Energetic Materials

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Outline

- Energetic Materials

What are Energetic Material

- **Energetic materials are classes of materials with a high amount of stored chemical energy**
- **Energetic materials usually contain a fuel and oxidizer in the same molecule or in separate molecules**
- **Upon initiation, they are capable of rapidly releasing a large amount energy producing heat, light, sound, and large volumes of gases**

Types of Energetic Material

- Fuels
  - Gasoline, Diesel, etc.
- Pyrotechnics
- Propellants
- Explosives

Pyrotechnics

Pyrotechnics

- **Pyrotechnic** is a material containing a fuel and oxidizer that when ignited produce heat, flames, sound, colored light, smoke, and some gas.

Pyrotechnics

- **Pyrotechnic** characteristics
  - Usually the fuel is metal and the oxidizer is salts or metal oxides
  - Chemically metastable
  - Very low reaction rates
  - Produces a large amount of energy

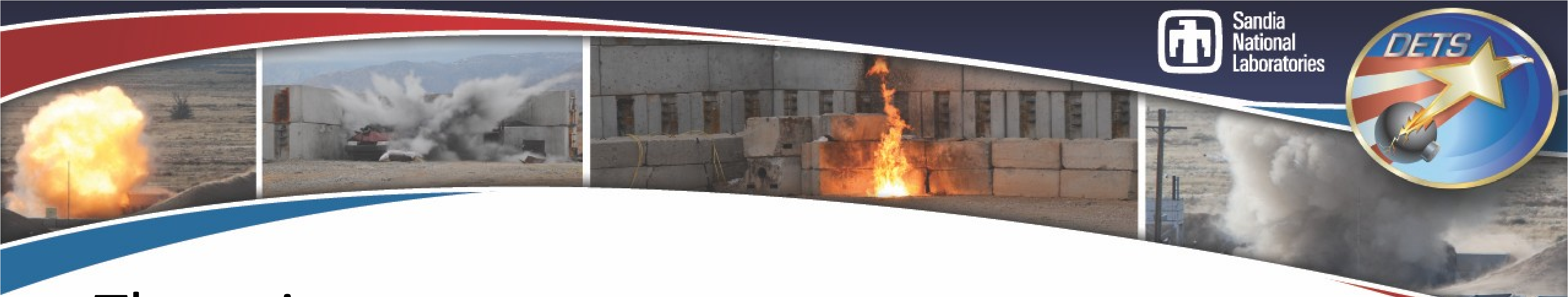
Fuels	Oxidizers	Reactants
Aluminum	Ammonium Nitrate	Aluminum Oxide
Boron	Ammonium Perchlorate	Barium Oxide
Iron	Barium Chlorate	Boron Oxide
Magnesium	Barium Nitrate	Carbon Dioxide
Phosphorus	Barium Peroxide	Carbon Monoxide
Silicon	Iron Oxide	Chromium Oxide
Titanium	Lead Chromate	Lead Oxide
Lactose	Lead Oxide	Magnesium Oxide
Shellac	Lead Peroxide	Nitrogen
Hexachloroethane	Potassium Chlorate	Potassium Carbonate
Starch	Potassium Nitrate	Potassium Chloride
Anthracene	Potassium Perchlorate	Potassium Sulfide
PVC	Sodium Nitrate	Silicon Dioxide
	Strontium Nitrate	Sodium Chloride
		Strontium Oxide
		Titanium Dioxide
		Water
		Zinc chloride

Pyrotechnics

- **Types**
  - Heat
  - Light
  - Sound
  - Smoke
  - Delay

Pyrotechnics

- **Heat**
  - Usually metal-salt or metal-metal oxide mixture with no binders
  - Uses
    - Ignition mixtures
    - Thermites
    - Incendiaries
    - Heat pellets for thermals batteries
  - Metal-salt mixture
    - Sensitive to impact, flame, and sparks
    - Used mainly in ignition mixtures
  - Metal-metal oxide
    - Not sensitive to impact, flame, and spark
    - Used mainly as thermite material and heating devices



Thermite

- With Termite the more reactive metal (Aluminum) reduces the metal Oxide (Iron Oxide Fe_2O_3), Oxidizing itself and releasing a substantial amount of energy during the reaction.
- The two most common types of Thermite are made using either Iron(III) Oxide, Fe_2O_3 (also known as Hematite), or using Iron(II, III) Oxide, Fe_2O_4 (also known as Magnetite).
  - The Iron Oxide is mixed with finely powdered Aluminum metal.
- When the Thermite reacts, liquid Iron metal and Aluminum Oxide, Al_2O_3, is produced as a result.
  - Al melting point is ~1,221˚F
  - Alumina melting point ~3,763˚F
  - Fe melting point is less than 3,000˚F
  - Ignition temperature is above 2,200˚F
  - Reaction temperature is between ~3,632˚F to 5,000˚F**
  - This temperature of the sun is ~10,000˚F

$$2Al + Fe_2O_3 \xrightarrow{heat} Al_2O_3 + 2Fe$$

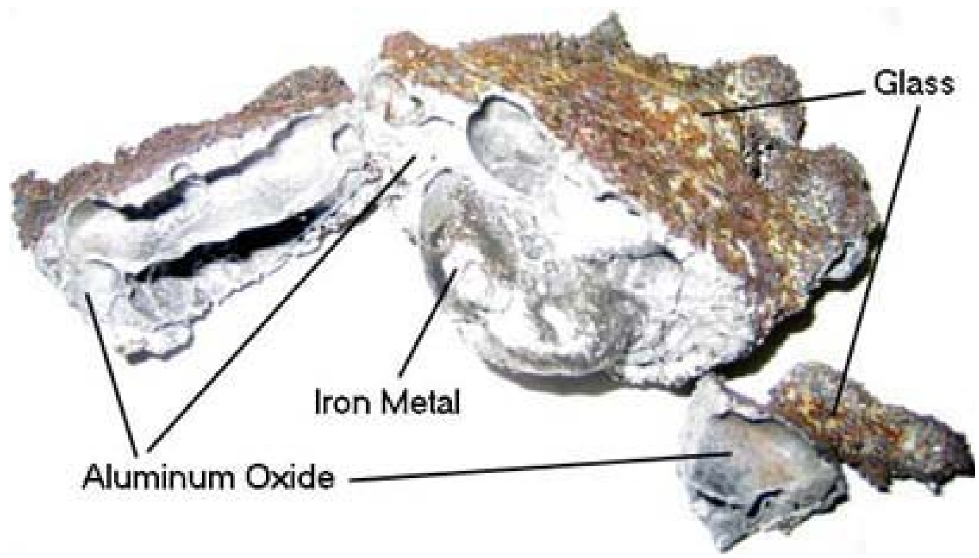
**Chemistry of Pyrotechnics, Conkling, 2nd Edition

Pyrotechnics

- **2000 grams** of Fe_2O_3 thermite, filling a large coffee can, reacts on top of a ¼" thick, steel, I-Beam. The resulting reaction is so intensely hot that it melts its container and the steel beam, spilling vast amounts of molten Iron and Al_2O_3 everywhere.

Thermite

- Al/Fe_2O_3 is the most common Thermite used today for welding
- The products from this reaction are
  - Molten Iron
  - Alumina
- The molten Iron is the heat transfer medium to perform the specific work
  - Welding of railroad tracks together



Exothermic Torch

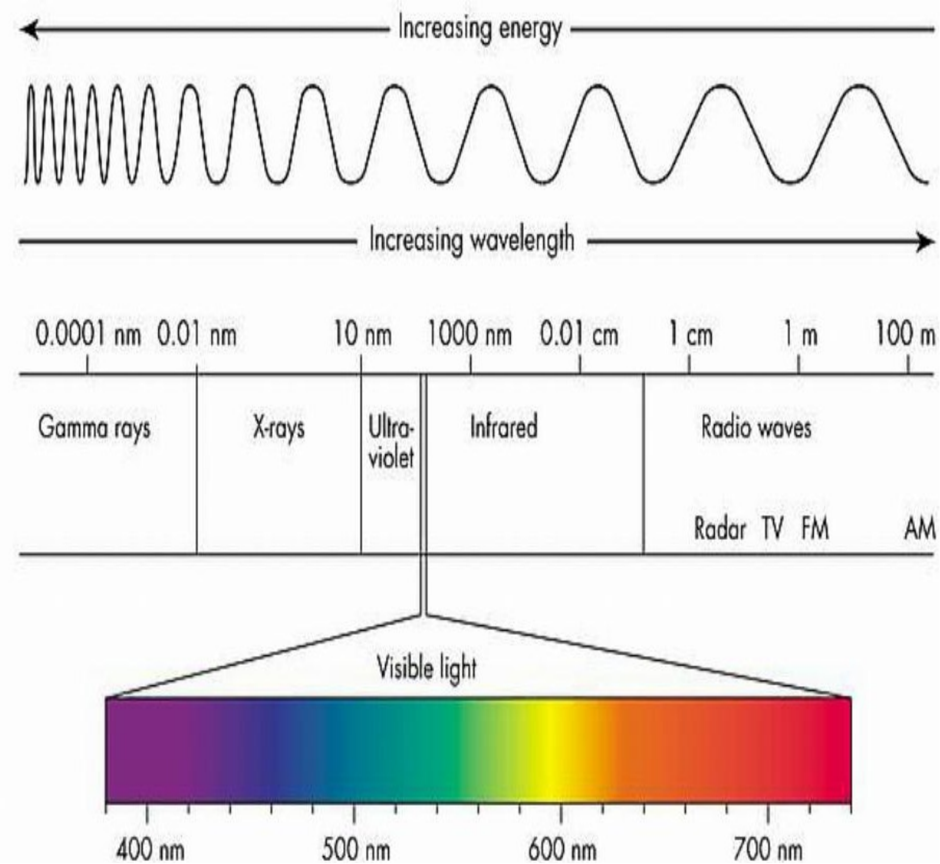
- An exothermic cutting torch is a copper pipe packed with metal wires.
- Pure oxygen gas is passed through the pipe from an oxygen cylinder and regulator.
- The end of the pipe is lit with a high temperature source.
- The copper sleeve burns and is used as a pre-heating source for the metal inside the sleeve.
- The iron in the steel burns in the oxygen coming down the pipe to produce enormous heat and a liquid slag of iron oxides and other materials, which dribbles and splashes out.
- The temperature reached in the center of the combustion zone is ~10,000˚F or greater. This is significantly higher than the melting point of any substance on earth.
  - Concrete melts at ~3500˚F
  - Steel at less than 3000 ˚F
- The flow and pressure of the oxygen also helps to blow the slag out of the cut zone.

Pyrotechnics

- **Light**
  - Two Categories
    - Flash Powder
    - Flares
  - Flash Powders
    - Metal-salt mixtures
    - Burn very rapidly where some almost produce detonation velocities
      - Reaction rates as high as 1 km/s
    - Usually packed loose or pressed lightly
    - Used to produce delays, stun individuals, or simulate detonations
  - Flare
    - Metal-salt and binder mixture
    - Burns slowly
    - Used to produce a sustained light

Pyrotechnics

- **Light** (cont'd)
  - Physics
    - Material's electrons are in a lowest energy state
    - Electrons are excited to a higher energy state
      - Electrons in higher energy state are unstable and want to return back to their ground state
  - Upon return to ground state energy is released as
    - Heat
    - Phonon (Light)
      - Electromagnetic radiation which gives it a wave speed and length (Frequency)



Pyrotechnics

- **Sound**
  - Two Types
    - Loud, sharp, short duration sound
    - Whistle sound for long durations
  - Loud, sharp, short duration sound
    - Black powder or photoflash mixtures used in light cardboard tubing
  - Whistle sound for long durations
    - Mixture compressed and burned in an open-ended container which produces the whistling sound

Pyrotechnics

- **Smoke**
  - Reaction produces a large amount of gases which, disperse the smoke into the environment
  - Reaction burns at low temperatures
  - Organic dyes used produce different colors
    - Dye sublimes and condenses into the air to form small solid particles
    - These dyes are strong absorbers of light
    - In essence, the small particles act like filters by absorbing a certain spectrum of wavelength and reflecting the rest
    - The reflected light is what is seen

Pyrotechnics

- **Delay**
  - Use controlled burn rates
  - Metal-metal oxide and metal-salt mixtures used
  - Used in safety fuse
  - Some mixtures produce gas

Propellants

Definition

- Presence of a fuel and oxidizer
    - Many propellants consist of explosive materials
- Chemically metastable
- Minimal porosity
    - Great efforts are taken during propellant production to reduce the level of porosity
- Thermally initiated
- **Propellants** undergo a rapid auto combustion that proceeds at subsonic rates
    - **Combustion** not **detonation**
- The reaction produces thermal energy, gases and hot particles

Definition

- Burn rate controlled by design pressure of the rocket or gun chamber
- Confinement enhance reaction
- **Power**
  - Thrust
- Propellants are also known as low explosives
- The rate of reaction is usually between a few cm/s up to approximately 1000 m/s

Propellants

- **Types**
  - Gun Propellants
    - Single-base
    - Double-base
    - Triple-base
    - Composite
    - High energy
    - Liquid
  - Rocket
    - Double-base
    - Composite
    - Liquid

Propellants

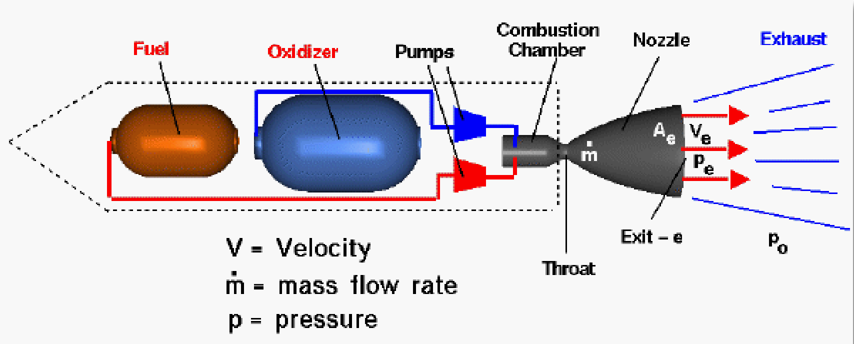
- **Single-base**
  - Composed of one energetic material (nitrocellulose) and a binder material
  - Guns
    - Used in pistols to artillery weapons
- **Double-base**
  - Composed of two energetic materials (nitrocellulose - nitroglycerine) and a binder material
  - Guns
    - Used in pistols and mortars
    - Disadvantage is the excessive erosion of the gun barrel due to high flame temperatures and muzzle flash
  - Rockets
    - Small grains used in small rocket motors
    - Cast large grain used in large rocket motors

Propellants

- **Triple-base**
  - Composed of three energetic materials (nitrocellulose – nitroglycerine - nitroguanidine) and a binder material
  - Guns
    - Used in tanks and large caliber guns
  - Nitroguanidine helps to reduce flame temperature and muzzle flash
- **Composite**
  - Composed of a fuel and oxidizer that chemically solidify when mixed together with a polymer binder
  - Guns
    - Used in pistols and mortars
    - Disadvantage is the excessive erosion due to high flame temperatures and the presence of muzzle flash
  - Solid rocket propellant mixture examples
    - Ammonium perchlorate (oxidizer), Carboxy or Hydroxy-terminated polybutadiene (fuel), Aluminum and other additives

Propellants

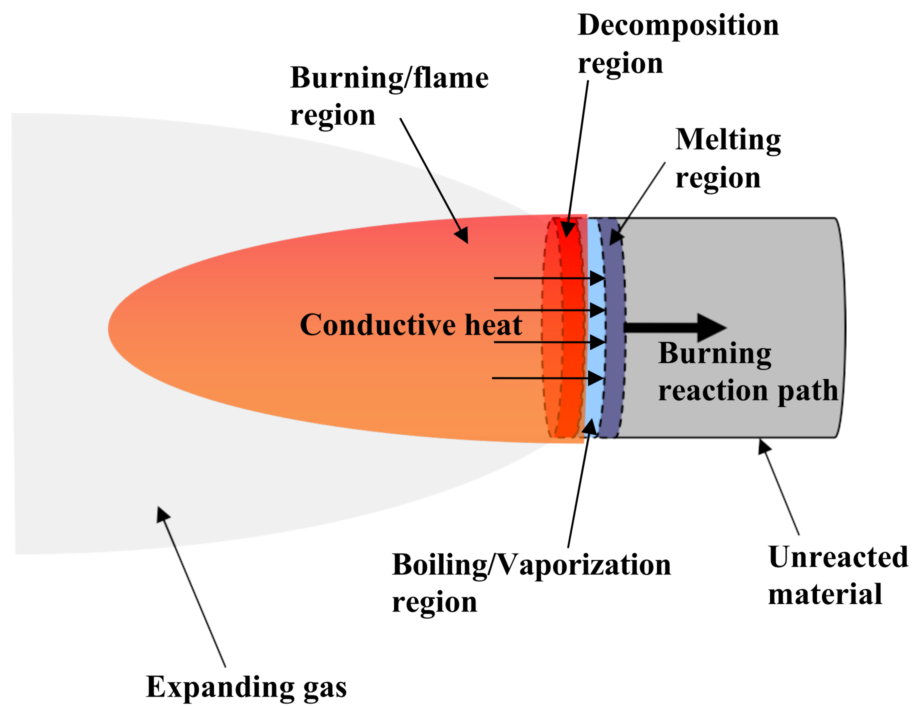
- **High Energy**
  - Nitroguanidine replaced by RDX to increase the power
  - Used in tank guns
  - Disadvantage of extensive gun barrel erosion from very high temperatures and the possibility of a detonation



- **Liquid**
  - Two types
    - Monopropellant
      - Single material
      - Hydrazine, Hydrogen peroxide, etc.
    - Bipropellant
      - Two separate materials mixed together in the combustion chamber
      - Unsymmetrical Dimethylhydrazine (UDMH) and Inhibited Red Fuming Nitric Acid (IRFNA); etc.
  - High energy output per unit volume
  - Cheap and lightweight
  - Less vulnerable to accidental initiation
  - High storage capacity
  - Drawbacks
    - Toxic

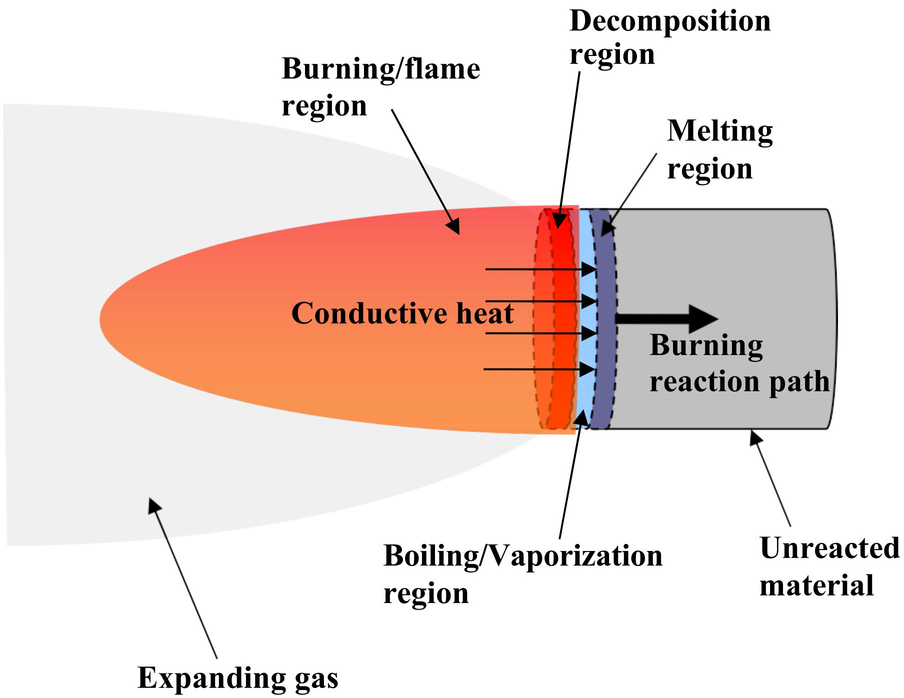
Initiation

- Propellants are usually thermally ignited
- Thermal ignition causes surface to melt
- As the temperature at the melted surfaces continues to increase boiling and vaporization occurs



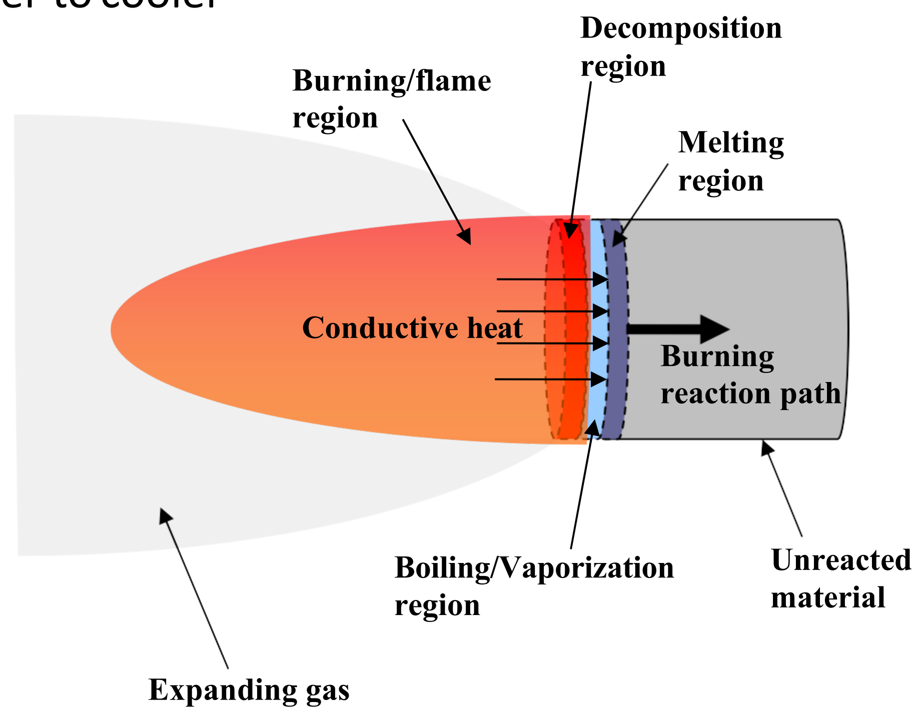
Propellants

- Thermal energy (usually in the form of a flame), gases and hot particles
- Heat from this process is transferred back into the next surface layer producing a self-sustaining subsonic deflagration
  - Conduction
  - Convection
  - Radiation



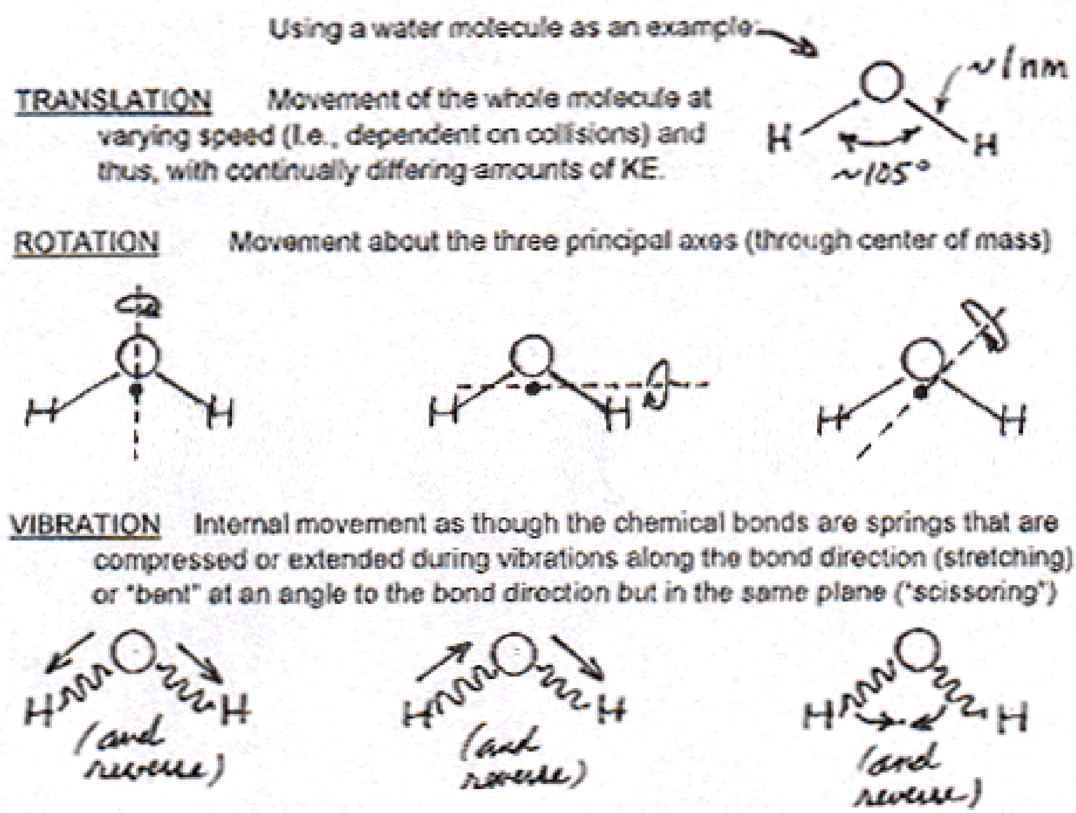
Initiation

- **Conduction**
  - Thermal energy (molecular vibration) is conducted along solids from hotter to cooler
  - Factors maximizing conductive feedback
    - Compacted composition
    - Metal fuels
    - Metal casing and core wire



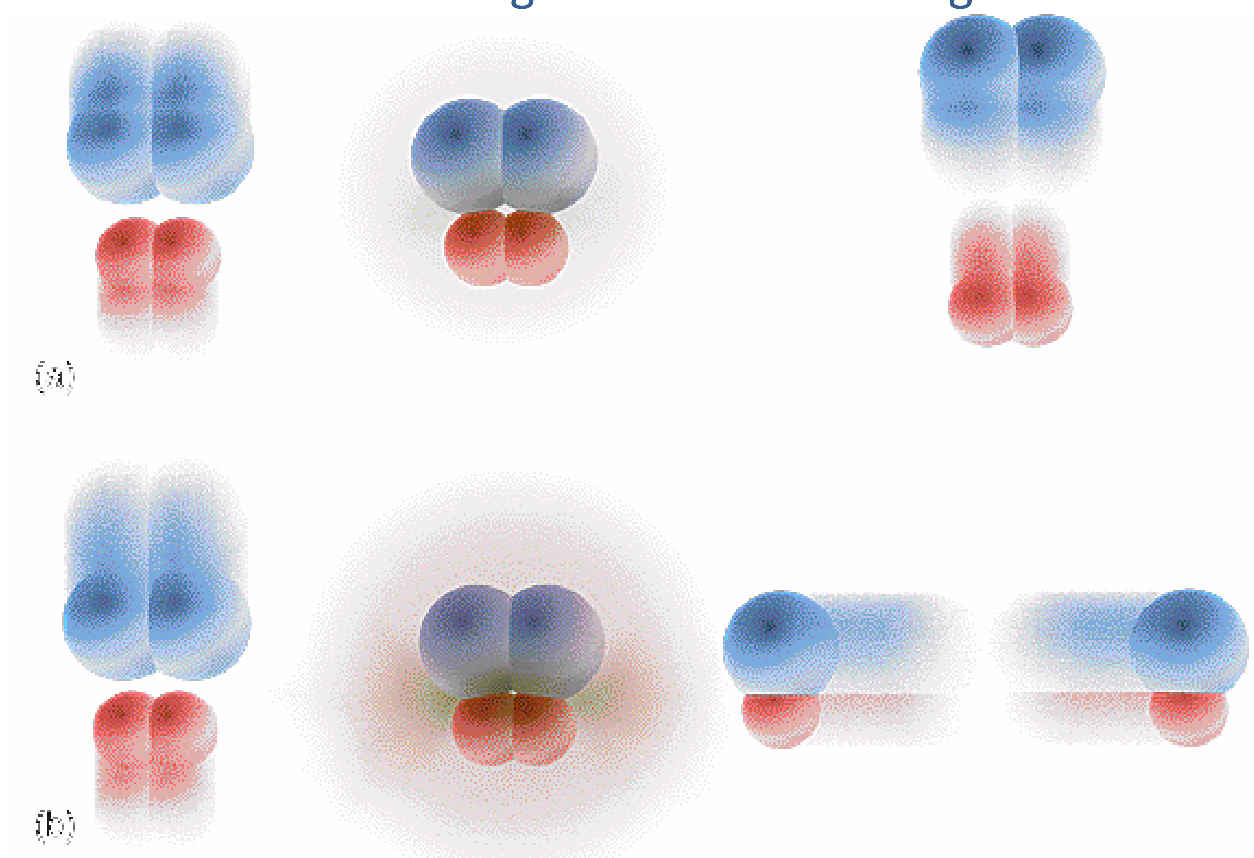
Propellants

- Decomposition occurs in the boiling and vapor region
  - The energy in that area is enough to break the bonds of molecules
  - The bonds break because of motion or kinetic energy of the atoms within the molecules



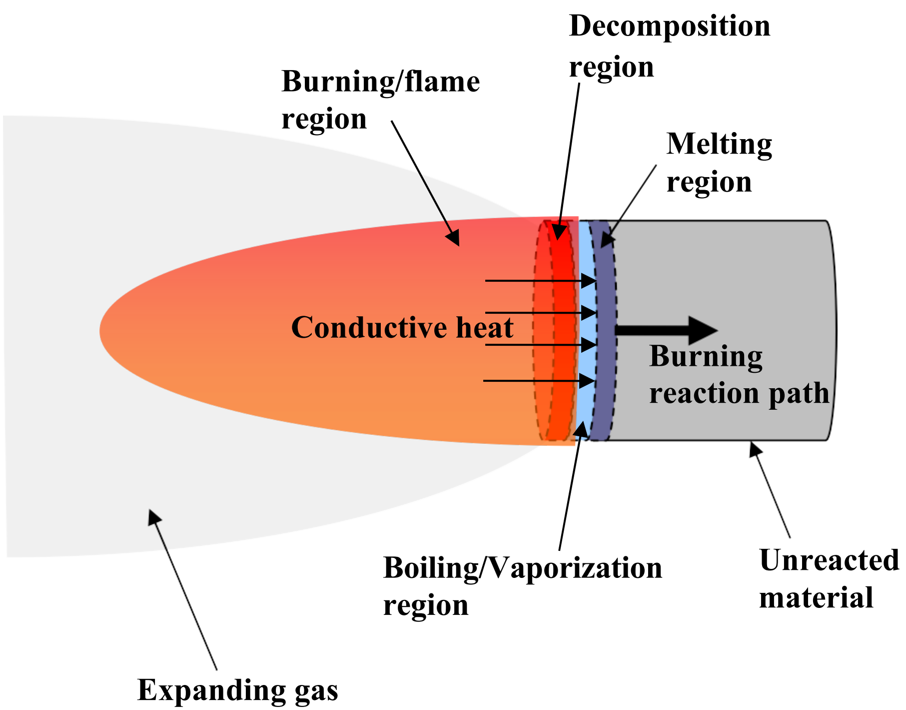
Chemical Kinetics

- Example of bonds not breaking and bonds breaking



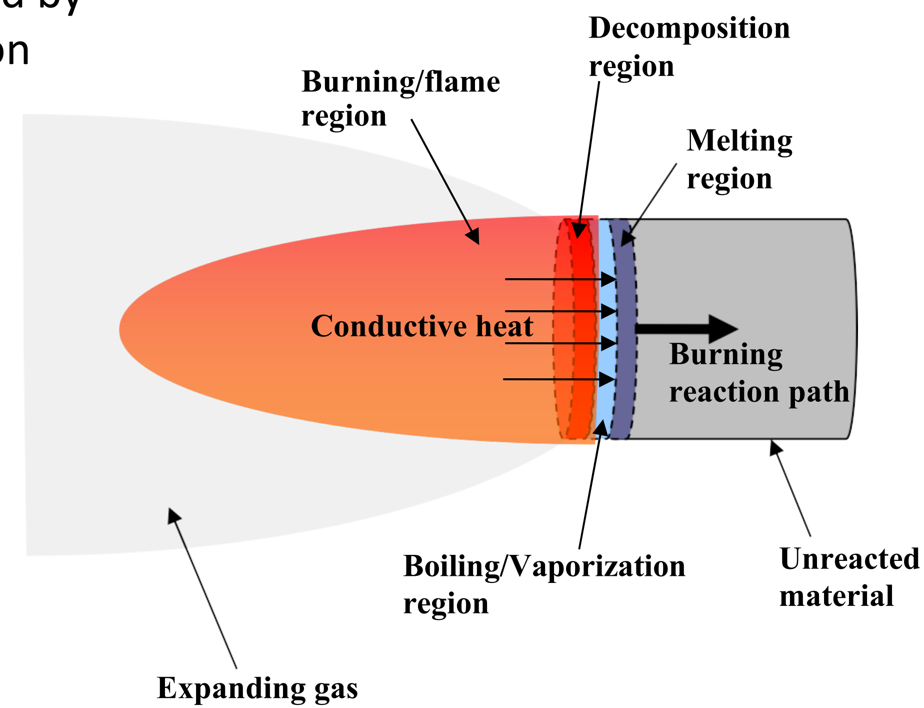
Initiation

- **Convection**
  - Hot gases penetrate the solid composition along spaces between grains (fire path)
  - Factors maximizing convective feedback
    - Uncompact composition
    - Granulated composition
    - Cracks in composition
    - Damaged composition



Initiation

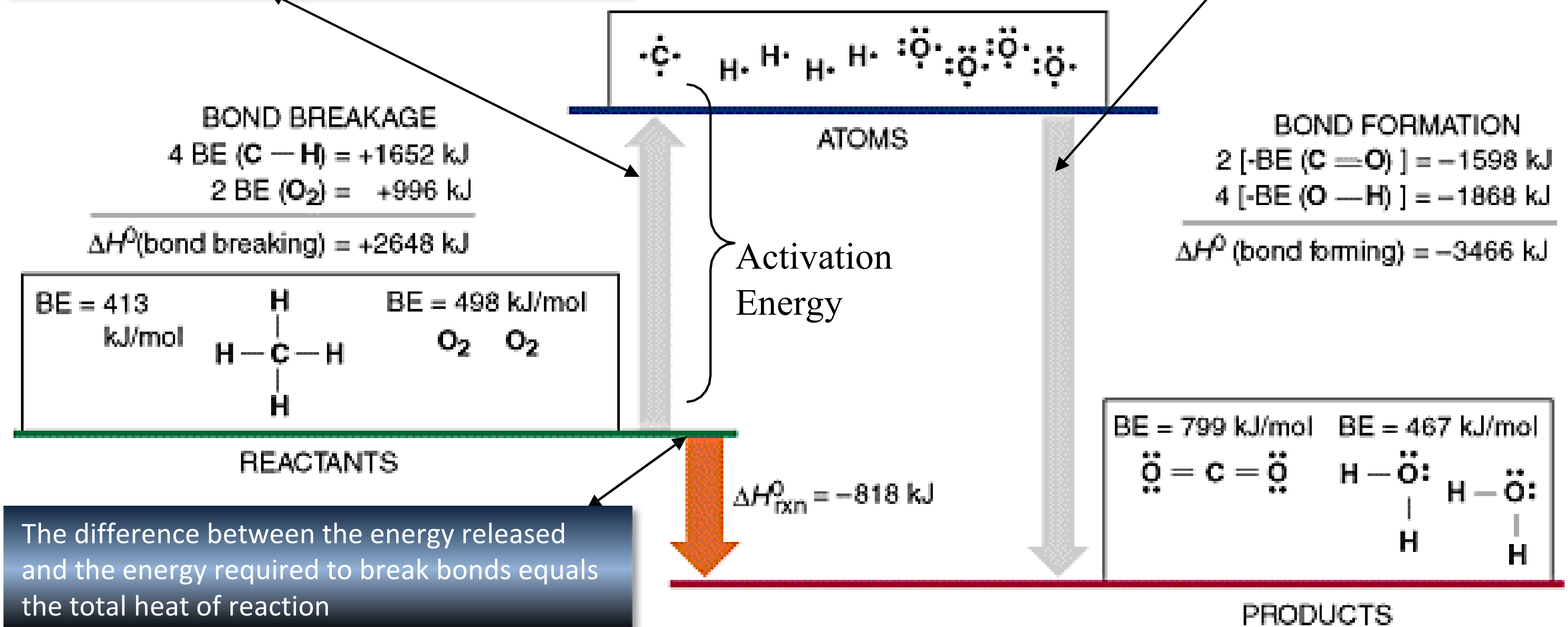
- **Radiation**
  - Thermal (infrared) radiation, emitted from flame and glowing particles, is absorbed by incompletely reacted composition
  - Factors favoring radiative feedback
    - Solid or liquid particles in flame
    - Dark or black composition



Chemical Reaction

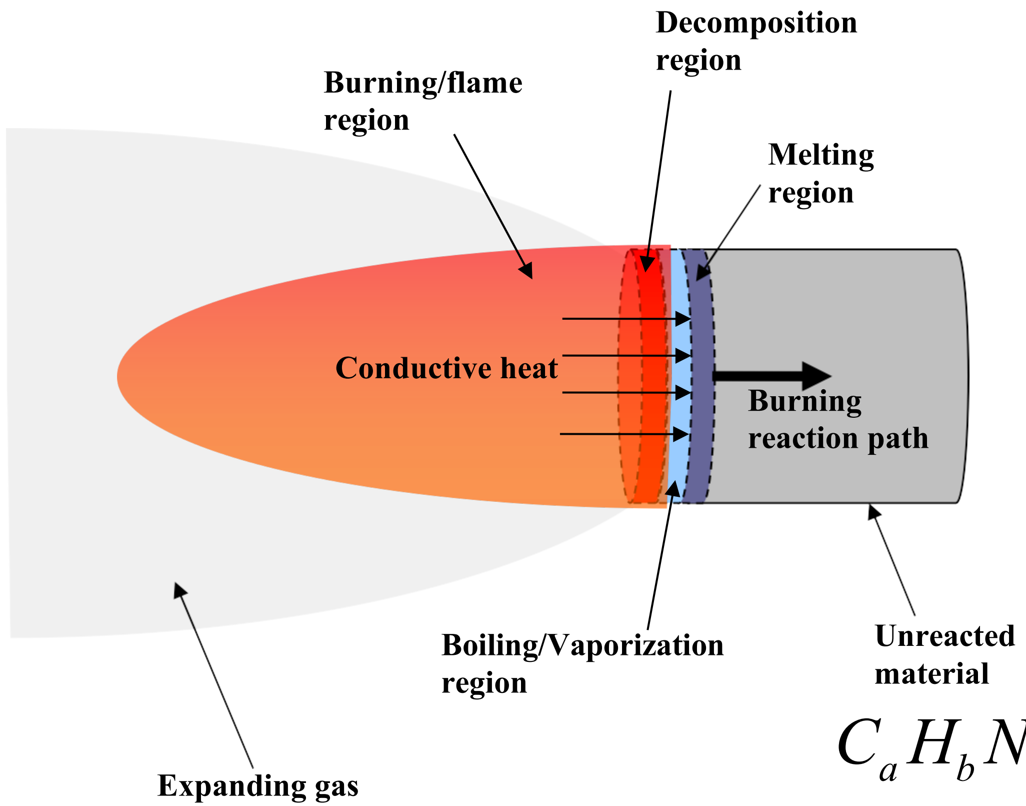
- Energy imparted into the material
- Each material will have a characteristic energy required to break bonds

Energy released when new bonds are formed to produce more stable molecules



The difference between the energy released and the energy required to break bonds equals the total heat of reaction

Propellants

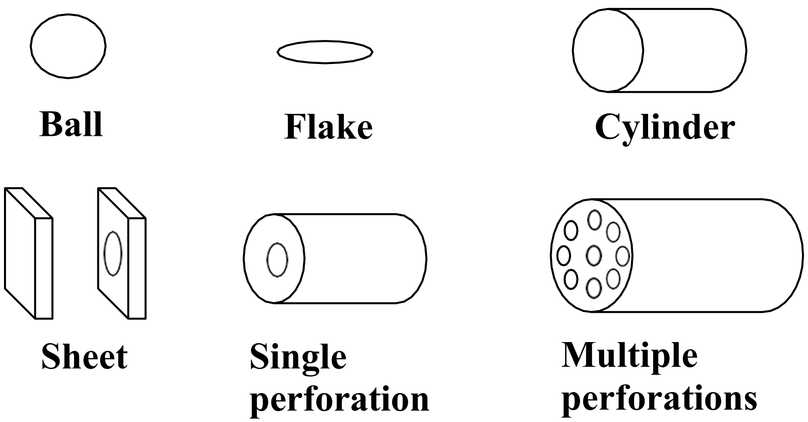


$$C_aH_bN_cO_d$$

$$n_1CO_2 + n_2H_2O + n_3N_2 + n_4CO + n_5H_2$$

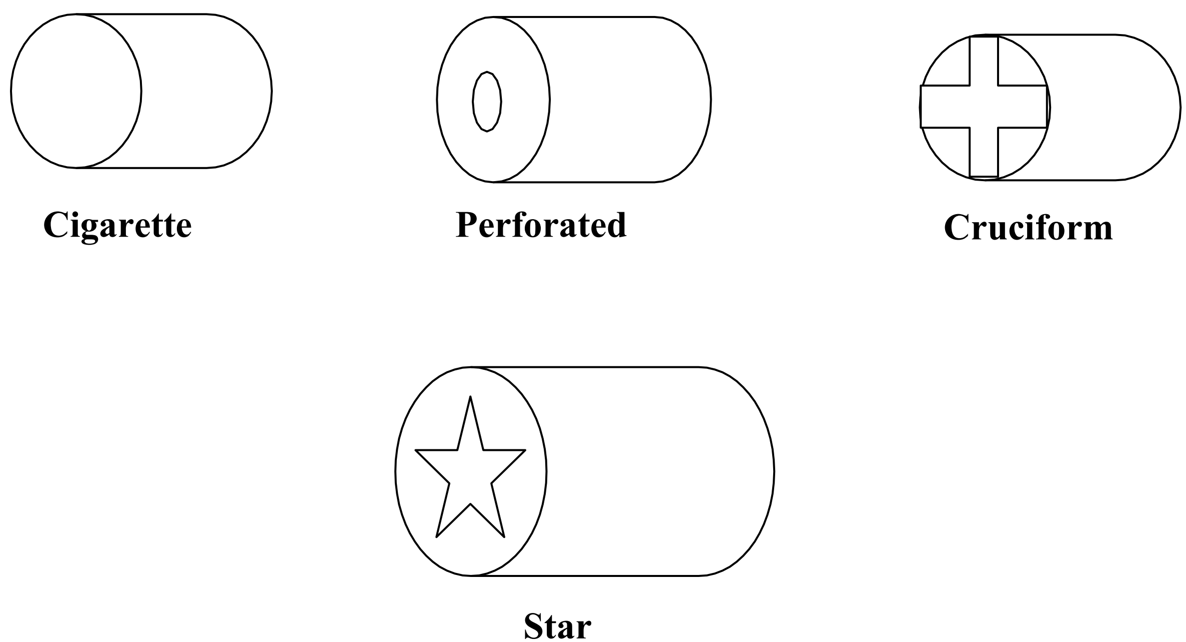
Propellants

- The profile of the burn is very dependent upon the geometry of the grain
- Some common types of grain for guns
  - Ball
  - Flake
  - Cylinder
  - Single perforation
  - Multiple perforation
  - Sheet



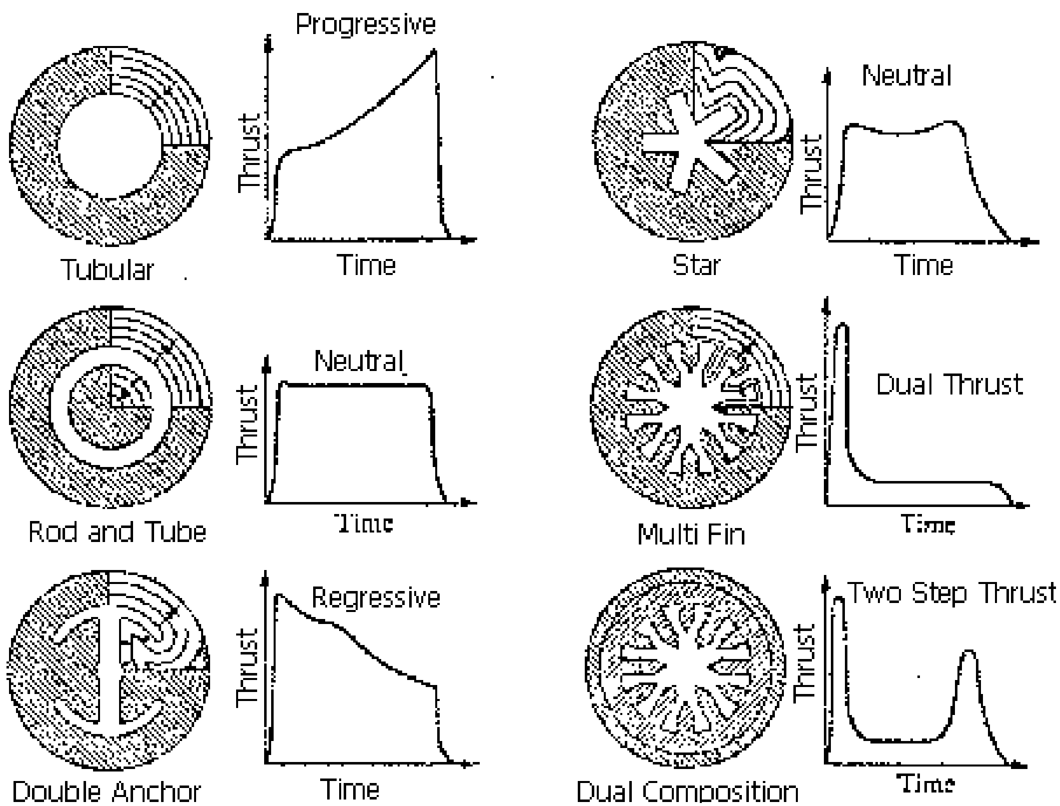
Propellants

- Some common types of grains for rockets
  - Cigarette
  - Perforated
  - Cruciform
  - Star



Propellants

- Typical thrust profiles

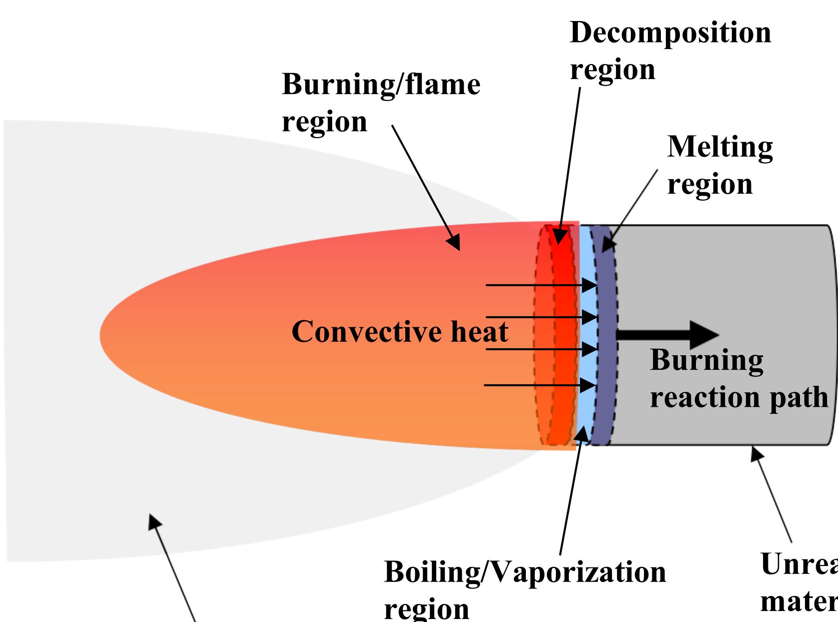


Gun Propellants Grain Performance

- The burn rate of propellants follows the pressure exponent law
  - $r = aP^n$
    - r is the burn rate in in/s or mm/s
    - P is the pressure in psi or Mpa
    - n is a constant dependent upon the chemical composition of the propellant (it is dimensionless)
    - a is a constant dependent upon the initial chemical composition and the temperature of the propellant [(in/s)/(psi) or (mm/s)/(MPa)]
  - In Paul Cooper and Stanley Kurowski’s book, Introduction to the Technology of Explosives, on page 43, table 2.1, shows a list of some common gun propellants along with the above constants “a” and “n”
    - Based on these values, one may adjust the pressure to see how the burn rate increases

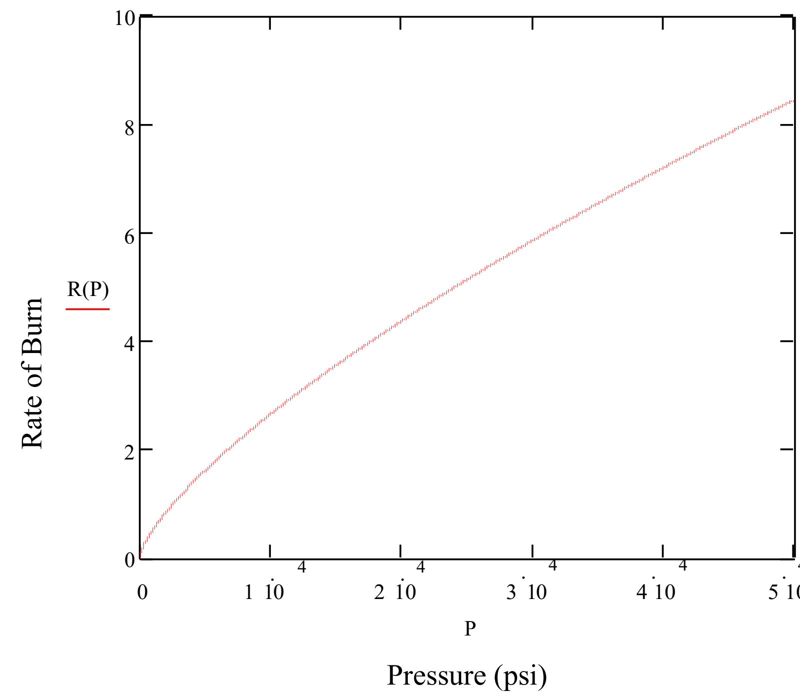
Gun Propellants Grain Performance

- From Cooper's book, Red Dot propellant constants are
  - a= 0.00350 and n = 0.720



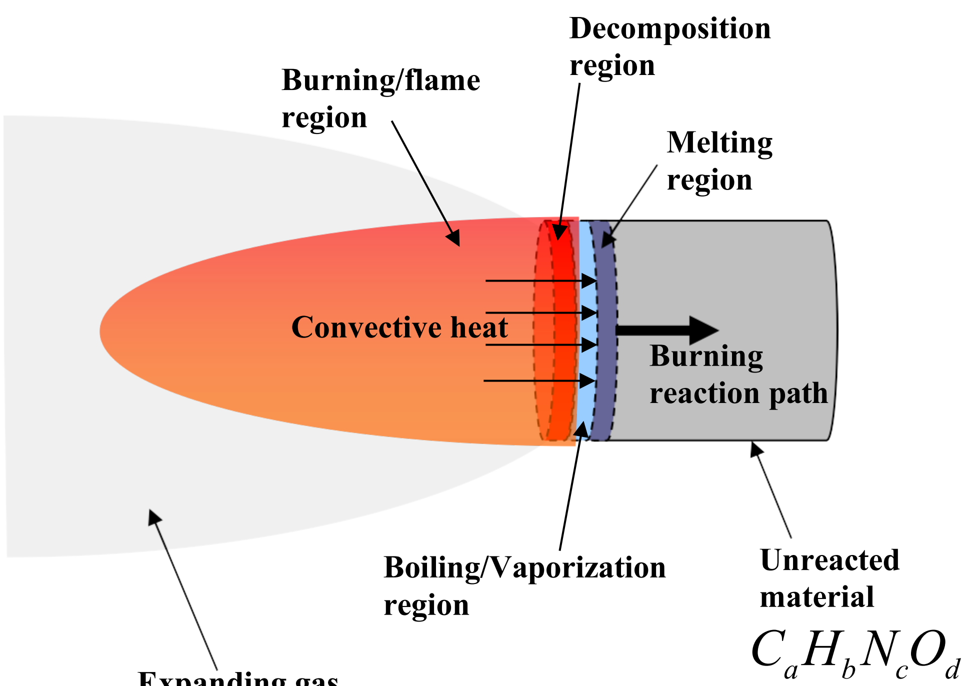
$$C_aH_bN_cO_d$$

$$n_1CO_2 + n_2H_2O + n_3N_2 + n_4CO + n_5H_2$$

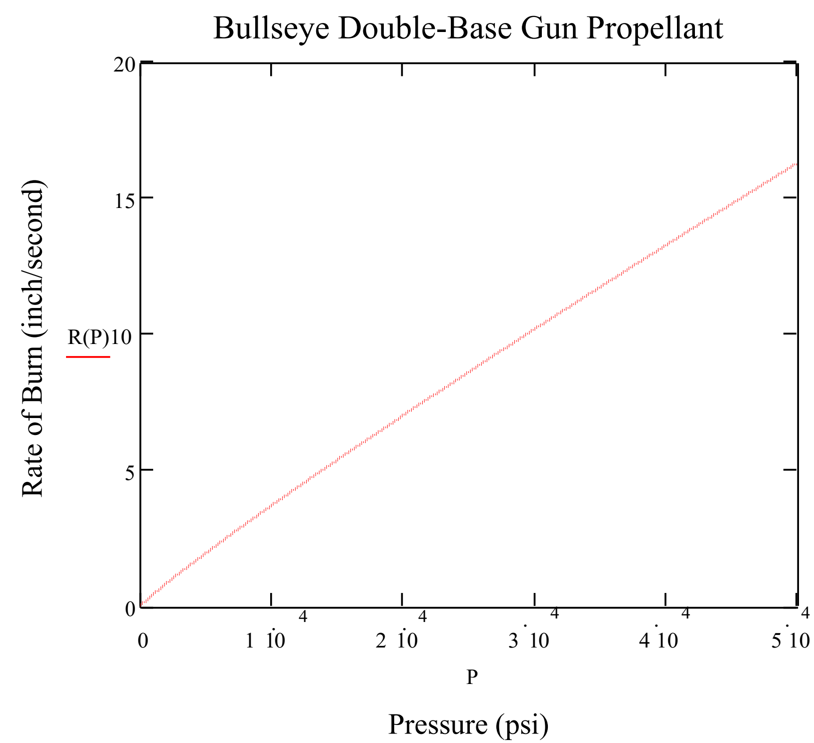


Gun Propellants Grain Performance

- From Cooper's book, Bullseye propellant constants are
  - a= 0.000775 and n = 0.920



$$n_1 CO_2 + n_2 H_2O + n_3 N_2 + n_4 CO + n_5 H_2$$



Interior Ballistics

- By knowing the reaction temperature, one may the use equation below to find the specific energy or force constant of the propellant (used in ballistics)
  - The maximum amount of work done by the unit mass of propellant
  - The force exerted on the projectile

$$f = PV = nRT_a$$

- f = specific energy (Joule/gram)
- P = pressure
- V = volume of system
- n = mols/gram
- R = universal gas content (3.314 Joule/mol – Kelvin)
- T_a = adiabatic flame temperature (Kelvin)

Interior Ballistics

- By dividing the force constant equation by the total volume ($V = A_i \cdot l_b$) that the gaseous products will occupy then multiply by the total weight of the propellant charge, one may find the average pressure

$$P_{avg} = \frac{nRT_a}{V} M_p$$

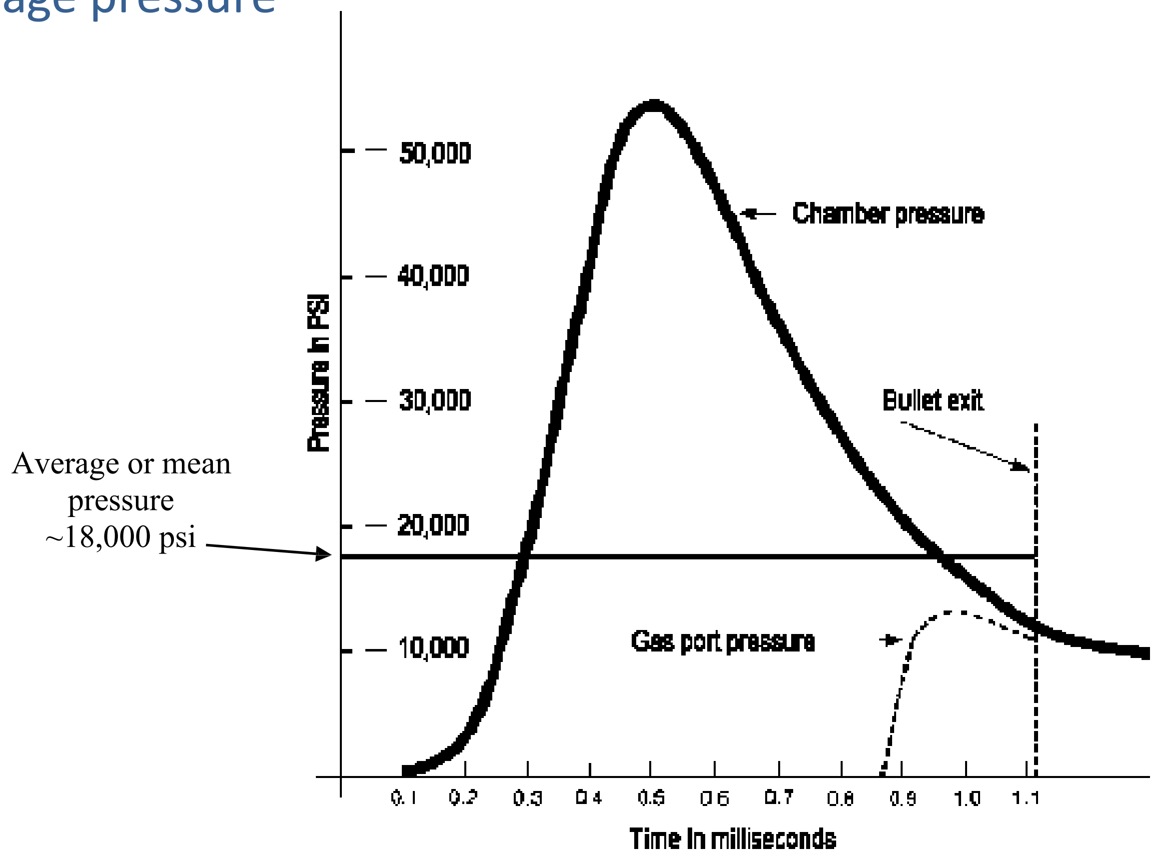
- Based on the average pressure the approximate velocity of the bullet or projectile exiting the end of the barrel is

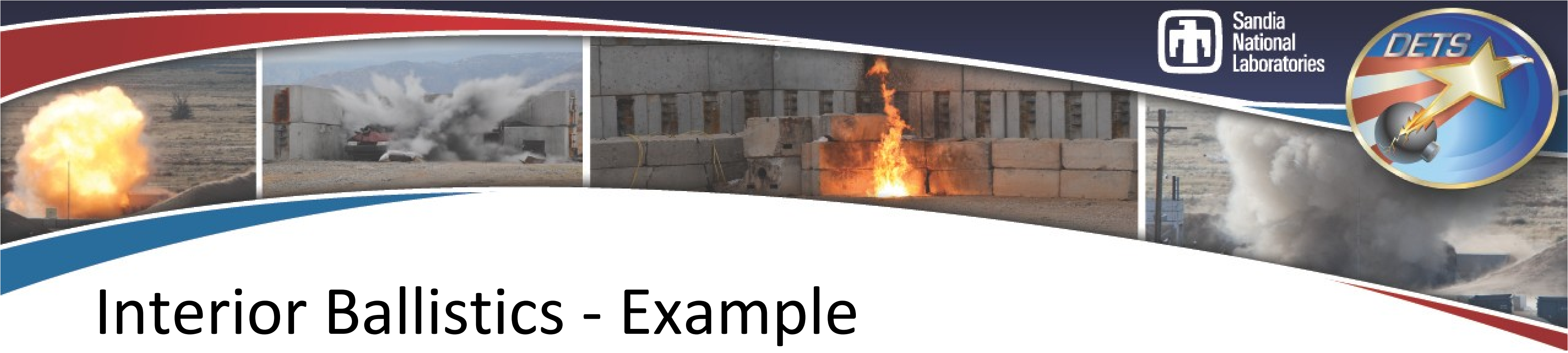
$$V_{be} = \sqrt{\frac{2 \times \left(P_{avg}\right) L_b A_{bi}}{M_p}}$$

  - V_{be} = velocity of the bullet at the end of the barrel
  - P_{avg} = the average pressure
  - L_b = length of the barrel
  - A_{bi} = the cross-sectional area of the inside the barrel
  - M_p = the mass of the projectile

Interior Ballistics

- The average pressure





Interior Ballistics - Example

- Using red-dot propellant, where n = 0.037 mol/gram and T_a = 3200 Kelvin (from Cooper's book, mentioned earlier, page 54)

$$P_{avg} = \frac{nRT_a}{V} = \frac{(0.037\,mol/gm)(8.314\,J/mol \times K)(3200K)}{(0.192\,in^2)\,(30\,in)} \times 105\,grain = 10{,}366\,psi$$

- Using a 12 gauge shotgun shooting a slug, where
  - Diameter = 0.5 in
  - Length of the barrel is 30 in
  - Cross-sectional area is $\pi r^2 = 0.192\ in^2$
  - Mass of slug is 437.5 grain

$$V_{be} = \sqrt{\frac{2 \times (P_{avg}) L_b A_{bi}}{M_p}} = \sqrt{\frac{2 \times (10{,}366\,psi)(30\,in)(0.192\,in^2)}{437.5\ grain}} = 1616\frac{ft}{s}$$

- It takes 105 grains of red-dot propellant to produce a velocity of ~1600 ft/s

Gun Propellants Grain Performance

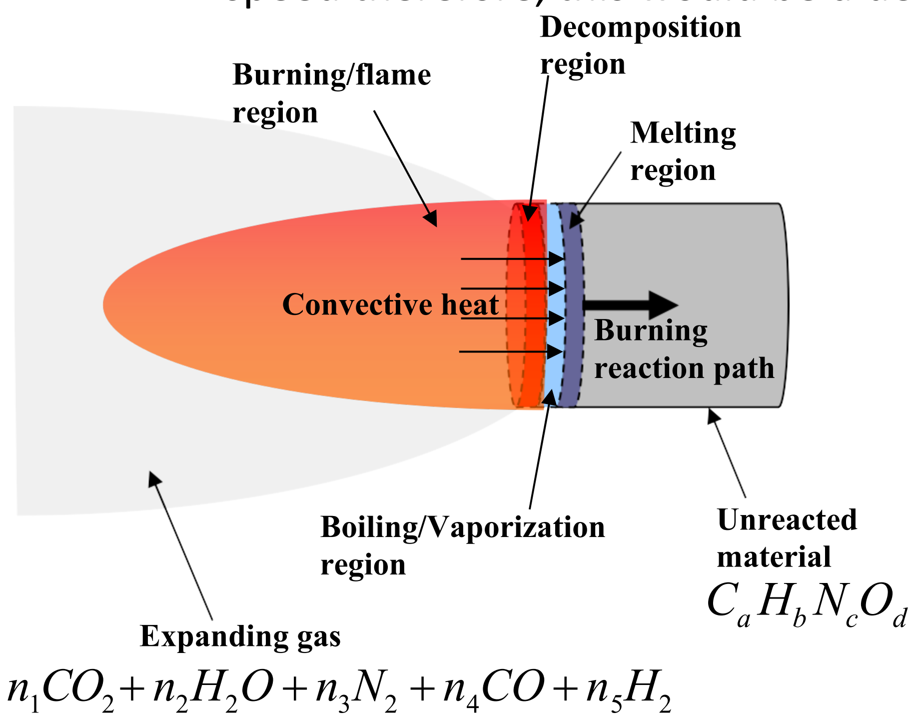
- $r = aP^n$
  - r is the burn rate in in/s or mm/s
  - P is the pressure in psi or MPa
  - n is a constant dependent upon the chemical composition of the propellant (it is dimensionless)
    - It describes the pressure dependency
      - n < 1 energetic material deflagrates
        - 0.7 – 0.9 or greater for gun propellants
        - 0.2 0.5 for DB rocket propellant
        - 0.1 – 0.4 for AP based composite rocket propellant
      - n > 1 energetic material detonates
  - a is a constant dependent upon the initial chemical composition and the **temperature** of the propellant [(in/s)/(psi) or (mm/s)/(MPa)]

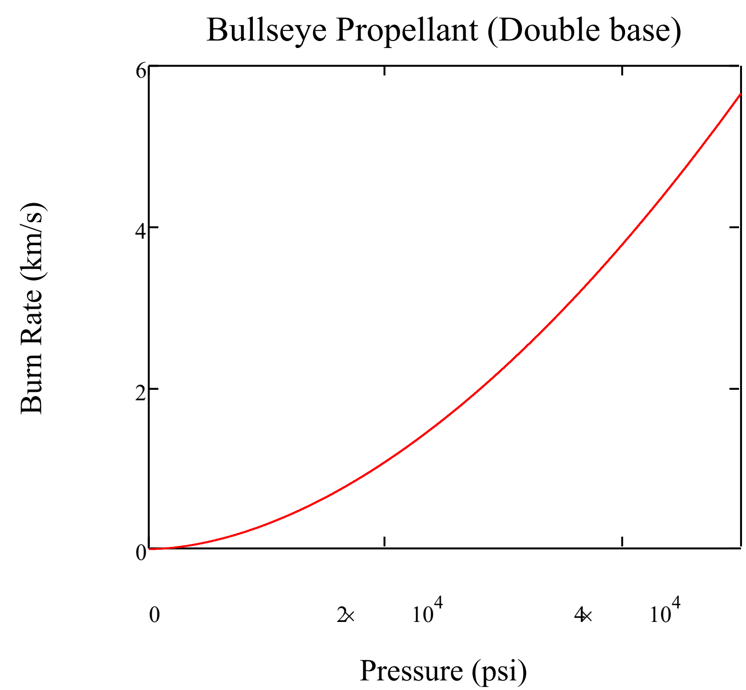
Gun Propellants Grain Performance

- The thermal energy generated by propellant combustion is distributed to various non-effective energies
- The energy losses of a caliber gun are approximately
  - Sensible heat of combustion gas - 42%
  - Kinetic energy of combustion gas - 3%
  - Heat loss to gun barrel and projectile - 20%
  - Mechanical losses - 3%
- The remaining part of the energy, 32 %, is used to accelerate the projectile.
- It is obvious that the major energy loss is the heat exhausted from the gun barrel.
- This is an unavoidable heat loss based on the thermodynamic law
  - the pressure in the gun barrel cannot decrease until the combustion gas is at the atmospheric temperature

Gun Propellants Grain Performance

- From Cooper's book, Bullseye propellant constants are
  - a= 0.000775 and n = 1.8
  - $2{\cdot}10^5$ in/s = 16,670 ft/s (5080 m/s) which is well above this materials sound speed therefore, this would be a detonation





Propellants

- Can Propellant detonate?

Propellants

- Can Propellant detonate?

Propellants

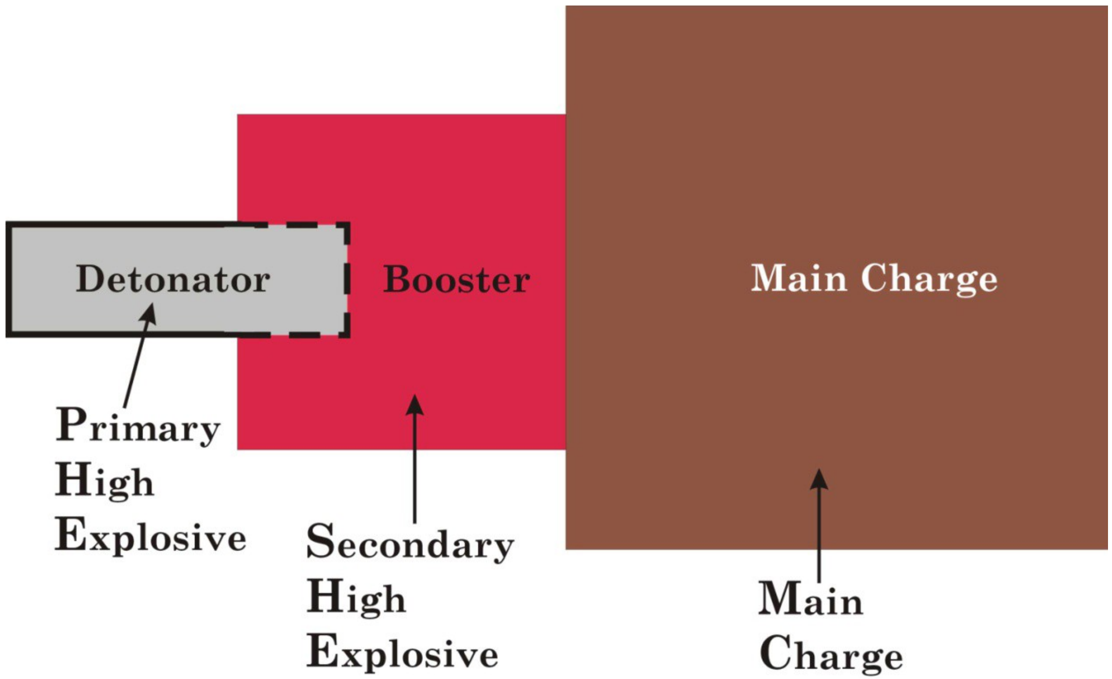
- Can Propellant detonate?

High Explosives

- Explosive materials upon initiation will produce a detonation
- A detonation is a chemical reaction that converts a solid or liquid explosive material into:
  - Large volume of stable product gases (CO, CO_2, H_2O, N_2, etc.) that expand at high velocities
    - Right at the explosive surface the expansion velocity can be approximately equal to ¾ of the detonation velocity to ~ the detonation velocity of the explosive
    - Expansion velocity decreases as the volume of the gaseous products increase
  - High temperatures
    - 3000 – 5000 degrees Fahrenheit
  - High pressures (millions of psi)
    - Blast wave (shock wave in air)
    - Shock wave inert material

High Explosives

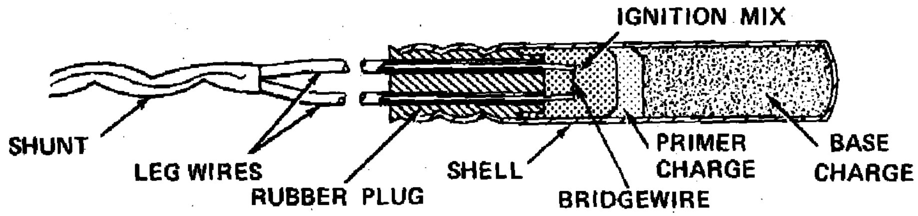
- Types of Sensitivity
  - Primary
  - Secondary
  - Tertiary



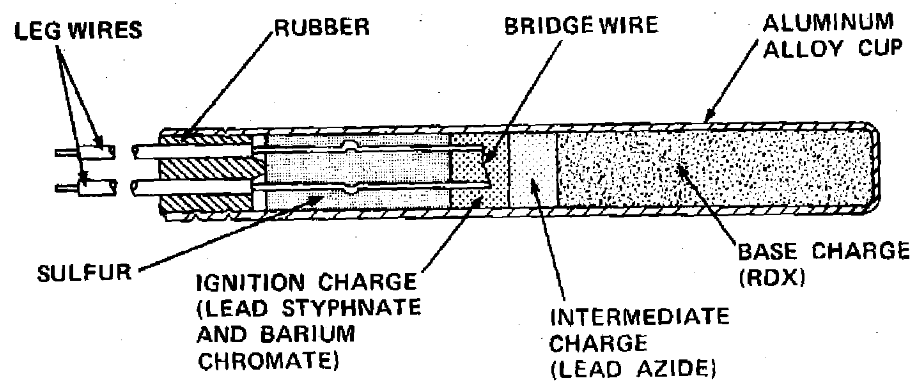
Three Step Explosive Train

High Explosives

- Primary
  - Extremely sensitive to shock, friction and heat
  - Usually used in detonators
  - Most primary explosives are inorganic
  - Some common primary explosives are
    - Mercury Fulminate
      - $HgC_2N_2O_2$
      - ΔH_{exp} = 1755 KJ/kg (J/g)
    - Lead Styphnate
      - $PbC_6H_3N_3O_9$
      - ΔH_{exp} = 1855 KJ/kg (J/g)
    - Lead Azide
      - PbN_6
      - ΔH_{exp} = 1610 KJ/kg (J/g)



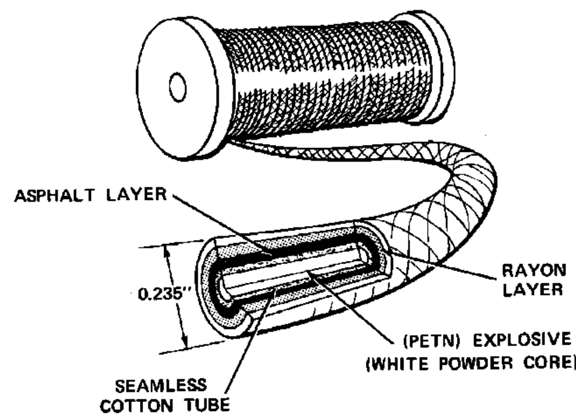
DUPONT NO. 6 COMMERCIAL ELECTRIC BLASTING CAP

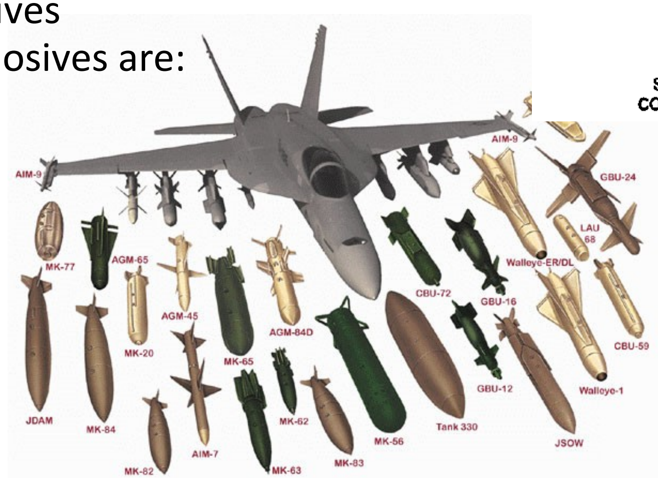


MILITARY CORPS OF ENGINEERS, SPECIAL NO. 8 ELECTRIC BLASTING CAP

High Explosives

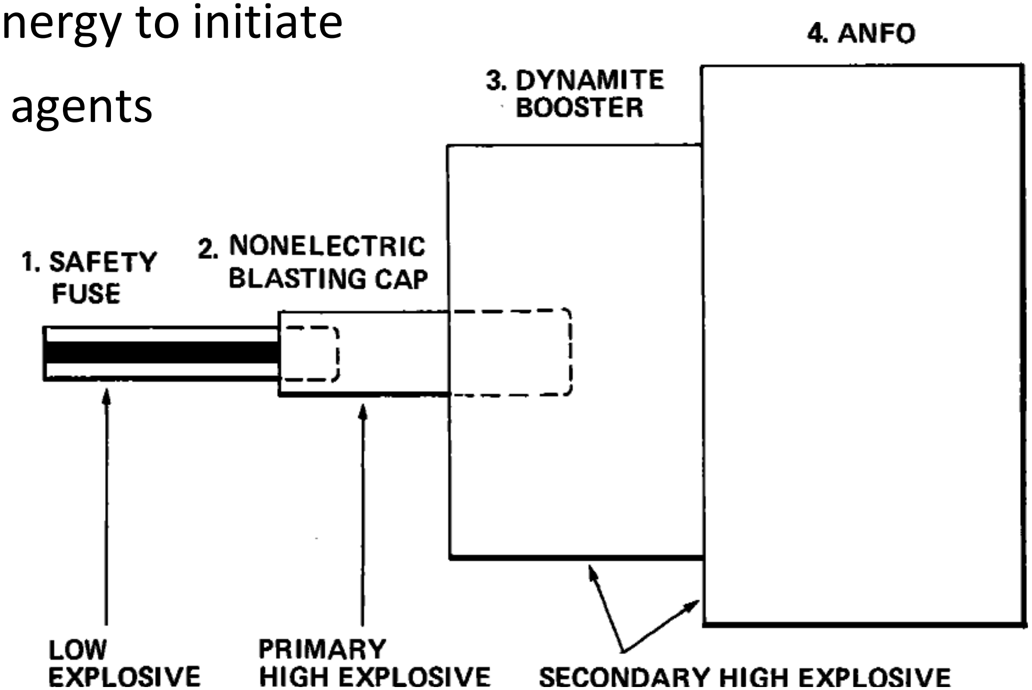
- Secondary
  - Relatively insensitive to shock, friction and heat
  - Tend to be more powerful than primary explosives
  - Needs a greater amount of energy to initiate than primary explosive
  - Usually the main payload in Military weapons or demolition explosives
  - Some common secondary explosives are:
    - TNT
      - $C_7H_5N_3O_6$
      - ΔH_{exp} = 4247 KJ/kg (J/g)
    - PETN
      - $C_5H_8N_4O_{12}$
      - ΔH_{exp} = 5794 KJ/kg (J/g)
    - RDX
      - $C_3H_6N_6O_6$
      - ΔH_{exp} = 5036 KJ/kg (J/g)
    - HMX
      - $C_4H_8N_8O_8$
      - ΔH_{exp} = 5010 KJ/kg (J/g)





High Explosives

- Tertiary
  - Very insensitive to shock, friction and heat
  - Need a large amount of energy to initiate
  - Mainly consist of blasting agents
    - ANFO
      - ΔH_{exp} = 3890 KJ/kg

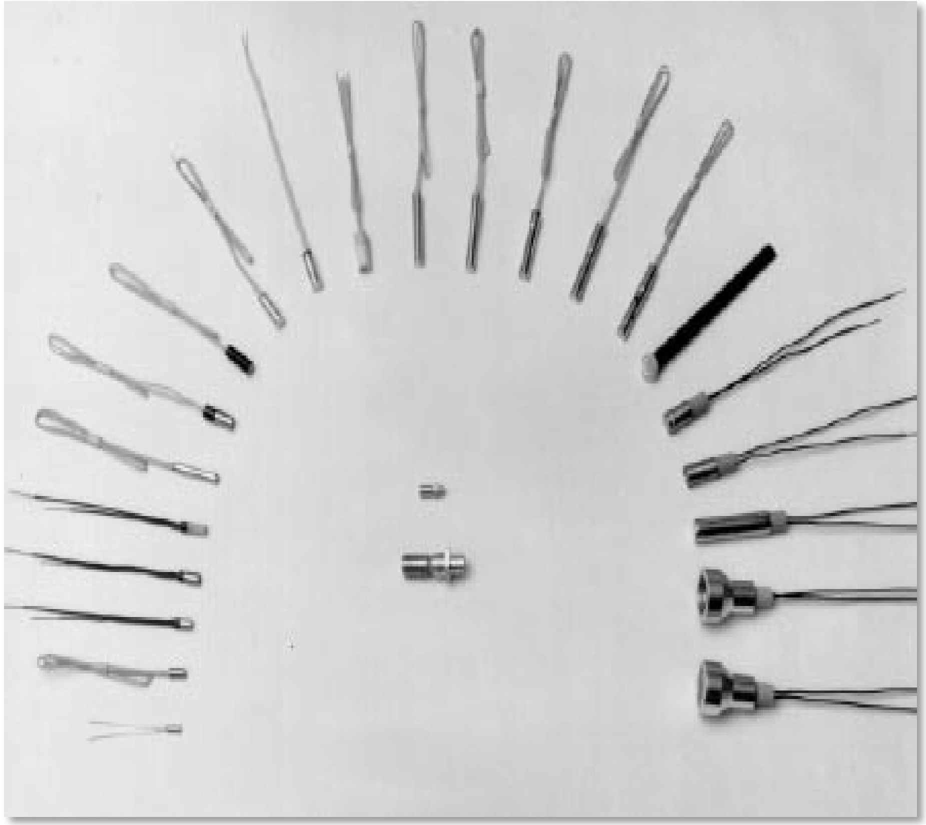


High Explosives

- Forms
  - Pressed
  - Plastic bonded
  - Cast
  - Putty
  - Rubber
  - Extrudable or paste
  - Slurry and emulsion
  - Binary
  - Blasting agents
  - Dynamites
  - Liquid
  - Metal additives

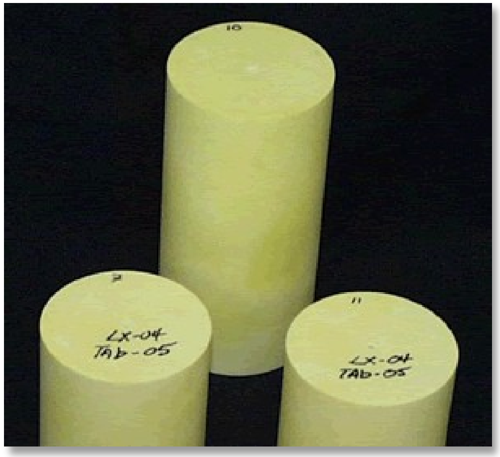
High Explosives

- Pressed
  - Process used to make pure explosive material into billets usually in canisters, cup or cartridges
  - Process usually used to make detonators



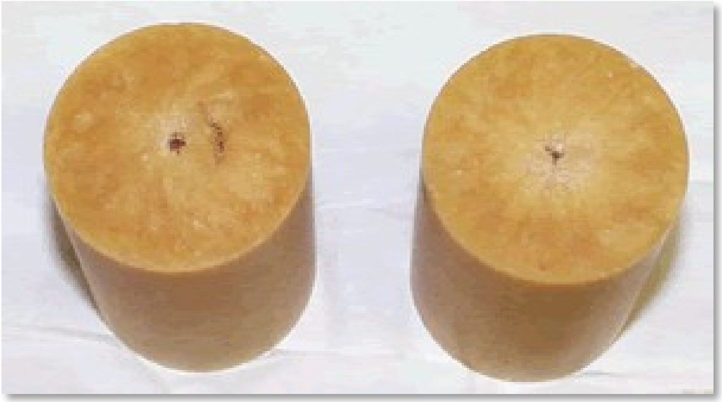
High Explosives

- Plastic bonded
  - Is a process where the pure explosive powder is coated with a plastic binder and then pressed obtaining ~97% of the theoretical densities
  - Possess good mechanical and machineable properties
  - Common process for DOE explosives



High Explosives

- Cast
  - A simple, economical, efficient and flexible process to produce large volumes of filled items
  - Usually a mixture of molten TNT with some other fine powder explosive
  - DoD uses in their ordnance and bulk demolition charges



High Explosives

- Putty
    - Process that mixes fine powdered RDX with plasticizers
    - The explosive has a moldable property like that of modeling clay
    - US produces Composition C4, UK produces PE-4, Portugal produces PE-4A, Czech produces Semtex, etc.

1A (PETN)

1H (RDX/PETN)

10 (PETN)

High Explosives

- Rubber
  - Process that mixes fine powdered RDX or PETN with rubber-type polymers and plasticizers to produce rubber mat like, varying thickness, sheet
  - Durable, easy to handle, and easy to cut into desired shape
  - DoD uses for demolition
  - Private sector uses it for explosive
    welding and explosive forming of metal components
- Extrude-able or paste
  - Viscous materials made from PETN, silicone rubber and curing agent
  - Capable of pumping (with low pressure) material into holes, molds, channels or crevices (similar to caulking)
  - Once cured, material forms a hard rubber

High Explosives

- Slurry and emulsion
  - Solution mixture of AN, water, fuel and sensitizer
    - Fuels: Aluminum, glycols, alcohols, etc.
    - Oxidizer: AN
    - Sensitizers: PETN powder, TNT powder, glass micro-balloons, etc.
  - Mainly used in the mining industry
- Binary
  - Consists of two materials which, by themselves are non-explosive but when combined form an explosive mixture
  - Mainly used commercially and in the mining industry

High Explosives

- Blasting Agents
  - Mixtures of a fuel and oxidizer which, in themselves are not explosive material
  - Usually consist of 94% AN with 6% fuel oil (number 2 diesel)
  - The most used explosive in the world
  - Mainly used by the mining industry
- Dynamites
  - Develop to desensitize nitroglycerine
  - Straight or "Ditching Dynamites"
    - Consists of nitroglycerine, absorbent material and depending on its application, some other material
  - Mining industry
    - Ammonia, gelatin and ammonia gelatin
      - Ammonium nitrate and nitroglycerine
      - The gelatin portion is actually nitrocellulose
  - Military dynamites
    - 75% RDX, 15% TNT, 5% SAE motor oil and 5% cornstarch

High Explosives

- Liquids
  - Nitromethane and nitroglycerine
  - Nitroglycerine is rarely used by itself because it is **very shock sensitive**
  - Nitromethane is usually used commercially as fuel for automobiles or as an additive in the mining industry

High Explosives

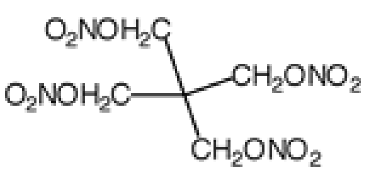
- Labeling of explosives
  - Names
    - Cyclotols RDX/TNT
    - Octols HMX/TNT
    - Torpex RDX/TNT/Al
  - The labs have the own type of labeling systems
    - LLNL usually is LX-##
    - LANL usually an X-##
  - Letter that follow
    - N = Navy (PBXN-5)
    - W = White Oak
    - C = China Lake
    - AF = Air Force
    - (Q) = following the number means qualified experimental explosives
    - (I) = interim qualified
  - Conventional numbering
    - 1-99 pressed
    - 100-199 cast
    - 200-299 extrude-able
    - 300-399 injection moldable

High Explosives

- Air Force numbering
  - AFX
    - 100 cast (RDX)
    - 200 cast (HMX)
    - 400 special mix
    - 500 special mix
    - 700 cast (RDX/Al)
    - 800 cast (HMX/Al)
    - 900 nitroquanidine
    - 1000 Foamed
    - 1100 TNT/Al
  - HMX is produced in two grades based on the maximum allowable amounts of RDX as an impurity
    - Grade B HMX – 2% RDX (only used in PBX’s)
    - Grade A HMX – 7% RDX

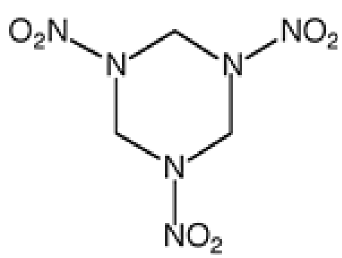
Initiation

- Characteristics
  - An explosive molecule is a metastable chemical species that reacts exothermically given the correct stimulus



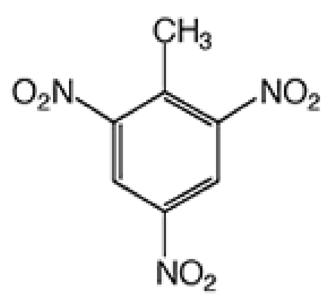
$C_5H_8N_4O_{12}$

PETN



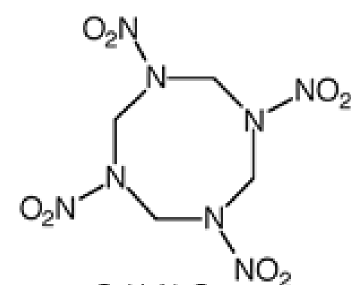
$C_3H_6N_6O_6$

RDX



$C_7H_5N_3O_6$

TNT



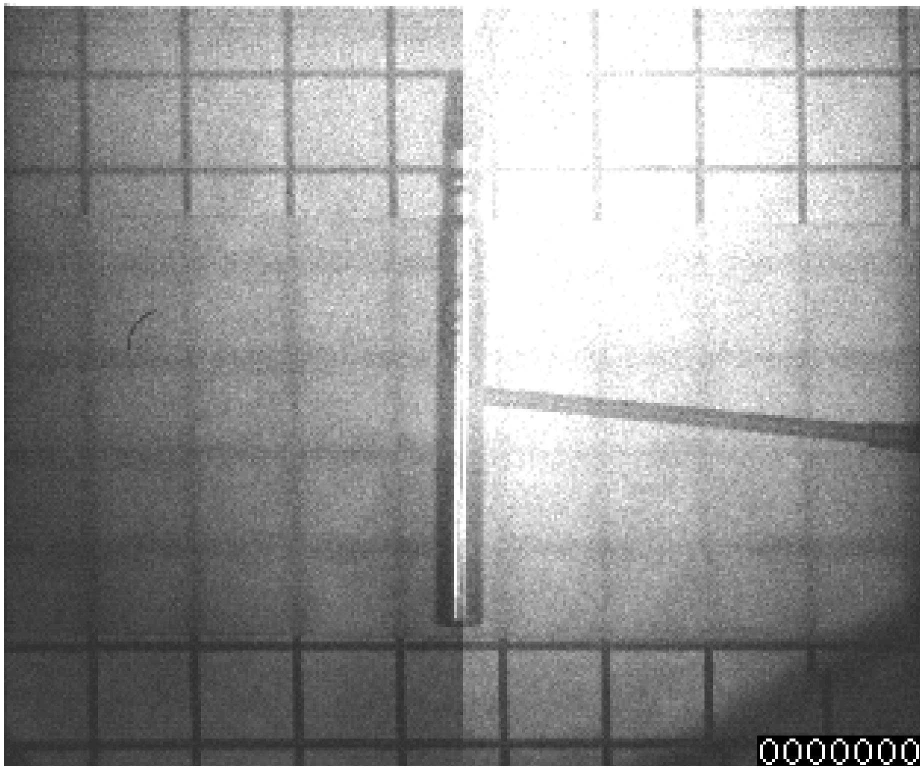
$C_4H_8N_8O_8$

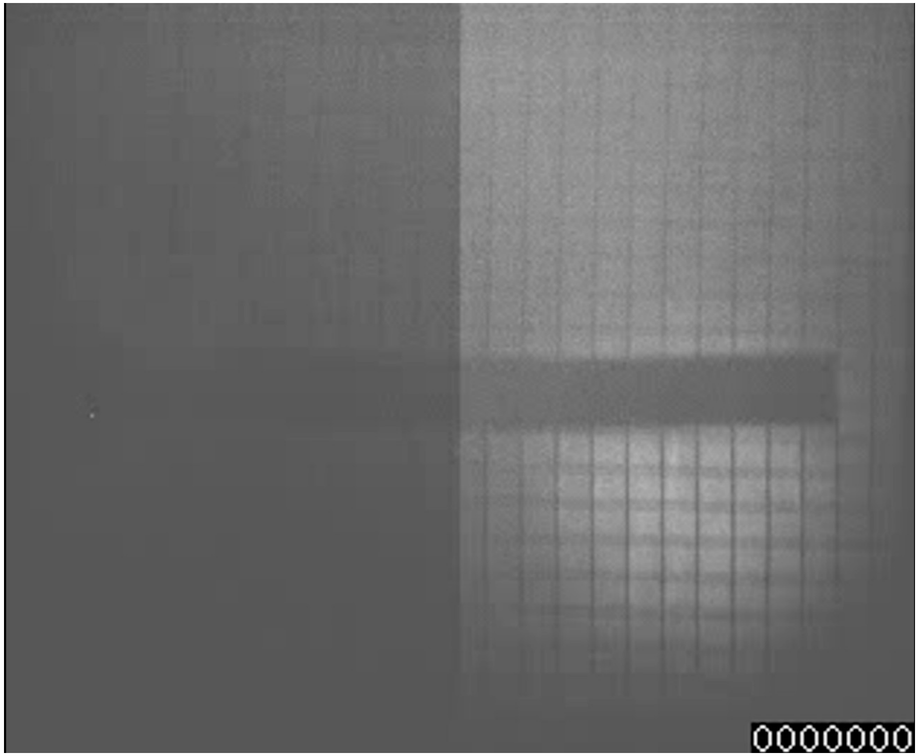
HMX

Initiation

- Imparting an explosive with a shockwave through either a chemical reaction or impact it a “Wake Up Call” or “Trigger” which compresses and heats the molecule
- Although unlikely, it is possible, given the right parameters for a detonation to occur from the other types of non-shock sources of imparted energy

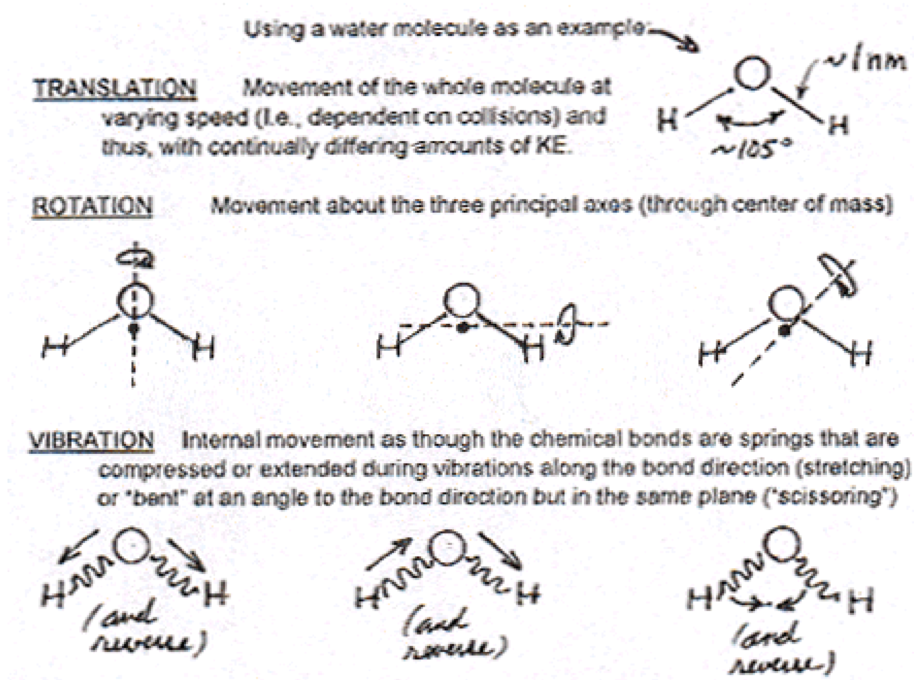
Initiation





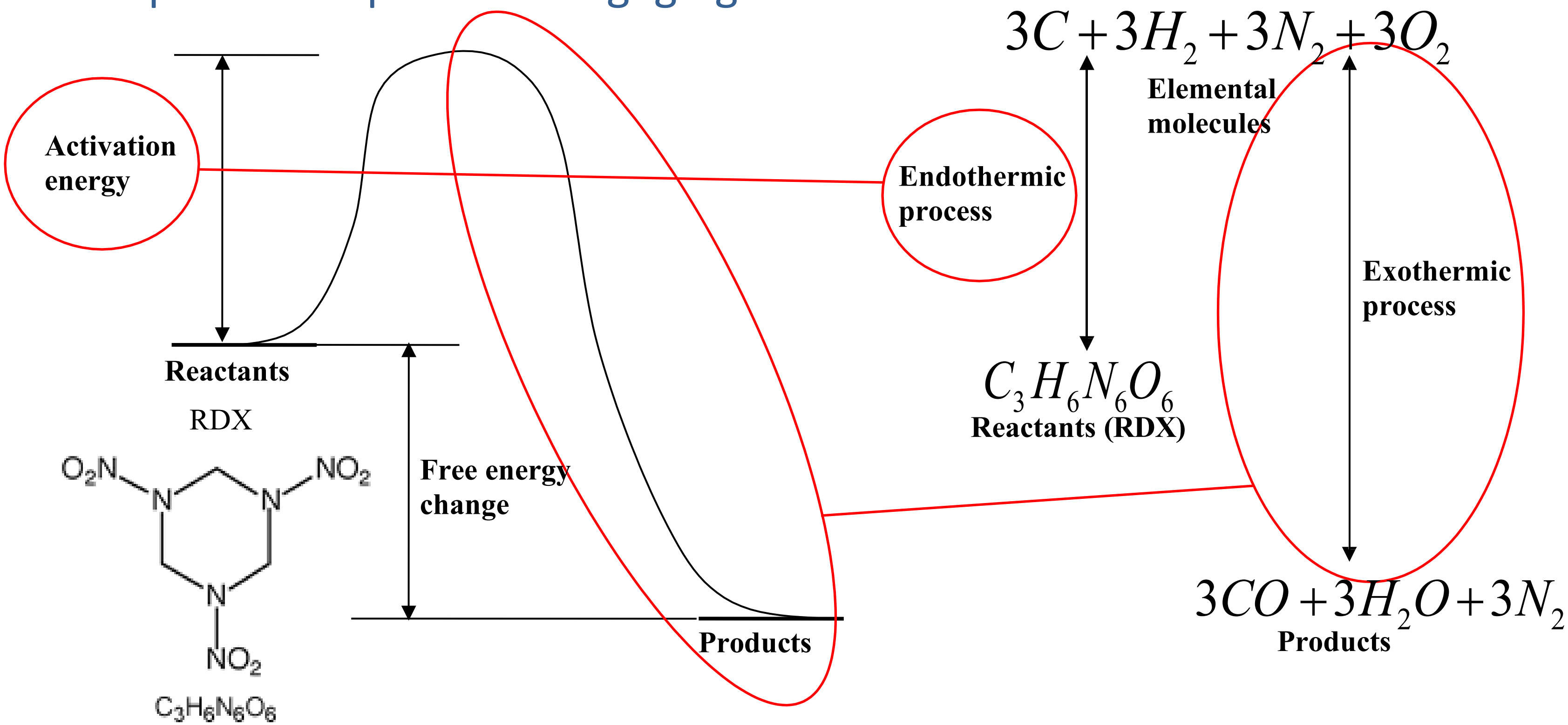
Initiation

- The energy deposited by the shockwave or other energy sources, activates the vibrational modes of the explosive molecule(s)
    - Transitional, rotational and/or vibrational motion
- The vibrational motion of atoms and/or molecules must be enough to break the bonds of the energetic material molecule
    - It is also possible to mechanically or physically break bonds



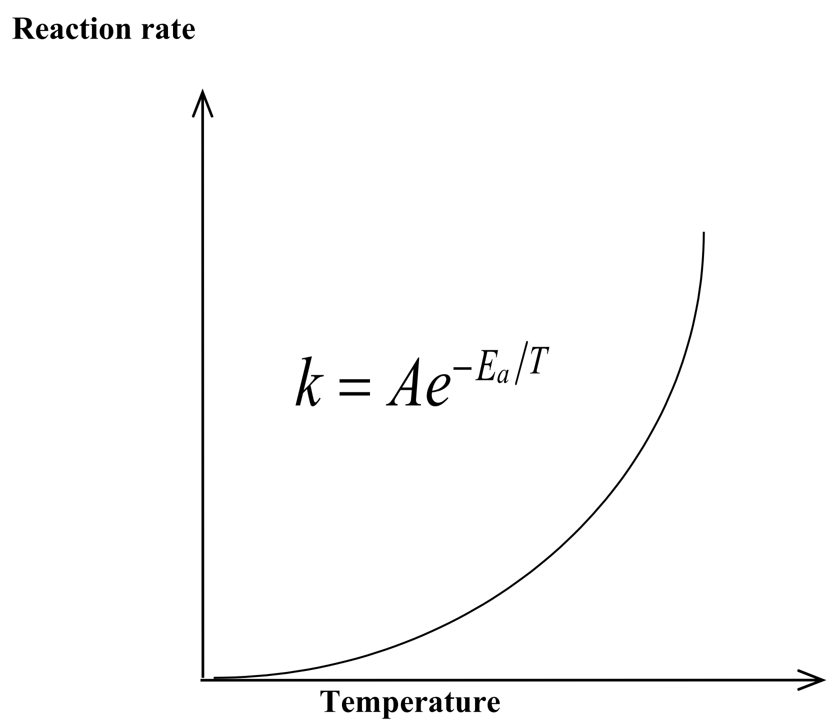
Initiation

- Local temperature increases through energy produced as the reactant decomposes into products engaging



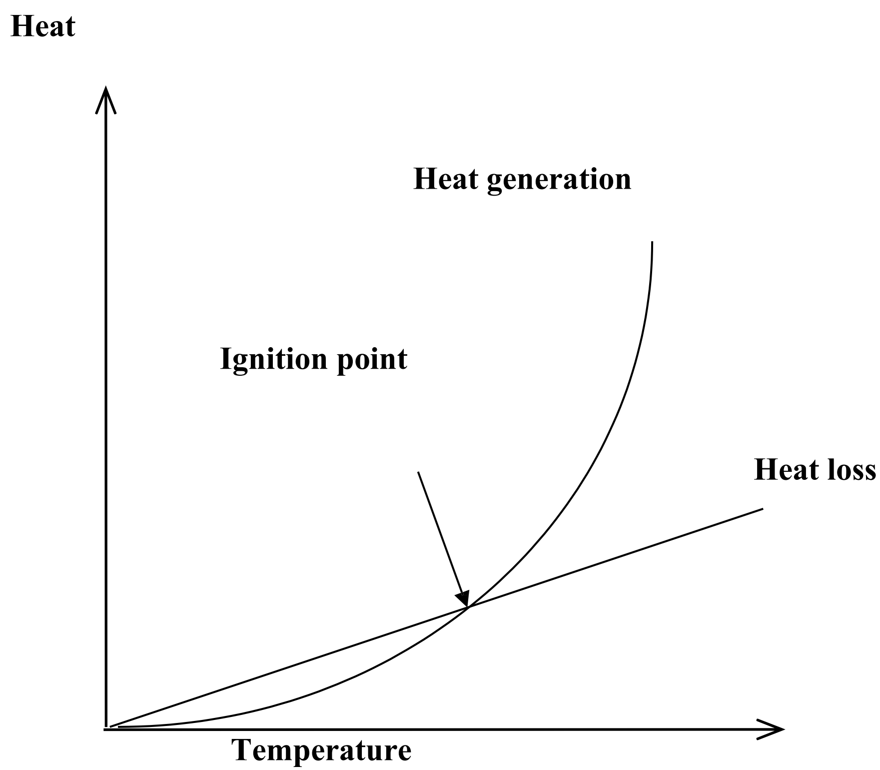
Rate of Reaction

- As the temperature increases, there is exponentially greater number of molecules that obtain the necessary activation energy



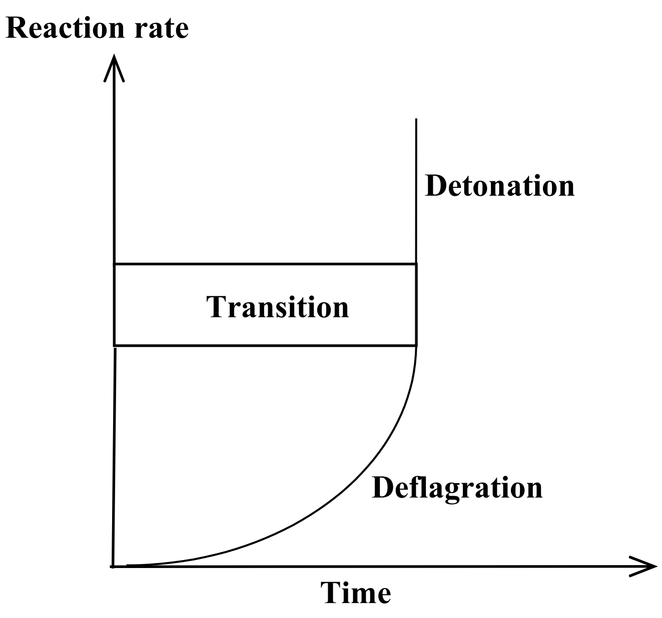
Ignition

- Self-sustaining ignition occurs when heat of generation equals heat loss



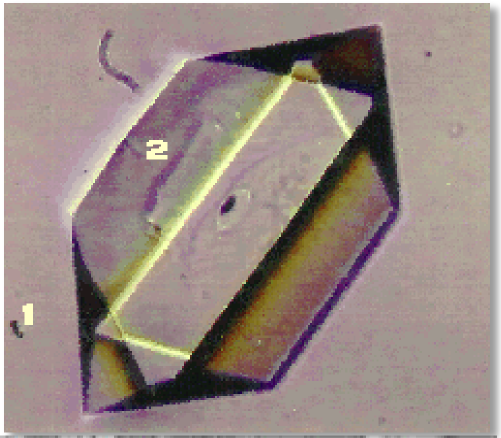
Transition to Detonation

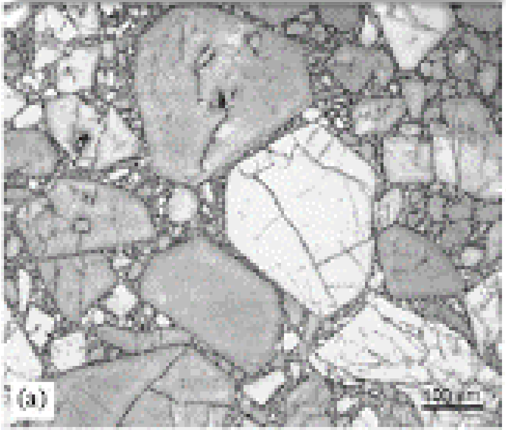
- The increase in temperature and rate of reaction also increases pressure
- If this trend continues, a shockwave (detonation wave) will develop ahead of the reaction zone producing a transition from deflagration to detonation (DDT)



Detonation

- The initiation process is different for homogeneous and heterogeneous explosive materials
  - Homogeneous explosive is an explosive with few or no defects or impurities
    - Pure crystal
    - Bubble free liquid
    - Cast TNT behave like a homogeneous material
  - Heterogeneous explosive is a composite material composed of explosive crystals surrounded by some type of binder
    - Imperfection occur at grain-grain and/or grain-binder interface

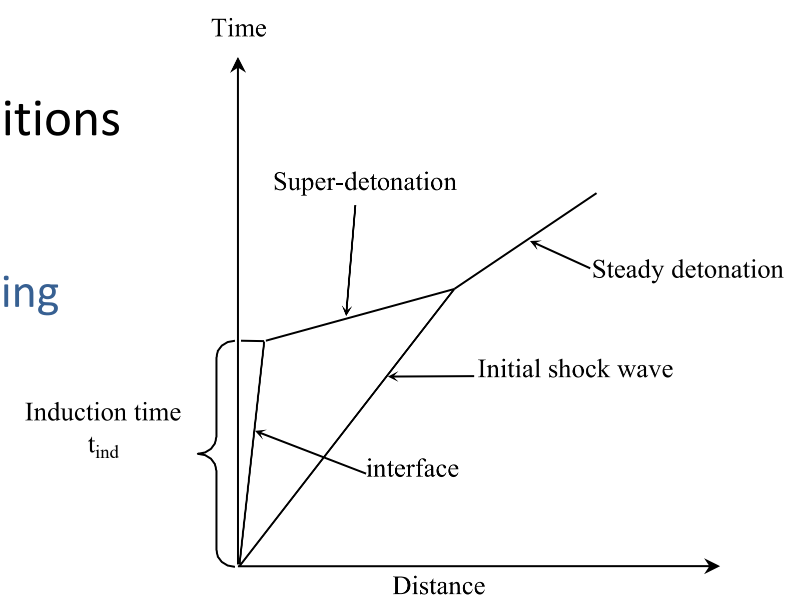




PBX 9501

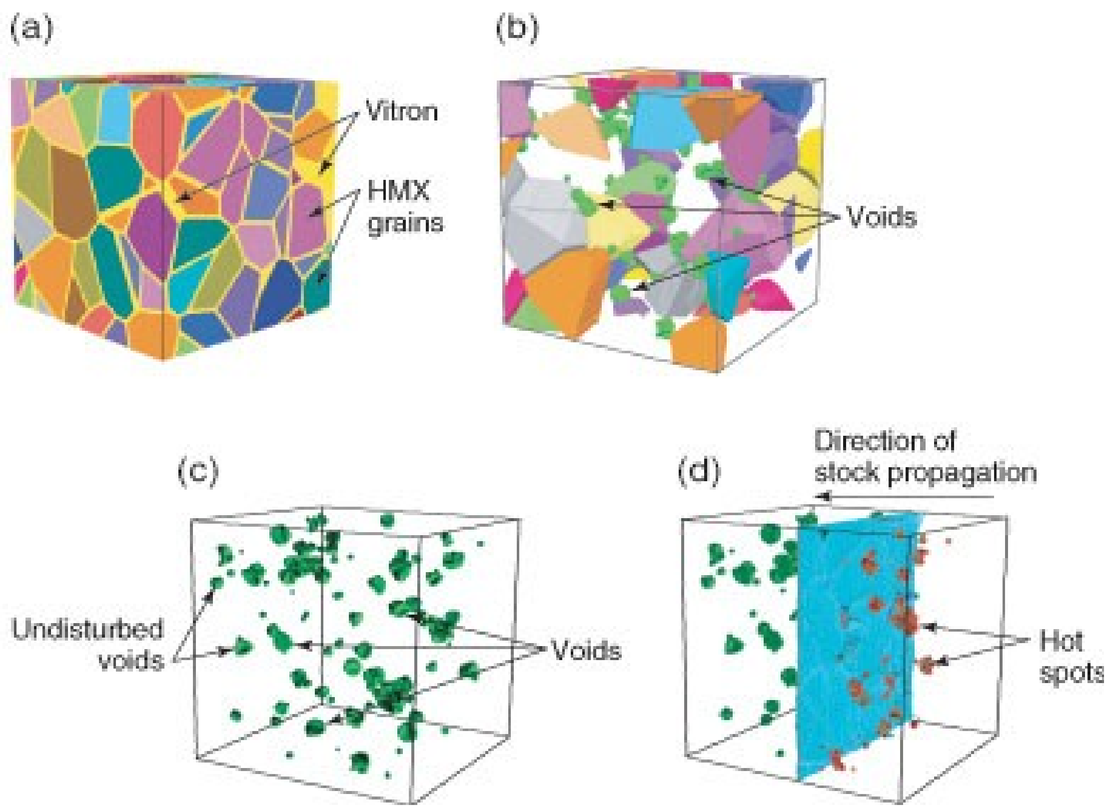
Detonation of Homogeneous

- Shock to detonation transition (SDT) for homogeneous explosives
  - Say flyer plate impacts a homogeneous explosive and generates a shock wave that travels into the material
  - The shock wave will heat up the material
  - The hottest area will occur near the explosive/impact interface producing a thermal explosion that quickly transitions into a detonation
    - This is the area where the material experiences a longer duration of heating

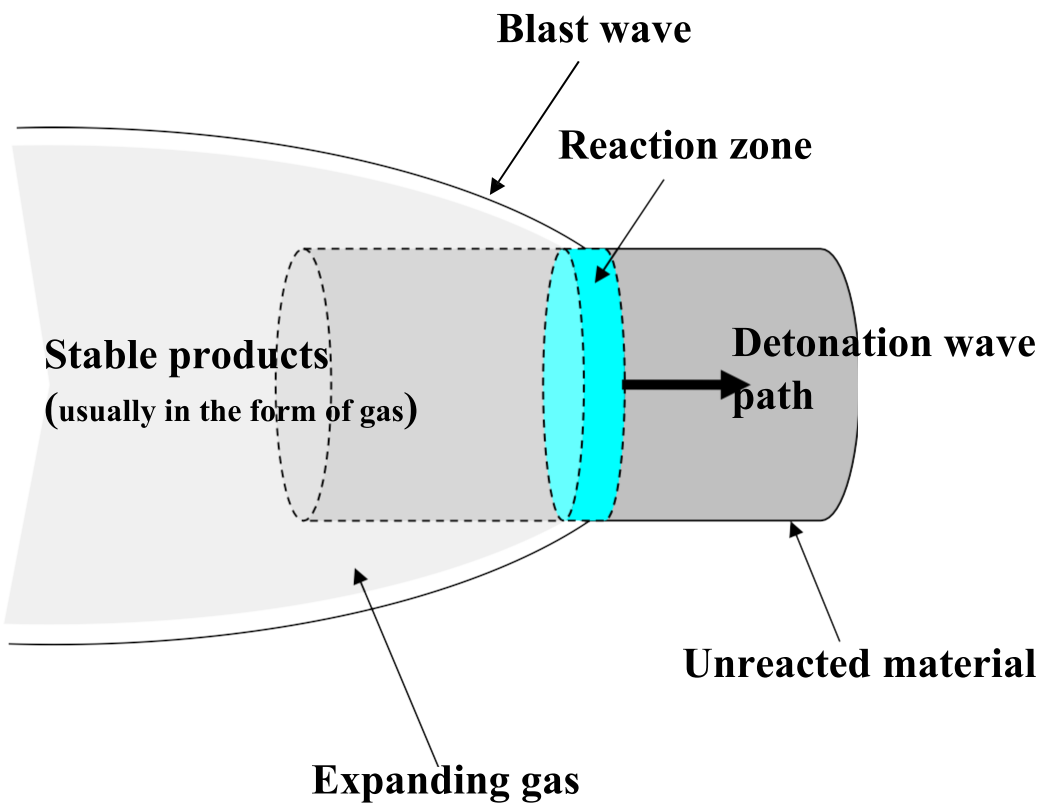


Detonation of Heterogeneous

- Shock to detonation transition (SDT) for heterogeneous

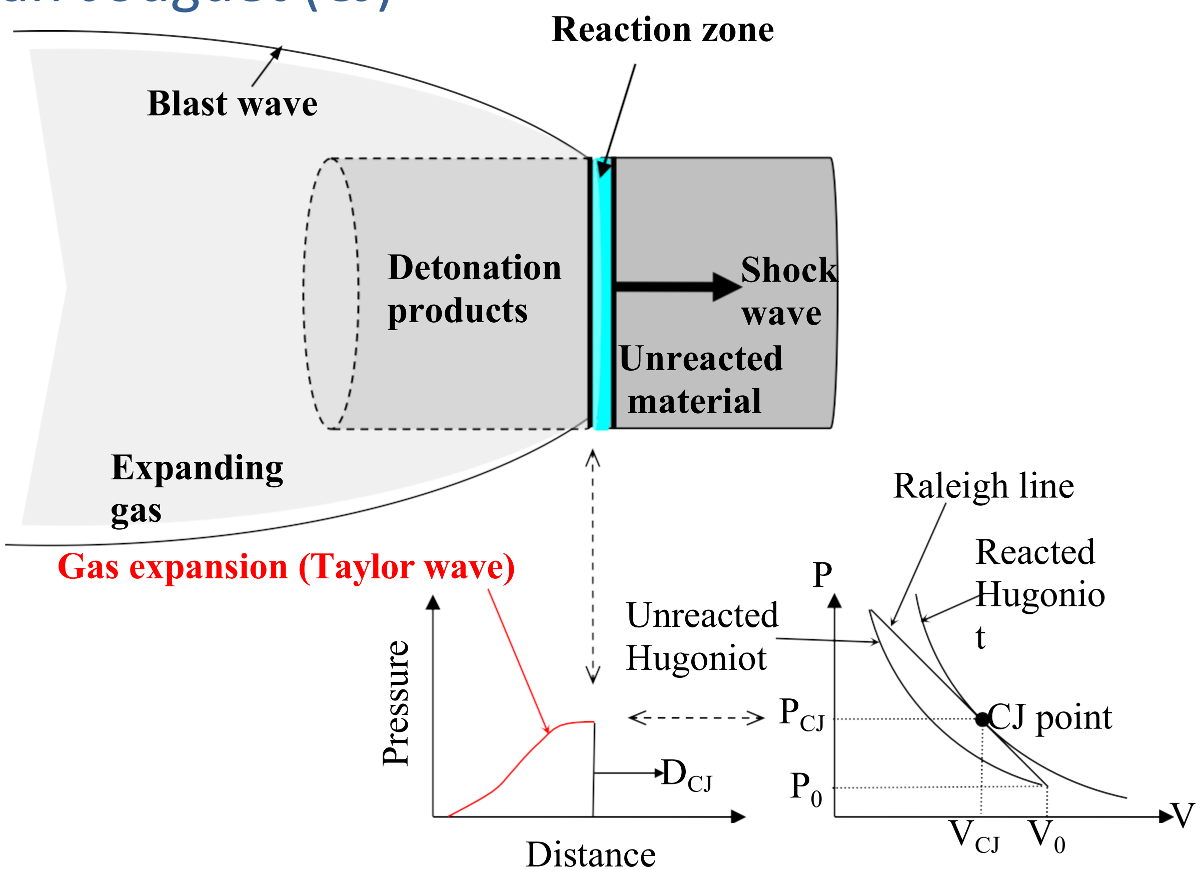


High Explosives



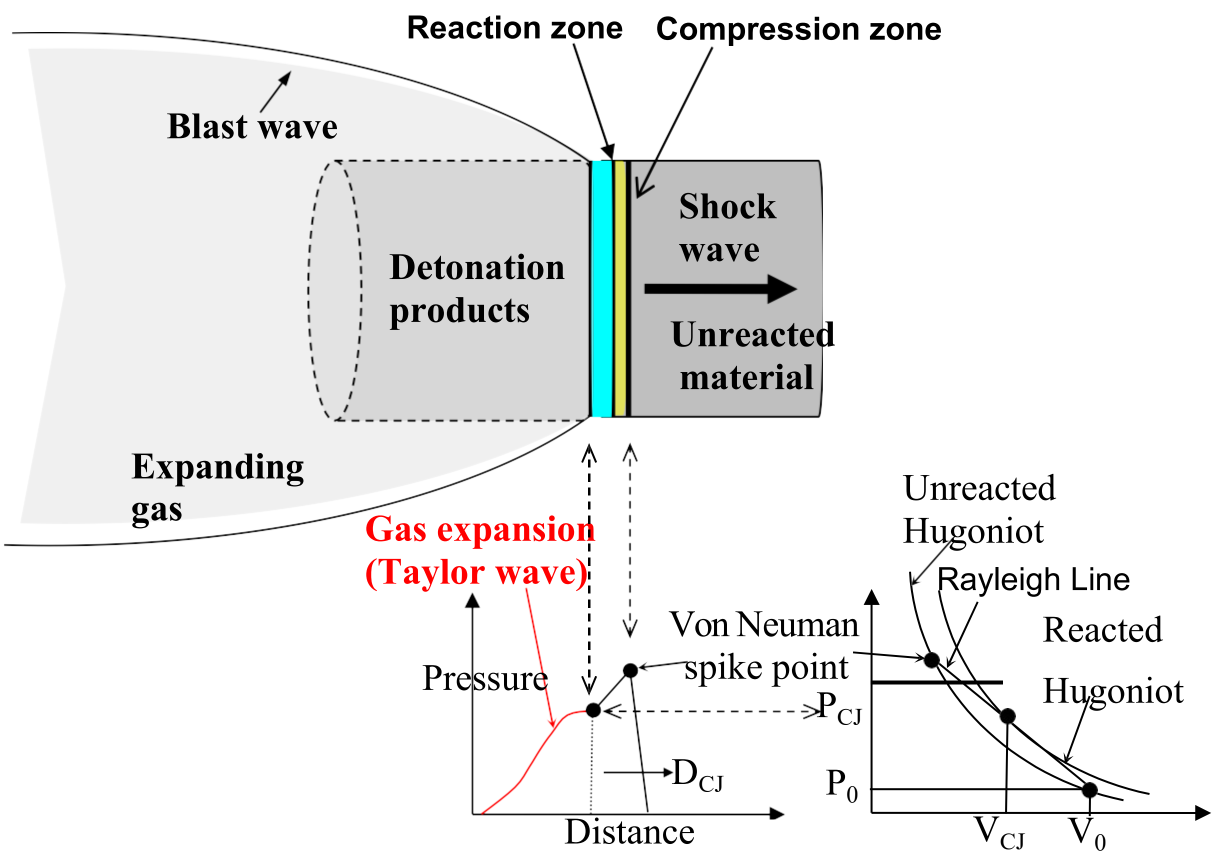
Detonation Theory

- Chapman-Jouguet (CJ)



Detonation Theory

- Zeldovich-Von Nuemann-Döring (ZND)



Non-Ideal

- Detonation process for a fuel and oxidizer contained in separate molecules
  - Initiation sequence is the same but the reaction process is slightly different
  - The reaction is a diffusion process
    - The fuel and oxidizer decompose separately first, each producing gaseous products
    - The products then react amongst themselves producing the final products
    - Part of this reaction occurs within the reaction zone supporting the detonation wave
    - Part happens to far away from the reaction zone therefore, producing heat that contributes to sustained pressure
  - This creates a larger reaction zone
  - Definition from Mader's Book "Numerical Modeling of Explosives and Propellants"
    - One may define a nonideal explosive as having a C-J pressure, velocity, or expansion isentrope significantly different from those expected from equilibrium, steady-state calculations
      - Pressure difference of 50 kbars (5 Gpa)
      - Velocity difference of 500 m/s

Non-Ideal

AN + Fuel

AN (Oxidizer): $NH_4NO_3 \rightarrow N_2 + 2H_2O + 1\ 2/O_2$

Fuel : $CH_3\left(CH_2\right)_n CH_3 + mO_2 \rightarrow \left(n+3\right)H_2O + \left(n+2\right)CO_2$

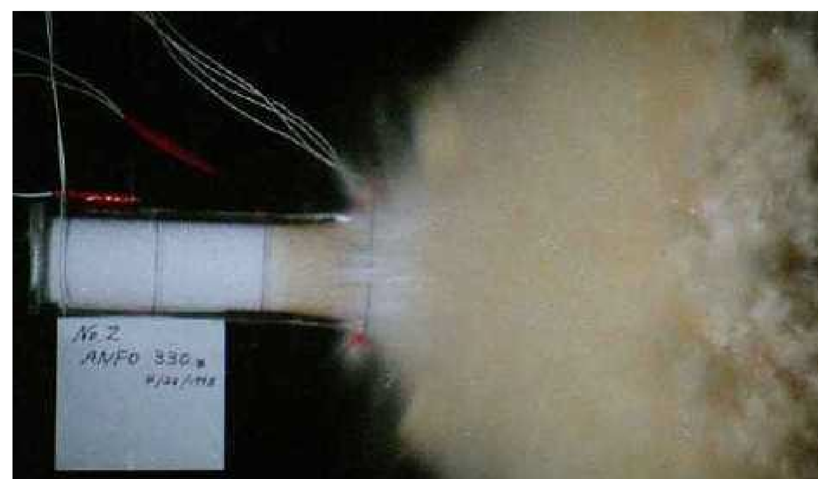
As onecan see, thefuel needs oxygen beforeit can react.

Setting $n = 10$ for Diesel, one gets

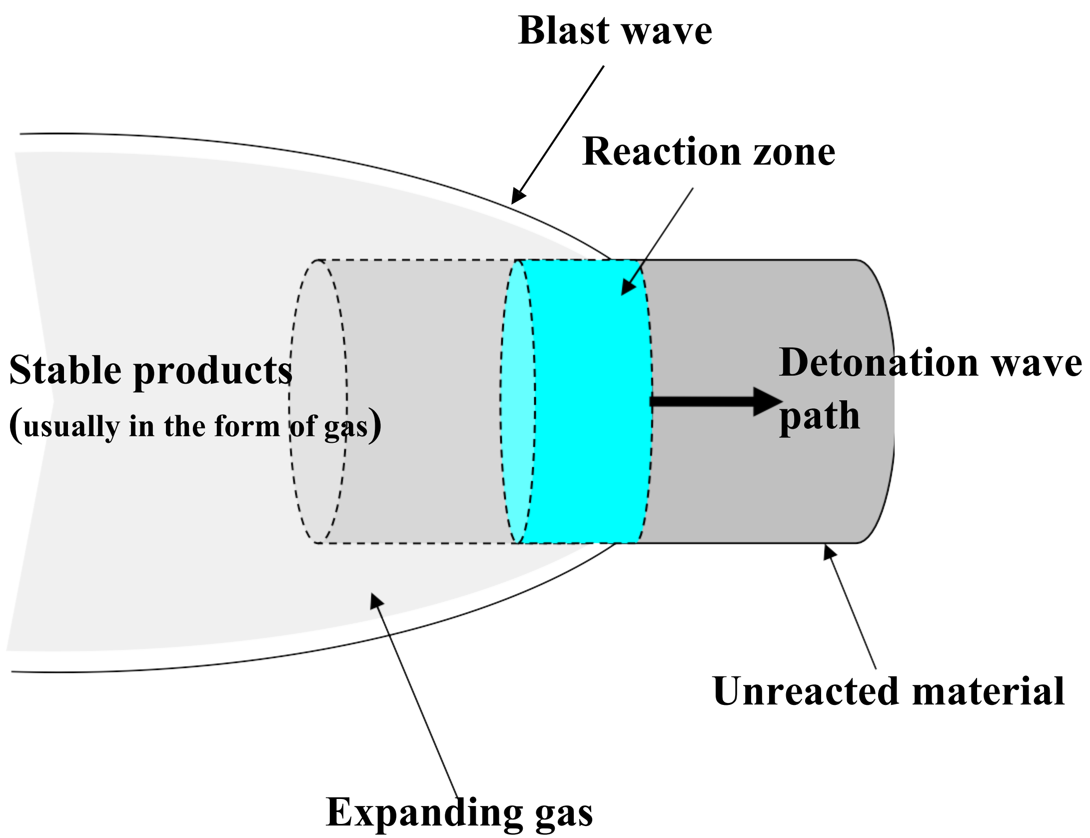
FO : $CH_3\left(CH_2\right)_{10} CH_3 + 18.5O_2 \rightarrow 13H_2O + 12CO_2$

AN + FO, then produces

$37NH_4NO_3 + CH_3\left(CH_2\right)_{10} CH_3 \rightarrow +87H_2O + 12CO_2 + 37N_2$



Non-Ideal

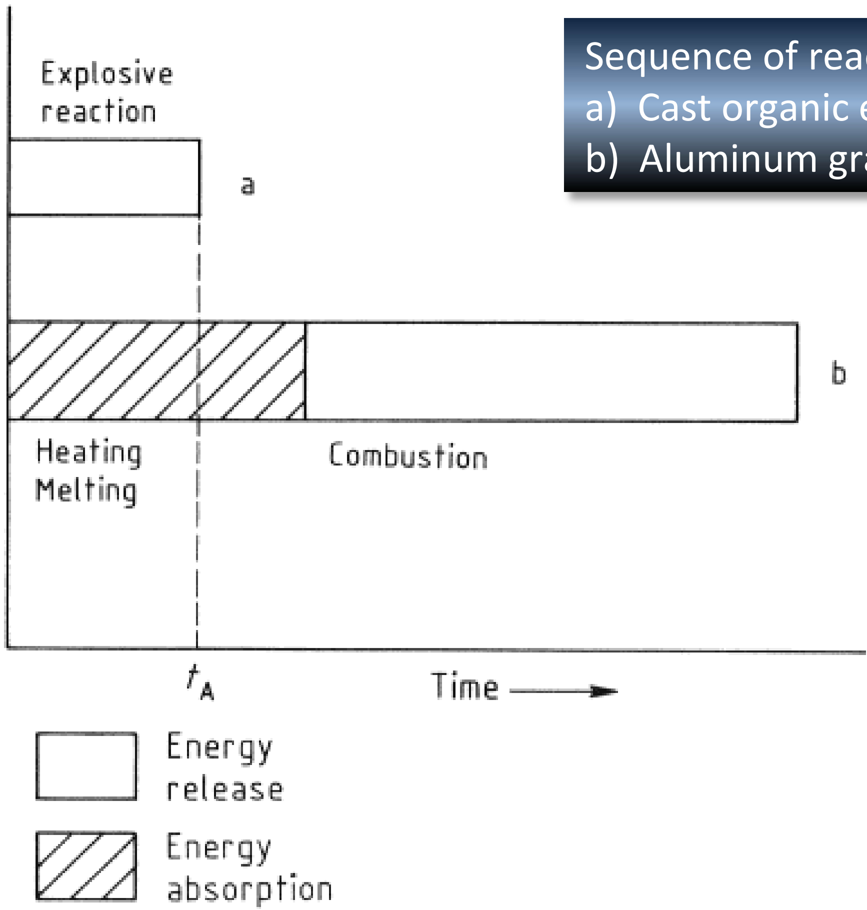


Blast wave
Reaction zone
Stable products
(usually in the form of gas)
Detonation wave
path
Unreacted material
Expanding gas

Non-Ideal

- Metal additive reaction process
  - Certain metal such as Aluminum produce a large amount of thermal energy upon oxidation
  - Metal added to an explosive material tends to react mainly with the stable gas products
    - The reaction zone temperatures strip the metal of its protective oxide layer
    - This process also reduces the rate of reaction by reducing the overall temperature
  - Some reaction, though, may occur in the reaction zone therefore, reducing the peak pressure produced
  - The increased temperature from the oxidation of the metal maintains the pressure magnitude longer

Non-Ideal



Sequence of reactions: Explosive and combustible additive

a) Cast organic explosive
b) Aluminum grains or flakes

High Explosives

- Metal additive reaction process
  - Energy from the explosives is loss heating the metal
  - When oxidation of the metal occurs from the oxygen with in the immediate environment, a large amount of heat is liberated

Oxidation of Aluminum with air or oxygen

$$2Al(s)+1.5O_2(g)\rightarrow Al_2O_3(s)+(Q=-1590\,kJ)$$

Oxidation of Aluminum with water

$$2Al(s)+3H_2O(g)\rightarrow Al_2O_3(s)+3H_2(g)+(Q=-866\,kJ)$$

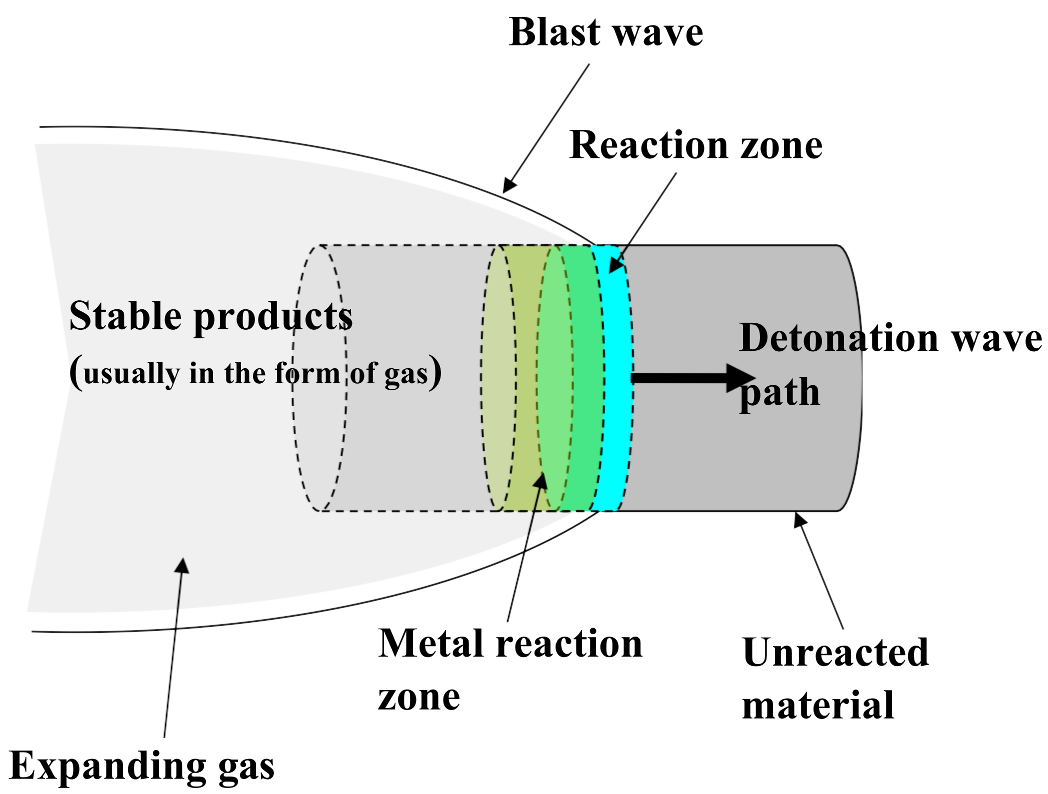
Oxidation of aluminum with detonation products

$$2Al(s)+3CO_2(g)\rightarrow Al_2O_3(s)+3CO(g)+(Q=-741\,kJ)$$

$$2Al(s)+3H_2O(g)\rightarrow Al_2O_3(s)+3H_2(g)+(Q=-866\,kJ)$$

$$2Al(s)+3CO(g)\rightarrow Al_2O_3(s)+3C(s)+(Q=-1251\,kJ)$$

High Explosives

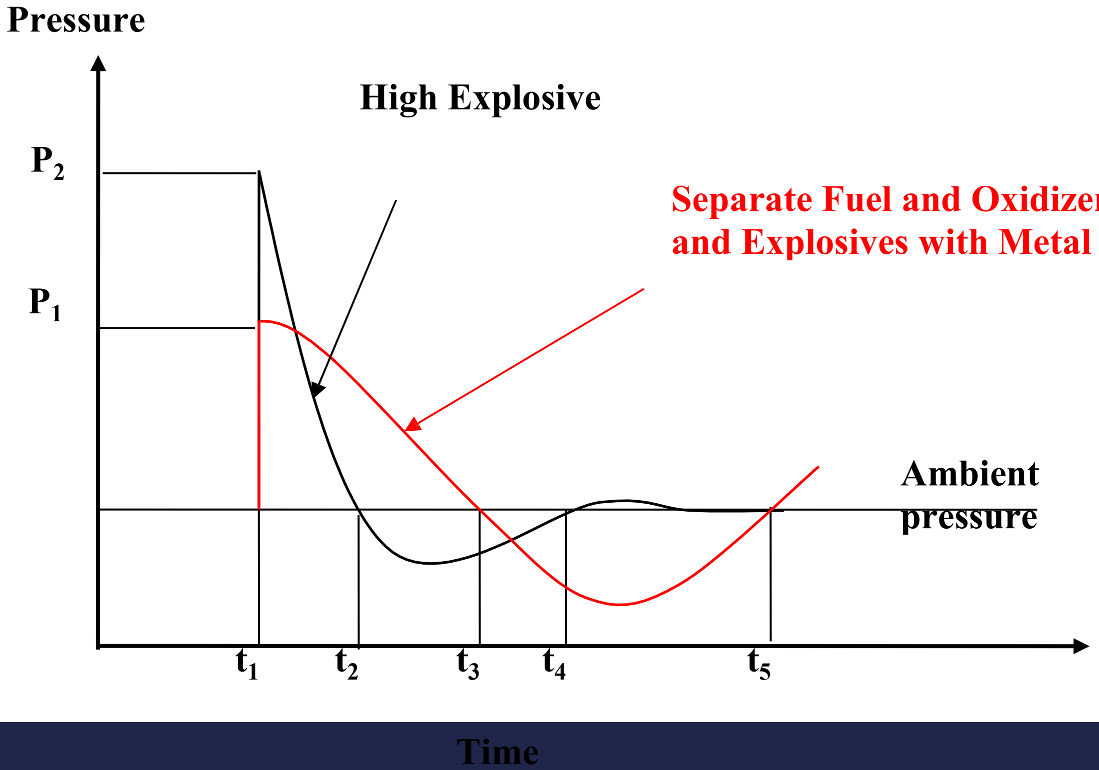


High Explosives

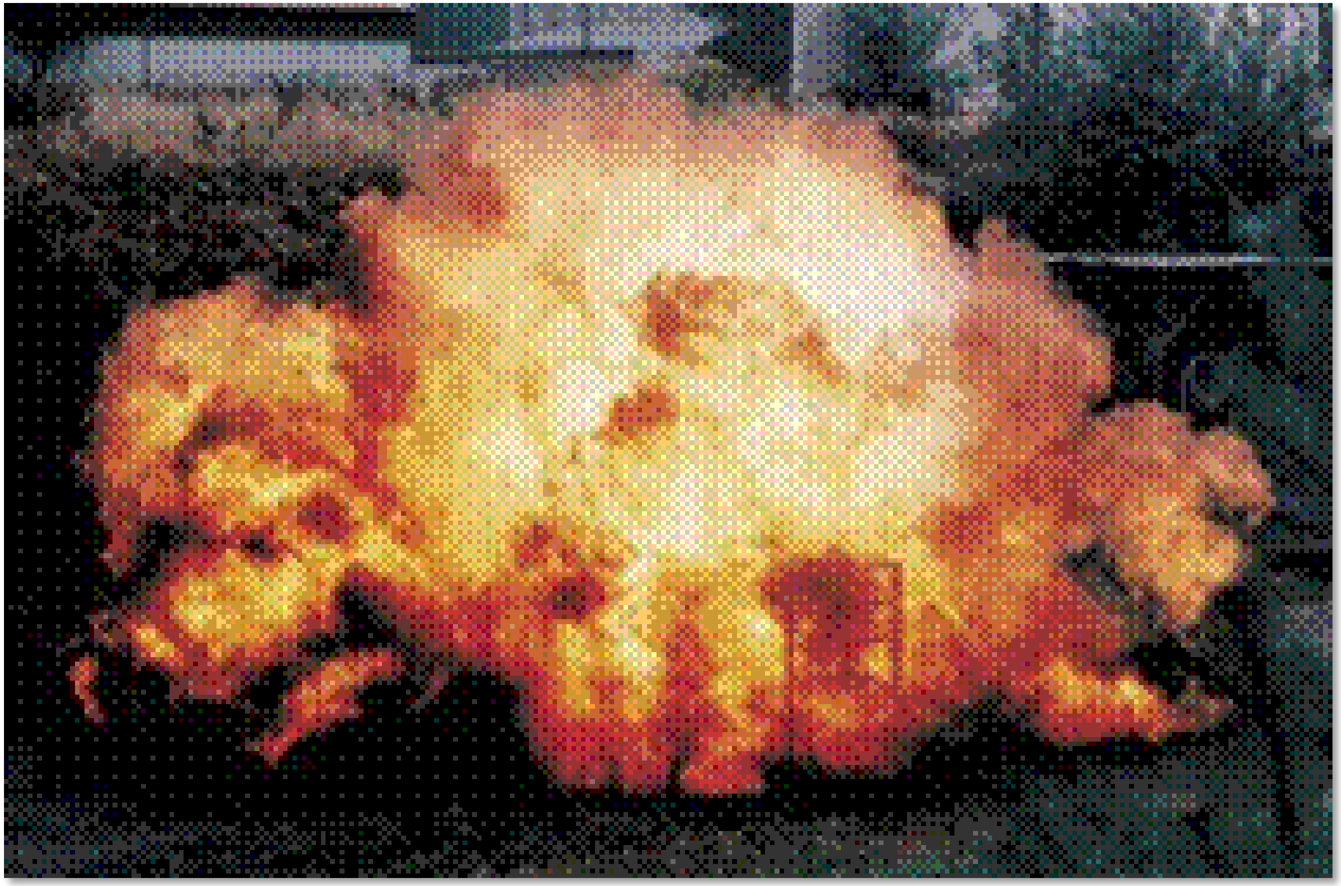
- Metal additive characteristics
  - Because aluminum is relatively cheap it is the most widely used
  - Increase the performance of explosive by:
    - Increasing the air blast (blast wave)
    - Produce large bubbles in underwater ordnance
    - Increasing lifting and heaving
    - Increase its sensitivity to external stimuli

High Explosives

- **Blast wave** is a shock wave in air
  - Shock front
  - Overpressure region
  - Negative pressure region
  - Wind force



Fuel-Air Explosives



Fuel-Air Explosives

- **Fuel-Air Explosive** is a fuel to air ratio that produces an explosive mixture in the form of a vapor or suspended particle cloud that when ignited produces a deflagration and/or detonation

Fuel-Air Explosives

- Characteristics
  - Fuels
    - Solid – fine particles
      - Dust, coal, grain, explosives, metal, etc…
    - Volatile Liquids
      - Diethyl ether, ethanol, gasoline, xylene, mineral spirits, oxirane, acetone, etc…
    - Gas
      - Hydrogen, acetylene, methane, propane, etc…

Fuel-Air Explosives

- Characteristics (cont.)
  - Reaction process is very dependent on fuel/air ratio

Name	LEL	UEL
Acetylene	2%	100%
Hydrogen	4%	75%
Ethylene oxide	3%	100%
Propane	2%	10%
Carbon Monoxide	12.5%	74%

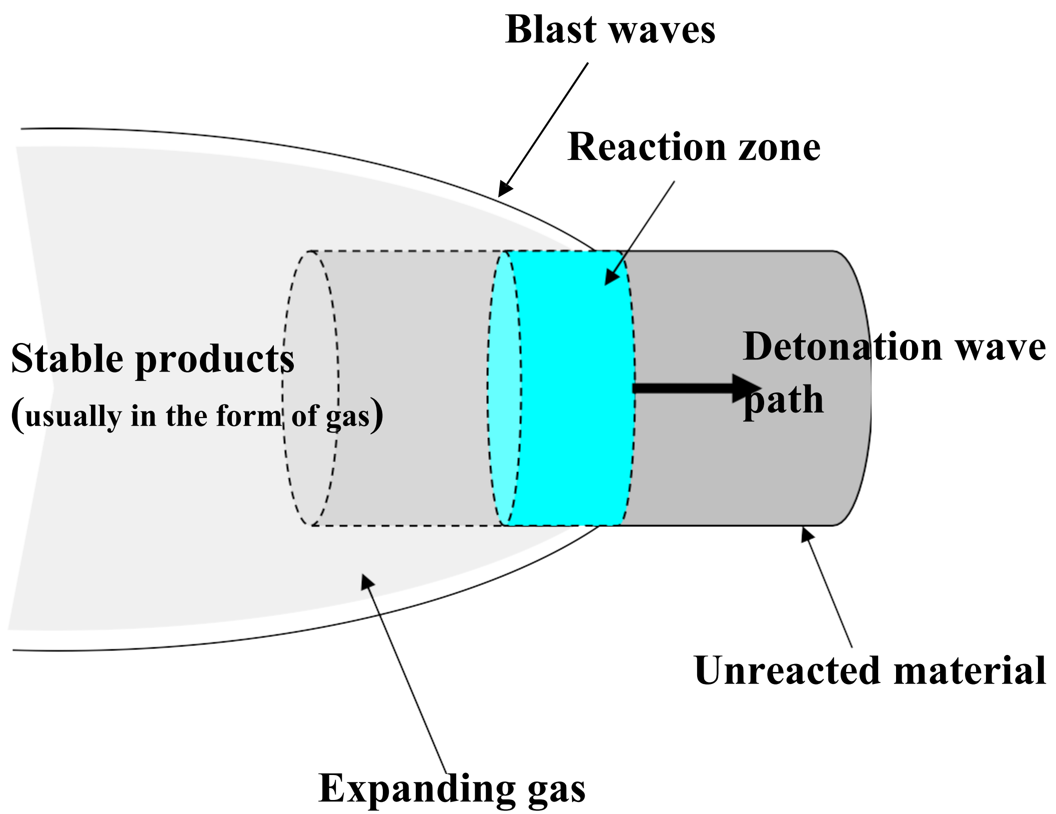
Fuel-Air Explosives

- Characteristics (cont.)
  - Chemically metastable
  - Detonation velocity between 1000 to 3500 m/s
  - Turbulence enhances reaction
  - Structures or obstacles create turbulence
  - Shock from detonation enhances mixing therefore, enhancing reaction
  - Power
    - Long duration pressure pulse

Fuel-Air Explosives

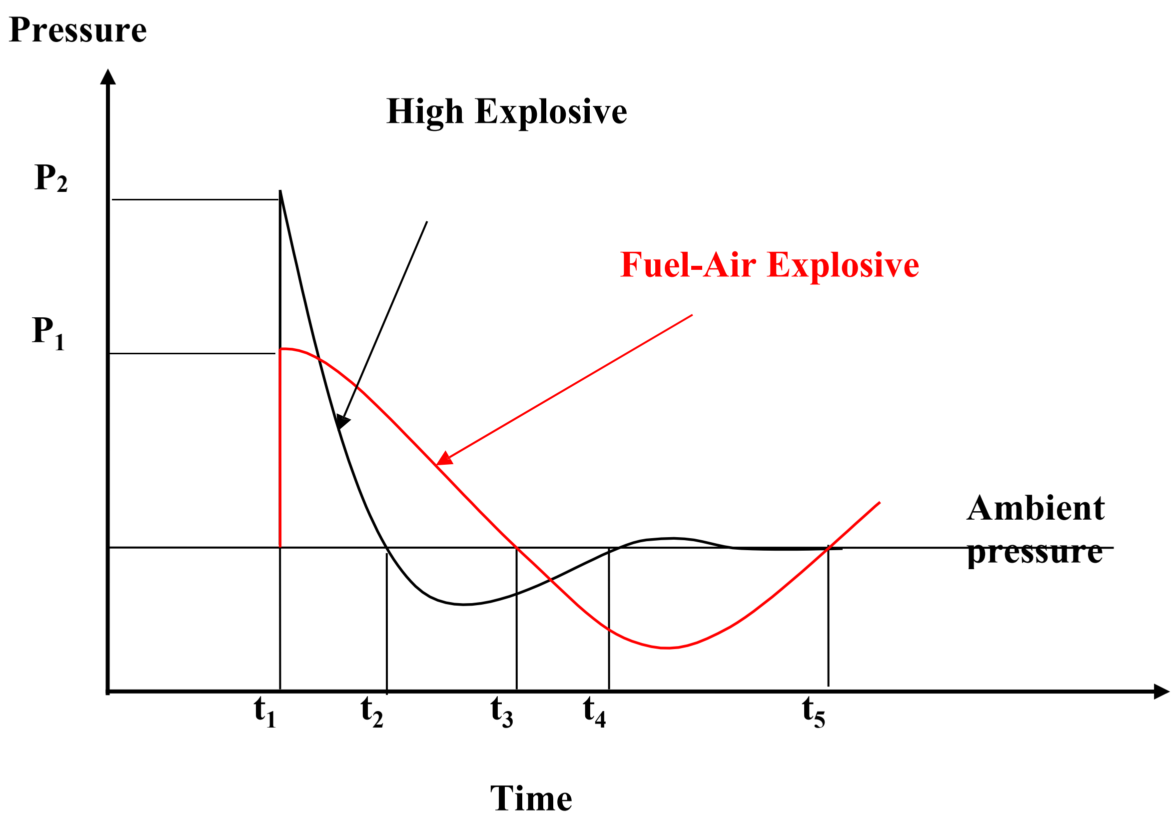
- Detonation process
  - Initiation sequence is the same but the reaction process is slightly different
  - The reaction is a diffusion process
    - The fuel and oxidizer decompose separately first, each producing gaseous products
    - The products then react amongst themselves producing the final products
    - Part of this reaction occurs within the reaction zone supporting the detonation wave
    - Part happens to far away from the detonation front therefore, producing heat that contributes to sustained pressure
  - This creates a larger reaction zone

Fuel-Air Explosives



Fuel-Air Explosives

- Blast profile



Fuel-Air Explosives

- Example

Fuel-Air Explosives

Explosives Performance

- An individual may also use the heat of detonation alone
  - In this Comparison, they should only compare explosive the behave the similar
    - TNT, Comp B, Comp C4, Sheet explosive, etc…
- There is no really easy way to figure out the chemical equilibrium. One of the more simpler conventions is:

$$C_aH_bN_cO_d \rightarrow \left(\frac{c}{2}\right)N_2 + \left(\frac{b}{2}\right)H_2O + \left[\left(\frac{d}{2}\right) - \left(\frac{b}{4}\right)\right]CO_2 + \left[a - \left(\frac{d}{2}\right) - \left(\frac{b}{4}\right)\right]C$$

Explosives Performance

- A more accurate way, but more work by the individual:

$$C_aH_bN_cO_d \rightarrow n_1CO_2 + n_2H_2O + n_3N_2$$

- The reaction for explosives and propellants usually follow
  - Nitrogen goes to N_2
  - Hydrogen burns to form H_2O
  - Oxygen left over form CO
  - Existing oxygen form CO_2
  - Any oxygen left forms O_2
  - Any carbon left form solid carbon C
- The heat of explosion is (simplified method)

$$\Delta H_d = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

$$Q_c = \frac{28.9b + 47.0\left(d - \frac{b}{2}\right) + \Delta H_f(\text{explosive})}{12a + b + 14c + 16d}$$

Explosives Performance

- Additionally, one may use the amount of gas liberated times the heat of detonation to compare explosives

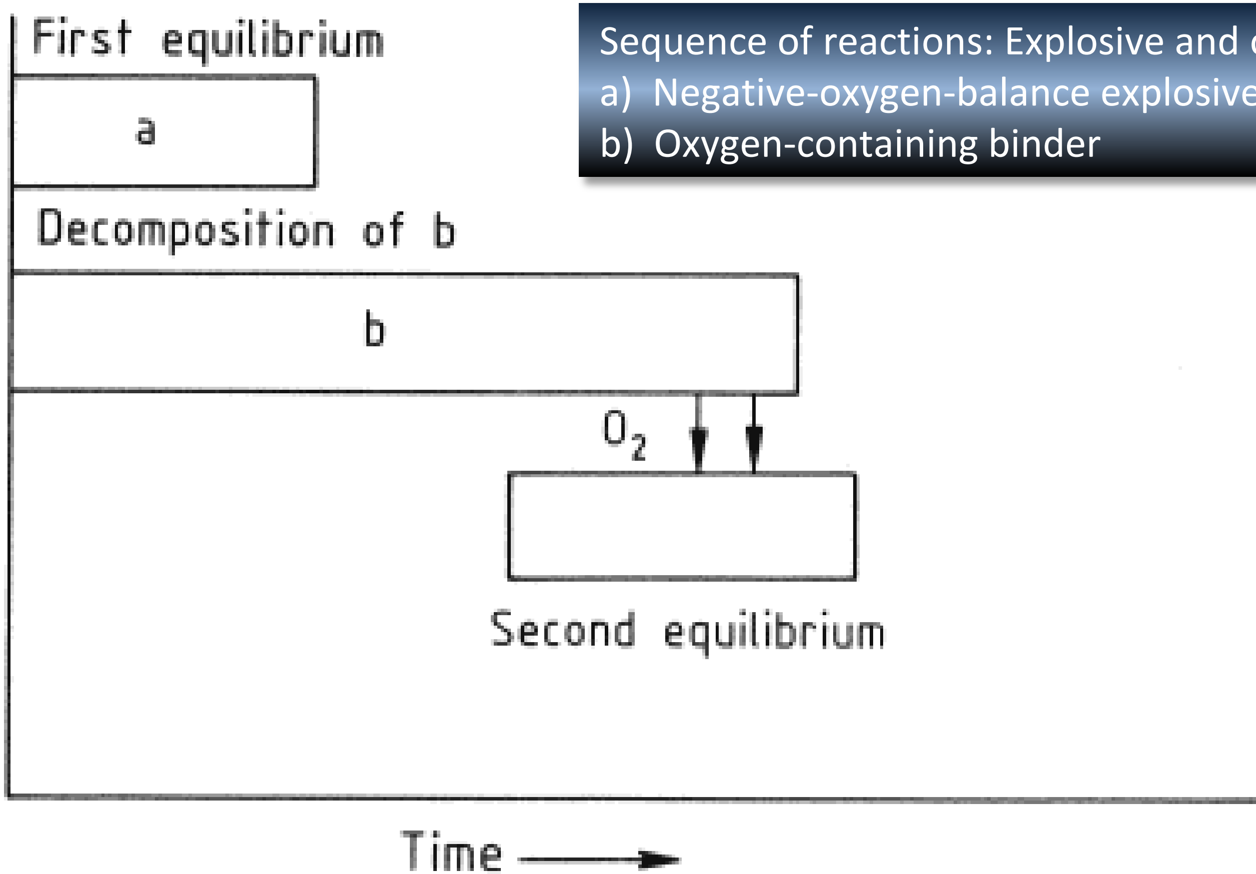
$$\underbrace{C_3H_6N_6O_6}_{\text{reactant}} \rightarrow \underbrace{3CO + 3H_2O + 3N_2}_{\text{products}} \quad \frac{9 \text{ mols of gas} \times 22.414 \text{ Liter/mol}}{222\text{gram}} = 908.8\frac{cm^3}{gm} \qquad \otimes H_d = -5036\frac{J}{gm}$$

$$\underbrace{C_7H_5N_3O_6}_{\text{reactant}} \rightarrow \underbrace{3.5CO + 2.5H_2O + 1.5N_2 + C}_{\text{products}} \quad \frac{7.5 \text{ mols of gas} \times 22.414 \text{ Liter/mol}}{227\text{gram}} = 740.5\frac{cm^3}{gm} \qquad \otimes H_d = -4247\frac{J}{gm}$$

$$Power\ Index = \frac{\otimes H_{RDX} \times V_{RDX}}{\otimes H_{TNT} \times V_{TNT}} \times 100 = \frac{5036 \times 908.8}{4247 \times 740.5} = 1.45 \Rightarrow 45\% \text{ more power}$$

Note: The excess carbon in the TNT reaction can combust with the surrounding environment generating an after burn, but it is usually seen as the black soot (solid carbon) seen after the detonation occurs

Secondary Reaction from TNT



Sequence of reactions: Explosive and oxygen-rich binder

a) Negative-oxygen-balance explosive
b) Oxygen-containing binder

Explosives Performance

- Furthermore, one can see how much is detonation energy or shock energy compared to push energy from gas expansion:

$$P = \frac{\rho D^2}{(1+\gamma)}, \quad Q_D = \frac{D^2}{2(\gamma^2 - 1)}, \quad Q_D = \frac{P}{2\rho(\gamma - 1)}, \quad \gamma = \left(\frac{P}{\rho D^2}\right)^{-1}$$

- Examples:
  - RDX (100%), PBXW-108 (85% RDX/15% Polymer binder), PBXW-109 (65% RDX/20% Al/15% Polymer binder), PBXW-115 (20% RDX/43% AP/25% Al/12% Polymer binder)

Explosive	Total Energy (Q)	Detonation Energy (Q_D)	Detonation Energy %
RDX	5036 J/gm	4774 J/gm	4774/5036 = 94.8
PBW-108	5180 J/gm	3694 J/gm	3694/5180 = 71.3
PBXW-109	7887 J/gm	3330 J/gm	3330/7887 = 42.2
PBXW-115	8473 J/gm	1469 J/gm	1469/8473 = 17.3

Explosives Performance

- Density
  - Detonation velocity
    - Once you find out the detonation velocity one my find the effect of density on pressure

$$D = A + B\rho$$

  - Pressure
    - In Cooper's book "Explosives Engineering" he shows on page 265

$$P = \rho_0 D^2 \left(1 - \frac{\rho_0}{\rho_{CJ}}\right)$$

    - He also shows on the same page a relationship from experimental data

$$P = \rho_0 D_2 \left(1 - 0.7125\rho_0^{0.04}\right)$$

    - Approximate rule of thumb (¼ $\rho_0 D^2$)

Critical Energy

- In 1965, Gittings conducted a series of experiments that showed the response of an explosive impacted by a thin flyer plate
  - E. F. Gittings, *Proceedings of the 4th International Detonation Symposium* 1965
- Walker and Wasley, in 1969, analyzed Gittings' findings and developed an initiation criterion for an explosive based on the shock wave energy imparted by an impacting flyer plate
- The critical energy, E_c, required to shock initiate an explosive relates the rate of work done per unit area to the shock pressure and its duration

$$E_c = \frac{P^2 t}{\rho U} \approx \frac{1}{2}\rho_o x_o u_o^2$$

P = amplitude of the shock pressure
t = pulse duration
p = density of the explosive
U = shock velocity of the explosive at pressure P

Critical Energy

- This represents the energy that flows through the impact area into the explosive. Roughly speaking, this is the kinetic energy from the impact transferred, as an inelastic collision, into the explosive
- Therefore, the compression of the explosive material consumes half of the energy while the other half gives the velocity to the explosive material
- Table below shows the critical threshold energy required to generate a SDT for a select group of energetic materials

Energetic material	Density (g/cm³)	Critical energy (J/mm²)
Comp B RDX/TNT (60/40)	1.73	1.84
HMX/nylon (89.5/10.5)	1.77	1.00
TNT (Cast)	1.62	4.20
TNT (Pressed)	1.64	1.34
Nitromethane (liquid)	1.12	16.90
PBX 9404 HMX/Nitrocellulose/cef (94/3/3)	1.84	0.63
RDX/Polybutadiene (86/14)	1.60	2.10

Pressure vs Run Distance

- A SDT is just that, a transition to detonation
- When an explosive experiences a shock, it does not instantaneously detonate
- In fact, there is a minimum strength and duration required of a pressure pulse to produce a detonation

Pressure vs Run Distance

- In 1965, Ramsay and Popolato conducted a series of experiments on various energetic materials
  - In these experiments, they impacted the energetic material with a flyer plate at different velocities to produce a range of induced shock pressures and recorded the distance it would take to generate a detonation
    - J. B. Ramsay, A. Popolato, *Proceedings of the 4th International Detonation Symposium* 1965
    - T. R. Gibbs, A. Popolato, *LASL Explosive Property Data*, University of California Press, Ltd., Berkeley and Los Angeles 1980
  - Empirical testing showed that the strength of the pressure pulse is related to a finite induction time and distance before the onset of a detonation

Pressure vs Run Distance

- Equation shows the pressure versus distance relationship

$$n\log(X) = \log(P) - m$$

X = minimum run distance in millimeters

P = pressure from shock in GPa

m, n = fit coefficent from empirical data

- Solving for X

$$\log(P) = m - \log(X^n)$$

$$-\log(X^n) = \log(P) - \log(b); \quad \log(b) = m$$

$$\log(X^{-n}) = \log(P/b)$$

$$X = (P/b)^{-\frac{1}{n}}$$

Pressure vs Run Distance

- This equation gives the relationship between input pressure and the distance it will take to produce a detonation

$$X = (P/b)^{-\frac{1}{n}}$$

- This is only true if the pressure is equal to or above the critical run distance empirically obtained for a given energetic material
    - P. W. Cooper, *Explosives Engineering*, Wiley-VCH, New York 1996
    - T. R. Gibbs, A. Popolato, *LASL Explosive Property Data*, University of California Press, Ltd., Berkeley and Los Angeles 1980

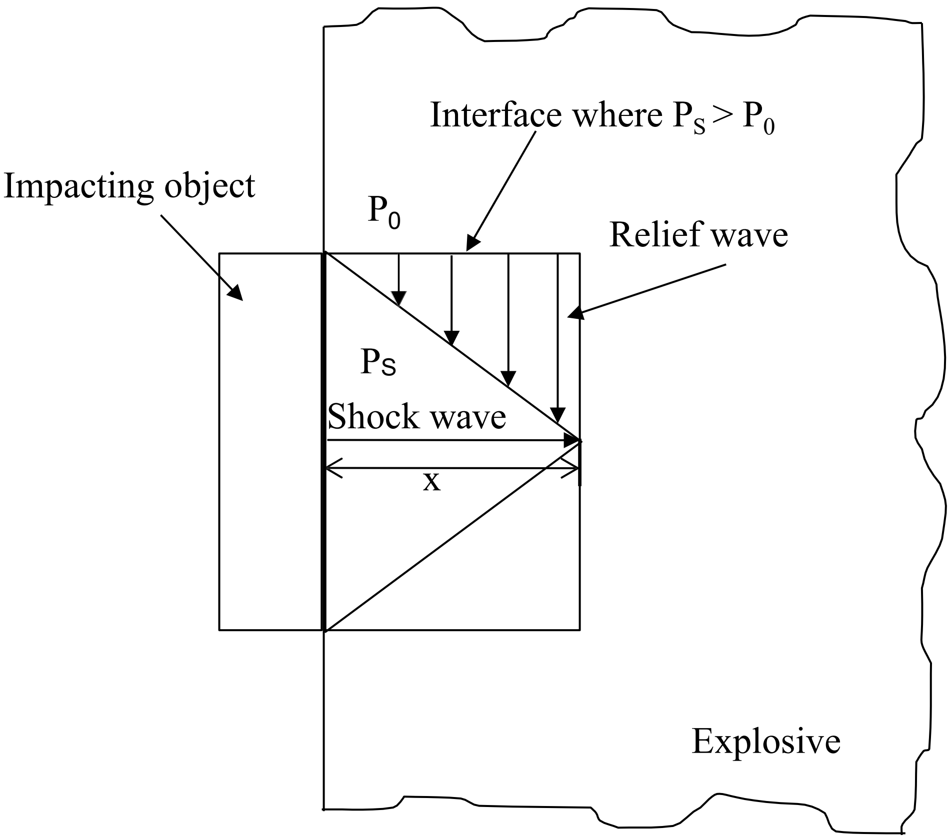
Pressure vs Run Distance

- Table below shows the pressure versus run distances required to generate a SDT for a select group of energetic materials

Energetic material	Density (g/cm^3)	$\log(P) = m - n\log(X)$	Pressure range (GPa)
PBX 9404 HMX/Nitrocellulose/cef (94/3/3)	1.84	$\log(P) = (1.1158) - (0.6696)\log(X)$	2.27< P <25.72
TNT (Cast)	1.62 to 1.64	$\log(P) = (1.40) - (0.32)\log(X)$	9.17< P <17.10
TNT (Pressed)	1.63	$\log(P) = (1.07) - (0.39)\log(X)$	4.00< P <12.00
Comp B RDX/TNT (60/40)	1.72	$\log(P) = (1.56) - (0.76)\log(X)$	3.7o< P <12.60

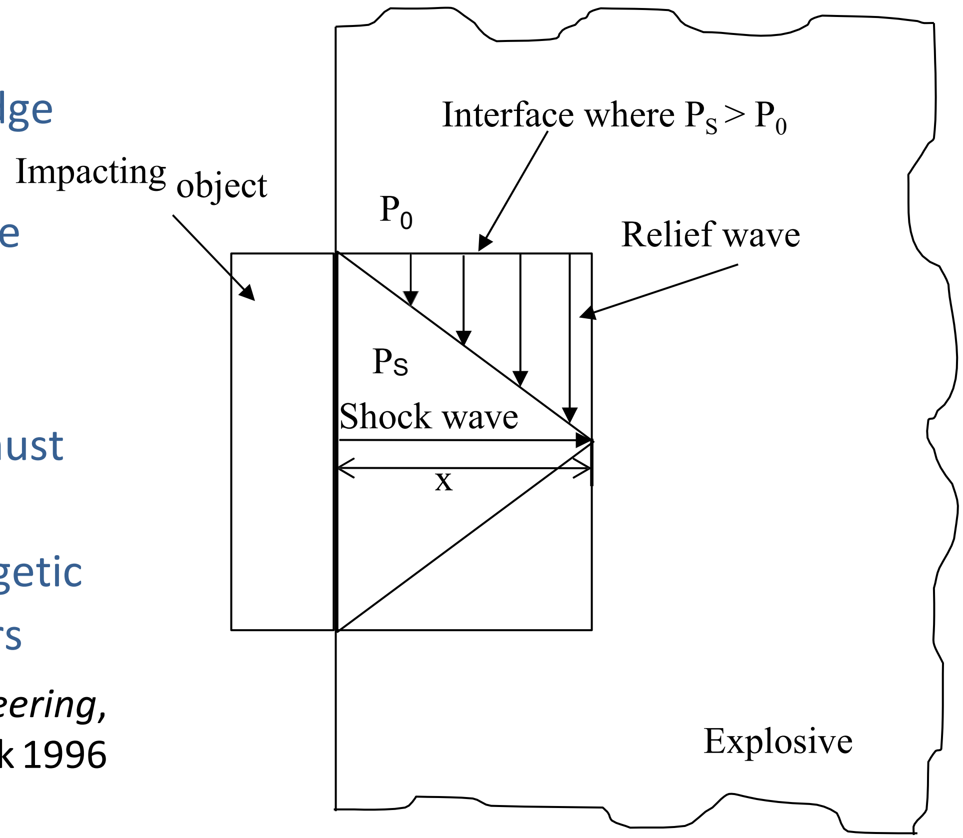
Critical Diameter

- The shock wave produces an interface or edge where the pressure produced from the shock is greater than the reference pressure of the explosive, $P_S > P_0$
- A relief wave (rarefaction) immediately starts to move inward effectively changing and reducing the shock pulse profile and amplitude



Critical Diameter

- "x" represents the maximum distance over which the shock pressure will sustain its amplitude before the edge relief wave overcomes it and starts to reduce the pressure of the wave
- Therefore, it is apparent that the diameter of an impacting object must exceed twice the minimum run distance characteristic of the energetic material to insure that a SDT occurs
  - P. W. Cooper, *Explosives Engineering*, Wiley-VCH, New York 1996



Critical Diameter

Energetic material	Density (g/cm³)	Critical diameter (mm)
Comp B RDX/TNT (60/40)	1.73	3.73 to 4.24
TNT (Cast)	1.61	7.00
TNT (Liquid)	1.44	62.60
Nitromethane	1.127	>11.76
PBX 9404 HMX/Nitrocellulose/cef (94/3/3)	1.846	~1.18
Pentolite (Cast) PETN/TNT (50/50)	~	6.70

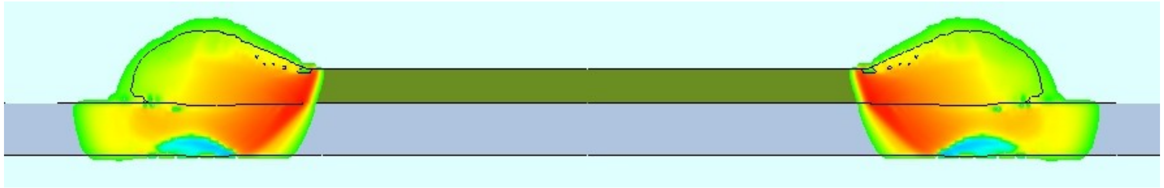
Explosives Performance

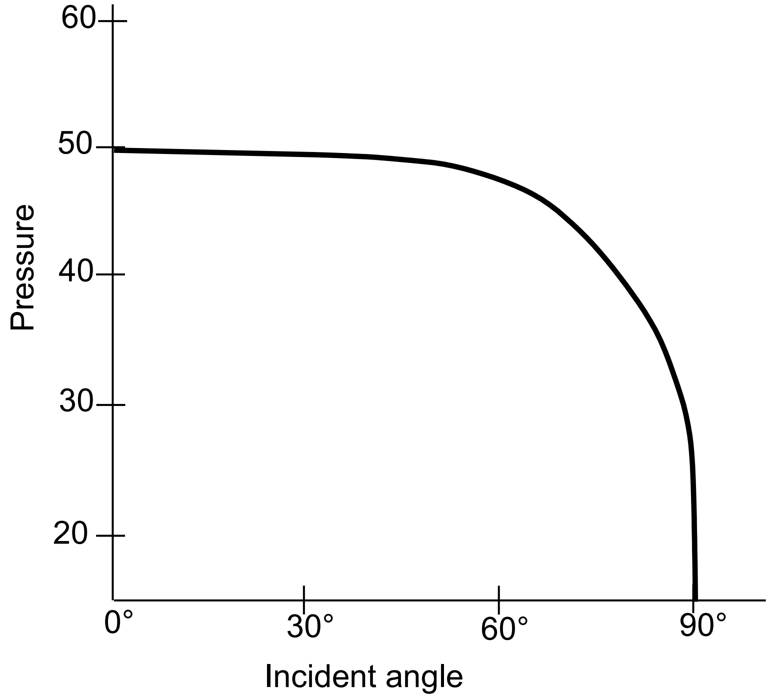
- Critical Diameter
  - Lead Azide (primary explosive)
    - 0.06 mm @ 3.50 gm/cc
  - RDX
    - 3 mm @ 1 gm/cc
    - 5.2 mm @ 0.9 gm/cc
    - 2 mm @ 1.2 gm/cc
  - PETN
    - 0.2 mm @ 1.68 gm/cc
  - TNT
    - 13 to 20 mm @ 1.62 gm/cc
  - Comp B
    - 4.3 mm @ 1.7 gm/cc
    - 2.54 mm @ 1.7 gm/cc **confined** in steel tube
  - Sheet Explosives
    - Primasheet 1000 (63% PETN/37% binder) is approximately 1 mm in thickness
    - Primasheet 2000 (88% RDX/ 12% binder) is approximately 2 mm in thickness

Work Capacity of Explosives

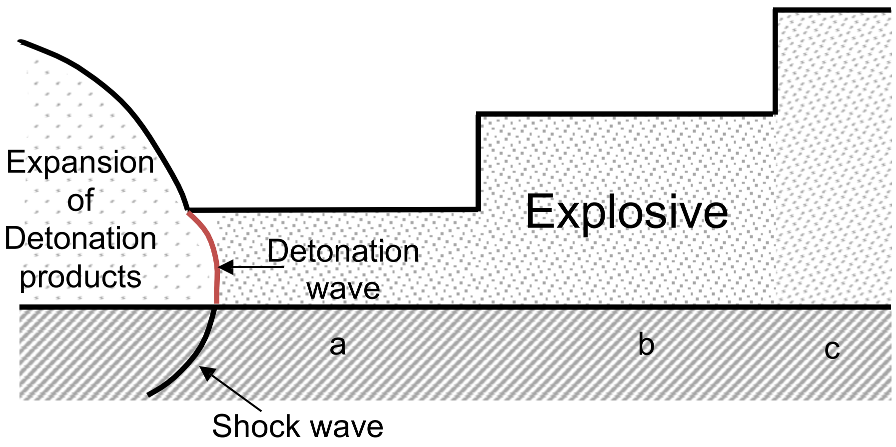
- There are many other types of empirical methods used to describe the performance ofan explosive. These test describe the brisance (shattering ability generated by pressure) and relative blast/effectiveness (power) of an explosive
  - Brisance
    - Sand test
    - Fragmentation test
    - Approximate rule of thumb ($\rho_0 D^2$)
  - Energy
    - Cylinder expansion test
  - Blasting and brisance (TNT equivalence methods)
    - Ballistic mortar test
    - Trauzl test
    - Plate dent test
    - Underwater explosion test

Sweeping Detonation Wave

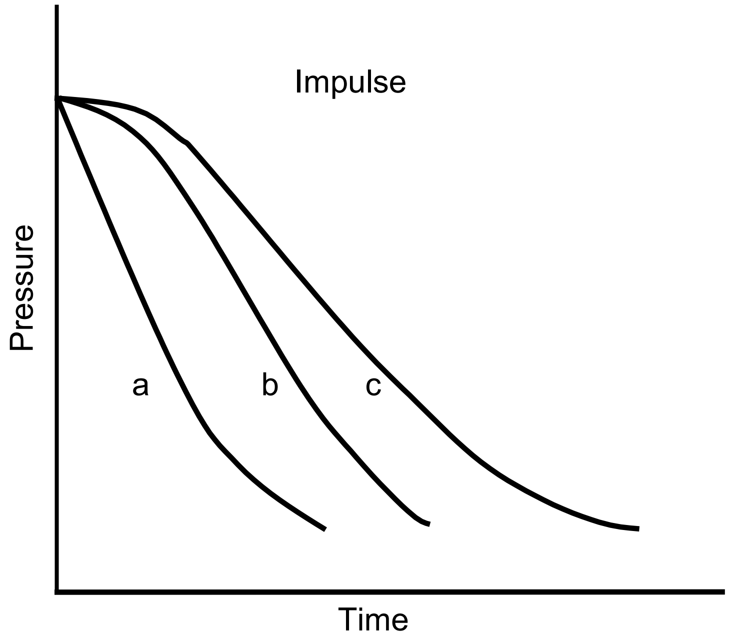




Thickness

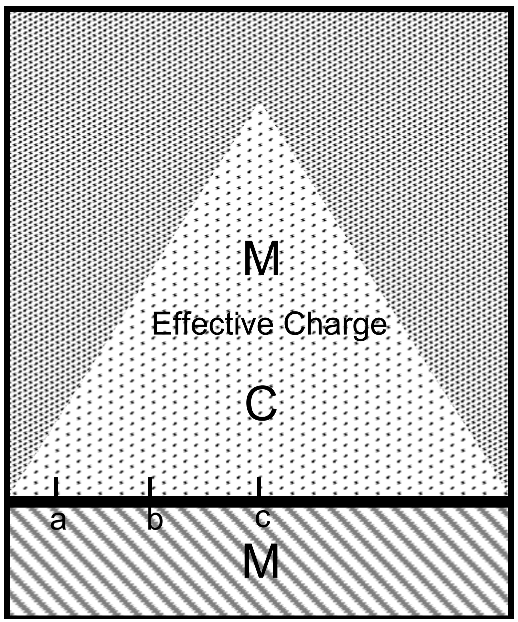


Expansion
of
Detonation
products
Detonation
wave
Explosive
a
b
c
Shock wave

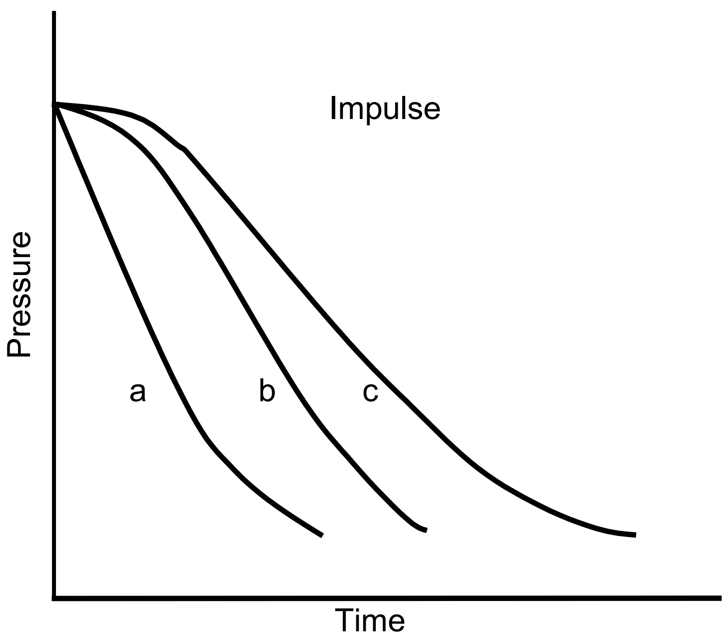


Impulse
Pressure
a
b
c
Time

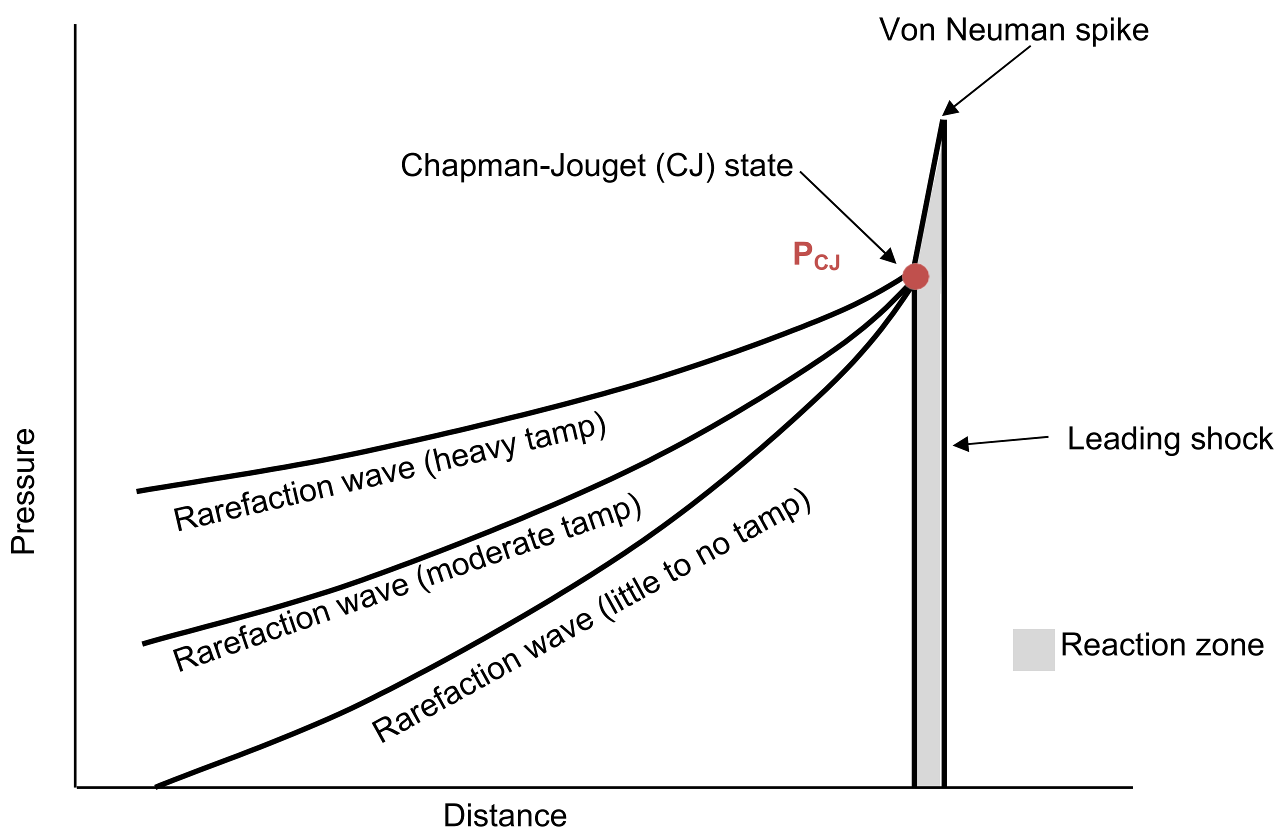
Effective Charge Volume



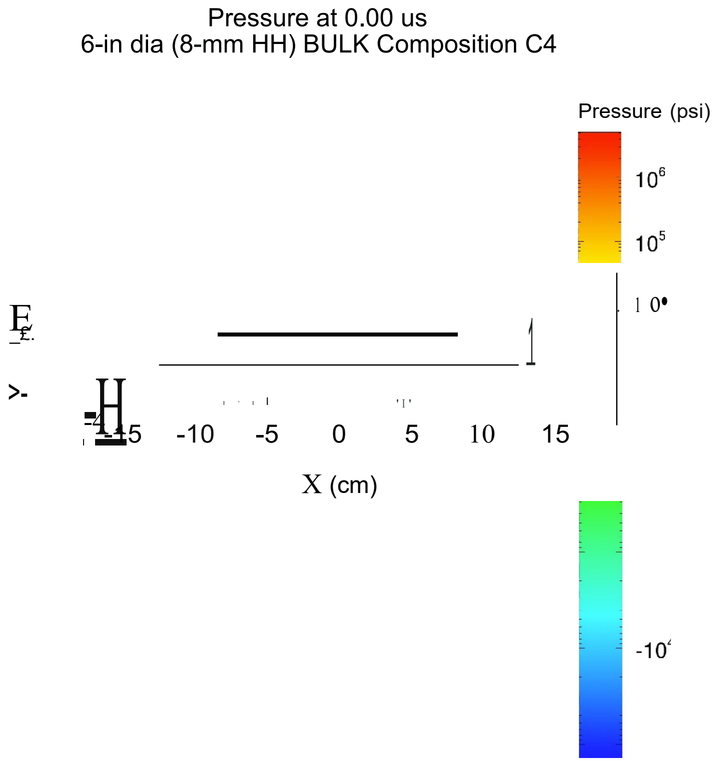
Tamping can increase the effective charge volume

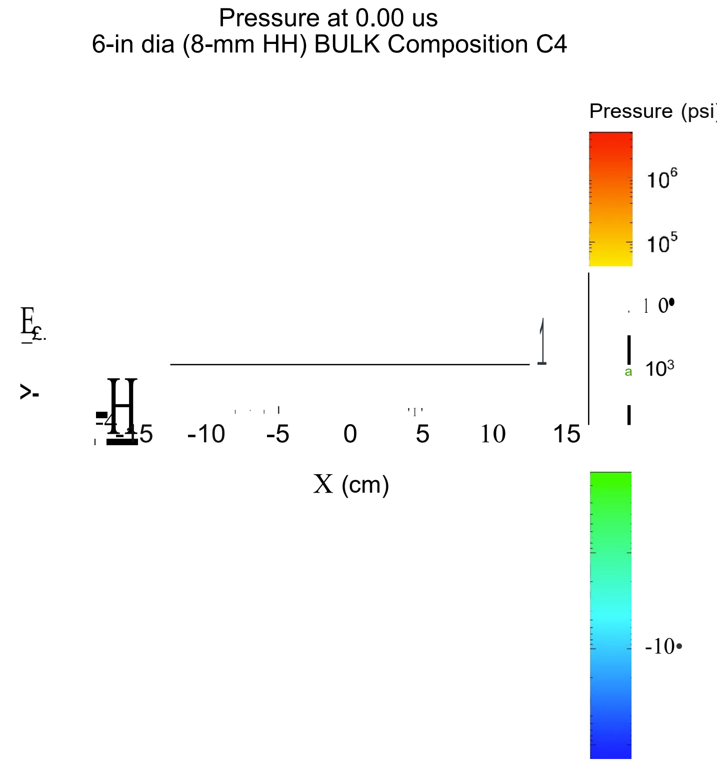


Confinement

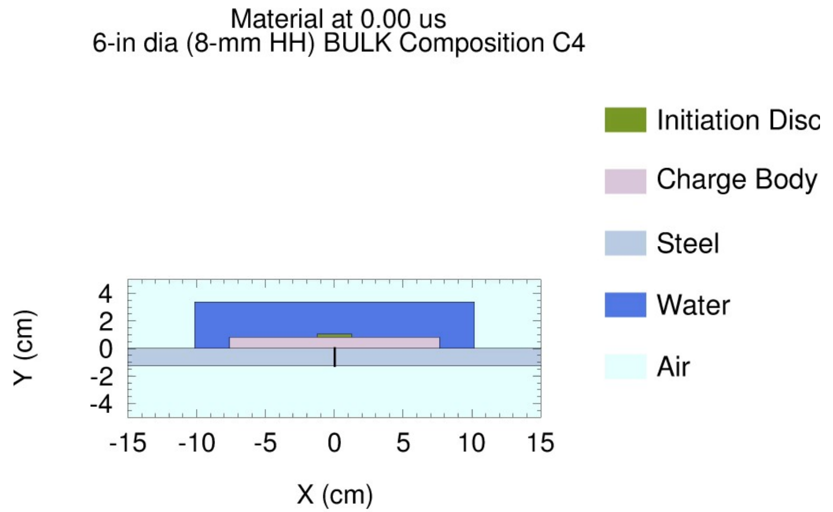


Confinement





Confinement



Summary of High Explosives

- Sensitive to external initiation stimuli
- Self-sustaining supersonic reaction without confinement (detonation wave)
- This self-sustained detonation wave is different from a deflagration, which propagates at a subsonic speed (i.e., slower than the sound speed of the explosive material itself), and without a shock or any significant pressure change
  - Additionally, one may control a rate of a deflagration by adjusting the pressure
- Because detonations generate high pressures, they are usually much more destructive than deflagrations
- Most explosive chemical compounds may usefully **deflagrate** as well as detonate, and are used in high as well as low explosive compositions
- This also means that under extreme conditions, a propellant can detonate
  - For example, **nitrocellulose** deflagrates if thermally ignited, but detonates if initiated by a detonator
- Last, when comparing explosive, be sure you have a complete understanding of their detonation process, work application, and then use the parameters associated specifically to your work application