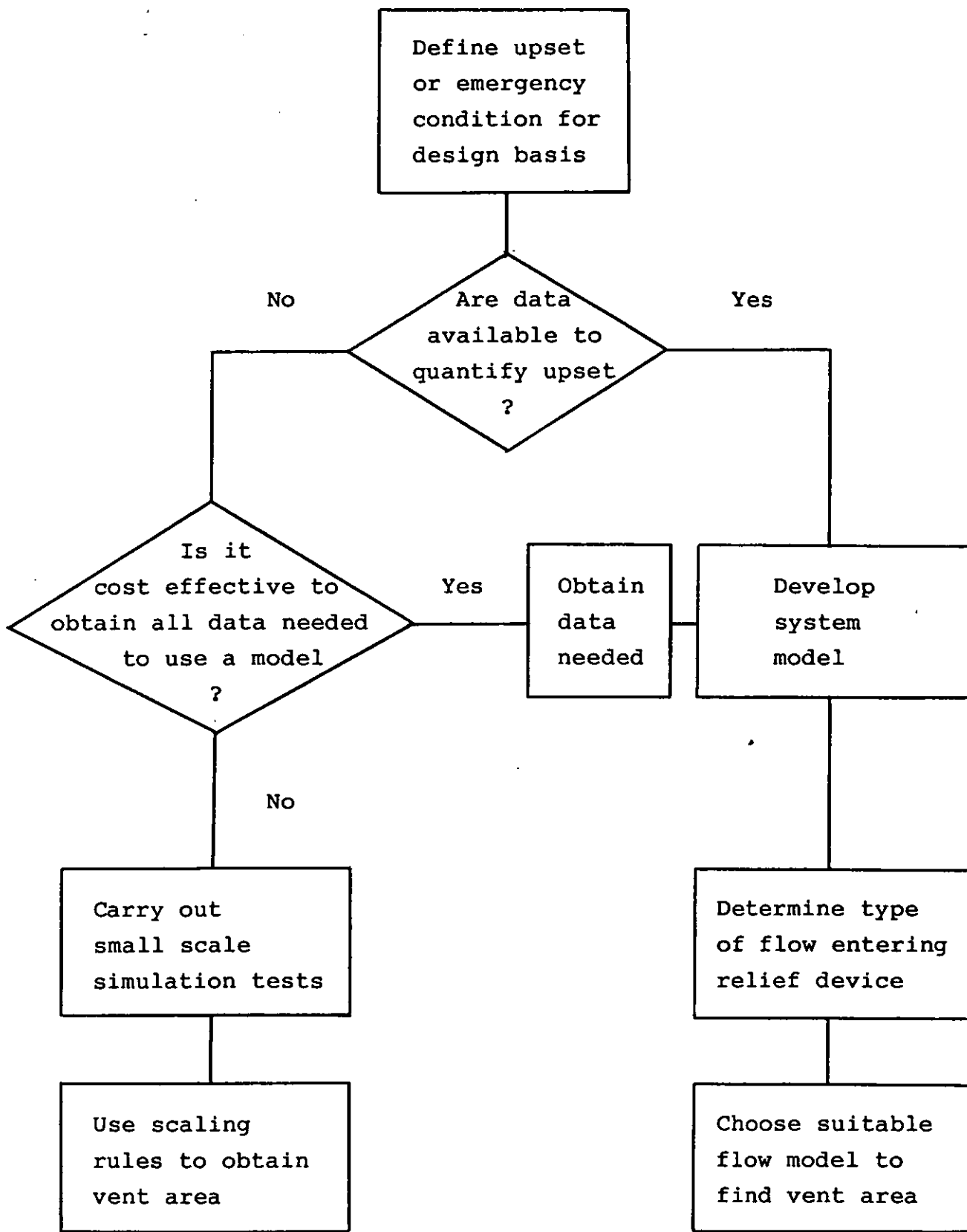


Figure 6.10 Elements of an ERS Design Strategy

## 7. PRESSURE RELIEF VALVES

### 7.1 Types of Pressure Relief Valves

"Pressure Relief Valve" is a generic term applied to the various types of valve - safety valve, relief valve, safety relief valve, etc. which are used to protect against over pressure. Unlike bursting discs, these are all pressure relief devices which are designed to reclose and prevent excess relief flow after normal conditions have been restored. Hence minimizing the loss of expensive or dangerous process material.

The American Petroleum Institute's API RP 520 (1963) (Recommended Practice for the Design and Installation of Pressure Relieving Systems in Refineries) recommends the use of three types of pressure relieving devices and gives the following definitions:

**SAFETY VALVE :** An automatic pressure relieving device actuated by the static pressure upstream of the valve and characterized by rapid full opening or "pop" action. It is normally used for gas or vapour operation.

**RELIEF VALVE :** An automatic pressure relieving device actuated by the static pressure upstream of the valve which opens further with the increase in pressure over the initial opening pressure. It is used primarily for liquid service.

**SAFETY-RELIEF VALVE** : An automatic pressure actuated relieving device suitable for use either as a safety valve or relief valve, depending on the application.

The corresponding British Standard does not make such distinctions, the underlying principles of design of the three valves being virtually the same, and generally refers to all valves for the automatic relief of pressure as safety valves, irrespective of the type of fluid on which they are designed to operate and of functional characteristics.

There are numerous types of safety/relief valves in use in the process industries to suit different combinations of temperature, pressure and other service conditions. In general, the three types of valve most frequently used are (a) conventional type, (b) balanced type bellows type and (c) pilot operated type.

#### 7.1.1 Conventional Type

This is the simplest type of valve most commonly used and adequate for most pressure relieving applications. The load is usually applied by means of a helical coil spring. To enable the conventional valve to function properly the pressure drop in the discharge system should not exceed 10% of the valve set pressure. These valves are particularly useful where back pressure is at a constant level.

The valves are usually of the closed bonnet type which protects the valve spring and internals from knocks and environmental effects, and prevents the leakage of fluid other than through the discharge pipe when the valve is called upon to operate.

### 7.1.2 Balanced Bellows Type

This type of valve minimizes the effects of back pressure caused by the discharge of another valve into a common discharge manifold. These valves are suitable therefore where the back pressure is likely to be variable.

Where possible the back pressure should be limited to a maximum of 30% of set pressure. Back pressure in excess of this figure tends to cause the valve to close nearer set pressure than is desirable, and this can lead to valve leakage.

Pressure build-up within the bonnet space will increase the pressure at which the valve lifts, so a safe venting device is normally provided for this type of valve.

### 7.1.3 Pilot Operated Type

Pilot operated valves use the pressure of the process fluid, sometimes in combination with the spring, for loading the valve seat. In all applications the action of the main valve is initiated and controlled by that of the pilot valve, which may itself be a direct operated safety/relief valve. A differential piston in the main valve is loaded through an orifice by the process pressure. The spring loaded pilot valve opens when set pressure is reached. This vents the pressure above the piston of the main valve allowing it to open wide. When the system blowdown pressure is reached, the pilot valve closes, and the full system pressure is immediately diverted to the main valve. The piston instantly moves downwards closing the main valve.

These types of valve are used for operation close to the set point. The main advantage of this valve is that it gives a very good seal up to set pressure, low overpressure and precise control of the blowdown and reseating pressure. In

addition, particularly in the case of larger types, the weight and height are considerably reduced compared with those of direct operated conventional valves.

The construction and performance of these valves in various services is generally documented in the literature and manufacturers catalogues. Guidelines for the use and design of most of the commercially available pressure relief valves is given in the relevant codes and standards including API RP 520 and ASME Boiler and Pressure Vessel Code, Draft British Standard for Safety Valves for use in the chemical, petroleum and allied industries, ISO 4126, etc.

## 7.2 Pressure Relief Valve Sizing

BS 5500 gives the following equations for the sizing of pressure relief valves:

For gas or vapour relief, under critical flow conditions:

$$A = \frac{WC}{KP} \sqrt{\frac{T}{M}} \quad (7.1)$$

where:

A = actual discharge area (m<sup>2</sup>)

K = manufacturer's coefficient of discharge (-)

M = molecular weight of the gas or vapour (kg/kmol)

P = absolute accumulation pressure (N/m<sup>2</sup>)

T = absolute inlet temperature (K)

W = rated capacity of valve (kg/s)

C = constant dependent on ratio of specific heats  
(constant pressure to constant volume) at standard conditions.

For liquid relief:

$$A = \frac{W}{K\sqrt{(2\Delta PG)}} \quad (7.2)$$

or

$$A = \frac{Q}{K} \sqrt{\frac{G}{2\Delta P}} \quad (7.3)$$

where:

- G = relative density at inlet temperature (kg/m<sup>3</sup>)
- ΔP = pressure drop (N/m<sup>2</sup>)
- Q = liquid flowrate (m<sup>3</sup>/s)
- A, W, K as above.

The following equations given by API RP 520 are also widely used for sizing pressure relief valves:

For gas or vapour under critical flow conditions:

$$A = \frac{W}{CKP_1} \sqrt{\frac{TZ}{M}} \quad (7.4)$$

where:

- A = effective discharge area (in<sup>2</sup>)
- W = flow through valve (lb/hr)
- T = temperature of inlet vapour (°R)
- Z = compressibility factor of gas (-)
- C = constant dependent on ratio of specific heats (C<sub>p</sub>/C<sub>v</sub>) at standard conditions
- K = manufacturers coefficient of discharge (-)
- P<sub>1</sub> = absolute upstream pressure (lb/in<sup>2</sup>)
- M = molecular weight of gas

for liquid flow:

$$A = \frac{\text{gpm}}{C} \sqrt{\frac{G}{\Delta P}} \quad (7.5)$$

where:

A = effective discharge area (in<sup>2</sup>)

gpm = flowrate (gal/min)

G = specific gravity of liquid at flow temperature (-)

ΔP = pressure drop (lb/in<sup>2</sup>)

C = constant (different to that shown above)

It should be emphasized that these are general sizing formulae and that for a given flow condition reference should be made to the relevant standard(s) for guidance.

As with bursting discs and other pressure relieving devices, the sizing of pressure relief valves for runaway reactions conditions remains a grey area and is essentially a matter for experts.

### 7.3 Pressure Relief Valve Setting and Capacity

The requirements for pressure relief valve setting and capacity differ somewhat between the existing standards and codes. Usually a distinction is made between pressure relief required for abnormal operation (e.g. runaway reaction conditions) and that for fire. The various requirements detailed in the principal codes are described in the ICI LFG code, which summarizes these as follows. For pressure relief for abnormal conditions only; the set pressure and the maximum pressure attained during relief should not exceed 100% and 110% of design pressure respectively. For pressure for fire only for vessels designed to the ASME Boiler and Pressure Vessel Code (Section VIII, Division 1), the set pressure and

the maximum relief pressure should not exceed 110% and 120% of design pressure, respectively. For combined abnormal operation and fire relief, the set pressure should not exceed 100% of the design pressure and the capacity should be at least equal to the greater of the two capacities calculated for the abnormal conditions and for fire relief.

BS 5500 requires that the set pressure and the maximum relief pressure should not exceed 100% and 110% of design pressure, respectively. If the relief capacity is provided by more than one valve, however, only one of the valves need to be set to operate before or at design pressure. The other(s) may be set to operate at a pressure not greater than 105% of design pressure, provided the capacity requirements are also met.

API RP 520 requires that where the set pressure is equal to the maximum allowable working pressure (MAWP), effectively the design pressure, then for pressure relief for abnormal conditions the maximum relief pressure should not exceed 110% of the MAWP and for pressure relief for fire the maximum relief pressure should not exceed 120% of the MAWP.

The pressure increase over set pressure of the (primary) relieving device is generally known as the overpressure and the pressure increase over the design pressure/MAWP is called the accumulation pressure.

These requirements apply equally well to bursting discs and other forms of pressure relief device.

All requirements as regards pressure relief should be carefully checked by reference to the appropriate codes and standards.



#### 7.4 Reliability of Pressure Relief Valves

A pressure relief valve should be able to discharge in a stable manner a given relief flow, whilst preventing the pressure increase exceeding a predetermined set level, and to reclose completely the installation it is protecting as the pressure build-up eventually subsides. It should then remain pressure tight up to the time of the next response to an overpressure situation, whereupon it should repeat the previous action.

In performing this essential protective function it is imperative that a pressure relief valve be extremely reliable, both in terms of structural reliability (ability to hold the required pressure without failure) and operational reliability (ability to perform the required function).

This can be achieved to a certain extent by ensuring good design, specification and construction of the valve, correct choice of materials of construction as regards corrosion, temperature and environmental factors, adequate tolerances and safety limits, regular testing and inspection etc.

On a more quantitative basis, it is extremely difficult to establish suitable reliability parameters for a device which is normally in a standby situation and which has no practical means of recording when or why it functioned once in service. Most companies now remove safety/relief valves periodically and test them on an appropriate test rig in order to determine their performance. They are then usually overhauled and reset before being returned to service. If a valve is judged to have failed then it is standard practice to reduce the time interval before the next inspection.

Whilst valves which have seized shut or open are obvious modes of failure, in between these two extremes there is an infinite range of possibilities (in terms of valve lift

performance) which may constitute valve failure. Clearly, certain guidelines need to be laid down. Consequently, it is very common to assume that valves which deviate by more than 10% from the cold set pressure have failed. Although the selection of this particular <sup>value</sup> ~~value~~ would seem to be rather arbitrary, its use is generally widespread as a criterion for valve failure.

Few studies have been carried out into the assessment of valve reliability. Recent work by Aird [56,57] and by Aird and Moss [58] in which the valve test data collected from the records of several companies was analyzed (using the 10% criterion) has shown no obvious trend as regards the proportion of failures recorded after different periods in service. Engineering instinct would suggest that the proportion of failures would be expected to increase as the period in service increases, but this was found not to be the case (as shown in Table 7.1).

Table 7.1 Proportion of Failures After Different Periods in Service[56,57,58]

Period in Service (weeks)	Mean (weeks)	Number of Valves	Number of Failures	Proportion (%)
1-39	17.1	104	46	44.2
40-57	48.6	104	36	34.6
58-90	70.6	107	52	48.6
91-112	103.0	103	44	42.7
113-147	130.2	103	43	41.7
148-182	160.9	106	51	48.1
183-364	261.0	103	55	53.4
ALL	119.1	746	332	44.5

For the total sample of valves the proportion of failures was found to be 44.5% and that the variation in each group could probably be attributed to sampling error rather than any underlying dependence on time.

Examination of the cumulative failure distribution (unreliability) given in Figure 7.1 indicates that safety/relief valves may be subject to certain mechanisms which give rise to sizable deviations (increase/decrease) in the lift pressure. Whatever these mechanisms are they must operate relatively quickly as evident by the considerable variation in performance in valves after relatively short periods in service. Whilst there are obvious causes, such as dirt on the valve seat or clogging with product, others are less extreme. One of the most widely investigated is spring relaxation (i.e. loss of loading force) and the effect of compression and temperature on springs is well documented. The significance of these phenomena is, however, relatively small (5-10% change in spring rate in the most extreme conditions) since the environment temperature of most valves is comparatively low ( $<100^{\circ}\text{C}$ ) and the load is designed to be well within the stress capabilities of the spring. This alone, therefore, would not account for the changes found.

Further work has been carried out by Aird [56,57] in order to study the effects of environmental factors on safety/relief valve performance. Two new valves were tested in the laboratory using a simple test rig. One valve was exposed to severe vibration and it was found that the initial lift pressure fell progressively until it reached a limit of 94% of the original valve. The second valve was subject to a temperature cycling between room temperature and  $80^{\circ}\text{C}$  for a period of a few days. A slight rise in initial lift pressure was observed. This valve was then soaked at  $80^{\circ}\text{C}$  for a longer period being allowed to cool before being tested at weekly intervals. This produced a significant increase in lift pressure as shown in Figure 7.2.

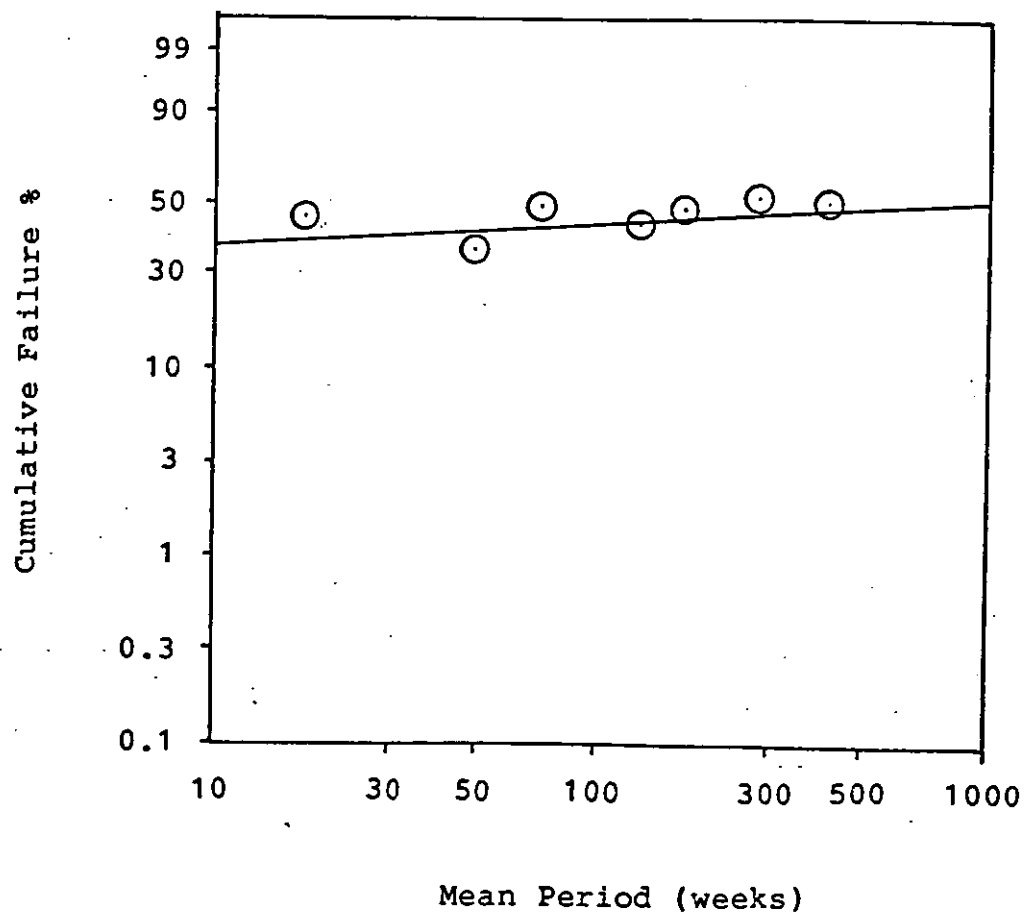


Figure 7.1 Cumulative Failure Distribution

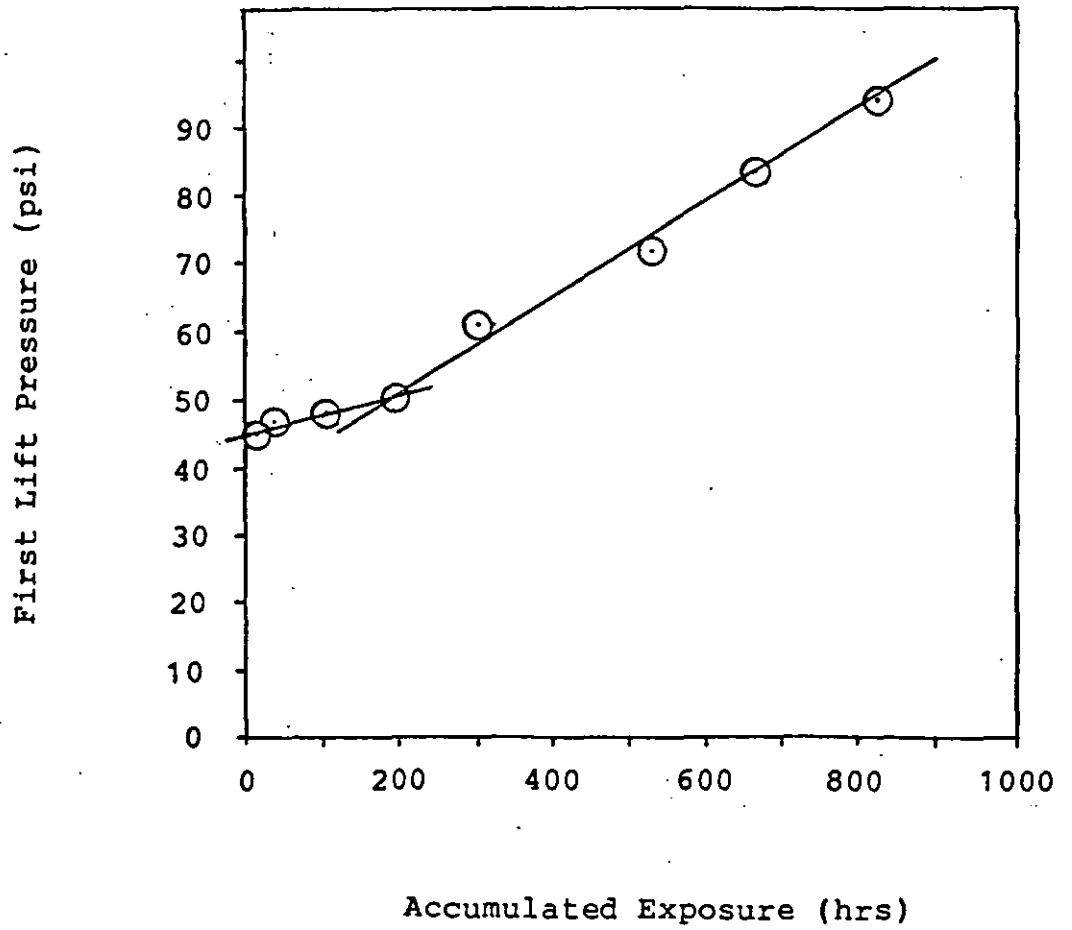


Figure 7.2 Lift Pressure versus Accumulated Exposure.  
for Valve Soaked at 80 °C

Work is still continuing in this area in order to determine, and hopefully eliminate, the mechanisms involved in valve failure.

Investigations are currently being conducted to identify the cause of the problem in terms of mechanical and metalurgical aspects, i.e. effects of temperature, oils, and contaminants on the valve seat/sealing rings, etc.

In a study [59] of 1378 performance tests carried out in West Germany on controlled (pilot operated) safety valves, it was found that there was a considerable difference between valves which use the process fluid as the control medium and those which used an external fluid (pneumatic or hydraulic). This was attributed mainly to the failure of control elements caused by contamination (e.g. dirt particles) in the control medium.

Another aspect of safety/relief valve failure is that a valve called upon to relieve an overpressure situation may stick or become blocked in the middle of the discharge due to plugging material, e.g. solid polymer. Reliability in this case is extremely difficult to quantify and as a result can limit the use of certain valves in particular pressure relief applications (especially as a primary means of relieving overpressure).

## 8. REACTORS AND REACTOR INCIDENTS

A quantitative estimate of the frequency of reactor overpressure may be made if information can be obtained on the total number of overpressure incidents in a given period and on the total number of reactors at risk during that period. The former has been obtained from the reactor study given in section 8.2 and the latter from the reactor inventory study described in this section 8.1.

### 8.1 Reactor Inventory Study

Three approaches were attempted in order to determine the total number of reactors in the country. These were to obtain the data for:

- (1) Publications on the chemical industry statistics.
- (2) Inventories of reactors insured by major insurance companies.
- (3) Sales of reactors by a major reactor vessel manufacturer.

A detailed account of the information obtained from the above sources is given in Appendix 2. The estimate obtained for the national reactor inventory is as follows.

The main estimate required is the average national reactor inventory for the period 1970-1981, say in 1976; this is the period for which there are full HSE records. The estimate is 2,100 reactors.

An estimate is also required of the average inventory for the period 1967-1981, say in 1974; this period is used only in relation to fatalities recorded by the HSE. This estimate is 1,987 reactors.

## 8.2 Reactor Incident Study

The sections below give details of the number of incidents associated with the reactor incident modes previously identified using data from both Nolan [2] and the HSE.

### 8.2.1 The Nolan Data

The large number of incidents collected by Nolan cover an unknown period world-wide. It is difficult therefore to determine the population of reactors at risk. The use of this collection has been limited, therefore, to the determination of the principal failure incident. For this purpose, however, the collection is very valuable, since it contains a much larger number of incidents than the HSE collection.

### 8.2.2 The HSE Data

An examination has been made of the HSE records of reactor incidents. These are the same records which are discussed in the Nolan collection but described in greater detail.

The records cover the period 1962-1982. The number of entries in each year is given in Table 8.1.



Table 8.1 HSE Incident Records: Number of Incidents

Year	Number	Year	Number
1962-67	16	1975	7
1968	4	1976	9
1969	2	1977	4
1970	7	1978	5
1971	10	1979	11
1972	10	1980	8
1973	12	1981	10
1974	6	1982	2
		Total	123

It was judged that the records might be incomplete for the years outside the period 1970-1981 and only those falling in this period have been examined in detail.

Not all the incidents are applicable to the present study. Those which are not have been excluded. However, the only two fatalities in the HSE records occurred in 1967 and 1968. For the purpose of reviewing fatalities, therefore, but for this purpose only, the period 1967-1981 has also been considered.

### 8.3 Incident Modes

The modes of failure in the Nolan set of incidents have been analyzed using the taxonomy given in Chapter 5. More detailed analyses have been carried out for the following types of reaction:

- (1) Sulphonation
- (2) Nitration
- (3) Polymerization

### 8.3.1 All Incident Modes

The classification for the complete list of reactions is given in Table 8.2.

Table 8.2 Analysis of Reactor Overpressure:  
Incident Modes - All Incidents

<u>Incident Mode</u>	<u>Number</u>
<u>Case 1: C1 Overpressure by Vaporized Liquid</u>	
D1 Regular Reaction Exotherm	
E1 Regular Reaction Inadequate Information	
E5 Incorrect Charging	
E6 Inadequate Cooling	
E7 Excessive Heating	
E8 Incorrect Agitation	
E9 Inadequate Batch Control	
E10 Undesired Catalysis	
E1 Regular Reaction Inadequate Information (7)	
E1.1 Unknown Exotherm	4
E1.2 Inadequate Definition of Operation	3
E5 Incorrect Charging (35)	
E5.1 Excess of Reactant	10
E5.2 Deficiency of Reactant	9
E5.3 Too Fast Addition of Reactant (see below)	
E5.4 Too Slow Addition of Reactant	
E5.5 Addition of Wrong Reactant	1
E5.6 Modification of Reactant	4
E5.7 Incorrect Order of Reactant Addition	2

E5.8 Too Slow Reaction of Solid (coarse particles)	1
E5.9 Too Fast Reaction of Solid (fine particles)	
E5.3 Too Fast Addition of Reactant	
E5.3.1 Automatic Control Failure	1
E5.3.2 Manual Control Failure	
Measurement/Alarm	
Operator Error	7
E6 Inadequate Cooling (26)	
E6.1 Underdesign (especially scaleup)	5
E6.2 Coolant Circulation Fault (see below)	
E6.3 Inadequate Agitation (for heat transfer)	2
E6.4 Internal Fouling	
E6.5 External Fouling	
E6.6 Evaporative Coolant Fault	1
E6.7 Condenser Fault (see below)	
E6.8 Moderating Solvent Fault	1
E6.9 Steam Jacket Cooling Inadequate	1
E6.10 Other Causes	2
E6.2 Coolant Circulation Fault	
E6.2.1 Coolant Source Failure	
E6.2.2 Power Failure	
E6.2.3 Pump Failure	1
E6.2.4 Coolant Turned Off	3
E6.2.5 Coolant Leak/Loss	
E6.2.6 Blockage	1
E6.2.7 Freezing	
E6.2.8 Automatic Control Failure	3
E6.2.9 Manual Control Failure	
Measurement/Alarm	
Operator Error	3

## E6.7 Condenser Fault

E6.7.1 Condenser Vapour Inlet Blockage	1
E6.7.2 Condenser Flooding	1
E6.7.3 Condenser Frozen	1

## E7 Excessive Heating (19)

E7.1 Initial Overheating	3
E7.2 Heating/Cooling Changeover Fault	3
E7.3 Unintended Heating or Heating Instead of Cooling	2
E7.4 Pump Energy	1
E7.5 Agitator Energy	2
E7.6 Steam Leak	2
E7.7 Live Steam	1
E7.8 Automatic Control Failure	2
E7.9 Manual Control Failure	
Measurement/Alarm	1
Operator Error	1
E7.10 Overheating in Flange Joints	1

## E8 Inadequate Agitation (for mixing) (20)

## E9 Incorrect Batch Control (18)

E9.1 Initial Temperature Low	2
E9.2 Initial Temperature High	
E9.3 Too Fast Reactant Addition Relative to Temperature	4
E9.4 Incorrect Cycle	3
E9.5 Inadequate Chemical Moderation	1
E9.6 Stewing	4
E9.7 Other Causes	4

## E10 Undesired Catalysis (5)

E10.1 Excess, or Too Rapid Addition of Catalyst	2
E10.2 More Active Catalyst	
E10.3 Catalyst Maldistribution	
E10.4 Catalyst Impurity	2
E10.5 Catalyst Left Over from Previous Batch	1
D3 Impurity Reaction Exotherm (21)	
D3.1 Water	11
D3.2 Air	
D3.3 Materials Left Over in Reactor	1
D3.4 Heat Transfer Fluid	1
D3.5 Other Impurities	8
<u>Case 2: C2 Overpressure by Decomposition Gas</u>	
D4 Regular Reactants Decomposition (16)	
E2 Regular Reactant Unknown Decomposition	11
As Above (Side Reaction)	5
D5 Impurity Reaction Decomposition	
E4 Impurity Decomposition	
<u>Case 3: C3 Overpressure by Water Vapour</u>	
D6 Water Ingress and Vaporization	1
<u>Case 4: C4 Overpressure by Flammable Gas</u> (Ignition of Explosive Mixture)	
D7 Air Ingress and Combustion (7)	7

Check that air is present in these cases; otherwise classify under decomposition.

Case 5: Overpressure by Other Gas/Vapour

D8 High Pressure Gas Ingress	1
------------------------------	---

Miscellaneous Cases

X1 Overpressure following unknown exotherm, where it is unclear if exotherm is a decomposition	7
--	---

X2 Overpressure following operator attempts to recover from fault conditions	4
--	---

Cases Where Causes are Unknown

Z1 Causes unknown	12
-------------------	----

### Summary

		Incidents	
		Number	%
Vaporized	Regular Reactant	7	3.5
Liquid	Inadequate Information		
	Incorrect Charging	35	17.6
	Inadequate Cooling	26	13.1
	Excessive Heating	19	9.5
	Incorrect Agitation	20	10.1
	Inadequate Batch Control	18	9.0
	Undesired Catalysis	5	2.5
	Impurity Reaction Exotherm	21	10.6
Decomposition	Regular Reactant Unknown	16	8.0
Gas	Decomposition		
Other		32	16.1
Total		199	100.0

Number of applicable incidents is 199.

### 8.3.2 Sulphonation Reactions

The classification of sulphonation reactions is given in Table 8.3.

Table 8.3 Analysis of Reactor Overpressure:  
Incident Modes - Sulphonation Reactions

#### Case 1: C1 Overpressure by Vaporized Liquid

D1 Regular Reaction Exotherm

E1 Regular Reaction Inadequate Information	
E1.1 Unknown Exotherm	1
E7 Excessive Heating	
E7.6 Steam Leak	1
E8 Inadequate Agitation (for mixing)	4
D3 Impurity Reaction Exotherm	
D3.1 Water	3

Case 2: C2 Overpressure by Decomposition Gas

D4 Regular Reactants Decomposition	
E2 Regular Reactant Unknown Decomposition	2

Summary

		Incidents	
		Number	%
Vaporized	Regular Reactant	1	9.1
Liquid	Inadequate Information		
	Incorrect Charging	0	0.0
	Inadequate Cooling	0	0.0
	Excessive Heating	1	9.1
	Inadequate Agitation	4	36.4
	Inadequate Batch Control	0	0.0
	Undesired Catalysis	0	0.0
	Impurity Reaction Exotherm	3	27.3
Decomposition	Regular Reactant Unknown	2	18.2
Gas	Decomposition		
Total		11	100.0



### 8.3.3 Nitration Reactions

The classification of nitration reactions is given in Table 8.4.

Table 8.4 Analysis of Reactor Overpressure:  
Incident Modes - Nitration Reactions

#### Case 1: C1 Overpressure by Vaporized Liquid

D1 Regular Reaction Exotherm

E5 Incorrect Charging

E5.2 Deficiency of Reactant 1

E5.5 Addition of Wrong Reactant 1

E5.3 Too Fast Addition of Reactant

E5.3.2 Manual Control Failure  
Operator Error 2

E6 Inadequate Cooling

E6.2 Coolant Circulation Fault

E6.2.4 Coolant Turned Off 1

E6.2.8 Automatic Control Failure 1

E7 Excessive Heating

E7.1 Initial Overheating 1

E7.2 Heating/Cooling Changeover Fault 1

E7.4 Pump Energy 1

E7.5 Agitator Energy 1

E7.6 Steam Leak 1

E8 Inadequate Agitation (for mixing) 4

## E9 Incorrect Batch Control

E9.1 Initial Temperature Low

E9.3 Too Fast Reactant Addition Relative to Initial Temperature 2

E9.6 Stewing 1

## D3 Impurity Reaction Exotherm

D3.1 Water 1

## Case 2: C2 Overpressure by Decomposition Gas

### D4 Regular Reactants Decomposition

E2 Regular Reactant Unknown Decomposition 2

Ditto (side reaction) 1

## Case 4: C4 Overpressure by Flammable Gas (Ignition of Explosive Mixture)

D7 Air Ingress and Combustion 1

## Miscellaneous Cases

X1 Overpressure following exotherm, where it is unclear if the exotherm is a decomposition 3

X2 Overpressure following operator attempts to recover from the fault conditions 2

## Summary

		Incidents	
		Number	%
Vaporized	Regular Reactant	0	0.0
Liquid	Inadequate Information		
	Incorrect Charging	4	13.8
	Inadequate Cooling	2	6.9
	Excessive Heating	5	17.2
	Inadequate Agitation	4	13.8
	Inadequate Batch Control	4	13.8
	Undesired Catalysis	0	0.0
	Impurity Reaction Exotherm	1	3.4
Decomposition	Regular Reactant Unknown	3	10.3
Gas	Decomposition		
Flammable Gas	Air Ingress and Combustion	1	3.4
Miscellaneous	Exotherm of Unknown Type	3	10.3
	Recovery from Fault	2	6.9
	Conditions		
Total		29	100.0

### 8.3.4 Polymerization Reactions

The classification for polymerization reactions is given in Table 8.5.

Table 8.5 Analysis of Reactor Overpressure:

#### Incident Modes - Polymerization Reactions

#### Case 1: C1 Overpressure by Vaporized Liquid

D1 Regular Reaction Inadequate Information

E1.2 Inadequate Definition of Operation	2
E5 Incorrect Charging	
E5.1 Excess of Reactant	1
E5.2 Deficiency of Reactant	3
E6 Inadequate Cooling	
E6.1 Underdesign (especially scaleup)	3
E6.2 Coolant Circulation Fault - see below	
E6.2.8 Automatic Control Failure	1
E6.2.9 Manual Control Failure	
Measurement/Alarm	
Operator Error	2
E6.7 Condenser Fault	
E6.7.1 Condenser Vapour Inlet Blockage	1
E6.7.2 Condenser Flooding	1
E7 Excessive Heating	
E7.1 Initial Overheating	2
E7.2 Heating/Cooling Changeover Fault	1
E7.8 Automatic Control Failure	1
E8 Inadequate Agitation (for mixing)	2
E9 Incorrect Batch Control	
E9.5 Inadequate Chemical Moderation	1
E10 Undesired Catalysis	
E10.1 Excess, or Too Rapid Addition of, Catalyst	1

### Miscellaneous Cases

X2 Overpressure following operator attempts to recover from the fault conditions	1
---	---

### Cases where Cause is Unknown

Z1 Cause Unknown	5
------------------	---

### Summary

		Incidents	
		Number	%
Vaporized	Regular Reactant	2	7.1
Liquid	Inadequate Information		
	Incorrect Charging	4	14.3
	Inadequate Cooling	8	28.6
	Excessive Heating	4	14.3
	Inadequate Agitation	2	7.1
	Inadequate Batch Control	1	3.6
	Undesired Catalysis	1	3.6
	Impurity Reaction Exotherm	0	0.0
Decomposition	Regular Reactant Unknown	0	0.0
Gas	Decomposition		
Miscellaneous	Recovery from Fault	1	3.6
	Conditions		
	Unknown	5	17.9
Total		28	100.0

#### 8.4 Overpressures

The information on the relief arrangements and the effect of these on the course of the overpressure event in the Nolan case histories are not sufficiently detailed and only the HSE case histories are considered.

The relief arrangements for the HSE case histories have been analyzed and are given in Table 8.6.

Table 8.6 Analysis of Reactor Overpressure:  
Relief Arrangement

Relief Arrangement	Number
Bursting Discs	11
Relief Valve	8
Relief Valve + Bursting Disc	2
Relief Valve, Vent Partially Closed	1
Bursting Disc - Recommended Larger Bursting Disc	2
Relief Valve - Recommended Bursting Disc	1
Bursting Disc - Vessel Open	1
No Bursting Disc	4
Recommend Bursting Disc	4
No Relief	1
Manual Vent Valve	1
Small Vent(s)	1
Vent - Recommended Bursting Disc	1
Small Holes	1
Vessel Open	15
Vessel Open - Recommended Bursting Disc	1
Unknown	13
Total	68

The overpressure incidents for the HSE case histories have been analyzed and are given in Table 8.7. Two of the incidents given in Table 8.1 are discarded as far as the analysis of overpressure is concerned. These are because one involves frothing, a potentially less serious incident, and in the other the mix was run off into an open vessel while it was still reacting.

Table 8.7 Analysis of Reactor Overpressure: Overpressures

Overpressure Incident	Number	%
Vessel Open, Hazardous Release <sup>(1)</sup>	18	27.3
Glass Work Shattered, Hazardous Release <sup>(2)</sup>	16	24.2
Vessel Ruptured, Hazardous Release	19	28.8
Vessel Ruptured	1	1.5
Explosion	5	7.6
Hazardous Release	5	7.6
Catchpot Ruptured	1	1.5
Catchpot Fire	1	1.5
Total	66	100.0

The relief system behaviour for the HSE case histories has been analyzed and are given in Table 8.8.

Twenty of the incidents given in Table 8.6 are discarded as far as the analysis is concerned. These are vessel open (18 incidents) and others (2 incidents) leaving 48 incidents given in Table 8.8.

Table 8.8 Analysis of Reactor Overpressure:  
Relief System Behaviour

Relief System Behaviour	Number	%
Relief Operated:		
Glassware Ruptured	3	6.3
Vessel Ruptured	1	2.1
Explosion	1	2.1
Catchpot Ruptured	1	2.1
Catchpot Fire	1	2.1
Hazardous Release	3	6.3
Relief Lifted but failed:		
Glassware Ruptured <sup>(1)(2)</sup>	3	6.3
Vessel Ruptured	8	16.7
Explosion	2	4.2
Glassware Ruptured <sup>(3)</sup>	10	20.8
Vessel Ruptured <sup>(4)</sup>	11	22.9
Explosion	2	4.2
Hazardous Release	2	4.2
Total	48	100.0

Notes:

- (1) Relief valve fitted, but vent part closed in one case and bursting disc fitted, but larger bursting disc recommended in another.
- (2) Bursting disc failed to rupture.
- (3) Relief arrangements unknown in five cases. Bursting disc recommended in three cases. In one case there was no relief.
- (4) In six cases relief arrangements were unknown. In three cases there was no bursting disc. In one case a bursting disc was recommended and in one case there was a manual vent valve.



### 8.5 Fatalities

The Nolan case histories record 45 fatalities, only two of which occurred in this country, while the HSE case histories record only one. This is over the period 1967-1981.

## 9. REACTOR INCIDENT ANALYSIS

An analysis has been made of the incidents given in the HSE case histories. The incidents considered are the 66 overpressure incidents given in Table 8.7.

These cases are referred to as overpressure incidents, or simply incidents. Occasions where an abnormal pressure rise occurred which did not result in an overpressure incident are termed overpressure excursions, or simply excursions.

The principal causes of an incident, e.g. inadequate cooling or incorrect agitation, are referred to as incident modes. An incident mode may be sub-divided into sub-modes, e.g. inadequate cooling into coolant circulation fault or condenser fault.

An analysis is given below of the observed and predicted frequencies for some of the modes and sub-modes which are easiest to quantify. Even so it is necessary to make a number of assumptions concerning the effect of mitigating features. The purpose of this analysis is to illustrate the sort of assumptions which have to be made in order to reconcile the observed and predicted values. In many cases a mitigating feature is identified and assumed to have a considerable attenuating effect. An analyst would normally hesitate to claim such a large degree of credit for such features, but the analysis given below suggests that attenuations of the order proposed are necessary in order to reconcile the observed and predicted values. See Appendix 5.

The effect of trip and interlock systems has not been considered in the initial analysis, but is considered in discussing the analysis.

### 9.1 Incident Frequency

The basic data or estimates are used in the analysis are given in Table 9.1.

Table 9.1 Reactor Incident Analysis: Basic Data

Period of Study	= 12 years
Estimated Inventory of Reactors at Risk	= 2100
Number of Applicable Incidents	= 66
Estimated Number of Cycles	= 250 per year
Estimated Batch Time	= 16 hours

From the data given in Table 9.1 the frequency of incidents can be calculated as:

$$\begin{aligned}\text{Frequency of Incidents} &= 66 / (12 \times 2100) \\ &= 2.62 \times 10^{-3} \text{ incidents per} \\ &\quad \text{reactor year}\end{aligned}$$

The breakdown of incident modes might be based on the HSE or the world-wide data set. There are arguments for using either set. The HSE set, is, by definition, that more applicable to the UK and is unbiased by any process of selection of "interesting incidents", while the world-wide set is considerably larger. The latter has been considered the more important factor and it is the world-wide set which has been used; this includes the HSE set.

Some incident modes are difficult to predict, particularly the occurrence of unknown reactions and

decompositions. It is considered, however, that it is in principle possible to predict the incident modes given in Table 9.2, section A. The modes involving unknown reactions and decompositions are shown in Table 9.2, section B. The air ingress mode is shown in Table 9.2, section C. Together these three sets of modes cover 96.7% of all cases.

Table 9.2 Reactor Incident Analysis:  
Principal Incident Modes

	%
Section A	
Incorrect Charging	18.3
Inadequate Cooling	14.0
Excessive Heating	10.2
Incorrect Agitation	10.8
Incorrect Batch Control	9.7
Undesired Catalysis	2.7
Impurity Reaction Exotherm	11.3
Total	77.0
Section B	
Regular Reaction Inadequate Information	3.7
Regular Reaction Unknown Decomposition	8.6
Exotherm of Unknown Type	3.7
Total	16.0
Section C	
Air Ingress and Combustion	3.7
Total	3.7

## 9.2 Excursion Frequency

Only a proportion of overpressure excursions become notifiable overpressure incidents. The ratio of the two has been estimated from information obtained during the industrial visits on the relative frequency of the two. It is estimated, based on information obtained from industry, that

Proportion of Excursions which Become Incidents = 0.05

It may be noted that this proportion is a much higher figure than the probability of failure of a relief device such as a bursting disc or pressure relief valve, indicating that failure to vent by either of the latter is not the prime cause of escalation into an incident. Then:

$$\begin{aligned}\text{Frequency of Excursion} &= 2.62 \times 10^{-3} / 0.05 \\ &= 5.24 \times 10^{-2} \text{ excursions per} \\ &\quad \text{reactor year}\end{aligned}$$

## 9.3 Failure, Event and Human Error Data

The estimates of incident mode and sub-mode frequency given in the following sections require the data on frequency or probability of failures, events and human error. Some of the data used are summarized in Table 9.3.

Table 9.3 Some Failure, Event and Human Error Data

	Frequency (per year)	Source
Pump Failure	2.0	Lees [60] <sup>(1)</sup>
Agitator Failure	0.5	Industrial
Operator Fails to Start Agitator	0.5	Industrial
Manual Isolation	0.5 or 1.0	Lees [60]
Valve Wrongly Closed		
Temperature Measuring Device Failure	0.4	Lees [60] <sup>(2)</sup>
Control Valve Failure	0.3	Lees [60] <sup>(2)</sup>
Operator Fails to Intervene Opposite Undesirable Plant Condition	0.01 - 0.5	Lees [60]

Note: .

(1) See text for original sources

(2) Fail-to-Danger Failures are taken as 1/3 of ?  
total failures.

#### 9.4 Frequency of Inadequate Cooling

The following comparison may be made between observed and predicted frequency of inadequate cooling.

The observed frequency can be calculated as below:

$$\begin{aligned}
 \text{Frequency of Excursions} &= 0.14 \times 5.24 \times 10^{-2} \\
 \text{Involving Inadequate Cooling} & \\
 &= 7.34 \times 10^{-3} \text{ per year}
 \end{aligned}$$

The principal sub-modes are shown in Table 9.4.

Table 9.4 Reactor Incident Analysis: Inadequate Cooling -  
Principal Sub-Modes

	Number	%
Coolant Source Failure	0	0.0
Power Failure	0	0.0
Coolant Pump Set Failure	1	3.8
Coolant Turned Off	3	11.5
Automatic Control Failure	3	11.5
Manual Control Failure	3	11.5
Inadequate Agitation	2	7.7
Total	12	46.0

The coolant source failure and power failure have been included in the list given in Table 9.4, despite the fact that no instances are included of incidents in these sub-modes, because they are potentially important, since they could affect all the reactors in a plant. The other sub-modes are very heterogeneous.

For coolant source/power failure it is assumed for the purpose of comparing observed and predicted excursion rates that there was a single sub-mode. This is in line with the usual practice in failure rate estimation when no failure has been observed of assuming that a failure was just about to occur. Then the frequencies of excursions in selected sub-modes from Table 9.4 are as follows.

Frequency of excursion due to:

$$\begin{aligned}\text{Coolant Source/Power Failure} &= 0.038 \times 7.34 \times 10^{-3} \\ &= 2.8 \times 10^{-4} \text{ per year}\end{aligned}$$

$$\begin{aligned}\text{Coolant Pump Set Failure} &= 0.038 \times 7.34 \times 10^{-3} \\ &= 2.8 \times 10^{-4} \text{ per year}\end{aligned}$$

$$\begin{aligned}\text{Coolant Turned Off} &= 0.115 \times 7.34 \times 10^{-3} \\ &= 8.44 \times 10^{-4} \text{ per year}\end{aligned}$$

$$\begin{aligned}\text{Automatic Control Failure} &= 0.115 \times 7.34 \times 10^{-3} \\ &= 8.44 \times 10^{-4} \text{ per year}\end{aligned}$$

$$\begin{aligned}\text{Incorrect Agitation} &= 0.077 \times 7.34 \times 10^{-3} \\ &= 5.65 \times 10^{-4} \text{ per year}\end{aligned}$$

The predicted frequencies for the sub-modes just considered are now determined.

#### 9.4.1 Coolant Source Failure, Power Failure

$$\begin{aligned}\text{Frequency of Coolant Source/Power Failure} &= 2.8 \times 10^{-4} \\ &\text{per year}\end{aligned}$$

#### Assumptions:

- (1) Probability of coolant source/power failure sufficiently serious to give total loss of cooling is 0.1.
- (2) Proportion of time reactor is in a condition sufficiently critical for excursion to occur if coolant is lost is 0.2 of batch time or 0.1 of total cycle time.

Hence we can calculate:



$$\begin{aligned}\text{Frequency of Excursion by Coolant} &= 0.1 \times 0.1 \times 0.1 \\ \text{Source/Power Failure} &= 1.0 \times 10^{-3}\end{aligned}$$

#### 9.4.2 Coolant Pump Set Failure

Assumptions:

- (1) A standby system with one pump operating and one on standby.
- (2) Frequency of Pump Failure,  $\lambda$ , is 2 per year
- (3) Probability of Successful Switchover,  $R_{sw}$ , is 0.95
- (4) Batch Time is 16 hours i.e.  $1.83 \times 10^{-3}$  years

Then we can calculate the reliability over a batch,  $R$  as:

$$\begin{aligned}R &= e^{-\lambda t} (1 + R_{sw} \lambda t) \\ R &= 0.9998\end{aligned}\tag{9.1}$$

$$\text{Unreliability of a Batch, } Q = 1 - R = 0.0002$$

Hence frequency of pump set failure is given as:

$$\text{Pump Set Failure} = 250 \times 0.0002 = 0.05 \text{ per year}$$

#### 9.4.3 Coolant Turned Off

Frequency of manual isolation valve wrongly closed is 0.05 per year.

Assumptions:

- (1) Probability that operator fails to detect lack of cooling is 0.01.

(2) Probability that reactor is in a critical condition is 0.5.

(This is a higher value than proportion of time reactor is in critical condition for coolant loss, because it includes start-up)

Hence:

$$\begin{aligned}\text{Frequency of Inadequate Cooling} &= 0.05 \times 0.01 \times 0.5 \\ \text{Due to Coolant Turned Off} &= 2.5 \times 10^{-4} \text{ per year}\end{aligned}$$

#### 9.4.4 Automatic Control Failure

$$\begin{aligned}\text{Frequency of Failure of Temperature} &= 0.4/3 \\ \text{Measuring Device in Fail-to-Danger Mode} &= 0.13 \text{ per year}\end{aligned}$$

$$\begin{aligned}\text{Frequency of Failure of Control Valve} &= 0.3/3 \\ \text{in Fail-to-Danger Mode} &= 0.1 \text{ per year}\end{aligned}$$

$$\text{Loop Failure Rate in Fail-to-Danger Mode} = 0.25 \text{ per year}$$

Assumptions:

- (1) Proportion of time reactor is in a critical condition is 0.1.
- (2) Probability that operator fails to detect maloperation of control loop is 0.01.

Hence we can calculate:

$$\begin{aligned}\text{Frequency of Inadequate Cooling} &= 0.25 \times 0.1 \times 0.01 \\ \text{by Automatic Control Failure} &= 2.5 \times 10^{-4} \text{ per year}\end{aligned}$$

9.4.5 Incorrect Agitation

Frequency of Agitator Failure = 0.5 per year  
Frequency of Operator Failure = 0.5 per year  
to Start Agitator

Assumptions (for both of these cases):

(1) Probability that agitator failure is critical = 0.01

Hence:

Frequency of Inadequate Cooling =  $(0.5 + 0.5) \times 0.01$   
by Inadequate Agitation  
 $= 1.0 \times 10^{-2}$  per year

9.4.6 Comparison of Incident Frequencies

The predicted frequencies for inadequate cooling due to the sub-modes considered are then as given in Table 9.2.

Table 9.5 Reactor Incident Analysis: Inadequate Cooling - Comparison of Observed and Predicted Frequencies in Selected Sub-Modes

	Observed Frequency (per year)	Predicted Frequency (per year)
Coolant Source/Power Failure	$2.8 \times 10^{-4}$	$10.0 \times 10^{-4}$
Coolant Pump Set Failure	$2.8 \times 10^{-4}$	$50.0 \times 10^{-4}$
Coolant Turned Off	$8.4 \times 10^{-4}$	$2.5 \times 10^{-4}$
Automatic Control Failure	$8.4 \times 10^{-4}$	$2.5 \times 10^{-4}$
Inadequate Agitation	$5.7 \times 10^{-4}$	$100.0 \times 10^{-4}$

The relatively low observed frequency of the inadequate agitation sub-mode may be due to the relatively high effectiveness of agitator instrumentation. The probability of being able to devise effective protection against agitator failure is ranked high both by the authors and the field study.

The relatively low observed frequency of the coolant pump set failure sub-mode is unexplained. Generally predictions of pump set reliability from the types of expression used here tend to be optimistic, because such sets are liable to common cause failures not taken into account in the simpler expressions.

#### 9.5 Frequency of Incorrect Agitation

The observed frequency is given as:

$$\begin{aligned}\text{Frequency of Excursions Involving} &= 0.108 \times 5.24 \times 10^{-2} \\ \text{Incorrect Agitation} &= 5.66 \times 10^{-3} \text{ per year}\end{aligned}$$

The predicted frequency is given as:

$$\text{Frequency of Agitator Failure} = 0.5 \text{ per year}$$

$$\begin{aligned}\text{Frequency of Operator Failure} &= 0.5 \text{ per year} \\ \text{to Start Agitator}\end{aligned}$$

Assumptions:

$$(1) \text{ Probability that agitator failure is critical} = 0.01$$

Hence:

$$\begin{aligned}\text{Frequency of Excursion due} &= (0.5 + 0.5) \times 0.01 \\ \text{to Agitator Failure}\end{aligned}$$

$$= 1.0 \times 10^{-2} \text{ per year}$$

Also assume that:

- (1) Probability that operator restarts agitator after initial failure to start is 0.1.
- (2) Probability that such a restart is critical is 0.25

Then:

$$\begin{aligned} \text{Frequency of Excursion due} &= 0.5 \times 0.1 \times 0.25 \\ \text{to Operator Restarting} & \\ \text{the Agitation} & \\ &= 12.5 \times 10^{-3} \text{ per year} \end{aligned}$$

Hence for incorrect agitation overall:

$$\begin{aligned} \text{Frequency of Excursion due} &= (10 + 12.5) \times 10^{-3} \\ \text{to Incorrect Agitation} & \\ &= 22.5 \times 10^{-3} \text{ per year} \end{aligned}$$

A comparison between the observed and predicted frequencies for this mode are thus:

$$\begin{aligned} \text{Observed} &= 5.66 \times 10^{-3} \text{ per year} \\ \text{Predicted} &= 22.50 \times 10^{-3} \text{ per year} \end{aligned}$$

The relatively low observed frequency is again probably due to the effectiveness of agitator instrumentation, as discussed above.

## 9.6 Fatality Frequency

From the data in section 9.5 the frequency of fatalities may be estimated as follows:

The HSE records do not include the fatal incident at Bolsover. This has been included here so that for the HSE case histories:

Number of Case Histories =  $68 + 1 = 69$

Number of Fatalities = 2

Probability of Fatality =  $2/69 = 0.03$  per incident

For the Nolan case histories:

Number of Case Histories = 199

Number of Fatalities = 45

Probability of Fatality =  $45/199 = 0.23$  per incident

Also for the Nolan case histories excluding the national case histories:

Number of Case Histories =  $199 - 68 = 131$

Number of Fatalities =  $45 - 2 = 43$

Probability of Fatality =  $43/131 = 0.33$  per incident

The probability of fatality is much higher for the Nolan case histories than for the HSE case histories. It is thought that there are three reasons for this. One is that the case histories in the general literature are likely to be biased towards those which are most severe, and which cannot be kept quiet. Another is that standards in Britain tend to be higher. The third is that the Nolan figures are strongly affected by two multiple fatality incidents (with 11 deaths in each case)

and that so far in this country we have not had such an accident.

## 10. REACTOR FAULT TREES

### 10.1 Conventional Fault Trees

A fault tree for a process plant may normally be built up by starting with the fault tree for the unprotected system, or demand tree, and then adding on the branches which represent *on* the protection, by the process operator and/or instrument system.

This approach is illustrated in Figure 10.1. Figure 10.1.(a) shows a demand tree which contains two base events, an enabling event and an initiating event. The enabling event is one which occurs usually some time earlier and lies latent. The initiating event then occurs and sets off the top event.

Figure 10.1.(b) shows the final tree in which there have been added to the demand tree branches which allow for the effect of beneficial action by the process operator, by the instrument system, and by the relief system.

Several fault trees for batch reactors have been given in the literature. They include the generic tree given in the BPF Guide (1979) [44] and the trees given by Stockburger (1979) [61] and by Roy, Rose and Parvin (1984) [19]. The BPF tree is shown in Figure 10.2 (a) and (b). The tree given by Roy, Rose and Parvin is for an ethoxylate reactor and is shown in Figure 10.3. The simplified pictorial flowsheet of the plant to which this refers is shown in Figure 10.4.



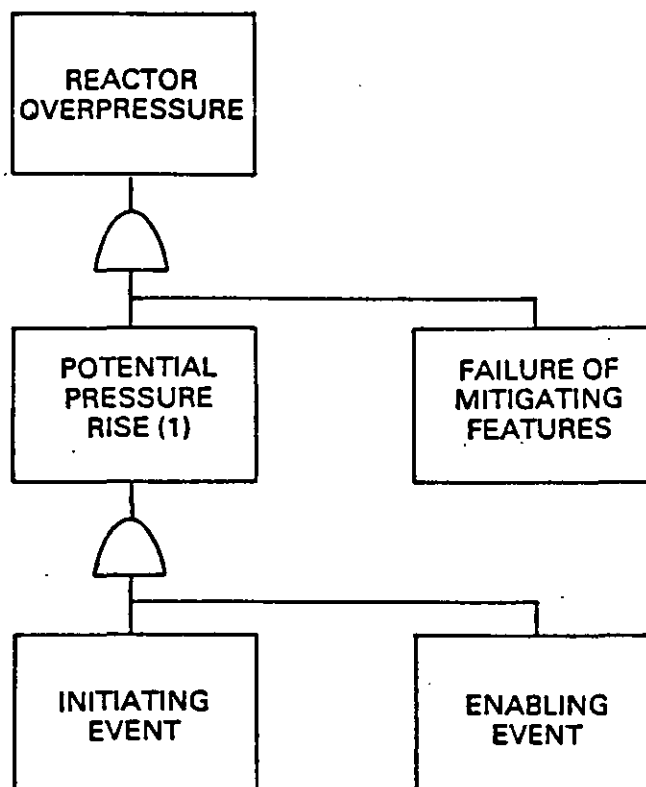


Figure 10.1 (a) Demand Tree with Base, Enabling and Initiating Events

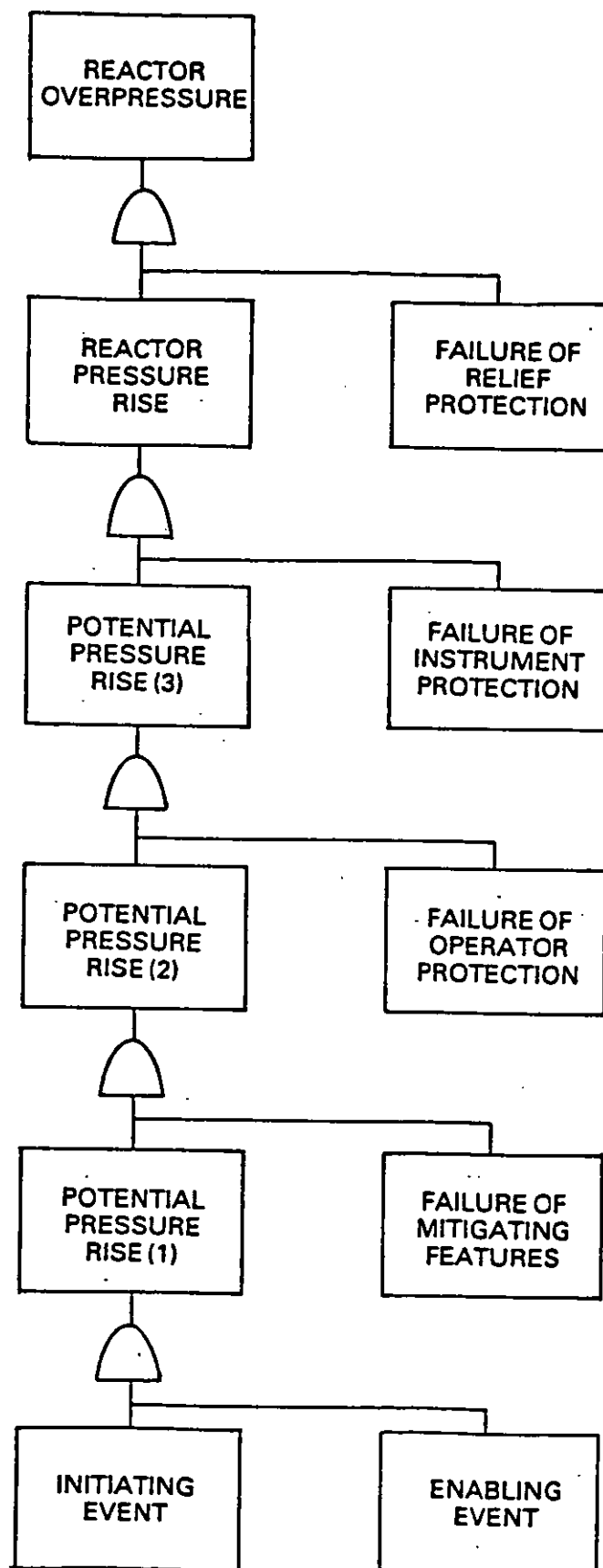


Figure 10.1 (b) Demand Tree Allowing  
for Beneficial Action

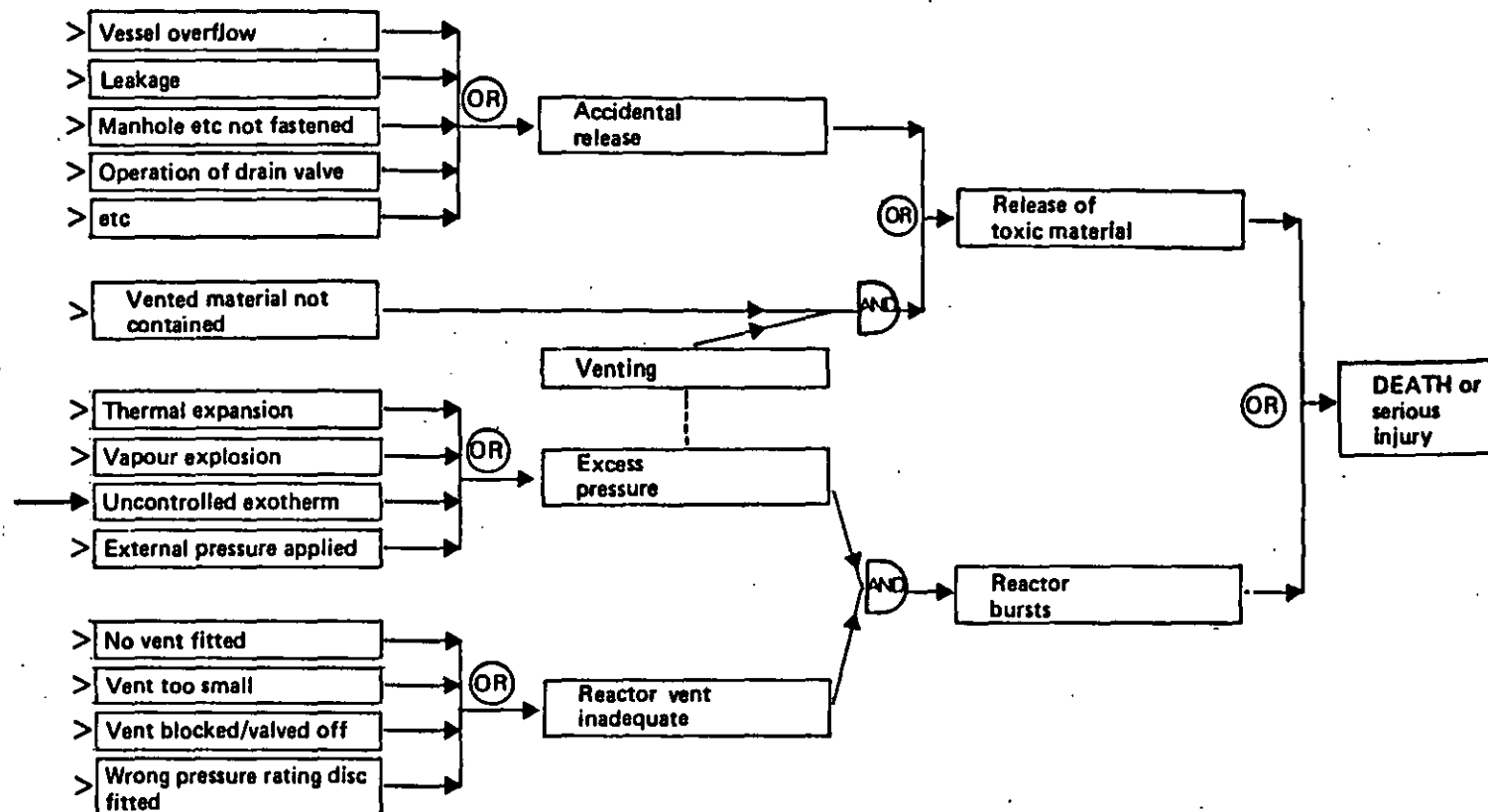


Figure 10.2 (a) Batch Phenolic Resin Process Fault Tree for Death or Serious Injury [44]

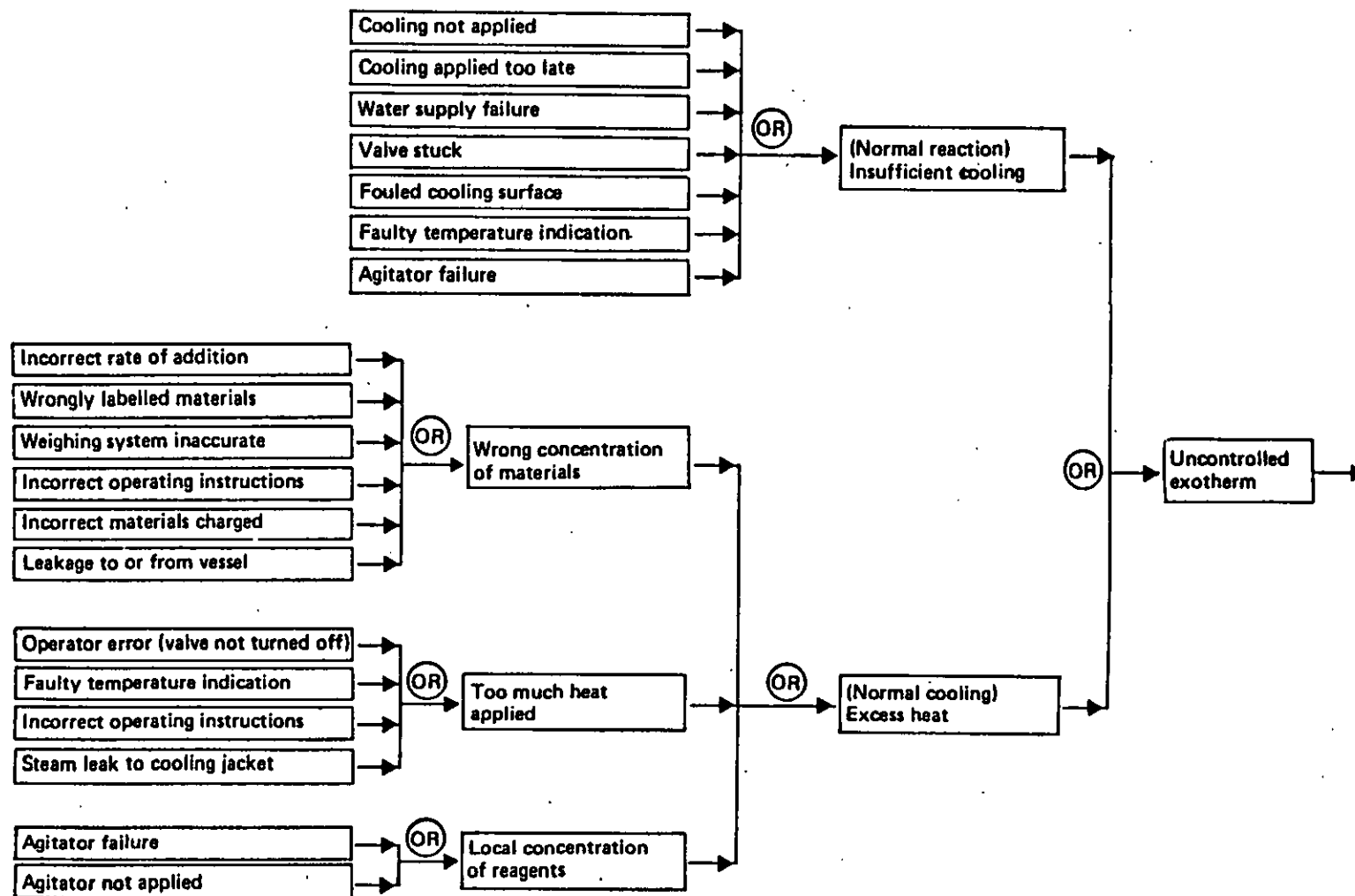


Figure 10.2 (b) Batch Phenolic Resin Process  
Continuation of Fault Tree [44]

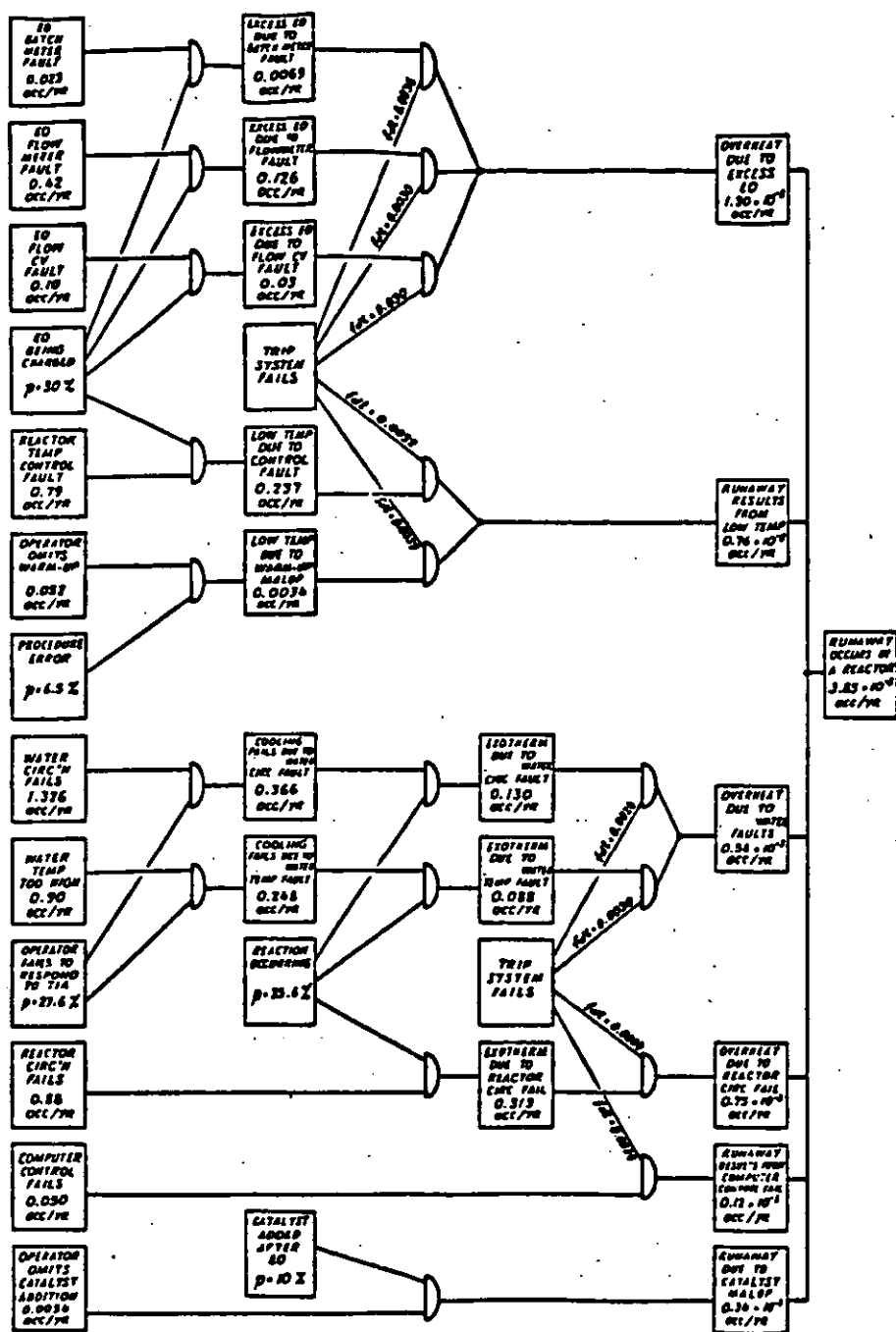


Figure 10.3 Fault Tree for an Ethoxylate Reactor [19]

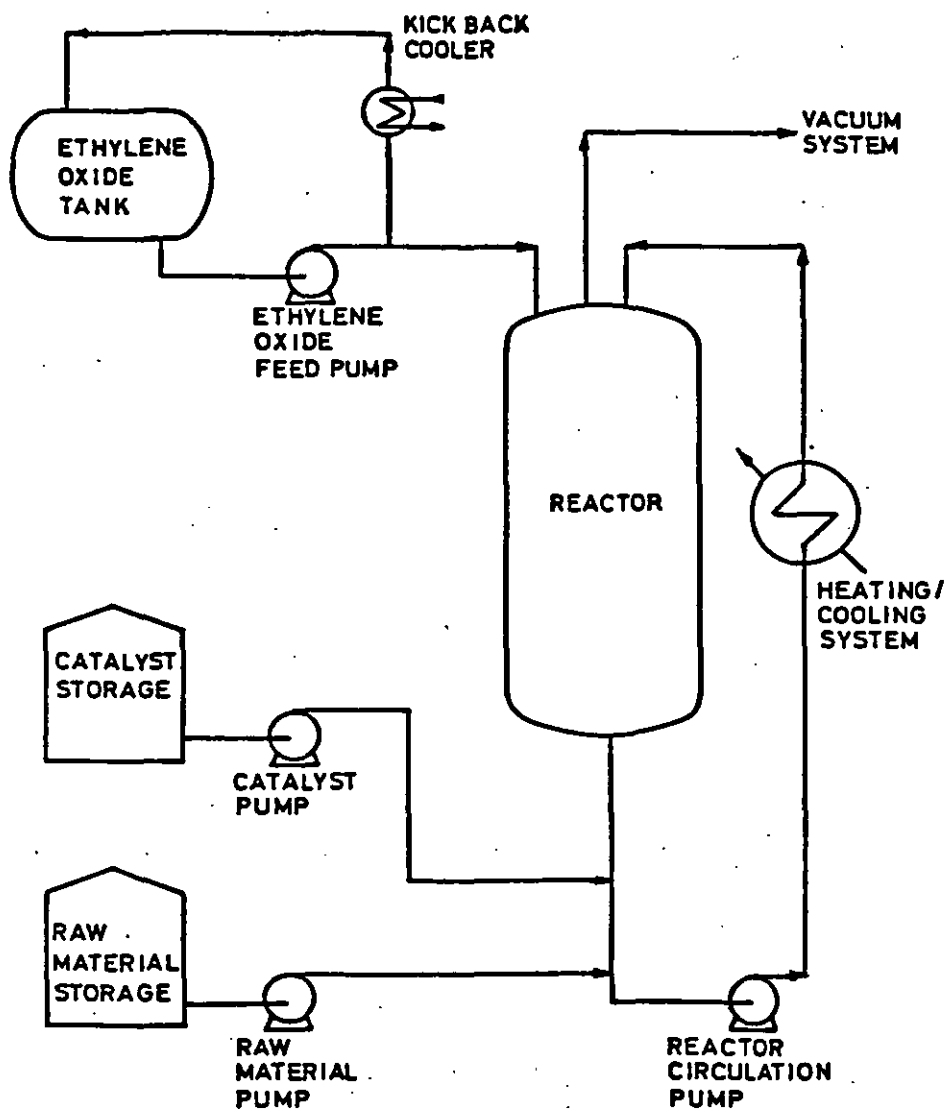


Figure 10.4 Simplified Pictorial Flowsheet  
of Ethoxylate Plant [19]

The initial intention of this project was to use a tree similar to the generic tree given by the BPF, building the tree up in the usual way by identifying a priori the various potential fault paths.

In the event this approach has not been used. The main reason for this is that such an a priori tree would be difficult to quantify. There are two basic difficulties. One is that there are various failure modes, including those involving human error, for which data are lacking or uncertain. The other is that it is also hard to estimate the effectiveness of mitigatory measures, particularly by the process operator.

This latter point may be illustrated by the case of the initiating fault of cooling water supply failure. Since this does occur sometimes and since there are at risk a quite large number of reactors, it would be expected that there would be incidents attributable to this initiating event. None have been found. This suggests that there are some strong mitigating features which result in a high attenuation between the frequency of the initiating event and that of a reactor incident.

## 10.2 Fault Tree Based on Incidents

In this project, therefore, a different approach has been taken. The fault tree used here is essentially an a posteriori tree, based on the incidents which have actually taken place. This means that the tree not only gives a qualitative fit to these incidents but also can be quantified from the relative frequency of the incidents.

The fault tree used is based on the taxonomy given in Chapter 5 and the analysis of incident modes given in Chapter 8. It is shown in Figure 10.5. This tree covers the great majority of the applicable incidents in the Nolan list, and

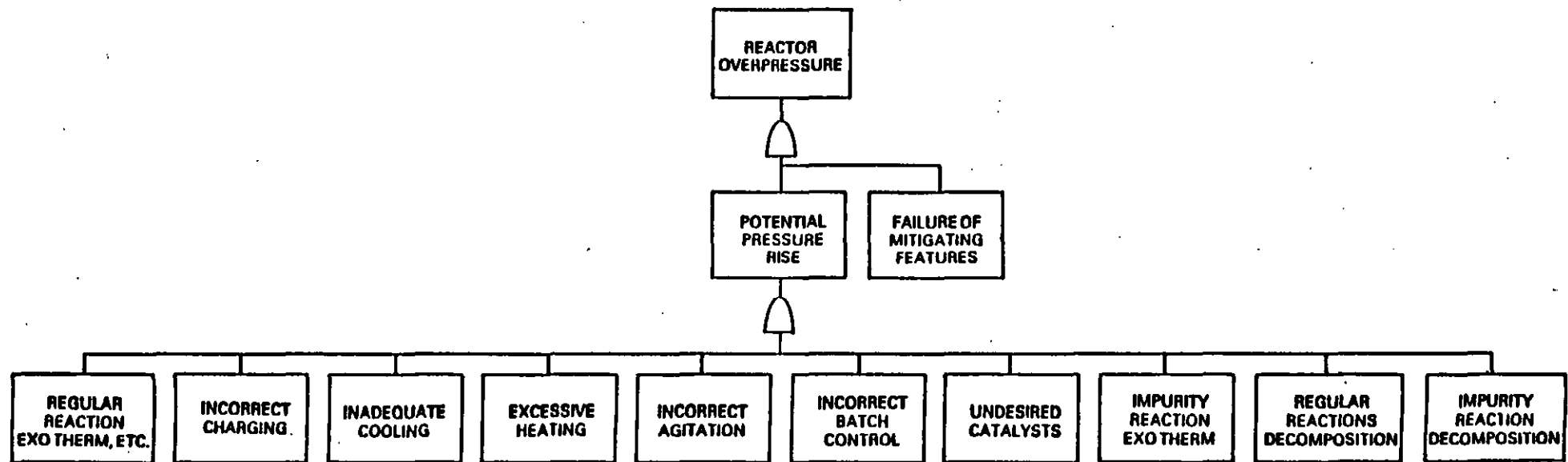


Figure 10.5 Fault Tree Based on Incident Mode Taxonomy



hence also in the HSE list, except those for which the cause is unknown.

Figure 10.5 is a demand tree. The quantification of this tree and the addition to it of the protective branches is considered in Chapter 11.

## 11. PROTECTION AGAINST OVERPRESSURE

### 11.1 Demand Tree

As just described, the generic demand tree used here is shown qualitatively in Figure 10.5.

The relative frequency of the initiating events may be obtained from the data on incident modes given in section 8. These data are summaries in Table 11.1, shown overleaf.

Values in brackets are based on redistribution of "causes unknown" among known causes in proportion to relative frequency of the latter.

- Notes: (1) Sulphonation reactions  
(2) Nitration reactions  
(3) Polymerization reactions

Table 11.1 Relative Proportions of Incident Modes

Mode	All	S <sup>(1)</sup>	N <sup>(2)</sup>	P <sup>(3)</sup>
Regular Reaction	3.5 (3.7)	9.1	0.0	7.1 (8.6)
Inadequate Information				
Incorrect Charging	17.2 (18.3)	0.0	13.8	14.3 (17.4)
Inadequate Cooling	13.1 (14.0)	0.0	6.9	28.6 (34.8)
Excessive Heating	9.6 (10.2)	9.1	17.2	14.3 (17.4)
Inadequate Agitation	10.1 (10.8)	36.4	13.8	7.1 (8.6)
Incorrect Batch Control	9.1 (9.7)	0.0	13.8	3.6 (4.4)
Undesired Catalysis	2.5 (2.7)	0.0	0.0	3.6 (4.4)
Impurity Reaction	10.6 (11.3)	27.3	3.4	0.0
Exotherm				
Regular Reactant	8.1 (8.6)	18.2	10.3	0.0
Unknown Decomposition				
Water Ingress and	0.5 (0.5)	0.0	3.4	0.0
Vaporization				
Air Ingress and	3.5 (3.7)	0.0	3.4	0.0
Vaporization				
High Pressure Gas	0.5 (0.5)	0.0	0.0	0.0
Ingress				
Recovery from Fault	2.0 (2.2)	0.0	6.9	3.6 (4.4)
Conditions				
Cause Unknown	6.1	0.0	0.0	17.9
Total	100.0	100.0	100.0	100.0

## 11.2 Non-Relief Protection

There are two principal types of protection other than pressure relief. These are the process operator and instrument systems consisting mainly of trips and interlocks.

The approach adopted here to estimate the potential effectiveness is as follows. For each incident mode, or

failure mode, such as inadequate cooling, the individual sub-modes such as coolant turned off have been examined and a decision made as to whether it is practical in principle to protect against them.

In making this decision only those types of protection are included which seem practical, bearing in mind that a given type of protection would generally need to be applied to all the reactors.

For this purpose four types of protection are defined as follows:

- (1) Design
- (2) Laboratory Screening
- (3) Instrumentation
- (4) Procedure

Then for each incident mode the proportion of incidents against which it is in principle practical to protect has been calculated. For example, for inadequate cooling it has been judged that protection is in principle possible in some degree for the sub-modes:

- (1) Underdesign
- (2) Inadequate agitation (for heat transfer)
- (3) Pump failure
- (4) Coolant turned off
- (5) Blockage
- (6) Automatic control failure
- (7) Manual control failure

Then for each incident sub-mode a probability  $P_1$  has been estimated which gives the probability that protection could in principle be provided. In most cases this is 1.0, but a few

instances it is some other value such as 0.5. In all cases the value is based upon examination of the individual case histories.

A further probability  $P_2$  has been estimated which is the probability that the protection, if provided, would be effective. In general, this probability is higher for control and for trip systems than it is for procedures.

The probability  $P$  that effective protection could be provided against a particular incident mode has then been calculated as the sum of the products of these two probabilities for the sub-modes.

$$P = \sum P_1 \times P_2 \quad (11.1)$$

The probability  $Q$  that effective protection could not be provided is the complement of  $P$ :

$$Q = 1 - P \quad (11.2)$$

The assessment of the effectiveness of non-relief protection is given in Appendix 5. The results of this assessment are summarized in Table 11.2.

Table 11.2 Reliability of Non-Relief Protection

Mode	Reliability
Regular Reaction Inadequate Information	0.90
Incorrect Charging	0.56
Inadequate Cooling	0.54
Excessive Heating	0.49
Inadequate Agitation	0.90
Incorrect Batch Control	0.48
Undesired Catalysis	0.20
Impurity Reaction Exotherm	0.05
Regular Reaction Unknown Decomposition	0.90
Water Ingress and Vaporization	0.00
Air Ingress and Combustion	0.80
High Pressure Gas Ingress	0.00
Exotherm of Unknown Type	0.90
Recovery from Fault Conditions	0.00

### 11.3 Relief Protection

The effectiveness of relief protection depends on both aspects of dependability: capability and reliability. It is necessary, therefore, to consider both of these.

Considering first reliability, the following estimates have been made in the bursting disc and vent system failure studies. For a bursting disc:

$$\text{Probability of Failure to Rupture} = 0.01$$

and for a vent system:

Probability of Failure by Blockage = 0.002

and from these figures:

Probability of Failure of Relief = 0.012

= 0.01, say

More detailed consideration of the HSE case histories provides further background. There are 13 cases where bursting disc protection is known to have been provided. There is one case out of the 13 where the bursting disc failed to rupture.

Hence for a bursting disc:

Probability of Failure to Rupture =  $1/13 = 0.08$

There are 33 cases where relief valve and/or bursting disc protection is known to have been provided. As just stated, in one of the these the bursting disc did not rupture, leaving 32 cases where there was a demand on the vent system. There is one clear case where the vent system was partly closed. This probably refers, however, to the normal vent rather than to the vent piping after the relief device. On this assumption there was no failure of a vent system. Then for a relief system:

Probability of Failure of Relief = 0.08

However, the HSE case histories are a biased set since

they cover only cases where reactor overpressure occurred. They may be regarded as a form of upper bound.

The foregoing discussion refers only to reliability. Capability is more difficult to assess. The main source of information on this is the HSE case histories for which the relief system behaviour is shown in Table 8.8. The 48 cases are summarized in Table 11.3, section A.

Table 11.3 Features of Relief Protection in HSE  
Case Histories.

<u>A - Behaviour of Relief Systems</u>	
	Number of Cases
Relief Operated;	
Bursting Disc	8
Relief Valve	2
Relief Fitted but Failed	13
Relief not, or Probably not, Fitted	25
Total	48



### B - Relief System Fitted but Failed

	Number of Cases
Relief Valve, but vent part closed	1
Relief Valve (including 4 known to be small or unsuitable)	7
Bursting Disc Failed to Rupture	1
Bursting Disc Known to be Small	1
Bursting Disc Details Unknown	1
Relief Valve and Bursting Disc	1
Relief Valve and Bursting Disc known to be large - 14 in.	1
Total	13

### C - Bursting Disc Failure

	Number of Cases
Capacity	12
Reliability	1

Classification into the first two categories in section A is somewhat arbitrary and has been influenced by the investigators' accounts.

It seems fairly clear that in the 10 cases where the relief operated but reactor overpressure, nevertheless, occurred the problem was one of capacity. The cases where relief was fitted but failed are less clear, but are summarized in Table 11.3, section B.

The cases where the bursting disc failed to rupture and that where the vent was closed have been considered above. There is one other case, that of the relief valve and 14 inch

bursting disc where bursting disc failure to rupture might be assigned as a bursting disc failure, but this was an incident where glassware shattered and it is uncertain that full design burst pressure was reached. It is concluded that of the 5 cases where a bursting disc was involved, the problem in four of them was capacity.

Hence the apportionment of bursting disc failure in the 13 applicable cases is as shown in Table 11.3, section C.

This is the basis of the judgement that a bursting disc is three times more likely to fail by undersizing than by failure to rupture and also that a vent system is three times more likely to fail by undersizing or otherwise incorrect design than by blockage. Hence for a bursting disc:

$$\begin{aligned}\text{Probability of Failure by Undersizing} &= 3 \times 0.01 \\ &= 0.03\end{aligned}$$

$$\begin{aligned}\text{Total Probability of Failure} &= 0.01 + 0.03 \\ &= 0.04\end{aligned}$$

For a vent system:

$$\begin{aligned}\text{Probability of Failure by Undersizing} &= 3 \times 0.002 \\ \text{or Incorrect Design} & \\ &= 0.006\end{aligned}$$

$$\begin{aligned}\text{Total Probability of Failure} &= 0.002 + 0.006 \\ &= 0.008\end{aligned}$$

and for a relief system:

$$\begin{aligned}\text{Probability of Failure of Relief} &= 0.04 + 0.008 \\ &= 0.048 \\ &= 0.05, \text{ say}\end{aligned}$$

#### 11.4 Overall Protection

The foregoing work provides a basis for making a comparative assessment of the dependability of non-relief and of relief protection.

For non-relief protection the analysis is given in Table 11.4.

Table 11.4 Dependability of Non-Relief Protection

Mode	Reliability of Protection	Incidents	
		(1)	(2)
Regular Reaction, Inadequate Information	0.90	3.5	3.2
Incorrect Charging	0.56	17.2	9.6
Inadequate Cooling	0.54	13.1	7.1
Excessive Heating	0.49	9.6	4.7
Incorrect Agitation	0.90	10.1	9.1
Incorrect Batch Control	0.48	9.1	4.4
Undesired Catalysis	0.20	2.5	0.5
Impurity Reaction Exotherm	0.05	10.6	0.5
Regular Reaction Unknown Decomposition	0.90	8.1	7.3
Water Ingress and Vaporization	0.00	0.5	0.0
Air Ingress and Combustion	0.80	3.5	2.8
High Pressure Gas Ingress	0.00	0.5	0.0
Exotherm of Unknown Type	0.90	3.5	3.2
Recovery from Fault Condition	0.00	2.0	0.0
Total		93.9	52.4

Notes: (1) Proportion of Incidents Requiring Protection.

(2) Proportion of Incidents Protected.

From Table 11.4 the proportion of incidents which have occurred which it is reasonable to expect might have been prevented by non-relief protection is 52.4%, or if the cause unknown cases are redistributed, 55.8%. Of the 52.4% some 13.7% is attributable to laboratory screening.

For relief protection the analysis is as follows. It might be thought that in this case a blanket probability might be used for the dependability of relief protection. There are, however, several reasons why a more detailed analysis has been done. One is that it seems appropriate to include credit for laboratory screening at this point. Another is that the dependability of relief protection must be a function of the sources of the overpressure, since the designer will find some sources more difficult to design against than others.

From the analysis given in section 11.3:

$$\text{Probability of Failure of Relief System} = 0.05$$

The dependability of relief protection is therefore assessed as 95%.

The treatment of relief protection has been put on the same basis as that for non-relief protection by estimating the effectiveness of such protection for each incident mode.

Then for relief protection the analysis is given in Table 11.5.

In Table 11.5 credit is taken for laboratory screening as well as for relief protection, where appropriate, so that the table is on the same basis as Table 11.4.

The extent to which, in a given incident mode, the relief

required can be predicted and designed for and the expected venting load on the relief protection is reflected in the figures used for the dependability of protection. For unknown reactions the main reliance is on screening so that there is a basic value of 0.9 credited to this source as in Table 11.3. The value of 0.95 actually used takes further credit for the relief protection itself. In the other incident modes the basic figures used are 0.9 and 0.8.

Notes: (1) Proportion of Incidents Requiring Protection.  
(2) Proportion of Incidents Protected.

Table 11.5 Dependability of Relief Protection

Mode	Reliability of Protection	Incidents	
		(1)	(2)
Regular Reaction, Inadequate Information	0.95	3.5	3.3
Incorrect Charging	0.80	17.2	13.8
Inadequate Cooling	0.80	13.1	10.5
Excessive Heating	0.80	9.6	7.7
Incorrect Agitation	0.90	10.1	9.1
Incorrect Batch Control	0.80	9.1	7.3
Undesired Catalysis	0.80	2.5	2.0
Impurity Reaction Exotherm	0.80	10.6	8.5
Regular Reaction Unknown	0.95	8.1	7.7
Decomposition			
Water Ingress and Vaporization	0.90	0.5	0.5
Air Ingress and Combustion	0.80	3.5	2.8
High Pressure Gas Ingress	0.90	0.5	0.5
Exotherm of Unknown Type	0.95	3.5	3.3
Recovery from Fault Condition	0.80	2.0	1.6
Total		93.9	78.6

From Table 11.5 the proportion of incidents which have occurred which is reasonable to expect might have been prevented by non-relief protection is 78.6%, or if the "cause unknown" cases are redistributed, 83.7%.

Thus comparing the proportion of incidents given in the HSE case histories which it is estimated realistically might not be prevented by relief or non-relief measures the proportions are:

Proportion Not Protected (%)	
Relief Measures	16.3
Non-Relief Measures	44.2

The non-relief protection considered so far, however, refers essentially to measures to handle specific faults such as agitator faults or cooling faults. In semi-batch plants, where one reactant is fed continuously, shut off of this feed provides a further means of protection. The estimate of the dependability of this is necessarily approximate, but it is estimated that some two thirds of the type of incident described would probably be averted by a trip from the reactor parameters onto the feed flow.

Hence, in round figures, it is estimated that for semi-batch reactors the dependability of relief measures is approximately equal, at 15 %.

## 12. EXPERT OPINION EVALUATION

In order to complement the other methods of estimation of reactor incidents and reactor overpressure a study of expert opinion was carried out. This involved the use of expert judgement to obtain estimates of the relative frequency and even absolute estimates of frequency of events.

### 12.1 Estimation of Expert Opinion

The technique used in the study was that of paired comparisons and draws on the work by Thurstone [62,63], Kendall [64], Pontecorvo [65] and Torgerson [66]. The method has previously been described by Hunns [67]. An outline of the method is given below with an example of how it can be used in Appendix 6.

### 12.2 Scaling by Paired Comparisons

The method of paired comparisons is a psychological scaling technique. It makes use of the human judgement dimension to obtain the ranking and scaling of a given set of items (stimuli) with respect to a specified attribute. The stimuli are presented in pairs to the assessor and for each pair he must decide which is the greater, or lesser, with respect to the given performance attribute. The stimuli are presented in all possible combinations of two and the complete set of "greater than" or "less than" decisions is recorded. For  $n$  stimuli the information set would comprise of  $n(n-1)/2$  decisions. The entire process is repeated many times in order

to produce a statistically usable population of information sets.

In theory it would be possible to use the same assessor for the repeated runs but normally the aim would be to use a different assessor on each occasion. It has been found that at least twelve assessors are required to get a meaningful result [64]. This total information can then be processed to produce a scaled ranking of the stimuli as shown diagrammatically in Figure 12.1.

The stimulus assessed as the lowest with respect to the attribute will be allocated a scale value of zero which serves as the base of a nominal scale along which the other attributes are positioned. The numerical magnitude and resolution of this scale potentially vary with the scale of the population of the information sets which produce it. The feature of importance is not the scale magnitude but the relative positions of the stimuli along it; the number of units within the scale merely reflects the resolution offered.

The scaled ranking is not, of course, absolute data; it is simply a nominal scale of relative values. We must have some method of relating these values to observable proportions.

### 12.3 The Scale Calculation Technique

The theory behind the construction of the following matrices can be found in Appendix 6.

#### 12.3.1 The F-Matrix

A given assessor is asked to rank each of a pair of items, the item with the higher ranking being assigned a value of one and the other zero. The F-matrix with columns A, B, C.... and rows A, B, C.... is then formed. An entry in column



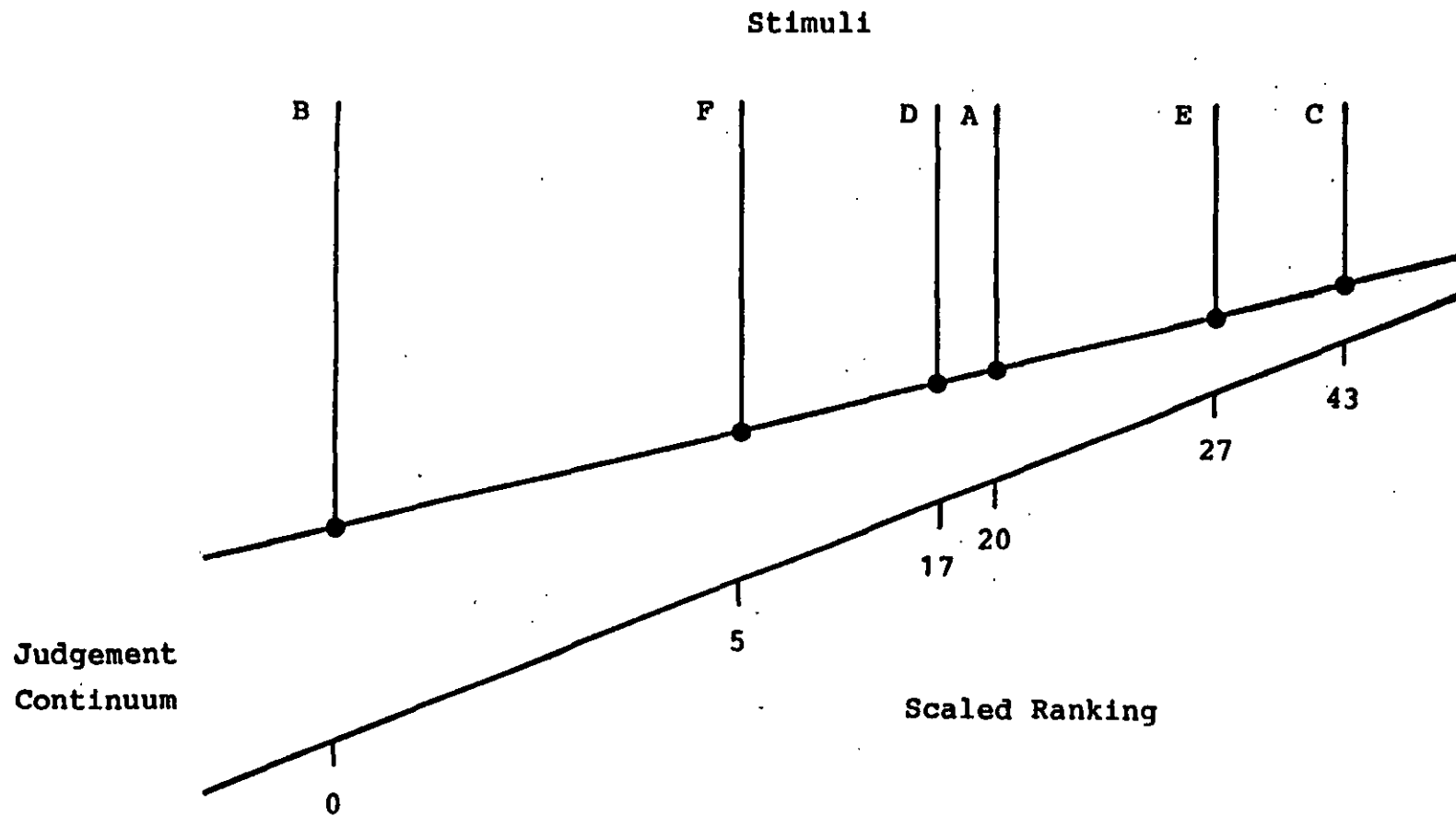


Figure 12.1 Diagrammatic Representation of the Scaled Ranking of Stimuli

B and row C means that B is ranked higher than C. The diagonal elements are blanked out. An F-matrix is compiled for each assessor and then summed to give the total F-matrix for all the assessors. For  $n$  items an  $n \times n$  F-matrix is produced, indicating the number of times any item was judged greater than every other item.

#### 12.3.2 The P-Matrix

The P-matrix, also of size  $n \times n$ , is formed from the F-matrix by dividing each term by the total number of assessors and is formally known as the normalized probability matrix.

#### 12.3.3 The X-Matrix

The P-matrix is converted into the X-matrix by using values of the cumulative normal distribution. Each element is converted into its equivalent unit normal deviate. This produces the basic transformation X-matrix. Values of zero and one in the P-matrix are ignored and left as gaps since these produce values of infinity for the X-matrix on the normal distribution. These values of zero and one occur when there is complete agreement between the assessors.

Each element of the X-matrix corresponds to a pair of stimuli and comprises an estimate (not the actual value since the population of assessors will be far from infinite) of the scale separation between the two items.

In order to obtain a scaled ranking of the  $n$  items,  $(n-1)$  data components are required, this representing the number of spaces along the scale. The X-matrix actually provides a total of  $n(n-1)/2$  estimated scale values giving up to  $n/2$  estimates to be averaged for each linear spacing along the scaled ranking. These averaged estimates of the scaled values are obtained using Torgerson's traditional procedure for incomplete matrices [66].

The column entries are summed and the columns then rearranged so that the column totals increases from left to right. Proceeding one column at a time, the difference between adjacent entries is found. For n items this produces a new matrix, the Z-matrix of n rows and n-1 columns.

#### 12.3.4 The Z-Matrix

The Z-matrix provides the separation between the items. The separation between items is the average of all the non zero terms in each column. Each column therefore provides one separation between items.

#### 12.4 Probability Values from a Scaled Ranking

The equations used to obtain absolute probability estimates from scale values were first postulated by Pontecorvo [65] who deduced them by experiment. A description of how he arrived at the following equations can be found in Appendix 6.

The upper and lower scale values ( $S_u, S_l$ ) can be related to the upper and lower probability values ( $P_u, P_l$ ) by the probability ratio r:

$$\frac{P_u}{P_l} = r(S_u - S_l) \quad (12.1)$$

$$\frac{P_x}{P_l} = r(S_x - S_l) \quad (12.2)$$

i.e. 
$$r = \left( \frac{P_u}{P_l} \right)^{1/(S_u - S_l)} \quad (12.3)$$

So 
$$\log_{10} P_x = A \cdot S_x + B \quad (12.4)$$

$$\text{when } r^e \quad A = \log_{10} r \quad (12.5)$$

$$\text{and} \quad B = \log_{10}(P_1 \cdot r^{-S_1}) \quad (12.6)$$

Thus we know the upper and lower scale values from the preceding calculations and if we assign a probability to the stimuli to which these values correspond then we can find the probability of any stimuli in between these limits. In actual fact these values of  $P_u$  and  $P_l$  corresponding to  $S_u$  and  $S_l$  need not be at the extreme limits as long as they can be correctly associated in the calculations and a check is made to ensure that the other values do not lie too far outside this range.

### 12.5 Evaluating Expert Performance

The technique used to evaluate the performance of an assessor is that suggested by Kendall [64]. It basically determines a level of consistency for an assessor and the degree to which the assessors agree amongst themselves.

The idea behind the technique can be simply conveyed by consideration of the following example. An assessor is asked to rank three items, A, B and C, according to some attribute. He may rank A above B and B above C. If he then ranks A above C he will have been completely consistent. However, if he ranks C above A he will have made a mistake in the ranking.

Consider the notation that if item X is ranked higher than item Y on a certain attribute then we can write  $X \rightarrow Y$  or  $Y \leftarrow X$ . Using this notation we can represent the above example diagrammatically, as shown below:

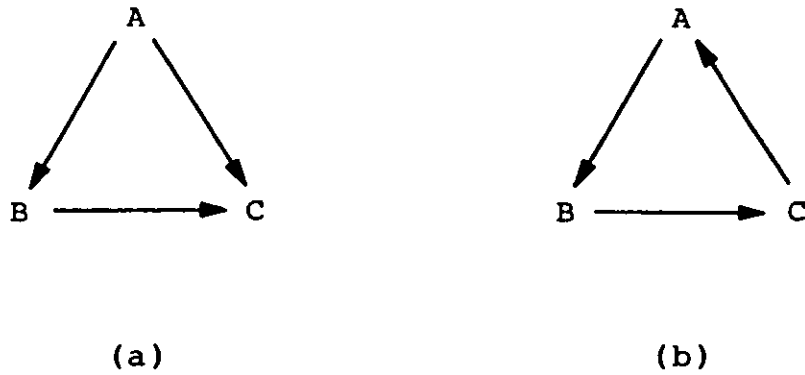


Figure 12.2  
Diagrammatic Representation of Expert Ranking  
and Triad Formation

For the case where the assessor is completely consistent, (a), one of the arrows is in an opposite direction to the others. When the judge shows an inconsistency, (b), all the arrows point in the same direction, i.e. they form a circular triad. Thus the formation of a triad between items can be used to measure the level of consistency of a particular assessor.

Kendall shows that for a number of items,  $n$ , being ranked that if  $n$  is odd then the maximum number of triads,  $n_T$ , is given by:

$$n_T = \frac{1}{24} (n^3 - n) \quad n \text{ odd} \quad (12.7)$$

and if  $n$  is even the maximum number of triads is given by:

$$n_T = \frac{1}{24} (n^3 - 4n) \quad n \text{ even} \quad (12.8)$$

The minimum number of triads is zero i.e. the assessor is 100% consistent.

#### 12.5.1 The Coefficient of Consistency

Using the definition above we can define a coefficient of consistency,  $\zeta$ , to indicate the level of performance of an assessor as shown below:

$$\zeta = 1 - \frac{24d}{(n^3 - n)} \quad n \text{ odd} \quad (12.9)$$

$$\zeta = 1 - \frac{24d}{(n^3 - 4n)} \quad n \text{ even} \quad (12.10)$$

where  $n$  is the number of items being ranked and  $d$  is the number of triads produced by the assessor which ranges between zero and  $n_T$ , the maximum number of triads given above.

The technique used to actually determine the number of triads from each assessors F-matrix is given in Appendix 6.

#### 12.5.2 The Coefficient of Agreement

The coefficient of agreement, which indicates how the assessors agree amongst themselves, can be calculated from the terms entered in the totalized F-matrix. For  $n$  items to be ranked this has  $n(n-1)$  entries with a blank leading diagonal. For each entry,  $\gamma_i$ , we find for  $m$  assessors the sum such that  $\Omega$  is the sum of the number of agreements between pairs of assessors:

$$\Omega = \sum_{i=1}^{i=n(n-1)} \gamma_i (\gamma_i - 1) \quad (12.11)$$

and

$$u = \frac{8\Omega}{m(m-1)n(n-1)} \quad (12.12)$$

The term  $u$  is called the coefficient of agreement. If there is complete agreement  $u$  equals one. The minimum possible value of the coefficient of agreement depends on the number of assessors,  $m$ . The minimum coefficient is  $1/2m$ , if  $m$  is even, or  $1/2(m+1)$  if  $m$  is odd.

### 12.5.3 The Chi-Squared Test

An additional test on the results produced by each assessor is the chi-squared test. Kendall [64] shows that in a certain sense it is possible to test the significance of a value of the coefficient of consistency,  $\zeta$ , by considering the distribution it would have if all the preferences were allotted at random. This will tell us whether the observed  $\zeta$  could have arisen by chance if the observer was completely incompetent, or, alternatively, whether there is some degree of consistency in his preferences notwithstanding a lack of perfection. Thus we can produce a probability from the chi-squared test which is the probability that a better value of  $\zeta$  can be attained by answering the questions at random.

Alternatively by finding the complement of this value it would be possible to determine the probability of getting a worse value for  $\zeta$  by answering the questions at random.

### 12.6 Field Study of Expert Opinion

The study used field visits to some 14 companies in each of which an individual expert with experience in the operation

of chemical reactors was interviewed. The interview was based on a questionnaire and the expert was taken through this question by question.

The main part of the questionnaire consisted of questions on the relative frequency of incident modes and sub-modes potentially capable of escalating to reactor overpressure and on the relative prospects of recovering from such modes and of devising practical and effective hardware/software measures of protection other than relief to counter these modes.

Details of, and results from the field study are given in Appendix 7.

#### 12.7 Results of Field Study

The results of the field study of expert opinion given in Appendix 7 may be compared to those obtained from the case histories and from the authors estimates. These comparisons are now given.

The comparison of the ranking of the incident modes is shown in Table 12.1.



Table 12.1 Comparison of Rankings from Case Histories and  
from Expert Judgement Field Survey: Incident Modes

	Case Histories		Field Study
	%	Rank	Rank
Unknown Exotherm/ Decomposition	15.1	2	6
Incorrect Charging	17.2	1	1
Inadequate Cooling	13.1	3	3
Excessive Heating	9.6	6	4
Incorrect Agitation	10.1	5	5
Inadequate Batch Control	9.1	7	2
Undesired Catalyst	2.5	8	8
Exotherm from Impurity	10.6	4	7

The degree of agreement given in Table 12.1 is considered good overall with two exceptions. Thus in both rankings incorrect charging and inadequate cooling are ranked high, undesired catalyst low and excessive heating, incorrect agitation and exotherm from impurity moderate. The exceptions are unknown exotherm/decomposition, which is ranked much lower by the experts than in the case histories and inadequate batch control which is ranked much higher.

The comparison of the ranking of the incorrect charging sub-mode is given in Table 12.2.

Table 12.2 Comparison of Rankings from Case Histories  
and from Expert Judgement Field Survey:  
Incorrect Charging

	Case Histories		Field Study
	%	Rank	Rank
Excess of Reactant	29.4	1	1
Deficiency of Reactant	26.5	2	3
Too Fast Addition of Reactant	23.5	3	2
Modification of Reactant	11.8	4	5
Incorrect Order of Reactant Addition	5.9	5	4

The degree of agreement shown in Table 12.2 is considered very good. The comparison of the ranking of the inadequate cooling sub-mode is given in Table 12.3.

Table 12.3 Comparison of Rankings from Case Histories  
and from Expert Judgement Field Survey:  
Inadequate Cooling

	Case Histories		Field Study
	%	Rank	Rank
Coolant Source/ Power Failure	0.0	5	5
Coolant Pump Set Failure	3.8	4	4
Coolant Turned Off	11.5	=1	2
Automatic Control Failure	11.5	=1	1
Condenser Fault	11.5	=1	3

The degree of agreement shown in Table 12.3 is considered fair. The comparison of the ranking of the

excessive heating sub-mode is given in Table 12.4.

Table 12.4 Comparison of Rankings from Case Histories  
and from Expert Judgement Field Survey:  
Excessive Heating

	Case Histories		Field Study
	%	Rank	Rank
Initial Overheating	15.8	=1	2
Heating/Cooling	15.8	=1	3
Changeover Fault			
Undesired Heating	10.5	=3	5
Automatic Control Failure	10.5	=3	4
Manual Control Failure	10.5	=3	1

The degree of agreement shown in Table 12.4 is considered fair. The comparison of the ranking of incorrect batch control sub-mode is given in Table 12.5.

Table 12.5 Comparison of Rankings from Case Histories  
and from Expert Judgement Field Survey:  
Incorrect Batch Control

	Case Histories		Field Study
	%	Rank	Rank
Initial Temperature			
Too Low	11.1	4	3
Initial Temperature			
Too High	0.0	5	5
Too Fast Addition of			
Reactant Relative			
to Temperature	22.2	=1	1
Incorrect Cycle	16.6	3	4
Excessive Holding.	22.2	=1	2

The degree of agreement in Table 12.5 is considered good. The comparison of the ranking of non-relief protection is given in Table 12.6. Here the comparison is between the authors' estimates and the experts estimates.

Table 12.6 Comparison of Rankings from Authors' Estimates and from Expert Judgement Field Survey:  
Non-Relief Protection

	Authors' Estimates		Field Study
	%	Rank	Rank
Incorrect Charging	0.56	=2	5
Inadequate Cooling	0.54	=2	3
Excessive Heating	0.49	=2	2
Inadequate Agitation	0.90	1	1
Incorrect Batch Control	0.48	=2	4

In view of the small differences in the authors' estimates for four of the items, these items are all shown ranked equal. A comparison of rankings is therefore not very meaningful in this case. The main point to be made is that both rankings rank highest the probability of devising measures to counter inadequate agitation.

No estimate has been made by the authors of the probabilities of recovery from incident modes and there is therefore no comparison for this case.

### 13. RISK AND RISK CRITERIA

The Fatal Accident Rate (FAR) indicated by the HSE records may be computed as follows. For the purpose of computing this, and for no other, the records for the period 1967-81 have been used. For this period the time period is 15 years. From Chapter 8 the reactor inventory is 1987.

Then, assuming 10 reactors and 2 operators per plant:

$$\begin{aligned}\text{Exposure Period} &= 1987 \times 15 \times 8760 \times 2 / 10 \\ &= 0.522 \times 10^8 \text{ operator (13.1)} \\ &\quad \text{hours}\end{aligned}$$

The FAR is defined as the number of deaths in  $10^8$  exposed hours. For a process which is manned around the clock it is equal to the number of hours in the year. It applies to the most exposed individual, which is taken here to be the reactor operator. Then for this individual we have:

$$\text{FAR} = \frac{2}{0.522 \times 10^8} \quad (13.2)$$

$$\text{FAR} = 3.8 \text{ per } 10^8 \text{ exposed hours (13.3)}$$

In the original work on the FAR as a risk criterion, the overall industry, or chemical industry, FAR was taken as 4. Allowing half of this for everyday hazards, such as falling down steps, etc., and half for special technological hazards and assuming there might be up to five of the latter, gives a target FAR for any single technological hazard of 0.4.

Thus the actual FAR is probably appreciably higher than the target value usually aimed for.

This is perhaps not surprising, since reactor overpressure is a recognized hazard. It indicates that the hazard of reactor overpressure is not an extraordinary one, but that it is appropriate to continue work to try to reduce it.

#### 14. CONCLUSIONS AND RECOMMENDATIONS

A study has been carried out of the problem of overpressure protection of chemical reactors, particularly by reaction runaways, and of the means of protection against such overpressure. Consideration has been given in particular to relief devices (bursting discs and relief valves) and to instrument systems (controls, trips and interlocks) as an alternative means of protection.

The work has included the following individual studies:

- (1) Survey of case histories
- (2) Review of specific reactions
- (3) Review of reactors
- (4) Creation of a taxonomy of reactor incidents
- (5) Study of national reactor inventory
- (6) Study of reactor incidents
- (7) Study of bursting disc failure
- (8) Study of vent system failure
- (9) Analysis of reactor incidents
- (10) Creation of fault trees for reactor incidents
- (11) Review of the means of protection against overpressure
- (12) Study of hazards of vent systems
- (13) Field study of expert opinion

The work has drawn heavily on the reactor overpressure incidents in the HSE records. The records principally used are

those for the period 1970-81. The conclusions drawn are therefore strongly influenced by the situation pertaining during that period.

A study has been made of the national reactor inventory. This is estimated to have been approximately 2,100 over the period 1970-81. This work provides the basis for virtually all estimates made of the absolute frequencies.

A study has been made of the fatalities caused by reactor overpressure. For this purpose, but for this purpose only, the period 1967-81 has been considered. There were two deaths from reactor overpressure during this period. The fatal accident risk is estimated to be  $6.8 \times 10^{-5}$  per reactor year.

The Fatal Accident Rate (FAR), which is defined as fatalities per  $10^8$  exposed hours, is estimated as 3.8, which is appreciably higher than the figure of 0.4 which is often taken as the target value. The work indicates, therefore, that the risk from overpressure of chemical reactors is a significant one and that the HSE is right to be concerned with it.

Moreover, there have been a number of incidents world-wide involving multiple fatality accidents. It would require only one such accident to cause a marked deterioration in the fatal accident risk in this country.

A study has been made of reactor overpressure incidents. Most of these incidents are from the HSE records for 1970-81 and from the world-wide collection by Nolan made for the HSE.

The case history information has been utilized in the following way. For the estimation of the absolute frequency of the principal events such as reactor overpressure or fatality the HSE case history data only has been used, in conjunction with the estimate of the national reactor inventory. For the



determination of the proportion of events in different categories, however, the larger world-wide data set has been used.

From these case histories a taxonomy of reactor overpressure has been created. The main headings of this taxonomy are system description, reaction type, pressurising fluid, pressurising event, process deviation, initiating fault, overpressure effect, bursting disc failure cause and release effects.

The main use of the taxonomy has been to classify the case history incidents first by pressurising fluid, then by pressurising event and finally by process deviation. For example, overpressure may be caused by vaporized liquid due to an exotherm of regular reaction resulting from incorrect charging.

The process deviations are also referred to as incident modes. These are the initiating events which in a proportion of cases escalate into a full overpressure incident. Typical incident modes are incorrect charging, inadequate cooling and excessive heating. A particular incident mode may be broken down into sub-modes. For example, sub-modes of inadequate cooling and cooling are coolant circulation fault and condenser fault.

The world-wide case histories have been classified using this taxonomy. Classifications have also been made for sulphonation, nitration and polymerization reactions. A summary of the proportions of incidents in the different incident modes is given in Tables 8.2-8.5 and 11.1.

Of the 66 HSE case histories considered relevant to this work 21 (32%) had an arrangement involving a bursting disc, a relief valve or both which does not appear to have been criticized by the HSE. In another 18 (27%) of cases the vessel

was open. In most of the remaining cases the vessel appears to have had neither an opening nor an adequate relief.

Of the 21 cases where there was a relief arrangement only 13 had a bursting disc. It is believed that a large proportion of these were undersized. Thus reactors which either have no bursting disc or which have one which is undersized contribute most to the incidents.

Attention is drawn also to the large proportion of incidents involving an open vessel, usually an open man-hole. Incidents of this sort will not be reduced by improved relief protection.

Of the 48 cases where the vessel was not open there were 10 (21%) where the relief operated but did not prevent the incident and 13 (27%) where a relief was fitted but failed in some way to prevent the incident for reasons which are unclear. Of other cases where there is known to have been no relief or where relief arrangements are unknown and where probably there was no proper relief 10 (21%) involve glassware shattering and 11 (23%) vessel rupture. These four situations account for 44 (92%) of the cases.

Failure of the relief arrangements therefore occurs in a significant proportion of overpressure incidents. The question is what form this failure takes.

Failure of a protective device such as a relief can be of two kinds. The dependability of such a device has two aspects: capability and reliability. The device must have the capability of performing the function for which it is intended and it must be reliable in performing that function when called on to do so. Frequently attention centres on reliability, but capability is equally important.

Studies have been made to investigate the reliability of relief systems. Two separate studies have been made. The first was a study of the reliability of bursting disc assemblies and the second was a study of the reliability of vent systems.

The study of bursting disc reliability included visits to bursting disc manufacturers to discuss failure modes and rates, review of the literature to obtain similar information and an investigation of bursting disc failure in a particular firm. The conclusion from this work is that the probability of failure on demand of a properly designed disc assembly is very low.

The study of vent system reliability was closely linked to that on bursting disc reliability. Vent system failure was discussed during the visits to the bursting disc manufacturers. An investigation of vent system failure was made in conjunction with that on bursting disc failure in the industrial firm. A review was also made of vent system failure data given in the British Plastics Federation guide on venting. The conclusion from this work is that the probability of failure on the demand of a properly designed vent system is also very low. It is therefore concluded that the majority of the relief failures occurring in the HSE case histories were caused by incorrectly designed vents. This conclusion is based primarily on the fact that the reliability of relief has been assessed as relatively high and that it appears to follow that the problem is one of capability rather than of reliability. There is, however, one piece of evidence which supports this conclusion. The BPF survey shows that in cases where there was failure of relief the relief was underdesigned.

With regard to the use of instrument systems as an alternative to relief, industrial contacts were asked whether they would prefer to dispense with relief systems and rely solely on instrumentation. No contact expressed any desire to adopt a general policy of dispensing with protection by

relief, but one or two would welcome the option of being able to use instrumentation where relief poses problems, particularly of disposal.

The work therefore supports HSE existing policy of promoting the use of relief devices and indicates that attention should be directed primarily to the proper sizing of such devices.

Several studies have been made which bear upon the practicality of devising instrumentation systems which offer alternative protection to relief devices.

The starting point is the study of incident modes. The important incident modes are shown in Table 11.1 and include incorrect charging (17.2%), inadequate cooling (13.1%), impurity reaction exotherm (10.6%), incorrect agitation (10.1%), excessive heating (9.6%) and incorrect batch control (9.1%). Also important is inadequate information on component and reaction characteristics (15.1%). These incident modes cover 85% of cases, or 90% if cases with unknown causes are redistributed among those with known causes.

The analysis of incident modes from the case histories has been supplemented by a field study in which experts have been asked to rank the relative frequency of incident modes. Comparisons are given in Tables 12.1-12.5. For the main incident modes there is broad agreement between the case history analysis and the field study, with two exceptions. The experts gave for unknown exotherm/decomposition a ranking much lower (6th out of 8) than the ranking in the case histories (2nd), while for incorrect batch control they gave a much higher ranking (2nd) than the ranking in the case studies (7th).

An analysis has been carried out of the reactor overpressure incidents. An overpressure incident occurs if an

initiating event, defined in terms of a particular incident mode, escalates sufficiently to cause such an incident; other lesser pressure rises are described as excursions.

What this analysis indicates is that initiating events are relatively frequent, but escalation to a full overpressure incident is infrequent. In other words there are mitigating features which in most instances are effective in preventing escalation and which thus introduce a large attenuation between the frequency of the initiating event and that of the overpressure incidents.

Important mitigating features are the fact that the reactor is in a critical condition only for a proportion of the time and the success of the operator taking corrective action. These and other similar mitigating features apply to virtually all reactors.

The mitigating feature which is of prime interest in the present context is the protective action of instrument systems, particularly trips and interlocks. Such systems are fitted, however, on only a proportion of reactors. This fact is quite significant in terms of the effect of such systems expressed as an attenuation factor applied to the national figures. Thus if half of the reactors in the country had trip systems which gave perfect protection, the attenuation factor obtained is still only 0.5. This is a relatively small attenuation compared with the total attenuation which is clearly taking place.

A study has been made of the practicality of providing non-relief protection. Such protection may be by hardware, primarily trips and interlocks, or by software, primarily operating procedures or computer programs.

For trip protection it is necessary to have a clearly defined action which the trip system can take. Here there is

an important distinction between a batch reactor, in which all the components are charged at the start, and a semi-batch reactor, in which all but one of the components are so charged while this other component is fed continuously. In this latter case the action of shutting off the feed is often sufficient to stop the reaction and render the system safe. This arrangement is therefore generally the preferred one where it is practical.

A study has been carried out of the practicality of devising non-relief protection to protect against the incidents which have actually occurred as given in the case histories. For each incident mode a judgement has been made of the proportion of incidents against which it might in principle be possible to devise practical and effective instrument counter-measures. This has been combined with an estimate of the proportion of occasions on which such counter-measures, if implemented, would actually have worked.

The outcome of this study is that there are three broad categories of incident mode. For the first category there is a high probability, assessed as about 90%, that such counter-measures would have prevented the incidents which occurred. In this category are inadequate information on component and reaction characteristics and inadequate agitation. For the second category the probability is assessed as about 50%. Incorrect charging, inadequate cooling, excessive heating and incorrect batch control come in this category. The probability for the third category is virtually zero. This category includes undesired catalysis, impurity reaction exotherm, water ingress and vaporization, high pressure gas ingress and recovery from fault conditions.

The implications of the foregoing discussion for the use of trip and interlock systems to provide protection and the use of fault trees to demonstrate the effectiveness of such protection are as follows.

All the evidence suggests that it is practical to provide instrumentation protection against incorrect agitation, which includes not only agitator failure but also undesirable restart of an agitator. The probability of being able to devise practical protection against this mode has been assessed as high. It is also assessed as high in the field study of expert judgement.

It is accepted that if a reaction runaway is likely to occur simply due to loss of agitation, it may be difficult to devise measures to counter this, unless feed shutoff is an available option and is effective. The proportion of cases where the hazard occurs in this extreme form is considered, however, to be low. Incidents due to situations such as agitator restart appear to be much more common.

It also appears practical to provide protection against a good proportion of sub-modes of most of the other incident modes such as incorrect charging, inadequate cooling, excessive heating and incorrect batch control. Unfortunately, for each of these incident modes there have occurred sub-modes which tend to be relatively obscure and rare against which it is judged that it would be difficult to provide specific protection.

Similarly, there are incident modes such as undesired catalysis and water ingress and vaporization against which it is judged that it is not practical to provide protection.

The conclusion which is drawn from these considerations is that for incident modes other than inadequate information and incorrect agitation it is difficult to devise counter-measures which are sufficiently comprehensive and difficult to demonstrate that this has been done.

As far as concerns the use of fault trees to demonstrate adequate protection, there are two factors which work in

opposite directions. One is that for the more common sub-modes only a small proportion of the initiating events escalate into overpressure incidents, since there are mitigating features which exert a strong attenuating effect. These factors are difficult to estimate and in many fault trees relatively little credit is claimed for them. The other is the occurrence of obscure and rare faults against which it is difficult to devise protection. Overall the mitigating features probably tend to operate mainly on the more common sub-modes which tend to be those for which protection can be devised. Thus there may be an excess of protection on these sub-modes, but a deficiency on the rarer sub-modes.

The alternative form of protection is relief. However, this also has its problems. Estimates have been made of the reliability of the relief system. But case histories suggest that failure probably occurs more often due to undersizing or otherwise incorrect design than due to failure of the disc to rupture or by blockage of the vent. Hence an assessment for relief systems also of the expected dependability.

The estimate made of the relative dependability of non-relief and of relief measures is that for the former the proportion of incidents currently occurring which would not receive protection is 44% and for the latter 16%. These are best estimates, but they involve many assumptions.

However, for semi-batch reactors when it is possible to have a trip where reactor parameters are measured and the feed is shut off, the dependability of relief and non-relief measures is estimated as approximately equal, at 15%.

Before considering policy on reactor protection, there is one further aspect which merits consideration. This is the possibility that operation of a relief system may itself give rise to a hazard. A study has been made of vent system hazard. The conclusion from this work is that in general the hazard is



not such as either to detract from the value of protection by a relief device or to tip the balance against a relief device and in favour of non-relief protection.

The work described forms the basis for the policy proposals now made.

There should be thorough screening of the components and reactions for exotherms of the regular reaction and for decomposition reactions. This mode is a major contributor to overpressure incidents. It is one which still appears to be rather underestimated by industry. The HSE policy of encouraging screening and assisting industry to perform it is strongly supported.

The default assumption in reactor design should continue to be that a relief system is provided. Failure of the relief system appears more likely to occur due to lack of capability rather than lack of reliability. Attention should focus primarily therefore on relief sizing. Relief and vent reliability should not, however, be neglected. The work which the HSE is doing on vent sizing, particularly as follow-up to the DIERS work, is timely.

A relief system may be regarded as a relatively passive form of protection compared with instrumentation, in that it is rather less susceptible to unrevealed failure and thus rather less dependent on proof testing. To this extent it is more suitable for use in a relatively unsophisticated environment.

The alternative option of the use of non-relief protection, typically a combination of hardware and software measures, should be permitted, particularly where there is a difficulty in disposal of materials vented. The effectiveness of such protection should be demonstrated, the normal method being the use of fault trees. Account should be taken of the

obscure and rare sub-modes revealed in actual incidents. Generally rather more credit than usually claimed may be allowed for mitigating features.

It is considered that the requirement to take account of obscure and rare sub-modes will not generally be excessively onerous. The actual FAR for reactors in the period studied is higher than the target value, but this results from a wide range of different practices. The practice of the better companies almost certainly already achieves an FAR below the target. It is expected that a well designed system will almost certainly give an assessed FAR below the target, even allowing for the rare sub-modes, not all of which will apply in a given case.

In reviewing a proposal for non-relief protection, it should be borne in mind that a process which can be rendered safe by the simple action of shutting off the feed is a much stronger candidate for non-relief protection than one where this is not the case.

It is necessary that the HSE policy be applicable to firms large and small, sophisticated and unsophisticated. The point has already been made that a relief system tends to be somewhat less prone to unrevealed failure and less dependent on proof testing and thus to be more robust than a non-relief system. The policy of making a relief system the default assumption is thus particularly suitable for firms which are less sophisticated and have fewer resources.

Some features which should figure in advice to small firms include the use of well defined operating procedures; the use of a limited range of instrumentation and trips; the sizing of the relief system; and the periodic inspection of the relief system.

The reporting of incidents within the HSE could also be improved. Some information which would be useful is summarized in Appendix 8.

There is need for advice to less sophisticated reactor operators. A minimal set of points is given in Appendix 9.

There remain aspects of the problem which it has not been possible to deal with in the present project and proposals are therefore made for further work.

Four principal areas of further work are suggested as follows. First, rules should be developed for the design of the overall system of protection of reactors. Second, work should be done to assist in the demonstration of the effectiveness of such protection, in particular to reconcile conventional fault trees and the incident-based fault trees developed here to furnish failure, event and human error data for use in such trees. Third, a more detailed study should be made of the hazard which may arise when material is vented. Fourth, more detailed guidance should be produced for reactor operators. This is closely linked with the first objective of developing rules.

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## 16. NOMENCLATURE

### 16.1 Symbols

A	actual discharge area	$\text{m}^2$
A	a probability ratio constant	(-)
A	reaction frequency factor	$\text{s}^{-1}$
$A_f$	cross sectional flow area in jacket	$\text{m}^2$
$A_H$	heat transfer area	$\text{m}^2$
$a_i$	row totals in F-Matrix	(-)
B	a probability ratio constant	(-)
C	constant in relief valve sizing	(-)
C	ratio of specific heats ( $C_p/C_v$ )	(-)
$C_p$	specific heat capacity of vessel contents at constant pressure	$\text{kJ/kg K}$
$C_v$	specific heat capacity of vessel contents at constant volume	$\text{kJ/kg K}$

$c$	constant standard deviation of the distribution of discriminial differences for Thurstone's case V model [62,63]	(-)
$D$	diameter of agitator blade	m
$D_c$	diameter of coil	m
$D_{c,i}$	outside diameter of coil	m
$D_{c,LM}$	log-mean diameter of coil	m
$D_{c,o}$	inner diameter of coil	m
$D_e$	equivalent diameter: four times the flow area divided by the wetted perimeter	m
$d$	discriminal difference between stimuli	(-)
$d$	number of triads	(-)
$d_{max}$	maximum number of triads	(-)
$d_i$	inside diameter of vessel	m
$E$	reaction activation energy	kJ/kgmol
$F$	constant multiplying factor	(-)
$F$	function of isentropic coefficient	(-)
$f$	entry in raw frequency matrix, F-Matrix	(-)
$f$	friction factor	(-)
$f_\mu$	liquid viscosity correction factor	(-)

G	mass flow of vapour or liquid	kg/s
G	relative density of liquid at inlet temperature to relief valve	kg/m <sup>3</sup>
G	specific gravity of liquid at flow temperature in relief valve	(-)
g	gravitational constant	m/s <sup>2</sup>
gpm	flowrate of liquid through relief valve	gal/min
$\Delta H_r$	heat of reaction	kJ/kg
$\Delta H_v$	latent heat of vaporization	kJ/kg
$h_{c,i}$	film heat transfer coefficient on inside of coil	W/m <sup>2</sup> K
$h_i$	film heat transfer coefficient on vessel inside surface or outside coil/jacket surface	W/m <sup>2</sup> K
$h_j$	film heat transfer coefficient on inside jacket surface	W/m <sup>2</sup> K
$h_o$	process side heat transfer coefficient	W/m <sup>2</sup> K
K	geometric constant	(-)
K	manufacturer's relief valve discharge coefficient	(-)
K	reaction rate constant	s <sup>-1</sup>
$K_D$	discharge coefficient	(-)

$K_H$	heat transfer factor: 0.150 for upward flow of heating fluid or downward flow of cooling fluid 0.128 for downward flow of heating fluid or upward flow of cooling fluid	W/m K
$K_T$	heat transfer constant	(-)
$k$	isentropic coefficient at inlet conditions to bursting disc	(-)
$k$	thermal conductivity	W/m K
$L$	average reactor life	years
$L$	reactor circumference	m
$M$	molecular weight of gas or liquid	kg/kgmol
$m$	number of assessors in scale ranking	(-)
$N$	national reactor inventory	(-)
$N$	number of trials	(-)
$N$	revolutions per second	revs
$N_{in}$	number of reactors insured	(-)
$N_{mn}$	number of reactors supplied by manufacturer	(-)
$N_{pc}$	average number of reactors purchased each year	(-)

$n$	number of items in scale ranking	(-)
$n$	scaleup exponent	(-)
$n_T$	maximum number of triads	(-)
$\Delta P$	pressure drop	$N/m^2$
$P$	pressure	$N/m^2$
$P$	probability	(-)
$P_w$	power input	W
$P_b$	backpressure	bar
$Q$	probability of effective protection	(-)
$Q$	unreliability	(-)
$Q$	pumping/flowrate	$m^3/s$
$Q_{mg}$	discharge capacity of gas	kg/hr
$Q_{ml}$	discharge capacity of liquid	kg/hr
$Q_{ms}$	discharge capacity of steam	kg/hr
$q$	heat transferred	W
$q_i$	entry in totalized F-Matrix	(-)
$R$	universal gas constant	$kJ/kgmol\ K$
$R$	reliability	(-)
$R_{sw}$	probability of successful switchover	(-)



r	correlation coefficient	(-)
r	probability ratio	(-)
r	reaction rate	kg/m <sup>3</sup> s
r <sub>d</sub>	fouling factor	(-)
S	number of successes	(-)
S	scale value	(-)
S <sub>in</sub>	insurer's market share	(-)
S <sub>mn</sub>	reactor manufacturer's market share	(-)
s	agitator tip speed	m/s
T	temperature	K
ΔT	temperature difference at equilibrium between initial and maximum allowable pressure	K
t	time interval to maximum allowable pressure	secs
t	time	secs
t	unit normal deviate	(-)
U	heat transfer coefficient	W/m <sup>2</sup> K
V	specific volume	m <sup>3</sup> /kg
V	volume of reactor	m <sup>3</sup>

V	volume of reaction mass	$\text{m}^3$
V	velocity of rotator	$\text{m/s}$
$V_n$	velocity of fluid leaving agitation nozzle	$\text{m/s}$
W	rated capacity of relief valve	$\text{kg/s}$
W	reaction mass	$\text{kg}$
$W_p$	mass flowrate of fluid leaving nozzle	$\text{kg/s}$
X	vessel wall thickness	$\text{m}$
x	difference between scale values	$(-)$
Y	scale value exponential term	$(-)$
Z	bulk viscosity correlation exponent	$(-)$
Z	compressibility factor of gas	$(-)$

## 16.2 Greek Letters

$\alpha$	discharge coefficient for bursting disc	$(-)$
$\beta$	coefficient of thermal expansion of fluid	$(-)$
$\phi$	fractional dead time	$(-)$
$\lambda$	failure rate	$\text{year}^{-1}$
$\theta$	temperature	$\text{K}$

$\Delta\theta$	temperature difference	K
$\Delta\theta_{LM}$	log-mean temperature difference	K
$\Omega$	sum of agreements between assessors	(-)
$\mu$	dynamic viscosity	Ns/m <sup>2</sup>
$\mu_w$	dynamic viscosity at temperature of heat transfer surface	Ns/m <sup>2</sup>
$\rho$	density	kg/m <sup>3</sup>
$\sigma$	standard deviation	(-)
$\tau_p$	proof test interval	years
$\xi$	coefficient of agreement	(-)
$\zeta$	coefficient of consistency	(-)

### 16.3 Subscripts

j	j th. term
k	k th. term
l	lower value
u	upper value
1	system one
1	upstream value

2            system two

2            downstream value

#### 16.4 Dimensionless Numbers

Nu	Nusselt number	$Nu = hd/k$
Re	Reynolds number	$Re = \rho Vd/\mu$
Pr	Prandtl number	$Pr = \mu C_p/k$

## APPENDIX 1 - FAILURE DATA CONFIDENCE LIMITS

The statistics for confidence limits of rates of failure are dealt with in the text books but confidence limits of failure on demand are not dealt with in books, especially in the case of a sample containing no failures. The information below gives a brief description of the use of confidence limits and how they are used in both these cases.

### A1.1 Confidence Limits

A sample of  $n$  units is randomly drawn from a very large population in which the proportion of units bearing a certain character,  $A$  is  $p$ . In the sample  $x$  individuals bear the character  $A$  and  $(n-x)$  do not. The value of  $p$  is unknown and the problem is to obtain limits  $p_1$  and  $p_2$  such that we may feel with a given degree of confidence that:

$$p_1 < p < p_2 \quad (A1.1)$$

The sections below provide a description of the method by which the limits  $p_1$  and  $p_2$  can be found by using charts developed by Clopper and Pearson [68].

### A1.2 The Binomial Theorem

When a sample of  $n$  components is taken from a population and the probability of successfully finding a faulty component

is  $p$  and the chance of failing to find a faulty component is  $q$ , where  $(p+q) = 1$ , then the probability of getting  $r$  successes and  $(n-r)$  failures in  $n$  trials from this sample can be found by the theory of compound probability as:

$$P(r) = {}_nC_r p^r q^{(n-r)} \quad (A1.2)$$

We can have any number of successes from zero to  $n$ , therefore  $r$  can also take any of the values from zero to  $n$ . Hence:

$$(p+q)^n = P(0) + P(1) + P(2) + \dots + P(r) + \dots + P(n) \quad (A1.3)$$

or alternatively:

$$(p+q)^n = {}_nC_0 q^n + {}_nC_1 p^1 q^{(n-1)} + \dots + {}_nC_r p^r q^{(n-r)} + \dots + {}_nC_n p^n \quad (A1.4)$$

where:

$${}_nC_r = \frac{n!}{(n-r)!r!} \quad (A1.5)$$

Thus if the probability of finding a failed item in the population, from which a sample of ten items is taken, is 0.2 we can calculate the probability of selecting two faulty items from the sample as shown below. From above definitions we can say that:

$$p = 0.2 \quad q = 1-p = 0.8 \quad n = 10 \quad \text{and} \quad r = 2$$

Hence the probability of finding two faulty items is:

$$P(2) = \frac{10!}{(10-2)!2!} (0.2)^2 (0.8)^8$$

$$P(2) = \underline{0.302}$$

Thus the probability of finding two failed items in this sample is 0.302. The problem is that if we examine each item in a sample and calculate a probability of failure for this sample how close is this to the correct population probability of failure which is unknown.

### A1.3 The Chi-Squared Distribution

If a sample is taken from the normal population and we determine the number of failures it contains the difference between the observed and expected frequency can be attributed to random sampling error.

We can define a term  $\chi^2$  which relates the observed value in the sample to the expected value in the population and which indicates the extent of the sampling error. This is defined as:

$$\chi^2 = \sum_{i=1}^{i=n} \frac{(y_i - x_i)^2}{x_i} \quad (A1.6)$$

for a sample of size  $n$  where the observed frequency of  $i$  failures is  $y_i$  and its expected frequency is  $x_i$ . The sample can contain between zero and  $n$  faulty items, the probability of successfully finding them being between zero and unity. The sum of the probabilities of the sample containing between zero

and  $n$  faulty items will always total one thus there are  $(n-1)$  degrees of freedom,  $\nu$ , thus we need only calculate  $\chi^2$  for obtaining upto  $(n-1)$  faulty items. i.e. we can write for a sample of size  $n$ , variance  $\sigma^2$ , and mean expected result  $\mu$ :

$$\chi^2 = \sum_{i=1}^{\nu} \frac{(y_i - \mu_i)^2}{\sigma_i^2} \quad (\text{A1.7})$$

where  $\nu = (n-1)$  and  $s_i^2 = (y_i - \mu_i)^2$ , referred to as the mean square estimate of the unknown value of a population variance.

This is the same for each probability hence:

$$\chi^2 = \frac{\nu s^2}{\sigma^2} \quad (\text{A1.8})$$

Chi-squared is tabulated in terms of a probability of achieving a mean square estimate,  $s^2$ , and varies with the number of degrees of freedom  $\nu$ , dependent on the sample size  $n$ . Then  $s^2$  is distributed as  $\chi^2 \sigma^2 / \nu$ . It follows that there is a probability,  $\alpha$ , that:

$$s^2 > \chi_{\alpha}^2 \sigma^2 / \nu \quad (\text{A1.9})$$

and  $s^2 < \chi_{1-\alpha}^2 \sigma^2 / \nu \quad (\text{A1.10})$  ?

where  $\chi_{\alpha}^2$  and  $\chi_{1-\alpha}^2$  are, respectively, the upper and lower  $100\alpha\%$  points of the  $\chi^2$  distribution for  $\nu$  degrees of freedom.



Thus there is a probability of  $\alpha$  that  $s/\sqrt{u}/\chi_\alpha > \sigma$  and a probability of  $\alpha$  that  $s/\sqrt{u}/\chi_{1-\alpha} < \sigma$ . Since for  $\alpha < 0.5$ ,  $\sqrt{u}/\chi_\alpha < \sqrt{u}/\chi_{1-\alpha}$ , it follows that the probability is  $1-2\alpha$  that the unknown  $\sigma$  is included between the limits:

$$\Pr \left\{ \frac{s/\sqrt{u}}{\chi_\alpha} < \sigma < \frac{s/\sqrt{u}}{\chi_{1-\alpha}} \right\} = 1-2\alpha \quad (\text{A1.11})$$

The value of  $\alpha$  can be taken as 0.025 or 0.005 to give a 95% or 99% probability that the value of the population  $\sigma$  lies between the above limits.

For the case where no failures are observed it is possible to make an estimate of the upper confidence limit in a similar fashion with appropriate values of  $S$  and  $N$  (number of successes and number of trials respectively).

Further accounts of confidence limits on failure data are given by Bazovsky [70] and by Green and Bourne [71].

#### A1.4 Clopper and Pearson Charts

Using the above information charts can be constructed to determine the limits between which the population  $\sigma$  lies. From equation (A1.2) for a sample of size  $N$  and standard deviation  $\sigma$  we can calculate a probability of finding  $S$  faulty items (successes) as  $P(S)$ . The value of  $\chi^2$  can be found for  $(N-1)$  degrees of freedom from tables using this probability. For the required confidence limits, i.e. mean square error  $s^2$ ,  $us^2/\sigma^2$  can be calculated and the two probabilities,  $P_A(S)$  and  $P_B(S)$  such that  $P_A(S) < P_B(S)$  found from chi-squared tables. These values are plotted versus  $S/N$  for  $100\alpha\%$  confidence limits. The charts are plotted for varying sample sizes from  $N=8, 10, 12$  to  $100, 400, 1000$ . Examples of these charts are given by Pearson and Hartley [69].

### A1.5 Example Calculations of Confidence Limits

From above, the probability of finding two faulty items in a sample of ten when the probability of success was known to be 0.2 was calculated as 0.302. If we did not know the probability of success we could calculate probability limits with, for instance 95% confidence, between which the probability lies.

In this case  $S=2$  and  $N=10$  thus using charts [69] we can read the limits as 0.025 and 0.555. Thus the probability of finding two failed items in a sample from this population lies, with 95% confidence, between 0.025 and 0.555.

When there are no recorded failures in the sample we can treat the information as indicated by the following example.

If we have a sample of ten items i.e.  $N=10$  and there are no recorded failures then  $S=0$ . Hence  $S/N$  is zero and from charts [69] we can find the upper 95% confidence limit as 0.31, the lower confidence limit being 0.

## APPENDIX 2 - REACTOR INVENTORY STUDY

An investigation has been made to obtain an estimate of the population, or inventory, of reactors in use in the country. Two basic approaches have been taken to arrive at this estimate. The first, method one, is to derive the estimate from:

- (a) The number of reactors insured by a major insurance company, and
- (b) The company's estimate of the market share.

The second approach is to derive the estimate from:

- (a) The number of reactors supplied to the market by a major reactor manufacturing company, and
- (b) The companies estimate of its market share, and
- (c) An estimate of the average life of a reactor obtained from the insurance company data.

In both cases the data were supplied in confidence so only the formulae for the estimation of the reactor inventory and the final result will be given here and not the crude data.

For method one the formula used takes the form:

$$N = \frac{N_{in}}{S_{in}} \quad (A2.1)$$

where  $S_{in}$  is the insurers' market share,  $N$  the national reactor inventory and  $N_{in}$  the number of reactors insured by the insurer.

The initial estimate obtained using the insurer's own estimate of the market share was  $N = 1680$  reactors.

It was subsequently concluded that allowing for self-insurance, particularly with small laboratory reactors, the insurer's estimate of the market share was somewhat high and that this estimate should be reduced to 70% of the given value. In this case  $N = 2400$ .

For method two the formula used is:

$$N = L \times N_{pc} \quad (A2.2)$$

where  $L$  is the average life of a reactor and  $N_{pc}$  the average number of reactors purchased each year.  $N_{pc}$  is estimated from the formula:

$$N_{pc} = \frac{N_{mn}}{S_{mn}} \quad (A2.3)$$

Where  $N_{mn}$  is the number of reactors supplied by the manufacturer to the market each year and  $S_{mn}$  the manufacturers market share.

The average life of a reactor was obtained from the insurer's data as shown in Table A2.1, which gives the proportion of reactors first insured in the periods shown. The proportion of the total inventory which is renewed each year is approximately 4.2%. The rate of purchase has been fairly

steady over the period 1966-1984. The average life  $L$  is thus some 23.8 years.

Table A2.1 Reactor Inventory Study: Year of Reactor Insurance

	Proportion (%)
1914 - 1950	1.9
1951 - 1955	6.3
1956 - 1960	6.2
1961 - 1965	9.6
1966 - 1970	16.8
1971 - 1975	21.2
1976 - 1980	23.5
1981 - 1984	14.5
Total	100.0

The manufacturer produces a variety of vessels some of which are reactors and some of which are various types of jacketed tanks and storage vessels. It has been necessary to estimate the proportion of the first two which are actually used as reactors. This is because the buyer can acquire his own agitator and reactant feeding devices and attach them to the vessel on site rather than have them fitted by the manufacturer of the vessel. A previously used set of equipment can also be used for this purpose. This then enables the vessel to be used as a reactor or blending vessel etc. Thus it has been assumed that two thirds of the "reactors" are used as actual reactors and the others for operations such as mixing, distillation, crystallization, etc. and that one quarter of the other jacketed vessels, which are much smaller in number than the "reactors", are used as reactors.

It was possible to obtain from the manufacturer the figures for the number of vessels manufactured over the period 1979 to 1985 and a detailed breakdown for the year 1985 as

well as his estimates for the proportion exported and of his market share in this country. It was thus possible to calculate  $N_{mn}$  and  $S_{mn}$ . From this data:

$$N_{pc} = 122 \text{ reactors per year and}$$

$$N = 2900 \text{ reactors}$$

The two estimates obtained by methods one and two are thus 2400 and 2900. There is no reason to suppose one method more accurate than another and therefore taking an average of these two values the number of reactors is 2650.

A further cross check can be made on this figure by making added estimates based on:

- (a) The number of firms with reactor inventories of more than 100 and
- (b) The proportion of reactors attributable to such firms as given by the insurers data.

The figure which was obtained in this way for the national reactor inventory is much more approximate but it suggests that the above values are of the right order.

The estimate of the national reactor inventory just given is for 1985. An estimate is also required for the period covered by the full HSE case histories records, which cover the period 1970-1981. From data given in Table A2.1 the proportions of reactors installed in 1984 which were already installed in 1970 and in 1981 are 41% and 65%. In both cases there will have been others installed which were taken out of commission by 1981. The proportions of the 1984 national reactor inventory in 1970 and 1981 are taken as 65% and 95%. Then for mid-period, say, 1976, the proportion is taken as the

average of these two values, i.e. 80%. Hence for the period considered we have approximately:

$$N = 0.8 \times 2650 = 2100$$

A further estimate of the national reactor inventory is required for the period 1967-1981, which covers a slightly longer period of HSE records and which includes two fatal accidents. The proportion of the 1984 national reactor inventory in 1967 and 1981 are taken as 54% and 95%. Then for mid-period, say 1974, the proportion is taken as the average of these values, i.e. 75%. Hence for the period considered we have approximately:

$$N = 0.75 \times 2650 = 1987$$

Thus there were 1987 reactors in commission in the period 1967-1981.

Some further information gathered for the reactor inventory study is shown in the following tables:

Table A2.2 Reactor Inventory - Reactors Classified by Age

Year		Proportion %
1914 - 1950		2.5
1951 - 1960		12.2
1961 - 1970		25.7
1971 - 1980		45.1
1981 - 1985		14.5
Total	1914 - 1985	100.0

Table A2.3 Reactor Inventory - Reactors Classified by Type

Type	Proportion %
Autoclave	2.7
Reaction Vessel	11.7
Jacketed Reactor	18.1
Jacketed Pan	42.7
Jacketed Vessel	11.3
Limpet Coil Reactor	6.3
Limpet Coil Vessel	1.2
Mixing Vessel	0.4
Mixing Reactor	0.2
Jacketed Mixer	5.3
Limpet Coil Blending Vessel	0.1
Total	100.0

Table A2.4 Reactors Classified by Material of Construction

Material	Proportion %
Mild Steel	25.6
Mild Steel Glass Lined	44.9
Mild Steel Enamel Lined	0.1
Mild Steel Stainless Steel Lined	4.3
Cast Iron	0.1
Stainless Steel	23.0
Stainless Steel Glass Lined	1.9
Aluminium	0.1
Total	100.0



Table A2.5 Reactors Classified by Working Pressure

Internal Pressure	Proportion %	Jacket Pressure	Proportion %
-15 - 0	4.5	0 - 15	4.1
0 - 15	14.0	16 - 30	7.7
16 - 30	8.5	31 - 45	7.5
31 - 45	44.5	46 - 60	13.5
46 - 60	6.7	61 - 75	39.9
61 - 75	1.9	76 - 90	10.0
76 - 90	2.0	91 - 105	8.3
91 - 105	9.1	106 - 120	0.3
106 - 120	0.3	121 - 150	4.0
121 - 150	3.9	151 - 180	0.2
151 - 180	0.2	181 - 210	0.2
181 - 210	0.1	211 - 300	1.7
211 - 300	1.0	301 - 355	2.0
500 - 751	3.1	356 - 550	0.4
Total	100.0	Total	100.0

### APPENDIX 3 - BURSTING DISC FAILURE STUDY

A study has been carried out of bursting disc and vent system failure using records made available by a chemical manufacturer.

Information was obtained on the reactor system at risk. For each reactor this included the period of operation and the existence of a bursting disc and vent system. There were records on the type and manufacturer of the bursting disc system for some 50% of the installations.

From the operating records it was possible to obtain data on incidents and on inspections. The basic data obtained from the analysis are shown in Table A3.1. Bursting disc entries are characterized as fail dangerous or fail safe (safe as far as reactor overpressure is concerned) or as successful operations of the disc. Detection modes are inspection or operation. Vent entries are characterized as fail dangerous or successful operations of the vent system and detection modes again as inspection or operation.

The notation used in the following tables is as indicated below:

(1) Failure Modes:

FD = Fail Dangerous Failure.

FD\* = Fail Dangerous Failure, i.e. in dangerous direction, but not such as to permit significant overpressure.

FS = Fail Safe Failure.

SO = Successful Operation of the Bursting Disc.

(2) Relief Devices:

Relief devices are given in order of arrangement starting with the inner device.

C = Conventional Disc.

G = Graphite Disc.

RB = Reverse Buckling Disc.

RV = Relief Valve.

V = Vent.

Table A3.1 Bursting Disc and Vent System Failure Study:  
Basic Data

A - Fail Dangerous Failures

Case Number	Unit	Relief	Detection	Failure Mode
FD1*	Tank	C/RB/V	I	Reversal
2*	Tank	C/RB/V	I	Reversal
3*	Reactor	C/C/V	I	Reversal
4*	Reactor	C/C/V	I	Reversal
5	Reactor	RB/RB/V	I	Roll Through
6	Reactor	RB/RB/V	I	Roll Through
7	Tank	RB/V	I	Roll Through
8*	Reactor	RB/RB/V	I	Incomplete Petal
9	Reactor	RB/RB/V	I	Roll Through
10	Reactor	RB/RV/V	I	Roll Through
11*	Reactor	G/V	I	Polymerization
12*	Reactor	G/V	I	Polymerization

## B - Fail Safe Failures

Case Number	Unit	Relief	Detection	Failure Mode	Vent Clear /Operated
FS1	Tank	C/V	O	Corrosion	Y
2	Tank	C/V	O	Corrosion	Y
3	Tank	C/V	O	Corrosion	Y
4	Tank	C/V	O	Corrosion	Y
5	Tank	C/V	O	Corrosion	Y
6	Tank	C/V	O	Corrosion	Y
7	Tank	C/V	O	Corrosion	Y
8	Tank	C/V	O	Corrosion	Y
9	Tank	C/V	O	Corrosion	Y
10	Tank	C/V	O	Corrosion	Y
11	Tank	C/V	O	Corrosion	Y
12	Tank	C/V	I	Damaged	-
13	Reactor	C/C/V	I	Pinholing	-
14	Reactor	C/C/V	I	Wrinkled	-
15	Tank	RB/V	I	Pinholed, Inner Disc	-
16	Tank	G/RV/V	O	Burst	-
17	Tank	G/RV/V	O	Burst	-
18	Tank	G/RV/V	O	Burst	-
19	Tank	G/RV/V	O	Burst	-
20	Tank	G/RV/V	O	Burst	-
21	Tank	RV/G/V	O	Burst	-
22	Tank	RV/G/V	O	Burst	-
23	Tank	RV/G/V	O	Burst	-
24	Tank	RV/G/V	O	Burst	-
25	Reactor	G/RV/G/V	I	Cracking	-
26	Reactor	C/C/V	I	Pinholed, Inner Disc	-
27	Tank	C/C/V	O	Reversal Under Vacuum (inner disc)	-
28	Tank	C/C/V	O	Pinholing	-

29	Vaporizer	G/G/V	0	Burst (inner disc)	-
30	Vaporizer	G/G/V	0	Cracked (inner disc)	-
31	Reactor	C/C/V	0	Reversal Under Vacuum (inner disc)	-
32	Reactor	C/C/V	0	Fatigue Cracking (inner disc)	-
33	Reactor	C/C/V	0	Fatigue Cracking (inner disc)	-
34	Reactor	C/C/V	0	Fatigue Cracking (inner disc)	-
35	Reactor	C/C/V	0	Fatigue Cracking (inner disc)	-

## C - Successful Operations

Case Number	Unit	Relief	Cause of Overpressure	Vent Operation
S01	Tank	C/V	Unknown	Y
2	Vaporizer	RB/V	Operational	Y
3	Vaporizer	RB/V	Pressure Test	Y
4	Vaporizer	RB/V	Line Blowing	Y
5	Reactor	G/G/V	Steaming	Y
6	Catchpot	G/V	Nitrogen	Y
7	Reactor	RB/RB/V	Experiments	Y
8	Reactor	G/RV/G/V	Unknown	Y
9	Reactor	G/RV/G/V	Unknown	Y
10	Reactor	G/RV/G/V	Unknown	Y
11	Reactor	G/RV/G/V	Unknown	Y
12	Reactor	G/RV/G/V	Unknown (inner disc)	-
13	Reactor	G/RV/G/V	Unknown (top disc)	-
14	Vaporizer	G/G/V	Operational	Y
15	Vaporizer	G/G/V	Operational	Y
16	Vaporizer	G/G/V	Operational	Y
17	Reactor	RB/RV/V	Reaction Runaway	Y
18	Reactor	RB/RV/V	Operational	Y
19	Reactor	RB/RV/V	Operational	Y

The reactor pressure regimes are characterized as reaction runaway, reactor overpressure, operational overpressure (including line blowing and nitrogen overpressure), normal pressure, reverse pressure (vacuum) and unknown. The distinction between reactor overpressure and operational overpressure is based on interpretation of the records. The former means not necessarily reaction runaway, but some pressure excursion due to the reaction, while operational overpressure is due to other operations such as inerting and line clearing.

The entries in Table A3.1 are by reactor rather than by time sequence. The failure modes therefore tend to be grouped, with a sequence of similar failures characteristic of that reactor or set of reactors, though the actual failures may have taken place over a period of years.

An analysis of the data on bursting discs given in Table A3.1 is shown in Table A3.2. The vent system failure data given in Table A3.1 are analyzed in Appendix 4.

Table A3.2 Bursting Disc Failure Study: Analysis of Failures

	Number of Incidents (all vessels)
<u>A - Fail-to-Danger Modes</u>	
FD	
Reverse Buckling Disc:	
Roll Through	5
Total	5
FD*	
Conventional Disc:	
Reversal	4
Reverse Buckling Disc:	
Incomplete Petalling	1
Graphite Disc:	
Some Polymerization	2
Total	7

## B - Fail-Safe Modes

FS

### Conventional Disc:

Corrosion	11
Damage	1
Pinholing	3
Reversal Under Vacuum	2
Fatigue Cracking	4

### Reverse Buckling Disc:

Pinholing	1
-----------	---

### Graphite Disc:

Cracking	2
Burst	10

Total	35
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## C - Summary

	Number of Incidents					I/O Total	
	Overpressure Runaway	Other	Normal	Pressure Reverse	Unknown		
Successful Bursts	1	11	-	-	7	-	19
Fail-to-Danger; Operation	-	-	-	-	-	-	0
Inspection	-	-	-	-	-	12	12
Fail-Safe; Operation	-	-	27	2	-	-	29
Inspection	-	-	-	-	-	6	6
Total							66



Note:

(1) This consists of inspections and tests by observation, etc.

This data may be analyzed to obtain an estimate of the probability that a bursting disc will fail in the fail-to-danger mode when a demand occurs.

For reactors only of which there are 24:

Total Exposure Period	= 164 reactor years
Number of Failures (in FD mode)	= 4
Failure Rate	= 4/164
	= 0.024 faults/reactor year

Number of Demands = 11

Number of Failures on demand = 0

From this data estimates can be made of the predicted and observed fractional dead times, or probabilities of failure on demand. For the predicted value:

$$\phi = \frac{\lambda \tau_p}{2} \quad (\text{A3.1})$$

where  $\lambda$  is the failure rate (failures per year),  $\tau_p$  the proof test interval (years) and  $\phi$  the fractional dead time.

From inspection of the records, the test interval is rather irregular but it is generally of the order of one year. Thus we have:

Inspection Interval,  $\tau_p = 1$  year

Fractional Dead Time,  $\phi = 0.024 \times 1/2 = 0.012$

For the observed value there is no failure on demand. The usual approach in such a case is to assume that a failure would have occurred at the next demand. The point estimate is then:

Failure Probability =  $1/(11+1) = 0.083$

The confidence limits for failure probability are given by Clopper and Pearson [68]. Applying this method.

Number of Trials,  $N = 11$

Number of Successes,  $S = 11$

$S/N = 11/11 = 1$

95% confidence limits on probability of success.

Upper Limit = 1.00

Lower Limit = 0.68

and thus on failure:

Lower Limit = 0.00

Upper Limit = 0.32

The predicted and observed values of the fractional dead time (fdt) are thus:

Predicted Dead Time = 0.012

Observed Dead Time = 0.083

95% confidence limits on the observed fractional dead time is 0-0.32.

As usually occurs in cases where there are insufficient data points, the confidence limits are very wide and the value of the upper limit of the observed failure dead time is very pessimistic.

The demand rate from the reactors on the bursting discs is:

Number of Demands = 11

Demand Rate =  $11/164 = 0.067$  demands/reactor year

#### APPENDIX 4 - VENT SYSTEM FAILURE STUDY

The study of bursting disc and vent system failure using the records of a chemical manufacturer described in Appendix 3 yields information on the failure of vent systems as well as of bursting discs.

In this study there were no vent system failures on demand but there were a number of successful ventings. These were of two types: venting following an overpressure and venting following fail safe disc rupture.

For the case of vents the vents on all the discs are considered. Then the successful ventings were;

Number of Ventings following Overpressure = 17

Number of Ventings following Fail Safe        = 11  
Disc Rupture

Total Number of Ventings                        = 28

There were two blockages which were detected by inspection. One was a small column of water, which is not considered to constitute a fail-to-danger failure. The other was polymerization due to leakage of material from the relief system on another vessel on a common vent system. This is considered to be a potential fail-to-danger failure.

These data may be analyzed in a manner similar to the analysis made for bursting discs to obtain an estimate of the probability that a vent system will fail in the fail-to-danger mode when a demand occurs.

For all vessels:

Number of Vessels	= 41
Total Exposure Period of Vessels	= 262 vessel years
Number of Failures	= 1
Failure Rate	= $1/262$
	= 0.0038 per vessel year
Number of Demands	= 28
Number of Failures on Demand	= 0

From this data estimates can be made of the predicted and observed fractional dead times. For the predicted value:

Inspection Interval	= 1 year
Fractional Dead Time	= $0.0038 \times 1/2$
	= 0.0019

For the observed value:

Failure Probability	= $1/(28 + 1)$
	= 0.034

S/N	= $28/28 = 1$
-----	---------------

95% confidence limit on failure:

Lower Limit	= 0.00
Upper Limit	= 0.15

The predicted and observed fractional dead (fdt) times are thus:

Predicted Dead Time = 0.0019

Observed Dead Time = 0.0340

95% confidence limits on observed fdt = 0 - 0.15

Another source of information on vent system failure is the work of the British Plastics Federation on venting, which is described in the BPF guide [44] and also by Singh [72]. Details of several specific incidents are given by Booth, Karmarkar, Knight and Potter [73].

The work is concerned primarily with vent sizing, but it includes a survey of relief and vent failures.

Singh gives a graph in which incidents are plotted on an FIA type plot of vent diameter versus reactor capacity. There are some 43 points, of which 40 did not involve vessel damage and 3 did. The three damage points are all in the small vent diameter region and probably the reliefs were undersized by the FIA criterion. If it is assumed that in these three cases vessel damage was due to an undersized relief and not due to vent system failure, then excluding these three cases there were 40 successful ventings out of 40 demands.

However, we understand from our contacts with the BPF workers that although there were 43 reaction runaway incidents, in only 10 of these was there either operation of the relief device or damage to the vessel. The others were presumably less severe excursions. In the two cases there was no relief fitted, in two cases the relief was apparently undersized and in one the material went solid in the vent.

There was therefore in this survey one case which may be categorized as vent system failure.

It is concluded, however, that the information from this survey is not such as to allow quantitative estimates to be drawn from it.

Vent failures have been one of the incidents about which we have inquired on the industrial visits. The following incidents were mentioned:

- (1) Overpressure of a polypropylene vent system after operation.
- (2) Fragments of bursting disc stuck in vent pipe.
- (3) Bursting disc grid was entrained down vent pipe.
- (4) Baffle plate on end of vent deflected material onto side of building.
- (5) Blockage of vent pipe due to solidification of vented material (This is the incident in the BPF survey already mentioned).

## APPENDIX 5 - NON-RELIEF PROTECTION STUDY

As described in Chapter 11, the incident modes have been analyzed to determine the effectiveness of possible methods of protection. The method of analysis used is that described in Chapter 11. The analysis for the individual incident modes are as follows:

### A5.1 Regular Reaction Inadequate Information

This mode has two aspects. Originally it was defined as regular reaction unknown exotherm, but it was clear from the incidents that the question was rather wider than this and that in some cases the problem was the failure of the laboratory to define sufficiently closely the conditions under which the process was to be operated.

For this mode protection is by:

- (1) Laboratory screening.
- (2) Procedure for transfer of information from laboratory to plant.

Effectiveness is estimated as:

$$\begin{array}{ll} P_1 = 1.0 & P = P_1 \times P_2 \\ P_2 = 0.9 & P = 0.9 \end{array}$$

This assumes a highly competent laboratory.



A5.2 Incorrect Charging

Protection:

- (1) Procedures for quality control of reactants, including particle size, stabilizers.
- (2) Control of reactant flows, including metering systems, weighing machines.
- (3) Trip on reactant flows.
- (4) Procedures for reactant addition, particularly where one reactant has been initially omitted or where batch seems not to be reacting.

Effectiveness:

Mode	P <sub>1</sub>	P <sub>2</sub>	Incidents	Weighted Incidents
E5.1	0.8	0.9	11	7.9
E5.2	0.7	0.8	10	5.6
E5.3.1,	0.8	0.9	8	5.8
E5.3.2				
E5.6	0.5	0.5	4	1.0
E5.7	0.5	0.5	2	0.5
Total			35	20.8

Taking into account all the E5 incidents (see section 8.1)

$$\text{Number of Incidents} = 35$$

$$\text{Probability} = 20.8/35 = 0.594$$

### A5.3 Inadequate Cooling

#### Protection:

- (1) Design for high reliability coolant source.
- (2) Alarm on coolant pressure, flow, temperature.
- (3) Control of reactant temperature.
- (4) Trip on reactor temperature.

#### Effectiveness:

Mode	P <sub>1</sub>	P <sub>2</sub>	Incidents	Weighted Incidents
E6.1	1.0	0.7	5	3.5
E6.3	1.0	0.9	2	1.8
E6.2.3	1.0	0.9	1	0.9
E6.2.4	1.0	0.9	3	2.7
E6.2.8,	1.0	0.8	6	4.8
E6.2.9				
Total			17	14.2

Number of Incidents = 26

Probability =  $14.2/26 = 0.54$

### A5.4 Excessive Heating

#### Protection:

- (1) Batch cycle controller/computer.
- (2) Control of reactor temperature.
- (3) Trip on reactor temperature.

- (4) Procedures for batch start-up, and changeover from heating to cooling.

Effectiveness:

Mode	$P_1$	$P_2$	Incidents	Weighted Incidents
E7.1, E7.2, E7.3	0.8	0.9	8	5.8
E7.8, E7.9	1.0	0.9	4	3.6
Total				9.4

Number of Incidents = 19

Probability =  $9.4/19 = 0.49$

A5.5 Inadequate Agitation

Protection:

- (1) Alarm on agitator rotation.
- (2) Alarm on agitator paddle.
- (3) Interlock to inhibit feed on loss of agitation.
- (4) Procedures on failure to start agitator or loss of agitation.

Effectiveness:

$$P_1 = 1.0$$

$$P_2 = 0.9$$

$$P = 1.0 \times 0.9 = 0.9$$

A5.6 Incorrect Batch Control

Protection:

- (1) Batch cycle controller/computer.
- (2) Procedures on batch cycle control, including avoidance of excessive holding, or stewing.

Effectiveness:

Mode	P <sub>1</sub>	P <sub>2</sub>	Incidents	Weighted Incidents
E9.1	1.0	0.9	2	1.8
E9.3	1.0	0.9	4	3.6
E9.6	1.0	0.9	4	3.2
Total				8.6

Number of Incidents = 18

Probability = 8.6/18 = 0.48

A5.7 Undesired Catalysis

Protection:

- (1) Procedures for cleaning out after batch.
- (2) Procedures for catalyst addition, particularly where batch seems not to be reacting.

Effectiveness:

Mode	P <sub>1</sub>	P <sub>2</sub>	Incidents	Weighted Incidents
E10.1	1.0	0.5	2	1.0
Total				1.0

Number of Incidents = 5

Probability =  $1.0/5 = 0.2$

A5.8 Impurity Reaction Exotherm

Protection:

(1) Procedures for quality control of reactants.

Effectiveness:

Mode	P <sub>1</sub>	P <sub>2</sub>	Incidents	Weighted Incidents
D3.1	0.3	0.3	11	1.0
Total				1.0

Number of Incidents = 21

Probability =  $1.0/21 = 0.05$

#### A5.9 Regular Reactant Unknown Decomposition

Protection:

- (1) Laboratory screening.

Effectiveness:

$$\begin{aligned} P_1 &= 1.0 & P &= 1.0 \times 0.9 = 0.9 \\ P_2 &= 0.9 \end{aligned}$$

#### A5.10 Water Ingress and Vaporization

Protection:     None

Effectiveness:

$$P = 0$$

#### A5.11 Air Ingress and Combustion

Protection:

- (1) Design to avoid air ingress.
- (2) Procedures to avoid air ingress.

Effectiveness:

$$\begin{aligned} P_1 &= 0.9 & P &= 0.9 \times 0.9 = 0.8 \\ P_2 &= 0.9 \end{aligned}$$

#### A5.12 High Pressure Gas Ingress

Protection:      None

Effectiveness:

$$P = 0$$

#### A5.13 Exotherm of Unknown Type

Protection:

(1) Laboratory screening.

Effectiveness:

$$\begin{aligned} P_1 &= 1.0 & P &= 1.0 \times 0.9 = 0.9 \\ P_2 &= 0.9 \end{aligned}$$

#### A5.14 Recovery from Fault Condition

Protection:      None

Effectiveness:

$$P = 0$$

The foregoing estimates are summarized in Table A5.1.

Table A5.1 Reliability of None-Relief Protection

Mode	Reliability
Regular Reaction, Inadequate Information	0.90
Incorrect Charging	0.59
Inadequate Cooling	0.54
Excessive Heating	0.49
Inadequate Agitation	0.90
Incorrect Batch Control	0.48
Undesired Catalyst	0.20
Impurity Reaction Exotherm	0.05
Regular Reaction, Unknown Decomposition	0.90
Water Ingress and Vaporization	0.00
Air Ingress and Combustion	0.80
High Pressure Gas Ingress	0.00
Exotherm of Unknown Type	0.90
Recovery from Fault Conditions	0.00



## APPENDIX 6 - EXPERT OPINION EVALUATION

Described below is the basic theory behind the method used to evaluate expert opinion. It covers the techniques on how to rank information by a given attribute and then scale this ranking. The equations are those used in Chapter 12.

### A6.1 Thurstone's Judgement Scaling Model

Thurstone presented a mathematical model [62,63] for relating scale values of a set of stimuli to observable proportions. The basic model is as follows:

We take, as given, a series of stimuli to which the subject can respond differentially with respect to a given attribute. The task is to locate these on a subjective or psychological continuum in such a way that we can account for the magnitudes of responses given by the observer. In Thurstone's terminology, each psychological magnitude is mediated by a "discriminal process" between stimuli.

A given stimulus does not always excite the same discriminial process between observers, but may excite one with a higher or lower value on the psychological continuum. As a result, instead of a single discriminial process always associated with a given stimulus, we have a number of discriminial processes forming a frequency distribution for that stimulus. The postulate is made that the discriminial processes associated with a stimulus forms a normal distribution on the psychological continuum.

The standard deviation of this distribution is called the discriminial dispersion of that stimulus. The discriminial dispersions, as well as the scale values, may be different for different stimuli and are characteristic of the stimuli. The scale value of the stimulus on the psychological continuum is defined as the value of its modal discriminial process. In a normal distribution the mode, median and mean coincide so the scale value of the stimulus can also be considered to be the median or mean discriminial process associated with this stimulus. Figure A6.1 gives an illustration of such a continuum along with the distributions associated with four stimuli: 1,2,3 and 4. Thus the scale value of stimulus  $j$  is  $s_j$ .

The observer cannot report directly the value of the discriminial process on the psychological continuum. Hence, we cannot obtain directly from the observer the frequency distribution associated with a stimulus. Scaling the stimuli must always be done indirectly.

We can however deduce equations relating judgements of relations among stimuli to the scale values and dispersions of the stimuli on the psychological continuum. We can then use these equations to estimate the scale values and dispersions of the stimuli. Finally, we can test the model by determining the goodness of fit of the theory to the observed data. The equations to be used are known collectively as the law of comparative judgement and use the principles of paired comparisons to relate two stimuli.

#### A6.2 The Law of Comparative Judgement

The law of comparative judgement is a set of equations relating the proportion of times any given stimulus  $k$  is judged greater on a given attribute than any other stimulus  $j$  to the scale values and discriminial dispersions of the two stimuli on the psychological continuum. The equations are

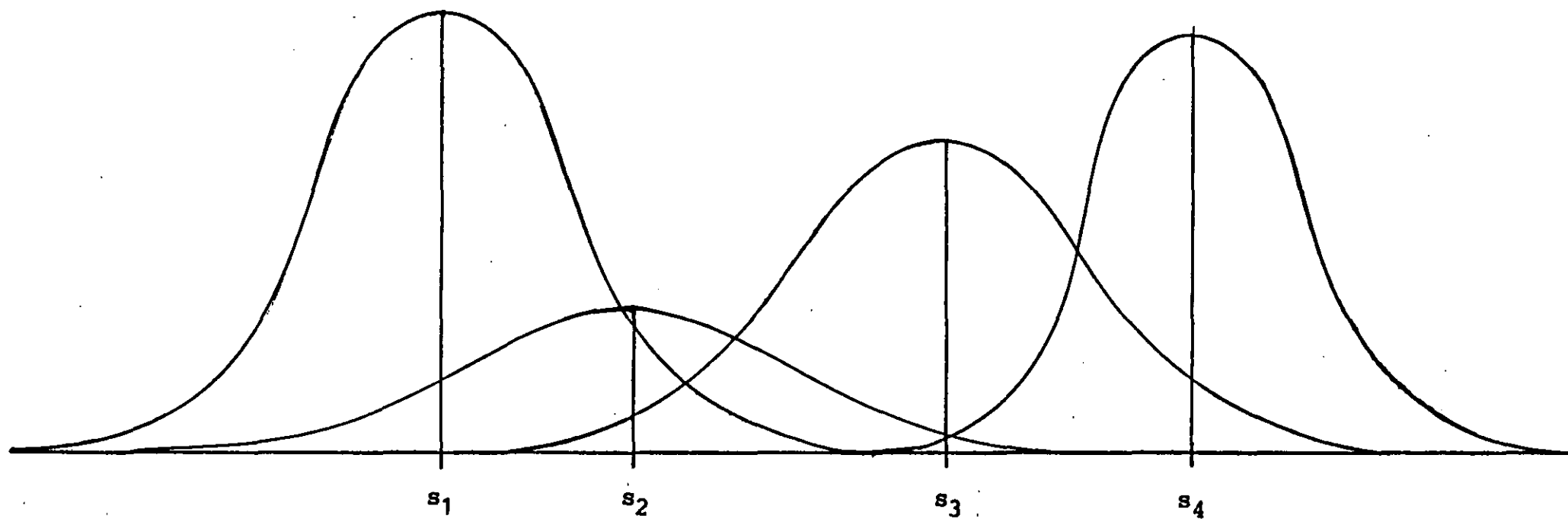


Figure A6.1 Distribution of the Discriminal Processes Associated with Four Stimuli

derived from the postulates presented above.

Consider the theoretical distributions of discriminial processes for any two stimuli  $j$  and  $k$  as shown in Figure A6.2. Let  $s_j$  and  $s_k$  correspond to the scale values of the two stimuli and  $\sigma_j$  and  $\sigma_k$  to their discriminial dispersions. If the two stimuli were presented together to the observer, each would excite a discriminial process:  $d_j$  and  $d_k$ . The difference in discriminial processes ( $d_k - d_j$ ) for any single presentation of the pair of stimuli is called a discriminial difference. If the two stimuli were presented together a large number of times, the discriminial differences themselves would form a normal distribution on the psychological continuum. The mean of this distribution is equal to the difference in the scale values of the two stimuli, since the difference between means is equal to the mean of differences. In like manner, from the well known equation for the standard deviation of differences, we know that:

$$\sigma |(d_k - d_j)| = (\sigma_j^2 + \sigma_k^2 - 2r_{jk}\sigma_j\sigma_k)^{1/2} \quad (A6.1)$$

where  $r_{jk}$  is the correlation between momentary values of discriminial processes associated with stimuli  $j$  and  $k$ .

Each time the two stimuli are presented to the observer, he is required to judge which is the higher on the psychological continuum (e.g. which is louder, heavier more valuable etc). It is assumed that judgement "stimulus  $k$  is greater than stimulus  $j$ " occurs whenever the discriminial process for stimulus  $k$  is greater than that for stimulus  $j$ , that is, whenever the discriminial difference ( $d_k - d_j$ ) is positive. Whenever the discriminial difference is negative, the judgement "stimulus  $j$  is greater than stimulus  $k$ " will be obtained. When the two distributions overlap, as in Figure A6.2, it is possible for the discriminial difference to be

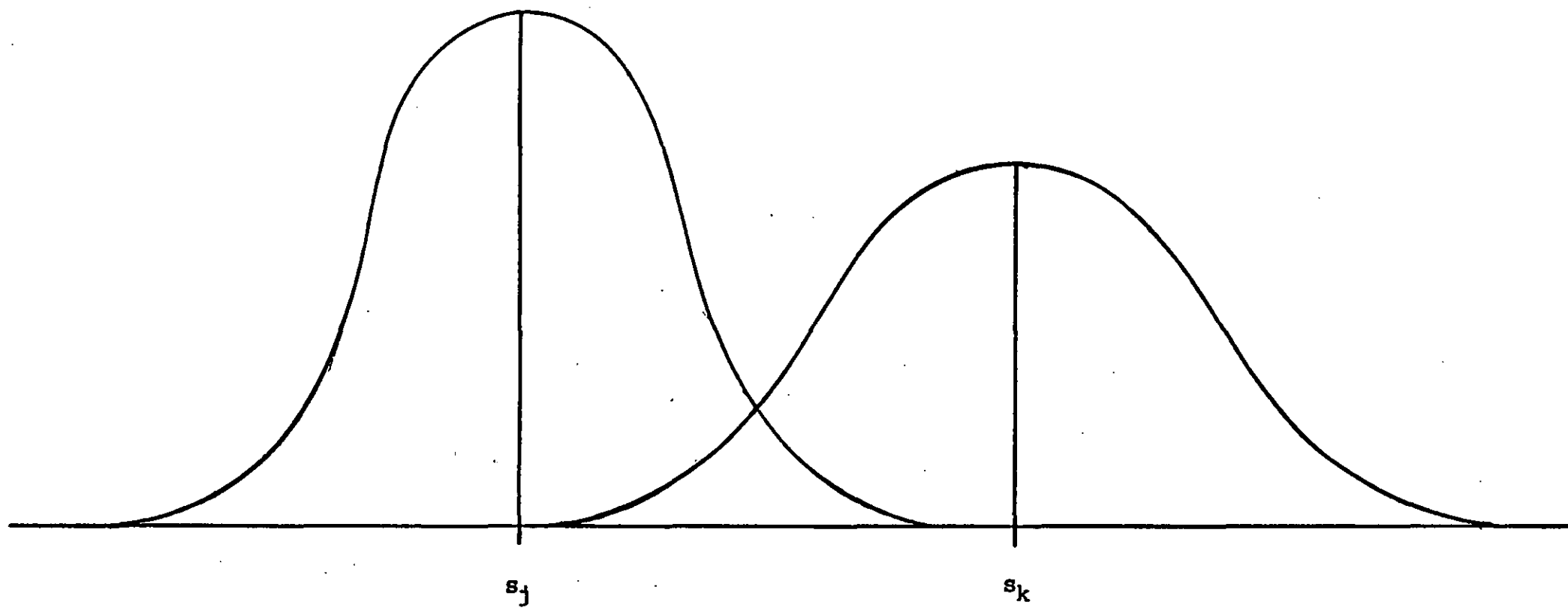


Figure A6.2 Distributions of Discriminal Processes Associated  
with Stimuli  $j$  and  $k$  on the Psychological Continuum

negative for any particular trial even though the scale value  $s_k$  is greater than  $s_j$ .

From a large number of judgements, the proportion of times stimulus  $k$  is judged greater than stimulus  $j$  can be determined. The distribution of of discriminial differences on the psychological continuum is illustrated in Figure A6.3.

The shaded region to the right of the zero point corresponds to the proportion of times  $(d_k - d_j)$  is positive, and hence, the proportion of times stimulus  $k$  is judged greater than stimulus  $j$ . The unshaded part to the left corresponds to the proportion of times  $(d_k - d_j)$  is negative, or the proportion of times stimulus  $j$  is judged greater than stimulus  $k$ . The mean of the distribution is equal to the difference in scale values of the two stimuli  $(s_k - s_j)$ . From the theoretical proportion of times stimuli  $k$  is judged greater than stimulus  $j$  we can determine the difference in scale values  $(s_k - s_j)$  from a table of areas under the unit normal curve. The difference is called  $x_{jk}$  and is measured in standard deviation units. We can thus write the equation:

$$s_k - s_j = x_{jk} \sigma \mid (d_k - d_j) \quad (\text{A6.2})$$

Since we know the relation between the standard deviation of the differences and the discriminial dispersions of the two stimuli, equation (A6.1), we can write:

$$s_k - s_j = x_{jk} (\sigma_j^2 + \sigma_k^2 - 2r_{jk}\sigma_j\sigma_k)^{1/2} \quad (\text{A6.3})$$

Equation A6.3 is the complete form of the law of comparative judgement, where:

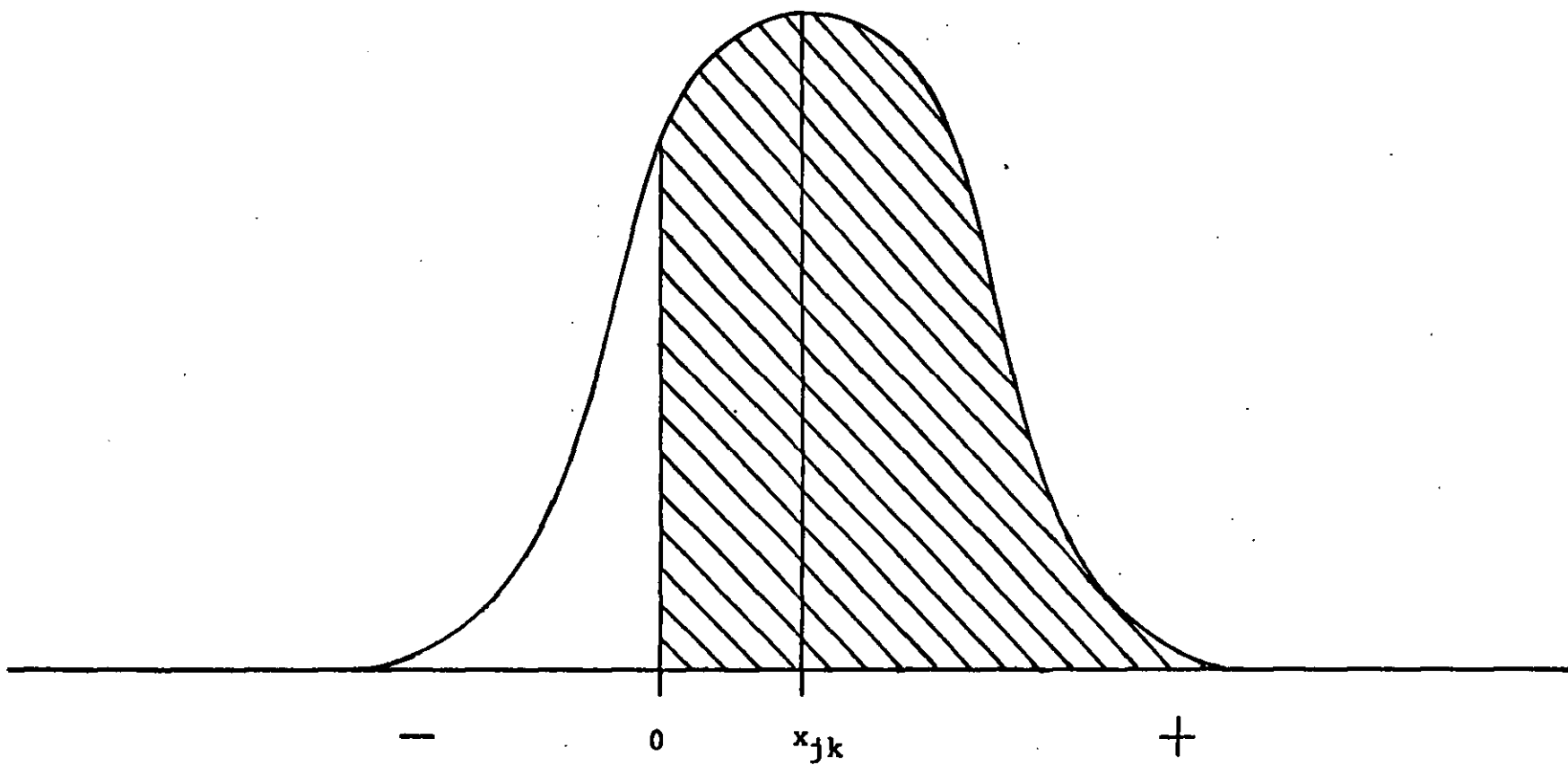


Figure A6.3 Distribution of Discriminal Differences on the Psychological Continuum

$s_j, s_k$  denote the scale values of stimuli  $j$  and  $k$ .

$\sigma_j, \sigma_k$  denote the discriminial dispersions of stimuli  $j$  and  $k$ .

$r_{jk}$  is the correlation between the pairs of discriminial processes  $d_j$  and  $d_k$ .

$x_{jk}$  is the normal deviate corresponding to the theoretical proportion of times stimulus  $k$  is judged greater than stimulus  $j$ .

The law of comparative judgement is not solvable in its complete form, since, regardless of the number of stimuli, there are always more unknowns than observation equations. For example, with  $n$  stimuli, there are  $n$  scale values,  $n$  discriminial dispersions, and  $n(n-1)/2$  independent correlations which are unknown. The zero point of the scale can be set arbitrarily at the scale value of one stimulus, and the unit can be taken as one of the unit dispersions, leaving a total of  $2(n-1)+n(n-1)/2$  unknowns.

Against this we have a total of only  $n(n-1)/2$  observation equations, one for each independently observable proportion. The number of equations is always  $2(n-1)$  less than the unknowns. Simplifying hypotheses are thus necessary in order to make the law workable.

#### A6.3 Simplifying Assumptions to the Law of Comparative Judgement

Thurstone has presented five cases of the law of comparative judgement [62,63]. These are described in depth by Torgerson [66]. Each case uses slightly different simplifying assumptions to the law of comparative judgement to give a usable solution and workable extension of the above equations.



Case one refers to the complete law of comparative judgement as developed above, involving a single trial with several individuals. Case two is applicable by replication of trials over a single individual. There is an intermediate condition involving the replication of trials over several individuals and is very similar to case one.

The last three cases are simplifications of the first two cases to arrive at a workable set of equations. No practical solution has been found for case three, however, it is solvable in theory. Case four assumes that the correlation terms are all equal and, in addition, that the differences between discriminial dispersions are small, an approximate equation is:

$$s_k - s_j = x_{jk} \cdot F \cdot (\sigma_k + \sigma_j) \quad (\text{A6.4})$$

where 
$$F = [1/2(1 - r)]^{1/2} \quad (\text{A6.5})$$

Since  $F$  is a constant multiplying factor, and since the unit is arbitrary anyway, equation (A6.4) can be written:

$$s_k - s_j = x_{jk} (\sigma_k + \sigma_j) \quad (\text{A6.6})$$

Case five assumes that the standard deviation of the distribution of discriminial differences is constant for all pairs of stimuli. If we denote this constant standard deviation by  $c$  then equation (A6.3) reduces to:

$$s_k - s_j = c \cdot x_{jk} \quad (\text{A6.7})$$

Thurstone's original equation was obtained by assuming zero correlations and equal discriminial dispersions. If we define these assumptions as:  $\sigma_j = \sigma_k = \sigma$ , and  $r = 0$  then equation (A6.3) becomes:

$$s_k - s_j = x_{jk} \cdot \sigma \cdot (2)^{1/2} \quad (\text{A6.8})$$

which is Thurstone's original case five. Since we can say that  $\sigma \cdot (2)^{1/2}$  is a constant order of magnitude then:

$$s_k - s_j = x_{jk} \quad (\text{A6.9})$$

Case five is preferred to case four in the majority of instances due to the fact that it is easier to apply and has some inherent application advantages.

The basic conditions of the method can be satisfied by the use of several individuals and replication of trials if after analysis discrepancies have arisen. This enables certain problems to be overcome such as; the problem of making successive runs independent of prior knowledge and bias which would be difficult if only one individual were used with replication of trials; secondly with many individuals a wider catchment of experience is tapped; thirdly after careful selection of these individuals to ensure a similar level of experience we can be more certain that their discriminial differences will also be similar hence the correlation coefficient,  $r_{jk}$ , between pairs of discriminial processes  $d_j$  and  $d_k$  can be taken to be close to, if not equal to, zero; and finally when taking several individuals of similar experience the discriminial dispersions of all the stimuli can reasonably be taken to be approximately equal.

This case also provides for some future problems which may arise during analysis. For example six stimuli will produce fifteen values for  $x_{jk}$  (the unit normal deviate) and only five differential scale values are required. The solution is therefore over determined. This is desirable since it enables an averaging process to take place which to some extent compensates for the fact that the paired ranking probabilities, not coming from an infinite population of observers, will never be more than sample estimates and therefore subject to error. Furthermore some data will be lost when the observers either make inconsistent judgements within their own paired rankings or alternatively when they return 100% agreement about one or more paired rankings. When 100% agreement is recorded a probability estimate of unity and an indeterminate value of infinity for the unit normal deviate occurs; such data are unusable for scaling.

#### A6.4 The Three Basic Matrices : F, P and X

After each of the  $n(n-1)/2$  pairs of stimuli have been presented a large number of times, we have as raw data the number of times each stimulus was judged greater than each other stimulus. These observed frequencies may be arranged in the  $n \times n$  square matrix F as shown over leaf:

Figure A6.4 Raw Frequency Matrix F

		Stimuli (k = 1,2,.. .,n)						
		1	2	3	.	k	.	n
Stimuli (j = 1,2,.. .n)	1	-	$f_{12}$	.	.	$f_{1k}$	.	$f_{1n}$
	2	$f_{21}$	-	.	.	$f_{2k}$	.	$f_{2n}$
	.	.	.	.	.	.	.	.
	j	$f_{j1}$	.	.	.	$f_{jk}$	.	$f_{jn}$
	.	.	.	.	.	.	.	.
	n	$f_{n1}$	.	.	.	$f_{nk}$	.	-

This matrix is the result of adding all the individual raw frequency matrices produced by each judge. The general element  $f_{jk}$ , which appears at the intersection of the  $j$ th row and  $k$ th column, denotes the observed number of times stimulus  $k$  was judged greater than stimulus  $j$ .

The diagonal cells of the matrix  $F$  will ordinarily be left vacant. Since the symmetric cells (e.g.  $f_{23}$  and  $f_{32}$ ) sum to the total number of judgements of the pair made, the matrix contains  $n(n-1)/2$  independent cells. Matrix  $P$  is constructed from matrix  $F$  by dividing each term by the number of individuals questioned. The element  $p_{jk}$  is the observed proportion of times stimulus  $k$  was judged greater than stimulus  $j$ . Diagonal cells are again left vacant ordinarily. Diagonal cells now sum to unity (e.g.  $p_{23} + p_{32} = 1$ ).

From matrix P in turn is constructed matrix X, the basic transformation matrix. The element  $x_{jk}$  is the unit normal deviate corresponding to the element  $p_{jk}$ , and may be obtained by referring to a table of areas under the unit normal curve. The element  $x_{jk}$  will be positive for all values of  $p_{jk}$  over 0.50, and negative for all values of  $p_{jk}$  below 0.50. Proportions of 1.00 and 0.00 cannot be used since the x values corresponding to these are unboundedly large. When such proportions occur, the corresponding cells in the matrix X are left vacant. Zeros are entered in the diagonal cells since we can ordinarily assume that when we have  $k=j$  then  $s_k-s_j = 0$ . The matrix is skew-symmetric, that is, the elements sum to zero, since, e.g.  $x_{23} = -x_{32}$ .

The matrix X contains the sample estimates  $x_{jk}$  of the theoretical values found in the equation of the law of comparative judgement. The element  $x_{jk}$  is an estimate of the difference  $(s_k-s_j)$  between scale values of the two stimuli measured in the units of the standard deviation of the distribution of discriminial differences i.e.  $\sigma|(d_k-d_j)$ .

Each independent element of matrix X is an estimate of a value for one equation of the law. However, since the elements are observed quantities, each will be somewhat in error. Analytical procedures have been devised to allow the errors to cancel one another and thus give reasonably good estimates of the unknowns. Since there may be unfilled cells in the matrix X, as mentioned above, the treatment that will be used to produce the matrix Z is the traditional procedure for the analysis of an incomplete matrix as described by Torgerson [66].

#### A6.5 The Production of the Matrix Z.

From equation (A6.9) if we use a unit of measurement such that c is equal to unity, it follows that the theoretical equations for stimulus k and stimulus k+a can be written:

$$s_k - s_j = x_{jk} \quad (j = 1, 2, \dots, n) \text{ and} \quad (\text{A6.10})$$

$$s_{k+a} - s_j = x_{j,k+a} \quad (j = 1, 2, \dots, n) \quad (\text{A6.11})$$

Subtracting equation (A6.10) from equation (A6.11), we have:

$$s_{k+a} - s_k = x_{j,k+a} - x_{jk} \quad (j = 1, 2, \dots, n) \quad (\text{A6.12})$$

It is thus seen that, for errorless data, the difference in the observed  $x$  values ( $x_{j,k+a} - x_{jk}$ ) for any value of  $j$  is an estimate of the difference in scale values ( $s_{k+a} - s_k$ ). For any two stimuli ( $k$  and  $k+a$ ), there will be as many such estimates as there are filled pairs of cells in the  $k$  and  $(k+a)$ th columns of matrix  $X$ . The average of the estimates is taken as the estimate of the difference  $d_{k,k+a}$ :

When  $n_k$  equals the number of terms summed over:

$$d_{k,k+a} = (s_{k+a} - s_k) = \frac{1}{n_k} \sum_{j=1}^{n_k} (x_{j,k+a} - x_{jk}) \quad (\text{A6.13})$$

Theoretically,  $a$  in equation (A6.13) may take any value from 1 to  $(n-k)$ . In actual practice, however, differences are obtained only for stimuli that are adjacent on the attribute being scaled. Adjacent stimuli will ordinarily have more filled cells in common and will give more reliable estimates of differences. The usual procedure when constructing the matrix  $X$  is to arrange its columns in rank order with respect to the attribute. The rank order of the columns is given by

the rank order of the sums of the columns in the matrix P.

This produces a new column order such that the most probable stimuli is in the first column and the least probable stimuli is in the last column.

Given matrix X with columns arranged in rank order, the differences  $d_{k,k+1}$  are obtained using equation (A6.13). If the zero point of the scale is now located arbitrarily (say let  $s_1$  equal zero), the scale values for all the stimuli are obtained simply by cumulating the successive differences:

$$\begin{aligned}s_1 &= 0 \\s_2 &= d_{12} \\s_3 &= s_2 + d_{23} \\&\cdot \\&\cdot \\&\cdot \\s_n &= s_{n-1} + d_{n-1,n}\end{aligned}$$

Thus we average of values in the matrix Z for each column and then cumulate them from left to right to form the scale rankings. The construction of these various matrices is illustrated by the example shown in Appendix A6.7. ✎

#### A6.6 Probability Values from a Scaled Ranking

In asking individuals to consider whether they would place event A above event B with respect to a certain attribute they are placing these events on a scale in the psychological continuum. If they were to place equal units of this scale between A and B and between B and C then the assessor felt that B was more probable than A and with the same conviction would believe that C was more probable than B.

In other words he felt that:

$$\frac{P_b}{P_a} = \frac{P_c}{P_b} = r \quad (\text{A6.14})$$

where  $r$  symbolizes the probability ratio equivalent to one scale unit. If the assessor expressed two units of conviction between C and D on the same scale we have:

$$\frac{P_d}{P_c} = \left( \frac{P_b}{P_a} \right)^2 = \left( \frac{P_c}{P_b} \right)^2 = r^2 \quad (\text{A6.15})$$

Thus we can write a hypothetical statement, which follows:

Given that a scaled ranking effectively exists for a set of stimuli in the (communal) mind of assessor(s), it is postulated that where one unit of scale value represents a probability ratio of  $r$ ,  $s$  units of scale value represent a probability ratio of  $r^s$ .

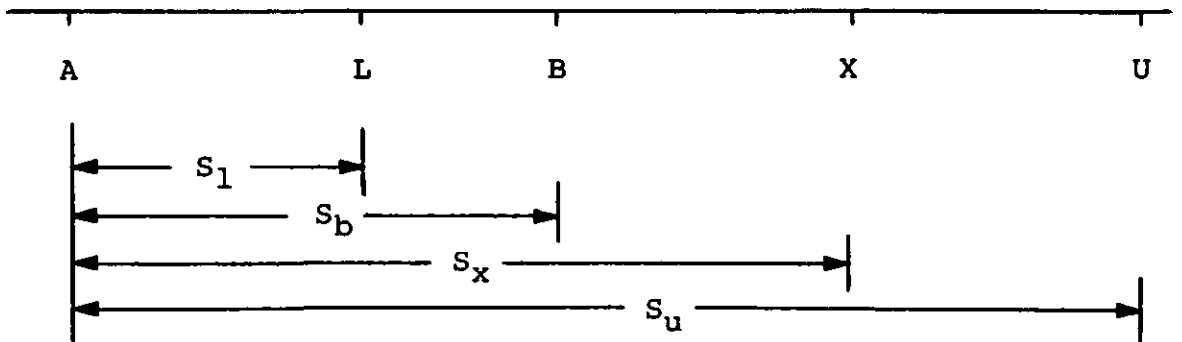


Figure A6.5 Diagrammatic Representation of Scale Values



From the foregoing and defining  $r$  as previously, the following may be written:

$$\frac{P_u}{P_1} = r^{(S_u - S_1)} \quad (\text{A6.16})$$

i.e. 
$$r = \left( \frac{P_u}{P_1} \right)^{1/(S_u - S_1)} \quad (\text{A6.17})$$

Similarly for any probability  $P_x$  we have:

$$\frac{P_x}{P_1} = r^{(S_x - S_1)} \quad (\text{A6.18})$$

Substitution of equation (A6.17) into equation (A6.18)

If we write that: 
$$Y = \frac{S_x - S_1}{S_u - S_1} \quad (\text{A6.19})$$

then we have:

$$P_x = P_1 \left( \frac{P_u}{P_1} \right)^Y \quad (\text{A6.20})$$

or in logarithmic form from equation (A6.18) we can write:

$$\log_{10} \left( \frac{P_x}{P_1} \right) = (S_x - S_1) \log_{10} r \quad (\text{A6.21})$$

Rearranging any probability  $P_x$  can be expressed as:

$$\log_{10} P_x = S_x \log_{10} r + \log_{10} (P_1 \cdot r^{-S_1}) \quad (\text{A6.22})$$

$$\text{or} \quad \log_{10} P_x = A.S_x + B \quad (\text{A6.23})$$

$$\text{when} \quad A = \log_{10} r \quad \text{and} \quad B = \log_{10} (P_1 \cdot r^{-S_1}) \quad (\text{A6.24})$$

Thus we know the upper and lower scale values from the preceding calculations and if we assign a probability to the stimuli to which these values correspond then we can find the probability of any stimuli in between these limits. In actual fact these values of  $P_u$  and  $P_l$  corresponding to  $S_u$  and  $S_l$  need not be at the extreme limits as long as they can be correctly associated in the calculations and a check is made to ensure that the other values do not lie too far outside this range.

#### A6.7 Evaluating Expert Performance

The performance of an assessor can be determined by counting the number of circular triads his answers produce in the individual F-matrix. The exact proof of the following equations can be found in Kendall [64] the equations below being a summary of this.

Consider a polygon with  $n$  vertices each linked to every other vertex representing a ranking of the  $n$  items (as shown by Chapter 12.5) by a particular assessor. There are  $(n-1)$  lines emanating from each vertex. Let  $a_i$  be the number of arrows which leave the vertices, then:

$$\sum_{i=1}^n a_i = \binom{n}{2} \quad (\text{A6.25})$$

The mean value of  $a$  is  $1/2(n-1)$ , so we can define the variance of the  $a$ -numbers by  $T$  when:

$$T = \sum_{i=1}^n \left\{ a_i - \frac{1}{2}n(n-1) \right\}^2 \quad (\text{A6.26})$$

i.e.

$$T = \sum_{i=1}^n a_i^2 - \frac{1}{4}n(n-1)^2 \quad (\text{A6.27})$$

The variance  $T$  is a maximum when the items are all ranked and in this instance  $\sum a_i^2$  becomes the sum of the squares of the first  $n$  real numbers, i.e.

$$\sum_{i=1}^n a_i^2 = \frac{1}{6}n(n+1)(2n+1) \quad (\text{A6.28})$$

Substituting we have  $T_{\max}$ :

$$T_{\max} = \frac{1}{12}(n^3 - n) \quad (\text{A6.29})$$

By examining a simple polygon it can be found that increasing the number of triads,  $d$ , by one decreases the value of  $T$  by two enabling us to write:

$$d = \frac{1}{2}(T_{\max} - T) \quad (\text{A6.30})$$

The minimum value for  $T$  can be found by setting up all the possible preferences for a simple polygon. For a polygon with an odd number of vertices,  $n$ , the value of each  $a_i$  will be given as  $(n-1)/2$  so that from equation (A6.27)  $T=0$ , a minimum.

For an even number of vertices there will be  $n/2$  vertices with  $a=n/2$  and  $n/2$  vertices with  $a=(n-2)/2$ . In this case  $T=n/4$  and again this is a minimum. So letting  $T=T_{\min}$  for odd and even values of  $n$  and substituting  $T_{\max}$  from equation (A6.29) into equation (A6.30) the maximum number of triads  $d_{\max}$  is given by:

$$d_{\max} = \frac{1}{24} (n^3 - n) \quad n \text{ odd} \quad (\text{A6.31})$$

$$d_{\max} = \frac{1}{24} (n^3 - 4n) \quad n \text{ even} \quad (\text{A6.32})$$

The actual number of triads produced by an assessor can be found by substituting equations (A6.27), (A6.28) and (A6.29) into equation (A6.30). Which after simplification yields:

$$d = \frac{1}{12} n(n-1)(2n-1) - \frac{1}{2} \sum_{i=1}^n a_i^2 \quad (\text{A6.33})$$

The values of  $a_i$  are the row totals of the assessor's in question F-matrix.

#### A6.8 An Example of Expert Evaluation

This paired comparisons exercise involved the questioning of 32 personnel working on, or associated with, a certain process plant. This example was first given by Hunns [67]. The experts were asked to compare the likelihood of five postulated operational events.

The events were:

- A. Following the testing of an alarm system the test engineer fails to restore the alarm "inhibit/normal" switch to the "normal" position.
- B. The sudden and catastrophic failure of a plant section produces a violent release of a white pungent vapour which rapidly envelopes the whole plant; the operators respond by shutting down the plant totally, failing to recognize that isolation of the failed section was all that was necessary.
- C. Without apparent reason an experienced plant operator goes to the area of a fully revealed flammable gas release and deliberately establishes a naked flame.
- D. From a row of six level gauges an operator notes down in his log the reading of gauge G3, describing this as the reading of G4.
- E. In a routine very regularly performed operation involving liquor transfer from tank A to tank B the operator instead vents tank A to drain.

The votes registered in the paired comparisons exercise are summarized in the raw frequency matrix F overleaf:

### F-Matrix

	A	B	C	D	E
A	-	12	29	19	23
B	20	-	32	21	25
C	3	0	-	4	9
D	13	11	28	-	22
E	9	7	23	10	-

Deduce the scale ranking of the five events given that:

Probability of Event A = 0.02

Probability of Event E = 0.0005

Dividing the above matrix F by the number of judges (32) we have the probability P matrix as shown overleaf:

### P-Matrix

	A	B	C	D	E
A	-	0.38	0.91	0.59	0.72
B	0.62	-	1.00	0.66	0.78
C	0.09	0.00	-	0.13	0.28
D	0.41	0.34	0.87	-	0.69
E	0.28	0.22	0.72	0.31	-
Sum	1.40	0.94	3.50	1.69	2.47

Rearranging the order to get the highest column total on the left (i.e. least probable) to the lowest on the right (i.e. most probable) and using the normal distribution curve we have the X matrix. If the probability  $P(t)$  is greater than 0.5 then the unit normal deviate,  $t$  is found by first subtracting 0.5 from  $P(t)$  and then looking up the tabulated value of  $t$  for the new  $P(t)$ .

If  $P(t) = 0.91$  then  $P(t) = 0.91 - 0.5$

$P(t) = 0.41$  and  $t = 1.339$

If the probability  $P(t)$  is less than 0.5 then the unit normal deviate,  $t$  is found by first subtracting the  $P(t)$  from 0.5. The tabulated value of  $t$  for the new  $P(t)$  can then be found and must be multiplied by -1 to give the correct answer.

If  $P(t) = 0.28$  then  $P(t) = 0.5 - 0.28$

$$P(t) = 0.22$$

From tables  $t = -0.581$  (see overleaf)

X-Matrix

	C	E	D	A	B
A	1.34	0.58	0.23	-	-0.30
B	-	0.77	0.41	0.30	-
C	-	-0.58	-1.12	-1.34	-
D	1.12	0.50	-	-0.23	-0.41
E	0.58	-	-0.50	-0.58	-0.77

Tabulated values for the cumulative normal distribution curve are shown overleaf:



Table A6.1 Tabulated Values for the Cumulative Normal  
Distribution Function

Probability	Unit Normal Deviate	Probability	Unit Normal Deviate
P(t)	t	P(t)	t
0	0	0.30	0.839
0.01	0.026	0.31	0.877
0.02	0.051	0.32	0.913
0.03	0.078	0.33	0.952
0.04	0.103	0.34	0.995
0.05	0.126	0.35	1.037
0.06	0.151	0.36	1.079
0.07	0.174	0.37	1.124
0.08	0.200	0.38	1.173
0.09	0.225	0.39	1.225
0.10	0.250	0.40	1.280
0.11	0.276	0.41	1.339
0.12	0.302	0.42	1.403
0.13	0.329	0.43	1.474
0.14	0.355	0.44	1.552
0.15	0.382	0.45	1.644
0.16	0.409	0.46	1.748
0.17	0.440	0.47	1.878
0.18	0.470	0.48	2.050
0.19	0.498	0.49	2.327
0.20	0.525		
0.21	0.552		
0.22	0.581		
0.23	0.611		
0.24	0.642		
0.25	0.673		
0.26	0.703		
0.27	0.736		
0.28	0.770		
0.29	0.803		

Calculating the column differences in the matrix Z we have:

Z-Matrix

	C-E	E-D	D-A	A-B
A	0.76	0.35	0.23	0.30
B	-	0.36	0.11	0.30
C	0.58	0.54	0.22	-
D	0.62	0.50	0.23	0.18
E	0.58	0.50	0.08	0.19
Average	0.64	0.45	0.17	0.24
Magnitude	64	45	17	24
Cumulating	64	109	126	150

Calculating the scale ranking we have:

stimuli	C	E	D	A	B
Scale	0	64	109	126	150

Using these values as  $S_x$  we can write

$$\log_{10} P_x = A.S_x + B$$

when:

$$r = \left( \frac{P_u}{P_l} \right)^{1/(S_u - S_l)} = 1.0613$$

$$A = \log_{10} r \quad \text{and} \quad = 0.0258$$

$$B = \log_{10}(P_l \cdot r^{-S_l}) = -4.955$$

$$\log_{10} P_x = 0.0258 \cdot S_x - 4.955$$

$$P_u = 0.02 \quad S_u = 126 \quad \text{Event A}$$

$$P_l = 0.0005 \quad S_l = 64 \quad \text{Event E}$$

Therefore we can calculate:

$$P_a = 0.2 \times 10^{-1}$$

$$P_b = 0.83 \times 10^{-1}$$

$$P_c = 1.1 \times 10^{-5}$$

$$P_d = 7.3 \times 10^{-3}$$

$$P_e = 5.0 \times 10^{-4}$$

The minimum coefficient of agreement can be calculated to be -0.0323 and the maximum 1.000. The actual coefficient is 0.3040 i.e. approximately 32.6% of the available range.

The individual assessors results can be broken down as shown below:

Number of Assessors	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
28	0	1.000	97.0
3	1	0.800	92.0
1	3	0.400	52.0

## APPENDIX 7 - RESULTS FROM EXPERT OPINION SURVEY

The format of the questionnaire used in the evaluation of expert opinion is as described below:

### A7.1 Field Study Questionnaire

The questionnaire used to collect the information was as follows:

#### A7.1.1 Background

These questions were designed to give some idea as to the level of experience of the assessor who would be asked to carry out the paired comparisons exercise.

- (1) What is your current position?
- (2) What experience of reactors have you:
  - (a) In your current position?
  - (b) In previous positions?
- (3) How long is your experience on reactors in the plant(s) with which you are concerned?
- (4) What processes do you operate?
- (5) How many reactors do you operate (by process)?

- e.g.
- |                    |                     |
|--------------------|---------------------|
| (1) Alcoholysis    | (9) Hydrogenation   |
| (2) Amination      | (10) Hydrolysis     |
| (3) Condensation   | (11) Isomerization  |
| (4) Cyclization    | (12) Methylation    |
| (5) Diazotization  | (13) Nitration      |
| (6) Electrolysis   | (14) Oxidation      |
| (7) Esterification | (15) Polymerization |
| (8) Halogenation   | (16) Sulphonation   |

(6) What are the overpressure arrangements?

The order can be indicated by starting from the inner most device:

- (a) C = Conventional Disc.
- (b) G = Graphite Disc.
- (c) RB = Reverse Buckling Disc.
- (d) RV = Relief Valve.
- (e) V = Vent.

(7) Does relieved material go to:

- (a) Atmosphere?
- (b) Scrubber?
- (c) Expanse Tank?

(8) Do you have any of the following crash shut down arrangements:

- (a) Reaction Shortstop?
- (b) Dump Tank?

(9) What is the average reactor cycle time?

(10) What is the average reactor utilization?

(11) Have you ever experienced a situation where fire relief of a reactor would have been necessary?

#### A7.1.2 Incidents

These questions are intended to gain some idea of the frequency of over pressure incidents and the frequency of incidents which almost lead to an overpressure.

- (1) How many overpressure incidents do you recall?
- (2) How long is the period which you are recalling?
- (3) How many were all vented safely through a bursting disc?
- (4) What happened in the other cases?

#### A7.1.3 Incident Modes

How would you rank the following as potential causes of an overpressure incident:

- (1) Unknown exotherm or decomposition reaction
- (2) Incorrect charging
- (3) Inadequate cooling
- (4) Excessive heating
- (5) Incorrect agitation
- (6) Inadequate batch control
- (7) Undesired catalysis
- (8) Exothermic reaction due to impurity

#### A7.1.4 Non-Relief Protection

How would you rank the following in terms of the practicality of devising hardware and/or software measures to prevent the incident mode from ever occurring:

- (1) Incorrect charging
- (2) Inadequate cooling
- (3) Excessive heating
- (4) Incorrect agitation
- (5) Incorrect batch control

#### A7.1.5 Initiating Events

How would you rank the following as causes of incorrect charging:

- (1) Excess of reactant
- (2) Deficiency of reactant
- (3) Too fast addition of reactant
- (4) Modification of reactant (1)
- (5) Incorrect order of reactant addition

How would you rank the following as causes of inadequate cooling:

- (1) Coolant source failure
- (2) Coolant pump failure
- (3) Coolant turned off
- (4) Automatic control failure
- (5) Condenser fault

How would you rank the following as causes of excessive heating:

- (1) Initial overheating (2)
- (2) Heating/cooling changeover fault/error
- (3) Unintended heating
- (4) Automatic control failure
- (5) Manual control failure

How would you rank the following as causes of incorrect batch control:

- (1) Initial temperature too low
- (2) Initial temperature too high
- (3) Too fast addition of reactant relative to temperature (3)
- (4) Incorrect cycle(4)



- (5) Excessive holding (stewing) (5)

Notes:

- (1) Reactant is in some way different from intended, e.g. stabilizer removed, different particle size, etc.
- (2) This excludes heating/cooling changeover fault or error, which is the next item.
- (3) Especially relative to initial temperature.
- (4) This refers to any incorrect sequence of actions.
- (5) This refers to cases where the batch is kept on hold, often for long periods such as a holiday weekend.

A7.1.6 Mitigating Features

How do you rank the probability of recovery from the following initiating events:

- (1) Agitator failure
- (2) Coolant circulation failure (1)
- (3) Condenser fault (2)
- (4) Excess of reactant
- (5) Deficiency of reactant
- (6) Too fast addition of reactant
- (7) Heating/Cooling changeover fault
- (8) Excess of catalyst (3)

Notes:

- (1) In other words, loss of cooling. This includes a failure by the automatic or manual control system to provide adequate cooling.
- (2) This refers to a fault sufficiently serious to cause loss of condenser cooling, even though the coolant is still circulating.

- (3) Say double the correct amount.

#### A7.2 Preliminary Information

The preliminary questions asked in the study yield the following information. On number of reactors and period of experience of experts the response was 137 reactors covered with a total experience of the assessors as 1203 years.

Several experts answered the questions in relation to a limited group of reactors within their works. In these cases the number of reactors covered by the expert's experience was much greater than the foregoing figures indicate. For example an expert might answer in respect of ten out of say, fifty in the works.

On reactor cycle times and reactor utilization the response produced an average reactor cycle time of 15.6 hours and a utilization of 71.2%. Hence the average number of cycles can be calculated as:

$$\text{Average No. of Cycles} = 0.712 \times 8760/15.6 = 400 \text{ cycles/year}$$

On fire relief no expert could recollect an incident where fire relief was or might have been necessary. One stated that fire relief was taken into account in at least one reactor design.

#### A7.3 Ranking and Associated Information

The main part of the field study involved the ranking of incident modes and sub-modes and of non-relief protection and mitigating features and the estimation of associated probabilities.

The ranking was done in two ways. First, the expert was asked to rank the items in pairs, i.e. he was asked to make paired comparisons. These data were then analyzed formally using the method of paired comparisons as described by Hunns [67]. Second, the expert was then asked to carry out a simple ranking of all the items in the list. The ranking obtained from the latter is simpler to understand and avoids problems such as inconsistency of responses, but the former allows quantitative estimates to be made of the position of items on a scale and hence their relative probabilities.

The probabilities of the items ranked were calculated using equations 12.1 to 12.6, making use of the fact that the sum of the probabilities for a set of mutually exclusive and exhaustive events is unity. The method by which this was achieved was described in Chapter 12.

#### A7.4 Incident Modes

The simple ranking of incident modes is given in Table A7.1. A low rank number means that the mode is ranked as having a relatively high frequency.

Table A7.1 Expert Judgement Field Study: Incident Modes - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Sum	Rank
Unknown Exotherm/ Decomposition	8	8	7	6	4	5	6	8	5	5	6	8	6	8	90	8
Incorrect Charging	1	1	2	1	3	4	1	1	1	2	1	1	1	3	23	1
Inadequate Cooling	4	2	1	2	6	1	8	3	7	8	2	3	3	1	51	3
Excessive Heating	6	4	4	3	7	2	3	4	2	1	7	4	4	2	53	4
Incorrect Agitation	7	5	6	5	1	6	2	7	6	3	8	2	5	5	68	5
Inadequate Batch Control	2	3	3	4	2	3	4	2	4	6	5	6	2	4	50	2
Undesired Catalysis	3	6	5	7	8	8	7	5	8	7	4	5	8	7	88	7
Exotherm from an Impurity	5	7	8	8	5	7	5	6	3	4	3	7	7	6	81	6

The ranking of incident modes by paired comparisons and the associated information is given in Table A7.2 in the next section.

A7.4.1 Ranking and Probability Estimates

Table A7.2 Expert Judgement Field Study: Incident Modes - Ranking by Paired Comparisons

	Scale Location	Probability
Undesired Catalysis	0.0	0.006
Exotherm from Impurity	45.2	0.012
Unknown Exotherm/Decomposition	83.6	0.022
Incorrect Agitation	128.0	0.042
Excessive Heating	158.1	0.065
Inadequate Cooling	206.3	0.133
Inadequate Batch Control	240.7	0.222
Incorrect Charging	295.0	0.497

#### A7.4.2 Information on Judges

Judge	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
1	1	0.950	99.0
2	0	1.000	99.0
3	0	1.000	99.0
4	1	0.950	99.0
5	1	0.950	99.0
6	0	1.000	99.0
7	0	1.000	99.0
8	1	0.950	99.0
9	0	1.000	99.0
10	2	0.900	99.0
11	4	0.800	99.0
12	2	0.900	99.0
13	0	1.000	99.0
14	0	1.000	99.0

Maximum possible number of triads = 20 per judge

Coefficient of Agreement; Actual Agreement Value = 0.2606

Minimum Possible Value = -0.0769

Maximum Possible Value = 1.0000

#### A7.5 Incorrect Charging

The simple ranking of incorrect charging submodes is given in Table A7.3. A low rank number means that the sub-mode is ranked as occurring on a relatively high proportions of occasions.

Table A7.3 Expert Judgement Field Study: Incorrect Charging - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	Sum	Rank
Reactant Excess	3	1	1	1	2	3	2	1	2	1	2	3	22	1
Reactant Deficiency	2	3	2	2	4	4	3	2	3	2	1	1	29	2
Too Fast Addition of Reactant	1	4	4	3	1	1	1	3	4	3	5	4	34	3
Modification of Reactant	5	2	3	5	3	5	4	5	1	4	4	5	46	4
Incorrect Order of Reactant Addition	4	5	5	4	5	2	5	4	5	5	3	2	49	5

The ranking of incorrect charging sub-modes by paired comparisons and the associated information is given in Table A7.4:

A7.5.1 Ranking and Probability Estimates

Table A7.4 Expert Judgement Field Study: Incorrect Charging Ranking by Paired Comparisons

	Scale Location	Probability
Modification of Reactant	0.0	0.034
Incorrect Order of Addition	21.0	0.046
Deficiency of Reactant	100.0	0.147
Too Fast Addition of Reactant	146.3	0.290
Excess of Reactant	181.0	0.483

#### A7.5.2 Information on Judges

Judge	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
1	0	1.000	97.0
2	0	1.000	97.0
3	0	1.000	97.0
4	0	1.000	97.0
5	0	1.000	97.0
6	0	1.000	97.0
7	0	1.000	97.0
8	0	1.000	97.0
9	0	1.000	97.0
10	3	0.400	52.0
11	0	1.000	97.0
12	0	1.000	97.0

Maximum possible number of triads = 5 per judge

Coefficient of Agreement; Actual Agreement Value = 0.2121

Minimum Possible Value = -0.0909

Maximum Possible Value = 1.0000

#### A7.6 Inadequate Cooling

The simple ranking of inadequate cooling submodes is given in Table A7.5. A low rank number means that the sub-mode is ranked as occurring on a relatively high proportions of occasions.

Table A7.5 Expert Judgement Field Study: Inadequate Cooling - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	Sum	Rank
Coolant Source/ Power Failure	4	5	3	1	5	2	3	5	5	4	5	1	43	5
Coolant Pump Set Failure	3	4	4	2	4	3	1	4	1	3	1	5	35	2
Coolant Turned Off	2	3	1	3	3	1	5	3	4	5	4	4	38	4
Automatic Control Failure	1	2	2	5	1	5	2	2	3	1	2	2	28	1
Condenser Fault	5	1	5	4	2	4	4	1	2	2	3	3	36	3

The ranking of inadequate cooling sub-modes by paired comparisons and the associated information is given in Table A7.6:

#### A7.6.1 Ranking and Probability Estimates

Table A7.6 Expert Judgement Field Study: Inadequate Cooling - Ranking by Paired Comparisons

	Scale Location	Probability
Coolant Source Power Failure	0.0	0.036
Coolant Pump Set Failure	53.9	0.077
Condenser Fault	87.6	0.123
Coolant Turned Off	146.4	0.282
Automatic Control Failure	184.7	0.482



#### A7.6.2 Information on Judges

Judge	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
1	0	1.000	97.0
2	0	1.000	97.0
3	0	1.000	97.0
4	0	1.000	97.0
5	0	1.000	97.0
6	1	0.800	92.0
7	0	1.000	97.0
8	0	1.000	97.0
9	0	1.000	97.0
10	1	0.800	92.0
11	0	1.000	97.0
12	0	1.000	97.0

Maximum possible number of triads = 5 per judge

Coefficient of Agreement; Actual Agreement Value = 0.0424

Minimum Possible Value = -0.0909

Maximum Possible Value = 1.0000

#### A7.7 Excessive Heating

The simple ranking of excessive heating submodes is given in Table A7.7. A low rank number means that the sub-mode is ranked as occurring on a relatively high proportions of occasions.

Table A7.7 Expert Judgement Field Study: Excessive Heating - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	13	Sum	Rank
Initial Overheating	3	2	2	1	4	2	4	5	4	5	2	2	4	40	3
Heating/Cooling Changeover Fault	2	4	4	4	5	3	5	1	1	4	3	3	2	41	4
Unintended Heating	4	5	5	3	2	4	1	4	5	2	4	4	5	48	5
Automatic Control Failure	1	3	3	5	3	5	3	3	3	3	1	5	1	39	2
Manual Control Failure	5	1	1	2	1	1	2	2	2	1	5	1	3	27	1

The ranking of excessive heating sub-modes by paired comparisons and the associated information is given in Table A7.8:

#### A7.7.1 Ranking and Probability Estimates

Table A7.8 Expert Judgement Field Study: Excessive Heating - Ranking by Paired Comparisons

	Scale Location	Probability
Unintended Heating	0.0	0.074
Automatic Control Failure	29.1	0.105
Heating/Cooling Changeover Fault	60.9	0.152
Initial Overheating	87.0	0.206
Manual Control Failure	155.7	0.463

#### A7.7.2 Information on Judges

Judge	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
1	2	0.600	77.0
2	0	1.000	97.0
3	0	1.000	97.0
4	0	1.000	97.0
5	0	1.000	97.0
6	0	1.000	97.0
7	0	1.000	97.0
8	0	1.000	97.0
9	0	1.000	97.0
10	0	1.000	97.0
11	0	1.000	97.0
12	0	1.000	97.0
13	0	1.000	97.0

Maximum possible number of triads = 5 per judge

Coefficient of Agreement; Actual Agreement Value = 0.0308

Minimum Possible Value = -0.0769

Maximum Possible Value = 1.0000

#### A7.8 Incorrect Batch Control

The simple ranking of incorrect batch control submodes is given in Table A7.9. A low rank number means that the sub-mode is ranked as occurring on a relatively high proportions of occasions.

Table A7.9 Expert Judgement Field Study: Incorrect Batch Control - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	Sum	Rank
Initial Temperature Too Low	1	3	4	3	4	4	3	4	3	2	5	5	41	4
Initial Temperature Too High	5	2	3	1	5	5	2	5	2	4	2	1	37	3
Too Fast Addition of Chemicals Relative to Temperature	2	4	2	4	1	1	1	3	1	1	1	3	24	1
Incorrect Cycle	4	1	5	5	3	3	4	1	5	3	4	4	42	5
Excessive Holding	3	5	1	2	2	2	5	2	4	5	3	2	36	2

The ranking of incorrect batch control sub-modes by paired comparisons and the associated information is given in Table A7.10:

A7.8.1 Ranking and Probability Estimates

Table A7.10 Expert Judgement Field Study: Incorrect Batch Control - Ranking by Paired Comparisons

	Scale Location	Probability
Initial Temperature Too High	0.0	0.066
Incorrect Cycle	28.4	0.089
Initial Temperature Too Low	60.9	0.124
Excessive Holding	130.0	0.254
Too Fast Addition of Chemicals Relative to Temperature	189.0	0.467

#### A7.8.2 Information on Judges

Judge	Number of Triads	Coefficient of Consistency	Probability of Worse Result by Chance
1	0	1.000	97.0
2	0	1.000	97.0
3	1	0.800	92.0
4	0	1.000	97.0
5	0	1.000	97.0
6	0	1.000	97.0
7	0	1.000	97.0
8	0	1.000	97.0
9	0	1.000	97.0
10	0	1.000	97.0
11	0	1.000	97.0
12	0	1.000	97.0

Maximum possible number of triads = 5 per judge

Coefficient of Agreement; Actual Agreement Value = 0.0818

Minimum Possible Value = -0.0909

Maximum Possible Value = 1.0000

#### A7.9 Non-Relief Protection

The simple ranking of non-relief protection modes is given in Table A7.11. A low rank number means that the probability of being able to devise practical and effective hardware/software to counter an incident mode (i.e. to prevent it occurring or escalating) is ranked relatively highly.

Table A7.11 Expert Judgement Field Study: Non-Relief  
Protection - Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	Sum	Rank
Incorrect Charging	5	4	4		4	5	1	5	4	5	5	1	43	5
Inadequate Cooling	3	3	3		3	3	5	2	2	3	2	3	32	3
Excessive Heating	2	2	2		2	3	3	1	3	2	3	2	25	2
Incorrect Agitation	1	1	1		1	4	2	3	1	4	1	5	24	1
Incorrect Batch Control	4	5	5		5	1	4	4	5	1	4	2	40	4

#### A7.10 Mitigating Features

The simple ranking of mitigating feature modes is given in Table A7.12. A low rank number means that the probability of being able to recover from an incident mode is ranked as occurring on a relatively high proportion of occasions.

Table A7.12 Expert Judgement Field Study: Mitigating Features  
Simple Ranking

Judge	1	2	3	4	5	6	7	8	9	10	11	12	13	Sum	Rank
Agitator Failure	6	5	2	6	8	1	5	2	7	3	8	8	7	68	6
Coolant Circulation Fault	5	7	7	1	3	6	2	8	8	5	3	7	8	70	7
Condenser Fault	8	6	1	2	4	5	3	1	2	4	2	6	6	50	3
Excess of Reactant	7	4	4	5	6	7	7	7	6	4	4	5	5	71	8
Deficiency of Reactant	1	3	3	4	5	3	6	4	1	6	1	1	4	42	1
Too Fast Addition of Reactant	4	1	8	3	7	4	8	5	5	1	5	4	1	56	4
Heating/Cooling Changeover Fault	3	2	6	7	2	2	1	3	4	7	6	3	3	49	2
Excess of Catalyst	2	8	5	8	1	8	4	6	3	8	7	2	2	64	5

## APPENDIX 8 - INCIDENT REPORTING

In the course of the project it has been necessary to examine in detail the HSE incident case histories. These have been extremely valuable, but in a number of cases crucial information has been missing. It is very desirable that in every investigation certain basic information be obtained. This is necessary particularly for statistical analyses.

It is suggested that the minimum information which is desirable for each incident should include the following items.

### A8.1 Reaction and Batch Sequence

A brief account of the reaction conducted and of the batch sequence for conduct of the reaction. It is important to say whether the sequence is batch or semi-batch, i.e. whether both main reactants are charged at the start or one reactant is charged and the other fed continuously. This has a significant effect on the ability to stop the reaction, since the quickest way to stop a semi-batch operation is to stop the feed. This is not possible, of course, in a pure batch operation and hence these are harder to stop.

### A8.2 Reactor System

A sketch of the reactor system including the arrangements for cooling and heating, relief and vent system, control loops, trips and interlocks, etc. is required.

### A8.3 Reactor Vessel

Reactor vessel information would include the vessel volume, design pressure and temperature and the working pressure and temperature.

### A8.4 Reactor Pressure Relief

The reactor relief arrangements as far as the type of the relief device, the size of the device and the state of the device would be needed. Any other reactor relief, e.g. small atmospheric vent or an open man-hole, should be listed.

### A8.5 The Incident

A general account of the incident, with information on the following specific aspects (taxonomy of Table 5.1 may be used as a guide):

- (C) Pressurising fluid
- (D) Pressurising event
- (E) Process deviation
- (F) Initiating fault
- (G) Overpressure effect
- (H) Bursting disc failure cause (if applicable)
- (I) Release effects

Investigation should distinguish between the initiating event which led to the incident, any enabling or unrevealed fault which already existed and allowed the incident to happen, and failure of any protective device which allowed the incident to escalate.

### A8.6 Injury

A brief account of the person injured and of how the injury occurred would be required.



