

# Passive Fire Protection

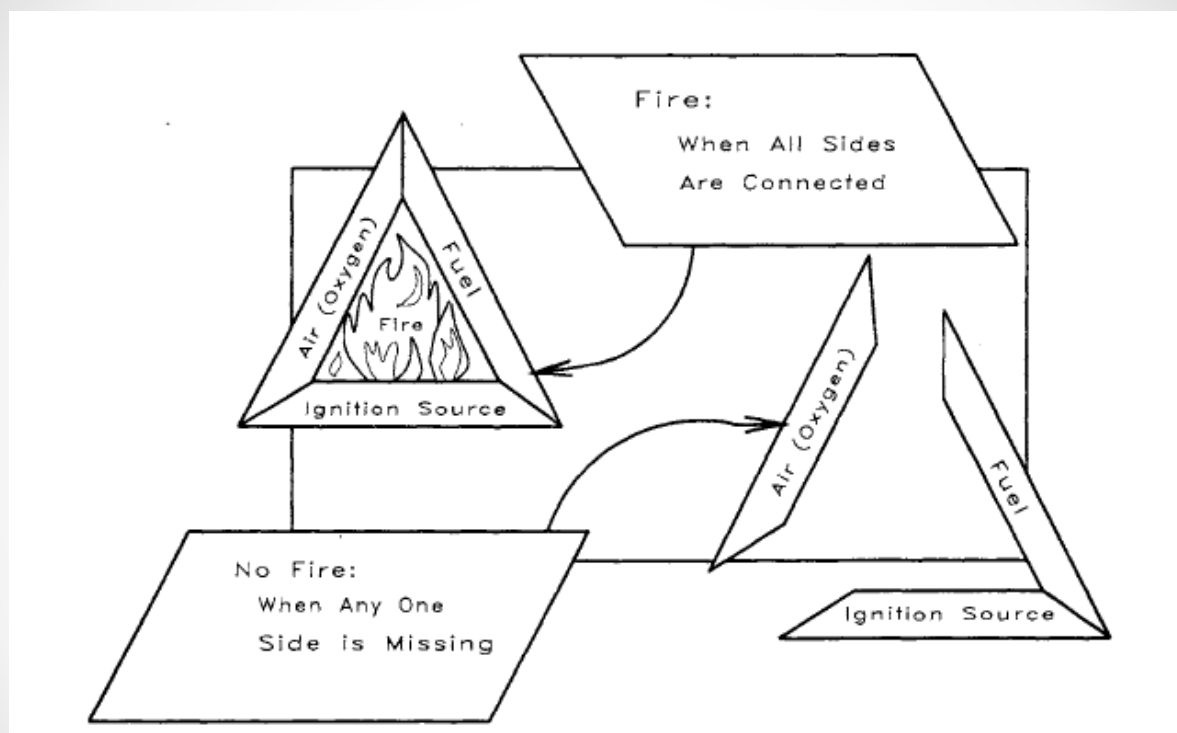
## Lec 4: Designs to Prevent Fires and Explosions

Flammability limits and diagrams, detonation and deflagration, Fire Risk Estimation

**Dr. Zayed Al-Hamamre**

Chemical Engineering Department | University of Jordan | Amman 11942, Jordan  
Tel. +962 6 535 5000 | 22888

### The fire triangle



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Tel. +962 6 535 5000 | 22888

## **Fuels**

Liquids: gasoline, acetone, ether, pentane

Solids: plastics, wood dust, fibers, metal particles

Gases: acetylene, propane, carbon monoxide, hydrogen

## **Oxidizers**

Gases: oxygen, fluorine, chlorine

Liquids: hydrogen peroxide, nitric acid, perchloric acid

Solids: metal peroxides, ammonium nitrite

## **Ignition sources**

Sparks, flames, static electricity, heat

## **Fires and Explosions**

- The major distinction between fires and explosions is the rate of energy release.
- Fires release energy slowly, whereas explosions release energy rapidly, typically on the order of microseconds.
- Fires can also result from explosions, and explosions can result from fires.
- A good example of how the energy release rate affects the consequences of an accident is a standard automobile tire.
  - The compressed air within the tire contains energy. If the energy is released slowly through the nozzle, the tire is harmlessly deflated.
  - If the tire ruptures suddenly and all the energy within the compressed tire releases rapidly, the result is a dangerous explosion.

## Definitions

**Combustion or fire:** Combustion or fire is a chemical reaction in which a substance combines with an oxidant and releases energy. Part of the energy released is used to sustain the reaction.

**Ignition:** Ignition of a flammable mixture may be caused by a flammable mixture coming in contact with a source of ignition with sufficient energy or the gas reaching a temperature high enough to cause the gas to autoignite.

**Autoignition temperature (AIT):** A fixed temperature above which adequate energy is available in the environment to provide an ignition source.

**Flash point (FP):** The flash point of a liquid is the lowest temperature at which it gives off enough vapor to form an ignitable mixture with air. At the flash point the vapor will burn but only briefly; inadequate vapor is produced to maintain combustion. The flash point generally increases with increasing pressure.

## Definitions

**Explosion:** An explosion is a rapid expansion of gases resulting in a rapidly moving pressure or shock wave. The expansion can be mechanical (by means of a sudden rupture of a pressurized vessel), or it can be the result of a rapid chemical reaction. Explosion damage is caused by the pressure or shock wave.

**Mechanical explosion:** An explosion resulting from the sudden failure of a vessel containing high-pressure nonreactive gas.

**Deflagration:** An explosion in which the reaction front moves at a speed less than the speed of sound in the unreacted medium.

**Detonation:** An explosion in which the reaction front moves at a speed greater than the speed of sound in the unreacted medium.

**Confined explosion:** An explosion occurring within a vessel or a building. These are most common and usually result in injury to the building inhabitants and extensive damage.

## Unconfined explosion:

- Unconfined explosions occur in the open.
- This type of explosion is usually the result of a flammable gas spill.
- The gas is dispersed and mixed with air until it comes in contact with an ignition source.
- Unconfined explosions are rarer than confined explosions because the explosive material is frequently diluted below the LFL by wind dispersion.
- These explosions are destructive because large quantities of gas and large areas are frequently involved.

## Flammability limits:

- Vapor-air mixtures will ignite and burn only over a well-specified range of compositions.
- The mixture will not burn when the composition is lower than the lower flammable limit (LFL); the mixture is too lean for combustion.
- The mixture is also not combustible when the composition is too rich; that is, when it is above the upper flammable limit (UFL).
- A mixture is flammable only when the composition is between the LFL and the UFL.
- Commonly used units are volume percent fuel (percentage of fuel plus air).
- Lower explosion limit (LEL) and upper explosion limit (UEL) are used interchangeably with LFL and UFL.

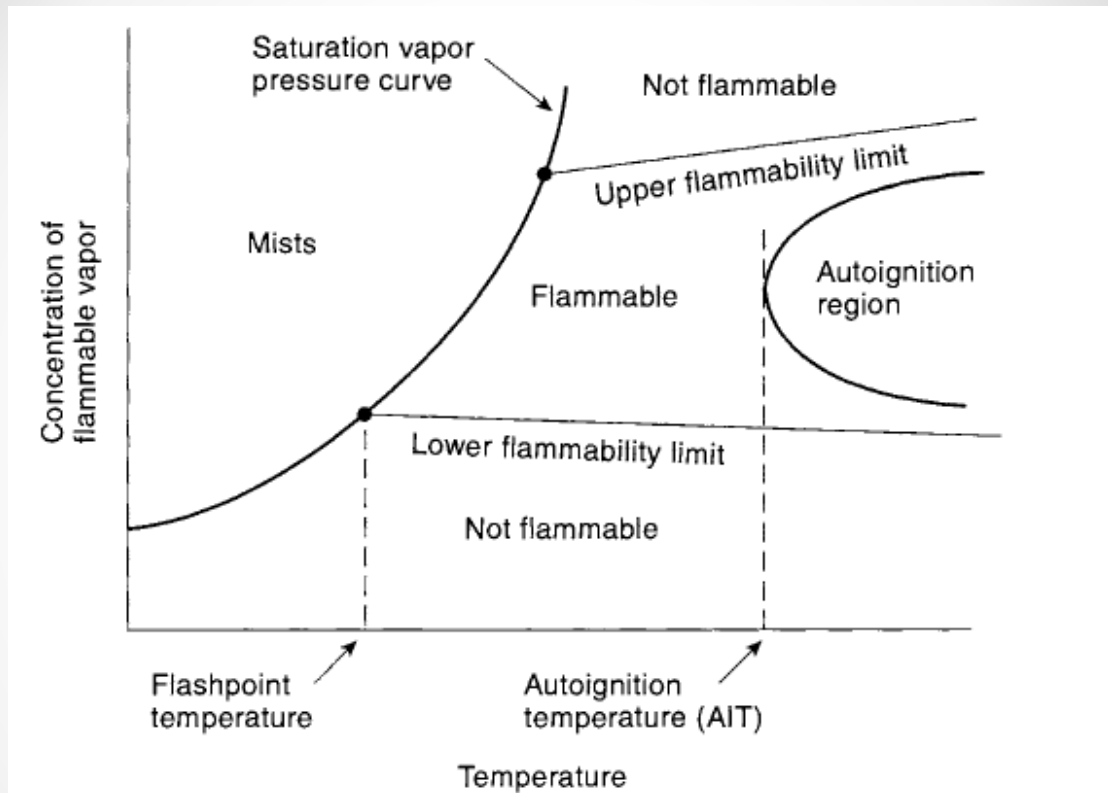
## Boiling-liquid expanding-vapor explosion (BLEVE):

- A BLEVE occurs if a vessel that contains a liquid at a temperature above its atmospheric pressure boiling point ruptures.
- The subsequent BLEVE is the explosive vaporization of a large fraction of the vessel contents; possibly followed by combustion or explosion of the vaporized cloud if it is combustible.
- This type of explosion occurs when an external fire heats the contents of a tank of volatile material.
- As the tank contents heat, the vapor pressure of the liquid within the tank increases and the tank's structural integrity is reduced because of the heating.
- If the tank ruptures, the hot liquid volatilizes explosively.

*Dust explosion:* This explosion results from the rapid combustion of fine solid particles. Many solid materials (including common metals such as iron and aluminum) become flammable when reduced to a fine powder.

*Shock wave:* An abrupt pressure wave moving through a gas.

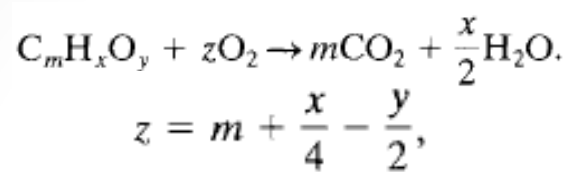
- A shock wave in open air is followed by a strong wind; the combined shock wave and wind is called a blast wave.
  - The pressure increase in the shock wave is so rapid that the process is mostly adiabatic.
- *Overpressure:* The pressure on an object as a result of an impacting shock wave.



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## Limiting Oxygen Concentration and Inerting

For general combustion reaction



where  $z$  has units of moles  $O_2$ /mole fuel.

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1},$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1}.$$

OR

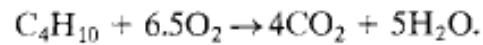
$$LFL = \frac{-3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.80,$$

$$UFL = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5,$$

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$$\text{LOC} = \text{LFL} \left( \frac{\text{moles O}_2}{\text{moles fuel}} \right)$$

for butane (C<sub>4</sub>H<sub>10</sub>).



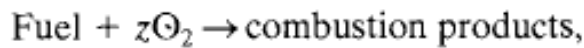
$$\begin{aligned} \text{LOC} &= \left( 1.9 \frac{\text{moles fuel}}{\text{total moles}} \right) \left( \frac{6.5 \text{ moles O}_2}{1.0 \text{ moles fuel}} \right) \\ &= 12.4 \text{ vol. \% O}_2. \end{aligned}$$

Below the limiting oxygen concentration (LOC) the reaction cannot generate enough energy to heat the entire mixture of gases (including the inert gases) to the extent required for the self-propagation of the flame.

## Flammability Diagram

- A general way to represent the flammability of a gas or vapor is by the triangle diagram
- Concentrations of fuel, oxygen, and inert material (in volume or mole %) are plotted on the three axes.
- Each apex of the triangle represents either 100% fuel, oxygen, or nitrogen.
- The tick marks on the scales show the direction in which the scale moves across the figure.
- Thus point A represents a mixture composed of 60% methane, 20% oxygen, and 20% nitrogen.
- The zone enclosed by the dashed line represents all mixtures that are flammable.
- Because point A lies outside the flammable zone, a mixture of this composition is not flammable.

- The air line represents all possible combinations of fuel plus air.
- The air line intersects the nitrogen axis at 79% nitrogen (and 21 % oxygen), which is the composition of pure air.
- The UFL and the LFL are shown as the intersection of the flammability zone boundary with the air line.
- Any gas mixture containing oxygen below the LOC is not flammable

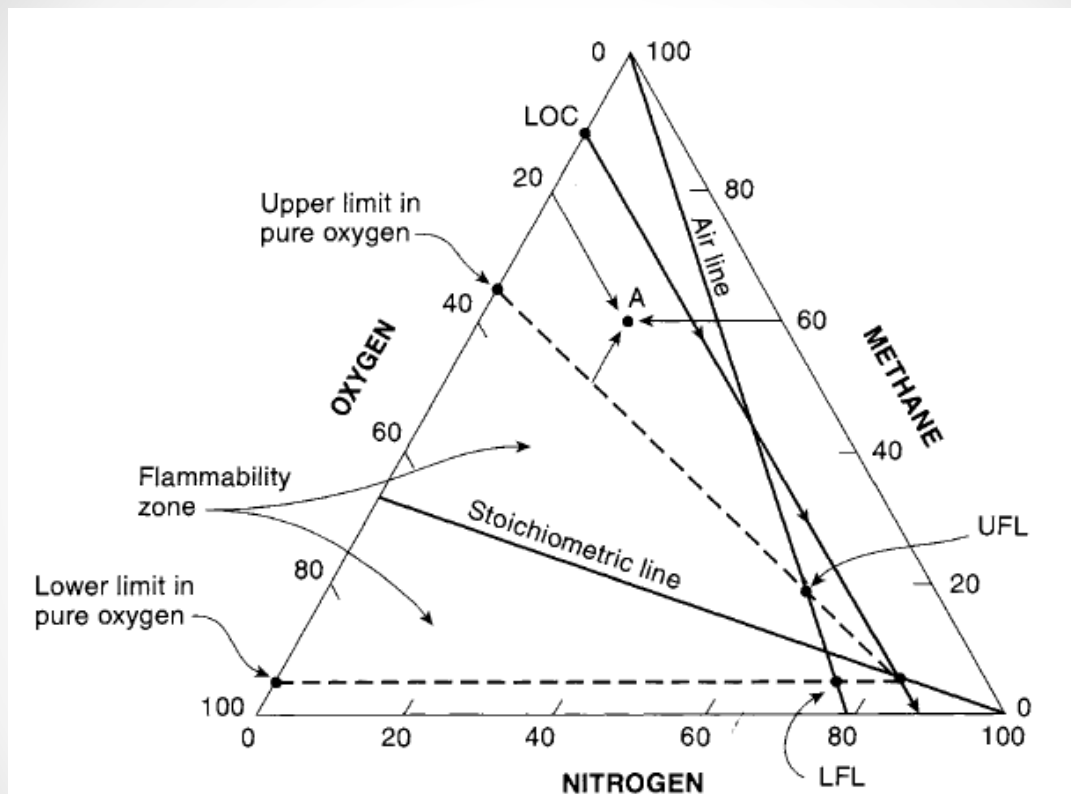


where  $z$  is the stoichiometric coefficient for oxygen.

- The intersection of the stoichiometric line with the oxygen axis (in volume % oxygen) is given by

$$100\left(\frac{z}{1+z}\right)$$

The stoichiometric line is drawn from this point to the pure nitrogen apex.





- The ratio of oxygen to fuel along the stoichiometric line is constant and is given by

$$\frac{x_{O_2}}{x_{Fuel}} = z.$$

At the specific fuel concentration of  $x_{Fuel} = LFL$  it follows

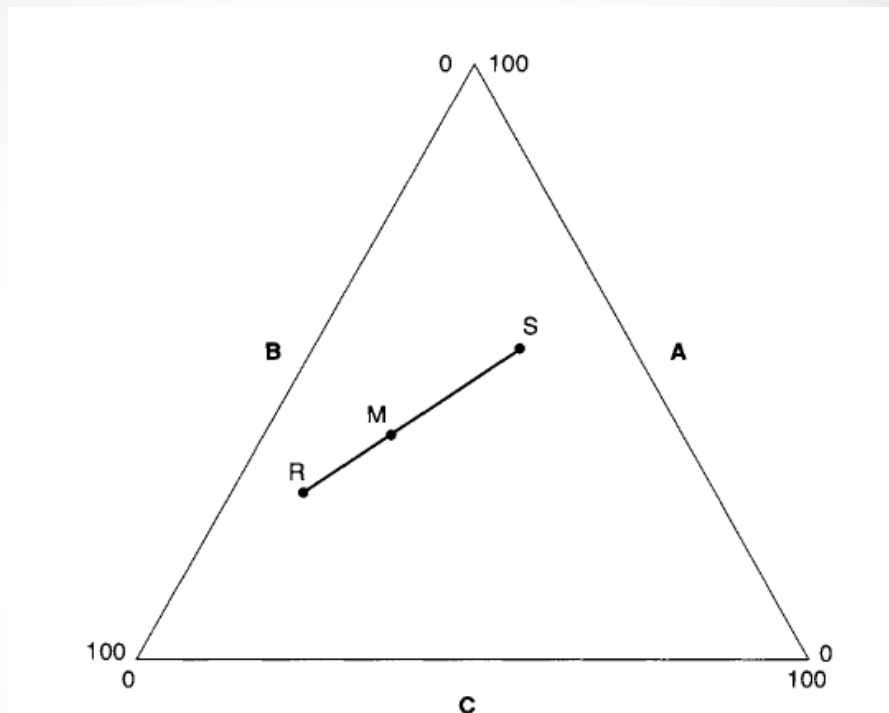
$$x_{O_2} = z(LFL).$$

- The expression is derived by realizing that on the oxygen axis no nitrogen is present.
- Thus the moles present are fuel (1 mole) plus oxygen ( $z$  moles).
- The total moles are thus  $1 + z$ , and the mole or volume percent of oxygen is given by

$$100\left(\frac{z}{1 + z}\right)$$

The shape and size of the flammability zone on a flammability diagram change with a number of parameters, including fuel type, temperature, pressure, and inert species. Thus the flammability limits and the LOC also change with these parameters.

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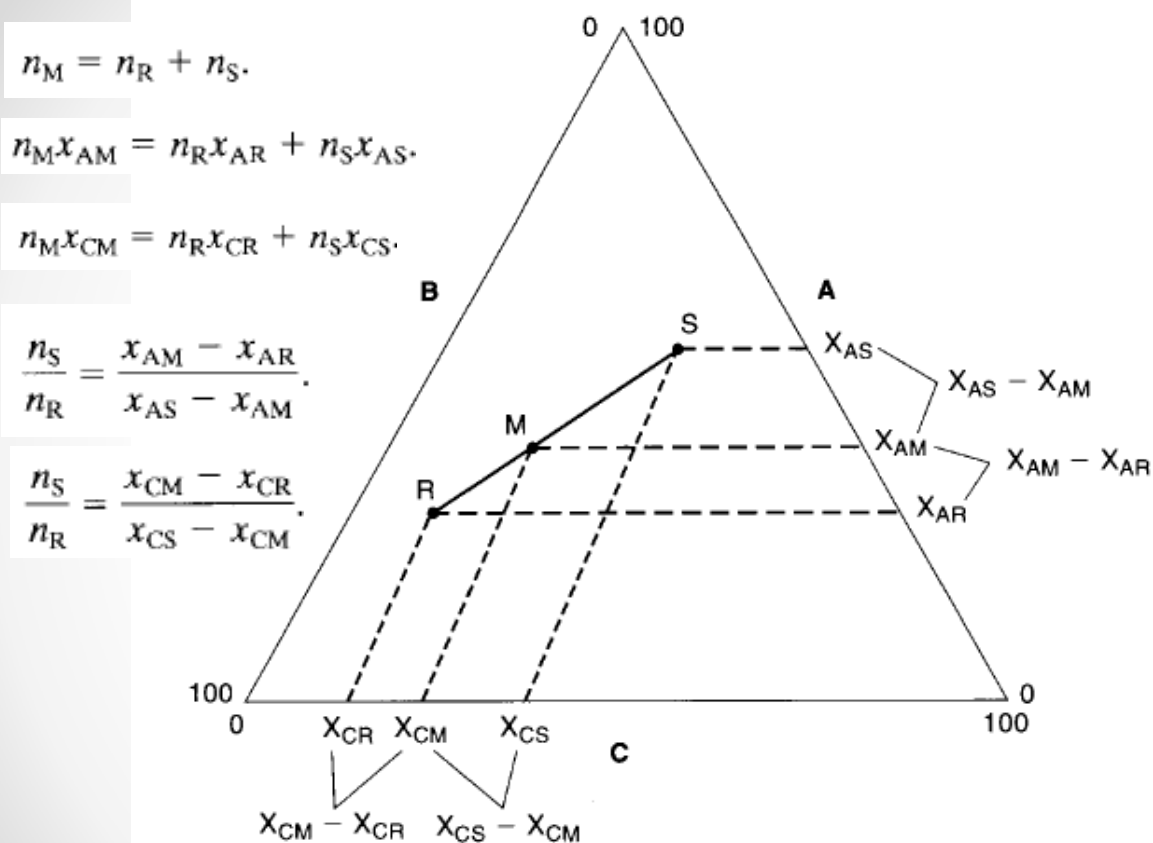
**Figure AC-1** Two mixtures R and S are combined to form mixture M.

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1. If two gas mixtures R and S are combined, the resulting mixture composition lies on a line connecting the points R and S on the flammability diagram. The location of the final mixture on the straight line depends on the relative moles of the mixtures combined. If mixture S has more moles, the final mixture point will lie closer to point S. This is identical to the lever rule used for phase diagrams.
2. If a mixture R is continuously diluted with mixture S, the mixture composition will follow along the straight line between points R and S on the flammability diagram. As the dilution continues, the mixture composition will move closer and closer to point S. Eventually, at infinite dilution, the mixture composition will be at point S.
3. For systems having composition points that fall on a straight line passing through an apex corresponding to one pure component, the other two components are present in a fixed ratio along the entire line length.
4. The limiting oxygen concentration (LOC) is estimated by reading the oxygen concentration at the intersection of the stoichiometric line and a horizontal line drawn through the LFL. This is equivalent to the equation

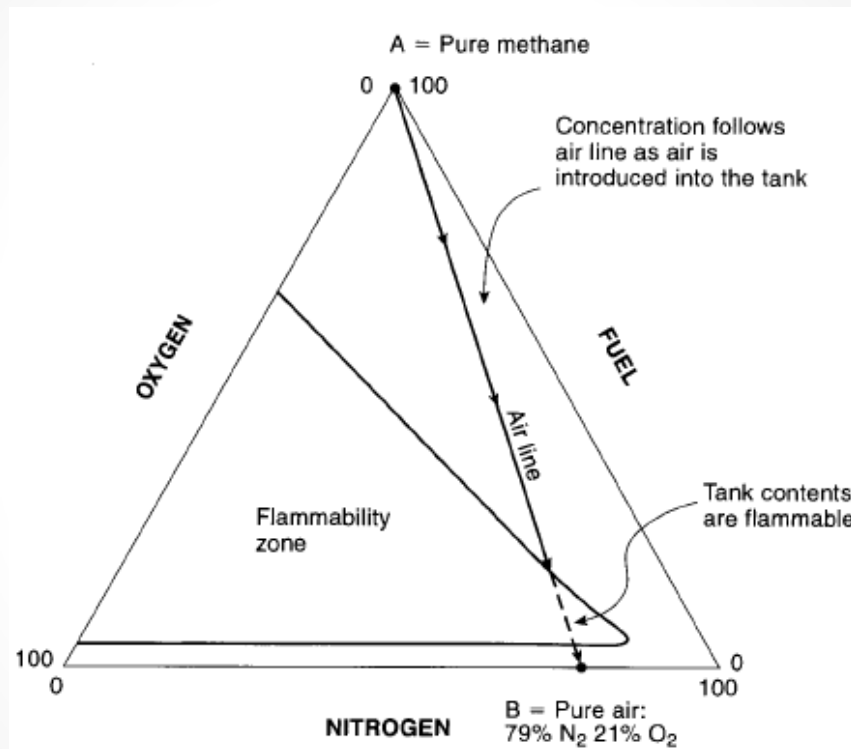
$$\text{LOC} = z(\text{LFL}). \quad (\text{AC-1})$$

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Tracking the gas composition during a process operation to determine whether a flammable mixture exists during the procedure.



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- For example, consider a storage vessel containing pure methane whose inside walls must be inspected as part of its periodic maintenance procedure.
- For this operation the methane must be removed from the vessel and replaced by air for the inspection workers to breathe.
- The first step in the procedure is to depressurize the vessel to atmospheric pressure.
- At this point the vessel contains 100% methane, represented by point A.
- If the vessel is opened and air is allowed to enter, the composition of gas within the vessel will follow the air line in until the vessel gas composition eventually reaches point B, pure air.
- Note that at some point in this operation the gas composition passes through the flammability zone.

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- If an ignition source of sufficient strength were present, then a fire or explosion would result.
- The procedure is reversed for placing the vessel back into service.
- In this case the procedure begins at point B, with the vessel containing air.
- If the vessel is closed and methane is pumped in, then the gas composition inside the vessel will follow the air line and finish at point A.
- Again, the mixture is flammable as the gas composition moves through the flammability zone.
- The out-of-service fuel concentration (OSFC) is the maximum fuel concentration that just avoids the flammability zone when a vessel is being taken out of service

$$\text{OSFC} = \frac{\text{LFL}\%}{1 - z\left(\frac{\text{LFL}\%}{21}\right)},$$

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$$\text{OSFC} = \frac{\text{LOC}\%}{z\left(1 - \frac{\text{LOC}\%}{21}\right)},$$

where LOC% is the minimum oxygen concentration in volume percentage of oxygen.

- The in-service oxygen concentration (ISOC) is the maximum oxygen concentration that just avoids the flammability zone,

$$\text{ISOC} = \frac{z(\text{LFL}\%)}{1 - \left(\frac{\text{LFL}\%}{100}\right)},$$

$$\text{ISOC} = \frac{z(\text{LOC}\%)}{z - \frac{\text{LOC}\%}{100}},$$

where LOC% is the limiting oxygen concentration in volume percentage of oxygen.

### Flammability Limits in Pure Oxygen<sup>1</sup>

Compound	Formula	Limits of flammability in pure oxygen	
		Lower	Upper
Hydrogen	H <sub>2</sub>	4.0	94
Deuterium	D <sub>2</sub>	5.0	95
Carbon monoxide <sup>2</sup>	CO	15.5	94
Ammonia	NH <sub>3</sub>	15.0	79
Methane	CH <sub>4</sub>	5.1	61
Ethane	C <sub>2</sub> H <sub>6</sub>	3.0	66
Ethylene	C <sub>2</sub> H <sub>4</sub>	3.0	80
Propylene	C <sub>3</sub> H <sub>6</sub>	2.1	53
Cyclopropane	C <sub>3</sub> H <sub>6</sub>	2.5	60
Diethyl ether	C <sub>4</sub> H <sub>10</sub> O	2.0	82
Divinyl ether	C <sub>4</sub> H <sub>6</sub> O	1.8	85

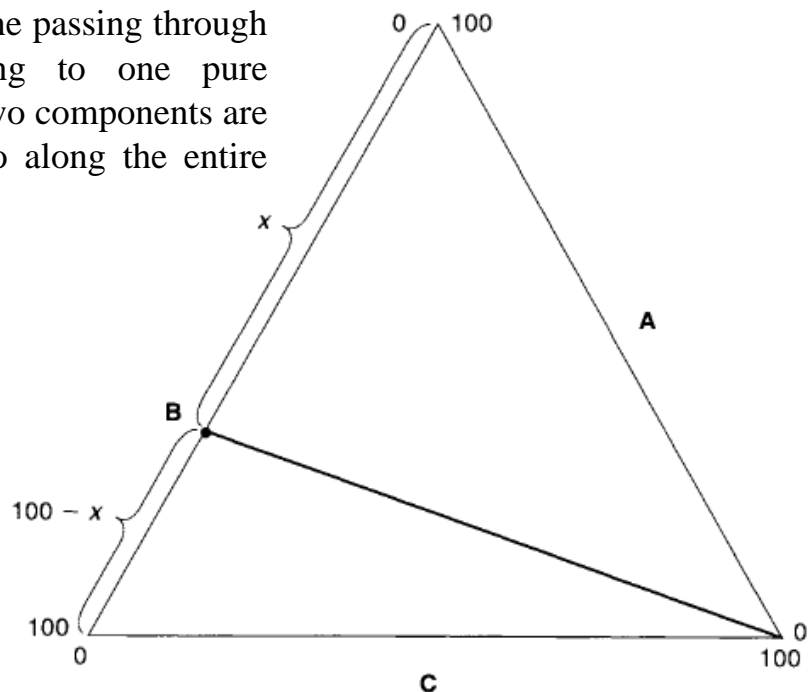
<sup>1</sup>Data from B. Lewis and G. von Elbe, *Combustion, Flames, and Explosions of Gases* (New York: Harcourt Brace Jovanovich, 1987).

<sup>2</sup>The limits are insensitive to  $p_{H_2O}$  above a few mm Hg.

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- For systems having composition points that fall on a straight line passing through an apex corresponding to one pure component, the other two components are present in a fixed ratio along the entire line length

$$\frac{x_A}{x_B} = \frac{x}{100 - x}$$



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## Ignition Energy

- The minimum ignition energy (MIE) is the minimum energy input required to initiate combustion.
- All flammable materials (including dusts) have MIEs.
- The MIE depends on the specific chemical or mixture, the concentration, pressure, and temperature

Experimental data indicate that

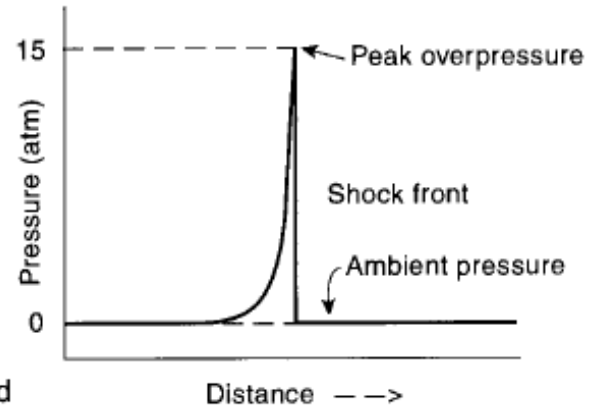
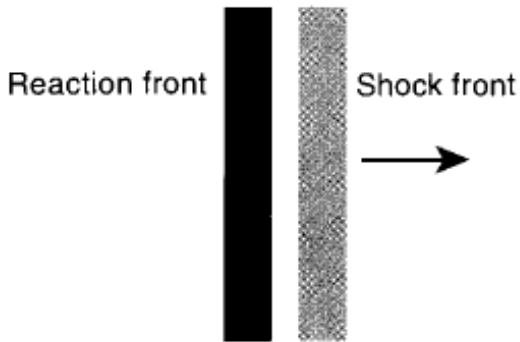
- the MIE decreases with an increase in pressure,
- the MIE of dusts is, in general, at energy levels somewhat higher than combustible gases, and
- an increase in the nitrogen concentration increases the MIE.

Chemical	Minimum ignition energy (mJ)
Acetylene	0.020
Benzene	0.225
1,3-Butadiene	0.125
<i>n</i> -Butane	0.260
Cyclohexane	0.223
Cyclopropane	0.180
Ethane	0.240
Ethene	0.124
Ethylacetate	0.480
Ethylene oxide	0.062
<i>n</i> -Heptane	0.240
Hexane	0.248
Hydrogen	0.018
Methane	0.280
Methanol	0.140
Methyl acetylene	0.120
Methyl ethyl ketone	0.280
<i>n</i> -Pentane	0.220
2-Pentane	0.180
Propane	0.250

<sup>1</sup>Data from I. Glassman, *Combustion*, 3d ed. (New York: Academic Press, 1996).

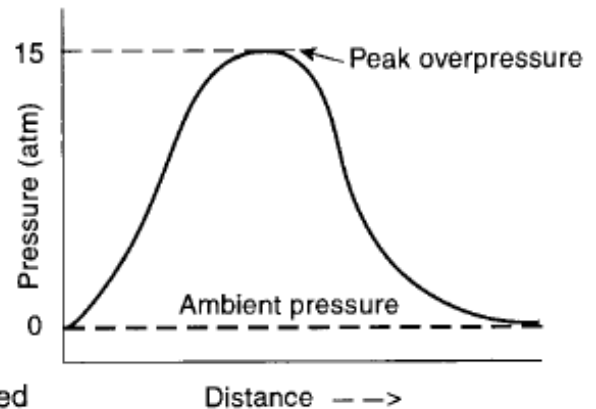
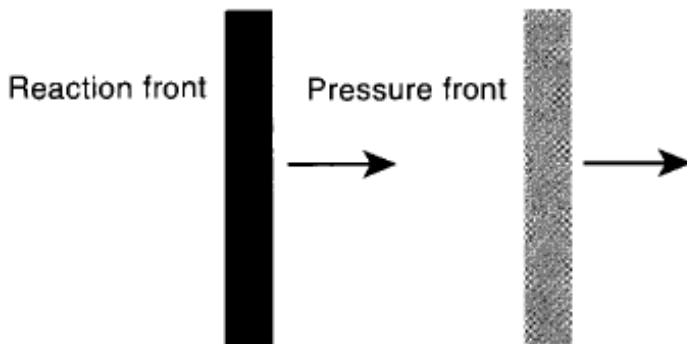
# Detonation and Deflagration

## DETONATION



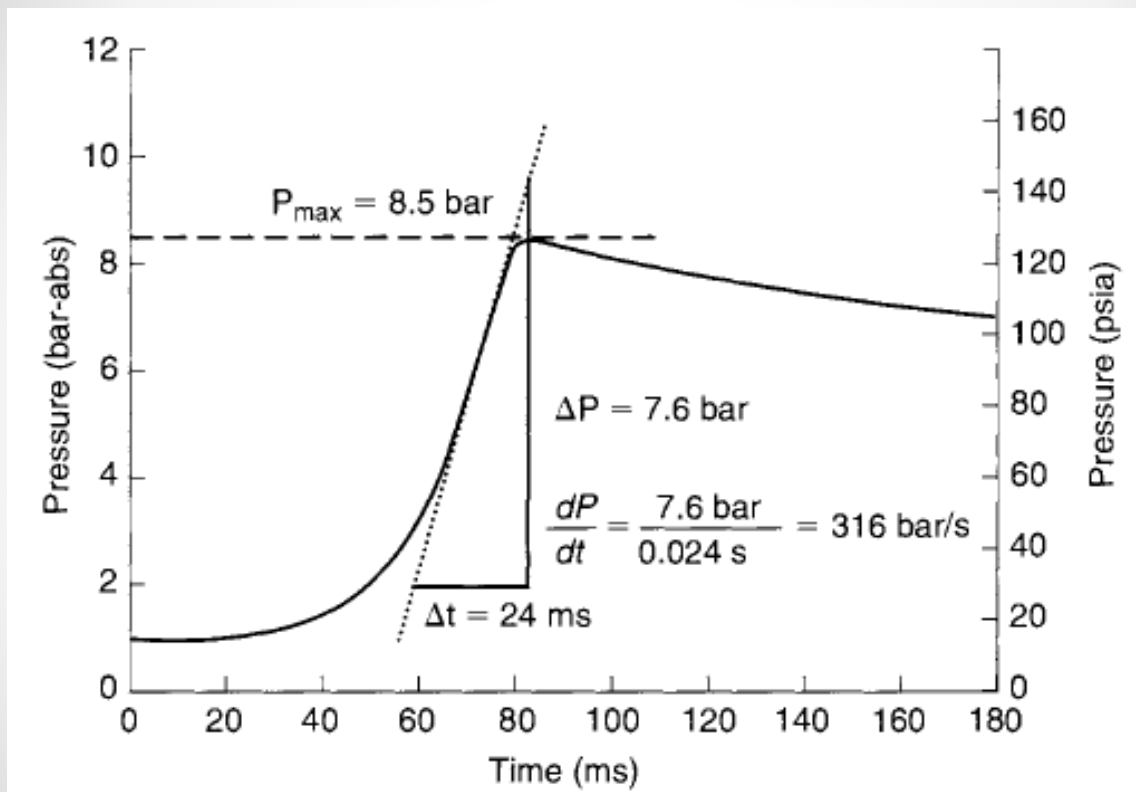
In a detonation, the reaction front moves at a speed greater than the speed of sound, driving the shock front immediately preceding it. Both fronts move at the same speed.

## DEFLAGRATION



In a deflagration, the reaction front moves at a speed less than the speed of sound, while the pressure front moves away from the reaction front at the speed of sound.

## Typical pressure versus time data obtained from gas explosion apparatus



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● 1-31

## Explosion Characteristics

The explosion characteristics determined using the vapor and dust explosion apparatus are used in the following way:

1. The limits of flammability or explosivity are used to determine the safe concentrations for operation or the quantity of inert material required to control the concentration within safe regions.
2. The maximum rate of pressure increase indicates the robustness of an explosion.
  - Thus the explosive behavior of different materials can be compared on a relative basis.
  - The maximum rate is also used to design a vent for relieving a vessel during an explosion before the pressure ruptures the vessel or to establish the time interval for adding an explosion suppressant (water, carbon dioxide, or Halon) to stop the combustion process.

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● 1-32



Experiments with explosives have demonstrated<sup>16</sup> that the overpressure can be estimated using an equivalent mass of TNT, denoted  $m_{\text{TNT}}$ , and the distance from the ground-zero point of the explosion, denoted  $r$ . The empirically derived scaling law is

$$z_e = \frac{r}{m_{\text{TNT}}^{1/3}} \quad \text{m/kg}^{1/3}$$

The equivalent energy of TNT is 1120 cal/g.

the scaled overpressure  $p_s$ ,

$$p_s = \frac{p_o}{p_a} = \frac{1616 \left[ 1 + \left( \frac{z_e}{4.5} \right)^2 \right]}{\sqrt{1 + \left( \frac{z_e}{0.048} \right)^2} \sqrt{1 + \left( \frac{z_e}{0.32} \right)^2} \sqrt{1 + \left( \frac{z_e}{1.35} \right)^2}}$$

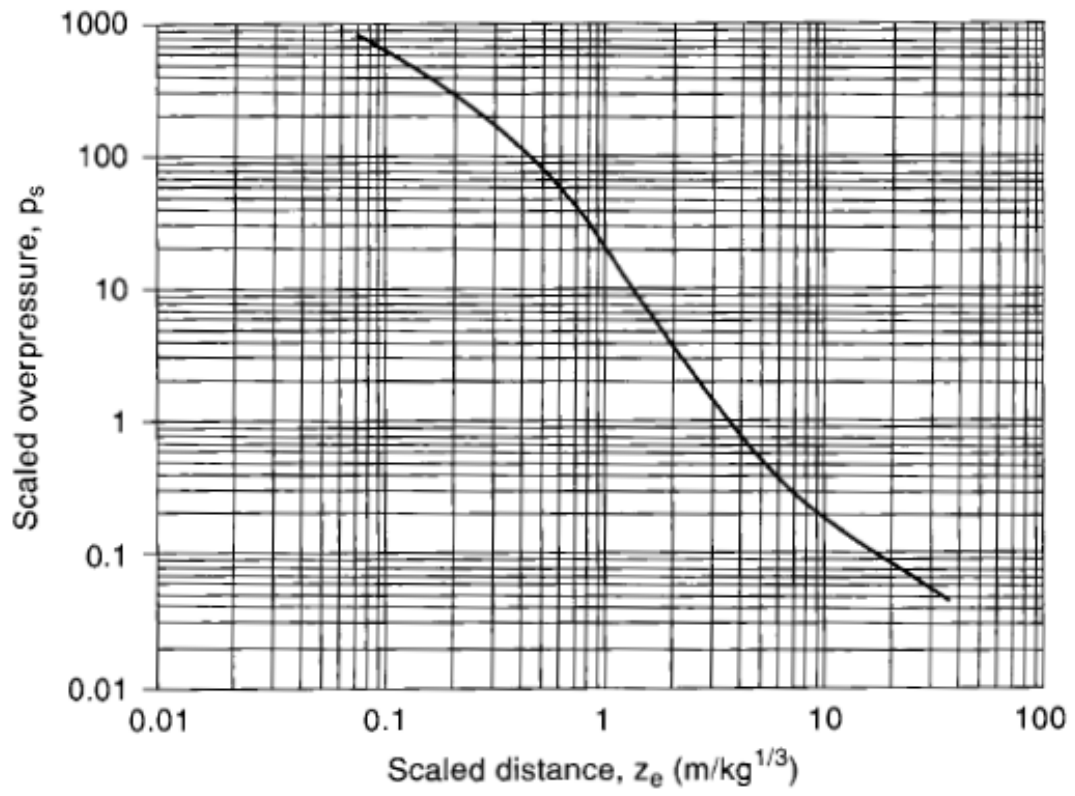
where

- $p_s$  is the scaled overpressure (unitless),
- $p_o$  is the peak side-on overpressure, and
- $p_a$  is the ambient pressure.

The procedure for estimating the overpressure at any distance  $r$  resulting from the explosion of a mass of material is as follows: (1) Compute the energy of the explosion using established thermodynamic procedures, (2) convert the energy to an equivalent amount of TNT, (3) use the scaling law and the correlations of Figure 6-23 to estimate the overpressure, and (4) use Table 6-9 to estimate the damage.

### Example

One kilogram of TNT is exploded. Compute the overpressure at a distance of 30 m from the explosion.



**Table 6-9** Damage Estimates for Common Structures Based on Overpressure (these values are approximations)<sup>1</sup>

Pressure		Damage
psig	kPa	
0.02	0.14	Annoying noise (137 dB if of low frequency, 10–15 Hz)
0.03	0.21	Occasional breaking of large glass windows already under strain
0.04	0.28	Loud noise (143 dB), sonic boom, glass failure
0.1	0.69	Breakage of small windows under strain
0.15	1.03	Typical pressure for glass breakage
0.3	2.07	“Safe distance” (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken
0.4	2.76	Limited minor structural damage
0.5–1.0	3.4–6.9	Large and small windows usually shatter; occasional damage to window frames
0.7	4.8	Minor damage to house structures
1.0	6.9	Partial demolition of houses, made uninhabitable
1–2	6.9–13.8	Corrugated asbestos shatters; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing), fastenings fail, panels blow in
1.3	9.0	Steel frame of clad building slightly distorted
2	13.8	Partial collapse of walls and roofs of houses
2–3	13.8–20.7	Concrete or cinder block walls, not reinforced, shatter
2.3	15.8	Lower limit of serious structural damage
2.5	17.2	50% destruction of brickwork of houses
3	20.7	Heavy machines (3000 lb) in industrial buildings suffer little damage; steel frame buildings distort and pull away from foundations
3–4	20.7–27.6	Frameless, self-framing steel panel buildings demolished; rupture of oil storage tanks
4	27.6	Cladding of light industrial buildings ruptures
5	34.5	Wooden utility poles snap; tall hydraulic presses (40,000 lb) in buildings slightly damaged
5–7	34.5–48.2	Nearly complete destruction of houses
7	48.2	Loaded train wagons overturned
7–8	48.2–55.1	Brick panels, 8–12 in thick, not reinforced, fail by shearing or flexure
9	62.0	Loaded train boxcars completely demolished
10	68.9	Probable total destruction of buildings; heavy machine tools (7000 lb) moved and badly damaged, very heavy machine tools (12,000 lb) survive
300	2068	Limit of crater lip

<sup>1</sup>V. I. Clancey, “Diagnostic Features of Explosion Damage,” paper presented at the Sixth International Meeting of Forensic Sciences (Edinburgh, 1972).

## TNT Equivalency

TNT equivalency is a simple method for equating a known energy of a combustible fuel to an equivalent mass of TNT. The approach is based on the assumption that an exploding fuel mass behaves like exploding TNT on an equivalent energy basis. The equivalent mass of TNT is estimated using the following equation:

$$m_{\text{TNT}} = \frac{\eta m \Delta H_c}{E_{\text{TNT}}}$$

where

- $m_{\text{TNT}}$  is the equivalent mass of TNT (mass),
- $\eta$  is the empirical explosion efficiency (unitless),
- $m$  is the mass of hydrocarbon (mass),
- $\Delta H_c$  is the energy of explosion of the flammable gas (energy/mass), and
- $E_{\text{TNT}}$  is the energy of explosion of TNT.

A typical value for the energy of explosion of TNT is  $1120 \text{ cal/g} = 4686 \text{ kJ/kg} = 2016 \text{ Btu/lb}$ . The heat of combustion for the flammable gas can be used in place of the energy of explosion for the combustible gas.

- The explosion efficiency is empirical, with most flammable cloud estimates varying between 1 % and 10%, as reported by a number of sources.
- Others have reported 5%, 10%, and 15%

The procedure to estimate the damage associated with an explosion using the TNT equivalency method is as follows:

1. Determine the total quantity of flammable material involved in the explosion.
2. Estimate the explosion efficiency, and calculate the equivalent mass of TNT
3. Use the scaling law to estimate the peak side-on overpressure.
4. Use Table 6-9 to estimate the damage for common structures and process equipment.

The procedure can be applied in reverse to estimate the quantity of material involved based on damage estimates.

### Example

One thousand kilograms of methane escapes from a storage vessel, mixes with air, and explodes. Determine (a) the equivalent amount of TNT and (b) the side-on peak overpressure at a distance of 50 m from the blast. Assume an explosion efficiency of 2%.

### Example

A reactor contains the equivalent of 10,000 lb of TNT. If it explodes, estimate the injury to people and the damage to structures 500 ft away.

**Table 2-4** Transformation from Percentages to Probits<sup>1</sup>

%	0	1	2	3	4	5	6	7	8	9
0	—	2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.50	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.80	4.82	4.85	4.87	4.90	4.92	4.95	4.97
50	5.00	5.03	5.05	5.08	5.10	5.13	5.15	5.18	5.20	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.50
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

$Y$  is 4.39. The percentage from Table 2-4 is 27%.

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**Table 2-5** Probit Correlations for a Variety of Exposures (The causative variable is representative of the magnitude of the exposure.)

Type of injury or damage	Causative variable	Probit parameters	
		$k_1$	$k_2$
<b>Fire<sup>1</sup></b>			
Burn deaths from flash fire	$t_e I_e^{4/3}/10^4$	-14.9	2.56
Burn deaths from pool burning	$t I^{4/3}/10^4$	-14.9	2.56
<b>Explosion<sup>1</sup></b>			
Deaths from lung hemorrhage	$p^o$	-77.1	6.91
Eardrum ruptures	$p^o$	-15.6	1.93
Deaths from impact	$J$	-46.1	4.82
Injuries from impact	$J$	-39.1	4.45
Injuries from flying fragments	$J$	-27.1	4.26
Structural damage	$p^o$	-23.8	2.92
Glass breakage	$p^o$	-18.1	2.79

$$Y = k_1 + k_2 \ln V.$$

The causative factor represents the dose  $V$ .

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$t_e$  = effective time duration (s)  
 $I_e$  = effective radiation intensity (W/m<sup>2</sup>)  
 $t$  = time duration of pool burning (s)  
 $I$  = radiation intensity from pool burning (W/m<sup>2</sup>)  
 $p^o$  = peak overpressure (N/m<sup>2</sup>)  
 $J$  = impulse (N s/m<sup>2</sup>)  
 $C$  = concentration (ppm)  
 $T$  = time interval (min)

For spreadsheet computations a more useful expression for performing the conversion from probits to percentage is given by

$$P = 50 \left[ 1 + \frac{Y - 5}{|Y - 5|} \operatorname{erf} \left( \frac{|Y - 5|}{\sqrt{2}} \right) \right],$$