Chemical Safety

Module 3

ROYAL SOCIETY OF CHEMISTRY

Health & Safety Essentials

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Control of hazardous operations – safe processing in the laboratory

A number of operations may be undertaken in laboratories that give rise to energetic reactions; these may involve reactions at high pressures, high temperatures, oxidation reactions and so on.

- You should keep energetic reactions as small as possible and know the flammable limits of gaseous mixtures.
- If possible work outside the flammable ranges, and change temperature and pressure to modify these ranges.
- Think about maximum energy releases, and ensure that the apparatus is designed to cope with this, or if not contained in an enclosure, and exclude persons from the area during the period of risk.
- Ensure that all fuel gas lines are colour coded, and labelled with identification along their length. They should be regularly inspected and maintained by competent staff for damage and leaks. Particular attention to connections and flexible hoses is required so that they are safe and secure.
- Ensure safe working for pyrophoric substances, such as metal hydrides and alkali metals, with an emphasis on weighing, addition to reactions, quenching and waste disposal.
- During the transfer of solids to vessels, traces of solids should not be left on the vessel walls as pyrophoric materials such as Raney nickel, cobalt, manganese and palladium may ignite vapours. Many materials not normally pyrophoric may become so when present in a finely divided state.

Inherently safe design of chemical processes

The principle of inherently safe processing is that due to the chemicals involved, the operating conditions and the reaction route, no or minimal control systems are required to prevent unacceptable (unsafe) deviations from the intended process.

There are different methods for achieving inherently safe design:

Intensification
This involves the use of smaller quantities or minimal amounts of hazardous material, so that even in the event of a release there is a risk reduction and no major emergency, even if all the contents are lost.

Energy limitation
Consideration should be made to limiting the amount of energy available in the process e.g. to limit the temperature of the heat exchange fluid.

Substitution
Substitution involves the use of safer materials that are less inherently hazardous; flammable, toxic, explosive etc. Consideration should also be given to the substances used in heating baths and condensers to ensure they are compatible with the reactants if there is an equipment failure.

Alternative reaction routes
This involves designing a reaction route that avoids the production of a harmful intermediate or by product that could be potentially released. For example, during the production of Carbaryl, at Bhopal , methyl isocyanate was produced, and its release caused a major accident. An alternative reaction route, using the same materials but in a different order, results in no methyl isocyanate being formed in the reaction, and thus no potential for its release during an incident.

Modified storage arrangements
If no reductions, substitutions or alternative reaction routes are possible to reduce the risk, then material should be handled in its least hazardous form, or stored on location in the most minimal quantities. You should look at delivery supplies on a daily or just-in-time basis, so that the inventory is kept to a minimum.

Simplicity
This means designing a process that is simpler, with less potential for electro-mechanical or human error.

Assessment of inherently safer processes:
If the lab work is 'pure research' then the selection of a synthetic route to produce a material or the study of reaction intermediates or kinetics will not involve considerations for scale-up and manufacture. However, as soon as scale-up with the associated complexities of process economics are to be considered, then much more detailed assessments will be required.

Dangerous substances risk assessment

Before work is carried out you need to assess the risks created by the use of dangerous substances

To complete a risk assessment you will need to identify:
- dangerous substances in the workplace
- the activities involving those substances
- the ways in which those substances and the way that they are handled, could cause harm to people

The purpose of this examination is to carry out a 'suitable and sufficient'[8] risk assessment to determine if anything needs to be done to eliminate or reduce the risks from these substances 'so far as is reasonably practicable,'[2] or eliminate them completely. The duty under COSHH is to reduce exposure to as low as is reasonably practicable.

The risk assessment should take into consideration:
- the hazardous properties of the substance (including information on the safety data sheet, given by the supplier)
- the circumstances of the work that include the work process, and the substances used
- the amount of substance involved
- the risk involved if more than one dangerous substance is present, if they have any interactions
- the arrangements in place for safe handling, storage and transport of dangerous substances and any waste materials
- any maintenance activities, particularly where there is a level of risk (such has hot work and flammable materials)
- the likelihood of an explosive atmosphere occurring, and how long for
- the types of ignition sources, their likelihood, including electrostatic discharges
- any places that can be connected via openings to places where explosive atmospheres may occur
- the scale of the anticipated effects of any fire or explosion
- any other safety information that you may need to complete the assessment

If during the assessment you discover that the risk is trivial, then nothing further is required to be done.

For further information on **Risk Assessment, please see Health & Safety Essentials – Risk Assessment**.

Five steps to risk assessment

When conducting a risk assessment the '5 steps to risk assessment' approach as recommended by the Health and Safety Executive can be used for chemical safety, dangerous substances and explosive atmospheres assessments.

If you can eliminate the risk completely, by replacing the dangerous substance altogether or using a different process or alternative reaction route, then this is the best solution.

1.	Identify hazards	Sources of ignition - flames/sparks, mantles/hot plates, soldering, chemical sources Sources of fuel - organic chemicals, solvents, paper, plastics, textiles Sources of oxygen - air/forced ventilation, oxidisers, oxygen, flammable gas Process hazards - energetic materials, runaway reactions, explosive substances Chemical hazards - toxic, corrosive, harmful, irritant, carcinogenic
2.	Identify people at risk	People (general) - in and around premises, students, employees, visitors, contractors People (specific risks) - people with impaired vision/hearing/mobility, lone workers
3.	Assess the risk and develop control measures	Evaluate risk of an event occurring - fire, failure of cooling water, incompatible storage, flammable atmospheres, exothermic reactions, explosion of energetic material maintenance operations, storage operations, dispensing, transport of materials, process or reaction considerations, safe operating parameters, quantities of materials Evaluate risk to people - from explosions, spread of fire/smoke, projectiles, chemical releases Control Measures in place/ required - storage considerations (segregation), control of ignition sources, appropriate equipment use (i.e. electrical), fuels, use of flammables /oxygen/ventilation sources, substitute for less hazardous materials, take alternative reaction routes (to prevent formation of a dangerous substance), use minimal quantities of materials, avoid or minimise release of substances, collect, contain or remove releases to a safe place, use of extraction systems, fume hoods, glove boxes (including for analysis), avoid adverse conditions (exceeding the limits of temperatures or pressures, or control limits), safe operating procedures, instructions, supervision, training, labelling of pipes and containers and use of personal protective equipment. Remove or reduce the risks to people - Fire precautions (access and escape routes, fire detection and alarm systems, maintenance of systems, training and routine checks and drills).
Remember the hierarchy of controls as:		Eliminate Reduce Isolate Control Use of Administrative Controls (Procedures), Instruction/Supervision/Training, Personal Protective Equipment (the last line of defence)

In addition to control measures, there are a number of other measures that are also required and these are termed **mitigation** measures, and they should be consistent with the risk assessment and the activities or operations taking place. These measures are about reducing the impact of an incident or accident if one occurred.

	These include considerations such as:	Limiting or reducing the number of persons at risk- by restricting access, isolating the area, access controls admitting competent trained persons only Providing equipment that is explosion resistant- pressure relief to a safe place, special cages around glass equipment, explosion suppression Taking measures to control the spread- of fires and explosions, fire suppression systems, use of inert gases, compartmentalisation
4.	Record, plan, inform, instruct and train	Record significant finding - record the control measures and actions required as soon as practicable after the assessment is completed Prepare an emergency plan - document the plan and use it for training Provide information, instruction, training - ensure all those impacted are aware of the significant findings of the risk assessment, any control measures put in place to control risks and any actions they need to take, and in the event of an emergency. They should also be aware of the nature of the dangerous substances and the risks they present, any hazard data information (safety data sheets) and applicable legislation
5.	Review	Keep your assessment under regular review to ensure it is up to date, and if you believe it is no longer valid or if there has been a significant change to the workplace, work process , or people, if new information comes to light, if you make a change to the process, new persons involved or after an incident. The review should be a regular part of your systems.
Remember		Control measures must be put in place to eliminate risks from dangerous substances, or reduce them 'so far as is reasonably practicable'. Where it is not possible to eliminate the risk completely measures must be taken to control the risks and reduce the severity (mitigate) of the consequences.

Hazardous area classification[9]

The areas where explosive atmospheres may occur should be identified and classified into zones, based on their likelihood and persistence.

If the assessment indicates that an area needs to be zoned, the following scheme should be used to allow the correct selection of equipment & protective systems.

The zone classifications are:

- **Zone 0 (Zone 20)** That part of a hazardous area in which an explosive atmosphere is continuously present, or present for long periods, or frequently.
- **Zone 1 (Zone 21)** That part of a hazardous area in which an explosive atmosphere is likely to occur occasionally in normal operation.
- **Zone 2 (Zone 22)** That part of a hazardous area in which an explosive atmosphere is not likely to occur in normal operation but, if it does occur, will persist for a short period only.

Zones 0, 1 and 2 are used for explosive atmospheres formed of flammable gases, vapours or mists.

Zones 20, 21 and 22 are used for explosive atmospheres formed of combustible dusts.

When a particular area has received hazardous area classification9, it needs to be marked at each entrance to that area with the approved sign, and everyone needs training in the special precautions to be adopted when working in that area.

This marking is shown on equipment and protective systems for use in hazardous areas. Further markings with the 'EX' symbol clarify which zone it is suitable for and the method(s) of protection.

Dangerous substances and explosive atmospheres in the laboratory

While Control of Substances Hazardous to Health (COSHH) relates to harm to health, the Dangerous Substances and Explosive Atmospheres Regulations (DSEAR3) is about harm to the physical environment.

On a laboratory scale, the primary source of a flammable atmosphere might be a vapour released when a volatile solvent is poured from one container to another. A secondary source could be a chemist knocking a container onto the floor. These kinds of flammable atmospheres are normally so small or transient that they are controlled by ventilation in the area, and the extent of the explosive atmosphere is negligible.

If precautions in handling, quantities used, ventilation, storage and dispensing controls are already adequate to prevent fire and explosion there is no need for zoning.

Whether work is done on the open bench, in a fume cupboard or a dedicated facility for larger scale work, a decision in a written risk assessment not to zone the laboratory must be justified on the basis that any incident will be of limited scale and could be safely and quickly controlled by those present; or that they could escape very quickly without leaving others in the building at risk. A high standard of controls of the type described above will help justify this assessment finding.

Factors to consider when assessing the risk

You should consider sudden releases, and specify a maximum release quantity. This assessment can be made from imagining what would happen if a glass flask fractured, how volatile the material is, what happens during a distillation if the cooling water failed, or if you are storing materials above their flash point.

Competence and training is also relevant to assessing the risk. Students and young persons may not have sufficient experience in laboratory work. Consequently they should have the necessary training to deal with any problems that might arise. Think also of security staff, cleaning staff or anybody that may be required to monitor reactions that are running in the area.

The degree of supervision of a continuous process needs to be considered. Would somebody be constantly available to take action? Consider if the cooling water failed, a flask cracked, a process boiled over? Would you be able to isolate all the equipment from a safe place (not in the vicinity that could create a spark)? Familiarity with a process should not be the basis for leaving the process unsupervised. If the risk exists, then the process should be supervised at all times and not left unattended.

Review the standard operating practices within your organisation that allow for unsupervised running of a reaction and make considerations for this as part of your assessment.

Strictly, hazardous area classification[9] takes no account of the consequences of a release, whether this is a fire or explosion, but selection of the necessary precautions must take the consequence factor into account and this approach is recognised in DSEAR.[3] If precautions already used are adequate to prevent fire and explosion risks to laboratory workers, then there is no need for zoning and `special precautions' in terms of the ignition risk from equipment will not be necessary.

For laboratory work, it is helpful to consider separately releases which occur suddenly, but where the maximum release quantity can be specified, e.g. the fracture of a glass flask; and those where the release once started will continue until some corrective action is taken to shut off the release, e.g. closing a valve following the failure of a plastic or rubber hose from a gas cylinder or mains supply.

The volatility of the product is also an important factor, but this must be considered in the context of the temperature at which it will be used. So if you are pouring a solvent from one open container to another at a temperature below its flash point, there should be no hazardous area, because too little vapour is present. If you then distil the same solvent and the condenser cooling fails, vapour will be released, and the risk is much greater. Consequently, the comments on flammable liquids apply whenever they are used or stored above their flash point. Most laboratories have good general ventilation, but this is not primarily intended to limit the extent of any explosive atmospheres that may form. More localised extraction is needed for this.

Very small and small scale operations

Looking first at operations with flammable liquids, at the very smallest scale of operations, the consequences of a spill may well be trivial. Quantities up to about 50mls can be mopped up, and if they ignite, so long as the fire does not quickly spread, they may well burn out before anyone is at risk, or before a laboratory worker could take any action to extinguish a fire. If these are the conclusions of a risk assessment, formal zoning is clearly inappropriate, though it may well be appropriate to avoid the use of naked flames and other powerful or constant ignition sources in the immediate vicinity. Where the evaporation of a solvent is deliberately intended, e.g. from a coated surface, the operation may need to be carried out in a fume cupboard. In these cases, if the health risks under COSHH are properly controlled, there may well be no need for additional precautions to control the fire and explosion risk.

Medium scale operations

Where quantities are larger but still manipulated on the open bench, for example up to 2.5 litres, in a Winchester bottle, the risks are more significant. The actual extent of a flammable atmosphere following a spill may well be a radius of up to a metre, but only a very small height above the liquid level. Any ignition of a spreading pool will produce a fire that quickly extends to the whole area of the spill, and could cause a risk to laboratory staff. Particular risks arise if the spill enters the drains, as an explosive atmosphere could then form in an enclosed space.

Direct heating by Bunsen burners and other obvious continuous ignition sources should be avoided, but the greatest risk probably comes from electrical equipment in use as part of the operation. Much of this cannot be avoided, and may well not be available in ignition-protected form, e.g. hot plates, heating mantles, stirrer controllers.

Precautions are likely to include:

- good handling techniques to minimise spills
- sills or other liquid retaining methods to minimise liquid spread
- proper support for glass equipment
- placing electrical equipment where it will not be splashed as a result of a spill (where practicable)
- constant supervision by trained staff (this is so that electrical equipment can be rapidly isolated, others warned of any dangers, and if safe to do so, first aid fire fighting started)

Most importantly, the risk that a fire following a spill will rapidly involve other containers of flammable liquids or other dangerous chemicals should be considered.

It is a common but **poor practice to store chemicals in fume cupboards** and these should be removed. Rapid failure of stored bottles in a small fire could produce sufficient vapour to prevent the extract fan diluting vapours sufficiently. Where these and similar precautions have been adopted, the risk assessment may conclude that there is no need for hazardous areas to be specified.

Instruments with internal flames

Some types of instrumentation use very small internal gas flames and in principle could ignite any surrounding explosive atmosphere, if for instance there was a release of vapour from some operation nearby. In addition, an explosive atmosphere could form from a leak in the fuel line to the flame, or in some cases from flammable liquids in the instrument. Such instrumentation needs specific consideration in the risk assessment. If the maximum size of a leak is very small, any release will form an explosive atmosphere of negligible extent. Best practice is to have an instrument room completely separate from the wet chemical lab.

Liquefied flammable gases

These may be handled either under pressure, or in refrigerated form. A small release of liquid is likely to vaporise immediately, creating a substantial size of explosive gas/air mixture. Pressurised systems need to be robustly constructed, and checks provided to ensure they are leak tight. Where liquids are handled in refrigerated form, the risks from loss of cooling or loss of insulation should be considered. Good ventilation around the apparatus will always be needed, but there may also be a need to designate a zone 2 area. This will depend on the foreseeability of a release of liquid, how rapidly it might be detected, and the ability of the ventilation to disperse it quickly.

Fume cupboards

Fume cupboards are often used for small and medium sized work, and the front sash will often give protection should an incident occur and a fire start.

Arrange work so that any foreseeable release of flammable gas or vapour will be rapidly diluted below the exposure limit by the airflow through the cupboard.

Precautions to reduce the fire risk such as retaining sills at the front edge of the floor of the hood, extraction ductwork kept free from flammable residues, and do not use a fume hood as a chemical store as rapid failure of bottles could result in the extraction being unable to cope with diluting the flammable atmosphere.

Remember **Releases into confined spaces such as fridges, ovens, and drains are most likely to result in an explosion and not a fire**

Larger scale laboratory work

Laboratory work involving equipment above a 2 litre scale, and pilot scale plants need more careful consideration. Pilot scale is taken to mean equipment with a capacity of 50-100 litres or more.

Most indoor laboratories are not designed for safe working with flammable liquids at 20 litres scale and above. Whilst fire precaution arrangements may (just) be adequate for personal safety, there is a 'business continuity' risk to consider as the impact from a large fire could be devastating to the continued use of the lab.

Particular risks come from the use of:

- glass equipment that may be fractured (by impact, thermal shock, overpressure, assembly technique)
- poor handling with open containers
- use of temporary hoses for flammable or other hazardous materials

Perhaps the most useful approach to controlling the ignition risks, is to limit the extent of any flammable atmosphere formed as a result of a release, by a combination of semi-enclosure, forced ventilation, and then to place all electrical equipment outside the enclosure, so far as possible. This may allow a hazardous area study to conclude that any zones are of a very small or even negligible extent. Direct heat sources, like an electric mantle may nevertheless need to be used, and could be exposed to flammable vapours following a major failure of a glass vessel. In this case the risk assessment should consider if the laboratory worker and any others nearby could be expected to escape safely, and how any subsequent fire could be prevented from spreading to affect other people and facilities.

Visitors

A further aspect to the control of hazardous operations is the possible impact on and by visitors to the lab. Included within this group are cleaners, security guards, chemists from other areas and even emergency responders.

When designing a chemical experiment, consideration should be given to labelling fume cupboards, apparatus and support equipment with warnings about hazards and operating limits. In extreme circumstances, demarcated areas may be required to control the particular risks.

Cleaners are part of a particularly vulnerable group and limits to their activities should be made clear in the contract regarding where to clean, what not to touch and how to report observations that concern them. In practice, a level of supervision will be required to achieve a good standard.

In the case of hazardous areas and dangerous substances that have a fire and explosion risk, it is generally an expectation that any maintenance operations must be carried out under a 'Permit to Work System'.

Learning assessment 2

Are the statements below true or false?		true	false
1.	Hazardous area classification zones 0, 1 and 2 are used for explosive atmospheres formed of combustible dusts.		
2.	When a particular area has received hazardous area classification, it needs to be marked with the approved sign at the main entrance only.		
3.	DSEAR: If precautions already used are adequate to prevent fire and explosion risks to laboratory workers, then there is no need for zoning.		
4.	It is OK to store chemicals in fume cupboards.		
5.	Personal Protective Equipment (PPE) should be used as the first line of defence.		
6.	When using a small of amount of a flammable liquid (up to 50 ml) the consequences of a spill are likely to be trivial.		
7.	In the case of hazardous areas and dangerous substances that have a fire and explosion risk, it is generally an expectation that maintenance operations must be carried out under a 'Permit to Work System'.		

Check your answers on the separate answer sheet.