SAND2011-0720P

Chemical

SAFETY AND SECURITY TRAINING

Hazards and Potential Consequences

Bangkok, Thailand

1 March 2011

SAND No.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

Sandia National Laboratories

Key acronyms

BLEVE = *boiling-liquid-expanding-vapor explosion*

VCE = *vapor cloud explosion*

LFL = *lower flammable limit*

LOC = *limiting oxygen concentration*

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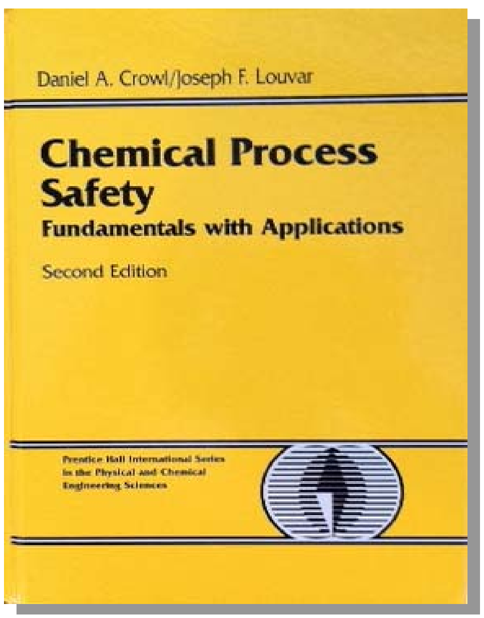
Hazards / consequences resources

D.A. Crowl and J.F. Louvar 2001. *Chemical Process Safety: Fundamentals with Applications, 2nd Ed.*, Upper Saddle River, NJ: Prentice Hall.

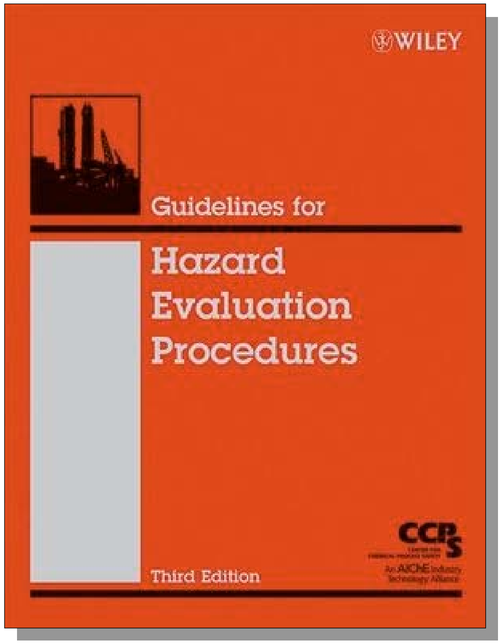


Chapter

- 2 • Toxicology
- 4 • Source Models
- 5 • Toxic Release and Dispersion Models
- 6 • Fires and Explosions
- 10 • Hazards Identification

Hazards/consequences resources

CCPS 2008a. **Center for Chemical Process Safety, *Guidelines for Hazard Evaluation Procedures, Third Edition*, NY: American Institute of Chemical Engineers.**



Chapter 3 • Hazard Identification Methods

3.1 Analyzing Material Properties and Process Conditions

3.2 Using Experience

3.3 Developing Interaction Matrixes

3.4 Hazard Identification Results

3.5 Using Hazard Evaluation Techniques to Identify Hazards

3.6 Initial Assessment of Worst-Case Consequences

3.7 Hazard Reduction Approaches and Inherent Safety Reviews

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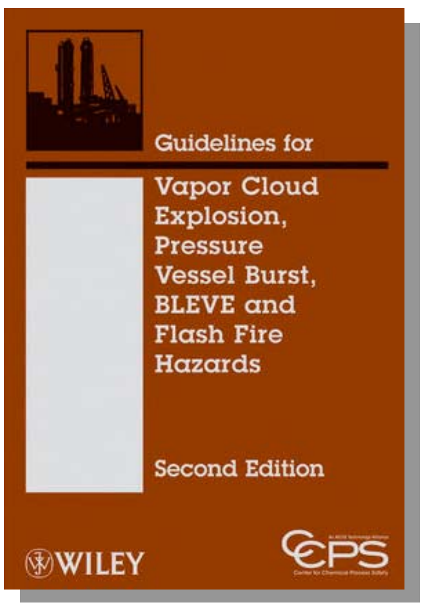
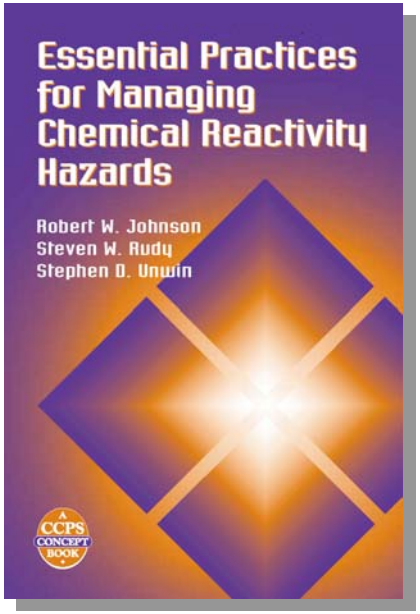
Hazards/consequences resources

CCPS 2010. **Center for Chemical Process Safety, *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE and Flash Fire Hazards, 2nd Edition*, NY: American Inst. of Chem. Engineers.**



Hazards/consequences resources

Johnson et al. 2003. ***Essential Practices for Managing Chemical Reactivity Hazards,*** **NY: American Institute of Chemical Engineers,** accessible free after registration on www.knovel.com**.**



Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- Chemical hazard data

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Identification of Hazards and Potential Consequences

- **“Process hazard” defined**

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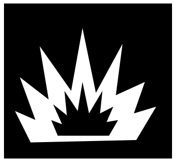
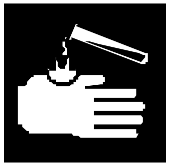
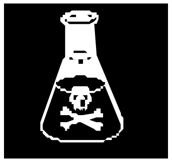
“Process Hazard” Definition



Presence *of a* ***stored or connected material or energy*** *with* ***inherent characteristics*** *having the* ***potential*** *for* ***causing loss or harm.***





Identification of Hazards and Potential Consequences

- “Process hazard” defined
- **Types of hazards and potential consequences**

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Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Note that these are not mutually exclusive categories

Types of process hazards and potential consequences

- **Toxicity and corrosivity hazards**
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Toxicity and corrosivity hazards

Nature of hazard	Potential exposure of people to materials having toxic and/or corrosive properties
What is required	Presence or generation of toxic/corrosive material **+** mechanism for physical contact
Typical examples	Chlorine used for water treatment; hydrogen sulfide as hydrocarbon impurity; sulfuric acid used for pH control
Consequences	Contact with toxic / corrosive material can cause various health effects, depending on material characteristics, concentration, route of exposure and duration of contact (see Day 1 information)

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Toxicity and corrosivity hazards

Video example	www.youtube.com; search term **Seward ammonia spill**
Area of effect	Liquid releases usually very localized; toxic vapor releases can extend many km
How calculated	• Toxic release dispersion models can be used to calculate release rates, downwind and cross-wind distances with various meteorological conditions • Some models can also calculate indoors concentration as a function of time
Free program	http://www.epa.gov/emergencies/content/cameo/aloha.htm

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- **Asphyxiation hazards**
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Asphyxiation hazards

- **An *asphyxiant* is a gas that can cause unconsciousness or death by suffocation (*asphyxiation*).**
  - ***Chemical asphyxiants*** **chemically interfere with the body's ability to take up and transport oxygen**
  - ***Physical asphyxiants*** **displace oxygen in the environment**
- ***Simple asphyxiants*** **have no other health effects**
- **Most simple asphyxiants are <u>colorless</u> and <u>odorless</u>.**

Physical asphyxiation hazards

- **Common industry asphyxiant: <u>Nitrogen</u>** N_2
- **Other simple asphyxiants:**
  - **Hydrogen** H_2
  - **<u>Argon</u>, helium, neon** Ar
  - **Hydrocarbon gases (e.g., <u>methane</u>, ethane, ethylene, acetylene, propane, propylene, butane, butylene)** CH_4
  - **<u>Carbon dioxide</u>** CO_2

Physical asphyxiation hazards

What is required	Reduced-oxygen atmosphere **+** situation allowing breathing of the atmosphere
Typical examples	Entry into vessel inerted with nitrogen; oxygen depletion by rusting over time; oxygen depletion by combustion; natural gas leak into enclosed room or area
Video	http://www.csb.gov/videoroom/detail.aspx?vid=11&F=0&CID=1&pg=1&F_All=y
Boundaries	• US OSHA: oxygen deficiency exists if concentration is less than 19.5% • ACGIH®: deficiency exists below 18% oxygen at 1 atm (equivalent to a partial pressure pO_2 of 135 torr)

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Types of process hazards and potential consequences

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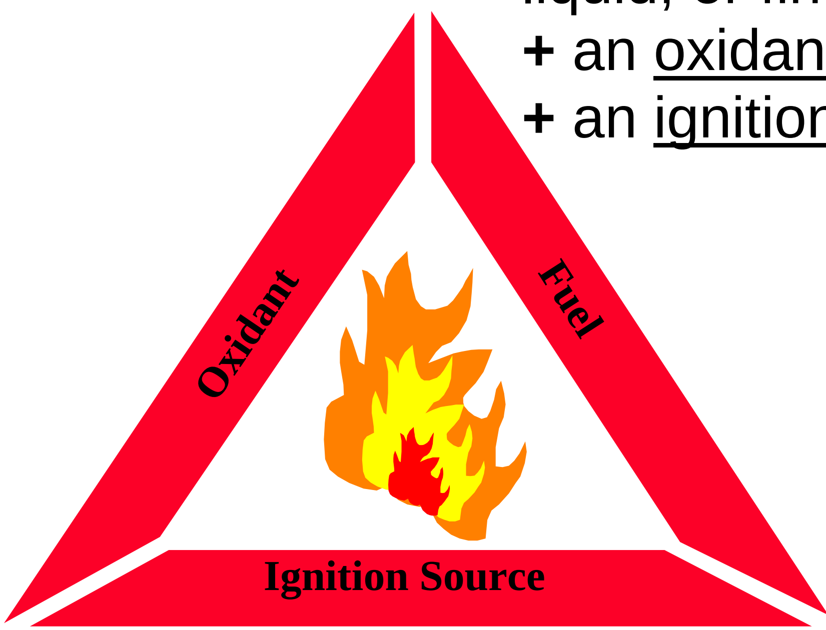
Combustion hazards

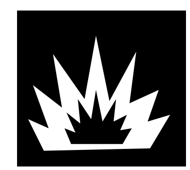
Nature of hazard — Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material

What is required — A fuel (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid)
+ an oxidant (usually atmospheric O_2)
+ an ignition source (unless pyrophoric)



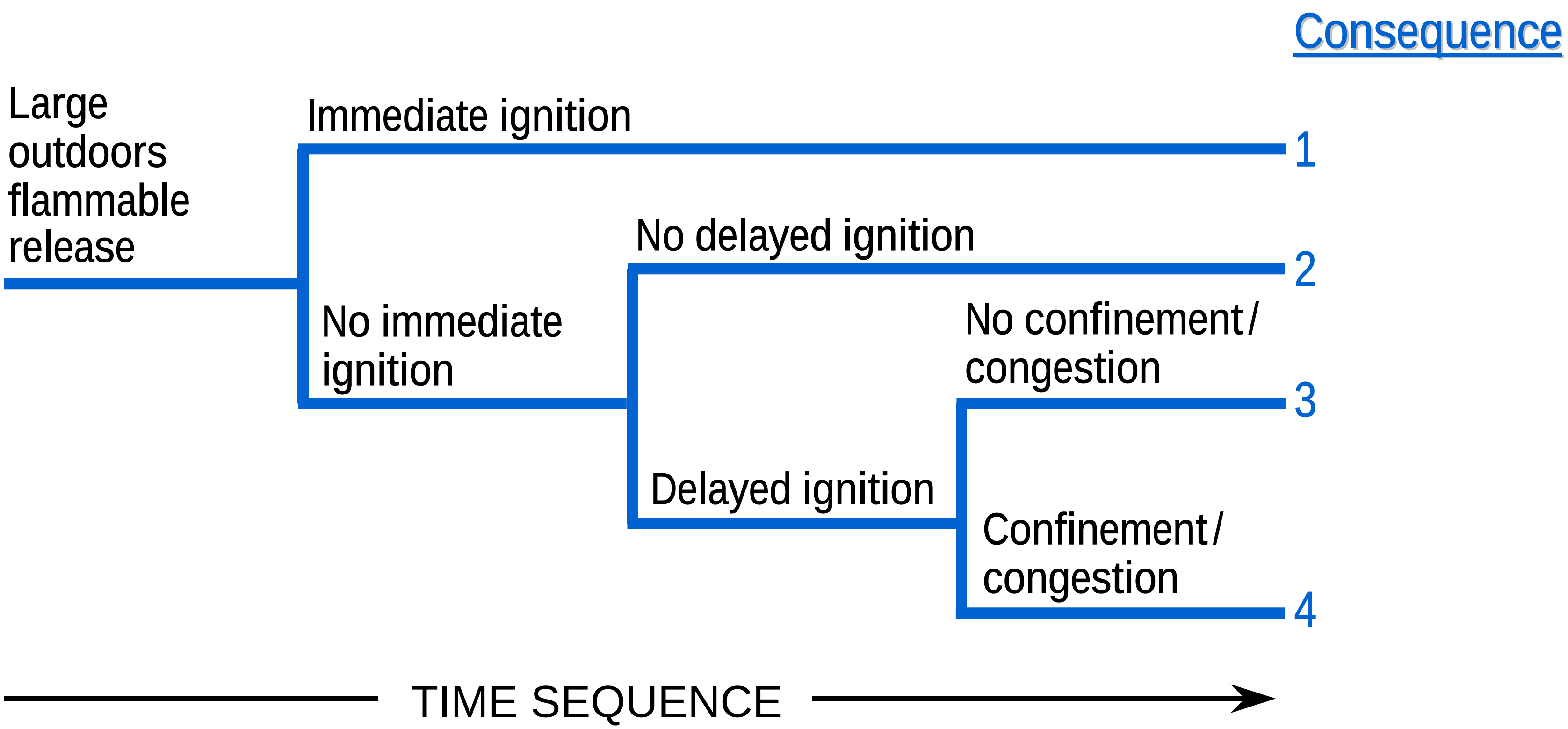
Combustion hazards

Nature of hazard	Potential for uncontrolled release of the heat of combustion upon rapid oxidation of a combustible material
What is required	A <u>fuel</u> (pyrophoric or flammable gas; pyrophoric, flammable or combustible liquid; or finely divided combustible solid) **+** an <u>oxidant</u> (usually atmospheric O_2) **+** an <u>ignition source</u> (unless pyrophoric)
Possible consequences	• **Flash fire**, **pool fire** and/or **jet fire** • **Confined vapor explosion** • **Vapor cloud explosion** • **Dust or mist explosion** • Toxic combustion products



EXERCISE

Describe each of the four possible outcomes.



Combustion hazards - Some definitions

Combustion	A propagating rapid oxidation reaction.
Oxidation	In this context, a reaction in which oxygen combines chemically with another substance.
Oxidizer	Any material that readily yields oxygen or other oxidizing gas, or that readily reacts to promote or initiate combustion of combustible materials.
Explosion	A rapid or sudden release of energy that causes a pressure discontinuity or blast wave.

Some definitions (continued)

Spontaneously combustible	Capable of igniting and burning in air without the presence of an ignition source.
Pyrophoric	Capable of igniting spontaneously in air at a temperature of 130°F (54.4°C) or below.
Hypergolic	Hypergolic behavior is characterized by immediate, spontaneous ignition of an oxidation reaction upon mixing of two or more substances.

Reference: Johnson et al. 2003

Combustion hazards

Area of effect — Small fires usually have very localized effects; a large fire or a combustion-related explosions can destroy an entire facility and affect nearby surroundings

How calculated — Available combustion energy:

Mass of combustible x heat of combustion *or*
Mass rate of combustion x heat of combustion

E.g., Ethanol pool fire in a 50 m^2 dike:

[Pool area x burning rate x liquid density] x heat of combustion
= (50 m^2) (0.0039 m/min) (789 kg/m^3) (26900 kJ/kg) = 4x10^6 kJ/min

Note: Only ~ 20% of this will be released as thermal radiation.

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Combustion hazards

Free program www.epa.gov/emergencies/content/cameo/aloha.htm

(can be used to calculate release rates, extent of a flammable vapor cloud, and vapor cloud explosion effect distances)

Online reference Gexcon Gas Explosion Handbook, www.gexcon.com/handbook/GEXHBcontents.htm

Other references **CCPS 2010; Crowl and Louvar 2001**

(See also the Chemical Data Sources at the end of this presentation)

Flammability limits

LFL **Lower flammability limit**

Below LFL, mixture will not burn, it is too lean.

UFL **Upper flammability limit**

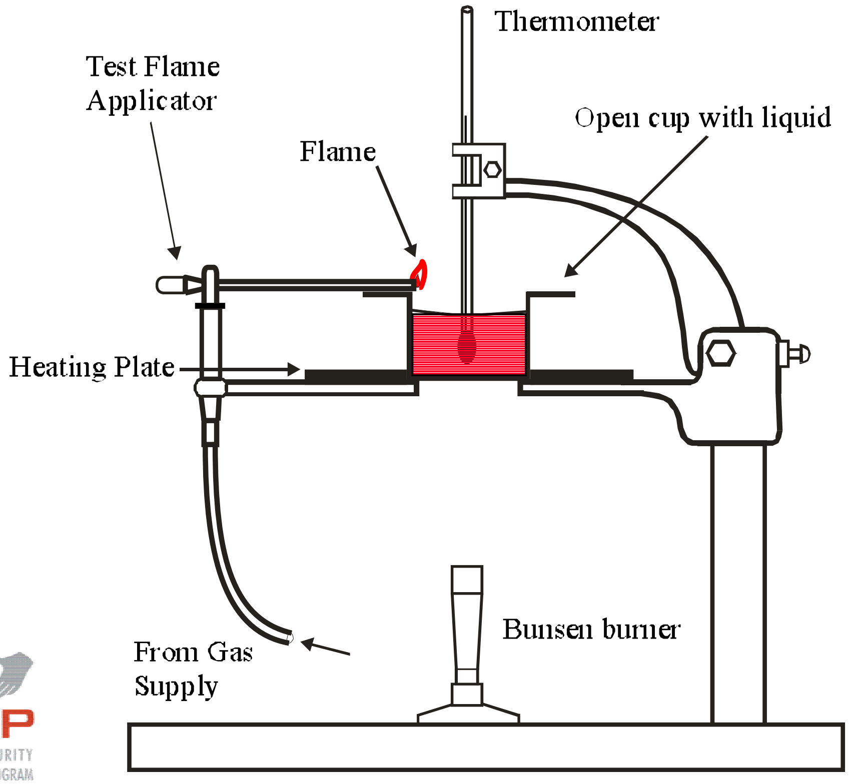
Above UFL, mixture will not burn, it is too rich.

- **Defined only for gas mixtures in air**
- **Both UFL and LFL defined as volume % fuel in air**

Flash point

Flash Point

Temperature above which a liquid produces enough vapor to form an ignitable mixture with air



(Defined only for liquids at atmospheric pressure)

Example values

	LFL	UFL
Methane	5%	15%
Propane	2.1%	9.5%
Butane	1.6%	8.4%
Hydrogen	4.0%	75%

	Flash point
Methanol	12.2 °C
Benzene	-11.1 °C
Gasoline	-40 °C
Styrene	30.5 °C

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Limiting oxygen concentration

Limiting oxygen concentration (LOC):

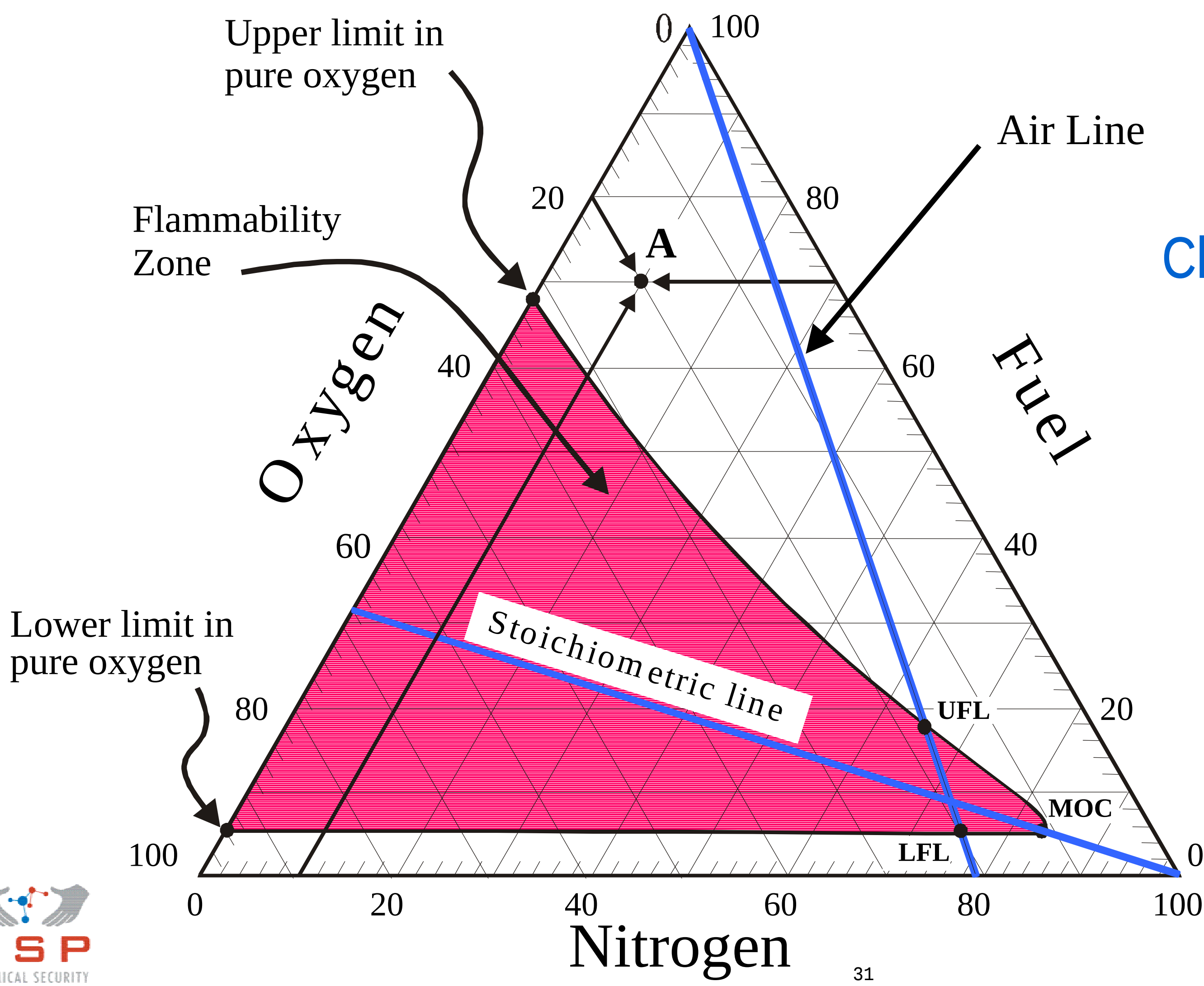
Oxygen concentration below which combustion is not possible, with any fuel mixture, expressed as volume % oxygen.

Also called: Minimum Oxygen Concentration (MOC)
Max. Safe Oxygen Concentration (MSOC)

Examples:

	LOC (volume % oxygen)
Methane	12 %
Ethane	11 %
Hydrogen	5 %

Flammability diagram



Chapter 6 of Crowl and Louvar 2002 shows how to prepare and use flammability diagrams

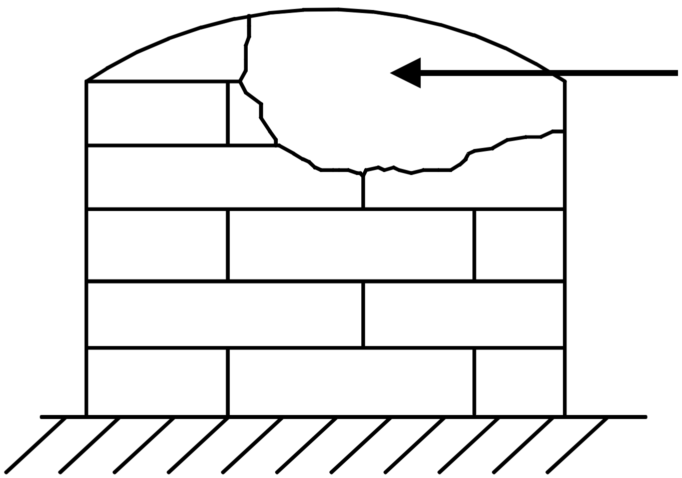
Design Criteria

1 **Avoid flammable mixtures**

2 **Eliminate ignition sources**

Inerting and purging

Purpose: To reduce the oxygen or fuel concentration to below a target value using an inert gas (e.g., nitrogen, carbon dioxide)



E.g., reduce oxygen concentration to **< LOC**

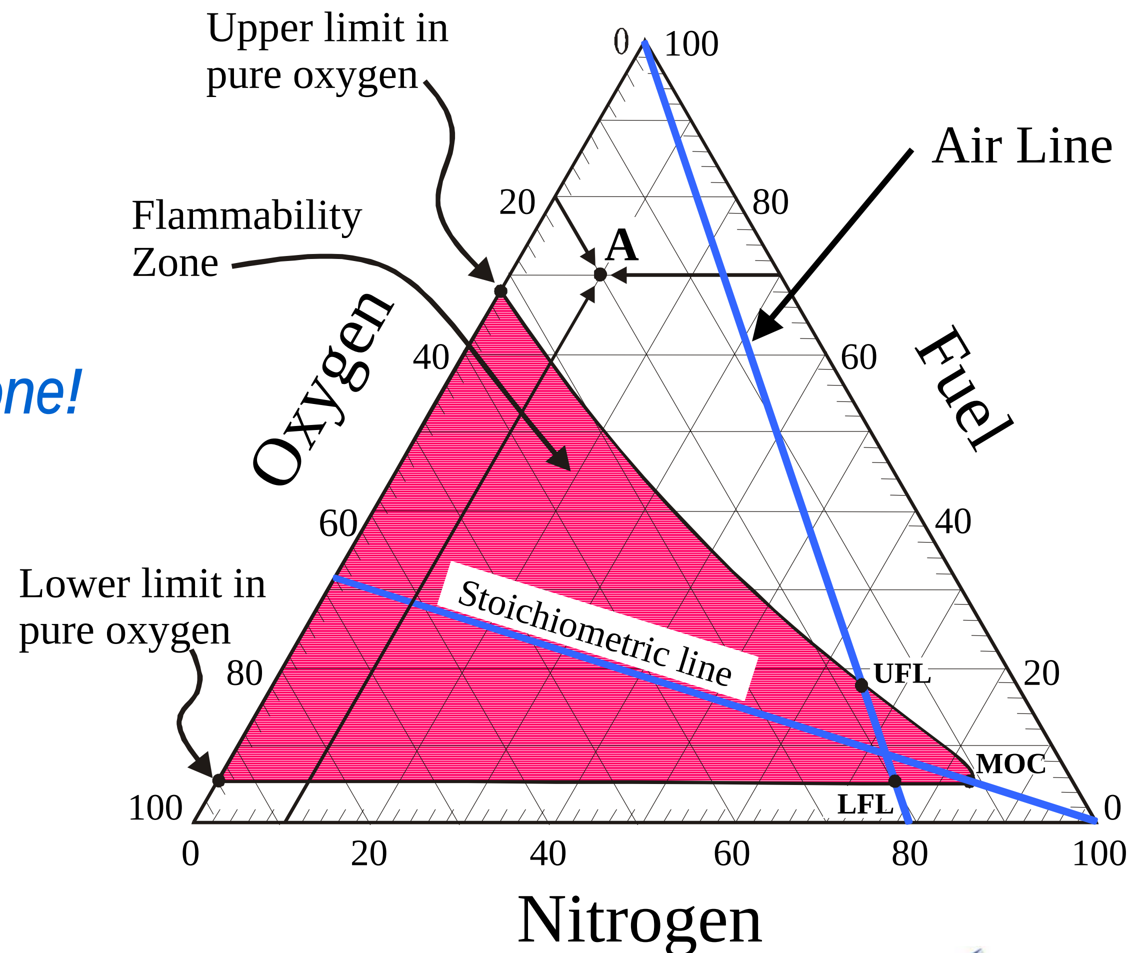
Inerting and purging options

- **Vacuum Purge** - evacuate and replace with inert
- **Pressure Purge** - pressurize with inert, then relieve pressure
- **Sweep Purge** - continuous flow of inert
- **Siphon Purge** - fill with liquid, then drain and replace liquid with inert
- **Combined** - pressure and vacuum purge; others

See Chapter 7 of Crowl and Louvar 2002 for details

Flammability diagram

OBJECTIVE:
***Stay out** of*
Flammability Zone!



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Ignition sources

- Obvious (e.g., flames, welding, hot surfaces)
- Spontaneous ignition at moderate temp's
- Electrical sources
  - Powered equipment
  - Static electricity
  - Stray currents
  - Radio-frequency pickup
  - Lightning
- Physical sources
  - Adiabatic compression
  - Heat of adsorption
  - Friction
  - Impact
- Chemical Sources
  - Catalytic materials
  - Pyrophoric materials
  - Thermite reactions
  - Unstable chemical species formed in system

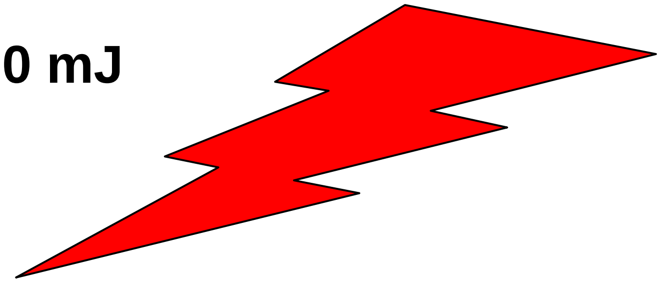
Minimum ignition energy

Minimum ignition energy (MIE) The electrical energy discharged from a capacitor that is just sufficient to ignite the most ignitable mixture of a given fuel-mixture under specific test conditions.

Typical values: (wide variation expected)

Vapors	**0.25 mJ**
Dusts	**about 10 mJ**

- **Dependent on test device, so not a reliable design parameter**
- **Static spark that you can feel: about 20 mJ**



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Autoignition temperature

Autoignition Temperature (AIT): **Temperature above which adequate energy is available from the environment to start a self-sustaining combustion reaction.**

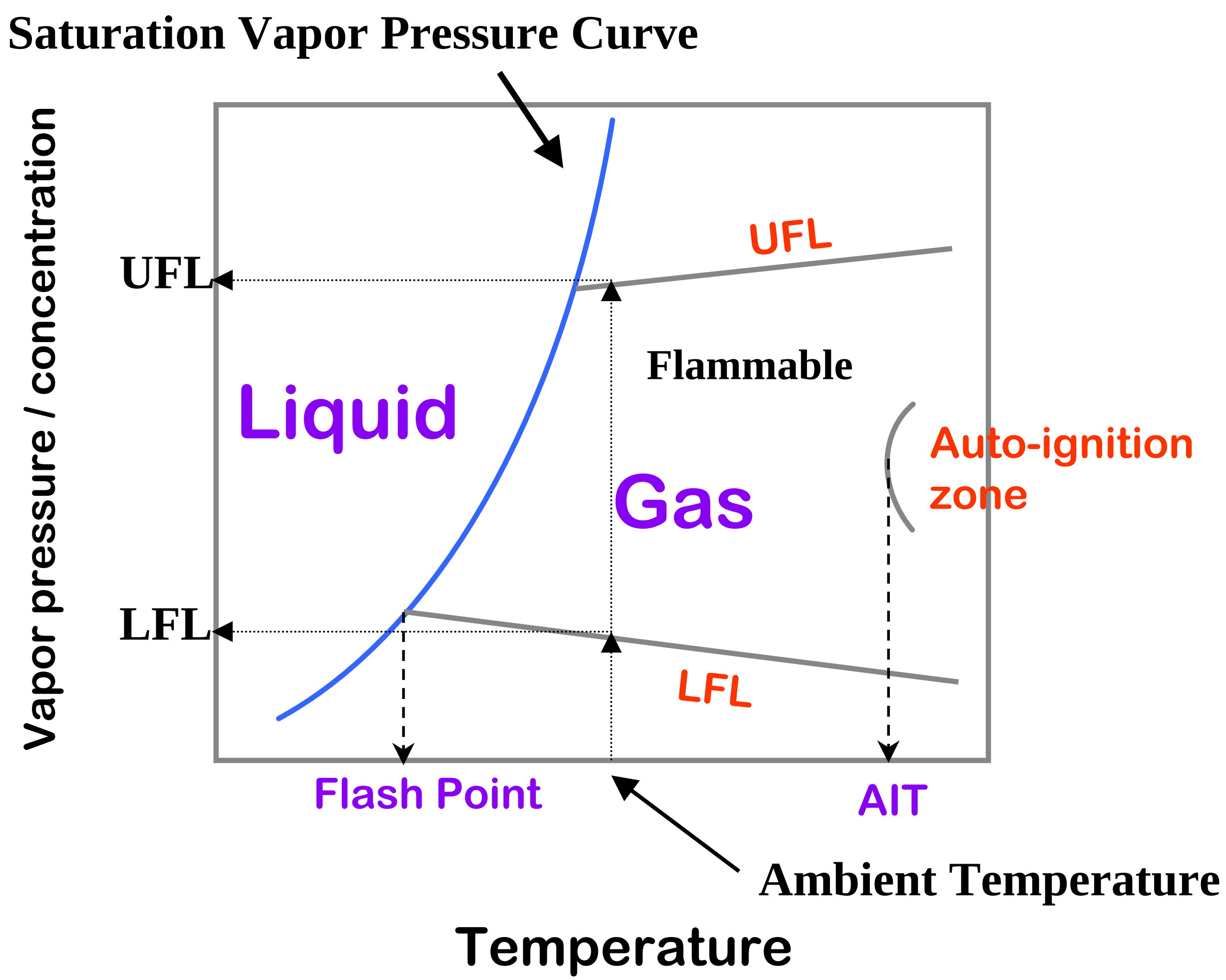
Example values:

	AIT
Methane	632 °C
Ethane	472
1-Pentene	273
Toluene	810
Acetaldehyde	185

There is great variability in reported AIT values! Use lowest reported value.

See Appendix B of Crowl and Louvar 2002 for a table of AITs

Flammability relationships



Ignition source control

- **Identify Ignition Sources**
  - Continuous ignition sources; e.g., fired equipment
  - Potential/intermittent ignition sources; e.g., traffic
- **Identify What Could Be Ignited**
  - Flammable atmospheres
  - Potentially flammable atmospheres
  - Likely leak/release locations
  - Avenues to unexpected locations; e.g., drains, sumps
- **Analyze for Adequate Control**

DISCUSSION

Which of these two design criteria can be more easily and reliably attained?

1 Avoid flammable mixtures

2 Eliminate ignition sources

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- **Detonation hazards**
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- Other physical hazards

Detonation hazards

Nature of hazard	Potential for generating a damaging blast wave by extremely fast chemical reaction
What is required	One of two typical mechanisms: (1) Direct initiation of a solid or liquid explosive material or mixture, or (2) Acceleration of a propagating gas-phase reaction to detonation velocity
Typical examples	(1) TNT; picric acid; unstable peroxides; commercial explosives (2) Vapor cloud explosion; flame acceleration in a long pipeline containing a flammable mixture

Detonation hazards

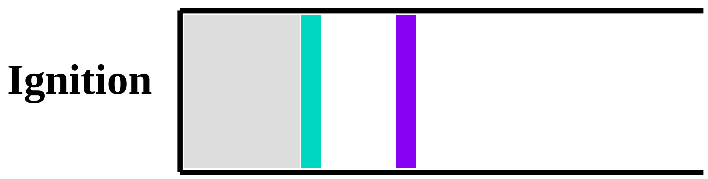
Possible consequences	• **Blast wave** (sometimes more than one) • Shrapnel (usually small fragments) • Toxic decomposition products See calculation example for Bursting vessel explosion hazards
Video	www.youtube.com; search term **Pepcon explosion**

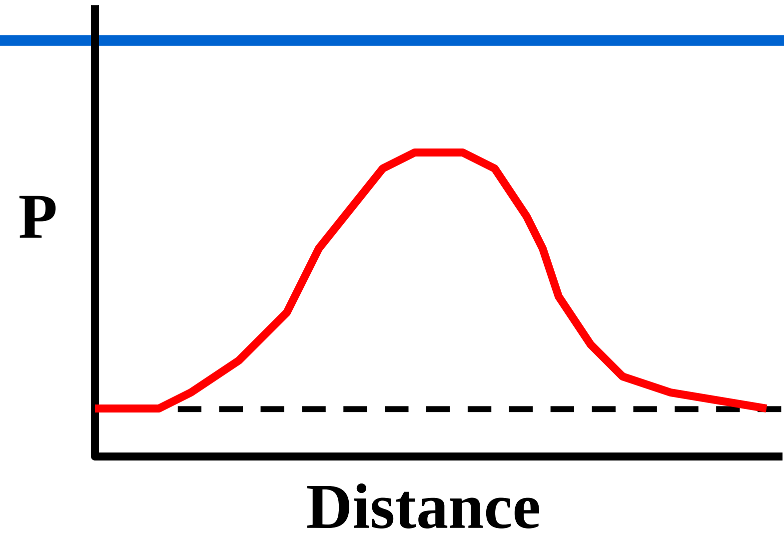
Detonation hazards - Some definitions

Deflagration	A chemical reaction propagating at less than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Detonation	A chemical reaction propagating at greater than the speed of sound relative to the unreacted material immediately ahead of the reaction front.
Deflagration-to-Detonation Transition (DDT)	Increase in the propagating velocity of a chemical reaction until the velocity exceeds the speed of sound relative to the unreacted material immediately ahead of the reaction front.

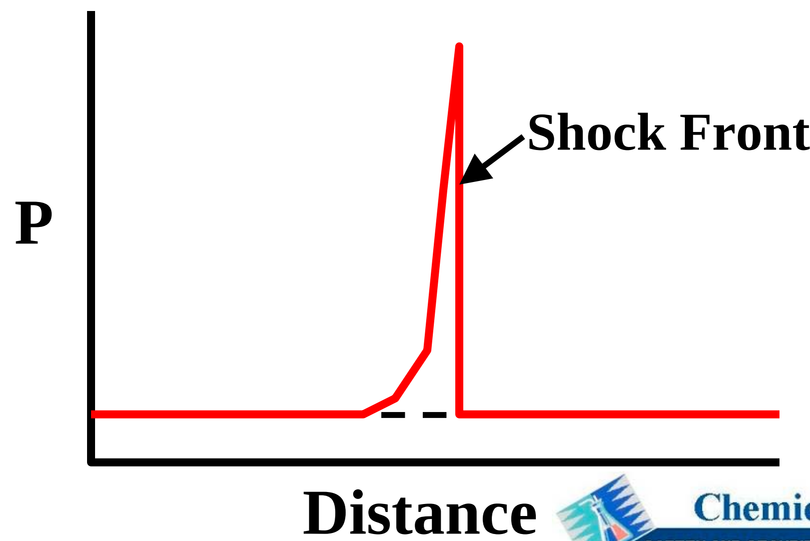
Deflagration *vs* Detonation

Deflagration:





Detonation:



- Reacted gases
- Reaction / Flame Front
- Pressure Wave
- Unreacted gases

Types of process hazards and potential consequences

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Chemical reactivity hazards

Nature of hazard	Potential for an uncontrolled chemical reaction that can result in loss or harm
Also known as	*Reactive chemical hazards*
What is required	Any situation where the energy and/or products released by a chemical reaction are not safely absorbed by the reaction environment
Typical examples	• Loss of control of an intended reaction • Initiation of an unintended reaction
Consequences	Fire, explosion, toxic gas release and/or hot material release

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Chemical reactivity hazards

Video	"Introduction to Reactive and Explosive Materials"
Types of chemical reactivity hazards	• Water-reactive • Oxidizing • Spontaneously combustible / pyrophoric • Peroxide forming • Polymerizing • Decomposing • Rearranging • Interacting (i.e., incompatible)
Reference	Johnson et al. 2003

Chemical reactivity hazards

Some chemicals have more than one reactive property.

R–O–O–R

For example, organic peroxides can be any or all of:

- **Oxidizing**
- **Decomposing** (shock-sensitive / thermally unstable)
- **Flammable** or **combustible**
- **Interacting** (incompatible with many other chemicals)

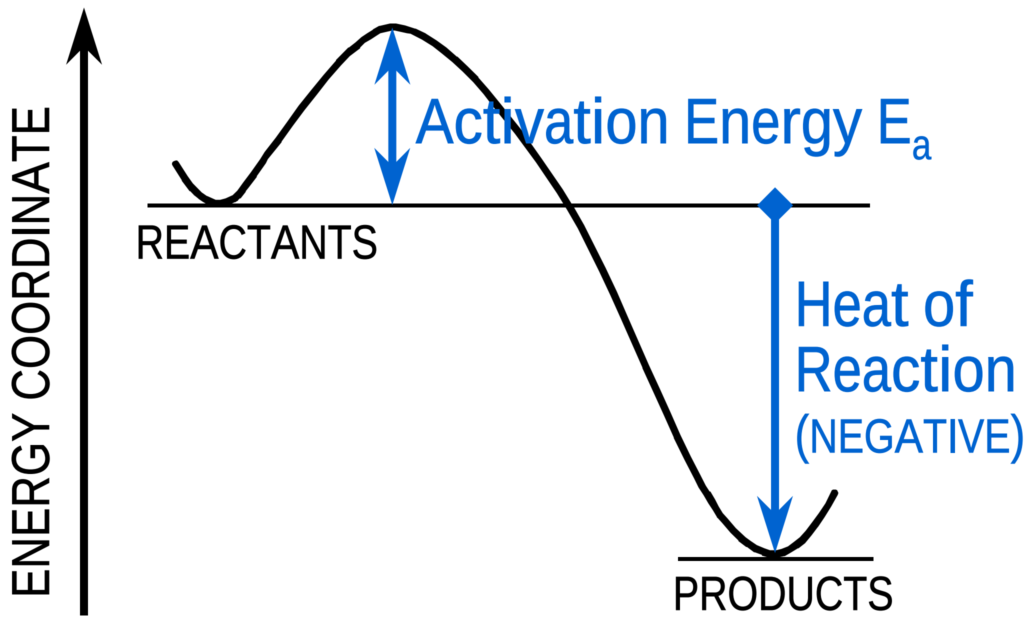
Chemical reactivity hazards

Some types of molecular structures tend to increase chemical reactivity, such as:

- Carbon-carbon double bonds not in benzene rings (ethylene, styrene, etc.)
- Carbon-carbon triple bonds (e.g., acetylene)
- Nitrogen-containing compounds (NO_2 groups, adjacent N atoms ...)
- Oxygen-oxygen bonds (peroxides, hydroperoxides, ozonides)
- Ring compounds with only 3 or 4 atoms (e.g., ethylene oxide)
- Metal- and halogen-containing complexes (metal fulminates; halites, halates; etc.)

Chemical reactivity hazards

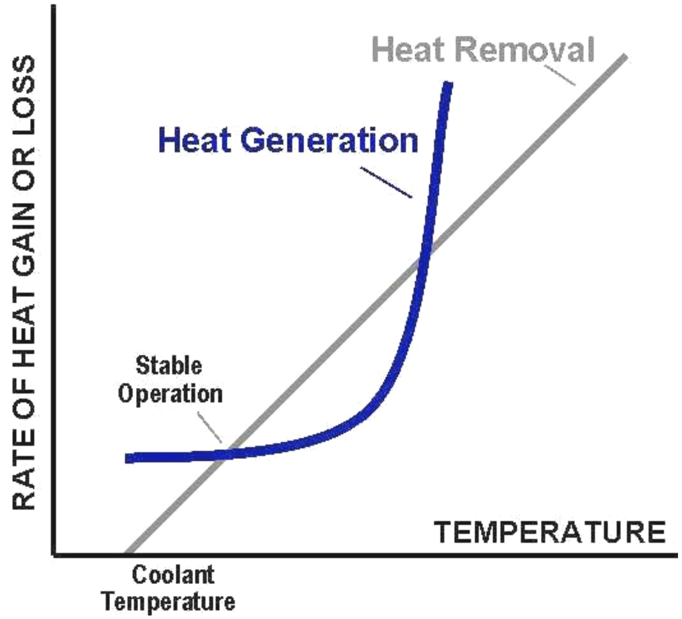
Energy diagram for exothermic chemical reaction:



- **Lower activation energy barrier → faster reaction**
- **Larger heat of reaction → more energy released**

Key term to understand:

“Runaway reaction”



For an exothermic chemical reaction:

FIRST-ORDER KINETICS

$$k = A\ e^{(-E_a/RT)}$$

- Reaction rate is exponential *f* (temperature)
- If reaction temperature increases, rate increases and more heat is released by exothermic reaction
- If this heat is not removed, it further increases the reaction rate
- Then even more heat is released, etc.
- Temperature can rise hundreds of °C per minute!
- Pressure is generated by product gases and/or liquid boiling
- Reactor may rupture if pressure not safely vented

Chemical reactivity hazards

Managing chemical reactivity hazards

- **More effort is required to identify and characterize the reactivity hazards**
- **This may require small-scale testing**
- See flowchart on next page

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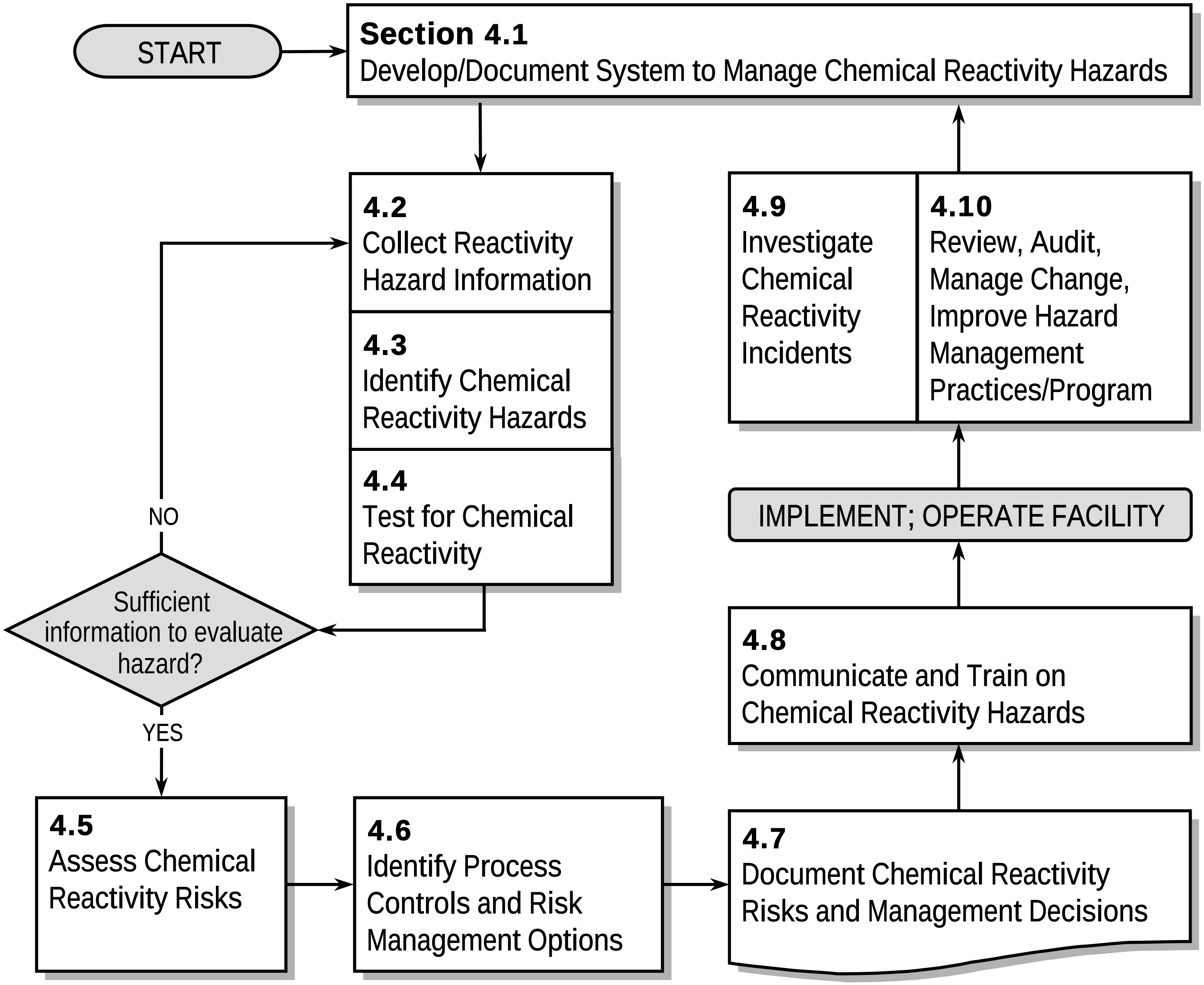
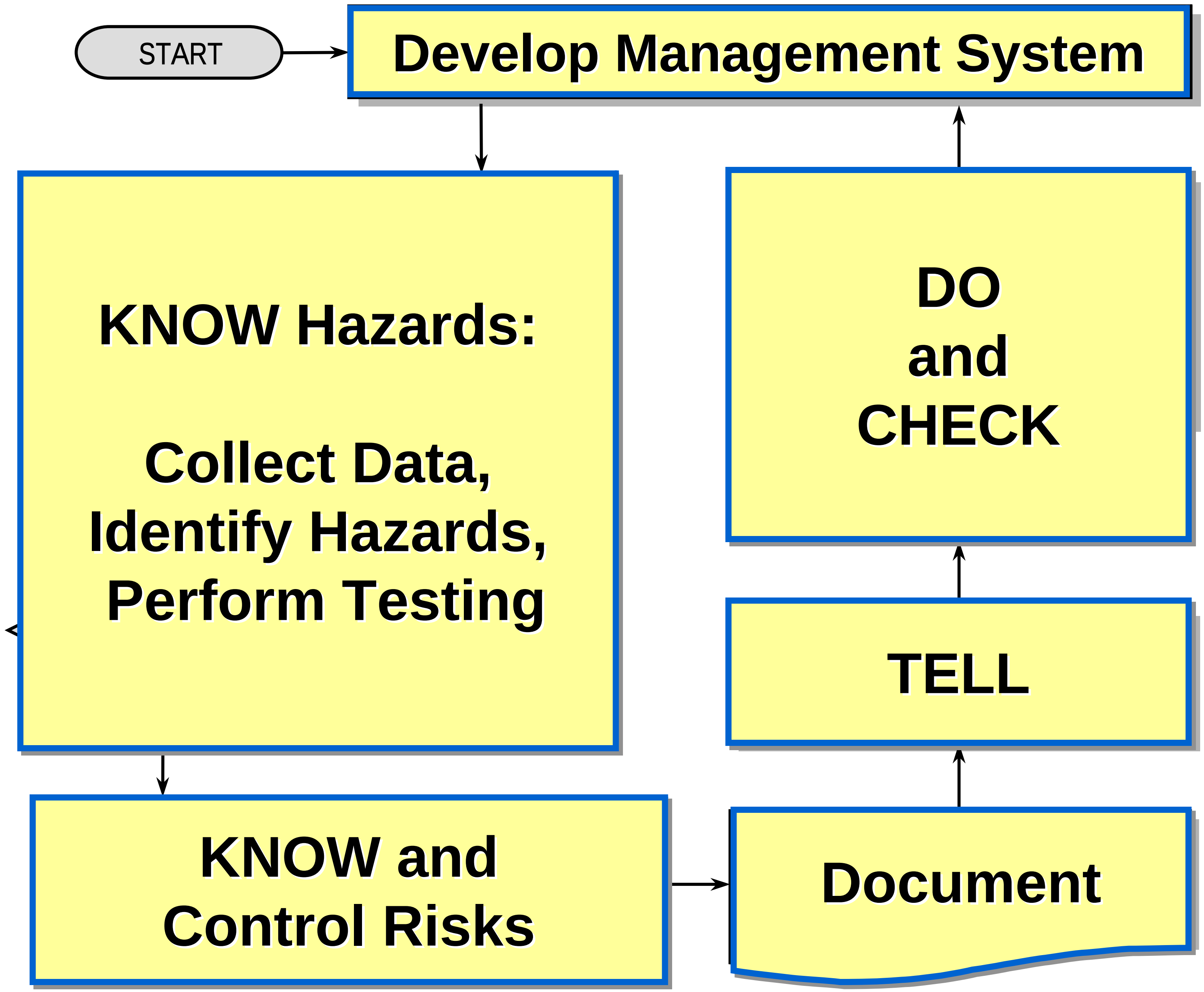
Flowchart for Implementing Chemical Reactivity Hazard Management (Johnson et al. 2003)



Flowchart for Implementing Chemical Reactivity Hazard Management (Johnson et al. 2003)



Chemical reactivity hazards


CCPS
Reactive Material Hazards
What You Need To Know
SAFETY ALERT
October 1, 2001

Key steps to avoid <u>unintended</u> chemical reactions

- ❑ Train all personnel to be aware of reactivity hazards and incompatibilities and to know maximum storage temperatures and quantities
- ❑ Design storage / handling equipment with all compatible materials of construction
- ❑ Avoid heating coils, space heaters, and all other heat sources for thermally sensitive materials
- ❑ Avoid confinement when possible; otherwise, provide adequate emergency relief protection
- ❑ Avoid the possibility of pumping a liquid reactive material against a closed or plugged line
- ❑ Locate storage areas away from operating areas in secured / monitored locations

Chemical reactivity hazards

Key steps to avoid <u>unintended</u> chemical reactions (continued)

- ❑ Monitor material and building temperatures where feasible with high temperature alarms
- ❑ Clearly label and identify all reactive materials, and what must be avoided (e.g., heat, water)
- ❑ Positively segregate and separate incompatible materials using dedicated equipment if possible
- ❑ Use dedicated fittings and connections to avoid unloading a material into the wrong tank
- ❑ Rotate inventories for materials that can degrade or react over time
- ❑ Pay close attention to housekeeping and fire prevention around storage/handling areas

Source: CCPS Safety Alert, “Reactive Material Hazards – What You Need to Know”, 2001

Chemical reactivity hazards

Key steps to control intended chemical reactions

- ❑ Scale up very carefully! – Heat generation increases with the system volume (by the cube of the linear dimension), whereas heat removal capability increases with the surface area of the system (by the square of the linear dimension).
- ❑ Ensure equipment can handle the maximum pressure and maxiumum adiabatic temperature rise of uncontrolled reactions
- ❑ Use gradual-addition processes where feasible
- ❑ Operate where the intended reaction will be fast
- ❑ Avoid using control of reaction mixture temperature as a means for limiting the reaction rate
- ❑ Use multiple temperature sensors in different locations
- ❑ Avoid feeding a material above the reactor contents' boiling point

For more details see D.C. Hendershot, "A Checklist for Inherently Safer Chemical Reaction Process Design and Operation," CCPS International Symposium, NY: AIChE, October 2002

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- Bursting vessel explosion hazards
- Other physical hazards

Rapid phase transition hazards

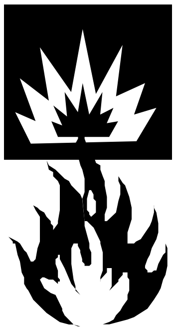
Nature of hazard	Near-instantaneous phase transition from liquid to gas, with large volume increase
Also known as	Boiling-liquid-expanding-vapor explosion (BLEVE)
What is required	<u>Any</u> liquefied gas stored under pressure above its boiling point
Typical example	Propane storage tank engulfed in fire with flame impinging on vapor space of tank, weakening the metal to point of failure
Consequences	Blast energy from both phase transition and bursting vessel; large tank fragments; huge fireball also if flammable liquid

Rapid phase transition hazards

Videos — www.youtube.com; search term **BLEVE**

Area of effect — Can be 1 km or more, depending on size of storage tank(s)

How calculated — Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity:



- Bursting vessel explosion
- Phase transition volume expansion
- Missiles / flying debris
- Fireball thermal radiation if flammable
- Follow-on (“domino”) effects

Reference — **CCPS 2010**

Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- **Bursting vessel explosion hazards**
- Other physical hazards

Bursting vessel explosion hazards

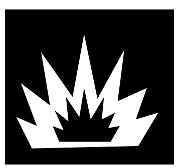
Nature of hazard	Near-instantaneous release of energy stored by a compressed vapor or gas
Also known as	Containment overpressurization; Vessel rupture explosion
What is required	Vapor or gas at elevated pressure inside some form of containment
Typical examples	Overpressurization of a reaction vessel from an unrelieved runaway reaction; ignition of flammable vapors in a tank
Consequences	Blast energy from bursting vessel; large vessel fragments thrown; expelling of remaining tank contents; follow-on effects

Bursting vessel explosion hazards

Videos
www.csb.gov; several examples in Video Room, including **Explosion at T2 Labs**

Area of effect
Highly dependent on amount of stored energy at time of rupture

How calculated
Calculate each mechanism separately and determine which has greatest effect; multiple mechanisms increases severity:



- Bursting vessel explosion (gas / vapor volume expansion)
- Missiles / flying debris
- Release of vessel contents
- Follow-on (“domino”) effects

References
CCPS 2010; Crowl and Louvar 2002

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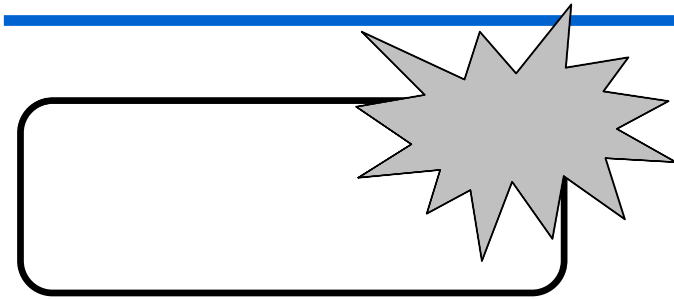
Bursting vessel explosion hazards



One equation used for calculating blast energy:

$$W_e = R_g T\left[\ln\left(\frac{P}{P_E}\right) - \left(1 - \frac{P_E}{P}\right)\right]$$

Maximum Mechanical Energy

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, T is absolute temperature.

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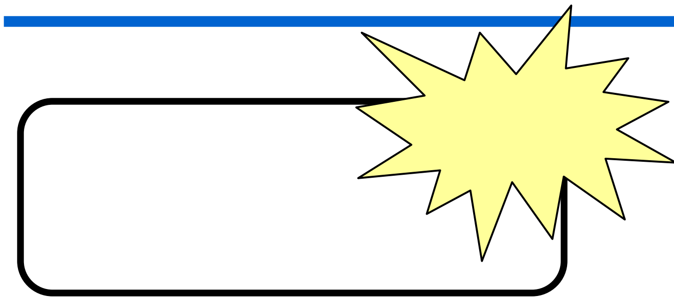
Bursting vessel explosion hazards



Another equation used for calculating blast energy:

$$W_e = \frac{(P - P_E)\,V}{\gamma - 1}$$

Brode's Equation

where W_e is the energy of explosion, P is absolute gas pressure in vessel, P_E is abs. ambient pressure, V is vapor volume, and γ is the ratio of specific heats

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Bursting vessel explosion hazards

EXAMPLE

- The vapor space of a 30 m^3 flammable liquid storage tank is nitrogen-inerted.
- The nitrogen regulator fails open, exposing the tank vapor space to the full 4 bar gauge nitrogen supply pressure. The tank relief system is not sized for this failure case.
- If the tank ruptures at 4 bar gauge when it is nearly empty of liquid, how much energy is released?

Bursting vessel explosion hazards

Data

P = 4 bar gauge = 400 Pa gauge = 501325 Pa abs

P_E = 0 bar gauge = 0 Pa gauge = 101325 Pa abs

V = 30 m^3

(= 1.4 for nitrogen (dimensionless)

Bursting vessel explosion hazards

Calculation

Using Brode's equation:

$$W_e = \frac{(501325\ \text{N/m}^2 - 101325\ \text{N/m}^2) \cdot 30\ \text{m}^3}{1.4 - 1}$$

$$W_e = 3\text{x}10^7\ \text{N-m} = 3\text{x}10^7\ \text{Joules}$$

Bursting vessel explosion hazards

Comparison

TNT (trinitrotoluene) has a heat of explosion of 4686 J/g, so a blast energy of $3 x 10^7$ J is equivalent to

$$3 x 10^7 / 4686 = 6400 \text{ g TNT} = \mathbf{6.4 \text{ kg TNT}}$$

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Bursting vessel explosion hazards

Consequences

Figure 6-23 in Crowl and Louvar 2001 (page 268) gives a correlation of scaled overpressure vs scaled distance.

If a control room building is 30 m away from the storage tank, the scaled distance is

$$z_e = 30 \text{ m} / (6.4 \text{ kg TNT})^{1/3} = 16.2$$

From Figure 6-23, the scaled overpressure p_s = 0.1, and the resulting overpressure is (0.1)(101 kPa) = <u>10 kPa</u>

Bursting vessel explosion hazards

Consequences

Table 6-9 of Crowl and Louvar 2001 (page 267) indicates that 10 kPa is sufficient to e.g.

- break windows
- cause serious damage to wood-frame structures
- distort the steel frame of clad buildings

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Types of process hazards and potential consequences

- Toxicity and corrosivity hazards
- Simple asphyxiation hazards
- Combustion hazards
- Detonation hazards
- Chemical reactivity hazards
- Rapid phase transition hazards (BLEVEs)
- Bursting vessel explosion hazards
- **Other physical hazards**

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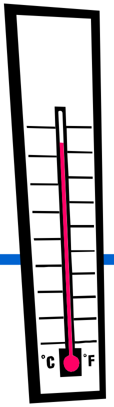
Other physical hazards



Physical hazard	**Typical examples**
Hydraulic pressure	High-pressure hydraulic fluid: *Jet spray from pinhole leak can cause severe cuts*
Vacuum	Contained sub-atmospheric pressure: *Pumping out of a tank or condensing steam with inadequate venting can cause tank implosion*

A railcar steam cleaning team went to lunch - but before they left, they put the manway back on the car on a cool and cloudy day. The steam condensed and created a vacuum.

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Process Safety Beacon
http: //www.aiche.org/ccps/safetybeacon.htm
Messages for Manufacturing Personnel

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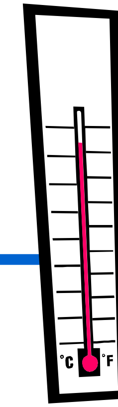
February 2007

Vacuum Hazards - Collapsed Tanks

The tank on the left collapsed because material was pumped out after somebody had covered the tank vent to atmosphere with a sheet of plastic. Who would ever think that a thin sheet of plastic would be stronger than a large storage tank? But, large storage tanks are designed to withstand only a small amount of ***internal*** pressure, not vacuum (external pressure on the tank wall). It is possible to collapse a large tank with a small amount of vacuum, and there are many reports of tanks being collapsed by something as simple as pumping material out while the tank vent is closed or rapid cooling of the tank vapor space from a thunder storm with a closed or blocked tank vent. The tank in the photograph on the right below collapsed because the tank vent was plugged with wax. The middle photograph shows a tank vent which has been blocked by a nest of bees! The February 2002 Beacon shows more examples of vessels collapsed by vacuum.

Other physical hazards



Physical hazard	Typical examples
Elevated temperature	High gas, liquid or surface temperature: *Contact with hot surface or leaking hot material can cause severe burns; prolonged exposure to high area temperature can cause heat exhaustion*
Cryogenic temperature	Liquid nitrogen; flashing liquefied gas: *Skin contact can cause cryogenic burns*

Other physical hazards

Physical hazard	Typical examples
Mass storage	Very large liquid storage tanks, silos: *Catastrophic failure can lead to fatalities*

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Process Safety Beacon

http://www.aiche.org/CCPS/Publications/Beacon/index.aspx

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The Great Boston Molasses Flood of 1919

May 2007

Before ↑ After ↓

On January 15, 1919, people in north Boston, Massachusetts heard a loud rumbling noise and watched in horror as a 50 foot (15 m) high tank containing 2.3 million US gallons (8700 cubic meters) of molasses suddenly broke apart, releasing its contents into the city. A wave of molasses over 15 feet (5 m) high and 160 feet (50 m) wide surged through the streets. How slow is molasses in January? This wave traveled at an estimated speed of 35 miles per hour (60 km/hour) for more than 2 city blocks. 21 people were killed, over 150 injured, and the damage estimate was equivalent to over 100 million US dollars in today's currency.

What caused this catastrophic tank failure? Some of the causes identified by the investigation included:

- The tank was not properly inspected during construction.
- The tank was not tested after construction and before filling it with molasses.
- The tank had been observed to be leaking at the welds between the tank's steel plates before the failure, but no action had been taken.

CCPS Process Safety Beacon (continued)

Do you know?

• You might think that an incident that occurred over 80 years ago is not relevant to today's industry. But, we still have catastrophic failures of storage tanks today (see pictures below), and for similar reasons.

• A large quantity of any liquid, even a non-hazardous material such as molasses or water, can be dangerous if rapidly released in large quantities, simply because of its volume and mass.

What You Can Do

• If you observe leakage, corrosion, or other indication of potential failure in a storage tank, report it immediately to management.

• Make sure that any new tank, or one being returned to service following repair or inactivity, is properly inspected and tested before filling.

• Ensure you know the operating capacities of your tanks and double check the level before filling.

• Don't throw out your old incident reports. Read them again, and remember the lessons. We can learn a lot from things that happened a long time ago.

January 1988 – Floreffe, Pennsylvania, USA, tank failure releases over 4 million US gallons (15,000 cu. m) of diesel oil into the Monongahela River. →

← January 2000 – Cincinnati, Ohio, USA, tank failure releases 365,000 gallons (1400 cu. m) of fertilizer solution into the Ohio River.

Remember the lessons of the past!

Other physical hazards

Physical hazard	Typical examples
Obscuring vapor cloud	Acid gases, titanium tetrachloride, cryogenic liquids: *Dense vapors, dust or condensed humidity can obscure vision and lead to e.g. vehicle collisions*

$$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$$

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Chemical SAFETY AND SECURITY TRAINING

Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- **Approaches and methods for systematically identifying process hazards**

US Chemical Safety Board

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Approaches and methods for systematically identifying process hazards

Some "HAZID" approaches and methods:

- Analyze material properties
- Analyze process conditions
- Use company and industry experience
  - Knowledge of the process chemistry
  - Experience at a smaller scale e.g. pilot plant
  - Examination of relevant previous incidents
  - Use relevant checklists e.g. CCPS 2008a Appx B
- Develop chemical interaction matrices

Approaches and methods for systematically identifying process hazards

Typical hazard identification results:

- List of flammable/combustible materials
- List of toxic/corrosive materials and by-products
- List of energetic materials and explosives
- List of explosible dusts
- List of hazardous reactions; chemical interaction matrix
- Fundamental hazard properties e.g. flash point, toxic endpoint
- Others e.g. simple asphyxiants, oxidizers, etc.
- Total quantities of each hazardous material
- List of chemicals and quantities that would be reportable if released to the environment
- List of physical hazards (e.g., pressure, temperature, etc.) associated with a system
- List of contaminants and process conditions that lead to a runaway reaction

Reference: CCPS 2008a, Table 3.4

One format for a "hazard inventory"

Last Updated:	PROCESS HAZARDS

CHEMICAL PROCESS HAZARDS						Inherent Safety:
Chemical, Concentration*	Quantity Stored or Rate Processed	Volatility	Health Hazards	Flammability; Fire Hazards	Chemical Reactivity; Other Hazards	Recommendation No.
*Include materials that may have dust or mist explosion hazards, as well as toxicity, fire, explosion, and other reactivity hazards						

PHYSICAL PROCESS HAZARDS						Inherent Safety:
Contained and Controlled Process Energy	Location Within or Connected To Process	Units of Measure	Range	Design	Comment	Recommendation No.
Pressurized Gas						
Hydraulic Pressure						
Vacuum						
Thermal Energy						
Radiant Energy						
Cryogenic Liquid						
Liquefied Gas						
Kinetic Energy; Material Movement						
Potential Energy; Mass Storage or Elevated Material						

One format for a “chemical interaction matrix”

Last Updated:	CHEMICAL REACTIVITY MATRIX

Abbreviation	Meaning
NR	Not reactive; no conditions identified for this process that would result in a chemical reaction between these materials
NS	No scenario identified that would result in this combination of materials coming into contact in this process
?	Unknown whether chemical reaction would occur between these materials at conditions found in this process
corr	One material corrosive to the other if these materials are combined
ht	Heat generation by chemical reaction or heat of solution; may cause pressurization if these materials are combined
R	Energetic chemical reaction, flammable gas generation, and/or toxic gas generation if these materials are combined
H#, F#, I#, W, OX	NFPA **H**ealth rating (0-4), **F**lammability rating (0-4), **I**nstability rating (0-4), vigorously or violently water reactive (**W**), oxidizer (**OX**)

Material	Abbv																								
		F_ H_ I_																							
			F_ H_ I_																						
				F_ H_ I_																					
					F_ H_ I_																				
						F_ H_ I_																			
							F_ H_ I_																		
								F_ H_ I_																	
									F_ H_ I_																
										F_ H_ I_															
											F														

Chemical interaction potentials based on scenarios and reactivity data listed [on separate page]

Reactivity represents only binary combinations.
See ASTM E 2012, "Standard Guide for the Preparation of a Binary Chemical Compatibility Chart," for methodology and example.

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Identification of Hazards and Potential Consequences

- "Process hazard" defined
- Types of hazards and potential consequences
- Approaches and methods for systematically identifying process hazards
- **Chemical hazard data**

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Chemical hazard data

Some sources of chemical hazardous property data:

- **Safety Data Sheets from chemical supplier**
- **Chemical-specific sources** (e.g., Chlorine Institute)
- **Many books and handbooks** (e.g., Sax, Brethericks)

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Chemical hazard data

Some internet-accessible data sources:

- **International Chemical Safety Cards**
  www.ilo.org/legacy/english/protection/safework/cis/products/icsc/dtasht/index.htm

- **CAMEO Chemicals**
  cameochemicals.noaa.gov

- **Chemical Reactivity Worksheet**
  response.restoration.noaa.gov/CRW

- **NIOSH Pocket Guide to Chemical Hazards**
  www.cdc.gov/niosh/npg

- **Wireless Information System for Emergency Responders**
  wiser.nlm.nih.gov

DISCUSSION

- **Select a familiar type of simple chemical process**
- **Identify what *process hazards* are present; i.e., generate a hazard inventory**
- **Discuss what could happen if the hazards were not contained and controlled**