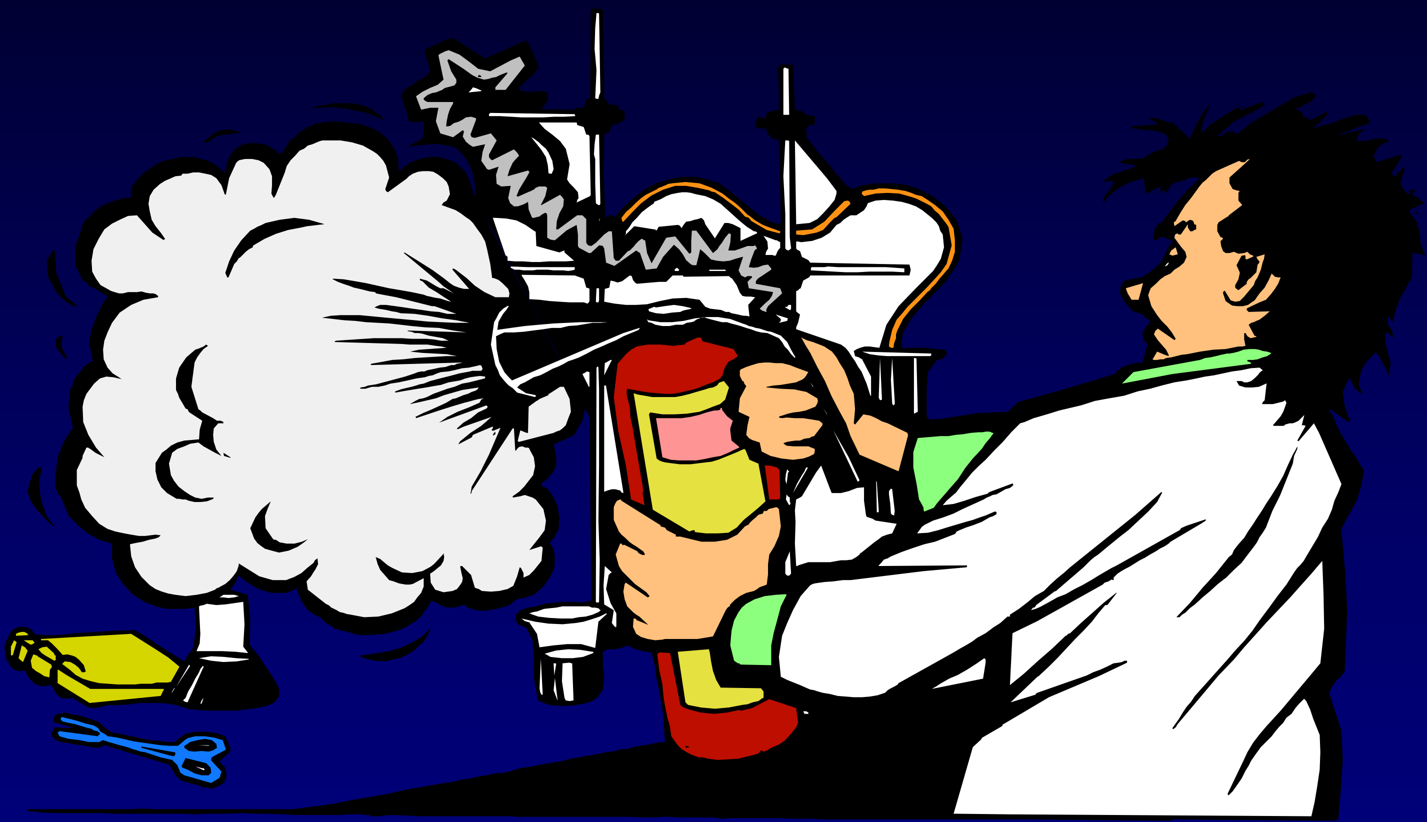
Reaction Safety Hazards



Unstable Compounds and Runaway Reactions

References:

Bretherick, L., *Handbook of Reactive Chemical Hazards*, 6th ed., Butterworths, London, 1999.

Steere, Norman V., editor, *Handbook of Laboratory Safety*, 2nd ed., The Chemical Rubber Co., Cleveland, 1971.

Uncontrolled Energy Release

- All chemical reactions involve energy changes. Most chemical reactions are exothermic, involving a net release of energy.
- Hazardous reactions release energy in quantities or at rates too high to be absorbed by the environment without damage.
- To minimize occurrence of reactive chemical hazards we must control the extent and rate of energy release.

WASTE DISPOSAL

1. Organize disposal to reduce risk of hazardous mixtures
2. Use separate labelled waste containers for:
    a) Halogenated solvents
    b) Hydrocarbons
    c) Polar organics not water soluble
    d) Polar organics - water miscible

3. Use small containers to encourage weekly disposal
4. Do not use metal solvent cans as waste receptacles

UNSTABLE MATERIALS AND INCOMPATIBLE MIXTURES

1. Incompatible Chemicals

- Sulfuric acid + sodium cyanide
- Perchloric acid + diethyl ether
- Arsenic or antimony salts + reducing agents
- Magnesium perchlorate + damp paper towels
- Nitric acid + toluene
- Sodium metal + acetone + water
- Potassium permanganate + acetone

PERMANGANATE (MnO_4^-) and ACETONE

Consider the reaction:

$$5\ CH_3COCH_3 + 16\ MnO_4^- + 48\ H^+$$

$$\longrightarrow 15\ CO_2 + 16\ Mn^{2+} + 39\ H_2O$$

Increase in volume of this system is > 10 fold, based only on stoichiometry and ignoring volume expansion due to the enthalpy of the reaction.

Polyethylene Bottles and Nitric Acid

- Polyethylene embrittles over time in contact with oxidizing agents such as nitric acid.
- These embrittled bottles can shatter when handled, spilling the contents.
- Nitric acid and other oxidizers should not be stored in polyethylene.
- If used for this purpose the bottles should be inspected and replaced at the first sign of loss of flexibility

Kinetic Factors and Reaction Hazards

Law of Mass Action

$$A + B \longrightarrow \text{products}$$

rate (forward reaction) = k [A] [B]

Rate is governed by:

1. Concentration of any catalyst present,
2. Presence of catalytic impurities
3. Inhibitors (induction period)

The Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

E_a = activation energy, T = temperature

- A 10°C increase can double or treble the rate.
- Exothermic reactions accelerate as they proceed.
- The rate of energy release increases exponentially with T.
- The rate of energy dissipation increases approximately linearly with T.
- When the exotherm is large, control may be lost.

Runaway Reactions

- Occur when exotherm is large and cooling capacity is inadequate.
- Fire or explosion may result from accelerating reaction rate.
- Rate of energy release is more important than the quantity of energy released.
- Can be avoided by providing adequate cooling.
- Always provide safety sheilding.
- Provide for pressure relief, away from the laboratory occupants.

Reaction Scale Up

- A frequent cause of runaway reactions
- Increasing the scale of a reaction increases reaction rate - requires greater heat dissipation.
- Doubling the volume of a reaction flask to scale up a reaction by a factor of two does not double the surface area.
- As volume increases, surface to volume ratio decreases.
- energy dissipation cannot increase as rapidly as energy production.
- Scale of a published reaction should never be increased without increased cooling capacity.

Peroxide Formation

- Acetylenes
- Ethers, oxygen heterocycles
- Isopropyl compounds
- Allyl compounds
- Haloalkenes
- Vinyl compounds
- Dienes
- Aldehydes
- Styrenes

1. Peroxides may form as solid precipitate or residues in threads of a screw cap.
2. Friction mechanical shock or temperature increases can readily cause detonation of peroxides.

IDENTIFICATION OF POTENTIALLY UNSTABLE COMPOUNDS

1. Master Chemical Energy Scale

The enthalpy of formation is useful for assessing the energy release that would accompany decomposition of a chemical species.

Enthalpy of formation is compared to that of carbon dioxide, the stable reference compound.

2. High Nitrogen Content Compounds

Azides	Diazo compounds
Diazonium salts	Hydrazinium salts
Nitro compounds	N-nitro compounds
Tetrazoles	Tetrazenes
Triazines	Dinitrophenylhydrazine

3. Oxygen balance

- Difference between the oxygen content of a compound and the oxygen required to fully oxidize the carbon, hydrogen and other oxidizable elements present to carbon dioxide, water and other oxides.

- Nitrogen is assumed to become N_2

- Explosive power of an unstable substance is maximum at zero oxygen balance.

Oxygen Balance Examples

1. Toluene:

$$C_7H_8 + 9O_2 = 7CO_2 + 4H_2O$$

Oxygen balance = 9

2. TNT:

$$2C_7H_5N_3O_6 + 3\tfrac{1}{2}O_2 = 7CO_2 + 2\tfrac{1}{2}H_2O + 3N_2$$

Oxygen balance = 2.5

3. Ethylene dinitrate:

$$C_2H_4N_2O_6 = 2CO_2 + 2H_2O + N_2$$

Oxygen balance = 0

Oxygen Balance or High Nitrogen Content

When faced with the prospect of working with an unfamiliar compound which has a high nitrogen content or a near zero oxygen balance, you should research the properties of the compound in a reference such as Bretherick before proceeding to use the material