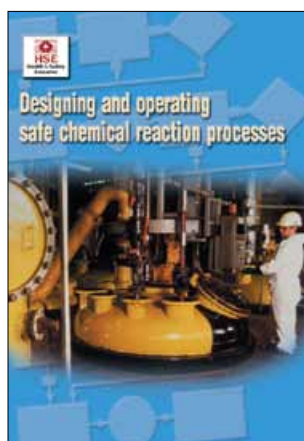# Designing and operating safe chemical reaction processes

**This is a free-to-download, web-friendly version of HSG143
(First edition, published 2000). This version has been adapted for online use
from HSE's current printed version.**

You can buy the book at www.hsebooks.co.uk and most good bookshops.

ISBN 978 0 7176 1051 8
Price £12.50

This publication is aimed at small to medium-sized chemical manufacturing
companies using batch and semi-batch processes to produce, for example,
resins, polymers, dyestuffs, pharmaceuticals and speciality chemicals.

It is aimed at those responsible for the development, design and operation of
chemical plant and processes. It explains how to prevent and control the risk of
exothermic runaway.

Front cover photograph supplied by Ciba Speciality Chemicals PLC

Contents

Preface

This guidance is aimed at those directly responsible for the development, design and operation of chemical plant and processes, particularly process chemists and process engineers.

It provides information on the assessment of chemical reaction hazards for batch and semi-batch processes, including selecting and specifying a basis of safety.

It sets out practical measures for the design, operation and modification of chemical reaction processes. These measures are designed to protect people at work and others who may be affected by the operations.

The guidance has been prepared by the Gas and Chemical Process Safety Unit, part of the Technology Division of the Health and Safety Executive (HSE).

Introduction

1   This publication provides guidance on the assessment of chemical reaction hazards for *batch* and *semi-batch processes,* including selecting and specifying a *basis of safety.* It describes how to prevent and control the risk of *thermal runaway* affecting people and the environment. It is aimed at those directly responsible for the development, design and operation of chemical plant and processes, particularly process chemists and process engineers. HSE has previously published guidance on this topic as a free leaflet.[1]

2   The objectives of the publication are to:

(a)   increase awareness of potential chemical reaction *hazards* associated with chemical manufacture in batch and semi-batch processes;

(b)   help in the assessment of *risks* from chemical reactions, and advise on how to prevent and control these risks;

(c)   provide a systematic approach for the design, operation and control of chemical reactions in batch and semi-batch processes;

(d)   advise on safe management procedures and appropriate precautions to prevent or reduce injuries and damage caused to property or the environment associated with chemical manufacture; and

(e)   advise on maintenance, training and information needs to prevent and control chemical reaction hazards.

3   It is aimed at those directly responsible for the development, design and operation of chemical plant and processes, particularly process chemists and process engineers.

4   The guidance does **not** cover in any detail: continuous processes; environmental hazards; toxicological hazards; storage of raw materials and product; drying and formulation of products; size reduction processes; physical separation processes; or the transport of chemicals. Further guidance on some of these aspects is available in the Further information section of this publication.

Legal requirements

5   Assessment by employers, of the risks to employees and others who may be affected by the work activities, is one of the requirements of the Management of Health and Safety at Work Regulations1999 (MHSW).[2]

6   This publication will help you in your assessment of the risks arising from chemical reaction processes, and gives advice on how you may control these risks.

7   This book also advises you on how to comply with relevant parts of the Health and Safety at Work etc Act 1974 (HSW Act)[3] and, where applicable, with the Provision and Use of Work Equipment Regulations 1998 (PUWER),[4] the Pressure Systems Safety Regulations 1999 (PSSR),[5] the Pressure Equipment Regulations 1999 (PER),[6] the Control of Substances Hazardous to Health Regulations 1999 (COSHH),[7] the Control of Major Accident Hazards 1999 (COMAH)[8] and other relevant legislation (see Appendix 1). The European Chemical Agents Directive (CAD)[9] requires you to avoid the conditions that can lead to harm from chemically unstable substances or mixtures. Legislation to implement the CAD requirements in

the United Kingdom will be forthcoming in 2001.

8   The reference section lists current legislation, guidance literature and the standards and codes of practice referred to in the text. They are subject to amendment from time to time. You need to make sure that these standards reflect the current legal requirements and accepted good practice at the time you carry out any work or modifications.

What is risk assessment?

9   A *risk assessment* is an organised study of your work activities using the following five steps:

Step 1	**Look for the hazards.**
Step 2	**Decide who may be harmed and how.**
Step 3	**Evaluate the risks arising from the hazards and decide whether existing precautions are adequate or if you need to do more.**
Step 4	**Record your significant findings.**
Step 5	**Review your assessment from time to time and revise it if necessary.**

10 Advice on carrying out risk assessments is contained in the HSE leaflet *Five steps to risk assessment*.[10]

11 The remaining sections of the publication will help you to identify the hazards associated with chemical reaction processes, and they give guidance on how to both assess and reduce the risks.

12 The guidance describes many of the issues you should consider when carrying out your risk assessments. It will help you to decide which precautions are appropriate to prevent and control the risks in your organisation.

13 A complete risk assessment made under the MHSW Regulations[2] also has to consider other hazards, for example transport safety and ionising radiation, which are not within the scope of this publication.

14 For the majority of businesses carrying out chemical reaction processes, there are four main events that individually, or jointly, have the potential to cause significant harm or damage:

(a) fire;

(b) *explosion;*

(c) release of a toxic substance; and

(d) release of a corrosive substance.

15 Your risk assessment needs to consider how these events could occur. Examples include:

Fire	■ mixing of incompatible chemicals ■ ignition following a spill or release ■ arson ■ hazardous activities - welding, smoking, etc ■ external events - lightning, impact, fire at an adjacent location, etc
Explosion	■ fire ■ ignition following a spill or release ■ exothermic runaway or decomposition ■ pressure build-up by gas generation
Releases	■ containment failure ■ impact ■ human error

16 The precautions you need to implement do not only relate to engineering design and installation standards, but also good management practices and operational procedures. The remainder of this publication concentrates on various measures you can use that can help to prevent and control *exothermic* runaways and *decompositions*.

17 You do not have to do anything if the risks are already low enough. However, if there is a significant risk that an incident could cause harm to people, or damage plant or the environment, you will have to consider additional measures.

18 If the COMAH Regulations[8] apply at your premises, then your risk assessment needs to be suitably detailed. It needs to be appropriate to the degree of risk and likely consequences of an incident. This includes covering on and off-site risks to people and the environment. The assessment will need to show that you have taken all measures necessary to prevent major accidents and to limit the consequences of any that do occur. HSE has issued guidance on these Regulations.[11]

19 Essentially, you need to identify the pathways to events that could lead to a major accident. The safeguards in place, to minimise the likelihood and the consequences of a major accident, will need to be of a suitably high standard.

Applying standards

20 The advice in this book provides suitable guidance for the design and operation of chemical manufacturing processes.

21 It may be inappropriate or impractical for you to adopt all the recommendations in this publication for existing processes. However, you should make any improvements that are reasonably practicable. This takes into account the risks of the process and the cost and feasibility of additional precautions. Providing adequate measures and procedures is a continuing responsibility rather than a one-off exercise. See the Glossary for a definition of the term *'reasonably practicable'* at the back of this publication.

22 This publication describes a number of ways to achieve an adequate standard of safety. You can obtain further advice on how to use it at specific sites from whoever inspects the site for health and safety, usually HSE.

Environmental protection

23 The spillage or release of dangerous materials can have environmental consequences and may be subject to controls under the Environmental Protection Act 1990.[12] Enforcement of this legislation is by the Environment Agency (EA) and the Scottish Environment Protection Agency (SEPA).

24 This guidance does not attempt to cover environmental issues in detail. However, the advice it contains for safe operations will generally also provide some protection of the environment by minimising the risk of spillage or release.

25 Further guidance is available from the EA in England and Wales,[13,14] or from the SEPA in Scotland.

Additional advice and information

26 You can find additional advice in documents listed in the Further Reading section at the back of this publication. Details of other organisations that can offer advice are also included.

Chemical process hazards

27 A chemical process goes through various stages of evolution. These stages are called *life* cycle stages.[15] The life cycle of a process begins with its initial concept, for example its discovery at the research stage. Then the process grows through stages of process development, design and construction, and matures with operations, maintenance, and modification. The process ends with decommissioning.

28 Much of the traditional approach to process safety is based on controlling the hazards associated with chemical processes and plants. This is done through improving procedures, installing additional safety interlocks and systems, and improving emergency response. Such control measures aim to reduce the risks.

29 The first step in your risk assessment procedure is to identify the hazards. Until you know these hazards it is not possible for you to assess the risks. Process hazards come from two sources:

(a) hazards that are characteristic of the materials and chemistry used; and

(b) hazards that are characteristic of the process variables and process plant.

30 You can use preventive or protective measures to reduce the risks. Traditionally these measures are classified into three types:

■ *Passive;* these minimise the hazard by process and equipment design features. They reduce either the frequency or consequence of the hazard without the active functioning of any device. Examples include firewalls, orifice plates or narrow bore piping to control flow, etc.

■ *Active;* these use engineering controls, safety interlocks and emergency shutdown systems to detect process deviations and take appropriate corrective or remedial action.

■ *Procedural;* these use operating procedures, emergency response and other management approaches to prevent incidents or to minimise the effects of an incident.

Inherently safer processes

31 However, a preferred philosophy is being used increasingly within industry. This is to eliminate a hazard completely or to reduce its magnitude sufficiently to avoid the need for elaborate safety systems and procedures.[16] This hazard elimination or reduction can be done by means that are inherent in the process. By definition, they are permanent and inseparable from it. Such an approach leads to what are called *inherently safer* processes or plant. It is easier to consider inherently safer processes or plant at the earliest stages of process development.

32 Risk control based on inherently safer concepts and passive protection measures is more reliable. This is because it depends on the physical and chemical properties of the system rather than the successful and correct operation of instruments, devices, procedures or people.

33 Changing the materials, chemistry or process conditions can reduce or eliminate hazards. Reduction of hazards in processes in this way are inherently safer processes.

34 Increasing the reliability of control measures also makes processes inherently safer.[17,18] For example, use of a passive protection measure is inherently safer than use of an active measure. Also, independent measures are inherently more reliable than protection measures that share common elements, ie that may be subject to common cause or common mode failure.

35 Approaches to the design of inherently safer processes and plants have been grouped into four strategies:

SUBSTITUTE replace a material with a less hazardous substance or a hazardous reaction with a less hazardous reaction;

MINIMISE use smaller quantities of hazardous substances in the process at any one time (also known as process intensification);

MODERATE use less hazardous conditions, a less hazardous form of a material or facilities which minimise the impact of a release of hazardous material or energy (also known as attenuation);

SIMPLIFY design facilities that eliminate unnecessary complexity and make operating errors less likely and which are forgiving of errors (also known as error tolerance).

36 Appendix 2 contains examples of inherently safer chemical reaction processes.

37 CAD[9] also adopts the hierarchy of controlling risks by:

(a) inherent safety (elimination or minimisation of the hazard);

(b) prevention of the hazard; and

(c) protection from the hazard.

Types of hazard in chemical processing

38 There are essentially four major hazards in chemical processing:

(a) chemical reactions hazards;

(b) fire and explosion hazards;

(c) health hazards; and

(d) environmental hazards.

39 You need to assess all these types of hazard. Fire, explosion, environmental and health hazards are **not** dealt with in any detail in this publication. However, Appendix 3 gives some basic information on fire, explosion and health hazards that you need to consider for a full risk assessment of chemical processes.

40 You can also find additional advice on these topics in the documents listed in the References and further information section of this publication.

Chemical reaction hazards

41 Chemical reactions either release heat (exothermic) or absorb heat (*endothermic*). The majority of chemical reactions carried out in industry are exothermic.

42 In some cases, an exothermic reaction can lead to a thermal runaway if the rate of heat generated by the reaction exceeds the removal rate. As the surplus heat begins to raise the temperature of the reaction mass, the *rate of reaction* starts to increase. This in turn accelerates the rate of heat production.

Figure 1 Effect of temperature on reaction and heat removal rates
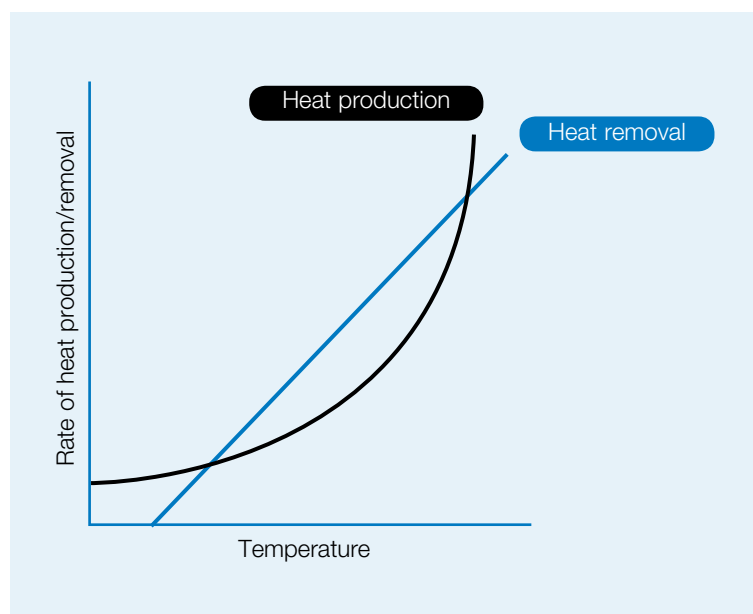
43 Thermal runaway can occur because, as the temperature increases, the rate of heat removal only increases approximately linearly but the rate of heat production increases exponentially (see Figure 1). For example, an increase in temperature of 10 K often results in a two- to three-fold increase in the rate of reaction. Once control of the reaction is lost, the temperature can rise rapidly leaving little time for correction. The elevated temperatures may initiate secondary, more hazardous runaways or decompositions.

44 A runaway exothermic reaction can have a range of results from the boiling over of the reaction mass, to large increases in temperature and pressure that lead to an explosion. Such violence can cause blast and missile damage. Release of flammable materials may result in fire or secondary explosions. Hot liquids and toxic materials may contaminate the workplace or generate a toxic cloud that may spread off-site.

45 There can be serious risk of injuries to plant operators, other personnel and the general public and damage to the local environment. At best, a runaway causes loss and disruption of production; at worst it has the potential for a major accident, as the incidents at Seveso and Bhopal have shown.

46 Hazards can also result from endothermic reaction processes - they can evolve gases, or can cause rapid crystallisation, etc and these may also need controlling.

Causes of exothermic runaway and decompositions

47 A number of factors can cause imbalance between the rates of heat production and heat removal that can result in exothermic runaway or decomposition. Studies of real runaway incidents show that the main causes are:

(a) mischarging of *reactants* eg addition of the wrong material or the wrong amount, addition in the wrong order or at the wrong rate or omission of a reactant;

(b) thermochemistry eg poor appreciation of the *heat of reaction*, unknown thermal instability of reactants, intermediates or products;

(c) temperature control eg failure to control temperature, misreading of temperature, incorrectly positioned or failed thermocouples or coolant failure;

(d) inadequate agitation eg omission to start agitation, agitator failure or incorrect specification;

(e) maintenance eg unauthorised modifications, build-up of residues, blockages, leaks or equipment restarted in an incorrect state;

(f) poor control of raw materials eg variable raw material specification or contamination; and

(g) others eg human errors, not following procedures or poorly defined procedures.

48 The underlying causes of many incidents involving chemical reactions are:

(a) an inadequate knowledge of the reaction chemistry/thermochemistry;

(b) inadequate engineering design for heat transfer;

(c) inadequate process control; and

(d) inadequate procedures and training.

Further information is available.[19,20]

The effects of scale-up

49 One particular factor that has a significant effect on the balance between the heat generated and the heat lost is the effect of scale-up from laboratory or pilot scale to full commercial size plant. This is not always appreciated. The heat produced in a reaction mass increases with its volume, which is proportional to the cube of the reactor diameter. The heat removed to the surroundings depends on the surface area available for heat transfer, which is only proportional to the square of the diameter (see Figure 2). As reactor scale, and the ratio of reactor volume to surface area, increases cooling may become inadequate. Incidents have occurred when processes are carried out on a plant scale that were uneventful in the laboratory.

Figure 2 Effect of scale up on heat flows

Rate of heat production proportional to volume

Natural cooling capacity proportional to surface area
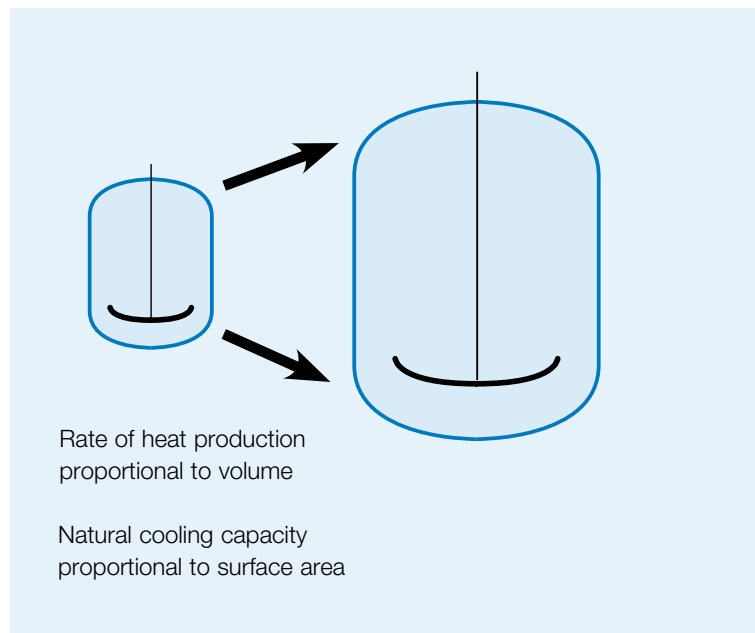
50 An illustration[21] of the effect of heat transfer in relation to vessel size and geometry is to consider the time taken for a 1 degree drop in temperature to occur by natural cooling from an initial temperature of 80°C when the surroundings are at 20°C.

2.5 m³ reactor	=	20 minutes
5 m³ reactor	=	40 minutes
12.7 m³ reactor	=	60 minutes
25 m³ reactor	=	230 minutes
10 ml test tube	=	10 seconds
100 ml glass beaker	=	20 seconds
1 l glass dewar	=	60 minutes
1 l stainless steel Dewar (adiabatic)	=	250 minutes

51 This data shows that conditions in a reactor with no supplementary cooling tend towards *adiabatic* (ie no heat losses) as reactor size increases. This is because the heat losses through the reactor external surfaces are so slow.

52 To additionally illustrate the effect of scale up on the heat balance consider an exothermic reaction where the heat of reaction is -416 kJ kg^{-1} of reactant mass; the specific heat of the reaction mass is 1.26 kJ kg^{-1} K^{-1}; and the reaction is carried out over one hour with a jacket-to-contents temperature differential of 80°C. The differences between laboratory scale and plant scale are:

	Laboratory scale	**Plant scale**
	(100 ml)	(4500 litres)
Heat loss (W kg^{-1} K^{-1})	2.3	0.04
Cooling rate (K hr^{-1})	520	9
Adiabatic temperature rise (K) (See paragraph 79)	330	330
Result	No exotherm seen	Possible runaway

An explosion occurred during the manufacture of a phenolic resin by a phenol-formaldehyde reaction catalysed by caustic soda in a 5.9 m^3 reaction vessel. The explosion ruptured the vessel and caused considerable damage to the building.

The incident occurred because of insufficient cooling capacity on scaling up the process. The reaction process was scaled up from 2.3 m^3 to 5.9 m^3 without taking due account of the reduction in vessel cooling capacity. This resulted in an increased reaction temperature that caused a runaway exothermic reaction.

The safe operating envelope

53 What the designer is trying to achieve is a controlled chemical reaction process that avoids a hazardous situation from occurring. The safe operating envelope defines the boundaries that contain the controlled reaction.

54 It is inherently safer if you develop processes with wide safe operating envelopes. These are less sensitive to variations in critical operating parameters. For example, controlling your process within a very small temperature band to avoid hazardous conditions means that the process has a narrow safe operating envelope. A process with a larger temperature band will have a wider safe operating envelope.

55 Discussion about the determination of the safe operating envelope occurs in paragraphs 123-125.

Hazard assessment of chemical reactions

56 The primary aim of this publication is to give you an understanding of the philosophies and stages you should go through when designing a safe chemical reaction process. It does not cover all aspects of this process but concentrates on the hazards that may be generated during the chemical reaction.

57 The three major chemical reaction hazards you need to consider are:

(a) the thermal instability of reactants, reactant mixtures and products (including any intermediates, potential contaminants and by-products);

(b) exothermic reactions which raise the temperature to produce decomposition reactions or violent boiling; and

(c) gas evolution.

58 The approach taken relies upon the life cycle concept[15] discussed earlier (paragraph 27) and the risk assessment you must carry out to comply with health and safety regulations.

59 A typical safety assessment procedure will include:

(a) defining the chemistry, the process operating conditions and the process plant;

(b) identifying the hazards;

(c) assessing the consequences, in terms of their severity and likelihood;

(d) selecting and specifying a basis of safety; and

(e) implementing and maintaining the safety measures.

60 For new processes and plant, beginning this assessment procedure at the earliest stages of research and development allows you to achieve the highest level of inherent safety. At this stage you can also minimise the costs of safety precautions. For existing plant and processes, you should consider your risk assessment to ensure you have taken all necessary steps to reduce risks to as low as is reasonably practicable.

61 Chemical reaction hazards need assessing by technically qualified people who have some experience of hazard evaluation and a good knowledge of process chemistry. Ideally they should be part of an independent team to avoid conflicts of interest between production and safety. However, they do need good communications with plant staff in order to minimise the chance of any misunderstandings.

62 The depth of the hazard assessment depends on the nature and magnitude of the hazards and on the scale of operation and its complexity. For example, it may be easy to show for some processes that they are unable to runaway from knowledge of the process chemistry combined with small scale screening tests. For others, you will need to do more detailed and accurate tests. There may be little justification for accurately measuring the rate of temperature rise of a runaway reaction if the process is only being operated at the gram scale in the laboratory.

Initial assessments

63 Research chemists and other research and development professionals play
a fundamental role in the development of a safe process. They must make an
in-depth investigation into the process chemistry and into the entire process
that may develop based on that chemistry. These professionals have many
opportunities to incorporate inherently safer design concepts. For example,
they can choose inherently safer synthesis routes. See Appendix 2 for further
information.

Literature surveys

64 The initial assessment you can carry out at this early stage involves a desktop
study of the potential reactants and routes to a given product. A literature search of
the chemicals to be used and the process chemistry can be useful, if it is thorough.

65 Bretherick's *Handbook of reactive chemical hazards*[22] and the National Fire
Protection Association's *Manual of hazardous chemical reactions*[23] are useful texts.
They give accounts of numerous previous incidents with many surprising and
unexpected exothermic runaway reactions. However, the absence of particular
information does not imply that no hazards exist.

66 It is at this early stage that you can consider inherently safer synthesis routes.
Examples of synthesis routes considered inherently safer include:

(a) Avoiding highly exothermic reactions or thermally unstable reactants and
intermediates.

(b) Replacement of batch reaction processes with semi-batch or continuous
processes. This reduces the quantity of reactant present and controlling the
addition rate may stop the reaction in the event of a hazard arising (see
paragraphs 131-135 on controlling reaction rates).

(c) Reactions in water as opposed to those which proceed in a more hazardous
organic solvent (provided water is compatible with the reaction mixture).

(d) The use of processes which are less sensitive to variations in operating
conditions, especially those defined as critical such as temperature or pressure.

(e) *Supercritical processing* uses relatively non-hazardous materials such as water
or carbon dioxide as solvents, albeit at high temperatures and pressures.

(f) The use of catalysts which can lead to less severe operating conditions, allow
the use of a less reactive reagent or the opportunity to reduce or eliminate
a hazardous solvent.

(g) Use of solvents to act as a heat sink. The addition of a higher boiling point
solvent may prevent the reaction mass boiling and overpressurising the
reactor. Alternatively, in some processes the use of lower boiling point solvents
allows the removal of energy from the system in the form of latent heat of
vaporisation. You need to take care when selecting either of these options. For
example, the solvent boiling point should be below any temperature at which a
decomposition reaction can occur; and with low boiling point solvents, the heat
capacity of the reaction mass should be such that evaporation to dryness
cannot occur.

Predicting reactivity and stability

67 It is possible for you to obtain a preliminary estimate of the reactivity and stability of chemicals from their molecular structure.

68 Certain molecular groupings are likely to introduce hazards into a process, and you need to identify these.[24] Examples are:

■ Double- and triple-bonded hydrocarbons
■ Epoxides
■ Hydrides and hydrogen
■ Metal acetylides
■ Nitrogen containing compounds, eg amides, imides, nitrides, azides, azo-, diazo-, diazeno- compounds, halogen-nitrogen bonded compounds, hydrazine-derived nitrogen compounds, nitrates, nitrites, nitroso, and nitro compounds, nitrogen-metal derivatives.
■ Oxygenated compounds of halogens
■ Peroxides

Many of these molecular groupings can be explosive or energetic materials.

69 You may not know the specific hazards of new compounds, but you may know the hazards of analogous compounds or those with the same or similar molecular groupings.

70 Many additional hazards result from the hazardous reactivity of combinations of chemicals. There are numerous lists of the reactivity of different types of chemical combinations to refer to.[25,26]

71 Another useful quick tool you can use, particularly for deciding whether a particular compound can decompose, deflagrate or *detonate* is the oxygen balance. It is designed primarily for the active oxygen in CHO compounds. It will give excessively conservative values for compounds like acetic acid (-107), and may provide non-conservative answers for non-oxygen containing compounds.

> If a molecule $C_xH_yO_z$ reacts completely with oxygen according to the stoichiometric equation:
>
> $$C_xH_yO_z + (2x + y/2 - z)O \longrightarrow xCO_2 + y/2H_2$$
>
> the oxygen balance is:
>
> $- 1600(2x + y/2 - z) \div$ molecular weight
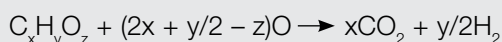
72 Almost all the recognised detonating explosives have oxygen balances between -100 and +40. You need to treat any substance with an oxygen balance more positive than -200 as a potentially high-risk chemical. If this is the case then you will need to subject the compound to additional specific explosibility testing.

73 Calculation of oxygen balance, and other explosibility indicators, is possible using the American Society for Testing Materials' computer program CHETAH.[27]

74 A simple test, which an experienced chemist could do, can indicate the possibility of *deflagration*. This is to drop a small quantity, no more than a few milligrams of the substance, onto a hot plate or to heat it on a spatula. Rapid decomposition or burning suggests that the substance is capable of deflagration.

75 More complicated explosibility tests need expert advice and specialised facilities. If your calculations or testing demonstrates potentially explosive properties then you should not use the material further until you have done a detailed evaluation of its properties. It is recommended that, where practicable, detonable materials are not handled in reactors. Such materials are outside the scope of this publication.

Thermochemistry

76 You can get a useful indication of the thermochemistry by considering the heat of reaction. Published references exist quoting many heats of reaction.[25,26] However, it is possible to calculate heats of reaction from the heats of formation of the reactants and products. The calculation assumes 100% conversion to the chosen products.

77 The accuracy of the calculation obviously depends on the accuracy of the heats of formation, but you must also take account of any changes of state that may occur. Not taking account of these heats of solution, vaporisation, etc can have a marked effect on the calculation and may lead to a false sense of security.

78 You can predict the approximate exothermicity of a chemical reaction by other methods, including calculations which sum average bond energies.[28,29] Computer programs such as CHETAH[27] use these types of calculations.

79 Once you have estimated the heat of reaction you can use it to predict the maximum temperature rise expected in the reaction mass under conditions of no heat loss. This assumes all the energy from the heat of reaction increases the temperature of the reaction mass. It is a maximum temperature rise depending only on the specific heat capacity of the reaction mass, and assumes no heat losses at all.

$$\Delta T_{ad} = - \Delta H / C_p$$

where:

ΔT_{ad} = adiabatic temperature rise (K)
ΔH = heat of reaction (kJ kg^{-1})
C_p = specific heat of reaction mixture (kJ kg^{-1} K^{-1})

80 Therefore, the maximum temperature that the reaction process can reach is the sum of the *adiabatic temperature rise* and the maximum expected processing temperature. This sum is an important value because if this maximum temperature is below the temperature at which:

(a) additional chemistry (eg decomposition);

(b) physical transition (eg boiling or gas generation); or

(c) overpressurisation from increased vaporisation can occur.

Then there is little hazard due to the heat release of the desired reaction, although there may be dramatic effects on product quality or yield.

Interpreting the information obtained

81 These simple but effective desktop screening methods are likely to have given you valuable information. They will have given an indication of the exothermicity of the desired reaction. They will have indicated if any of the reactants or products are thermally unstable, and they will have estimated the maximum reaction temperature of the desired reaction (sometimes referred to as the *maximum temperature of the synthesis reaction* or MTSR). These screening steps may not be necessary where generic chemistry and full testing are routine. Actual test results are always preferable to theoretical calculations.

82 Your initial screening may have given you sufficient information to narrow down the choices for a synthesis route, and to determine a safe operating strategy for the reaction, particularly at the laboratory stage.

83 However, you need to take care that you have adequately assessed the process. In particular, the temperature at which decomposition or a runaway can occur varies with the conditions under which the materials are held. The adiabatic temperature rise may also be underestimated, particularly if you have not taken account of any changes of state or side reactions.

84 What these screenings have not done is given you any information on:

(a) the kinetics of the desired reaction;

(b) the rate at which heat can be produced;

(c) any unwanted and potentially unsafe side reactions including decompositions;

(d) the effect of contaminants in the reaction mixture;

(e) the effect of any foreseeable variation in feed quality; and

(f) gas evolution.

85 You may need more accurate information on the heat of reaction and the rate of reaction to determine whether an exothermic runaway can occur.

86 To determine this additional information you need to carry out further screening involving physical testing.

Further screening

87 There are a number of small-scale test methods (0.01-10g sample size) available that you can use to give an indication of:

(a) the rates and quantities of heat and gas evolution;

(b) whether a runaway reaction may occur; and

(c) what the consequences are of a runaway in terms of the heat and gas evolution rates.

88 These include *differential scanning calorimetry* (DSC) and various forms of *differential thermal analysis* (DTA): the insulated exotherm test (IET); decomposition pressure test (DPT); and the Carius (or ICI) sealed tube test. Commercial variants of these tests are available.

89 It is not possible to obtain all the information needed for your chemical reaction assessment from a single simple test. Figure 3 shows a useful assessment strategy flow diagram.

90 Some of the screening tests are described briefly below. Further information is available.[19,30,31,32,33]

Differential scanning calorimetry
91 You can use DSC to indicate the thermal stability of a reactant, reaction mixture or product, and the heat of reaction or decomposition.

92 The temperature trace of the sample indicates exothermic or endothermic activity by means of peaks, troughs or discontinuities. The trace gives the total amount of energy released (ie measuring the area under the trace determines the heat of reaction or heat of decomposition, etc) and an estimate of the rate of the release (by measuring the slope of the peaks, etc). Both the total energy and the maximum rate of energy release are indicators of the degree of the hazard.

Insulated exotherm test
93 You can use this test to give early detection of the initial exothermicity. It is possible for you to estimate thermo-kinetic parameters (eg the activation energy and the adiabatic self-heat rate) and to estimate how the initial temperature for self-sustaining reactions will vary with the quantity of material present.

Decomposition pressure test
94 You can use the DPT to determine the pressure characteristics and gas generation rates where they occur during a decomposition reaction.

95 The output from the test is a pressure-time plot that you can use to determine the volume of gas generated in the decomposition reaction.

Carius (or ICI) sealed tube test
96 A number of variations of this test exist. An oven temperature is increased linearly. Continuous monitoring of the temperature and pressure outputs from a sample tube in the oven provides qualitative information about the thermal characteristics of the sample.

97 In many cases, the pressure data can also yield valuable information. Any discontinuity in a plot of 1n P against 1/T indicates non-condensable gas generation (the plot is often essentially a straight line if the pressure increase is due solely to the *vapour* pressure).

Interpreting screening data

98 The selection and use of testing equipment and procedures, and particularly the interpretation of the results, requires competent people. Some major companies have their own testing facilities, but there are a number of testing houses and consultancies available that you could use.

99 The tests are useful for:

(a) initial screening of a large number of samples;

(b) testing samples over a wide temperature range;

(c) samples only available in laboratory quantities;

(d) samples taken from reaction mixtures at various stages of the process, to see if there is any change in mixture stability;

(e) samples of distillation residues and recycled materials;

(f) mixtures containing the reactants in varying proportions, to check the effect of mischarging reactants; and

(g) ageing effects - changes in stability may occur after prolonged periods at elevated temperatures.

Note: see reference 30

Figure 3 Assessment strategy flow diagram
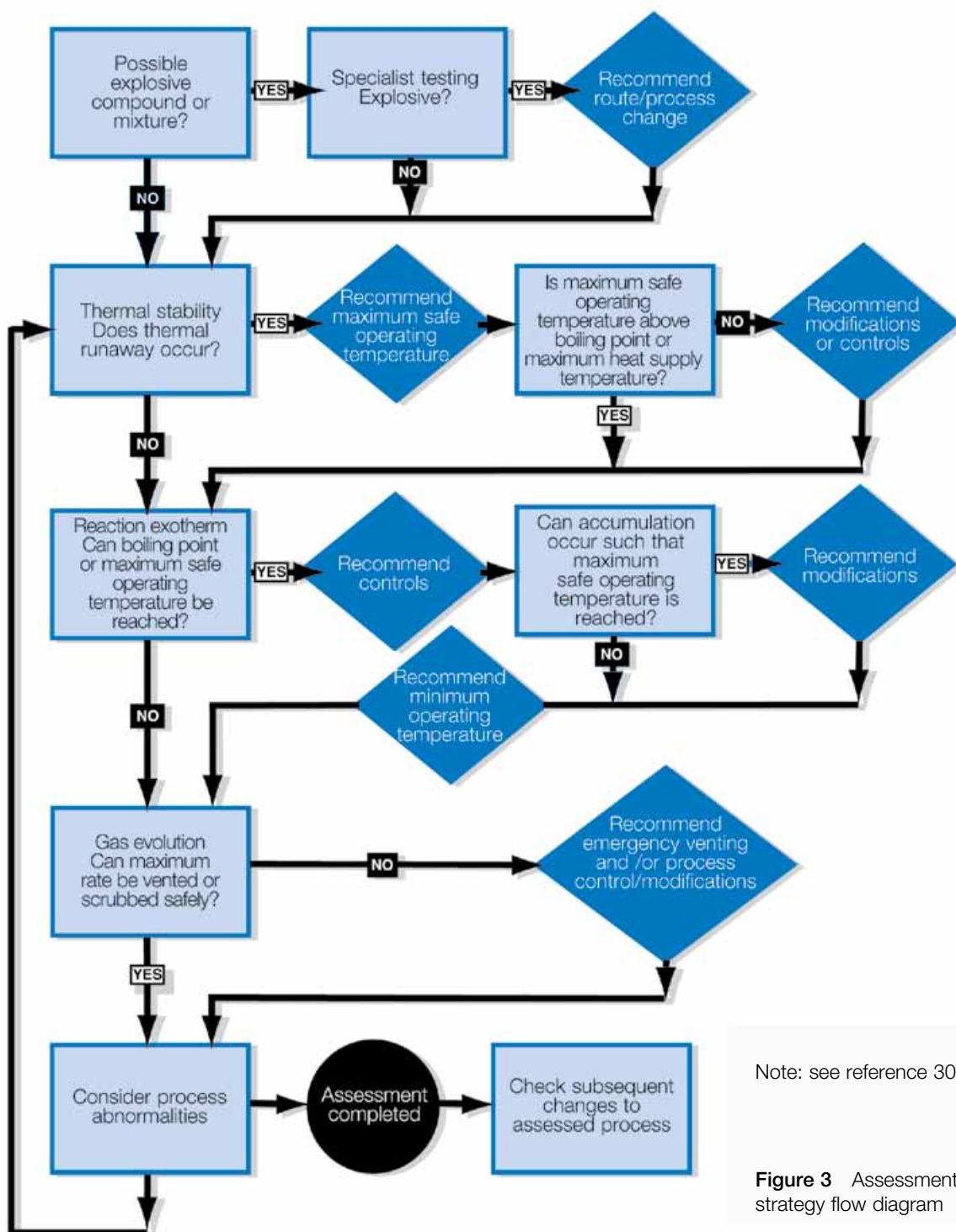
100 The results of the screening tests will give you a preliminary indication of:

(a) the possibility of thermal decomposition;

(b) the quantity and rate of heat release;

(c) gas evolution;

(d) induction time effects (*autocatalysis*) - ie the development of thermal instability after prolonged storage; and

(e) high-rate decompositions (showing that a substance could deflagrate).

101 Often the initial deviation in the temperature trace is quoted as the *initial exotherm temperature or the onset temperature* (see Glossary). You must take care in interpreting these temperatures. A number of factors affect the temperature that are unrelated to the inherent chemical stability of the test material. These include:

(a) the sensitivity of the test device;

(b) the sample size;

(c) the experimental heating mode and heating rate (eg the onset temperature increases as the rate of heating of the sample increases);

(d) heat losses from the sample container;

(e) reactions with the sample container; and

(f) sample vaporisation prior to decomposition.

An explosion occurred in a process vessel involving a thermally unstable material. Published values of the onset temperature for thermal decomposition in laboratory tests were in the range 270-300 $^{\circ}$C. However, following the incident, further investigation indicated that the material would decompose at around 150 $^{\circ}$C on the plant scale.

102 What you have achieved at this point in the assessment process is a good introductory understanding of your chosen chemical process and the hazards involved. You may now have sufficient information to define the safe operating envelope for full-scale plant, particularly if you are going to operate at temperatures well below the onset temperature for runaway or decomposition when related to the operating conditions.

103 However, in a number of cases, you will need to carry out more detailed tests to determine the safe operating envelope.

Reaction calorimetry

104 It is possible for you to directly measure the instantaneous heat output of a reacting system due to chemical or physical processes as a function of the process time. This quantity shows directly whether and how quickly chemical conversions occur in the process phase under consideration. Such an approach can be useful, not only from a safety perspective but also for process design and optimisation.

105 You can derive from the measured heat production rate the quantities important for safe process control such as the required heat removal rates and the expected temperature changes in the case of a malfunction.

106 You need to investigate the effects on the reaction kinetics and rates of heat generation and gas evolution. Factors such as, stirring speed, agitator configuration, materials of construction, variations in addition rate, reactant concentrations and hold times can affect these rates. You also need to establish the effects of any foreseeable process maloperations.

107 Experimental calorimetry methods have been developed which:

(a) simulate the full-scale reactant addition rates, batch temperature and time profiles and processing conditions (eg stirring, distillation, boiling under *reflux*, etc);

(b) include any other source of heat or heat loss (eg energy input from a stirrer, heat loss from a condenser, etc); and

(c) measure the effects of changes in physical properties (eg viscosity, specific heat, precipitation, etc) during the reaction.

108 Therefore, the data you can obtain from these tests, which will help in specifying the safe operating envelope on the full-scale plant, include:

(a) heat of reaction;

(b) heat capacity;

(c) rate of heat production;

(d) heat transfer properties of the reaction mixture;

(e) dependence of reaction kinetics on reactant concentrations;

(f) factors which affect *accumulation* or rate of heat production (temperature, catalysts, pH, etc); and

(g) amount and rate of gas evolution.

Types of calorimeters

109 There are a number of *calorimeters* that you can use to specify the safe operating envelope more accurately. However, the choice of calorimeter used needs careful consideration. Further advice is available.[19,31,32,33]

110 A reaction volume of the order of 0.5 to 2 litres allows the processes to perform under conditions resembling those on the plant, particularly concerning agitation, reactant addition rates and temperature profiles.

111 The instruments ensure that, in most cases, the determined quantities depend solely on the properties of the reaction mass. The instrument designs allow factors that are dependent on the scale and on the specific instrument properties to have a minimal influence on, or be eliminated from, the experimental result. Sometimes this is not possible. For example, it may be difficult to scale down agitation rates. In this case you need to obtain expert advice on how to take account of these effects.

112 For the purpose of this guidance, there are essentially three types of *reaction calorimeter*:

(a) *isothermal* - heat flow and power compensation;

(b) *adiabatic*;

(c) *isoperibolic*.

Isothermal calorimeters

113 Heat flow calorimeters simulate closely the operation of plant reactors. Removing the heat of reaction at the same rate as it is generated results in a constant reaction temperature. The temperature difference between the reactor and vessel jacket is a measure of the rate of heat production.

114 In power compensation calorimeters the *jacket temperature* is set slightly below the desired reaction temperature. A heater in the reaction mass maintains the set temperature. A change in electrical power to the heater compensates for any change in reaction temperature. This provides a direct measure of the heat produced by the chemical reaction.

115 Usually isothermal calorimeters are used to measure heat flow in batch and semi-batch reactions. They can also measure the total heat generated by the reaction. With careful design the calorimeter can simulate process variables such as addition rate, agitation, distillation and reflux. They are particularly useful for measuring the accumulation of unreacted materials in semi-batch reactions. You can select reaction conditions to minimise such accumulations.

Adiabatic calorimeters

116 There are a number of different types of adiabatic calorimeter. *Dewar* calorimetry is one of the simplest calorimetric techniques. Although simple it produces accurate data on the rate and quantity of heat evolved in an essentially adiabatic process.

117 Dewar calorimeters use a vacuum-jacketed vessel. The apparatus is readily adaptable to simulate plant configurations. They are useful for investigating isothermal semi-batch and batch reactions, and they can be used to study the:

(a) effects of mischarging;

(b) temperature range in which decomposition occurs; and

(c) kinetics (autocatalysis) of decomposition reactions.

118 By replacing the glass dewar with a stainless steel vessel, you can study reactions that generate pressure. Such equipment needs to be placed in a blast cell where it can be operated remotely.

119 Placing the dewar in an oven whose temperature is controlled to follow that in the reaction mass allows the study of the reaction under near adiabatic conditions.

120 In addition to the adiabatic dewar, there is a specific sub-set of adiabatic calorimeters that are commercially available that allow emergency pressure-relief system sizing. These include:

(a) *The Vent Sizing Package* (VSP™).

(b) The *Phi-Tec*™ adiabatic calorimeter.

(c) The pseudo-adiabatic *Reactive Systems Screening Tool* (RSST™).

(d) The Automatic Pressure Tracking Adiabatic Calorimeter (APTAC™).

121 The *Accelerating Rate Calorimeter* (ARC™) is another adiabatic test instrument that can be used to test small samples. It can be used to determine the onset of exothermicity where the reaction mixture can be accurately simulated.

Isoperibolic calorimeters
122 In this type of calorimeter the jacket temperature is held constant and the heat flow is measured by the change in the reaction temperature from a constant jacket temperature. It is difficult to increase the reaction temperature and simultaneously measure the heat flows. Therefore, this type of calorimeter is usually not used for safety assessments.

Determining the safe operating envelope

123 Armed now with the results of the simulation tests, you understand a great deal about the reaction hazards of the process. You have defined your safe operating envelope. You understand, for example, what happens if the agitator stops during the reaction; or if cooling stops; or if reactants are charged in the incorrect order, or too fast or too slow; or at lower or higher temperatures than desired.

124 You can use this knowledge now in relation to the design of your process. For example, you can:

(a) Use a heating medium whose maximum temperature will ensure safety in the event of loss of direct control.

(b) Install a restricting orifice in a feed pipeline to restrict the flow rate if a control valve or meter should fail.

(c) Size the reactor charge vessels so that the quantity of reactant that can be added at any one time is limited to a safe amount.

125 What you now need to do is design the process and plant, and operate the process and plant safely. That is, you need to specify a basis of safety.

Selecting and specifying a basis of safety

126 Take the opportunity at this stage to review the process chemistry and plant required. Try to use some of the principles discussed earlier to design an inherently safer process. You need to try and reduce the number, complexity and cost of 'add-on' safety features and increase the integrity of any features you do use. Ask yourself the following questions:

(a) Is it possible to eliminate hazardous raw materials, process intermediates or by-products by using alternative chemistry?

(b) Is it possible to substitute less hazardous raw materials?

(c) Have all in-process inventories of hazardous materials in storage tanks been minimised?

(d) Has all processing equipment handling hazardous materials been designed to minimise inventory?

(e) Is process equipment located to minimise the length of hazardous material piping?

(f) Is it possible to generate hazardous reactants in situ from less hazardous raw materials, rather than to have to store them on site?

(g) For equipment containing materials that become unstable at elevated temperatures or freeze at low temperatures, is it possible to use heating and cooling fluids that limit the maximum and minimum temperatures attainable?

(h) Can reaction conditions be made less severe by using a catalyst?

(i) Can the equipment be designed to totally contain the maximum pressure generated?

(j) Can equipment be designed so that it is difficult or impossible to create a potentially hazardous situation due to operating error?

(k) Can process units be located to reduce or eliminate adverse impacts from other adjacent hazardous installations?

(l) Can semi-batch processes be modified to reduce accumulation of reactants?

(m) Has the heating effect of the surroundings been considered under failure conditions when working below ambient temperatures or using reactor heating?

This list is not exhaustive, but it should give you a flavour of the thinking you can adopt in trying to produce an inherently safer process.

127 In many situations it will be necessary to provide additional safety measures. These can be of two types:

(a) preventive, ie they reduce the likelihood of a hazardous situation occurring; and

(b) protective, ie they reduce the consequences of a hazardous situation.

128 Whatever the basis of safety selected it is important that you consider:

(a) all foreseeable hazards; and

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

Preventive measures

129 Preventive measures relate to your defined safe operating envelope. These are the means by which you control the desired chemical reaction. They include measures to control:

(a) *Temperature:* the safety margin between the temperature at which an undesired exothermic reaction starts and the operating temperature.

(b) *Reactant addition:* to prevent addition of the wrong reactant; or the correct reactant(s) too early, too late, too quickly, too slowly, in too much or too little quantities, or in the wrong order.

(c) *Agitation:* what happens when the agitator or circulation pump fails, is started too late, is stopped or not turned on, or is operating at the wrong speed?

(d) *Other variables:* used to control reactions including varying pH, conductivity, concentration and pressure, etc.

130 Other measures include aspects of the design of the process and plant already discussed, particularly the inherently safer options. But they also include the engineering and procedural controls; the safety interlocks and emergency shutdown systems.[15]

Controlling rates of reaction

131 You can affect the heat balance by how you control the rate of reaction. If all the reactants are present in the reactor at the start of the process, and you then start the reaction (eg by heating), then this is a *batch* reaction. The main disadvantage of batch reactions is that because all the reactants are present, if something goes wrong (eg failure of cooling) then nothing can be done to control the reaction. You must then rely on protective measures to mitigate the consequences.

132 If you add one or more reactants gradually during the reaction then the process is a *semi-batch* reaction. The rate of reaction is controllable by a number of factors, in particular addition rate and temperature.

133 In most cases, stopping the addition will not completely stop the reaction. Some temperature rise can be developed in the reaction mass because some reaction of accumulated reactants continues. The effect of this accumulation and its extent depends on the balance between reaction kinetics and addition rate. It may be possible to control addition rates and temperatures so that there is only a small accumulation of unreacted material in the reactor. In this case the reaction mixture cannot reach an unsafe temperature. Isothermal calorimetry can be useful in determining the optimum conditions for this.

A serious explosion took place in a semi-batch plant for the nitration of benzene killing 11 people. The operator had filled the nitration reactor with benzene and started adding mixed acid without starting the stirrer. When the agitator was started the reaction was so violent that the reactor burst from overpressure and a fire started from the contact of the acid with organic material.

134 If there is a process malfunction, for example loss of agitation that may result in a runaway, it should be possible to detect this. Stopping the addition prevents an increase in the accumulation of unreacted material and the possibility of an exothermic runaway. In some cases, although complete control may not be possible, a reduced accumulation can reduce the level of protection required. For example the cross sectional area of emergency pressure relief needed may be smaller.

135 You will have been able to determine if accumulation occurs, and when in the process it occurs, from your testing.

The integrity of process control
136 Your preventive measures could rely upon operator intervention. This allows the operator to apply judgement and the measures taken can be very flexible. However, a number of factors can affect the reliability of this type of approach. These include:

(a) the complexity of the tasks;

(b) the system design;

(c) the time available for a response;

(d) operator availability; and

(e) operator training.

137 Automatic safety control systems have the advantage that high levels of safety integrity are achievable. You need, however, to take great care in designing the system. You need to consider what are the critical sequences of failures that can cause a hazard. This needs to be done in a systematic way. There are many techniques available for this type of analysis, eg hazard and operability study (HAZOP),[34] fault tree analysis,[35] etc.

138 Where loss of control could lead to significant injury to people, or damage to plant or the environment, then the integrity of the control system must be to a high standard. The integrity of the control systems can be increased, or the system can be made inherently safer, by a number of means.

139 Consider a semi-batch chemical process to produce a given desired product. There is a well-defined safe operating envelope concerning the reactor contents temperature. It is known that there is little or no accumulation even if the temperature is allowed to drop (see paragraph 133). Provided the temperature remains within the safe operating envelope not only are product yield and quality as required but also excursion into a region that could result in an exothermic decomposition of a by-product is avoided. Reactor contents temperature is therefore a safety-critical parameter. Examples of control options are:

System 1 - Process control of the reactor contents temperature could simply rely upon a single thermocouple giving an analogue output on a paper chart recorder. Operators have instructions to manually shut off the addition of reactant if the temperature approaches the upper limit of the safe operating envelope.

System 2 - The thermocouple could be the input to a temperature controller that controls the flow of the reactant through a pneumatically operated control valve within set temperature limits. Any deviation from these set temperature limits raises an audible alarm and the operator's instructions require the closure of a manual valve.

System 3 - As well as the process control offered by system 2, an independent reactor contents temperature switch is installed which is set at a specified level below the upper safe-temperature limit. The output from this switch is hardwired direct to a separate solenoid operated shut-off valve in the reactant supply line.

140 The integrity of the control system has increased in going from system 1 to system 3. Additional levels of integrity could be developed. In this case the level of integrity you require depends on the consequences of the exothermic decomposition by-product reaction.

141 System 1 may be adequate if the difference in temperature between the required reaction and the unwanted by-product decomposition reaction is large. This is so if the maximum achievable reactor contents temperature - ie the sum of the adiabatic temperature rise plus the maximum process temperature (set by the heating medium) - is below the onset temperature (see Glossary) of the decomposition reaction.

142 System 2 relies on a single temperature controller. It must be working correctly and calibrated and maintained; control is achieved by controlling the addition rate. The reactant addition should be stopped automatically by closure of the control valve. A back-up exists to ensure the addition is stopped by closure of a manual valve. This protects the system from re-opening the control valve as the temperature drops, and it gives added reliability if the control valve fails to close properly.

143 System 1 and 2 both rely on one temperature measurement and the availability of an operator to take the required action of manually closing the valve. All the safety measures are lost if the temperature sensor is faulty or incorrectly calibrated. Similarly, if the operator fails to take the appropriate and timely action then the reaction is not stopped.

144 System 3, therefore, increases the reliability by installing an additional temperature sensor. This is totally independent of the first system. If the two temperature sensors are of different types then you can avoid common mode failure. Reactant feed is stopped automatically by closure of an independent valve without the need for operator intervention. The integrity of the shutdown system is enhanced considerably. A high-integrity system (of which system 3 is just one possible solution) would be required if the upper limit of the safe operating envelope was relatively close to the onset temperature of the runaway decomposition.

145 Industry standards[17,18] address the issues of how to design, operate and maintain control and instrumentation systems to achieve the necessary level of functional safety. The scope of these standards includes hardware, software, human factors and management.

Protective measures

146 Protective measures mitigate the consequences of a hazard. They are rarely used on their own. Some preventive measures are usually present to reduce the demand on the protective system. Protective measures include:

(a) containment within the reactor system;

(b) emergency pressure relief or *venting*, and *dumping*;

(c) crash cooling;

(d) reaction inhibition;

(e) drown-out and *quenching*; and

(f) secondary containment.

147 All the protective measures, with the exception of containment and venting, normally rely on a control system to operate them. Therefore, the safety integrity of the protective measure and the integrity of the control system[17,18] are both important in its selection.

148 As with all other aspects of safe chemical processes, it is important that the design of any protective measure is adequate. For this to happen you must understand the runaway reaction process in detail. An undersized vent on a reactor will not totally protect the reactor against damage. As the protective measure is the last line of defence, it needs designing to protect against the worst case scenario.

Assessing the worst case scenario

149 The worst case scenario is the one in which a credible combination of equipment failures and process maloperations occur which places the highest demand on the protective system. It therefore depends on the basis of safety chosen.

150 For example, if emergency relief is the chosen basis of safety then the worst case scenario is that which results in the largest vent area being required to protect the reactor. If the basis of safety is to be containment then the worst case scenario is that which results in the highest final pressure and temperature.

151 The information you need to characterise the worst case scenario will vary with the protective measure selected. It may include:

(a) the worst rate of heat production at runaway;

(b) the worst rate of gas evolution and pressure development at runaway; and

(c) the maximum pressure and temperature developed in a closed vessel when a runaway occurs.

152 The problems associated with measuring heat generation and heat loss described previously also apply to the worst case scenario. For realistic simulation of the reaction under runaway conditions you need to measure these parameters using an adiabatic calorimeter with low thermal mass.

Containment within the reactor

153 In this case the design of the reactor system should withstand the maximum pressure generated by the runaway reaction.

154 You need to remember that all equipment open to the reactor, eg reflux condensers, charge vessels, instrument connections, piping and sample points must be capable of withstanding this maximum pressure. You may also need to consider the possibility of the maximum reactor pressure causing reverse flow, eg via reactant feed lines.

Emergency pressure relief or venting, or dumping

155 A common approach for chemical reactor systems has been to provide preventive measures including control systems and safety trips, etc backed up by an emergency pressure-relief system. The emergency relief or vent is simply a means of limiting the pressure build-up of vapour or gas during a runaway.

156 Although an emergency relief protects the reactor system you need to handle the discharge from the relief safely. In most cases the relieving fluids will still be reacting. If the reactor contents are hazardous or environmentally unfriendly it is unlikely you will be able to relieve direct to the atmosphere.

157 In these cases the relief discharge can be to a disposal system. Examples include:

(a) knock-out drums;

(b) quench tanks;

(c) flare stacks; and

(d) scrubbers.

158 Any disposal system needs to be adequately sized and designed to protect against the worst case scenario.

159 For systems that evolve non-condensable gases, relief from the bottom of the reactor (dumping) may be a more efficient way to reduce the pressure in the reactor. However, if a top relief system or process vent is also required, the efficiency of bottom relief may be impaired.[36]

160 Overpressure relief may additionally be installed on a reactor system to cope with:

(a) compressed air, nitrogen, steam or other service fluids that enter the system unexpectedly;

(b) venting of vapours produced during an external fire;

(c) pumping liquids into the vessel, or

(d) heating the vessel with the vent closed.

161 Relief systems sized to cope with these hazards are unlikely to be adequate to protect the reactor from the effects of a chemical reaction runaway or decomposition. Where there is the possibility of fire engulfing the reactor you need to take into account the thermal stability of the reaction mass when sizing the relief system.

162 It is important that your management systems clearly indicate that in these cases the relief is not part of the basis of safety concerning the chemical reaction hazards. There have been cases where operators have ignored process alarms, etc because they believed that when all else failed the system would be safe because

a relief vent was installed.

163 Appendix 4 contains further advice and guidance on the design of emergency relief systems.[36,37,38,39]

Crash cooling
164 In some cases it may be possible to bring a runaway reaction back under control, particularly in its early stages, by using additional cooling. The usual means of achieving this are to:

(a) bring a reflux condenser on-line;

(b) use a refrigerant in the reactor cooling coils or jacket; or

(c) pump the reactor contents through an external heat exchanger.

In all these cases you will need to assess the reliability and integrity of the system.

Reaction inhibition
165 It is possible to suppress some reactions by adding a chemical inhibitor to interrupt the reaction mechanism; eg by free-radical scavenger injection or by poisoning a catalyst.

166 You need to carefully design such systems. In the worst case scenario can you add the inhibitor and distribute it quickly enough? Can it be mixed into the reaction mass adequately? The worst case scenario may occur as a result of agitator failure. In such a case it may be unlikely that the injection of inhibitor would be successful. If the reaction mass becomes more viscous during a runaway, which is common for many polymerisation reactions, again it is unlikely that inhibition will work adequately.

Drown-out, quenching or dumping
167 These could be considered as special cases of crash cooling. The objective is to slow down the reaction by mixing a large quantity of cold liquid. This provides either a sufficient heat sink to remove the heat of reaction, or reduces the rate of reaction by lowering the temperature or by diluting the reactant concentrations.

168 The liquid used is usually water, unless it would react with the reaction mass. Even if this does happen, it may be possible simply to add sufficient water to cool the exothermic reaction with the water too.

169 If there is sufficient space within the reactor you can consider introducing the quench fluid directly into the reactor from a standby tank. This will need to be kept pressurised. Alternatively, you can simply dump the contents of the reactor into a separate containment vessel containing the quench fluid.

170 In all cases the measure needs to happen sufficiently quickly to avoid overpressurising the reactor.

Secondary containment
171 In certain circumstances, particularly when handling highly energetic substances, secondary containment may be considered. This may be necessary when venting of a reactor is inadequate. The blast may be diverted to a safe place by blast walls or mounds. This, however, is an expensive option. It also requires remote operation of the plant which is located away from any occupied areas. This method of protection is therefore rarely used in the chemical industry.

Management of chemical processes

172 The guidance so far has shown you how to assess chemical reaction hazards and how to design a safe process. Once you have selected a system of safe operation you need to record it, operate it correctly and monitor its performance. This means you need written procedures that cover:

(a) process instructions and safe operating procedures;

(b) process changes and modifications;

(c) operator training;

(d) plant maintenance;

(e) routine checks/safety audits of the safety systems; and

(f) emergency procedures.

Process instructions and safe operating procedures

173 You have gone to much effort to design and install a safe chemical manufacturing process. You have obtained a great deal of information about the process and you have used this to reduce the risks to as low a level as is reasonably practicable. You now need to ensure that it remains safe throughout the life cycle of the process. This means ensuring that:

(a) the design assessments and basis of safety are recorded and available for consultation; and

(b) the process is operated as required.

174 This involves two sets of process documentation:

(a) the detailed technical documentation; and

(b) safe operating instructions.

Detailed technical documentation
175 This should include all the information that defined the desired final process. Therefore, it should contain:

(a) a detailed description of the chemistry involved and the process, including flowsheets, process and instrumentation drawings (P&ID's), etc;

(b) the hazard assessments, including any screening or test results;

(c) the risk assessments, including the safe operating envelope, safety critical calculations, and results of HAZOPs, etc; and

(d) details of the basis of safety implemented to ensure safety.

176 The technical documentation may also contain many other pieces of information, eg quality specifications, yields, safety data sheets, environmental assessments, etc.

177 The technical documentation is the history of the design process. The intent and reasoning for the process should therefore be clear to someone new to the particular process.

Safe operating instructions

178 The safe operating instructions are for use by the plant operators. They need to be clear, simple and unambiguous. They should contain:

(a) the substances used in the process, their hazards and the precautions to be taken, eg the personal protective equipment (PPE) that must be used;

(b) any critical safety systems on the plant and the action to be taken when they operate - relate this to the safe operating envelope and the basis of safety;

(c) a step-by-step procedure to carry out the process; and

(d) emergency procedures.

179 It is a requirement of PSSR[5] that any person operating a pressure system is provided with adequate and suitable operating instructions.

180 Make the safe operating procedures easier to understand by stating the critical action points. For example, if you require an operator to control the reactor contents temperature, state in the instructions that the temperature should not exceed, say, 100 $^{\circ}$C and that activation of the emergency reactor cooling should occur at 90 $^{\circ}$C and that the reactor should be shutdown at 95 $^{\circ}$C.

181 You can give operators guidance on the magnitude of a specified action to achieve a specified goal. For example, rather than letting the operator guess how much to open a valve, suggest opening to a certain amount, then using minor adjustments to get the desired start-up flow. Give guidance on how to lead or lag in changing setpoints; or advise on how long to blow a line to clear it of liquid. Take out the guesswork.

Process changes and modifications

182 It is important that you do not modify the chemical reaction process system until you have considered the safety implications. You need a formal management system developed for modifications to plant, procedures and/or process chemistry.

183 Changes considered as minor can lead to hazardous conditions developing. For example, a change of catalyst can lead to a significant increase or decrease in the rate of reaction. Decreases in rate can cause accumulation of reactants. Changing the form of a reactant from a pellet to a powder can significantly increase the reaction rate.

A violent decomposition occurred when a reaction normally carried out in a stainless steel reactor was changed to a mild steel one. Traces of iron that had dissolved in the reaction mass catalysed the decomposition.

184 Other examples include:

(a) increases in process temperature - these may accelerate an exothermic reaction, increase reactor vapour pressure, cause thermal decomposition, or simply reduce the time available for corrective action;

(b) decreases in process temperature - these may cause unreacted material to accumulate (this can be a particular problem in addition controlled semi-batch reactions);

(c) changes in raw material specification - these can introduce unexpected side reactions;

(d) concentration changes - these can change the rate of reaction;

(e) increases in cycle process time - these may give a thermally unstable material time to decompose; and

(f) replacement of metal pipes or piping components by plastic ones - static electricity may build up and ignite flammable materials.

185 Make sure that you assess the effect of the modification on the original basis of safety. If the change affects the basis of safety then you should initiate a further assessment. All modifications should be fully documented.

Operator training

186 Adequate training and knowledge of the properties of the materials handled are essential for safe operations. Training is a requirement of the MHSW Regulations.[2] Carrying out the risk assessments required by these Regulations will identify how much information, training and retraining is needed. An Approved Code of Practice[40] gives further guidance on these Regulations. HSE has produced a leaflet concerning training and identifying training needs.[41]

187 You need to inform all staff (including contractors, etc) who are on the site of the hazards of handling the materials involved, in operating the process, and the precautions they need to take to ensure safety. Those directly responsible for the operations should also receive specific training in emergency procedures. Periodic retraining will normally be required. The training should include the following aspects:

(a) the types of materials handled, their properties and hazards;

(b) general procedures for safe handling;

(c) use of PPE and clothing;

(d) the need for good housekeeping;

(e) reporting procedures for faults and incidents, including minor leaks and spills; and

(f) emergency procedures, including raising the alarm, calling the emergency services and the use of appropriate emergency equipment.

188 Written procedures will be needed for controlling the risks from the operations, and these should be used as the basis for training. These procedures require updating when any modifications have taken place. To ensure that the procedures are still valid and that they are being complied with they also need auditing at regular intervals.

Plant maintenance

189 Maintenance of plant keeps it in a safe working condition. This involves carrying out maintenance to prevent problems arising (preventive maintenance) and putting faults right after a breakdown (breakdown maintenance).

190 Proper planning and assessment of the risks before starting maintenance work is necessary.

191 Preventive maintenance allows you to close down the plant at a convenient time and clean it out before starting on the maintenance work, making it safer for those doing the work. This also allows maintenance at the most convenient time in the production cycle and should reduce the amount of breakdowns and lost production you suffer.

192 Carrying out breakdown maintenance when the plant fails can lead to problems such as breaking into contaminated plant and making temporary repairs to keep the process going. This involves more risk for those doing the work and often leads to lost production.

193 Carrying out as much planned preventive maintenance as you can is a safer and usually a more cost-effective option.

194 Some of the main points to consider when carrying out maintenance are:

(a) Who will do the maintenance work - your staff or contractors?

You need to ensure that any staff or contractors who work on the process and the associated plant systems are competent to carry out the work required. They need to be aware of the hazards associated with the materials or processes involved.

The HSW Act[3] and the MHSW Regulations[2] place duties to ensure safe working practices on both the company using the services and the contractor. Guidance on selecting and managing contractors is available.[42] The PSSR[5] and PUWER[4] have maintenance requirements for any pressure systems.

(b) Is there a risk of fire?

Flammable substances need removing or reducing to a minimum, and any feeds to items of plant or equipment should be isolated. You will need to control sources of ignition.

(c) Is there a risk of explosion?

Any energetic substances (those that can decompose resulting in a fire or explosion) that could be affected by the work need removing. Again you will need to control sources of ignition.

Pressurised vessels or pipelines need depressurising following isolation from the plant before maintenance.

(d) Is there a risk of ill health?

Exposure to hazardous substances, for example during cleaning out reactors, can be avoided if the substance is removed and the plant washed. Where this is not possible, you will need appropriate PPE.

(e) Is there a risk from machinery or gaining access to the plant?

Isolating the power supply to plant with moving parts, and ensuring plant is readily accessible reduces these risks.

(f) Could the work involve entry into a confined space?

In such cases the Confined Spaces Regulations 1997[43] apply. The hazards that they address arise through the confined nature of the work and the possible presence of materials or conditions that, if taken together, could increase the risk to the safety or health of people. (See also paragraph 196)

The most likely hazards are:

(i) flammable materials and oxygen enrichment;

(ii) toxic gas, fume or vapour; and

(iii) oxygen deficiency.

Guidance[44,45] is available from HSE, together with information on exposure limits for toxic substances.[46]

195 It is essential that no maintenance work occurs until:

(a) the potential hazards of the work have been clearly identified and assessed;

(b) the precautions needed have been specified in detail;

(c) the necessary safety equipment has been provided; and

(d) adequate and clear instructions have been given to all those concerned.

196 Certain maintenance or repairs may require entry into confined spaces. In most cases, a permit-to-work (PTW) system[47] controls maintenance operations, particularly maintenance or repairs involving *hotwork* (eg welding) on systems that contain flammable materials. PTWs are formal management documents. Only those with clearly assigned authority should issue them. Requirements stated in the PTW must be complied with before it is issued and before the work is started. Individual PTWs need to relate to clearly defined individual pieces of work. PTWs should normally contain:

(a) the intended location and nature of the work;

(b) identification of the hazards, including any residual hazards and those introduced by the work itself;

(c) the precautions necessary, eg isolations;

(d) the PPE required;

(e) the proposed time and duration of the work;

(f) the time limits for which the permit is valid; and

(g) the person in direct control of the work.

Further advice on PTWs is available in a HSE leaflet.[48]

197 You will also need to check the plant is in a safe state before bringing it back into operation. This may mean carrying out various checks or tests, eg pressure testing.

Routine checks/safety audits

198 Active monitoring, before things go wrong, involves regular inspection and checking to ensure that the systems and procedures you have developed are actually being implemented and followed.

199 Audits, by your own staff or outsiders, complement monitoring activities by looking to see if your policy, organisation and systems are actually achieving the desired objectives.

200 For example, are your operators aware of the basis of safety, and that the vent installed on the reactor is not there to protect against an exothermic runaway? Why have the operators changed the sequence of valve operations to that stated in the safe operating procedures? Is it because they repeatedly have to walk up and down flights of stairs to comply with the correct procedure?

Emergency procedures

201 Initiating emergency procedures at the earliest stage of an incident can significantly reduce the impact of an incident on people and premises. You will need, therefore, a written procedure for dealing with any reasonably foreseeable incident, for example fires, spills or leaks. It should cover:

(a) raising the alarm;

(b) calling the emergency services;

(c) evacuating the area and providing safe havens; and

(d) tackling the fire or controlling the spill or leak (when it is safe to do so).

202 If you are a *top-tier COMAH site* (see Appendix 1), guidance is available on the details which should be present in your on-site emergency plan.[49] This may also help even if the COMAH Regulations[8] do not apply at your site.

203 You need to consider the range of possible events to take into account the following:

(a) the nature and quantities of the materials involved;

(b) the location of the process and its design; and

(c) the people and environment, both on-site and off-site that may be affected.

204 When the fire brigade arrive they will assume responsibility for firefighting and rescue operations. They may, at the discretion of the fire brigade incident

commander, undertake any other appropriate emergency operations to prevent and limit any environmental damage the incident might cause. It is therefore important that they are aware of the facilities and capabilities at your site. For top-tier COMAH sites the statutory consultees, which includes the emergency services, will have helped in the development of the emergency plans.

205 Where large numbers of employees on-site or people off-site may be at risk a nominated person should co-ordinate or manage the risk assessments and, in consultation with the emergency services, prepare an emergency action plan. Sites subject to the COMAH Regulations[8] require formal on-site and off-site emergency plans.[49] If you are a top-tier COMAH site it is a statutory requirement to periodically test your on-site and off-site emergency plans.

206 Also there are requirements in the PSSR[5] that any person operating a pressure system should have adequate and suitable emergency instructions.

Appendix one:
Legal requirements

1   It is a legal requirement under health and safety law that those responsible for work activities ensure that:

(a) hazards are adequately identified;

(b) risks are assessed; and

(c) suitable control measures are put into practice.

2   You must take measures to eliminate or control the risks unless doing so involves a sacrifice (time, trouble or cost) which is grossly disproportionate to the level of risk. However, the ability to pay for additional control measures is not a deciding factor as to whether they are necessary.

3   Where it is not possible to remove the risk then the arrangements for managing the activity safely are particularly important.

The Confined Spaces Regulations 1997

4   These Regulations apply when hazards exist because of the confined nature of certain work activities, and the possible presence of substances or conditions that, if taken together, could increase the risk to the safety or health of people. Guidance on the Regulations is available from HSE.[44,45]

The Control of Major Accident Hazards Regulations 1999

5   These Regulations[8] apply at two levels (top-tier and lower-tier) to certain premises where specified dangerous substances are stored or used at or above one of two threshold quantities. The main aim of these Regulations is to prevent major accidents occurring; a secondary objective is to limit the effects of any which do happen. A major accident, in relation to these Regulations, is a major emission, fire or explosion resulting from uncontrolled developments that lead to serious danger to people or the environment.

6   The general requirements apply at both levels and require the operator in control of the industrial activity to demonstrate that the major accident hazards have been identified and that the activity is being operated safely. The additional requirements that apply at the higher level include the submission of a written safety report, preparation of an on-site emergency plan and provision of certain information for the public. Guidance on the Regulations[11] and how to write a safety report[50] is available.

The Control of Substances Hazardous to Health Regulations 1999 (as amended)

7 These Regulations[7] require employers to assess the risks arising from substances hazardous to health at work and to decide on the measures needed to protect the health of employees. They also require the employer to take appropriate action to prevent or adequately control exposure to substances hazardous to health.

8 Substances covered by these Regulations include carcinogenic substances and those, which under the Chemicals (Hazard Information and Packaging for Supply) Regulations 1994,[51] are labelled as very toxic, toxic, harmful, corrosive or irritant. The Regulations also cover those substances assigned occupational exposure limits.[46]

Health and Safety at Work etc Act 1974

9 This Act[3] deals with securing the health, safety and welfare of people at work and with protecting those who are not at work from risks to their health and safety arising from work activities.

10 The general duties in sections 2 to 4 and 6 to 8 of this Act apply to all work activities that are the subject of this guidance.

The Highly Flammable Liquids and Liquefied Petroleum Gases Regulations 1972

11 These Regulations[52] apply when liquids that have a flashpoint of less than 32 °C and which support combustion (when tested in the prescribed manner) are present at premises subject to the Factories Act 1961.[53] The Regulations include provisions for these highly flammable liquids relating to:

(a) precautions to be taken during storage;

(b) precautions to be taken against spills and leaks;

(c) controlling sources of ignition in areas where accumulations of vapours may occur;

(d) preventing the escape of vapours; and

(e) dispersing dangerous concentrations of vapours.

Management of Health and Safety at Work Regulations 1999

12 These Regulations[2] require all employers and self-employed people to assess the risks to workers and others who may be affected by their undertakings so that they can decide what measures to take to comply with health and safety law. They go on to require the employer to implement appropriate arrangements for managing health and safety. This includes health surveillance (where appropriate), emergency planning, and the provision of information and training. An Approved Code of Practice[40] gives guidance on these Regulations.

The Personal Protective Equipment at Work Regulations 1992

13 These Regulations[54] aim to ensure the free provision of personal protective equipment (PPE) where the risk has not been controlled by other means, and its safe use. They include general duties covering the selection of suitable PPE, maintenance, information, instructions and training. Guidance[55] on the Regulations is available.

The Pressure Systems Safety Regulations 1999

14 These Regulations[5] set down a range of duties on users of installed pressure systems and owners of mobile systems. They include duties not to operate the system or allow its operation unless the safe operating limits of the pressure systems are known. The systems must have a suitable written scheme of examination.

15 A written scheme of examination is a planned scheme for periodic examination of those parts of a pressure system in which a defect may give rise to danger.

16 A pressure system includes any vessel and/or pipeline, with its associated pipework (including valves and pumps, etc) that contains a relevant fluid. The term 'relevant fluid' is defined in the Regulations and covers compressed or liquefied gases above 0.5 bar gauge pressure, pressurised hot water above 110 $^{\circ}$C and steam at any pressure.

17 An Approved Code of Practice[56] accompany the Regulations.

The Pressure Equipment Regulations 1999

18 These Regulations[6] apply to the design, manufacture and conformity assessment of pressure equipment and assemblies. They apply when the maximum allowable pressure is greater than 0.5 bar above atmospheric pressure.

19 If Schedule 1 (of PER) excludes a particular item of pressure equipment from PER, then the PSSR[5] may apply to the initial supply of the equipment.

20 Whichever set of Regulations cover the initial supply of the equipment, the PSSR cover the equipment while in-service.

Provision and Use of Work Equipment Regulations 1998

21 These Regulations[4] aim to ensure the provision of safe work equipment and its safe use. They include general duties covering the selection of suitable equipment, maintenance, information, instructions and training. They also address the need for equipment to be able to control selected hazards. Guidance is available.[57]

Appendix two: Inherently safer chemical reaction processes

1   The four strategies for the design of inherently safer processes and plants are:

(a) substitute;

(b) minimise;

(c) moderate; and

(d) simplify.

Some examples of inherently safer chemical synthesis routes have been given in paragraph 66 of the main text.

2   Inherently safer design represents a fundamentally different approach to chemical process safety.[15,16] Rather than accepting the hazards in a process, and then adding on safety systems and layers of protection to control those hazards, the challenge to the process designer is to reconsider the process and eliminate the hazards. If the designer cannot eliminate the hazards the challenge becomes to minimise or reduce them as much as possible by modifying the process, rather than by adding external layers of protection.

3   In considering inherently safer design alternatives, it is essential to remember that there are often, perhaps always, conflicting benefits and deficiencies associated with the different options. Chemical processes usually have many potential hazards, and a change that reduces one hazard may create a new one or increase the magnitude of a different existing hazard. For example:

(a) Chlorocarbon refrigerants are inherently safer with respect to fire, explosion and acute toxic hazards when compared to alternative refrigerants such as ammonia, propane and sulphur dioxide. However, they have been shown to cause long term environmental damage because of stratospheric ozone depletion.

(b) Supercritical processing may use relatively non-hazardous materials such as water or carbon dioxide as reaction and extraction solvents, but supercritical processing may require high temperatures and pressures.

(c) A solvent used in an exothermic reaction is non-volatile, and moderately toxic. An alternative solvent is less toxic, but also has a much lower boiling point. There is a trade-off between toxic hazards, the ability of the lower boiling point solvent to temper the exotherm at a lower temperature, and the possibility that the mixture may evaporate more rapidly.

(d) A wide variety of applications including chlorination, ethoxylation, hydrogenation, and polymerisation reactions use continuous processes in loop *reactors*. However, facilities may be needed to deal with off-specification material produced during start-up or process malfunction.

4   Examples of the use of the inherently safer strategies follow. Each of the highlighted examples generally illustrates more than one of the strategies.

Substitute

5   Substitution means the replacement of a hazardous material or process with an alternative that reduces or eliminates the hazard. Examples include:

(a)   The use of water under pressure as a heat transfer medium to replace flammable oils. However, you also need to consider the compatibility of the heat transfer fluid with the reaction mixture.

(b)   The use of fluorinated hydrocarbons as refrigerants instead of ammonia, propane or chlorocarbons.

(c)   New synthesis routes that avoid the use of hazardous raw materials or intermediates.

(d)   Changing the materials of construction of plant and equipment.

Six five-tonne batch reactors, used to produce an inorganic oxychloride by the reaction of the oxide with chlorine, have been replaced with one continuous loop reactor producing 500 m^3/hr.

Changing the chemistry, to the direct oxidation of the chloride already produced on site, eliminated the handling of chlorine. The oxidation reaction is rapid and exothermic, but the actual temperature rise seen in the reactor is less than 20 K. The product acts as a diluent for the reactants in the loop.

A tubular heat exchanger, with external cooling water sprays at atmospheric pressure, now cools the reaction mixture rather than a cooling water jacket. This has eliminated the hazard of water leaking into the reactor vessel and reacting with the reactor contents.

The processing of tonnage quantities of an energetic substance required a batch distillation step that took place in a glass-lined mild steel vessel. It was known that iron contamination could lead to a rapid decomposition reaction. Part of the basis of safety was that if breaching of the lining occurred, the steam to the vessel jacket would be shutoff, cooling water applied, and the batch dumped.

However, application of these precautions was not quick enough to prevent the vessel being overpressurised. A smaller remotely operated continuous distillation vessel, constructed of glass, replaced the batch still eliminating the iron-catalysed decomposition reaction.

Minimise

6   To minimise is to reduce the quantity or energy contained in a process or plant.

7   This can be achieved by reducing process inventories by applying good engineering design principles. Additionally, the term process intensification is used more specifically to describe new technologies that reduce the size of plant and equipment, particularly reactors.

8   Reactors are generally large because the reaction is slow. However, in many cases the chemical reaction has the potential to occur very quickly, but it appears to be slow due to inadequate mixing and contact of the reactants.

9   Innovative reactor designs can improve mixing and may result in much smaller reactors. Such designs are usually cheaper to build and operate, as well as being potentially safer due to their smaller inventory. These include:

(a) continuous stirred tank reactors (CSTR);

(b) tubular reactors; and

(c) loop reactors.

10 There are other forms of reactor currently being developed, for example, spinning disc reactors, heat exchanger reactors and micro-reactors.

Table 1 Comparison between batch stirred reactor and loop tank reactor

An organic material was originally chlorinated in a glass-lined batch stirred tank reactor, with the chlorine fed through a dip pipe. Replacement of the stirred reactor with a loop reactor, with chlorine fed to the recirculating liquid stream through an eductor, increased productivity, reduced chlorine usage and reduced reactor size; as summarised in Table 1.

Reactor type	Batch stirred reactor	Loop tank reactor
Reactor size (1)	8000	2500
Chlorination time (hr)	16	4
Productivity (kg/hr)	370	530
Chlorine usage (kg/100 kg product)	33	22
Caustic usage in vent scrubber (kg/100 kg product)	31	5

Nitroglycerin is produced by the nitration of glycerine with concentrated nitric and sulphuric acids. The reaction is very exothermic and if heat removal, by cooling and stirring, is inadequate an uncontrollable reaction is followed by explosive decomposition of the nitroglycerin.

The reaction was traditionally carried out batchwise in a large stirred pot containing about one tonne of material. The operators had to monitor the reactor temperature closely. To make sure they did not fall asleep they sat on one-legged stools. If they fell asleep, they fell off.

On redesigning the process, the engineers asked 'Why does the reactor have to contain so much material?' Although they initially thought this was because the reaction was slow, it was actually because of inadequate mixing. They therefore designed a small, well-mixed reactor holding about one kilogram of material.

The new reactor resembled a laboratory water ejector. The rapid flow of the acids through it creates a partial vacuum that sucks in the glycerine through a sidearm. Very rapid mixing occurs, and by the time the mixture leaves the reactor the reaction is complete. The residence time in the reactor fell from two hours to two minutes and the same output as the batch reactor was achieved.

The control system on the reactor is inherently safer than conventional control. If the flow of acids falls the flow of glycerine must fall in proportion without the intervention of a flow ratio controller or other instrument that may fail.

They also designed a simple emergency shutdown system. Deactivation of a solenoid will cause a lead weight to fall which opens a plug valve. Opening this valve allows air to enter into the reactor that breaks the partial vacuum created by the flowing acid. This causes the flow of glycerine to stop and hence the reaction.

Moderate

11 To moderate is to use hazardous materials under less hazardous conditions, that is: at lower temperatures or pressure; as a vapour; or dissolved in a safe solvent. For example:

(a) a polypropylene process uses gaseous propylene instead of liquid propylene dissolved in a flammable solvent; or

(b) in a continuous method for the production of nitro-aromatics, excess acid is used to dilute the aromatics and make a reaction runaway impossible.

Simplify

12 Simplify means designing to eliminate unnecessary complexity, reducing the opportunities for error and misoperation. A simpler plant is generally safer and more cost effective than a complex one. Examples include:

(a) building reactors with sufficiently high design pressures may result in the elimination or reduction in size of an emergency relief system; or
(b) in some cases, carrying out a multi-step batch process in several vessels each optimised for a single processing step may be inherently safer and far more

simple than carrying out all reaction steps in one complex vessel, particularly when it may need several chemical feeds.

A process involved two reaction stages both originally carried out in one vessel. If, by mistake, addition of the first-stage reactants (A and B) occurred during the second stage or second-stage reactants (C and D) during the first stage, a runaway reaction could occur. Originally the use of interlocks and training prevented such incidents.

A new plant used an inherently safer method: separate vessels for the two stages. Reactants A and B were piped only to the first vessel and C and D only to the second.

Appendix three:
Other hazards in chemical processing

Fire and explosion hazards

1   Flammable materials may be:

(a) gases or vapours;

(b) liquids;

(c) mists or aerosols; and

(d) solids (including dusts).

2   In all cases, for a fire or explosion to occur a flammable atmosphere and a
source of ignition must be present at the same time.

3   Examples of incidents that can occur during the operation of a reactor are:

(a) vapour or dust explosions during the charging of reactants;

(b) vapour or gas explosions in the reactor, eg ignited by a pyrophoric catalyst or
     when the hatches are opened, air enters and the contents are above their
     autoignition temperature;

(c) explosion of a vapour or dust cloud issuing from a vessel, ignited by an external
     source; and

(d) autoignition of product when run-off at too high a temperature.

4   There are five general principles for ensuring that the risks of fire and explosion
from the use of flammable materials can be controlled and minimised. The acronym
'VICES' will help you to remember them. The acronym implies no order of priority
of the principles.

V   Ventilation

Is there plenty of fresh air where the materials are used? Good ventilation means rapid dispersion of vapours given off from a spill, leak or release.

I   Ignition

Have all ignition sources been removed from the area? Ignition sources can vary widely. They include sparks from electrical equipment or welding and cutting tools, hot surfaces, smoking, open flames from heating equipment and electrostatic discharges from plant, process operators or materials being processed.

C   Containment

Are your flammable liquids contained adequately? Will a spillage be contained and prevented from spreading to other parts? Means of controlling spillage could be an impervious sill or low bund. An alternative is to drain the area to a safe place, such as a remote sump or a separator.

E   Exchange

Can you exchange a flammable liquid for a less flammable one? This is a basic question you should always ask. Can you eliminate the use of flammable materials from your operation altogether?

S   Separation

Are flammable materials stored and used well away from other processes and general storage areas? Can they be separated by a physical barrier, wall or partition?

Health hazards

5   Toxic substances vary widely in the hazards they create. Acute hazards arising from short-term exposure are more likely to arise than chronic effects from low-level long-term exposure.

6   Exposure to a chemical substance through inhalation, ingestion or skin absorption can lead to poisoning or other ill health. Of these routes of exposure, inhalation is generally the most serious as the probability of exposure to vapours during routine operations and incidents involving spills is much greater than from skin exposure or ingestion.

7   The Personal Protective Equipment Regulations 1992[54] require employers to provide suitable PPE to employees who may be exposed to a risk to their health or safety while at work unless the risk has been adequately controlled by other means that are equally or more effective.

8   The COSHH Regulations[7] require employers to prevent or control exposure to harmful substances. Guidance on these Regulations is contained in the Approved Codes of Practice (ACOPs) entitled *Control of substances hazardous to health (Fifth edition). The Control of Substances Hazardous to Health Regulations 2002 (as amended). Approved Code of Practice and guidance*.[58]

9   Many dangerous substances are harmful to health if inhaled, ingested or come into contact with eyes or skin. Some obvious precautions to take against skin and eye contact is to provide such items as gloves, protective clothing and eye protection (goggles). Decontamination facilities such as eyewash stations and showers should also be made available. Suitable respiratory protection may need to be worn during operations with toxic gases. Such protection may be needed in emergency situations to deal with spills and leaks, and possibly to enable evacuation.

Appendix four: Emergency pressure relief or vent design

1   The design of emergency pressure relief systems for exothermic runaway is complex. It requires a thorough understanding of the reaction during runaway, including any side reactions or unintended reactions that may occur, and relief system sizing methodology. You need information on:

(a) the credible maloperations and system failures that might occur during reaction;

(b) the kinetics of the reaction under runaway conditions;

(c) whether the reaction pressure is from vapour or non-condensable gas (or both);

(d) the flow regimes, both in the vessel and the relief system, during pressure relief; and

(e) the design and layout of the relief system.

Unless you use such information and apply it properly in the pressure relief system design, then the system may not be correctly sized.

2   The identification and characterisation of worst case scenarios have been discussed in paragraphs 149-152 of the main text.

3   State-of-the-art techniques for vent design have been developed by the Design Institute for Emergency Relief Systems (DIERS). A number of relief-system sizing methods are available.[59] HSE has published a workbook[36] that gives information on methods available.

What happens during relief?

4   During an exothermic runaway the reaction temperature increases exponentially. As the temperature increases the pressure in the reactor may also increase. This can occur in three ways:

(a) The pressure generated is due solely to the increasing vapour pressure of the reaction mass as the temperature increases - vapour pressure systems.

(b) The pressure generated is due to a permanent gas - *gassy systems*. This can occur in both synthesis and decomposition reactions.

(c) The pressure generated is due to both the vapour pressure and the permanent gas generation - *hybrid systems*.

5   Vapour pressure systems and some hybrid systems are 'tempered'. Providing the relief system is large enough, the vapour generation allows sufficient latent heat of vaporisation to moderate the runaway. This holds the temperature constant and keeps the reaction rate approximately constant.

6   Gassy systems are *'untempered'* because there is no available mechanism for the removal of significant amounts of heat from the vented system.

7   The fluid vented from an exothermic runaway is usually a two-phase gas/liquid or vapour/liquid mixture. DIERS recommend that two-phase flow be assumed for most reactor-relief system sizing calculations.

Flow regimes

8   The fact that the fluid vented is usually a two-phase mixture is due to the phenomenon of *level swell*. As the runaway generates vapour and/or gas, the bubbles produced attempt to rise through the liquid to disengage at the surface. These bubbles occupy volume, so that while they are within the liquid the bulk-liquid level rises or 'swells'.

9   The extent of the level swell is dependent on the type of flow regime occurring in the vessel. Many reacting systems are inherently foamy. This means that they vent a two-phase mixture that is homogeneous, that is, the fluid entering the vent has the same ratio of vapour or gas to liquid as the average in the vessel. Such systems will continue to vent a two-phase mixture until the vessel is empty.

10 In systems that are not inherently *foamy* the fluid entering the vent contains a higher proportion of gas or vapour. There are two main flow regimes in these circumstances: *bubbly*; and *churn-turbulent*.

11 In bubbly flow the bubbles are small and discrete and rise through the liquid relatively slowly, which makes two-phase flow into the vent more likely. In *churn-turbulent flow* the bubbles coalesce to form larger bubbles that rise faster.

12 You do not necessarily need to know the actual flow regime occurring in practice, if you assume the worst case when using the relief system sizing methods. However, it may sometimes be desirable to determine the flow regime because:

(a) for tempered systems, if gas or vapour-only venting can be shown to occur, a smaller relief size than for two-phase flow can be obtained;

(b) a number of the sizing methods (for tempered systems only) allow the disengagement from two-phase flow to single gas or vapour flow in order to reduce the relief size; and

(c) best estimates for the amount of two-phase mixture relieved are needed to reduce the size and cost of disposal systems downstream of the process.

Designing the vent

13 In practice, all vents have a discharge pipe and the calculated vent area may need increasing to allow for the effect on the flow. This can be due to:

(a) friction along the discharge pipe;

(b) the effect on flow by any disposal systems downstream; and

(c) *choked flow*.

Ideally, vent lines should be as short and straight as practicable and must discharge to a safe place.

14 Choking is a phenomenon that occurs in high-speed compressible flows. Its effect is to limit the flow rate of compressible flow for a given upstream pressure.

15 Having calculated the vent area required by an appropriate method you may need to apply a safety factor. This is to take care of errors introduced because of the assumptions in the calculation methods, or due to the accuracy of the kinetic data (which is directly proportional to the vent area).

16 As a minimum, the vent discharge-pipe diameter needs increasing to the next available standard pipe size above the calculated vent area. It should never be reduced to a size less than the calculated vent area.

References and further information

References

1   *Chemical reaction hazards and the risk of thermal runaway*
    Leaflet INDG254 HSE Books 1997 (single copy free or priced packs of 15
    ISBN 978 0 7176 1404 2) www.hse.gov.uk/pubns/indg261.pdf

2   *The Management of Health and Safety at Work Regulations 1999*
    SI 1999/3242 The Stationery Office 1999 ISBN 978 0 11 085625 4

3   *Health and Safety at Work etc Act 1974* (c. 37)
    The Stationery Office 1974 ISBN 978 0 10 543774 1

4   *The Provision and Use of Work Equipment Regulations 1998*
    SI 1998/2306 The Stationery Office 1998 ISBN 978 0 11 079599 7

5   *The Pressure Systems Safety Regulations 2000*
    SI 2000/128 The Stationery Office 2000 ISBN 978 9 99901760 2

6   *The Pressure Equipment Regulations 1999*
    SI 1999/2001 The Stationery Office 1999 ISBN 978 0 11 082790 2

7   *The Control of Substances Hazardous to Health Regulations 1999*
    SI 1999/437 The Stationery Office 1999 ISBN 978 0 11 082087 3

8   *The Control of Major Accident Hazard Regulations 1999*
    SI 1999/743 The Stationery Office 1999 ISBN 978 0 11 082192 4

9   'Council Directive 98/24/EC of 7 April 1998 on the protection of the health and
    safety of workers from the risks related to chemical agents at work (14th
    individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)'
    Official Journal of the European Communities 1998 **141** (L131) 11-23

10 *Five steps to risk assessment* INDG163(rev2) HSE Books 2006
    (single copy free or priced packs of 10 ISBN 978 0 7176 6189 3)
    www.hse.gov.uk/pubns/indg163.pdf

11 *A guide to the Control of Major Accident Hazard Regulations 1999
    (as amended). Guidance on Regulations* L111 HSE Books 2006
    ISBN 978 0 7176 6175 6

12 *Environmental Protection Act 1990* (c.43)
    The Stationery Office 1990 ISBN 978 0 10 544390 2

13 Environment Agency *Processes subject to integrated pollution control: IPC
    guidance note series 2:Chemical industry sector: Speciality organic chemicals*:
    IPC S2 4.02 The Stationery Office 1999 ISBN 0 11 310154 6 (Out of print)

14 Environment Agency *Processes subject to integrated pollution control: IPC
    guidance note series 2:Chemical industry sector: Speciality organic chemicals:
    Large volume organic chemicals* IPC S2 4.01 The Stationery Office 1999
    ISBN 0 11 310153 8 (Out of print)

15 Bollinger R E and Clark D G *Inherently safer chemical processes: A life cycle approach* American Institute of Chemical Engineers 1996 ISBN 978 0 8169 0703 8

16 Kletz T A *Process plants: A handbook for inherently safer design* Taylor and Francis 1998 ISBN 978 1 5603 2619 9

17 *Functional safety of electrical/electronic/programmable electronic safety-related systems Parts 1-7* BS IEC 61508 (1-7): 1998/2000

18 *Functional safety of safety instrumented systems in the process sector Parts 1-3* BS IEC 61511 (1-3): 2000

19 Barton J and Rogers R *Chemical reaction hazards: A guide to safety* Second edition Institution of Chemical Engineers 1997 ISBN 978 0 85295 341 9

20 Etchells J E 'Why reactions run away' *Hazards XIII Process safety: The future: A three day symposium organised by the Institution of Chemical Engineers (North Western Branch) and held at UMIST*, Manchester, UK *22-24 April 1997* 1997 **141** ISBN 978 0 85295 388 4

21 *Design for safe handling of industrial chemicals Sheffield 26-27 October 1998* short course Institution of Chemical Engineers 1998

22 Urben P G and Pitt M J *Bretherick's Handbook of reactive chemical hazards* Sixth edition Butterworth-Heinemann 1999 ISBN 978 0 7506 3605 6

23 National Fire Protection Association *Manual of hazardous chemical reactions* ANSI/NFPA 491M American National Standards Institute 1991

24 *Energetic and spontaneously combustible substances: Identification and safe handling* HSG131 1995 HSE Books 1995 ISBN 978 0 7176 0893 5

25 Pedley J B, Naylor R D and Kirby S P *Thermochemical data of organic compounds* Second edition Chapman and Hall 1986 ISBN 978 0 4122 7100 7

26 Cox J D and Pilcher G *Thermochemistry data of organic and organometallic compounds* Academic Press 1970 ISBN 978 0 1219 4350 9

27 Frurip D J, Freedman E 'A new release of the ASTM CHETAH program for hazard evaluation: Versions for mainframe and personal computer' *Plant/Operations progress* 1989 8 2 100-104

28 Sanderson R G *Chemical bond and bond energy* Academic Press 1971

29 Benson S W *Thermochemical kinetics. Methods for the estimation of Thermochemical data and rate parameters* Second edition Wiley-Interscience 1976 ISBN 978 0 4710 6781 8

30 *Guidelines for chemical reaction hazard evaluation* Association of the British Pharmaceutical Industry 1989

31 Grewer T *Thermal hazards of chemical reactions Industrial safety series 4* Elsevier Science 1994 ISBN 978 0 444 89722 0

32 Steinbach J *Safety assessment for chemical processes* Wiley-VCH 1999 ISBN 978 3 527 28852 6

33   *Guidelines for chemical reactivity evaluation and application to process design*
American Institute of Chemical Engineers 1995 ISBN 978 0 8169 0479 2

34   Crawley F, Tyler B J, Preston M *Hazop: Guide to best practice* Institution of
Chemical Engineers 1999 ISBN 978 0 8529 5427 0

35   Kletz T A *Hazop and Hazan: Identifying and assessing process industry hazards*
Fourth edition Institution of Chemical Engineers 1999 ISBN 978 0 8529 5421 8

36   *Workbook for chemical reactor relief system sizing* CRR 136 HSE Books 1998
ISBN 978 0 7176 1389 2

37   *Guidelines for pressure relief and effluent handling systems with CD-ROM*
American Institute of Chemical Engineers 1998 ISBN 978 0 8169 0476 1

38   Parry C F *Relief systems handbook* Institution of Chemical Engineers 1992
ISBN 978 0 85295 267 2

39   *Safe disposal of vented reacting fluids* CRR 100 HSE Books 1996
ISBN 978 0 7176 1107 2

40   *Management of Health and Safety at Work. Management of Health and Safety
at Work Regulations 1999. Approved Code of Practice and guidance* L21 HSE
Books 2000 ISBN 978 0 7176 2488 1

41   *Health and safety training: What you need to know* Leaflet INDG345 HSE
Books 2001 (single copy free or priced packs of 15 ISBN 978 0 7176 2137 8)
www.hse.gov.uk/pubns/indg345.pdf

42   *Managing contractors: A guide for employers: An open learning booklet*
HSG159 HSE Books 1997 ISBN 978 0 7176 1196 6

43   *The Confined Spaces Regulations 1997* SI 1997/1713
The Stationery Office 1997 ISBN 978 0 11 064643 5

44   *Safe work in confined spaces. Confined Spaces Regulations 1997. Approved
Code of Practice, Regulations and guidance* L101 HSE Books 1997
ISBN 978 0 7176 1405 9

45   *Safe work in confined spaces* INDG258 HSE Books 1997 (single copy free or
priced packs of 20 ISBN 978 0 7176 1442 4)
www.hse.gov.uk/pubns/indg258.pdf

46   *EH40/2005 Workplace exposure limits: Containing the list of the workplace
exposure limits for use with the Control of Substances Hazardous to Health
Regulations 2002 (as amended)* Environmental Hygiene Guidance Note EH40
HSE Books 2005 ISBN 978 0 7176 2977 0

47   Oil Industry Advisory Committee *Guidance on permit-to-work systems in the
petroleum industry* HSE Books 1997 ISBN 0 7176 1281 3

48   *Permit-to-work systems in the chemical industry* INDG98 HSE Books 1997
(Out of print)

49   *Emergency planning for major accidents: Control of Major Accident Hazards
Regulations 1999 (COMAH)* HSG191 HSE Books 1999
ISBN 978 0 7176 1695 4

50   *Preparing safety reports: Control of Major Accident Hazards Regulations 1999
     (COMAH)* HSG190 HSE Books 1999 ISBN 978 0 7176 1687 9

51   *The Chemicals (Hazard Information and Packaging for Supply) Regulations
     1994* SI 1994/3247 The Stationery Office 1994 ISBN 978 0 11 043877 1
     (as amended)

52   *The Highly Flammable Liquefied Petroleum Gases Regulations 1972*
     SI 1972/917 The Stationery Office 1972 ISBN 978 0 11 020917 3

53   *Factories Act 1961* (c. 37) The Stationery Office 1961 ISBN 978 0 10 850027 5

54   *The Personal Protective Equipment at Work Regulations 1992*
     SI 1992/2966 The Stationery Office 1992 ISBN 978 0 11 025832 4

55   *Personal protective equipment at work. (Second edition). Personal Protective
     Equipment at Work Regulations 1992 (as amended). Guidance on Regulations*
     L25 HSE Books 2005 ISBN 978 0 7176 6139 8

56   *Safety of pressure systems. Pressure Systems Safety Regulations 2000
     Approved Code of Practice* L122 HSE Books 2000 ISBN 978 0 7176 1767 8

57   *Safe use of work equipment. Provision and Use of Work Equipment
     Regulations 1998. Approved Code of Practice and guidance* L22 (Third edition)
     HSE Books 2008 ISBN 978 0 7176 6295 1

58   *Control of substances hazardous to health (Fifth edition). The Control of
     Substances Hazardous to Health Regulations 2002 (as amended). Approved
     Codes of Practice and guidance* L5 (Fifth edition) HSE Books 2005
     ISBN 978 0 7176 2981 7

59   Fisher H G *Emergency Relief System Design Using DIERS Technology: The
     Institute for Emergency Relief Systems (DIERS) Project manual* American
     Institute of Chemical Engineers 1992
     ISBN 978 0 8169 0568 3

Further reading

BS 5908: 1990 *Code of practice for fire precautions in the chemical and allied
industries* British Standards Institution

Chemical warehousing: The storage of packaged dangerous substances HSG71
(Second edition) HSE Books 1998 ISBN 978 0 7176 1484 4

Control of exothermic chemical reactions Video HSE Books 1993
ISBN 978 0 7176 1882 8

Control of exothermic chemical reactions IChemE Training package Institute of
Chemical Engineers 1993 ISBN 978 1 8989 45 222

*Formula for health and safety: Guidance for small and medium-sized firms in the
chemical industry* HSG166 HSE Books 1997 ISBN 978 0 7176 0996 3

Integrated pollution control: A practical guide Department of the Environment 1995
ISBN 978 1 85112 021 5

Monitoring strategies for toxic substances HSG173 (Second edition) HSE Books
2006 ISBN 978 0 7176 6188 6

Successful health and safety management HSG65 (Second edition) HSE Books
1997 ISBN 978 0 7176 1276 5

Safe use and handling of flammable liquids HSG140 HSE Books 1996
ISBN 978 0 7176 0967 3

The storage of flammable liquids in tanks HSG176 HSE Books 1998
ISBN 978 0 7176 1470 7

Further information

For information about health and safety ring HSE's Infoline Tel: 0845 345 0055
Fax: 0845 408 9566 Textphone: 0845 408 9577 e-mail: hse.infoline@natbrit.com or
write to HSE Information Services, Caerphilly Business Park, Caerphilly CF83 3GG.

HSE priced and free publications can be viewed online or ordered from
www.hse.gov.uk or contact HSE Books, PO Box 1999, Sudbury, Suffolk
CO10 2WA Tel: 01787 881165 Fax: 01787 313995. HSE priced publications
are also available from bookshops.

British Standards can be obtained in PDF or hard copy formats from the BSI online
shop: www.bsigroup.com/Shop or by contacting BSI Customer Services for hard
copies only Tel: 020 8996 9001 e-mail: cservices@bsigroup.com.

The Stationery Office publications are available from The Stationery Office,
PO Box 29, Norwich NR3 1GN Tel: 0870 600 5522 Fax: 0870 600 5533
e-mail: customer.services@tso.co.uk Website: www.tso.co.uk (They are also
available from bookshops.) Statutory Instruments can be viewed free of charge
at www.opsi.gov.uk.

Environment Agency (EA) general enquiries or requests for publications should be
directed to National Customer Contact Centre, PO Box 544, Rotherham S60 1BY.
General enquiries: Tel: 08708 506 506
e-mail: enquiries@environment-agency.gov.uk

Scottish Environment Protection Agency (SEPA) general enquiries should be
directed to SEPA, Erskine Court, Castle Business Park, Stirling FK9 4TR.
Tel: 01786 457700 Website: www.sepa.org.uk

Institution of Chemical Engineers, Davis Building, 165-189 Railway Terrace, Rugby
CV21 3HQ Tel: 01788 578214

Royal Society of Chemistry (RSC), Burlington House, Piccadilly, London W1J 0BA.
Tel: 020 7437 8656 Fax: 020 7237 8883 Website: www.rsc.org.

Glossary

Accelerating rate calorimeter (ARCTM): A type of **adiabatic calorimeter**.

Accumulation: A build-up of unreacted materials in a semi-batch or continuous reactor.

Adiabatic: No heat transfer occurs to or from the environment surrounding the sample, including the sample container.

Adiabatic temperature rise: The increase in temperature of a reacting mixture as a result of **exothermic** chemical reaction, when there is no heat transfer to or from the environment.

ARC™: see **accelerating rate calorimeter**.

Autocatalysis: The increase of the rate of reaction due to the catalysing effect of the reaction products.

Autoignition temperature: The minimum temperature at which a material will ignite spontaneously under specified test conditions. It can also be referred to as the minimum ignition temperature.

Basis of safety: The combination of measures relied upon to ensure safety. The basis of safety for a reactor highlights those aspects of the design and operation (hardware, protective systems and procedures) that are safety critical. The basis of safety can only be selected once all the significant **hazards** have been identified and evaluated.

Batch process: An operation in which all the **reactants** including any solvent are added to a reactor at the start of a reaction.

Batch reactor: Reactor in which all **reactants** and solvents are introduced before setting the reaction conditions. Products are only taken from the reactor upon conclusion of the reaction process.

Bubbly flow: A **two-phase** flow regime in which small discrete bubbles exist within a liquid.

Calorimeter: See **reaction calorimeter**.

Choked flow: The maximum flow rate of a compressible fluid (gas or **two-phase**) for a given upstream pressure.

Churn-turbulent flow: A two-phase flow regime in which large bubbles exist within a liquid.

Continuous reactors: Reactors that are characterised by a continuous flow of **reactants** into, and products from, the reactor system.

Continuous stirred tank reactor (CSTR): A tank reactor in which the contents are stirred by an agitator to promote mixing and characterised by a continuous flow of **reactants** into, and products from, the reaction system.

Decomposition: The breaking up of a chemical compound into gaseous products. The temperature at which decomposition occurs depends on scale and is markedly dependent on the sensitivity of the measuring equipment.

Deflagration: Chemical reaction propagating through a material by a reaction front or zone travelling at subsonic speed.

Detonate: see **Detonation**.

Detonation: Chemical reaction propagating through a material by a reaction front or zone in front of a shock wave travelling at supersonic speed.

Dewar: A vacuum flask that can be used in calorimetry.

DIERS: The Design Institute for Emergency Relief Systems of the American Institute of Chemical Engineers. A collaborative group of companies and organisations.

Differential scanning calorimetry (DSC): A technique in which the difference of energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. **DSC** and **DTA** are essentially equivalent.

Differential thermal analysis (DTA): see **differential scanning calorimetry**.

DSC: see **differential scanning calorimetry**.

DTA: see **differential thermal analysis**.

Dumping: Rapid discharge of the contents from the bottom of a reactor. Term sometimes used synonymously with 'bottom venting'.

Endothermic: A reaction is called endothermic if energy (heat) is absorbed during the reaction.

Exothermic: A reaction is called exothermic if energy (heat) is released during the reaction.

Explosion: A release of energy sufficient to cause a pressure wave.

Flow regime: An idealised model of the behaviour of a **two-phase** system that best describes the actual behaviour.

Foamy: see **foamy flow**.

Foamy flow: A flow regime in which the **vapour** and liquid phases are uniformly and homogeneously mixed as a foam.

Gassy systems: A system type for **relief system sizing** in which pressure increase is due to permanent gas generated by a reaction.

Hazard: The disposition of a thing, a condition or a situation to cause injury. The 'injury' of concern is physical injury and/or ill health to people, though this may be accompanied by harm to property and the environment.

Hazard and operability study (HAZOP): A technique to identify process hazards and potential operating problems using a series of guide words to study process deviations.

HAZOP: see **hazard and operability study**.

Heat of reaction: The total quantity of thermal energy liberated or absorbed during a chemical reaction.

Hybrid: A system type for relief sizing in which pressure is due to both vapour pressure of the reacting system and the generation of permanent gas from the reaction.

Inherently safer: A system is described as inherently safer if it remains in a non-hazardous situation after the occurrence of non-acceptable deviations from normal operating conditions. Inherently safer is used rather than inherently safe because all hazards cannot be removed.

Inhibition: A protective measure where the reaction can be stopped by addition of another material.

Isoperibolic: see **isoperibolic system**.

Isoperibolic system: A system in which the controlling **jacket temperature** is kept constant.

Isothermal: A system condition in which the temperature remains constant.

Jacket temperature: The temperature of the fluid contained in the reactor jacket used to indirectly heat or cool the reactor contents.

Kinetic data: Data associated with the conversion rate of a reaction.

Level swell: The increase in liquid level due to the presence of gas or vapour bubbles within the liquid.

Loop reactor: Continuous flow reactors that are characterised by the fact that part of the effluent stream is re-supplied to the reactor, either directly or mixed with a reactant supply stream.

Occupational exposure limit: The legal limits of concentration in the air of substances hazardous to health, averaged over a specified time: often referred to as an OEL.

Onset temperature: Defined as the temperature at which the heat released by a reaction can no longer be completely removed from the reaction vessel, and consequently, results in a detectable temperature increase. The onset temperature depends on detection sensitivity, reaction kinetics, vessel size and on cooling, flow and agitation characteristics. Scaling of onset temperatures and application of 'rules of thumb' concerning onset temperatures must be regarded as highly unreliable.

Permanent gas: A gas that cannot be condensed (or solidified) under the range of conditions of interest (eg temperature or pressure).

Phi-Tec™: A type of adiabatic calorimeter.

Pyrophoric: A material that will burn in air without the addition of an ignition source.

Quenching: Severe cooling of the reaction system in a short time.

Rate of reaction: The rate at which conversion of **reactants** takes place.

Reactants: Chemicals that are converted into products during the reaction process.

Reaction: The process in which chemicals (**reactants**) are converted into other chemicals (products).

Reaction calorimeter: A laboratory test apparatus for measuring thermal effects of chemical reactions or processes. For the purpose of this guidance, types of reaction calorimeters include **isothermal, isoperibolic** and **adiabatic systems**.

Reactive systems screening tool (RSST™): A type of pseudo-adiabatic calorimeter.

Reasonably practicable: The degree of **risk** in a particular job or workplace needs to be balanced against the sacrifice in time, trouble, cost and physical difficulty of taking measures to avoid or reduce the risk. Measures must be taken to eliminate or control the risks unless it is clear that the sacrifice incurred in doing so is grossly disproportionate to the level of the risk. However, the ability to pay for additional control measures is not a deciding factor as to whether they are necessary.

Reflux: A system condition in which a component in the **reaction** system (usually a solvent) is continually boiled off, condensed in a nearby condenser and subsequently returned to the reaction system.

Relief system sizing: the sizing of an emergency relief vent.

Relief system: All parts of the pressure-relief flow path from the protected vessel to atmosphere or containment within a disposal system. This includes relief device(s), piping and any containment and disposal system.

Risk: The chance of something adverse happening where 'something' refers to a particular consequence of the manifestation of a **hazard**. Risk reflects both the likelihood that harm will occur and its severity in relation to the number of people who might be affected, and the consequences to them.

Risk assessment: The process of identifying the hazards present in any undertaking (whether arising from work activities or other factors) and those likely to be affected by them, and of evaluating the extent of the risks involved, bearing in mind whatever precautions are already being taken.

RSST: see **reactive systems screening tool**.

Runaway: A **reaction** that is out of control because the rate of heat generation by an **exothermic** chemical reaction exceeds the rate of cooling available.

Semi-batch: An operation in which some materials are added to the reactor at the start, with one or more other **reactants** added in a controlled manner during the **reaction**. See also **semi-batch reactor**.

Semi-batch reactor: A type of reactor that is characterised by the supply, in a controlled manner, of one or more key **reactants** during the **reaction**. Products are only taken from the reactor upon conclusion of the reaction process.

Supercritical processing: Processing using supercritical fluids. In a gas-liquid equilibrium there is a certain temperature and pressure below which a gas and a liquid can co-exist but above which only a single phase (known as a supercritical fluid) can form.

Thermal runaway: see **runaway.**

Two-phase: Any system in which two phases exist.

Untempered: see **untempered system**.

Untempered system: A reacting system in which the temperature cannot be held constant at constant pressure, because there is insufficient vapour pressure to cause sufficient cooling by removal of latent heat.

Vapour: The gaseous phase released by evaporation from a material at normal temperatures and pressure.

Vapour pressure system: A system type in which pressure is due to the **vapour** pressure of the reacting system. Tempering will occur with pressure relief via an adequately sized relief.

Venting: Emergency flow of vessel contents out of the vessel through an opening provided. The pressure is reduced by venting, thus avoiding a rupture of the vessel by overpressurisation. The vent flow can be single phase or multiphase, each of which results in different flow and pressure characteristics.

Vent Sizing Package (VSP™): A type of adiabatic calorimeter.

VSP™: see vent sizing package.