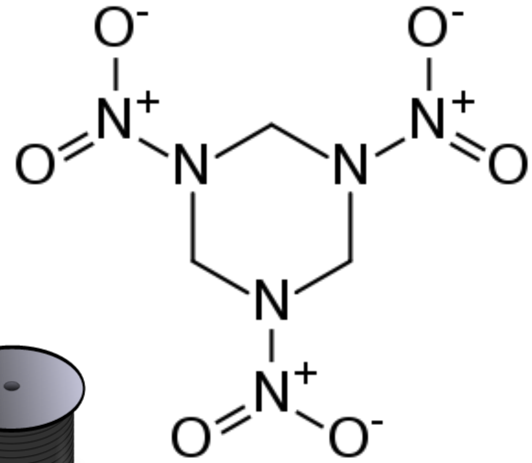
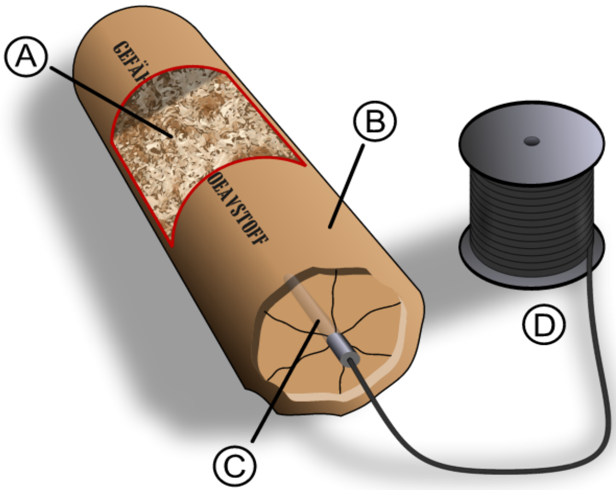




An Introduction to Chemical Reactions, Energy, Gases, and Chemical Explosives

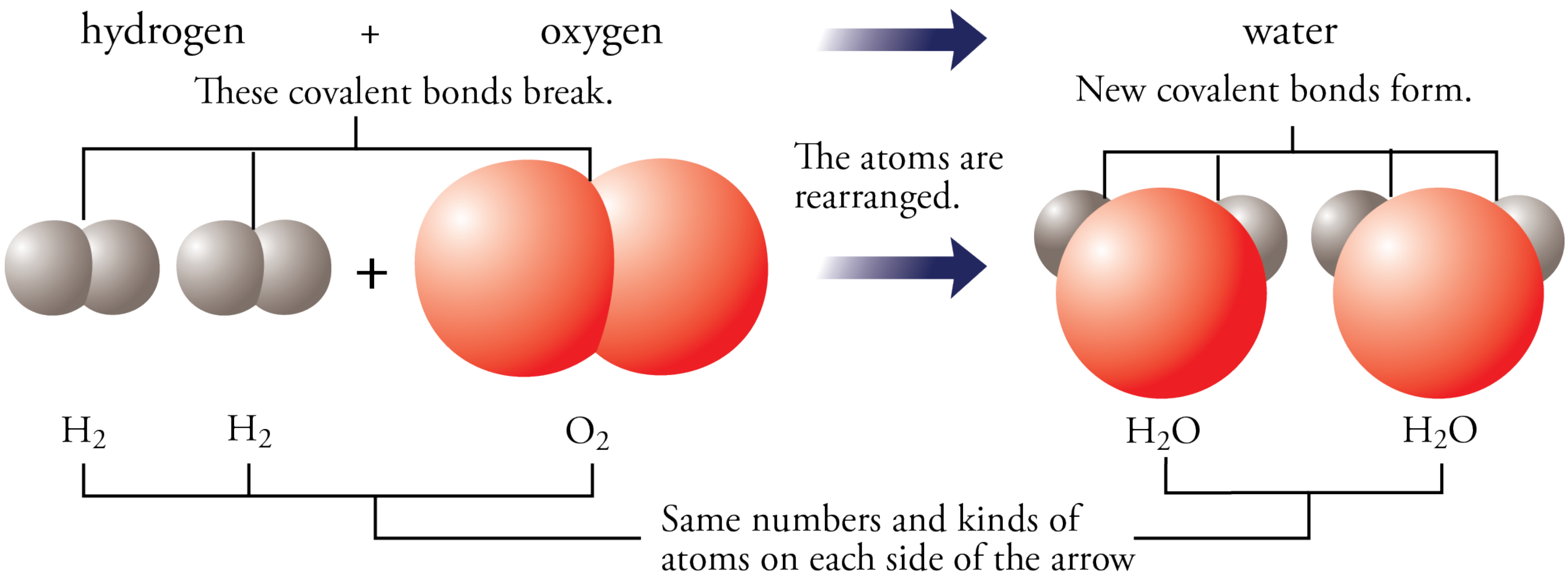
Chemical Explosives

- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the gas.

Chemical Reaction

- A ***chemical change*** or ***chemical reaction*** is a process in which one or more pure substances are converted into one or more different pure substances.

Chemical Reactions - Example



Chemical Equations (1)

- Chemical equations show the formulas for the substances that take part in the reaction.
  - The formulas on the left side of the arrow represent the ***reactants***, the substances that change in the reaction. The formulas on the right side of the arrow represent the ***products***, the substances that are formed in the reaction. If there are more than one reactant or more than one product, they are separated by plus signs. The arrow separating the reactants from the products can be read as *"goes to"* or *"yields"* or *"produces."*

Chemical Equations (2)

- The physical states of the reactants and products are provided in the equation.
  - A *(g)* following a formula tells us the substance is a gas. Solids are described with *(s)*. Liquids are described with *(l)*. When a substance is dissolved in water, it is described with *(aq)* for "aqueous," which means "mixed with water."

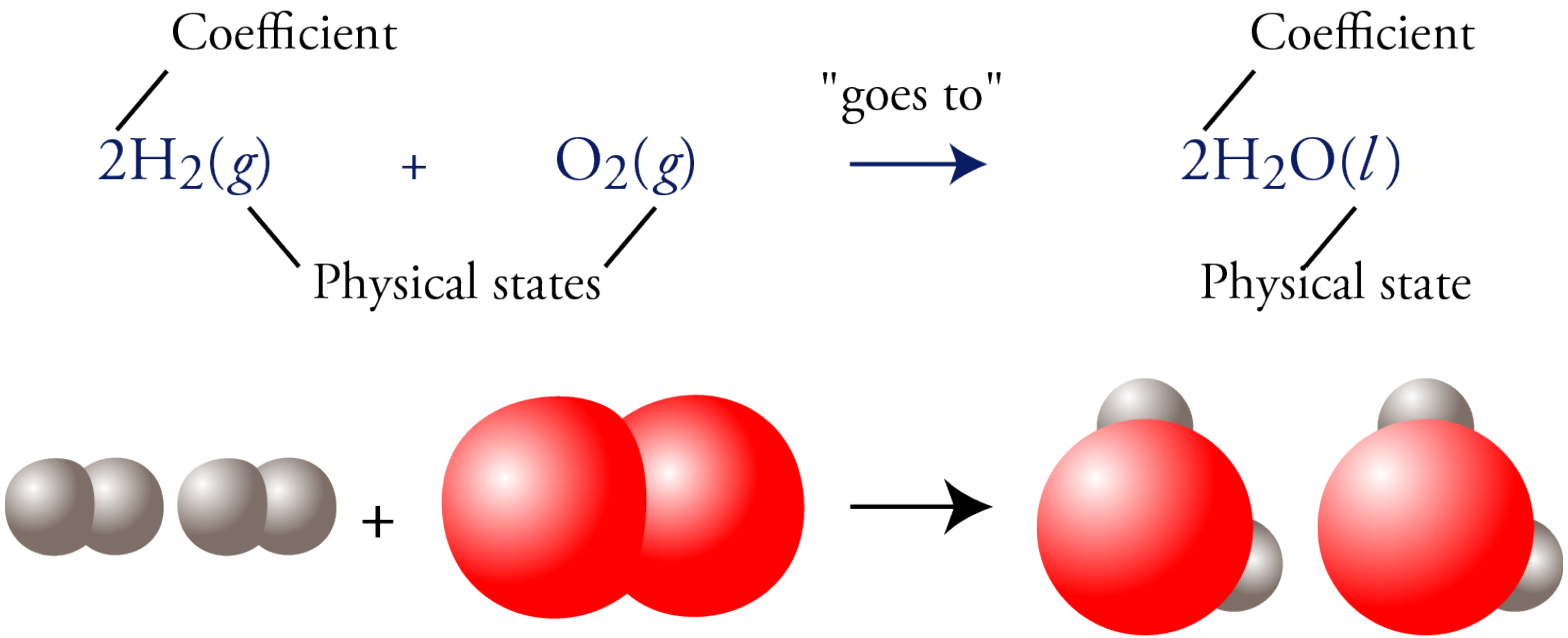
Chemical Equations (3)

- The relative numbers of particles of each reactant and product are indicated by numbers placed in front of the formulas.
  - These numbers are called ***coefficients***. An equation containing correct coefficients is called a balanced equation.
  - If a formula in a balanced equation has no stated coefficient, its coefficient is understood to be 1.

Chemical Equations (4)

- If special conditions are necessary for a reaction to take place, they are often specified above the arrow.
  - Some examples of special conditions are electric current, high temperature, high pressure, or light.

Chemical Equation Example



Special Conditions

A special condition

$$2H_2O(l) \xrightarrow{\text{Electric current}} 2H_2(g) + O_2(g)$$

This indicates the continuous addition of heat.

$$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$$

Decomposition Reactions

- In ***decomposition reactions***, one compound is converted into two or more simpler substances.

$$2H_2O(l) \xrightarrow{\text{Electric current}} 2H_2(g) + O_2(g)$$

$$2C_7H_5N_3O_6 \text{ (TNT)}$$

$$\rightarrow 7CO + 7C + 5H_2O + 3N_2$$

Chemical Explosives

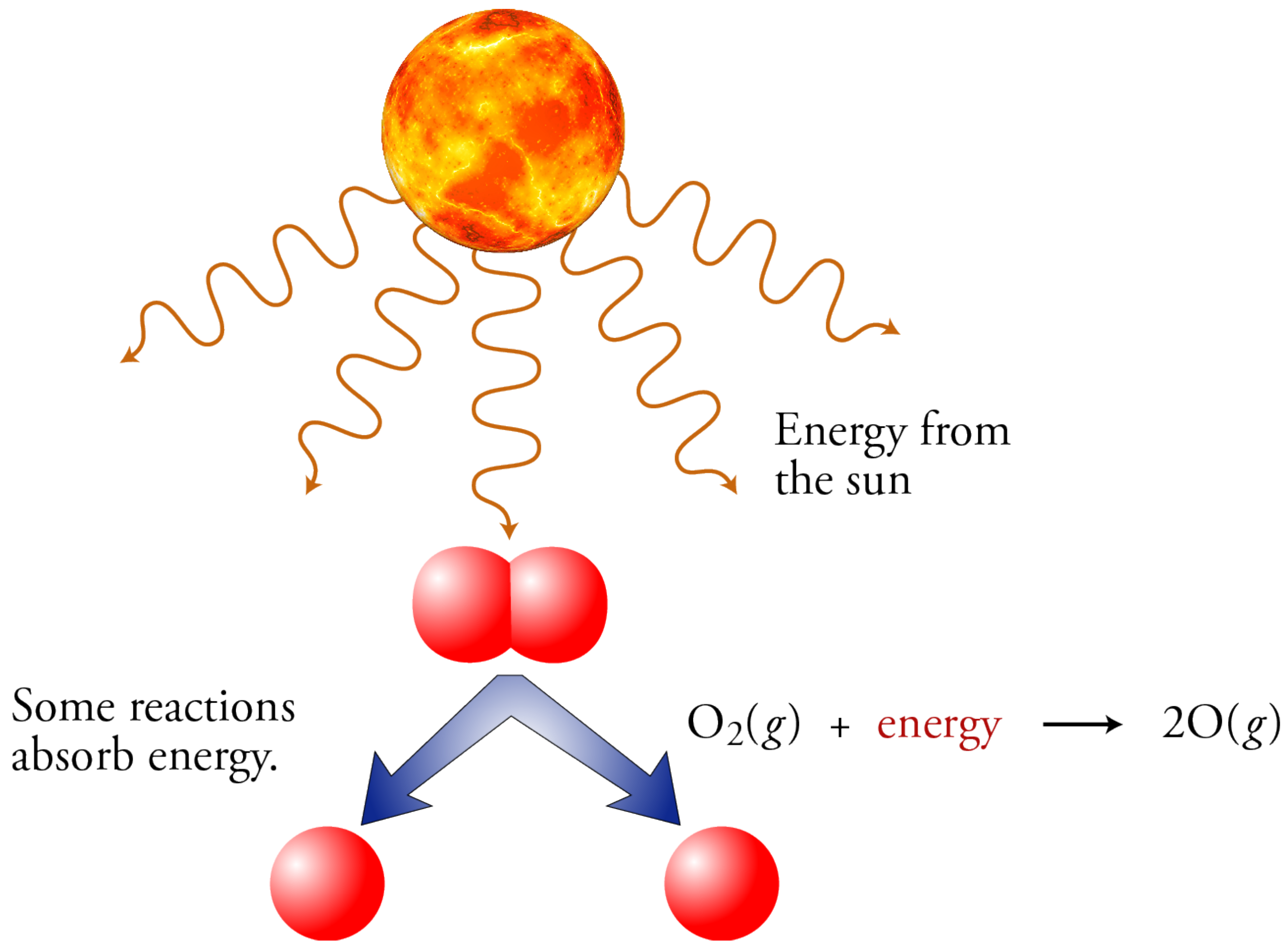
- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the gas.

Some Chemical Changes Release Energy

Combustion of Methane

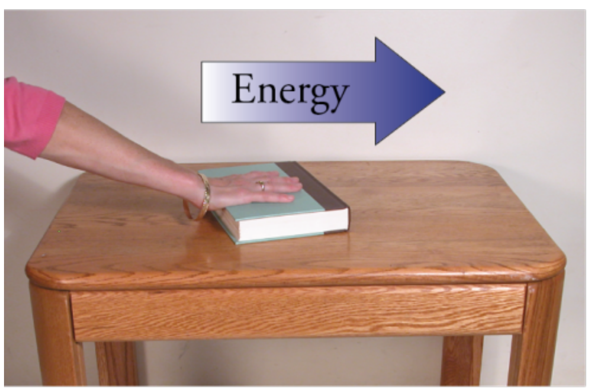
$$CH_4(g) + 2O_2(g)$$
$$\rightarrow CO_2(g) + 2H_2O(l) +$$

Some Chemical Changes Absorb Energy

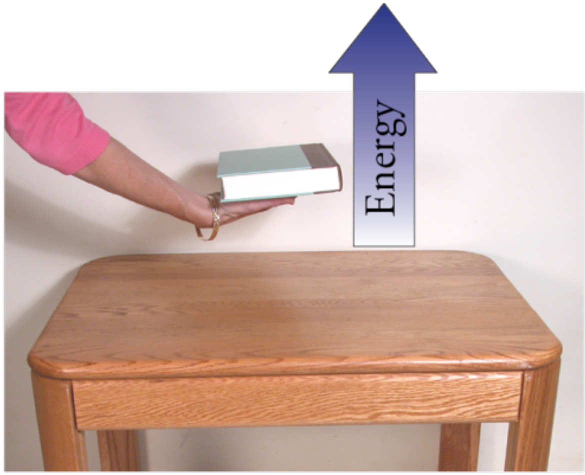


Energy Terms

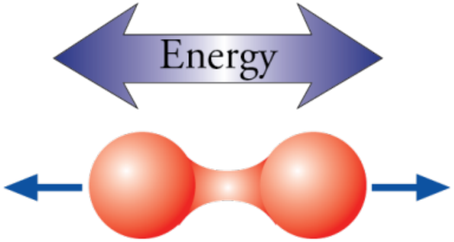
- **Energy** = the capacity to do work
- **Work**, in this context, may be defined as what is done to move an object against some sort of resistance.



Energy is required to push a book across a table and overcome the resistance to movement due to friction.



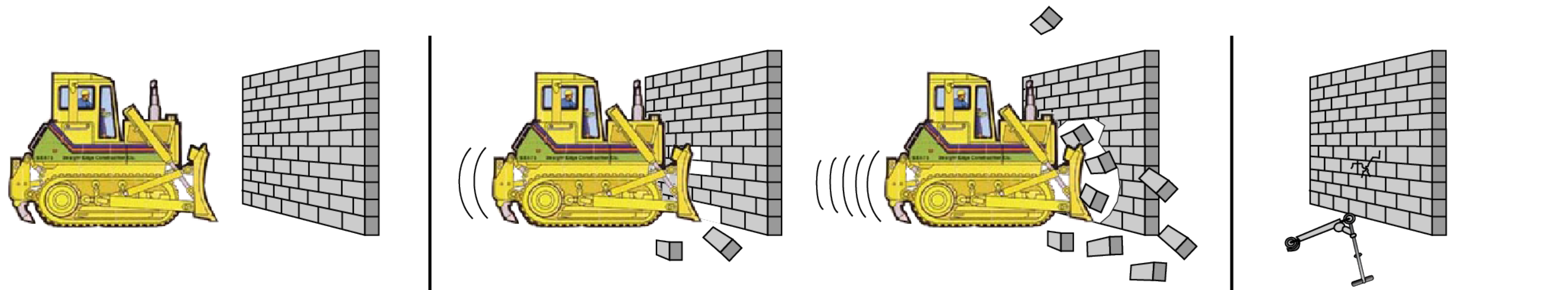
Energy is required to lift a book and overcome the resistance to movement due to gravity.



Energy is required to separate two atoms in a molecule and overcome the resistance to movement due to the chemical bond between them.

Two Types of Energy

- **Kinetic Energy** = the energy of motion
  $= 1/2\ m\mu^2$



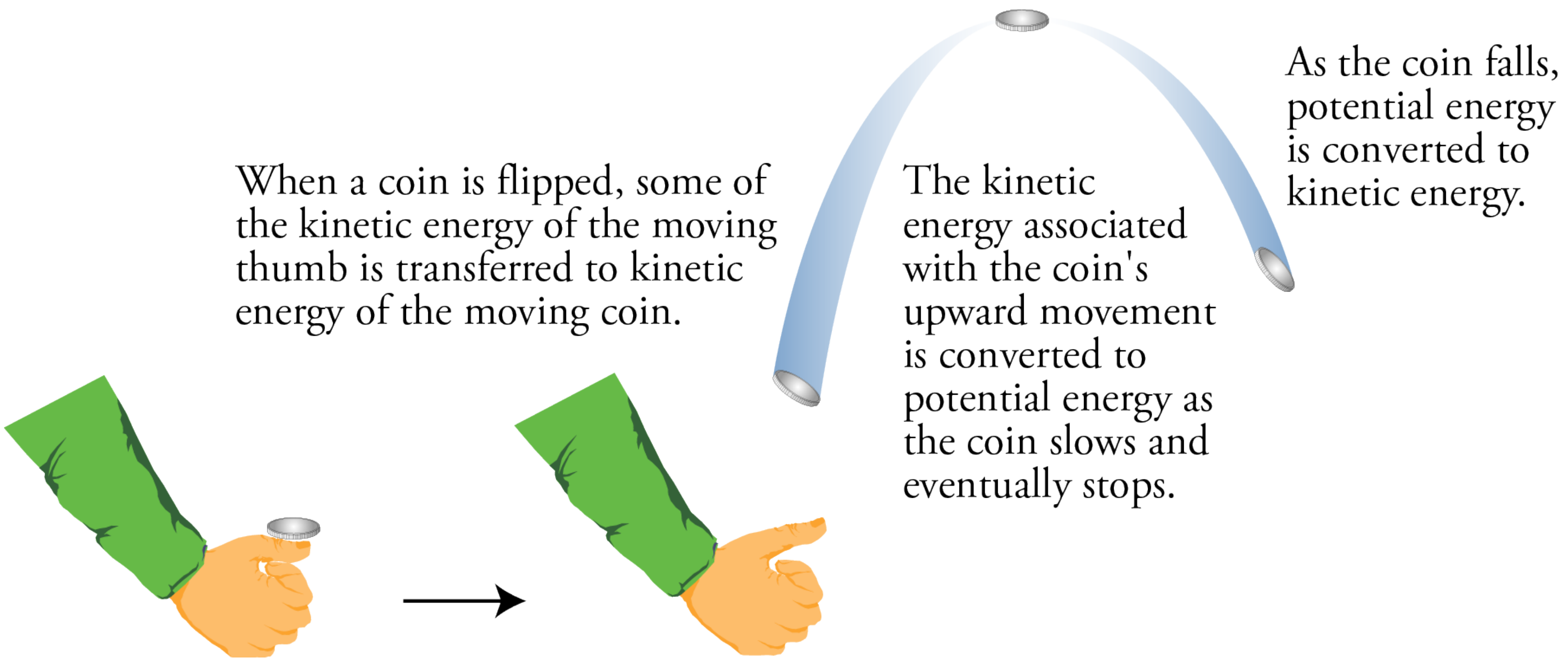
A stationary buldozer does not have the capacity to do the work of moving a wall.

The faster moving bulldozer does more of the work of moving the wall. The faster an object moves, the more work it can do, and the more kinetic energy it has.

A scooter moving at the same velocity as a bulldozer will do less work and therefore has less energy.

- **Potential Energy** = energy by virtue of position or state

Law of Conservation of Energy



Endergonic Change

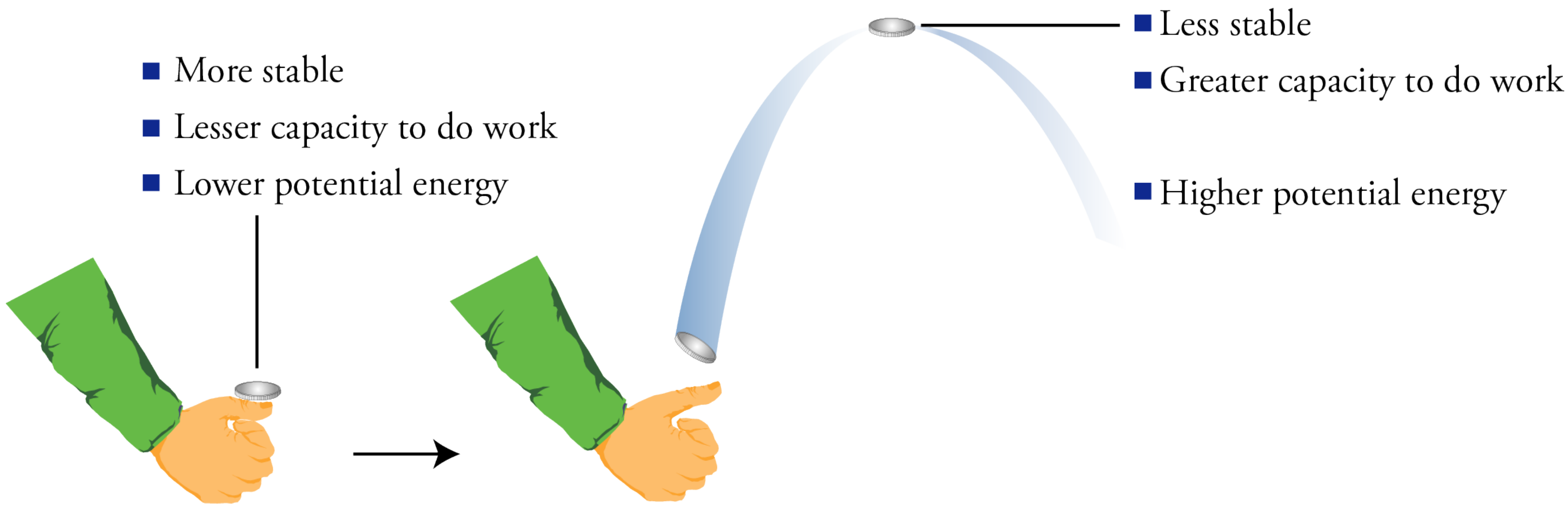
more stable + energy → less stable system

lesser capacity to do work + energy → greater capacity to do work

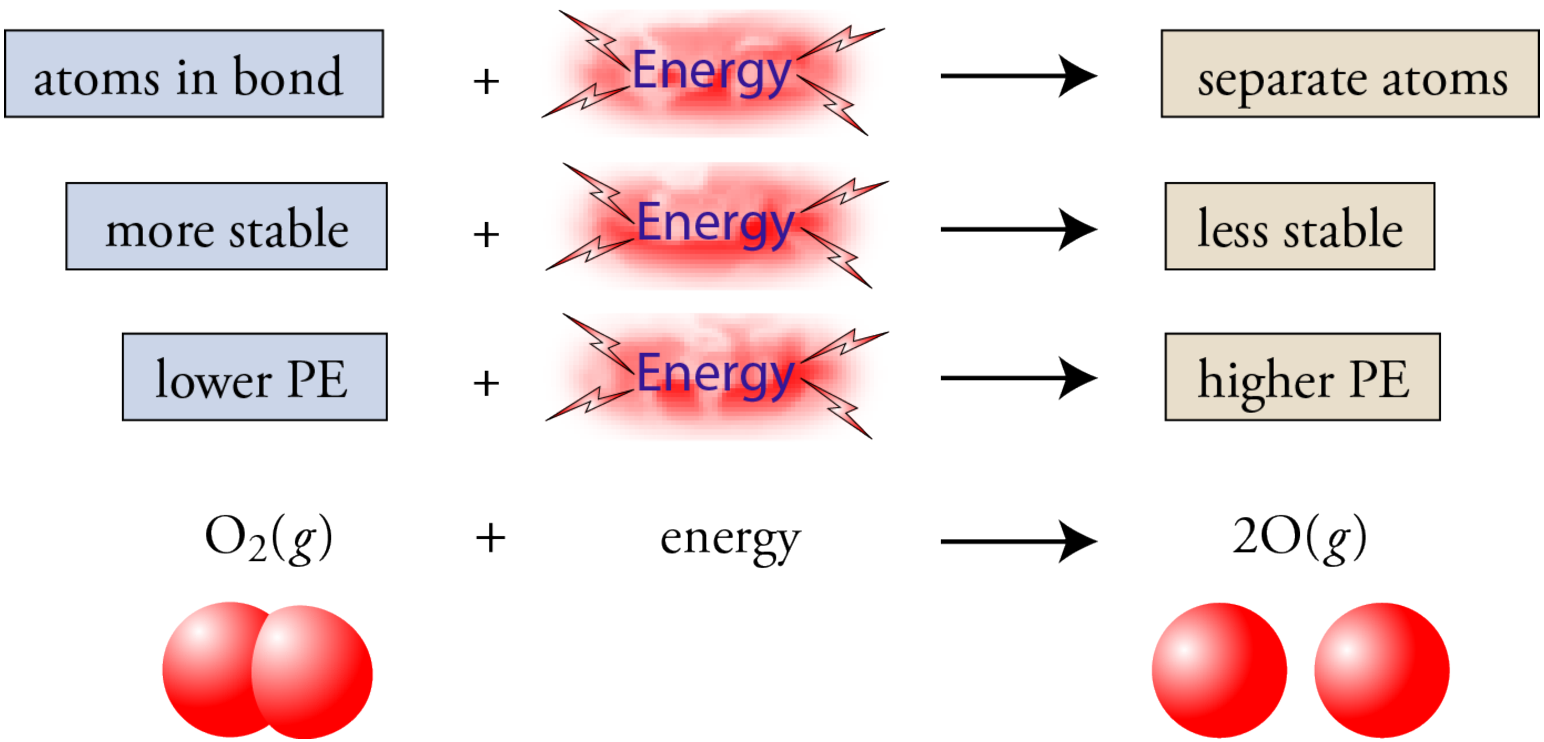
lower PE + energy → higher PE

coin in hand + energy → coin in air above hand

Coin and Potential Energy



Bond Breaking and Potential Energy



Exergonic Change

less stable system $\rightarrow$ more stable + energy

greater capacity to do work $\rightarrow$ lesser capacity to do work + energy

higher PE $\rightarrow$ lower PE + energy

coin in air above hand $\rightarrow$ coin on ground + energy

Bond Making and Potential Energy

separate atoms → atoms in bond + Energy

less stable → more stable + Energy

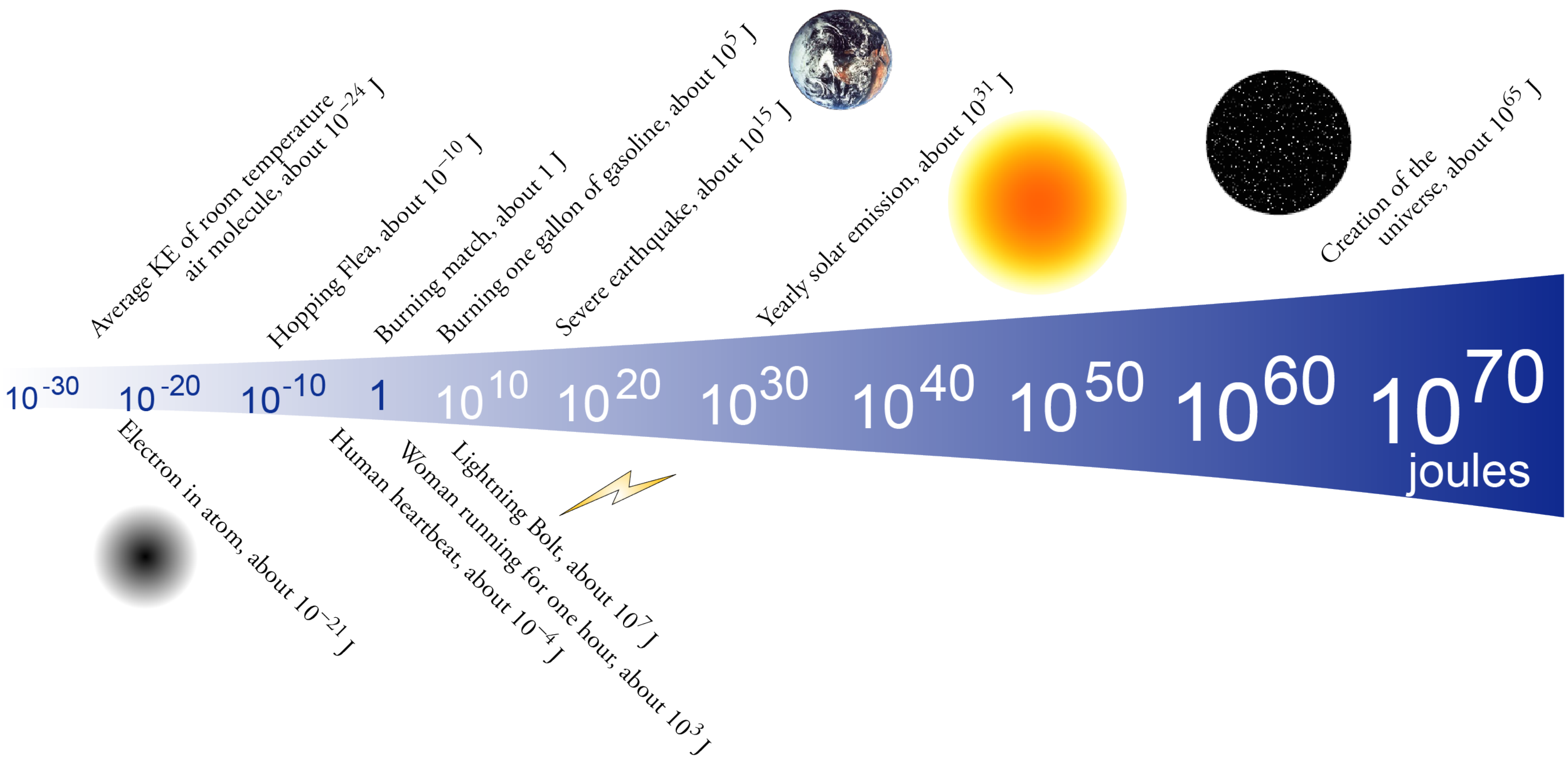
higher PE → lower PE + Energy

$$O(g) + O_2(g) \longrightarrow O_3(g) + \text{energy}$$

Units of Energy

- 4.184 J = 1 cal
- 4.184 kJ = 1 kcal
- 4184 J = 1 Cal (dietary calorie)
- 4.184 kJ = 1 Cal

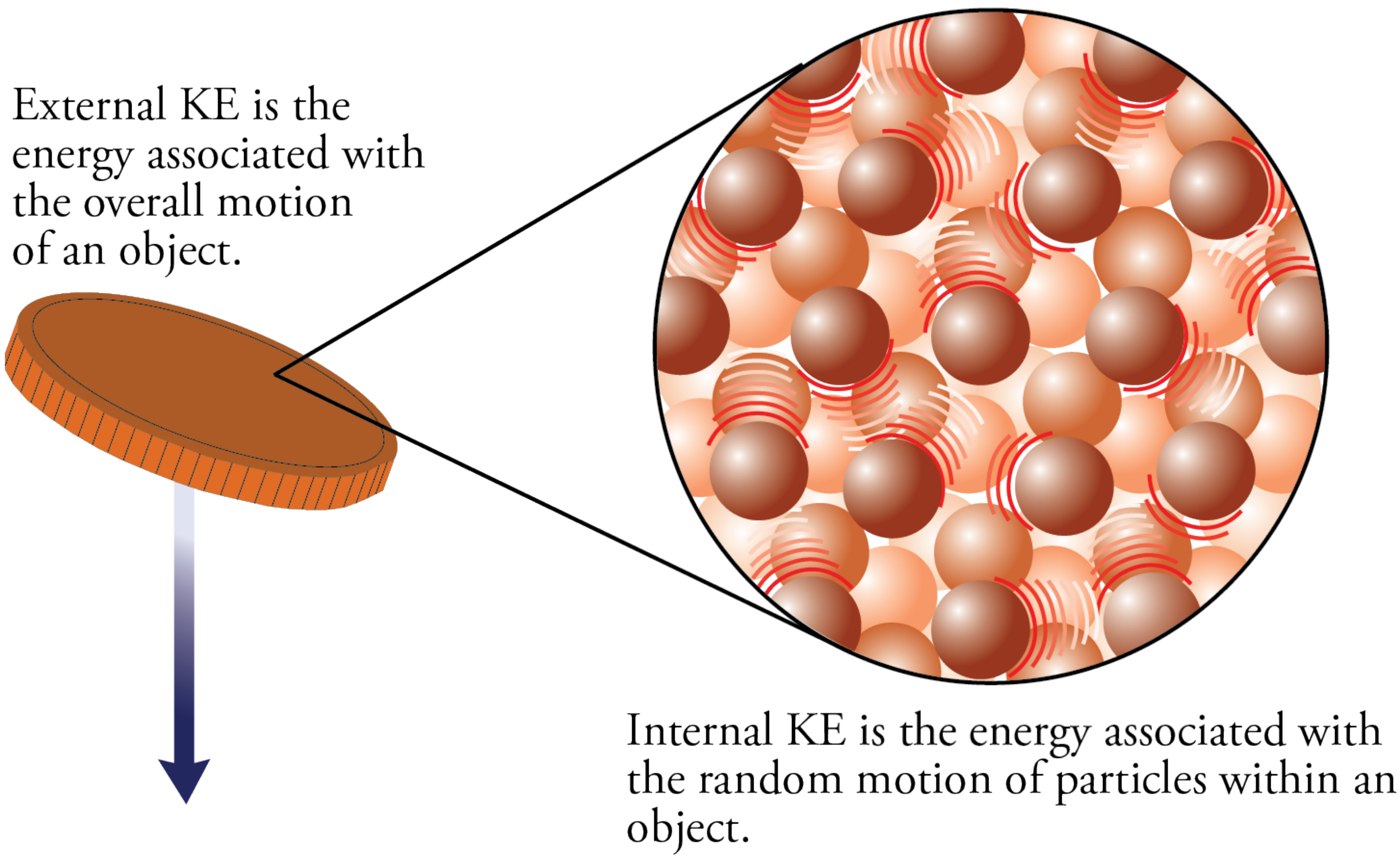
Approximate Energy of Various Events



More Terms

- **External Kinetic Energy** = Kinetic energy associated with the overall movement of a body
- **Internal Kinetic Energy** = Kinetic energy associated with the random motion of the particles within a body

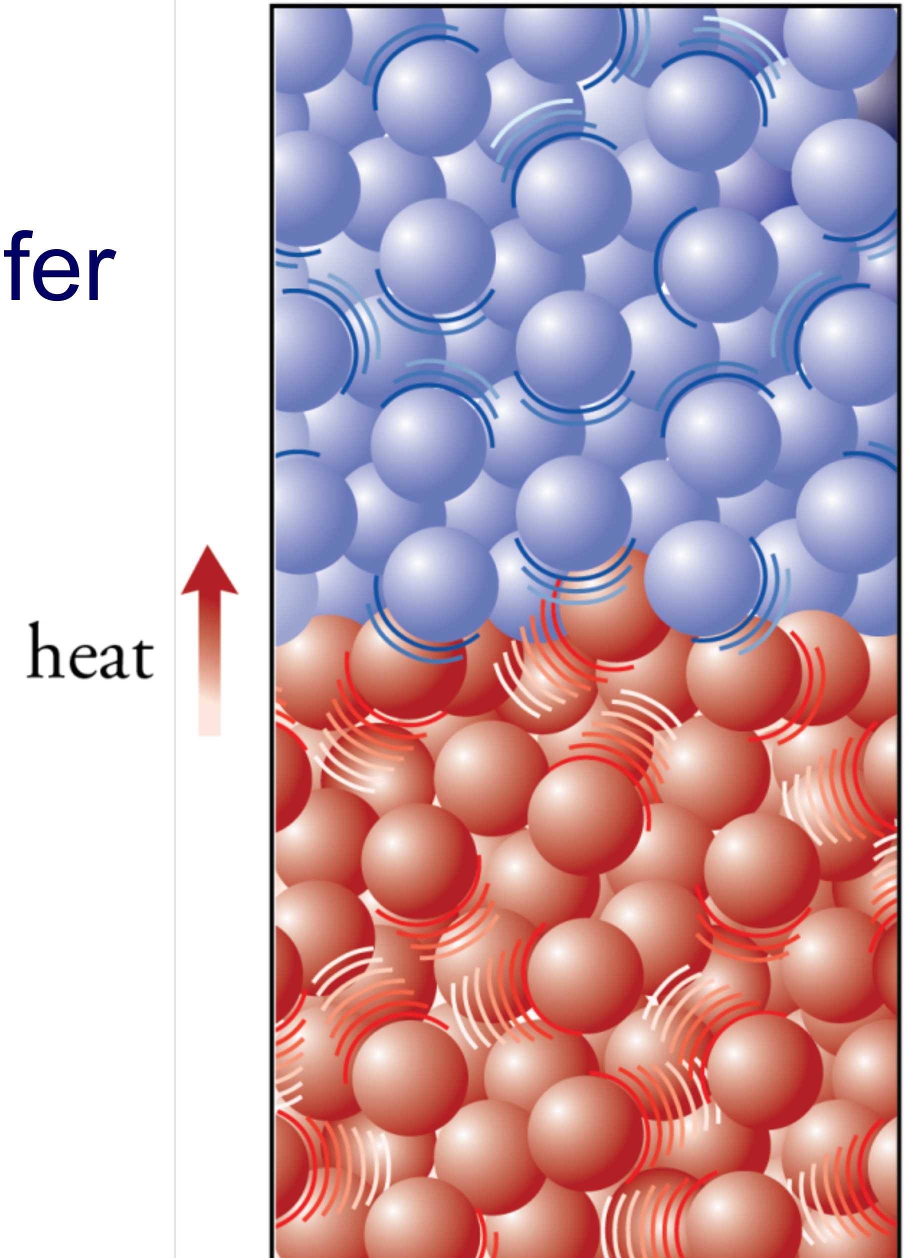
External and Internal Kinetic Energy



Heat

- **Heat** = Energy transfer from a region of higher temperature to a region of lower temperature due to collisions of particles.

Heat Transfer



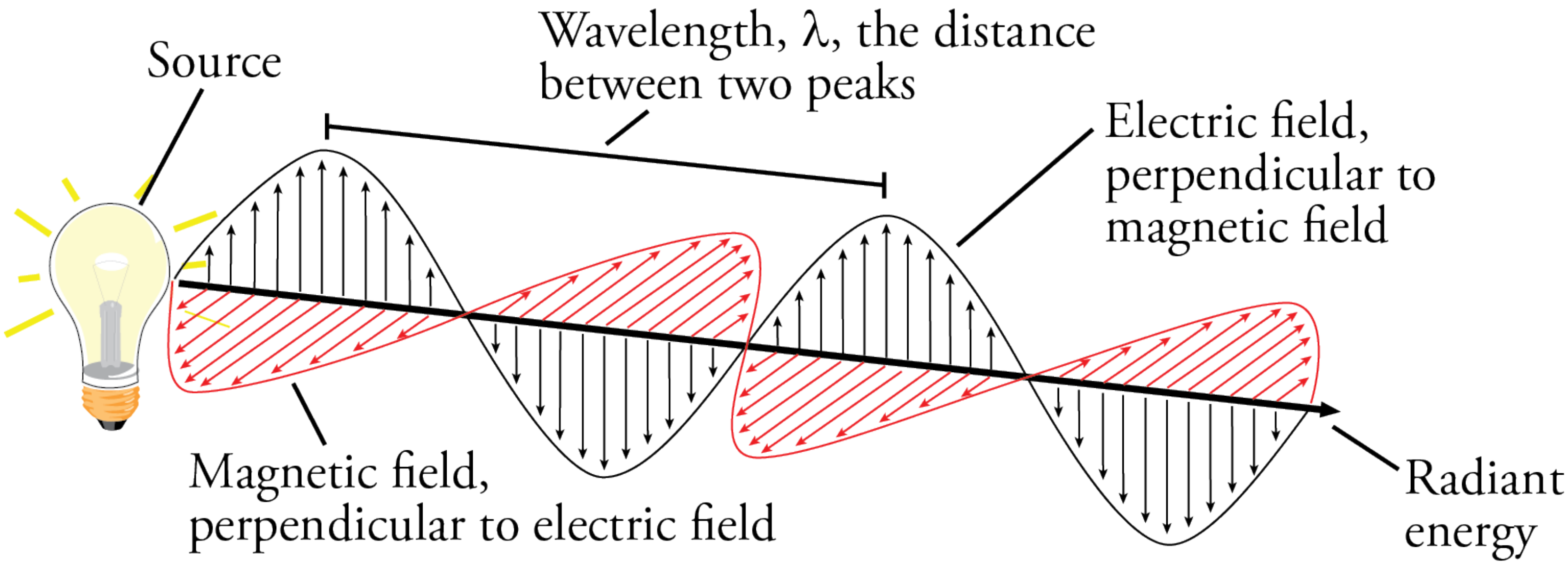
Lower-temperature object
↓
Lower average force of collisions
↓
Particles speed up when they collide with particles of the higher-temperature object.
↓
Increased energy

Higher-temperature object
↓
Higher average force of collisions
↓
Particles slow down when they collide with particles of the lower-temperature object.
↓
Decreased energy

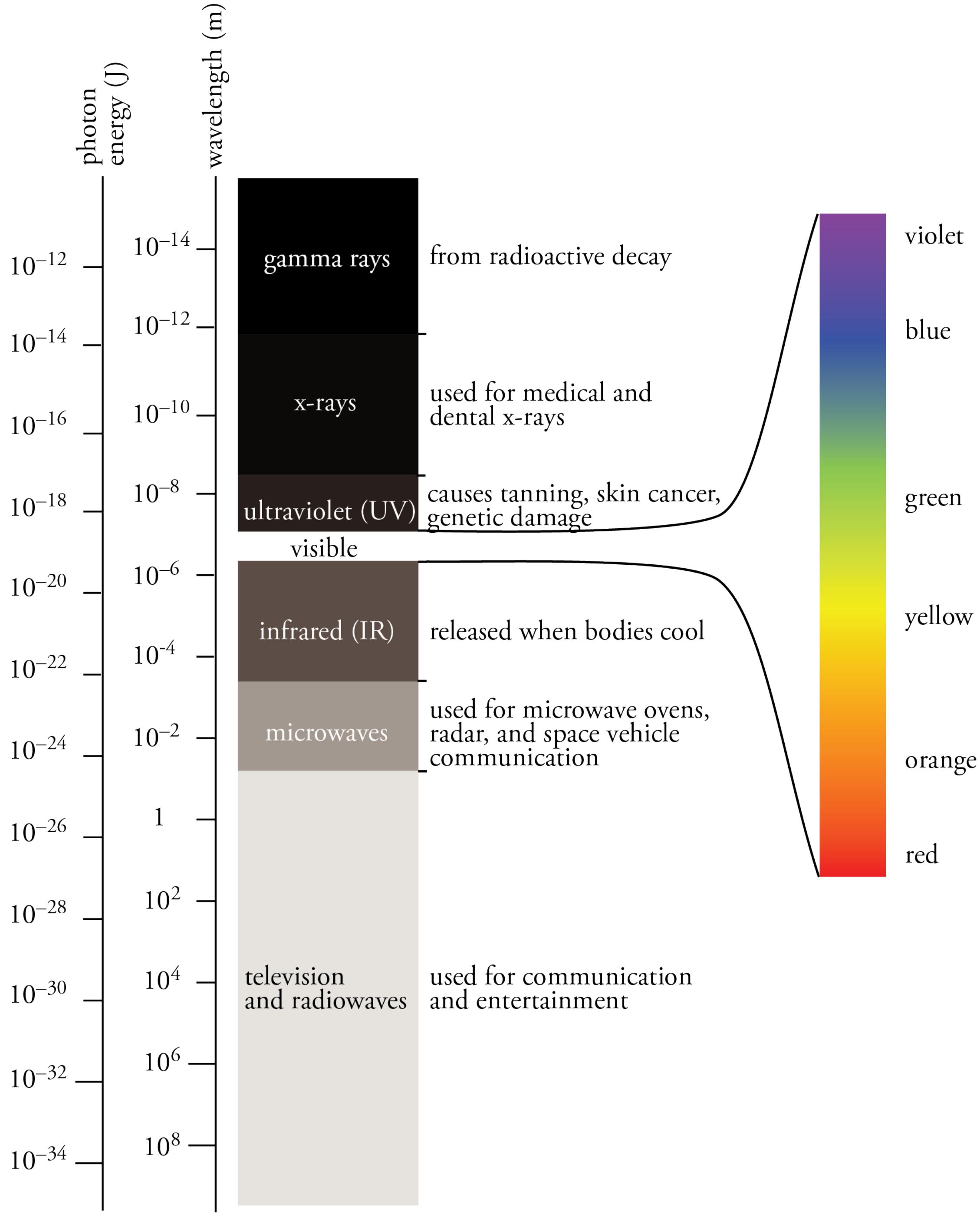
Radiant Energy

- **Radiant Energy** is electromagnetic energy that behaves like a stream of particles.
- It has a dual Nature
  - Particle
    - photons = tiny packets of radiant energy
    - 10^{17} photons/second from a flashlight bulb
  - Wave
    - oscillating electric and magnetic fields
    - describes effect on space, not true nature of radiant energy

A Light Wave’s Electric and Magnetic Fields



Radiant Energy Spectrum



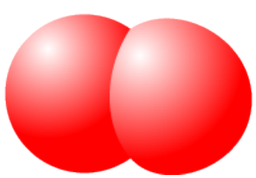
Bond Breaking and Potential Energy

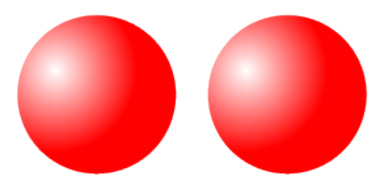
atoms in bond + Energy ⟶ separate atoms

more stable + Energy ⟶ less stable

lower PE + Energy ⟶ higher PE

$$O_2(g) + \text{energy} \longrightarrow 2O(g)$$





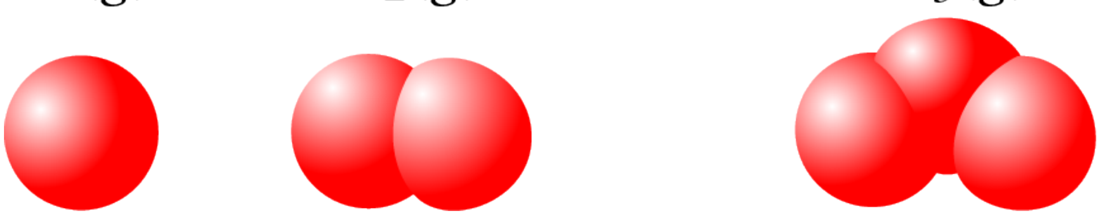
Bond Making and Potential Energy

separate atoms → atoms in bond + Energy

less stable → more stable + Energy

higher PE → lower PE + Energy

$$O(g) + O_2(g) \longrightarrow O_3(g) + \text{energy}$$



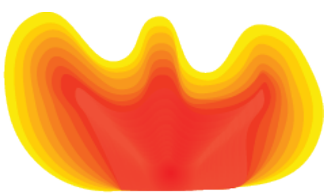
Exergonic (Exothermic) Reaction

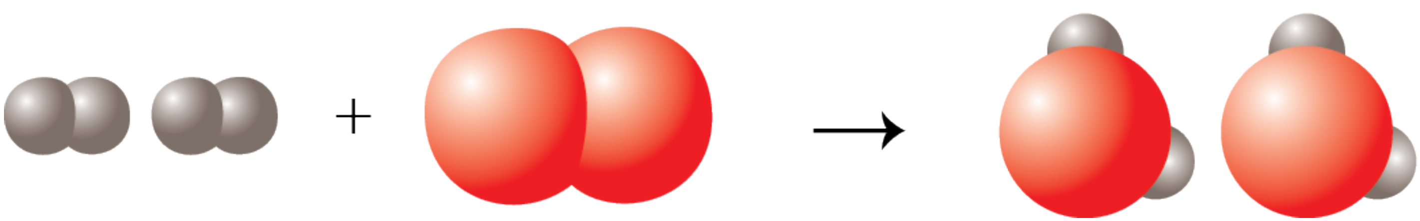
weaker bonds → stronger bonds + energy

less stable → more stable + energy

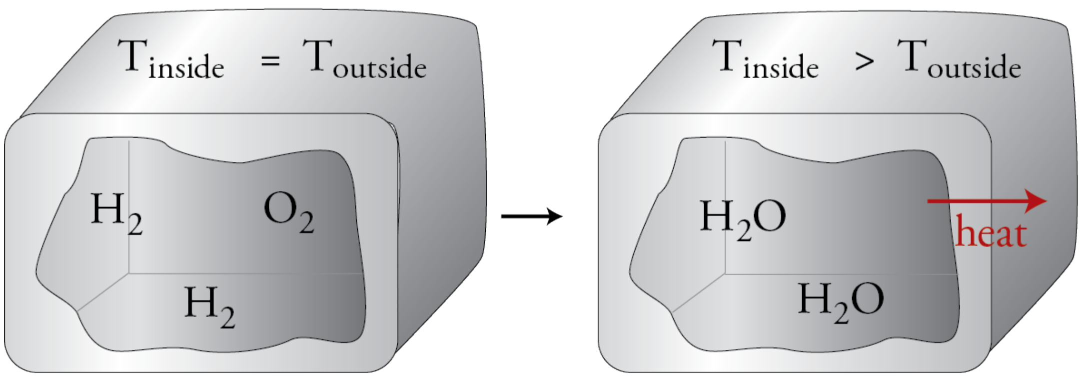
higher PE → lower PE + energy

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) +$$





Exothermic Reaction



Stronger bonds → More stable

↓

Energy released ← Lower PE

↓

Increases KE_{ave} of product particles

↓

Increased T → $T_{inside} > T_{outside}$

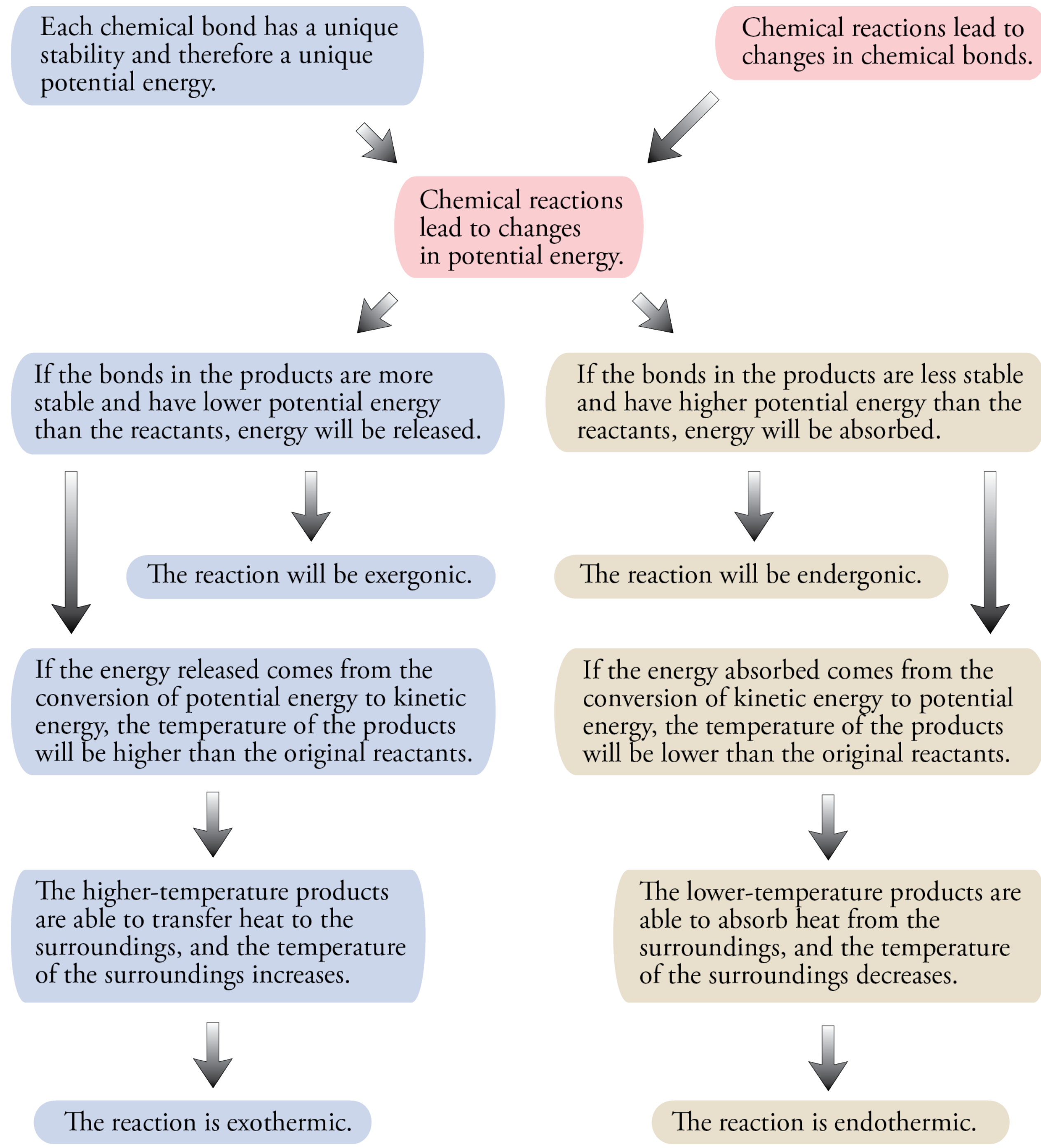
↓

Heat transferred to surroundings

↓

Exothermic

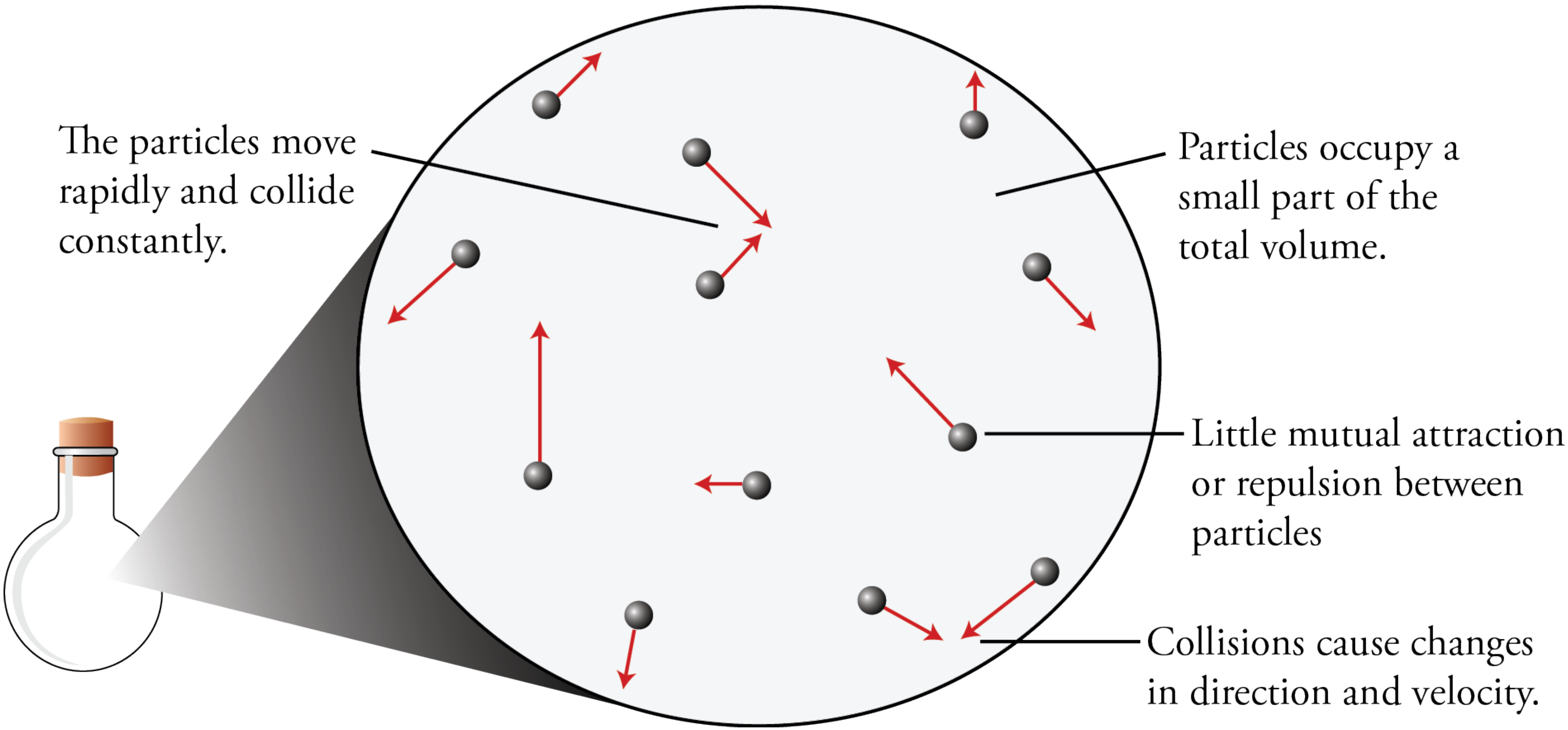
Energy and Chemical Reactions



Chemical Explosives

- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the gas.

Gas


The particles move rapidly and collide constantly.
Particles occupy a small part of the total volume.
Little mutual attraction or repulsion between particles
Collisions cause changes in direction and velocity.

Gas Model

- Gases are composed of tiny, widely-spaced particles.
  - For a typical gas, the average distance between particles is about ten times their diameter.

Gas Model (cont.)

- Because of the large distance between the particles, the volume occupied by the particles themselves is negligible (approximately zero).
  - For a typical gas at room temperature and pressure, the gas particles themselves occupy about 0.1% of the total volume. The other 99.9% of the total volume is empty space. This is very different than for a liquid for which about 70% of the volume is occupied by particles.

Gas Model (cont.)

- The particles have rapid and continuous motion.
  - For example, the average velocity of a helium atom, He, at room temperature is over 1000 m/s (or over 2000 mi/hr). The average velocity of the more massive nitrogen molecules, N_2, at room temperature is about 500 m/s.
  - Increased temperature means increased average velocity of the particles.

Gas Model (cont.)

- The particles are constantly colliding with the walls of the container and with each other.
  - Because of these collisions, the gas particles are constantly changing their direction of motion and their velocity. In a typical situation, a gas particle moves a very short distance between collisions. Oxygen, O_2, molecules at normal temperatures and pressures move an average of 10^{-7} m between collisions.

Gas Model (cont.)

- There is no net loss of energy in the collisions. A collision between two particles may lead to each particle changing its velocity and thus its energy, but the increase in energy by one particle is balanced by an equal decrease in energy by the other particle.

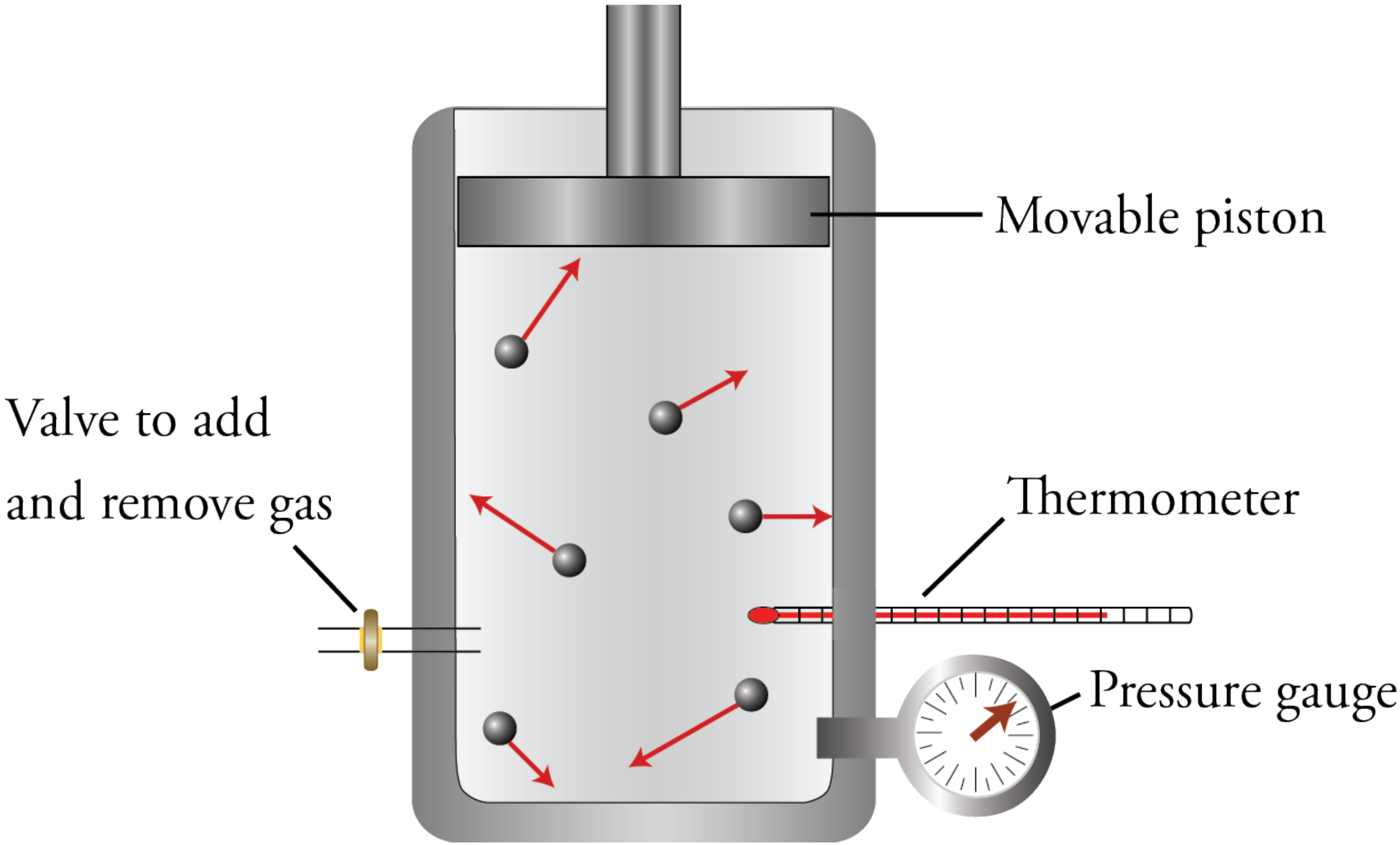
Gas Properties and their Units

- Pressure (P) = Force/Area
  - units
    - 1 atm = 101.325 kPa = 760 mmHg = 760 torr
    - 1 bar = 100 kPa = 0.9869 atm = 750.1 mmHg
- Volume (V)
  - unit usually liters (L)
- Temperature (T)
  - ? K = --- °C + 273.15
- Number of gas particles (n)

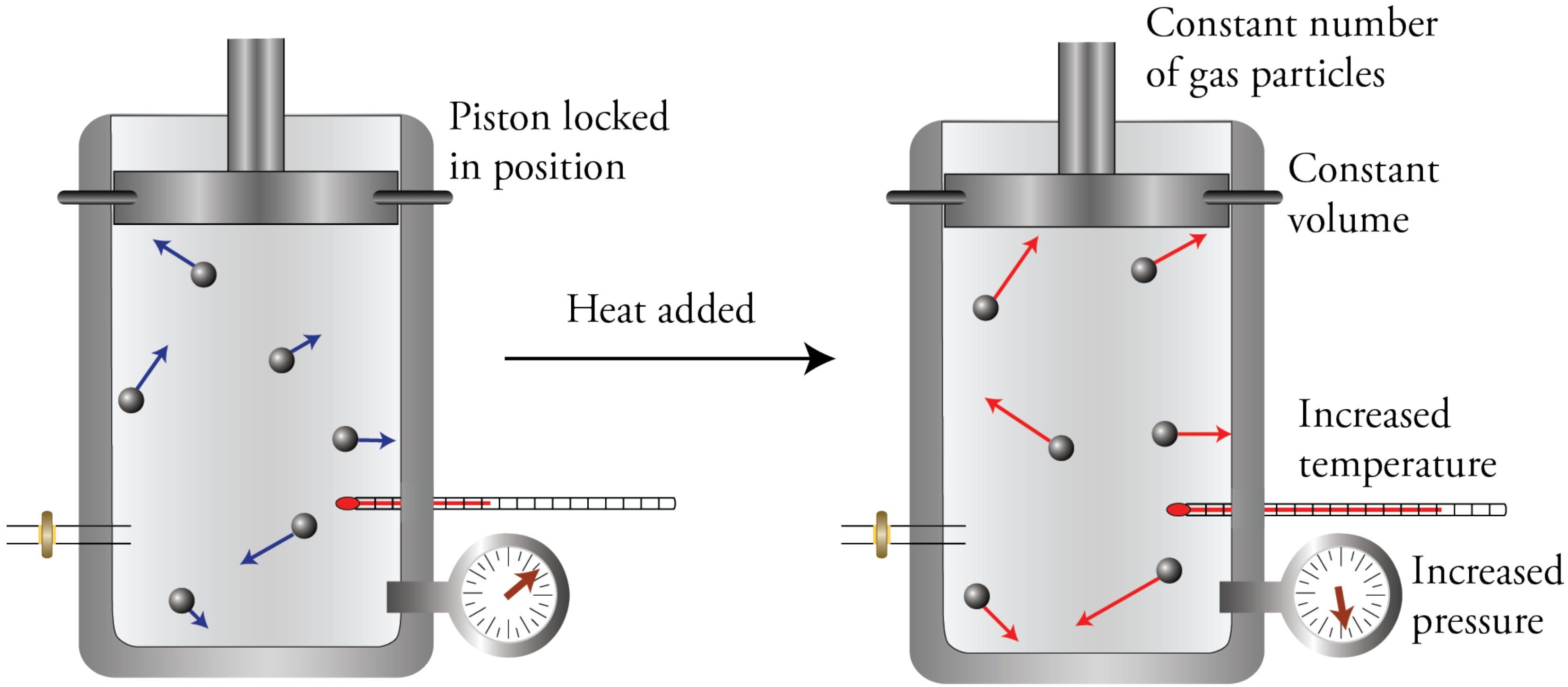
Two Gas Laws

- $P \propto T$ when n and V are constant
- $P \propto n$ when V and T are constant

Apparatus for Demonstrating Relationships Between Properties of Gases



Increased Temperature Leads to Increased Pressure



P α T   if n and V are constant

http://preparatorychemistry.com/Bishop_Gay_Lussac_Law_Flash1.htm

Relationship between P and T

Increased temperature

↓

Increased average velocity of the gas particles

↙ ↘

Increased number of collisions with the walls

Increased force per collision

↘ ↙

Increased total force of collisions

↓

$$\text{Increased } \frac{\text{force due to collisions}}{\text{area of wall}}$$

↓

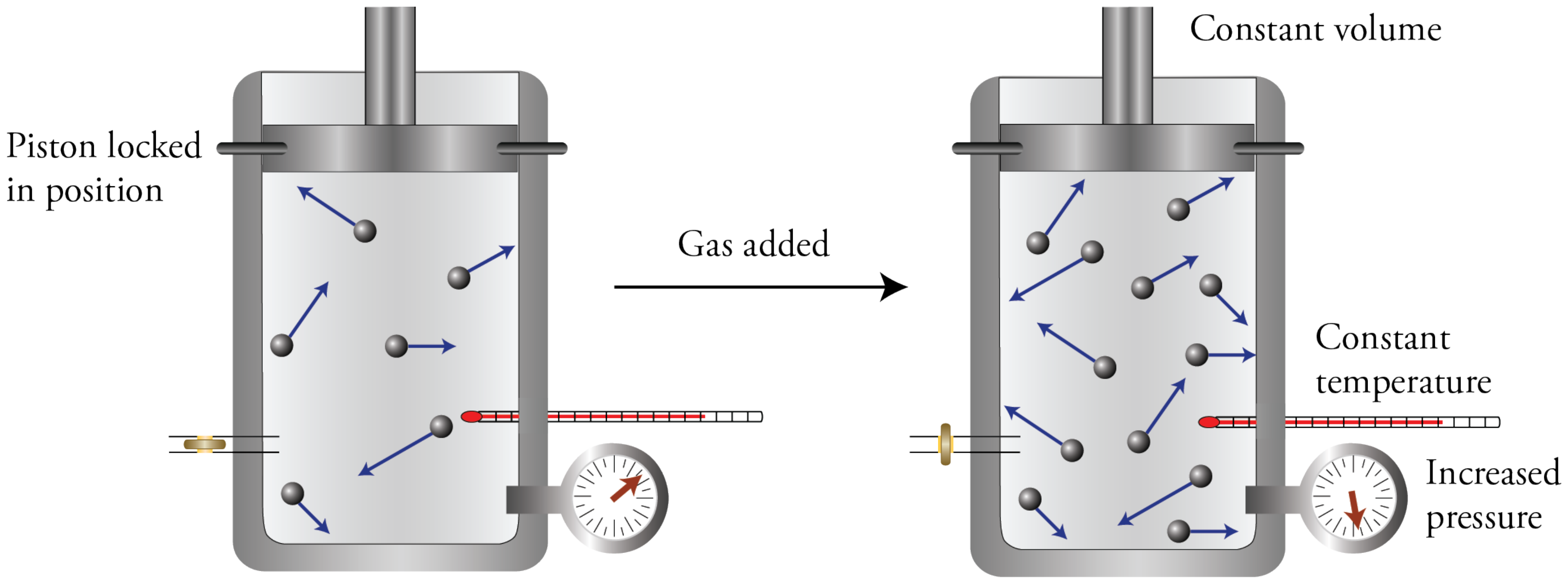
Increased gas pressure

Gay-Lussac's Law

- The pressure of an ideal gas is directly proportional to the Kelvin temperature of the gas if the volume and moles of gas are constant.

$$P \propto T \quad \text{if } V \text{ and } n \text{ are constant}$$

Increased Moles of Gas Leads to Increased Pressure



$P \propto n$ if T and V are constant

http://preparatorychemistry.com/Bishop_Moles_Pressure_Law_Flash1.htm

Relationship between n and P

Increased number of gas particles

↓

Increased number of collisions with the walls

↓

Increased total force of collisions

↓

Increased gas pressure

Relationship Between Moles of Gas and Pressure

- If the temperature and the volume of an ideal gas are held constant, the moles of gas in a container and the gas pressure are directly proportional.

  $P \propto n$ if T and V are constant

Chemical Explosives

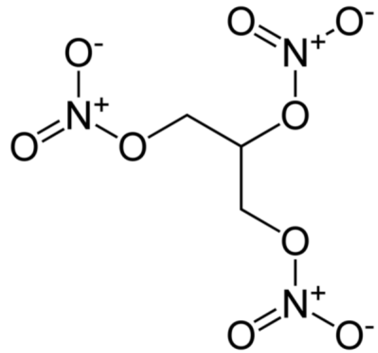
- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the gas.

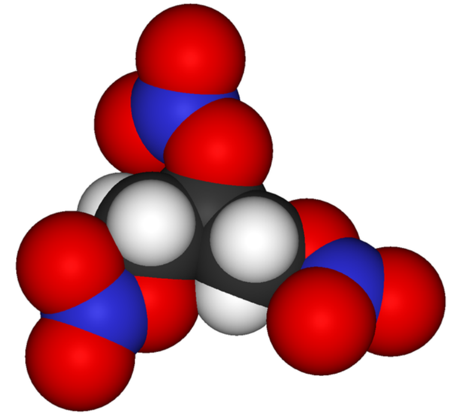
Combustion of Propylamine

$$4C_3H_7NH_2(l) + 21O_2(g)$$
$$\rightarrow 12CO_2(g) + 18H_2O(g) + 2N_2(g) + 8668\ kJ$$

- Releases a lot of energy
- Produces a lot of gas
- Does this too slowly to yield the high temperature and pressure necessary for the substance to be explosive.
- Goal: to speed up the process
- Solution: add the oxygen atoms necessary for the reaction to the combustible material

Nitroglycerine





$4C_3H_5N_3O_9(l)$

$$\rightarrow 6N_2(g) + 10H_2O(g) + 12CO_2(g) + O_2(g) + 9174 \text{ kJ}$$

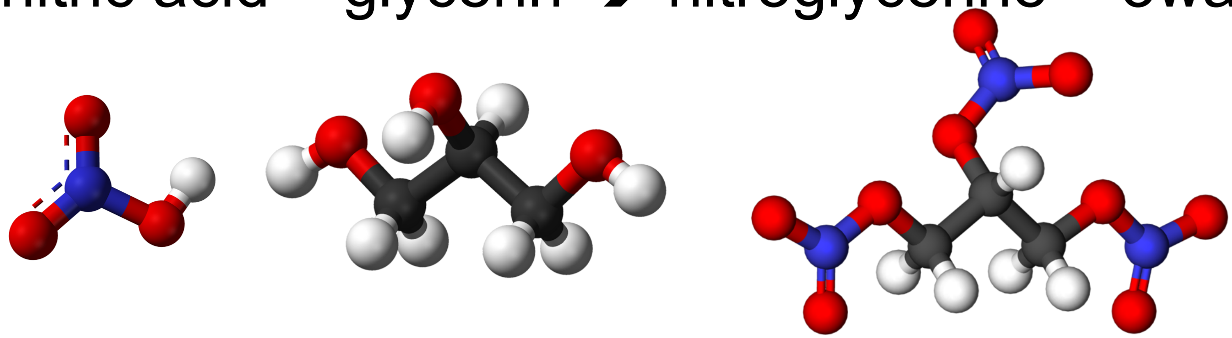
- First and most widely produced nitrate ester explosive
- Produces gases that would have a volume 1200 times the original volume at room temperature and pressure.
- Temperature rises to about 5000 °C (about 9000 °F)
- Produces a shock wave moving over 20 times the speed of sound – detonation velocity ≅ 7700 m/s

http://www.youtube.com/watch?v=r17czTWHFmU

Nitroglycerine Production

- Starts with 1:1 mixture of concentrated sulfuric acid and concentrated nitric acid.
- Reaction with glycerin is exothermic, so glycerin is added slowly and the mixture is cooled to keep the mixture at about 22 °C (72 °F)
- Not very difficult process, but need to be done very carefully to avoid danger

3nitric acid + glycerin ➔ nitroglycerine + 3water

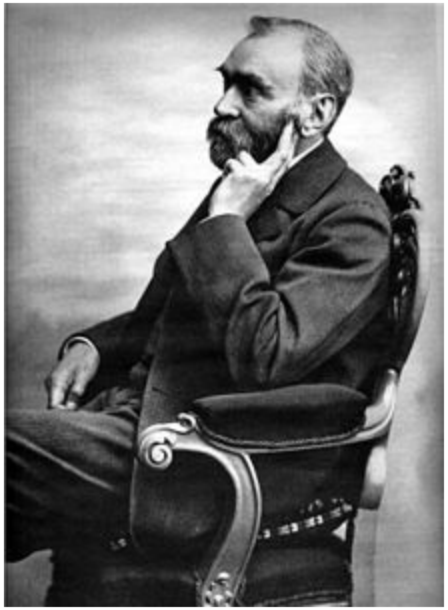


Nitroglycerine (cont)

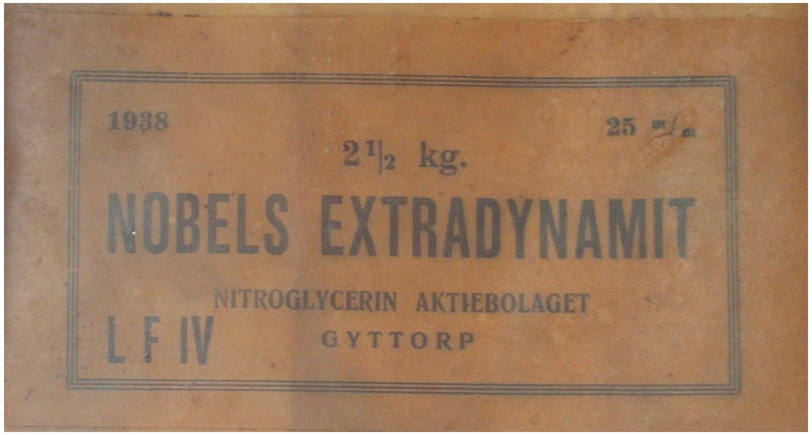
- Very sensitive to impact, so dangerous when pure
- Liquid forms microscopic bubbles that are more likely to react and start the detonation.
- Mixed with other substances and used in dynamite and propellants.
- More stable when absorbed in powdered absorbent (e.g. diatomaceous earth or sawdust), which minimizes microscopic bubbles.
  - Diatomaceous earth = ground up sedimentary rock formed from fossilized diatoms

Alfred Nobel's Contribution

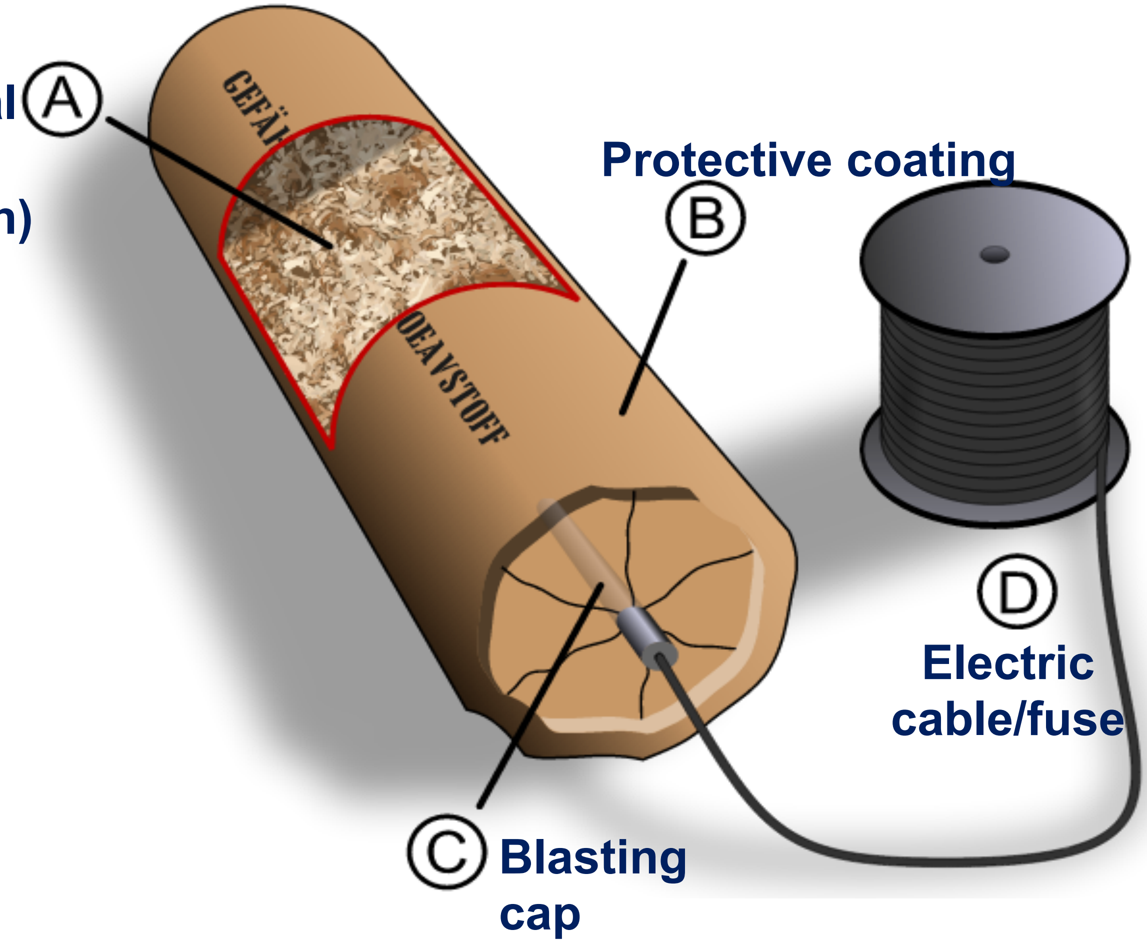
- Swedish chemist, engineer, innovator, and armaments manufacturer with 355 patents
- Most famous patent: Dynamite
- Invented first plastic explosive: Gelignite or 'blasting gelatin'
- Became rich due to these lucrative patents
- Willed his fortunes to creation of the "Nobel Prize"

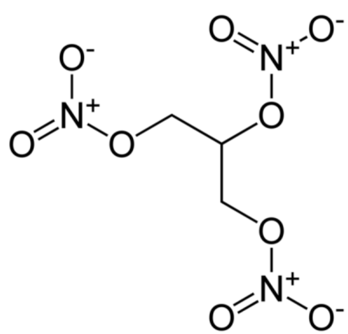


1833-1896



Dynamite
(Originally, “Nobel’s Blasting Powder)





Invented in 1860s, dynamite was the first safe and manageable chemical explosive.

Terms Related to Explosives

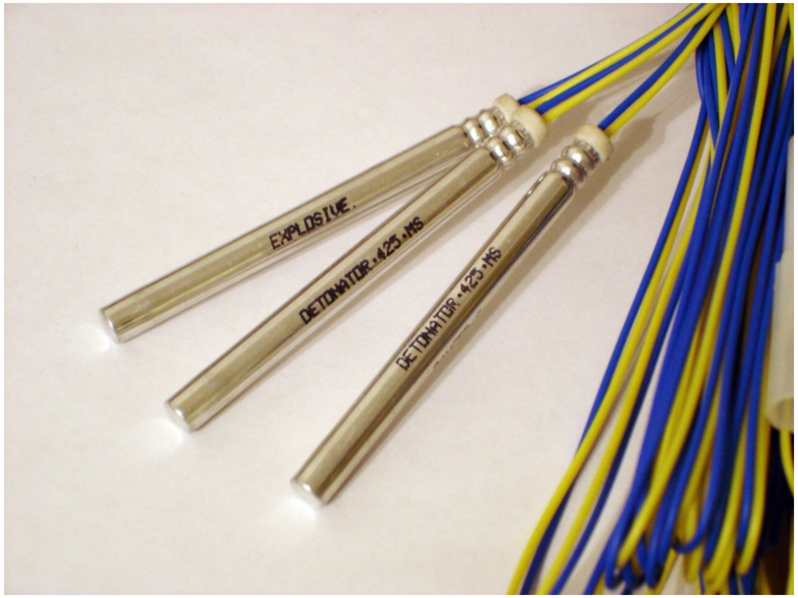
- **Explosion** = large-scale, noisy, rapid expansion of matter into a volume greater than the original volume
  - Can be due to a very fast *burning* of a material
  - Can be due to *detonating* an explosive material
- **Burning** (or **deflagration**) = relatively slow reaction (propagation less than the speed of sound)
- **Detonation** = very fast reaction (propagation greater than speed of sound, about 340 m/s)

Terms Related to Explosives

- **High explosive** = chemical that can detonate
  - **Primary** = very easy to detonate with flame, heat or shock (e.g. lead azide, PbN_6 or $Pb(N_3)_2$)
  - **Secondary** = do not easily go from burning to detonation (e.g. TNT and RDX)
  - **Tertiary** = hardest to detonate = insensitive high explosives, IHE (e.g. ANFO)
- **Low explosive** = cannot be caused to detonate by a common blasting cap
  - **Pyrotechnics** = when burned, produce heat, light, smoke, gas, and/or sound
  - **Propellants** = produce gases used to do mechanical work, such as propel a projectile or push a piston, e.g. black powder (charcoal, sulfur, and potassium nitrate) or nitrocellulose.

Terms Related to Explosives

- **Blasting cap** = a small, sensitive primary explosive device used to detonate a larger, more powerful and less sensitive secondary explosive, such as TNT, dynamite, or plastic explosive.
  - Main explosive designed to be insensitive enough to be easily handled without worry of detonation.
  - Blasting cap can be added just before detonation.



Terms Related to Explosives

- **Shock wave** = a high-pressure wave that moves through material at a speed faster than the speed of sound in that material.
- **Fragments and shrapnel** = missiles, e.g. from casings and other solid materials, that are scattered from an explosion.

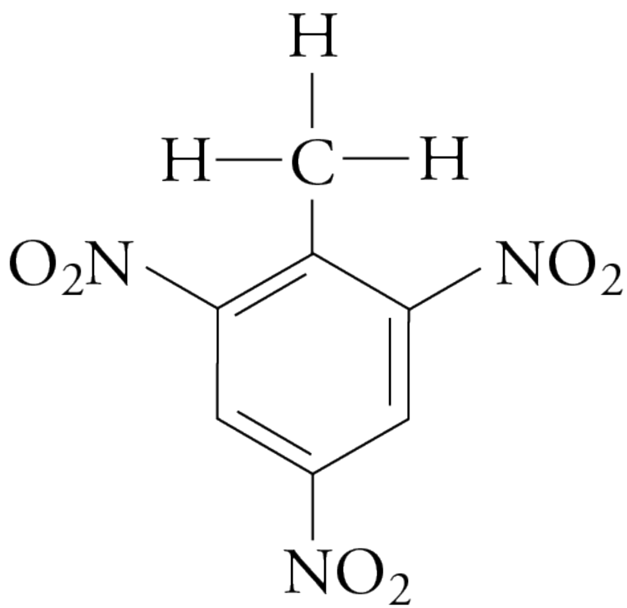
Explosives

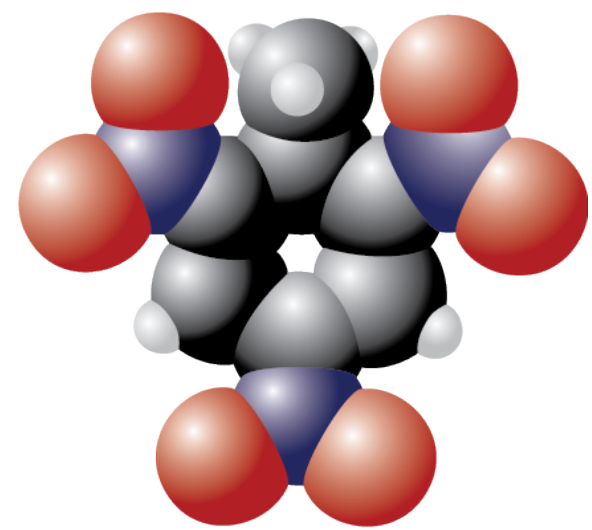
- Most explosives are composed of carbon, nitrogen, hydrogen, and oxygen …$C_cH_hN_nO_o$.
- Guidelines for the order of formation of products
  - Nitrogen forms N_2(g)
  - Hydrogen forms H_2O(g)
  - Any oxygen left converts carbon to CO(g)
  - Any oxygen left converts CO(g) to CO_2(g)
  - Any oxygen left forms O_2(g)
  - Traces of NO(g) and NO_2(g) are always formed.

Underoxidized or Fuel Rich Explosives

- Not enough oxygen to form CO_2
- Trinitrotoluene, TNT

$$2C_7H_5N_3O_6(s) \rightarrow 3N_2(g) + 5H_2O(g) + 7CO(g) + 7C(s)$$





TNT

Trinitrotoluene, TNT

- More produced than any other military explosive
- Stable, insensitive to shock, and nontoxic
- Carbon solid formed causes sooty appearance when pure TNT detonated
- Often mixed with oxygen-rich substances (e.g. ammonium nitrate) to convert the carbon to CO or CO_2, yielding more energy.
- Low melting point (81 °C) and relative safety so often blended with other explosives.
- Detonation velocity of $\cong$ 6900 m/s

TNT-Equivalent

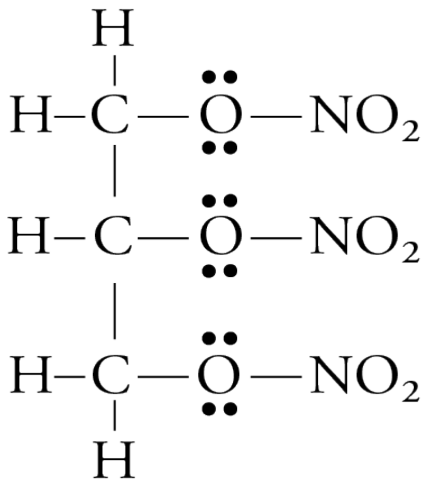
- **TNT Equivalent** = a measure of the energy released in an explosion
- **Ton** (or tonne) **of TNT** = 4.184 GJ (gigajoule or 10^9 joule) = approximate energy released in the detonation of one metric ton of TNT
- **Megaton** = 4.184 PJ (petajoule)
  $= 4.184 \times 10^{15}$ J
  = approximate energy released in the detonation of one megaton of TNT

Overoxidized or Fuel Lean Explosives

- More than enough oxygen to form CO_2
- Nitroglycerine (nitroglycerol)

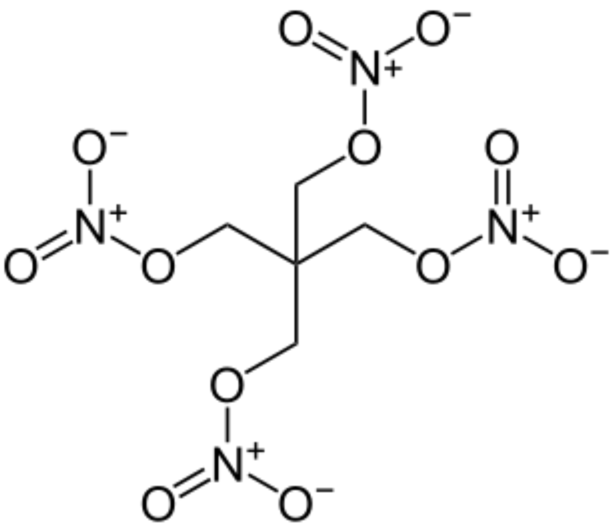
$4C_3H_5N_3O_9(l)$

$\rightarrow 6N_2(g) + 10H_2O(g) + 12CO_2(g) + O_2(g) + 9174\ \text{kJ}$



PETN
(pentaerythritol tetranitrate)

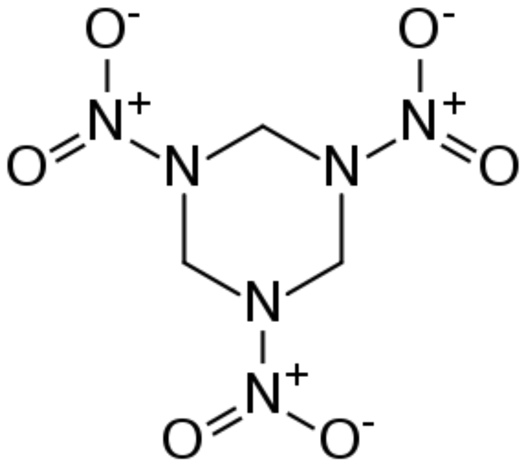
- One of the most sensitive of the secondary explosives
- Rarely used alone
- 1.66 relative effectiveness (R.E.) factor (measurement of explosive power for military purposes compared to TNT as 1)
- Detonation velocity ≅ 8400 m/s



Research Department Explosive, RDX (T4)

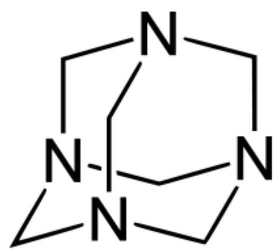
- Less sensitive than PETN
- High detonation velocity (≅ 8700 m/s)
- Relative effectiveness factor of 1.6

$$2C_3H_6N_6O_6(s) \rightarrow 3N_2(g) + 3H_2O(g) + 3CO(g)$$



RDX Production

- React white fuming nitric acid (WFNA) with hexamine, producing dinitromethane and ammonium nitrate as byproducts.



Hexamine + 10 nitric acid

→ RDX + dinitromethane + ammonium nitrate + 3 water

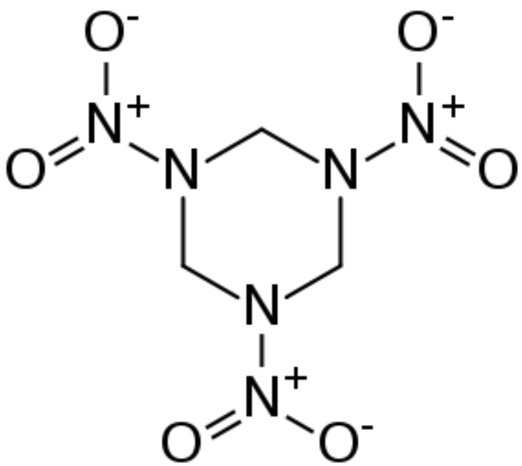
$$(CH_2)_6N_4 + 10HNO_3$$

$$\rightarrow (CH_2\text{-}N\text{-}NO_2)_3 + 3CH_2(NO_2)_2 + NH_4NO_3 + 3H_2O$$

C-4, a Plastic (Putty) Explosive

- **Plastic (putty) explosives** = an explosive that has been mixed with plasticizers, resulting in a moldable clay-like material that can be configured into any shape you want.
- C-4 is a very common explosive, can be molded by hand, used by U.S. military
- Composed of about 91% explosive (RDX), 5.3% plasticizer, 2.1% binder, and odorizing agent (for detection)

"RDX" (cyclotrime thylene trinitramine)

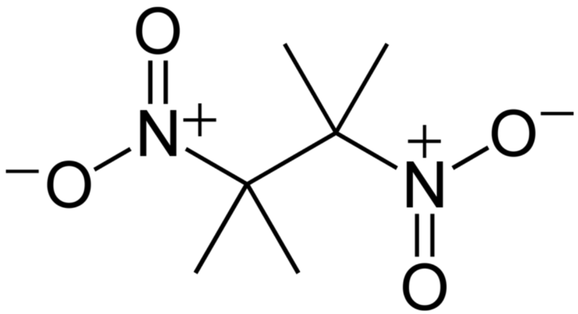


Semtex

- Plastic explosive with both RDX and PETN
- Easily-malleable and waterproof
- Useful over greater temperature range than other plastic explosives
- Widely exported in past
  - Vietnam War: North Vietnam received 14 tons
  - Used in 1988 Pan Am Flight 103 hijacking (~300 killed)
- Producer adds a chemical to aid detection (produces a unique chemical vapor signature)

Explosive Taggants

- Detection Taggants - volatile chemicals that slowly evaporate from the explosive and can be detected dogs or specialized instruments, such as ion mobility spectrometers.
  - Four possible detection taggants for plastic explosives
  - In U.S. it's 2,3-dimethyl-2,3-dinitrobutane (DMDNB or DMNB).



Explosive Taggants

- **Identification (or post-detonation) Taggants** - considered for industrial explosives so that the manufacturer and batch number can be determined if they are used illegally.
  - Must survive the detonation and not be contaminated by the environment afterwards.
  - Most common are microscopic polymer/ metallic particles.
  - Controversial – in general, law enforcement agencies want it and producers do not
  - Not done anywhere but Switzerland

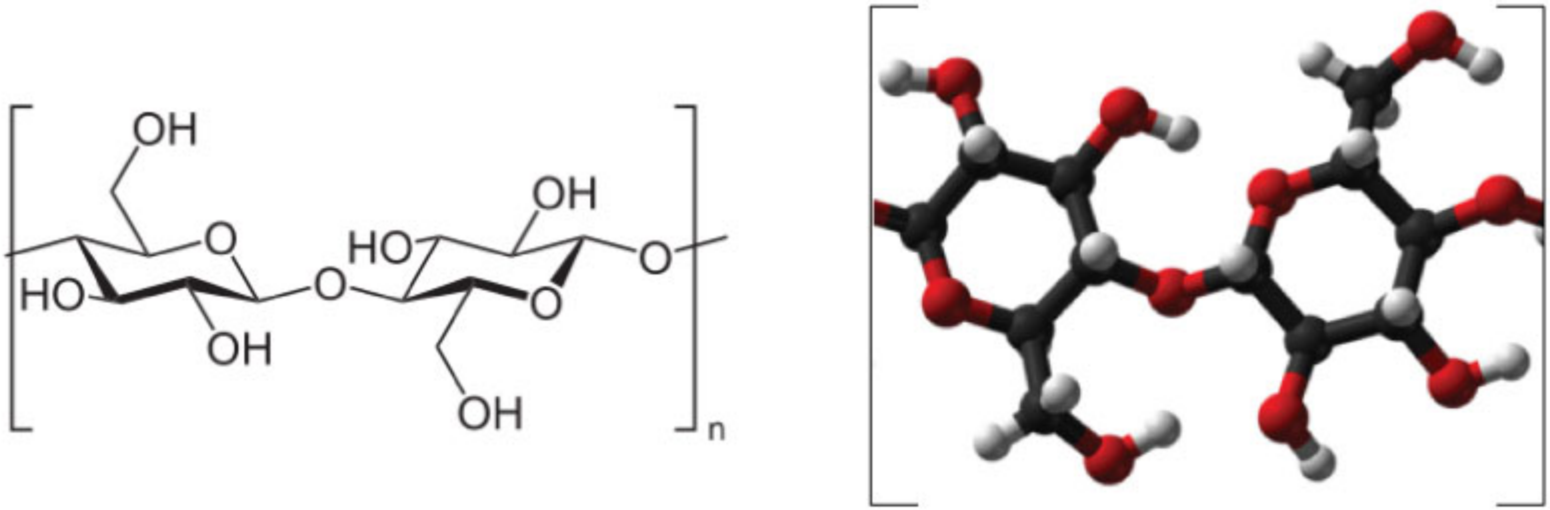
Propellants (Gun Powder)

- Low explosives, burn (deflagrate), not detonate
- Produces a lot of gas - $CO_2(g)$, $H_2O(g)$, $N_2(g)$ - which expands rapidly, propelling an object, such as a bullet.
- Example: black powder
  - Fuel: sulfur and charcoal
  - Oxidizer: usually potassium nitrate, KNO_3
  - Produces some solid substances, e.g. $K_2S(s)$, K_2CO_3, K_2SO_4, producing smoke

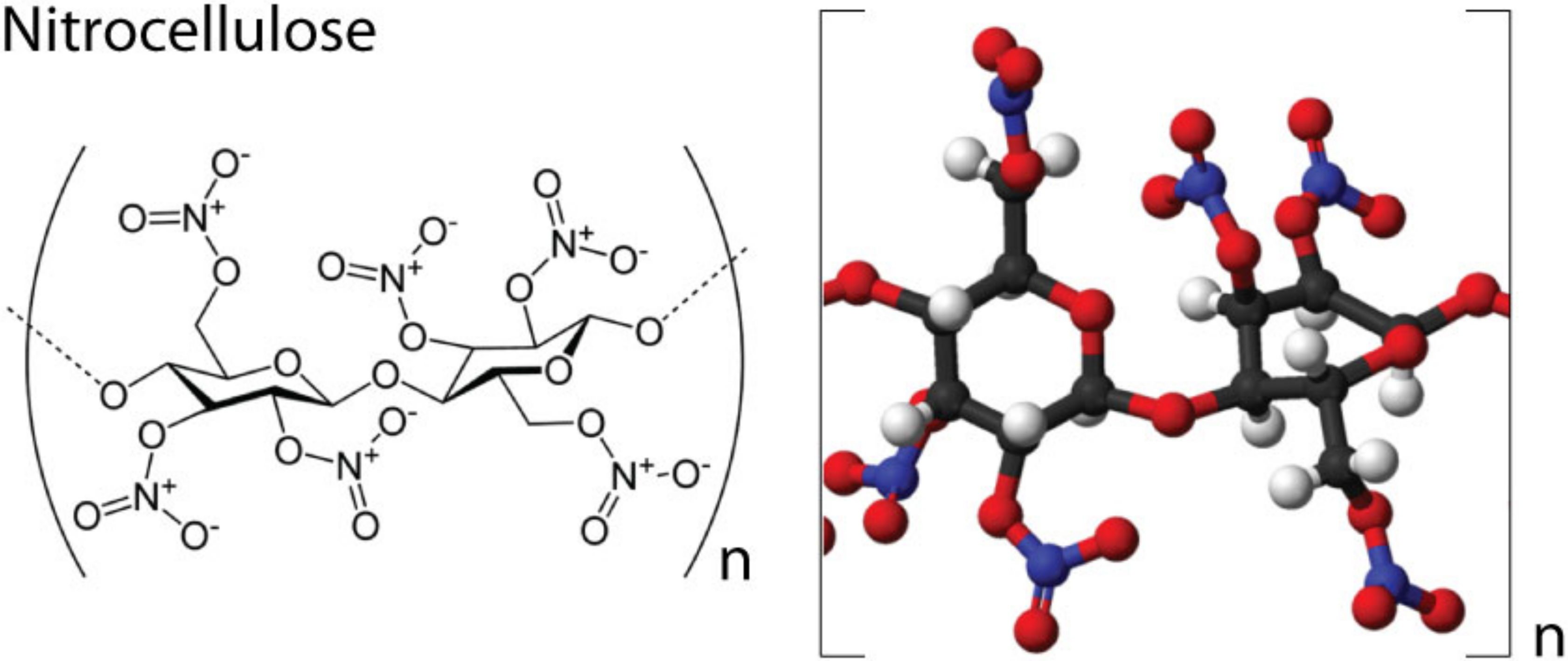
Propellants – Smokeless Powder

- **Single-base powder** – nitrocellulose, made by reacting cellulose, such as found in cotton, with nitric acid.
- **Double-base powder** – a mixture of nitroglycerine and nitrocellulose, e.g. Cordite

Cellulose



Nitrocellulose



Inorganic Explosives

- Ammonium nitrate, NH_4NO_3
  - Rather poor explosive
  - Very overoxidized
  - Difficult to initiate
  - Mixed with other explosives (e.g. ammonium nitrate fuel oil, ANFO)
- Lead azide, $Pb(N_3)_2$ or PbN_6

  $Pb(N_3)_2 \rightarrow Pb + 3N_2 + \text{energy}$
  - Extremely sensitive to sparks, friction, and impact
  - Major initiating explosive used in most blasting caps