An Introduction to Chemical Reactions, Gases, and Chemical Explosives

http://preparatorychemistry.com/Bishop_Book_atoms_7.pdf

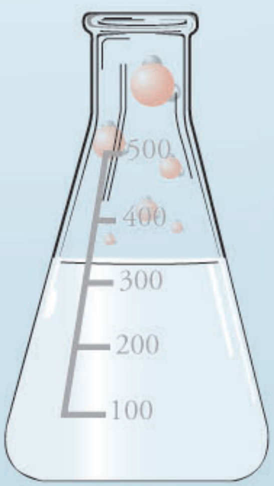
http://preparatorychemistry.com/Bishop_Book_atoms_11.pdf

Chemical Explosives

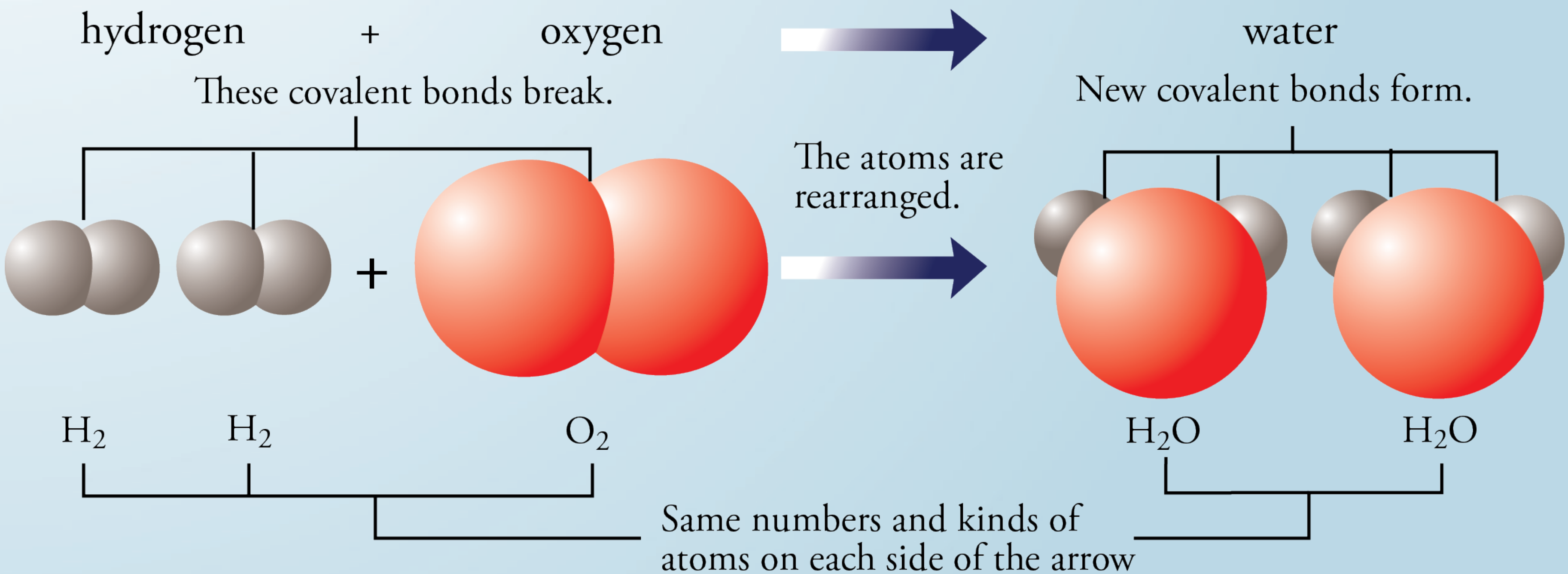
- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the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

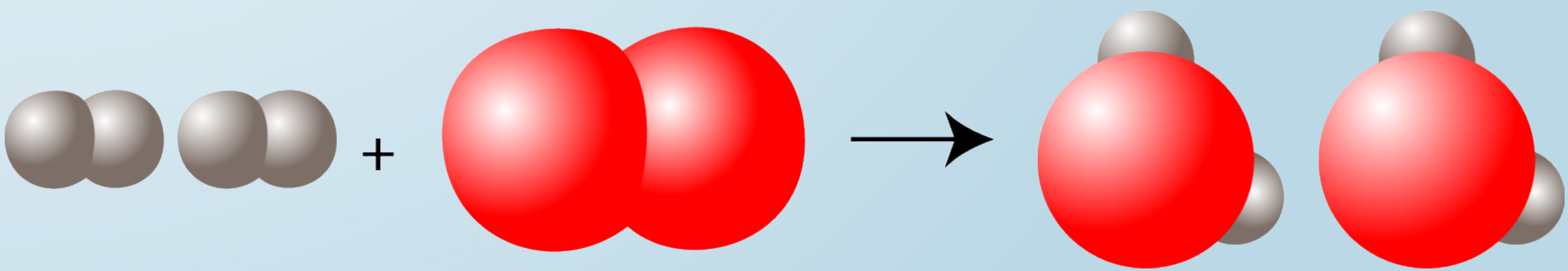
Coefficient

Coefficient

$$2H_2(g) + O_2(g) \xrightarrow{\text{"goes to"}} 2H_2O(l)$$

Physical states

Physical state



Special Conditions

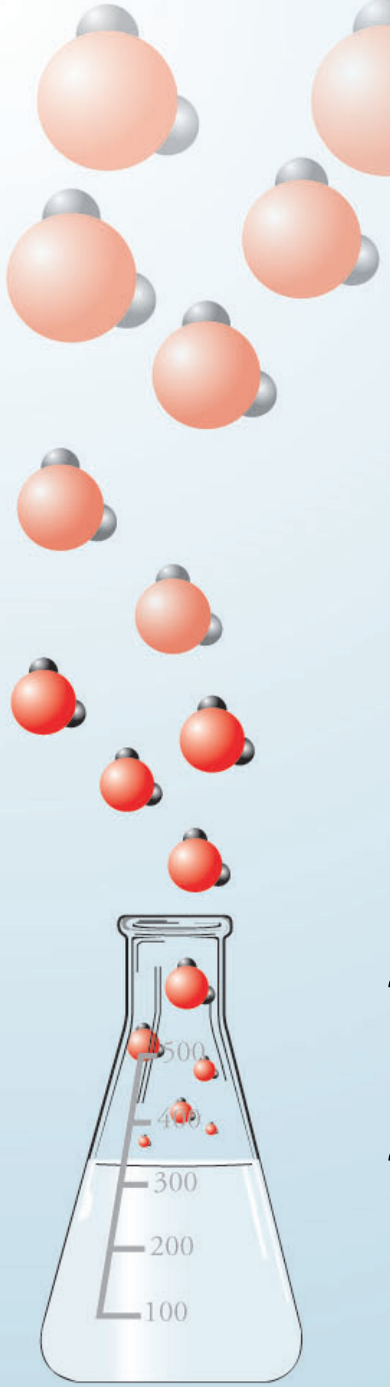
A special condition

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

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.

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

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

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

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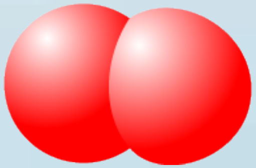
Bond Breaking and Potential Energy

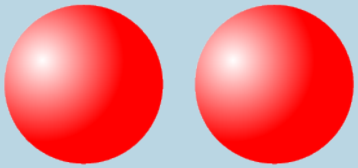
atoms in bond + Energy $\longrightarrow$ separate atoms

more stable + Energy $\longrightarrow$ less stable

lower PE + Energy $\longrightarrow$ higher PE

$O_2(g)$ + energy $\longrightarrow$ $2O(g)$





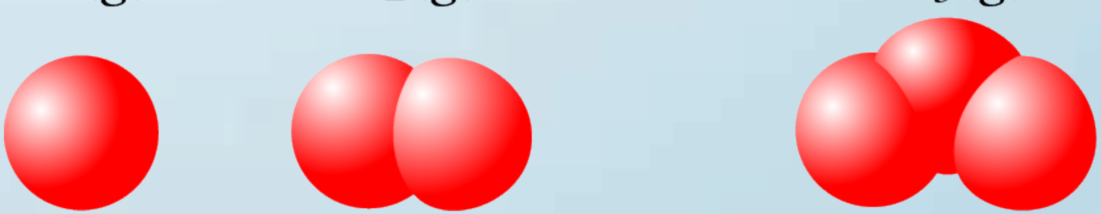
Bond Making and Potential Energy

separate atoms $\longrightarrow$ atoms in bond + Energy

less stable $\longrightarrow$ more stable + Energy

higher PE $\longrightarrow$ lower PE + Energy

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



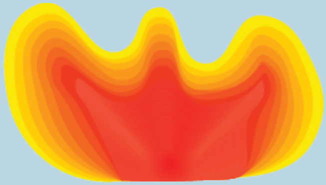
Exergonic (Exothermic) Reaction

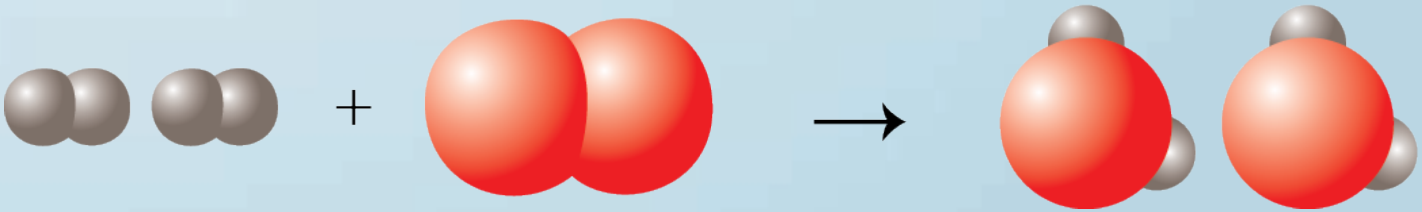
weaker bonds → stronger bonds + energy

less stable → more stable + energy

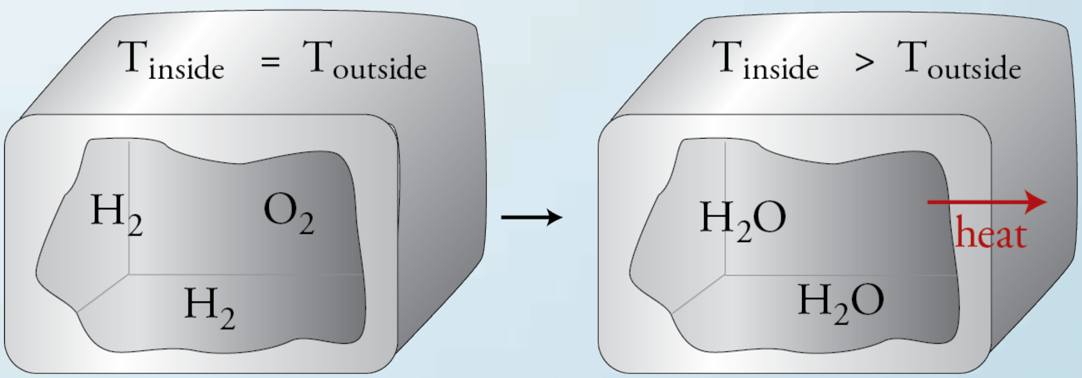
higher PE → lower PE + energy

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





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

Each chemical bond has a unique stability and therefore a unique potential energy.

Chemical reactions lead to changes in chemical bonds.

Chemical reactions lead to changes in potential energy.

If the bonds in the products are more stable and have lower potential energy than the reactants, energy will be released.

The reaction will be exergonic.

If the energy released comes from the conversion of potential energy to kinetic energy, the temperature of the products will be higher than the original reactants.

The higher-temperature products are able to transfer heat to the surroundings, and the temperature of the surroundings increases.

The reaction is exothermic.

If the bonds in the products are less stable and have higher potential energy than the reactants, energy will be absorbed.

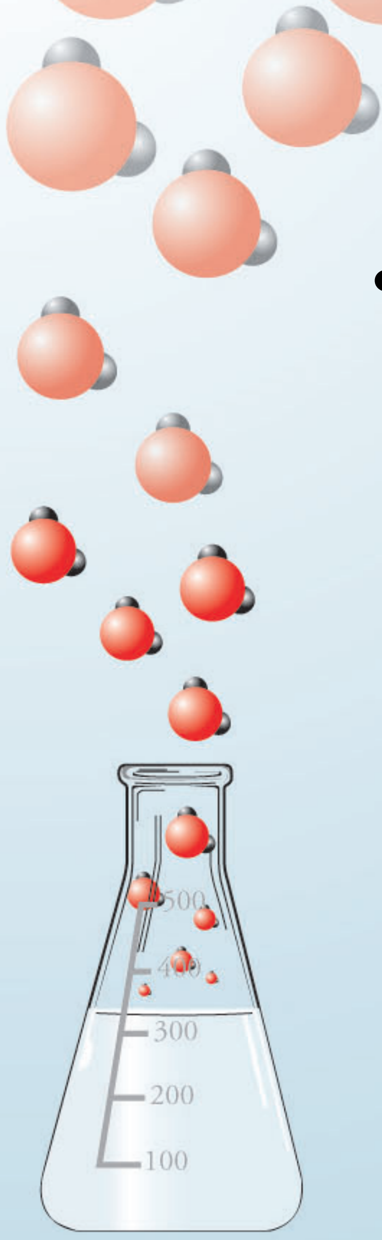
The reaction will be endergonic.

If the energy absorbed comes from the conversion of kinetic energy to potential energy, the temperature of the products will be lower than the original reactants.

The lower-temperature products are able to absorb heat from the surroundings, and the temperature of the surroundings decreases.

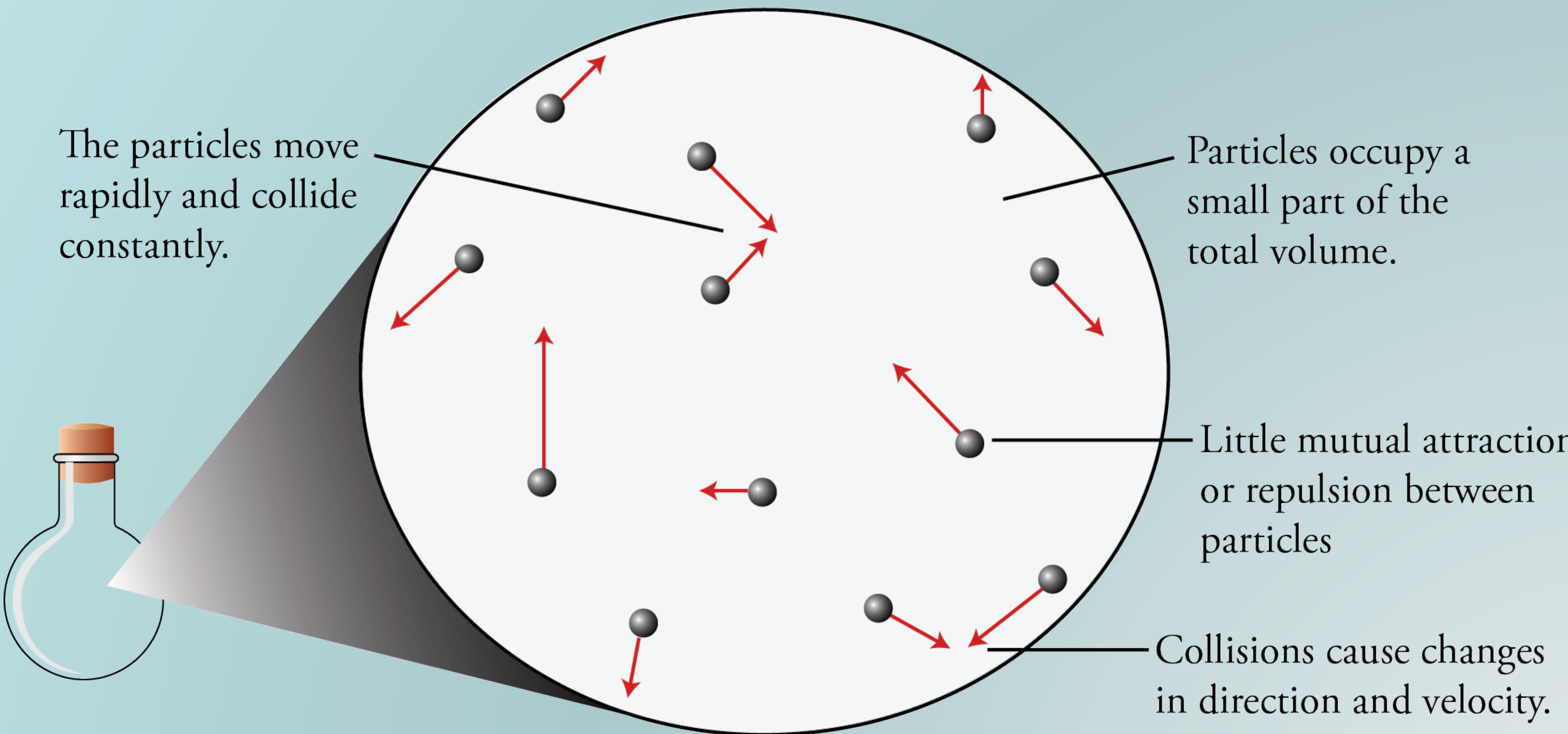
The reaction is endothermic.

Chemical Explosives

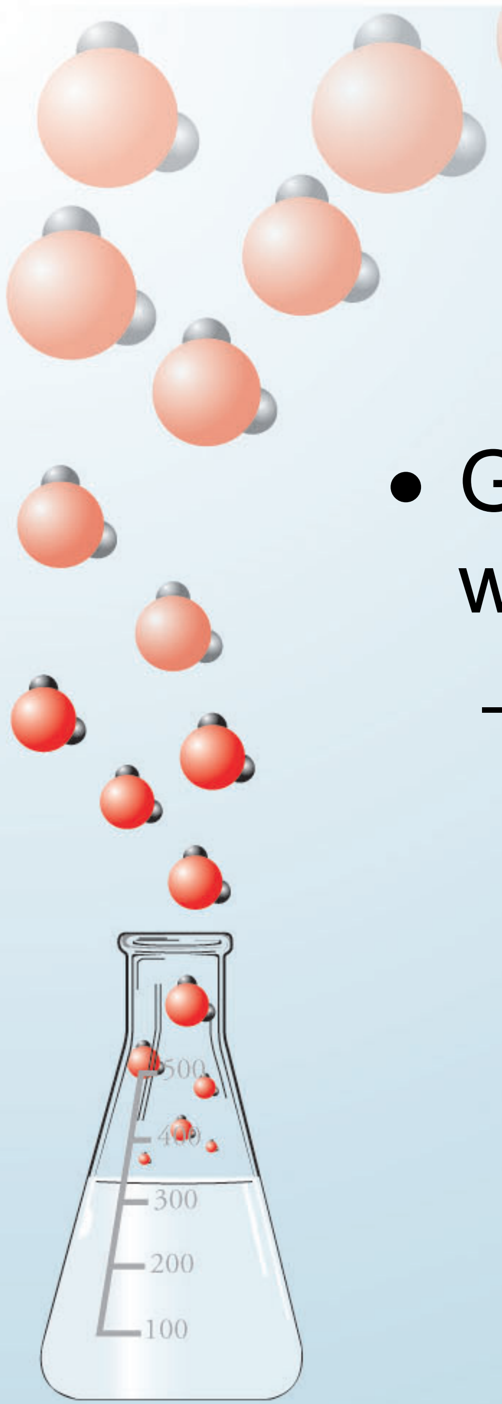


- For a substance to be a chemical explosive, it must undergo a chemical reaction that
  - releases a lot of energy, making the temperature and gas pressure rise rapidly.
  - produces lots of gas, leading to an increase in gas pressure.
  - does this very quickly, leading to a rapid expansion of the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

Gas

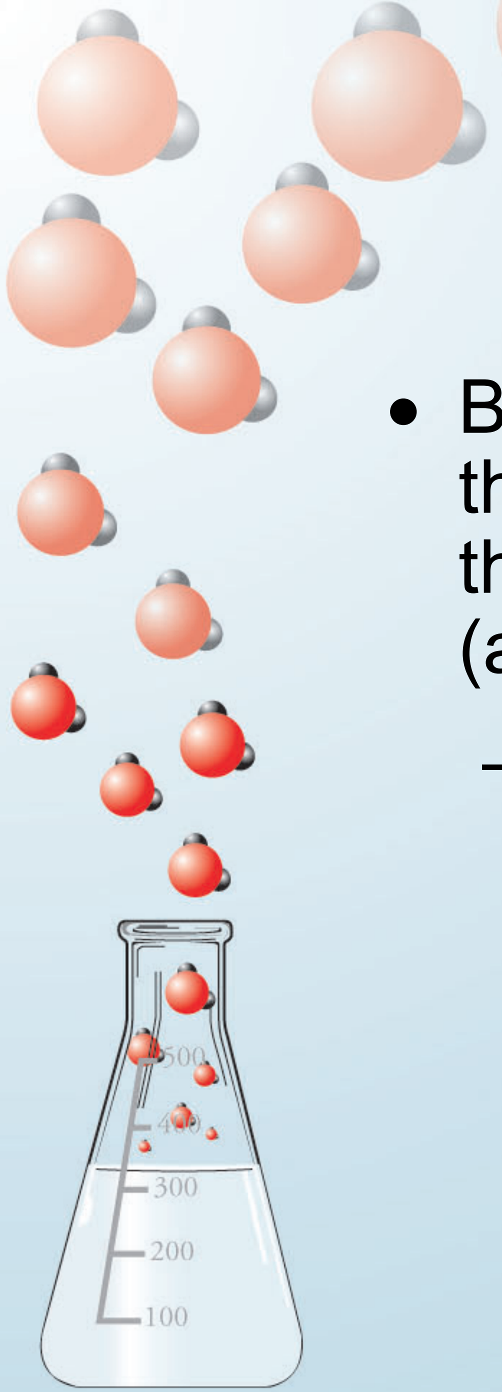

The particles move rapidly and collide constantly.
Particles occupy a small part of the total volume.
Little mutual attraction or repulsion between particles
Collisions cause changes in direction and velocity.

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.)



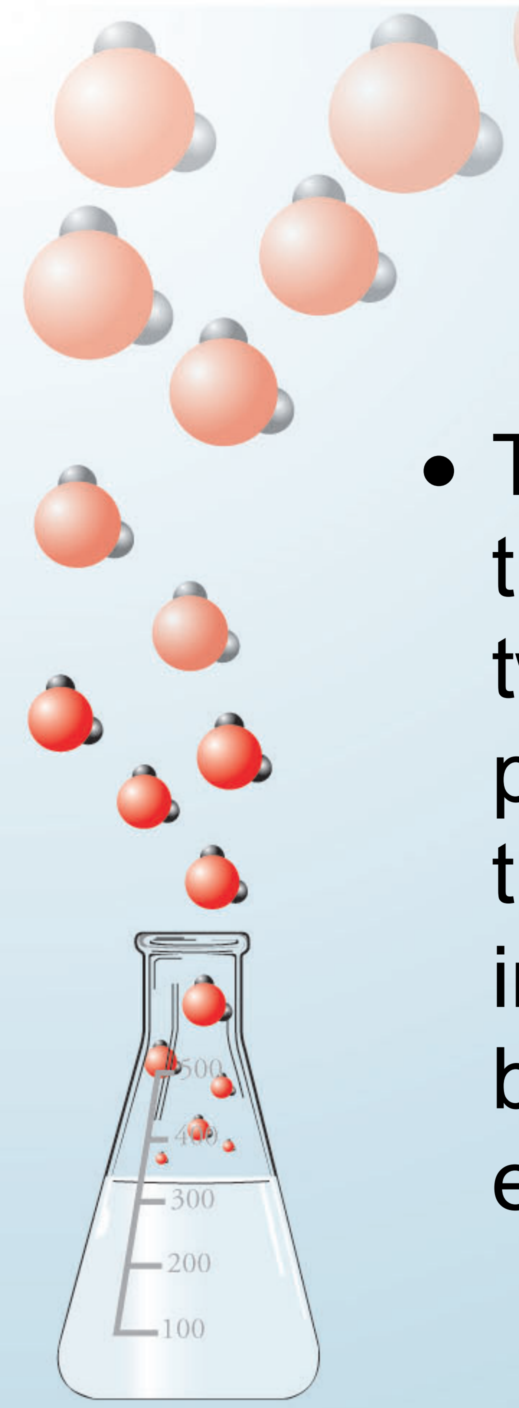
- Because of the large distance between the particles, the volume occupied by the particles themselves is negligible (approximately zero).
  - For a typical gas at room temperature and pressure, the gas particles themselves occupy about 0.1% of the total volume. The other 99.9% of the total volume is 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.)

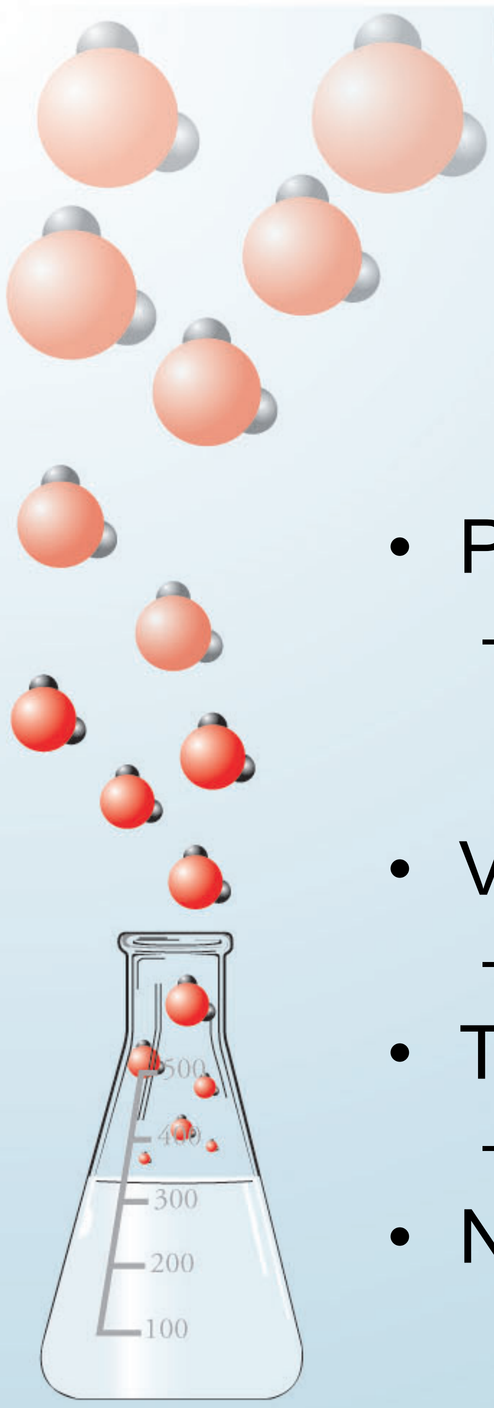
- The particles are constantly colliding with the walls of the container and with each other.
  - Because of these collisions, the gas particles are constantly changing their direction of motion and their velocity. In a typical situation, a gas particle moves a very short distance between collisions. 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

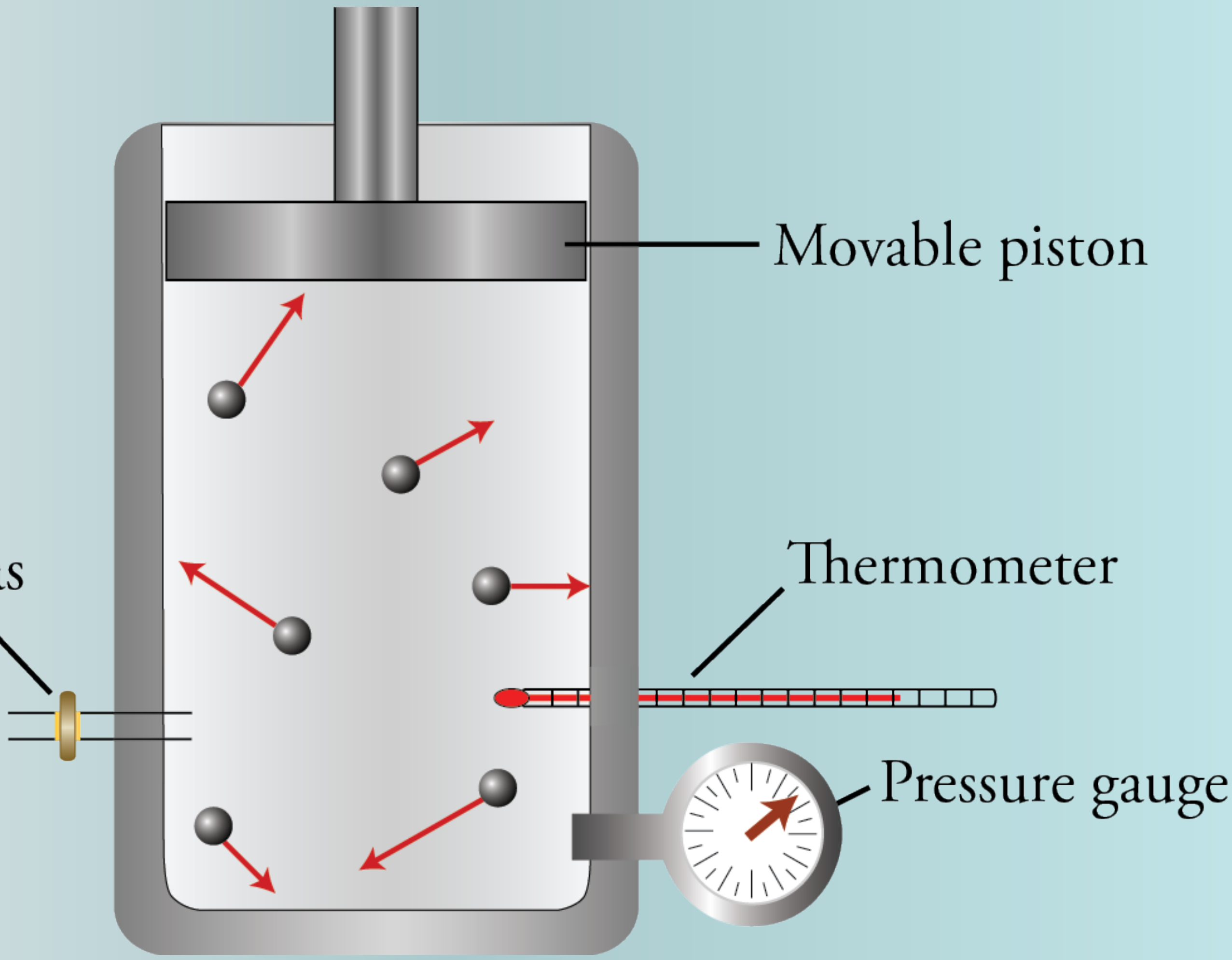


- Pressure (P) = Force/Area
  - units
    - 1 atm = 101.325 kPa = 760 mmHg = 760 torr
    - 1 bar = 100 kPa = 0.9869 atm = 750.1 mmHg
- Volume (V)
  - unit usually liters (L)
- Temperature (T)
  - ? K = --- °C + 273.15
- Number of gas particles (n)

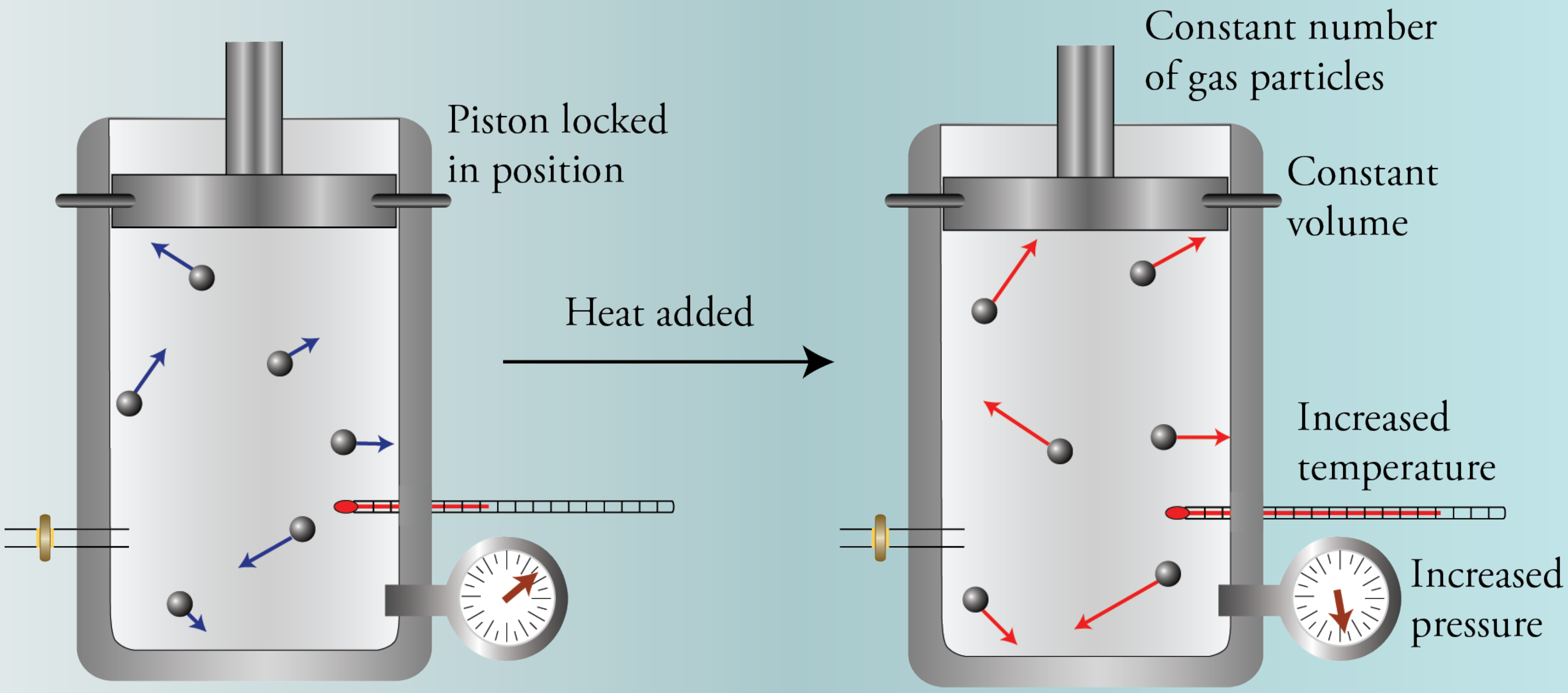
Two Gas Laws

- $P \propto T$ 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



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

http://preparatorychemistry.com/Bishop_Gay_Lussac_Law_Flash1.htm
http://preparatorychemistry.com/Bishop_Gay_Lussac_Law_audio.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

↓

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

↓

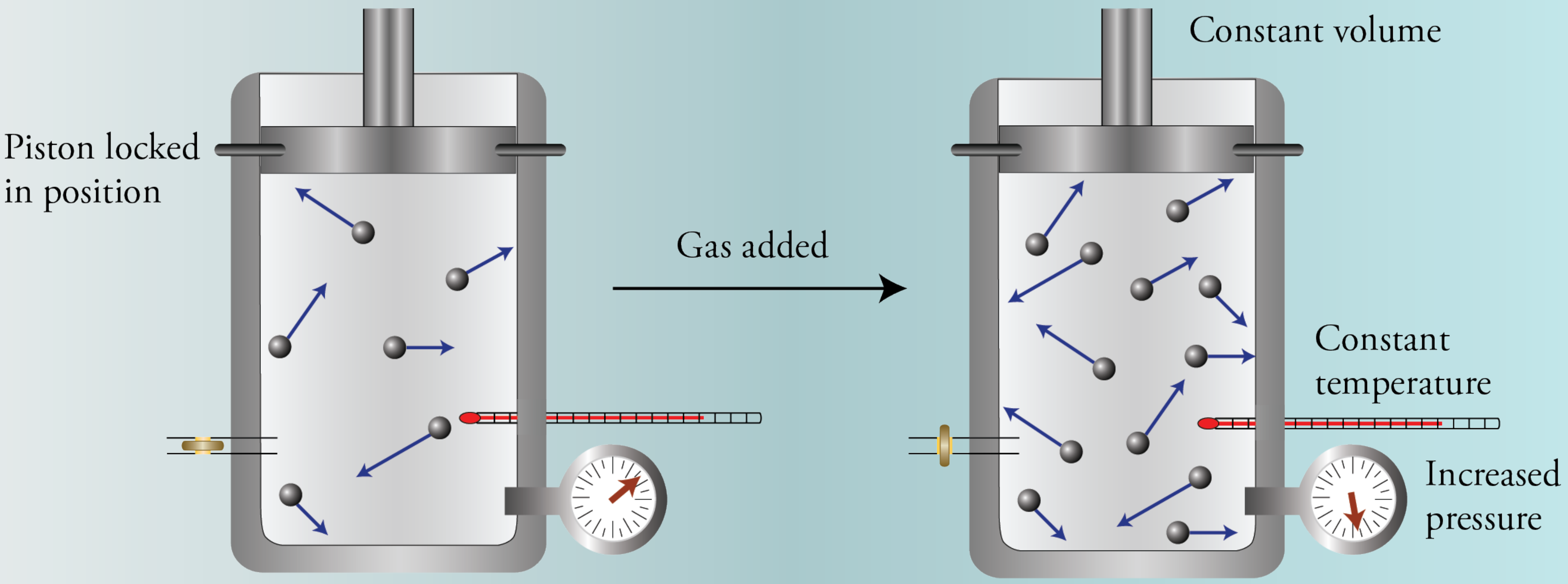
Increased gas pressure

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.

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

Increased Moles of Gas Leads to Increased Pressure



P α n   if T and V are constant

http://preparatorychemistry.com/Bishop_Moles_Pressure_Law_Flash1.htm
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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

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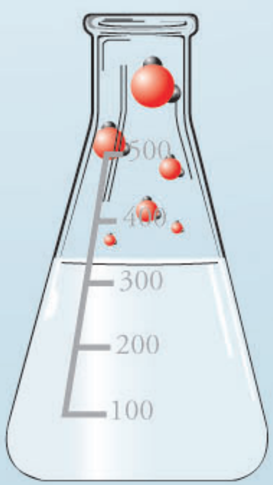
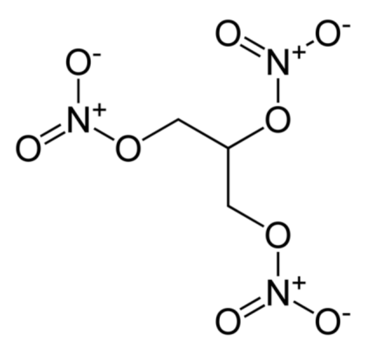


Combustion of Propylamine

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

- 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 about 30 times speed of sound – detonation velocity ≅ 7700 m/s

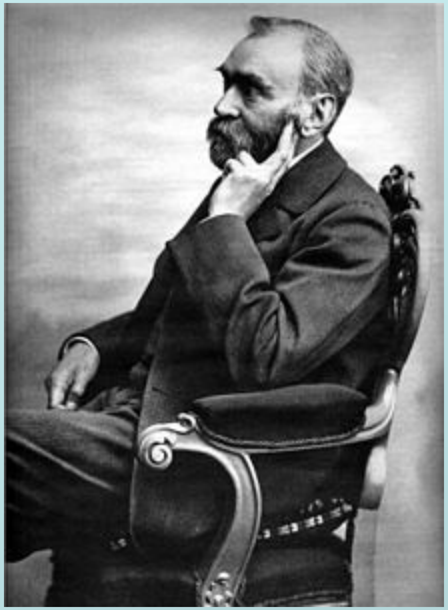
http://www.youtube.com/watch?v=r17czTWHFmU

Nitroglycerine (cont)

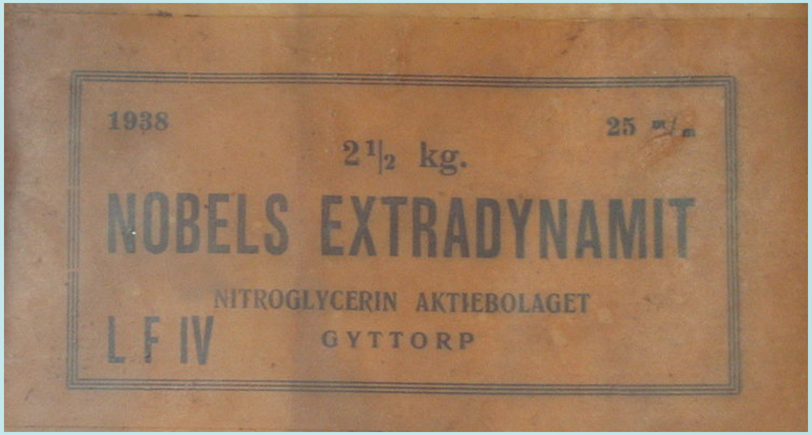
- Very sensitive to impact, so dangerous when pure
- Liquid forms microscopic bubbles that are more likely to react and start the detonation.
- Mixed with other substances and used in dynamite and propellants.
- More stable when absorbed in powdered absorbent (e.g. diatomaceous earth or sawdust), which 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"

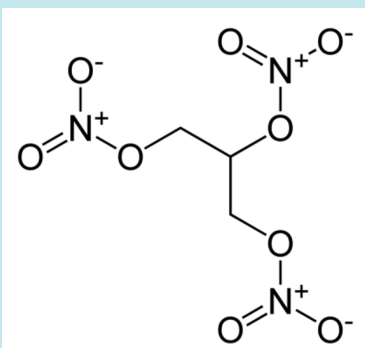


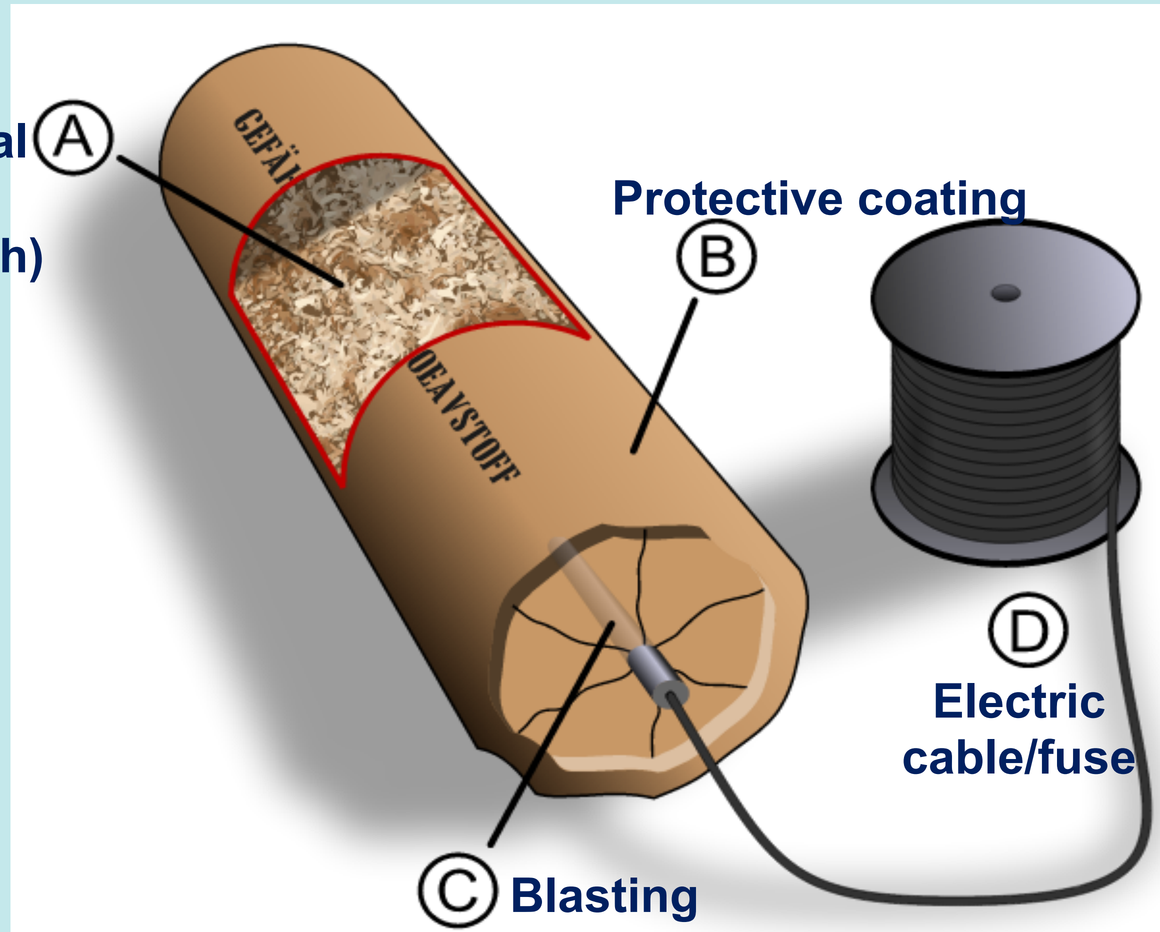
1833-1896



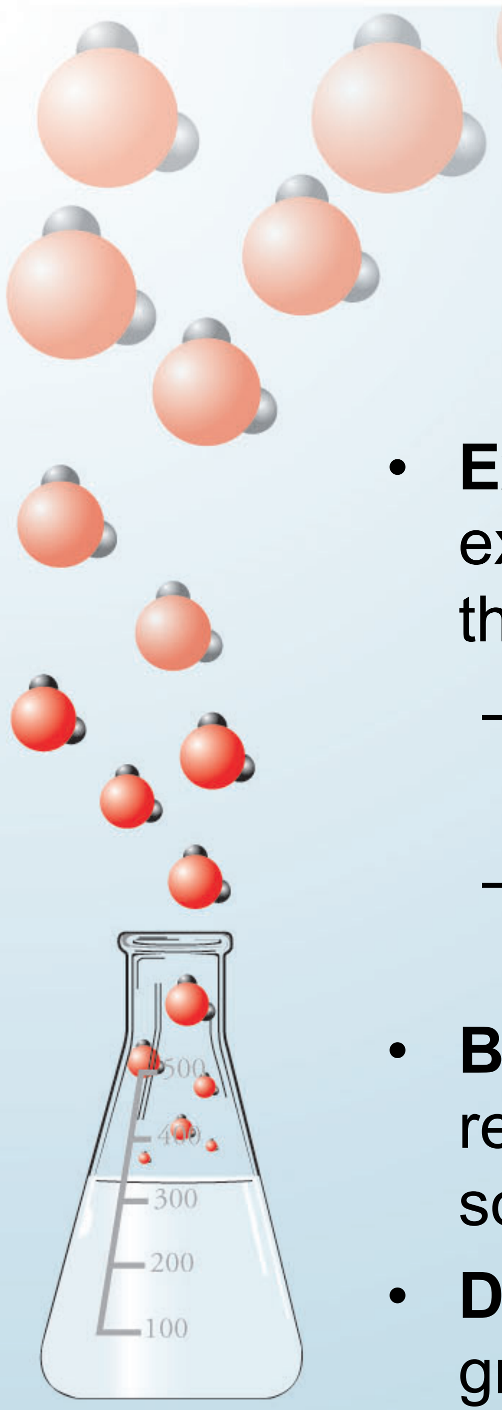
Dynamite
(Originally, “Nobel’s Blasting Powder)

Absorbent material (sawdust or diatomaceous earth) soaked in nitroglycerin





At the time of its invention (1860s), dynamite was the first safe and manageable chemical explosive.



Terms Related to Explosives

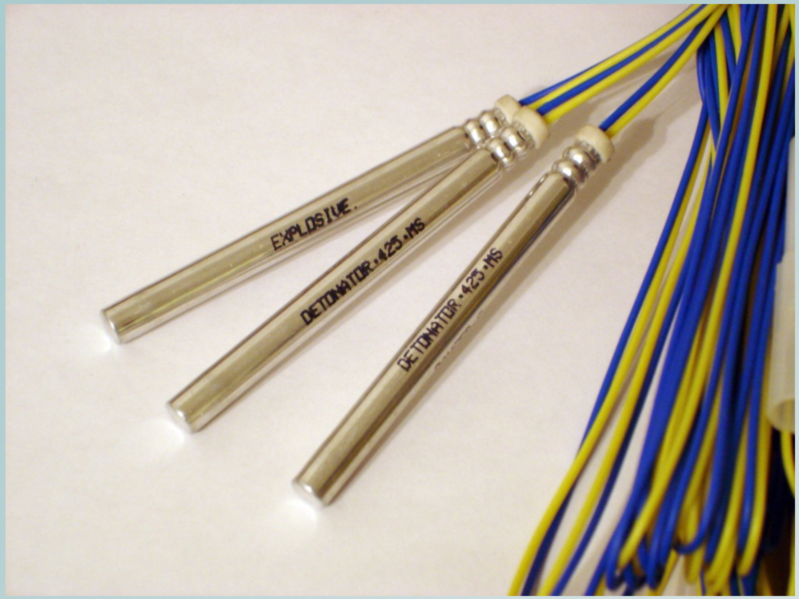
- **Explosion** = large-scale, noisy, rapid expansion of matter into a volume greater than the original volume
  – Can be due to a very fast *burning* of a material
  – Can be due to *detonating* an explosive material
- **Burning** (or **deflagration**) = relatively slow reaction (propagation less than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

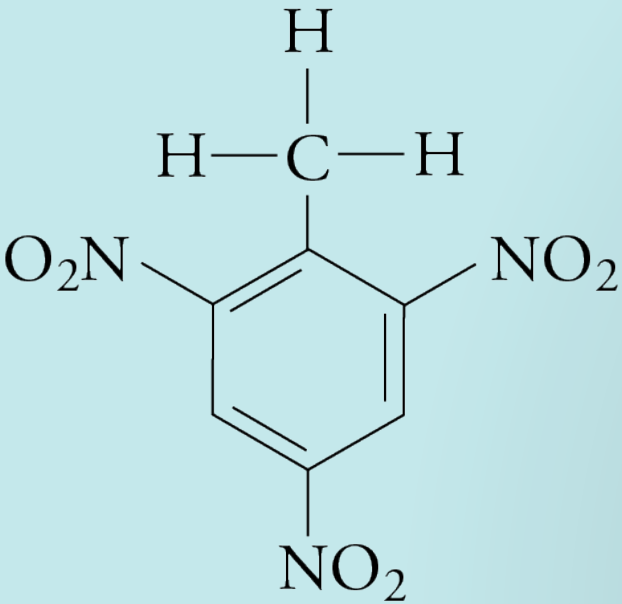
Explosives

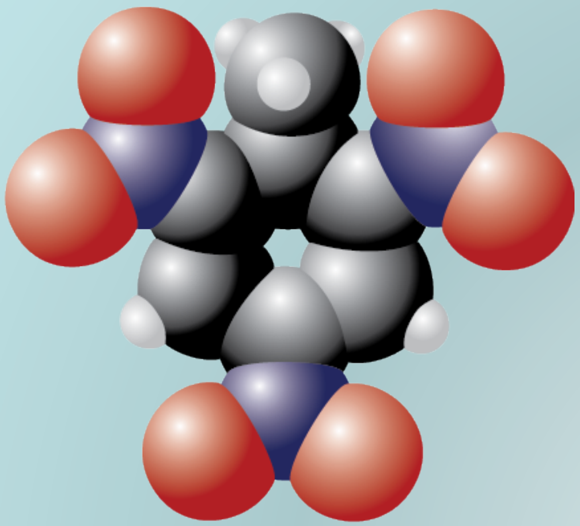
- Most explosives are composed of carbon, nitrogen, hydrogen, and oxygen … $C_cH_hN_nO_o$.
- Guidelines for the order of formation of products
  - Nitrogen forms $N_2(g)$
  - Hydrogen forms $H_2O(g)$
  - Any oxygen left converts carbon to $CO(g)$
  - Any oxygen left converts $CO(g)$ to $CO_2(g)$
  - 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

- 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

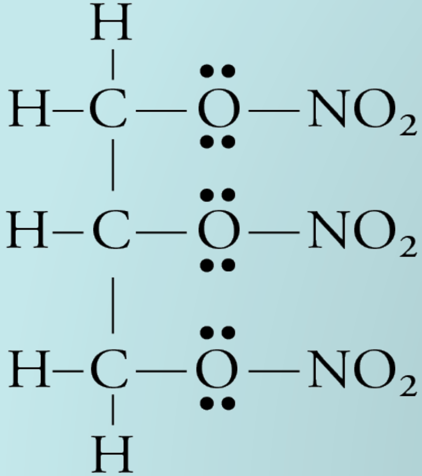
- **TNT Equivalent** = a measure of the energy released in an explosion
- **Ton** (or tonne) **of TNT** = 4.184 GJ (gigajoule or 10^9 joule) = approximate energy released in the detonation of one metric ton of TNT
- **Megaton** = 4.184 PJ (petajoule) = 4.184×10^{15} J
  = approximate energy released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

Overoxidized or Fuel Lean Explosives

- Enough oxygen to form CO_2
- Nitroglycerine (nitroglycerol)

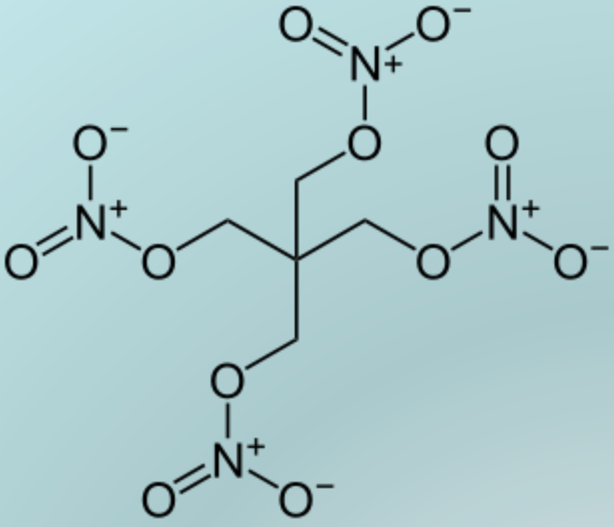
$4C_3H_5N_3O_9(l)$

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



PETN (pentaerythritol tetranitrate)

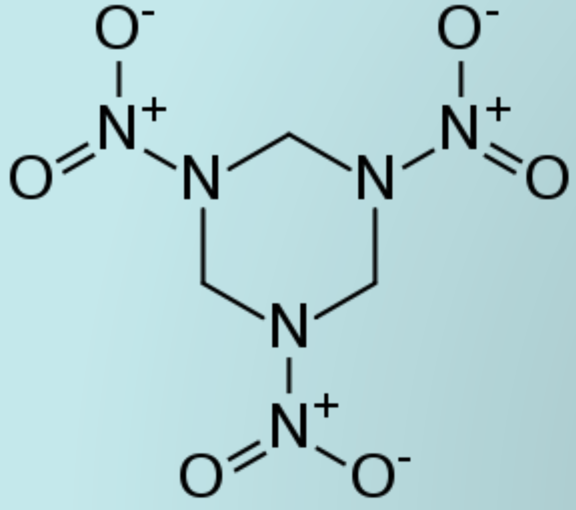
- One of the most sensitive of the secondary explosives
- Rarely used alone
- 1.66 relative effectiveness (R.E.) factor (measurement of explosive power for military purposes compared to TNT as 1)
- Detonation velocity ≅ 8400 m/s



Research Department Explosive, RDX (T4)

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

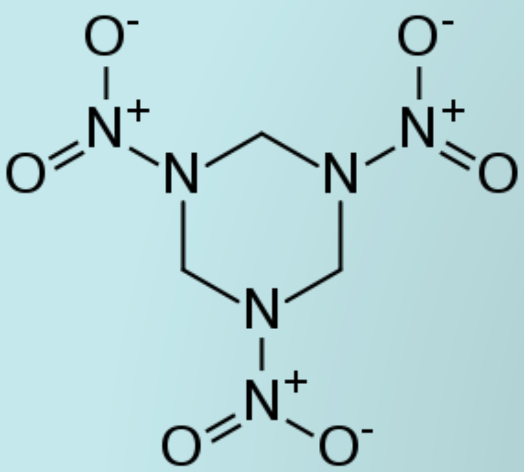
$$2C_3H_6N_6O_6(s) \rightarrow 3N_2(g) + 3H_2O(g) + 3CO(g)$$



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 and identification)

"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)

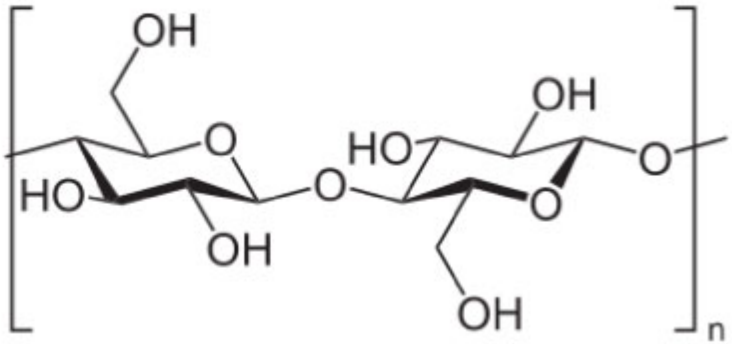
Propellants (Gun Powder)

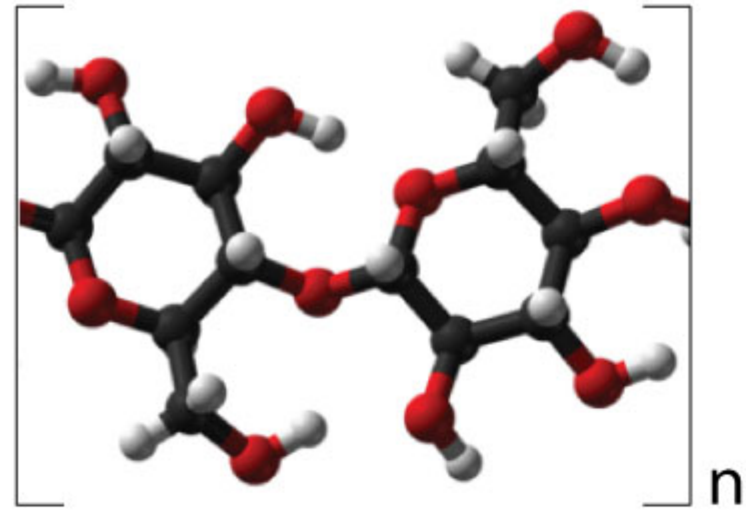
- Low explosives, burn (deflagrate), not detonate
- Produces a lot of gas - $CO_2(g)$, $H_2O(g)$, $N_2(g)$ - which expands rapidly, propelling an object, such as a bullet.
- Example: black powder
  - Fuel: sulfur and charcoal
  - Oxidizer: usually potassium nitrate, KNO_3
  - Produces some solid substances,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

Propellants – Smokeless Powder

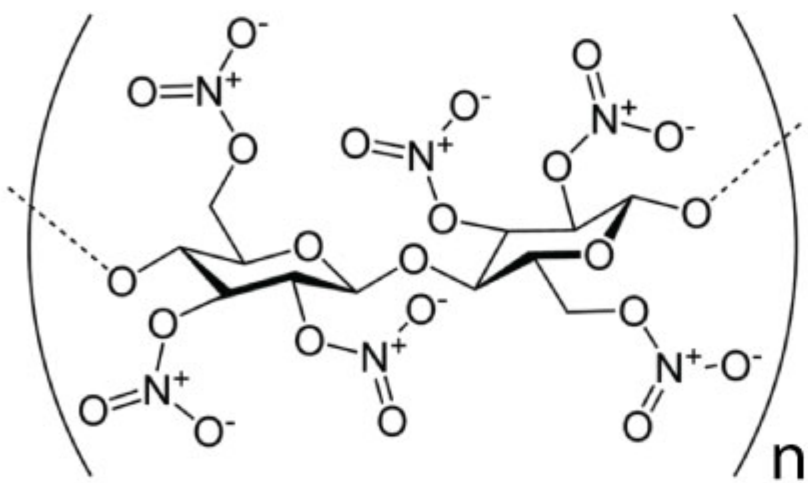
- **Single-base powder** – nitrocellulose, made by reacting cellulose, such as found in cotton, with nitric acid.
- **Double-base powder** – a mixture of nitroglycerine and nitrocellulose, e.g. Cordite

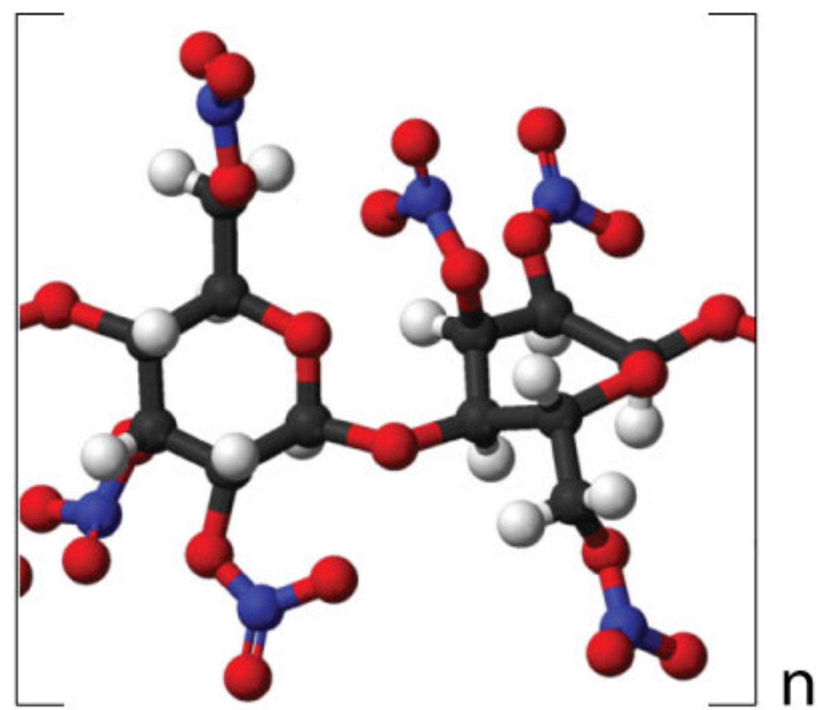
Cellulose

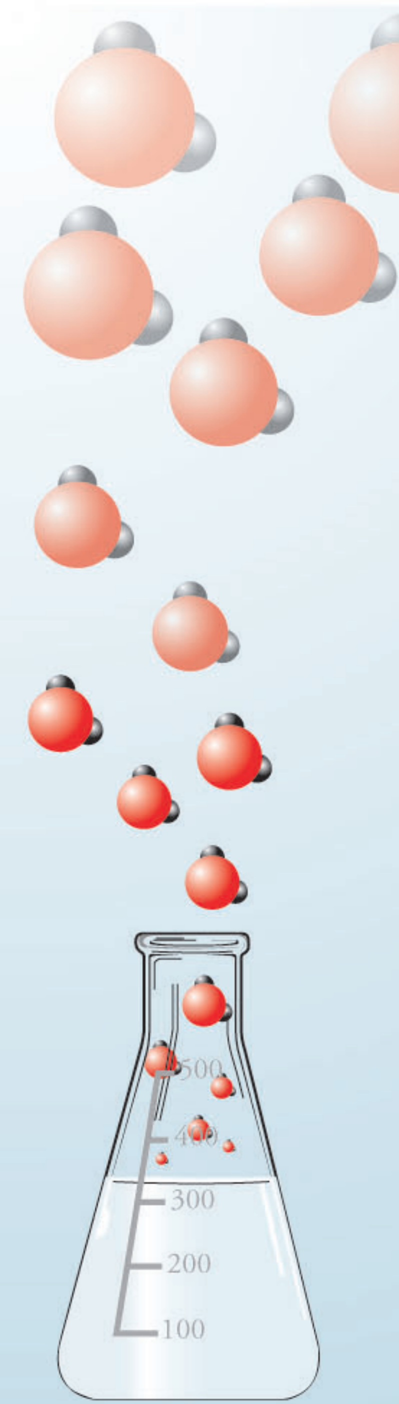




Nitrocellulose



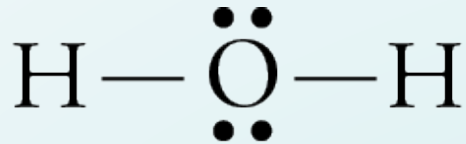


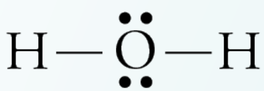


Inorganic Explosives

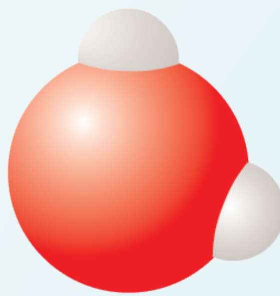
- Ammonium nitrate, NH_4NO_3
  - Rather poor explosive
  - Very overoxidized
  - Difficult to initiate
  - Mixed with other explosives (e.g. ammonium nitrate fuel oil, ANFO)
- Lead azide, $Pb(N_3)_2$ or PbN_6
  - Extremely sensitive to sparks, friction, and impact
  - Major initiating explosive used in most blasting caps

Water, H_2O

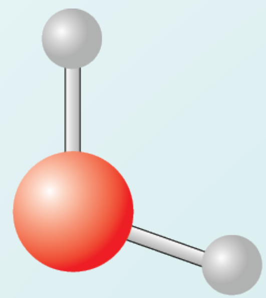




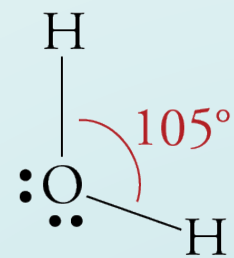
Lewis structure



Space-filling model

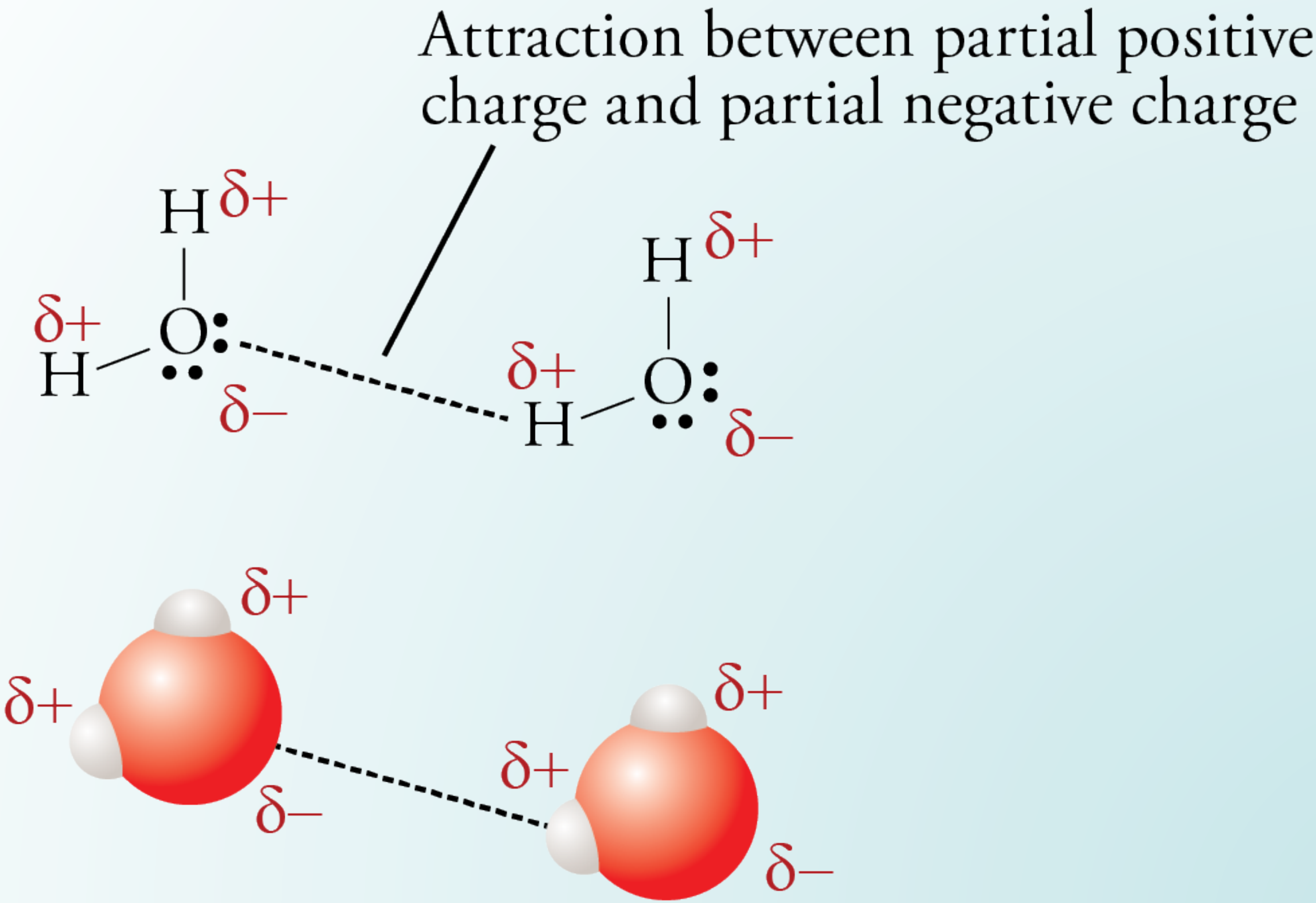


Ball-and-stick model

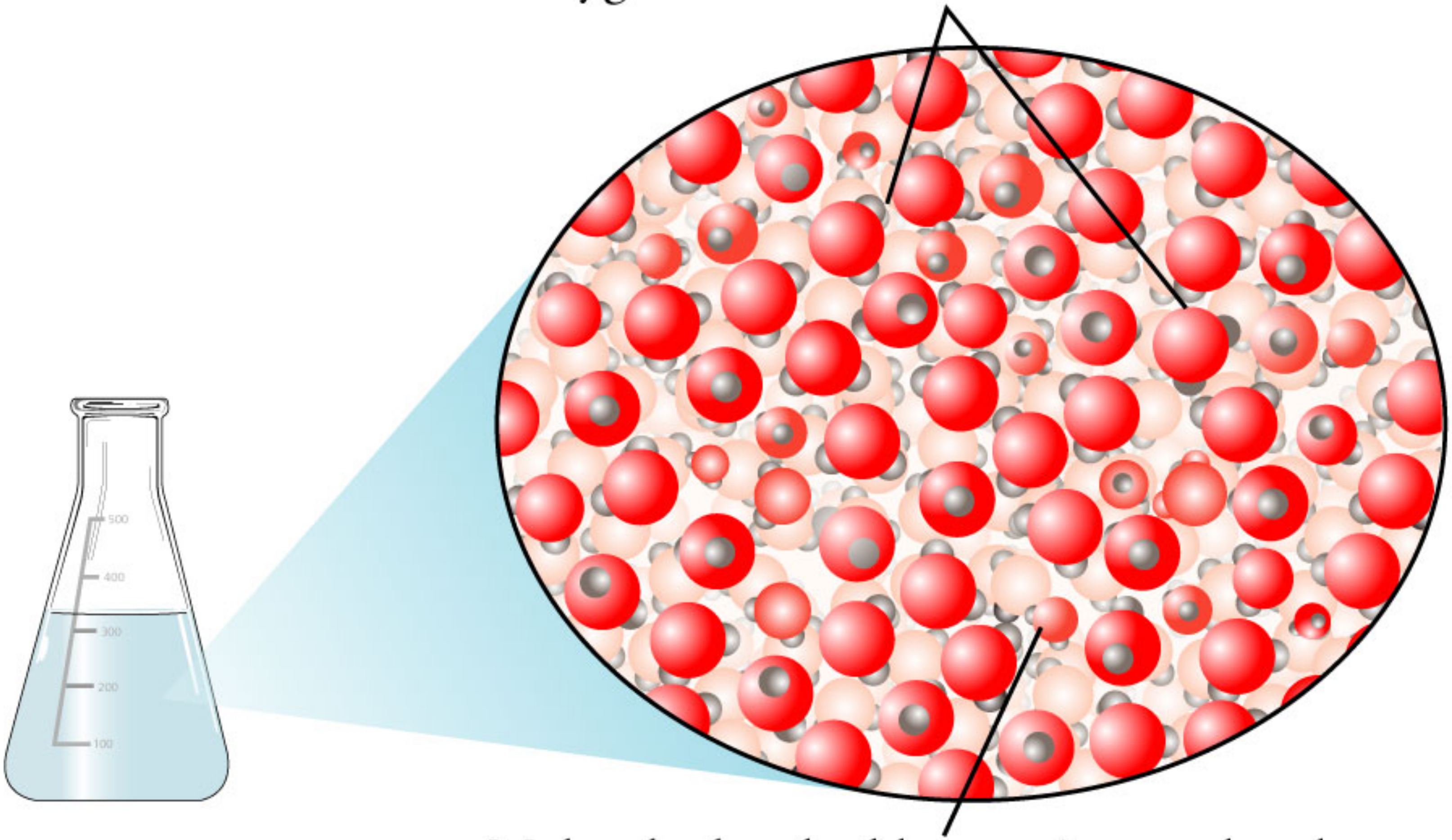


Geometric Sketch

Water Attractions

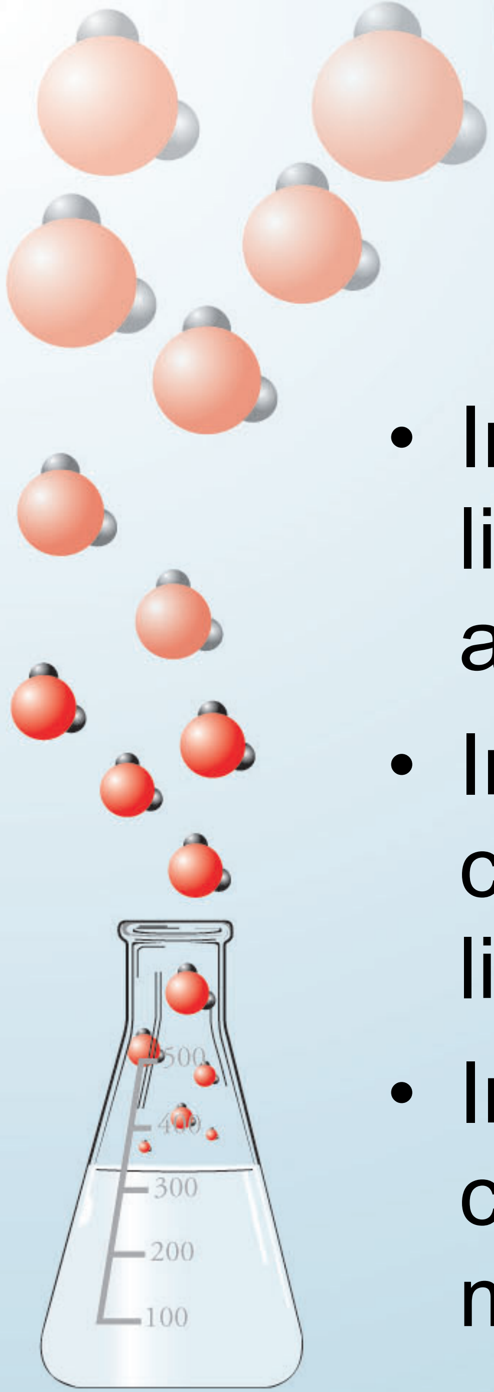


Attractions exist between hydrogen and oxygen atoms of different water molecules.



Molecules break old attractions and make new ones as they tumble throughout the container.

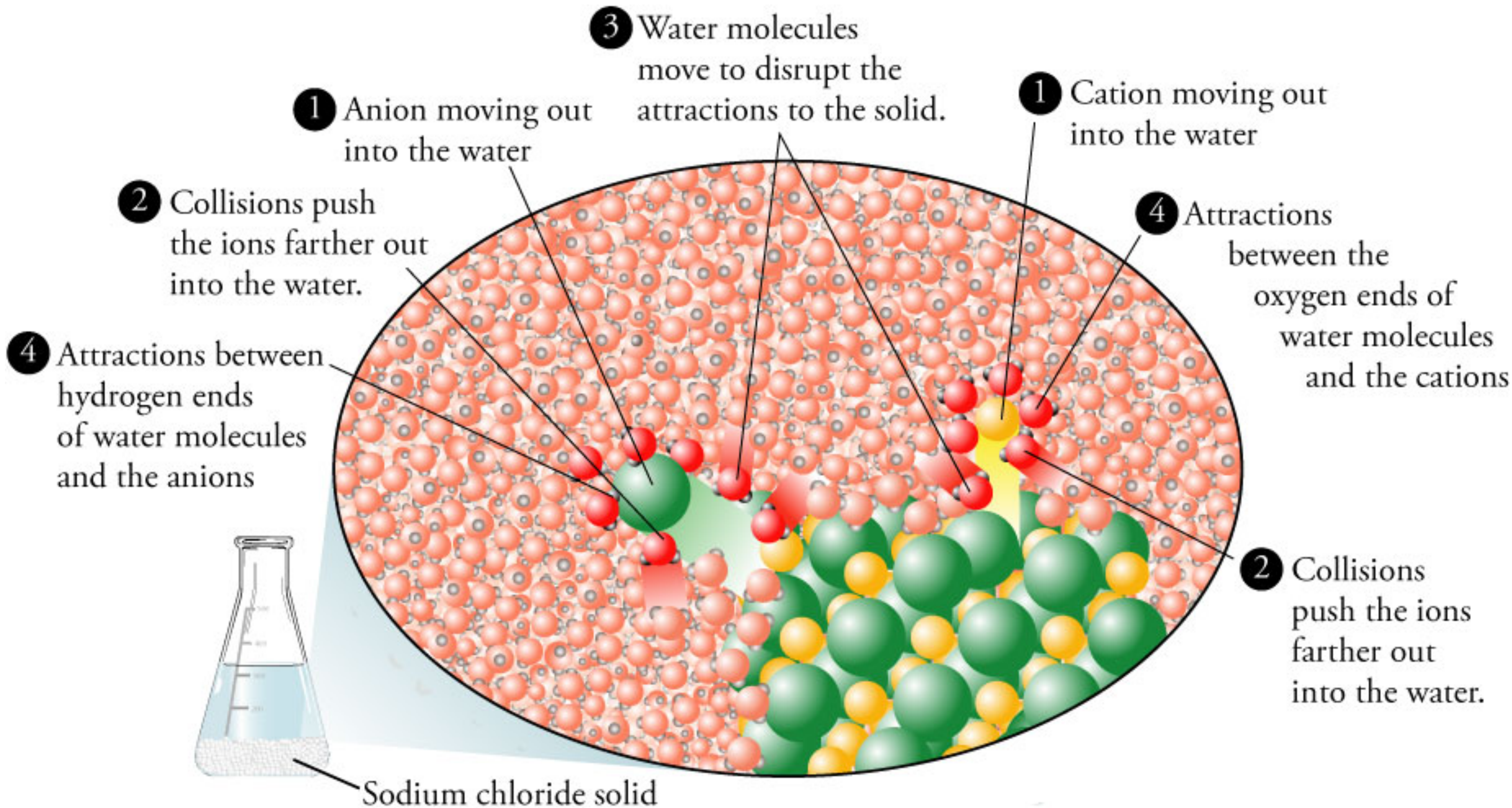
http://preparatorychemistry.com/water_flash.htm
http://preparatorychemistry.com/water_audio.html



Solute and Solvent

- In solutions of solids dissolved in liquids, we call the solid the ***solute*** and the liquid the ***solvent***.
- In solutions of gases in liquids, we call the gas the ***solute*** and the liquid the ***solvent***.
- In other solutions, we call the minor component the ***solute*** and the major component the ***solvent***.

Solution of an Ionic Compound



http://preparatorychemistry.com/NaCl_flash.htm
http://preparatorychemistry.com/NaCl_flash_audio.html

Solution of an Ionic Compound (cont.)