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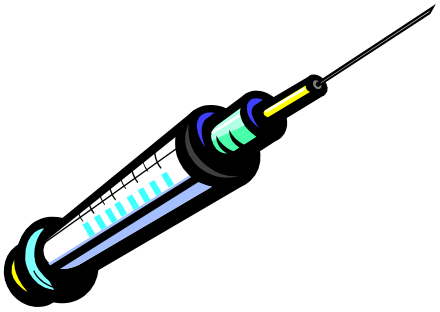
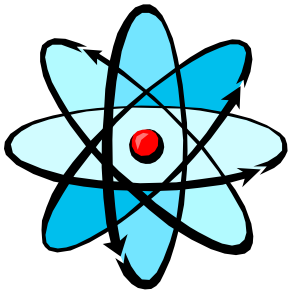
Chemistry: The Study of Change

Chapter 1

Chemistry: A Science for the 21st Century

- Health and Medicine
  - Sanitation systems
  - Surgery with anesthesia
  - Vaccines and antibiotics

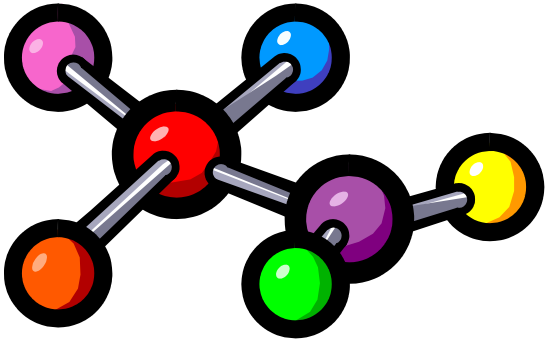


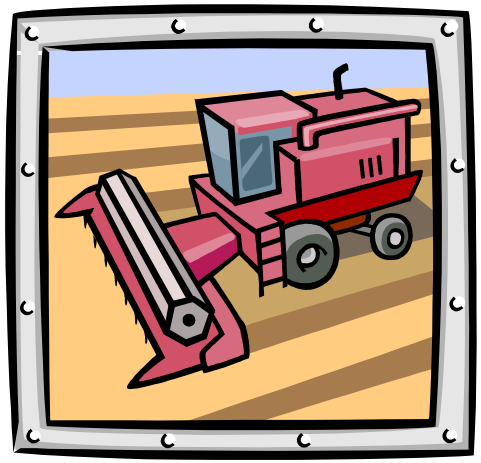


- Energy and the Environment
  - Fossil fuels
  - Solar energy
  - Nuclear energy

Chemistry: A Science for the 21st Century

- Materials and Technology
  - Polymers, ceramics, liquid crystals
  - Room-temperature superconductors?
  - Molecular computing?



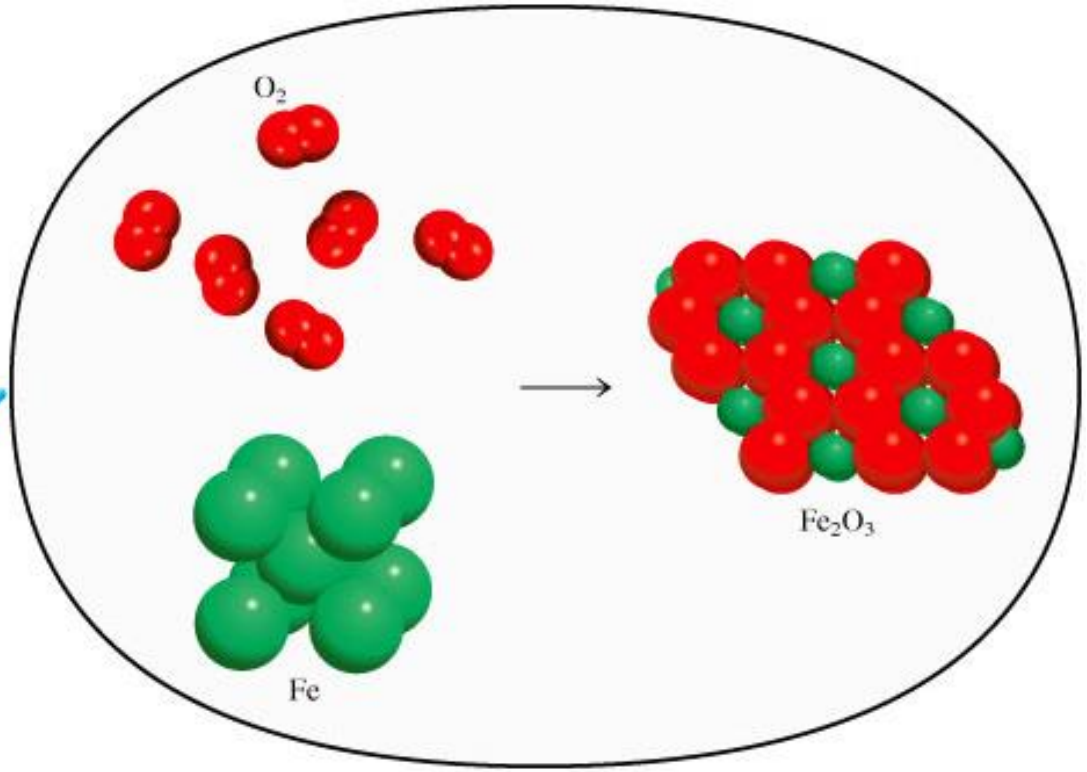


- Food and Agriculture
  - Genetically modified crops
  - “Natural” pesticides
  - Specialized fertilizers

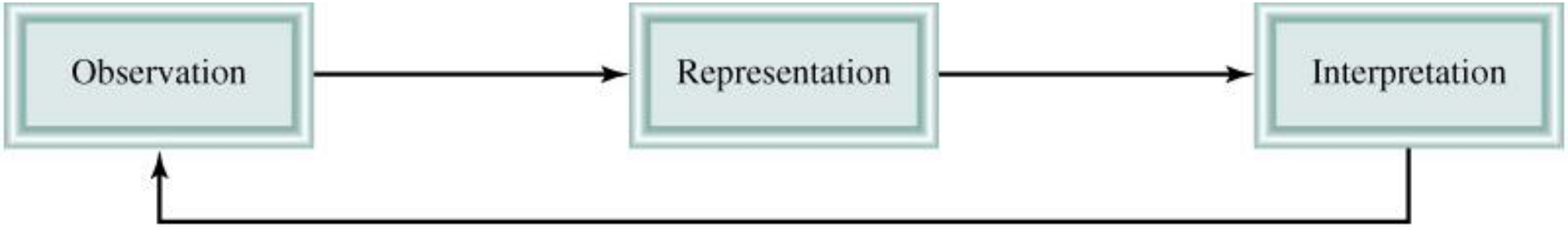
The Study of Chemistry

Macroscopic

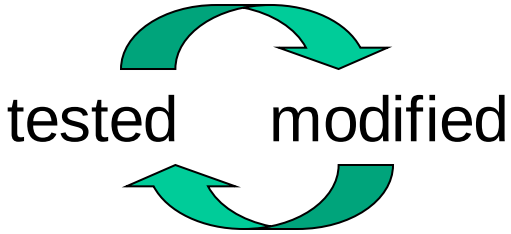
Microscopic



The ***scientific method*** is a systematic approach to research



A ***hypothesis*** is a tentative explanation for a set of observations

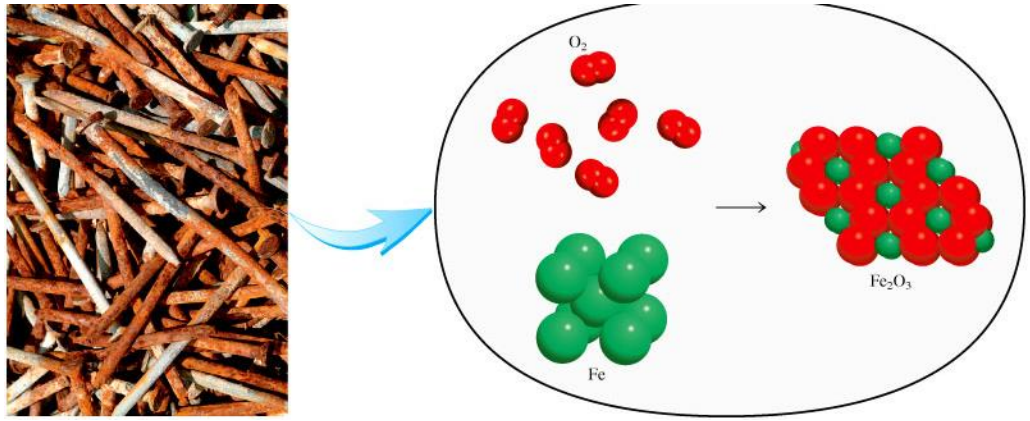


A ***law*** is a concise statement of a relationship between phenomena that is always the same under the same conditions.

Force = mass x acceleration

A ***theory*** is a unifying principle that explains a body of facts and/or those laws that are based on them.

Atomic Theory



Chemistry is the study of matter and the changes it undergoes.

1. ***Matter*** is anything that occupies space and has mass.
2. A ***substance*** is a form of matter that has a definite composition and distinct properties.

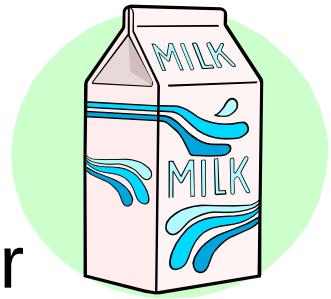
Water

Gold

Sugar

A ***mixture*** is a combination of two or more substances in which the substances retain their distinct identities.

1. ***Homogenous mixture*** (***solution***) – The composition of the mixture is the same throughout (at the atomic/molecular level).

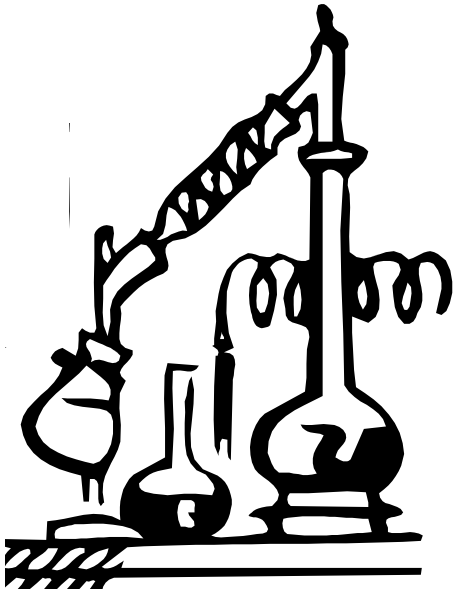


Are these homogeneous?
soft drink, milk, solder, salt water

2. ***Heterogeneous mixture*** – The composition is not uniform throughout.

Are these heterogeneous?
cement, iron filings in sand

Physical means can be used to separate a mixture into its pure components.



distillation

magnet

An ***element*** is a substance that cannot be separated into simpler substances by ***chemical means***.

- 114 elements have been identified
  - 82 elements occur naturally on Earth

    gold, aluminum, lead, oxygen, carbon
  - 32 elements have been created by scientists

    technetium, americium, seaborgium

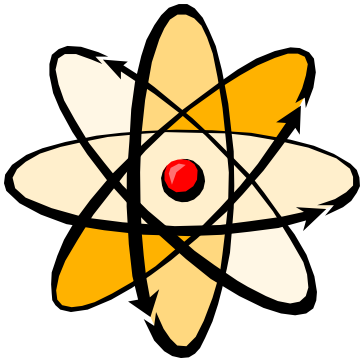


TABLE 1.1 Some Common Elements and Their Symbols

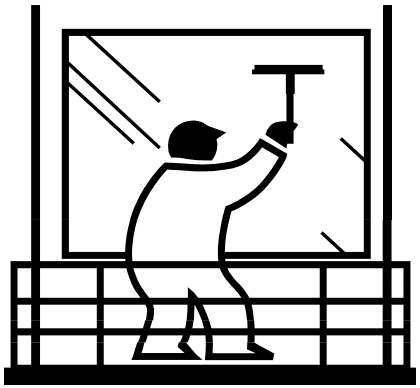
Name	Symbol	Name	Symbol	Name	Symbol
Aluminum	Al	Fluorine	F	Oxygen	O
Arsenic	As	Gold	Au	Phosphorus	P
Barium	Ba	Hydrogen	H	Platinum	Pt
Bismuth	Bi	Iodine	I	Potassium	K
Bromine	Br	Iron	Fe	Silicon	Si
Calcium	Ca	Lead	Pb	Silver	Ag
Carbon	C	Magnesium	Mg	Sodium	Na
Chlorine	Cl	Manganese	Mn	Sulfur	S
Chromium	Cr	Mercury	Hg	Tin	Sn
Cobalt	Co	Nickel	Ni	Tungsten	W
Copper	Cu	Nitrogen	N	Zinc	Zn

A ***compound*** is a substance composed of atoms of two or more elements chemically united in fixed proportions.

Compounds can only be separated into their pure components (elements) by ***chemical*** means.

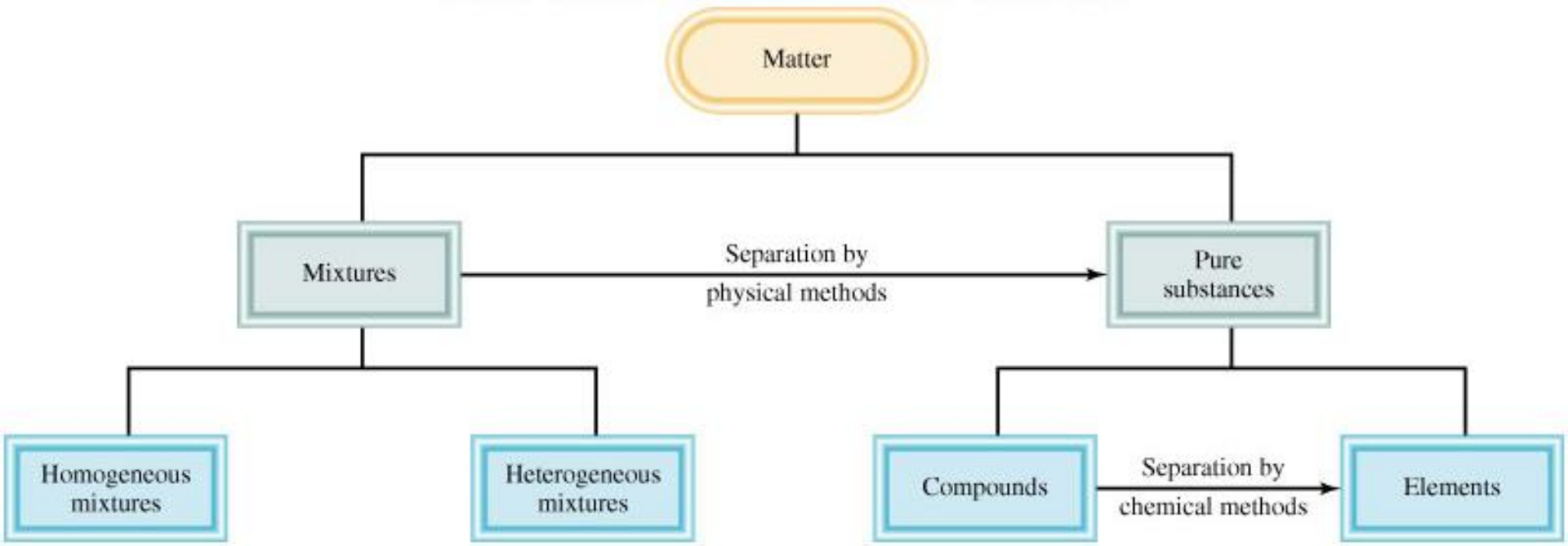
Water (H_2O)

Ammonia (NH_3)

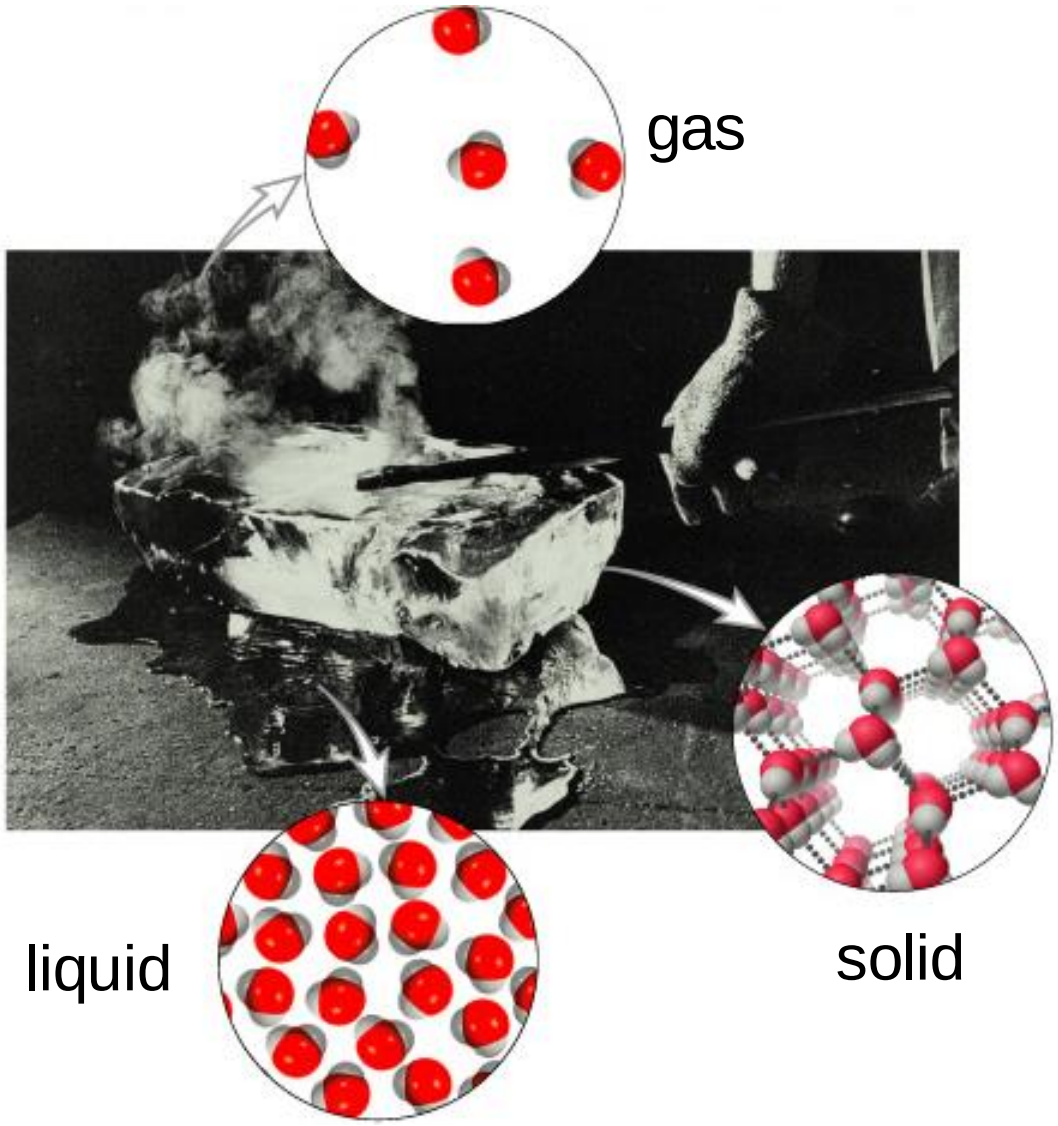


Glucose ($C_6H_{12}O_6$)

Classifications of Matter

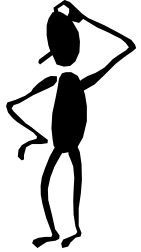


The Three States of Matter



States of Matter

Water Properties



Physical or Chemical?

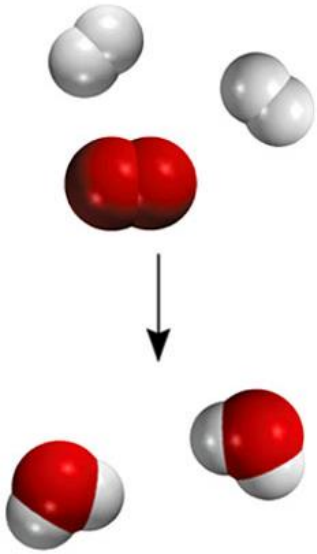
A ***physical change*** does not alter the composition or identity of a substance.

ice melting

sugar dissolving in water

A ***chemical change*** alters the composition or identity of the substance(s) involved.

hydrogen burns in air to form water

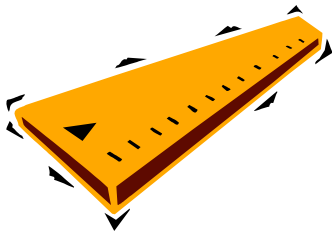


Formation of Sodium Chloride

Extensive and Intensive Properties

An ***extensive property*** of a material depends upon how much matter is is being considered.

- mass
- length
- volume



An ***intensive property*** of a material does not depend upon how much matter is is being considered.

- density
- temperature
- color

Matter - anything that occupies space and has ***mass***.

mass – measure of the quantity of matter

SI unit of mass is the ***kilogram*** (kg)

1 kg = 1000 g = 1 x 10^3 g

weight – force that gravity exerts on an object

weight = *c* x mass

on earth, *c* = 1.0

on moon, *c* ~ 0.1

A 1 kg bar will weigh

1 kg on earth

0.1 kg on moon

International System of Units (SI)

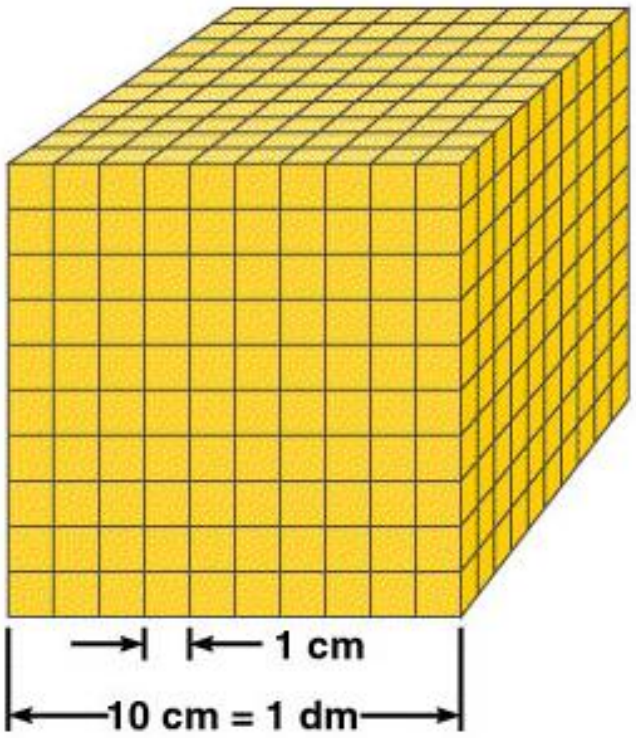
TABLE 1.2 SI Base Units

Base Quantity	Name of Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Electrical current	ampere	A
Temperature	kelvin	K
Amount of substance	mole	mol
Luminous intensity	candela	cd

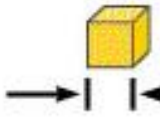
TABLE 1.3 Prefixes Used with SI Units

Prefix	Symbol	Meaning	Example
tera-	T	1,000,000,000,000, or 10^{12}	1 terameter (Tm) = 1×10^{12} m
giga-	G	1,000,000,000, or 10^{9}	1 gigameter (Gm) = 1×10^{9} m
mega-	M	1,000,000, or 10^{6}	1 megameter (Mm) = 1×10^{6} m
kilo-	k	1,000, or 10^{3}	1 kilometer (km) = 1×10^{3} m
deci-	d	1/10, or 10^{-1}	1 decimeter (dm) = 0.1 m
centi-	c	1/100, or 10^{-2}	1 centimeter (cm) = 0.01 m
milli-	m	1/1,000, or 10^{-3}	1 millimeter (mm) = 0.001 m
micro-	μ	1/1,000,000, or 10^{-6}	1 micrometer (μm) = 1×10^{-6} m
nano-	n	1/1,000,000,000, or 10^{-9}	1 nanometer (nm) = 1×10^{-9} m
pico-	p	1/1,000,000,000,000, or 10^{-12}	1 picometer (pm) = 1×10^{-12} m

Volume – SI derived unit for volume is cubic meter (m^3)



Volume: _cm^3; _mL



$1\ cm^3 = (1 \times 10^{-2}\ m)^3 = 1 \times 10^{-6}\ m^3$

$1\ dm^3 = (1 \times 10^{-1}\ m)^3 = 1 \times 10^{-3}\ m^3$

$1\ L = 1000\ mL = 1000\ cm^3 = 1\ dm^3$

$1\ mL = 1\ cm^3$

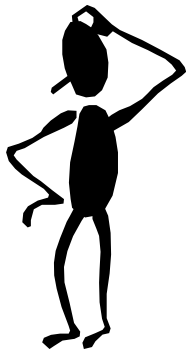
Volumetric flask

Density – SI derived unit for density is kg/m^3

$1\ g/cm^3 = 1\ g/mL = 1000\ kg/m^3$

$$\text{density} = \frac{\text{mass}}{\text{volume}} \qquad d = \frac{m}{V}$$

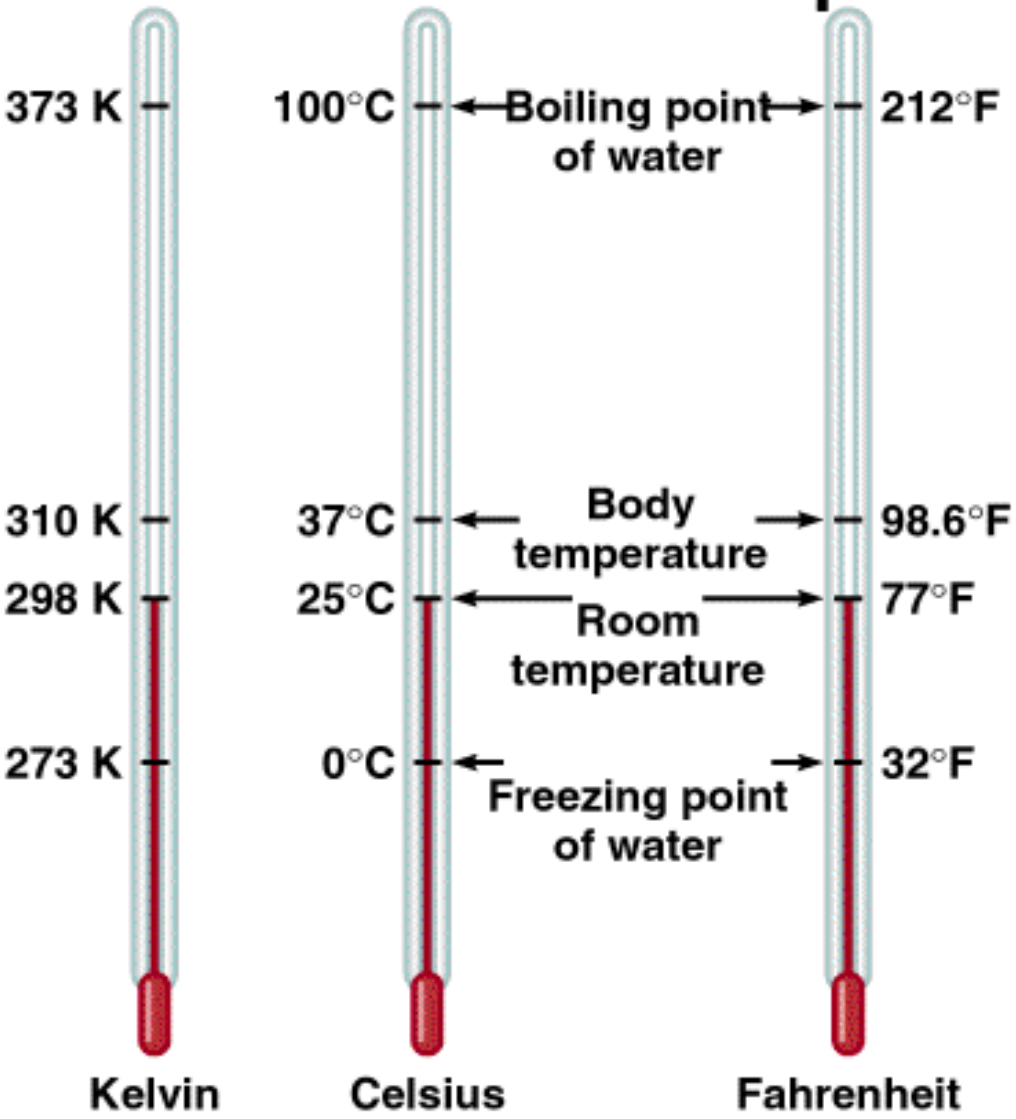
A piece of platinum metal with a density of 21.5 g/cm^3 has a volume of 4.49 cm^3. What is its mass?



$$d = \frac{m}{V}$$

$m = d \times V = 21.5\ g/cm^3 \times 4.49\ cm^3 = 96.5\ g$

Comparison of the Three Temperature Scales



$K = {}^0C + 273.15$

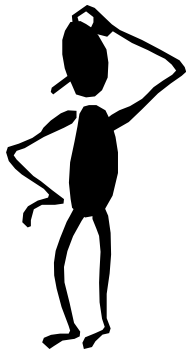
$273\ K = 0\ {}^0C$

$373\ K = 100\ {}^0C$

$${}^0F = \frac{9}{5} \times {}^0C + 32$$

$32\ {}^0F = 0\ {}^0C$

$212\ {}^0F = 100\ {}^0C$



Convert 172.9 ^{0}F to degrees Celsius.

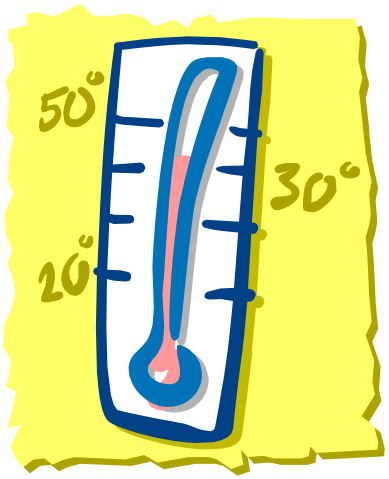
$$^0F = \frac{9}{5} \times {}^0C + 32$$

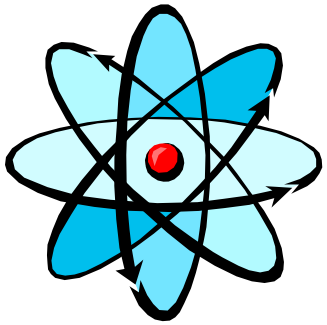
$$^0F - 32 = \frac{9}{5} \times {}^0C$$

$$\frac{5}{9} \times (^0F - 32) = {}^0C$$

$$^0C = \frac{5}{9} \times (^0F - 32)$$

$$^0C = \frac{5}{9} \times (172.9 - 32) = 78.3$$





Scientific Notation

The number of atoms in 12 g of carbon-12:

602,200,000,000,000,000,000,000

6.022×10^{23}

The mass of a single carbon atom in grams:

0.000000000000000000000199

1.99×10^{-23}

$N \times 10^{n}$

N is a number between 1 and 10

n is a positive or negative integer

Scientific Notation

568.762

← move decimal left

$n > 0$

$568.762 = 5.68762 \times 10^{2}$

0.00000772

→ move decimal right

$n < 0$

$0.00000772 = 7.72 \times 10^{-6}$

Addition or Subtraction

1. Write each quantity with the same exponent *n*
2. Combine N_1 and N_2
3. The exponent, *n*, remains the same

$4.31 \times 10^{4} + 3.9 \times 10^{3} =$

$4.31 \times 10^{4} + 0.39 \times 10^{4} =$

4.70×10^{4}

Scientific Notation

Multiplication

1. Multiply N_1 and N_2
2. Add exponents n_1 and n_2

$(4.0 \times 10^{-5}) \times (7.0 \times 10^{3}) =$
$(4.0 \times 7.0) \times (10^{-5+3}) =$
$28 \times 10^{-2} =$
2.8×10^{-1}

Division

1. Divide N_1 and N_2
2. Subtract exponents n_1 and n_2

$8.5 \times 10^{4} \div 5.0 \times 10^{9} =$
$(8.5 \div 5.0) \times 10^{4-9} =$
1.7×10^{-5}

Significant Figures

- Any digit that is not zero is significant

  1.234 kg 4 significant figures

- Zeros between nonzero digits are significant

  606 m 3 significant figures

- Zeros to the left of the first nonzero digit are **not** significant

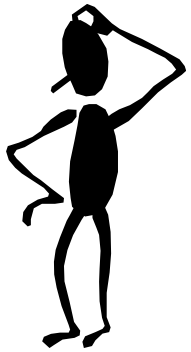
  0.08 L 1 significant figure

- If a number is greater than 1, then all zeros to the right of the decimal point are significant

  2.0 mg 2 significant figures

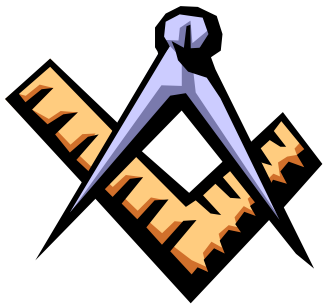
- If a number is less than 1, then only the zeros that are at the end and in the middle of the number are significant

  0.00420 g 3 significant figures



How many significant figures are in each of the following measurements?

24 mL	2 significant figures
3001 g	4 significant figures
0.0320 m^3	3 significant figures
6.4 x 10^4 molecules	2 significant figures
560 kg	2 significant figures



Significant Figures

Addition or Subtraction

The answer cannot have more digits to the right of the decimal point than any of the original numbers.

89.332
+1.1 ⟵ one significant figure after decimal point
90.432 ⟵ round off to 90.4

3.70 ⟵ two significant figures after decimal point
-2.9133
0.7867 ⟵ round off to 0.79

Significant Figures

Multiplication or Division

The number of significant figures in the result is set by the original number that has the ***smallest*** number of significant figures

$$4.51 \times 3.6666 = 16.536366 = 16.5$$

3 sig figs

round to 3 sig figs

$$6.8 \div 112.04 = 0.0606926 = 0.061$$

2 sig figs

round to 2 sig figs

Significant Figures

Exact Numbers

Numbers from definitions or numbers of objects are considered to have an infinite number of significant figures

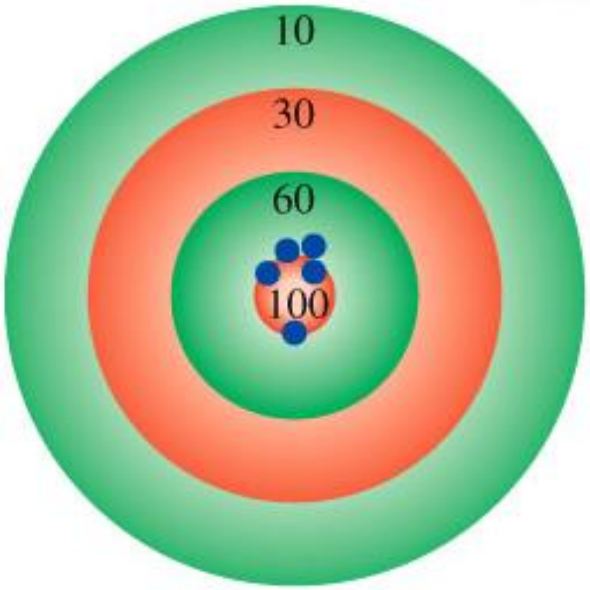
The average of three measured lengths; 6.64, 6.68 and 6.70 = ?

$$\frac{6.64 + 6.68 + 6.70}{3} = 6.67333 = 6.67 = \cancel{7}$$

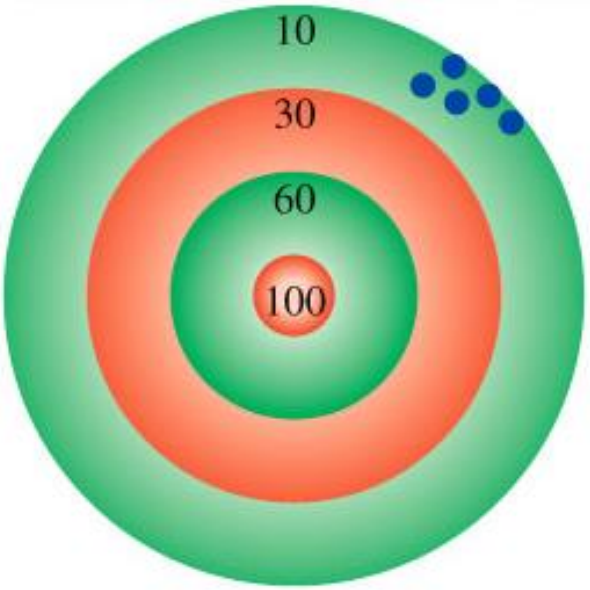
Because 3 is an ***exact number***

Accuracy – how close a measurement is to the *true* value

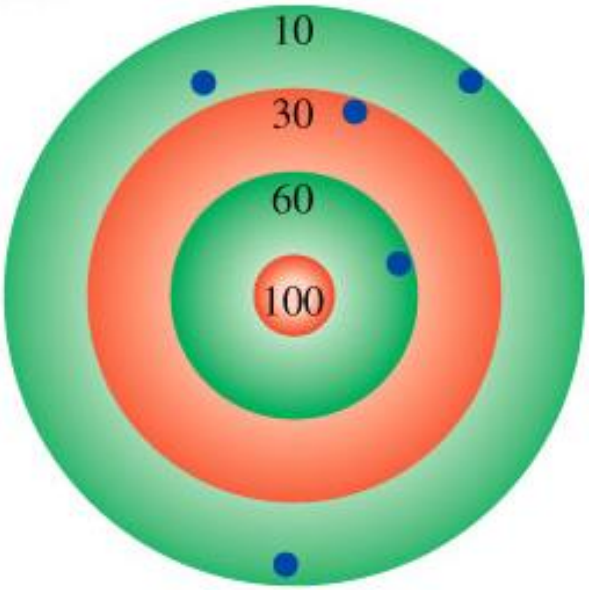
Precision – how close a set of measurements are to each other



accurate
&
precise



precise
but
not accurate



not accurate
&
not precise

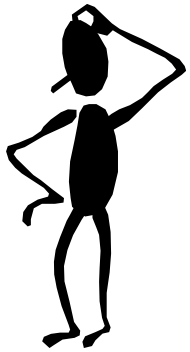
Dimensional Analysis Method of Solving Problems

1. Determine which unit conversion factor(s) are needed
2. Carry units through calculation
3. If all units cancel except for the ***desired unit(s)***, then the problem was solved correctly.

given quantity x conversion factor = desired quantity

$$\text{given unit} \times \frac{\text{desired unit}}{\text{given unit}} = \text{desired unit}$$

Dimensional Analysis Method of Solving Problems

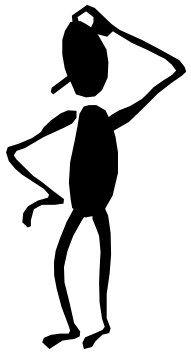


How many mL are in 1.63 L?

Conversion Unit 1 L = 1000 mL

$$1.63\ \cancel{L} \times \frac{1000\ mL}{1\cancel{L}} = 1630\ mL$$

$$1.63\ L \times \frac{1L}{1000\ mL} = 0.001630\ \frac{L^2}{mL}$$



The speed of sound in air is about 343 m/s. What is this speed in miles per hour?

conversion units

meters to miles

seconds to hours

1 mi = 1609 m 1 min = 60 s 1 hour = 60 min

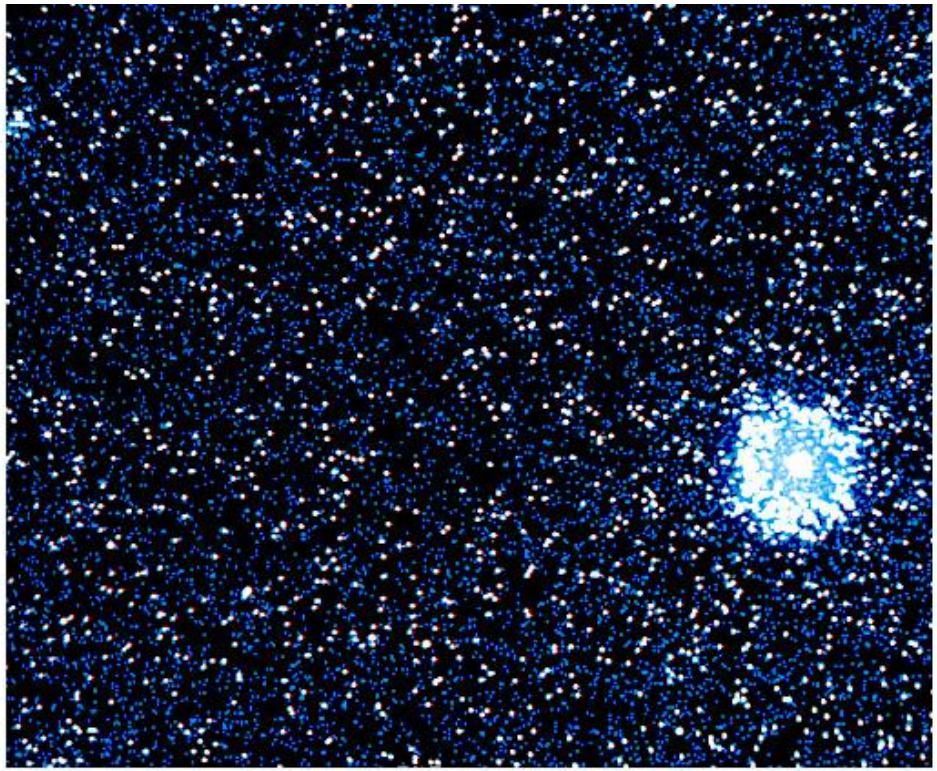
$$343 \frac{m}{s} \times \frac{1\ mi}{1609\ m} \times \frac{60\ s}{1\ min} \times \frac{60\ min}{1\ hour} = 767 \frac{mi}{hour}$$


END

Chemistry In Action:

Primordial Helium and the Big Bang Theory

In 1940 George Gamow ***hypothesized*** that the universe began with a gigantic explosion or big bang.



<u>Experimental Support</u>

- expanding universe
- cosmic background radiation
- primordial helium

Chemistry In Action

On 9/23/99, $125,000,000 Mars Climate Orbiter entered Mar's atmosphere 100 km (62 miles) lower than planned and was destroyed by heat.

1 lb ≠ 1 N

1 lb = 4.45 N

"This is going to be the cautionary tale that will be embedded into introduction to the metric system in elementary school, high school, and college science courses till the end of time."

Reactions in Aqueous Solution

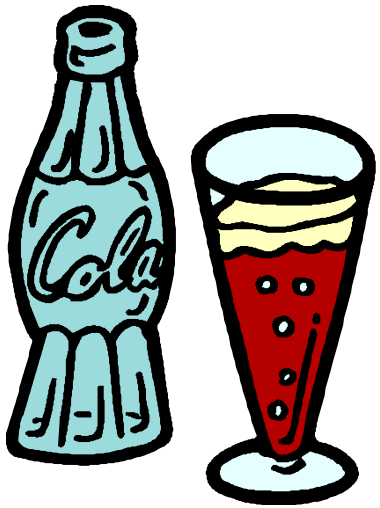
Chapter 4

A ***solution*** is a homogenous mixture of 2 or more substances

The ***solute*** is(are) the substance(s) present in the smaller amount(s)

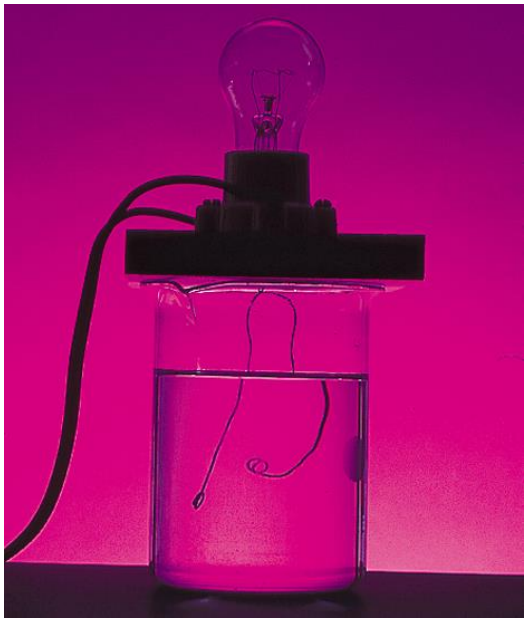
The ***solvent*** is the substance present in the larger amount

Solution	Solvent	Solute
Soft drink (*l*)	H_2O	Sugar, CO_2
Air (*g*)	N_2	O_2, Ar, CH_4
Soft Solder (*s*)	Pb	Sn

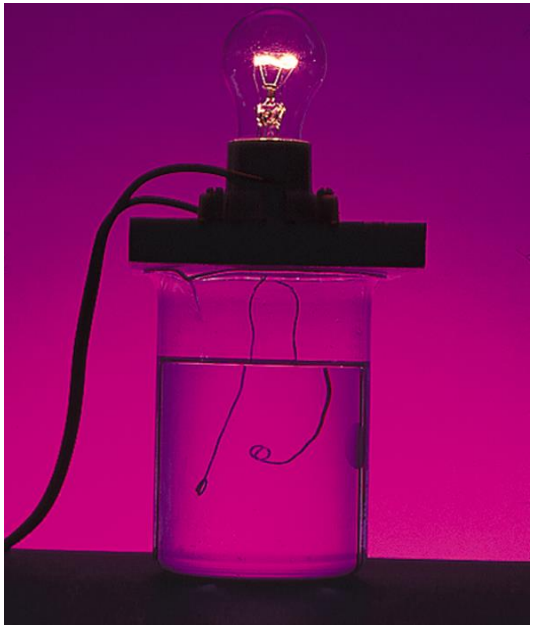


An ***electrolyte*** is a substance that, when dissolved in water, results in a solution that can conduct electricity.

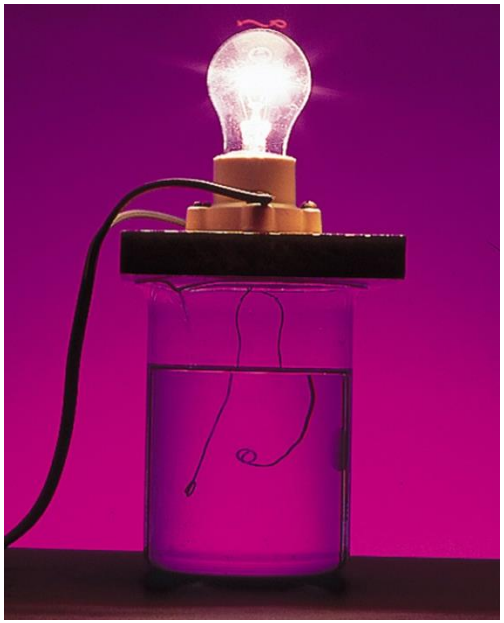
A ***nonelectrolyte*** is a substance that, when dissolved, results in a solution that does not conduct electricity.



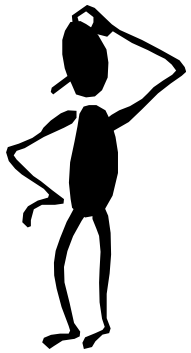
nonelectrolyte



weak electrolyte



strong electrolyte



Conduct electricity in solution?

Cations (+) and Anions (-)

Strong Electrolyte – 100% dissociation

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Weak Electrolyte – not completely dissociated

$$CH_3COOH \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

Ionization of acetic acid

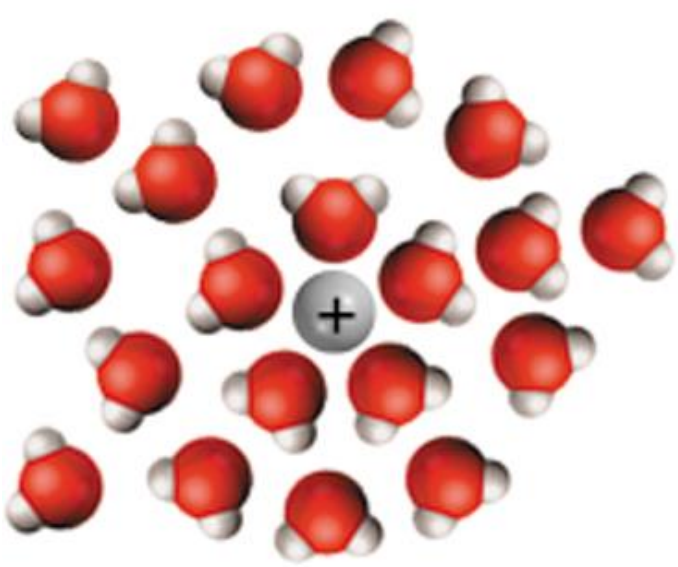
$$CH_3COOH \rightleftharpoons CH_3COO^- (aq) + H^+ (aq)$$

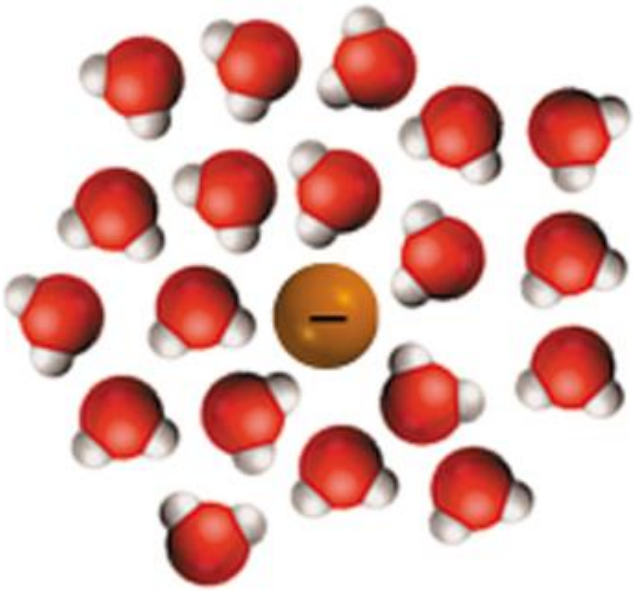
$\rightleftharpoons$

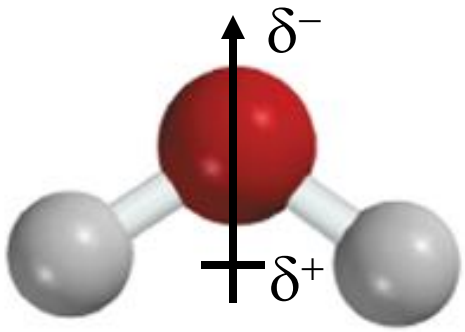
A ***reversible*** reaction. The reaction can occur in both directions.

Acetic acid is a ***weak electrolyte*** because its ionization in water is incomplete.

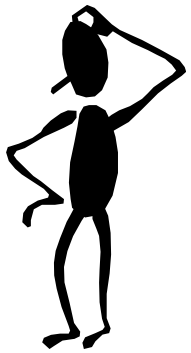
Hydration is the process in which an ion is surrounded by water molecules arranged in a specific manner.







H_2O



Nonelectrolyte does not conduct electricity?

No cations (+) and anions (-) in solution

$$C_6H_{12}O_6\,(s) \xrightarrow{H_2O} C_6H_{12}O_6\,(aq)$$

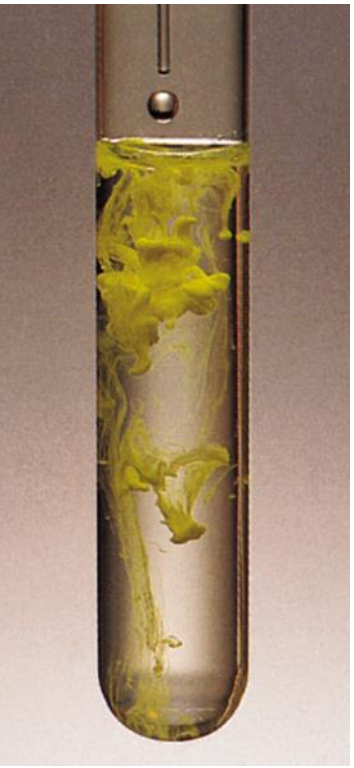
TABLE 4.1 Classification of Solutes in Aqueous Solution

Strong Electrolyte	Weak Electrolyte	Nonelectrolyte
HCl	CH_3COOH	$(NH_2)_2CO$ (urea)
HNO_3	HF	CH_3OH (methanol)
$HClO_4$	HNO_2	C_2H_5OH (ethanol)
H_2SO_4*	NH_3	$C_6H_{12}O_6$ (glucose)
NaOH	H_2O†	$C_{12}H_{22}O_{11}$ (sucrose)
$Ba(OH)_2$		
Ionic compounds		

*H_2SO_4 has two ionizable H^+ ions.
†Pure water is an extremely weak electrolyte.

Precipitation Reactions

Precipitate – insoluble solid that separates from solution



PbI_2

precipitate

$$Pb(NO_3)_2\ (aq) + 2NaI\ (aq) \longrightarrow PbI_2\ (s) + 2NaNO_3\ (aq)$$

molecular equation

$$Pb^{2+} + \cancel{2NO_3^-} + \cancel{2Na^+} + 2I^- \longrightarrow PbI_2\ (s) + \cancel{2Na^+} + \cancel{2NO_3^-}$$

ionic equation

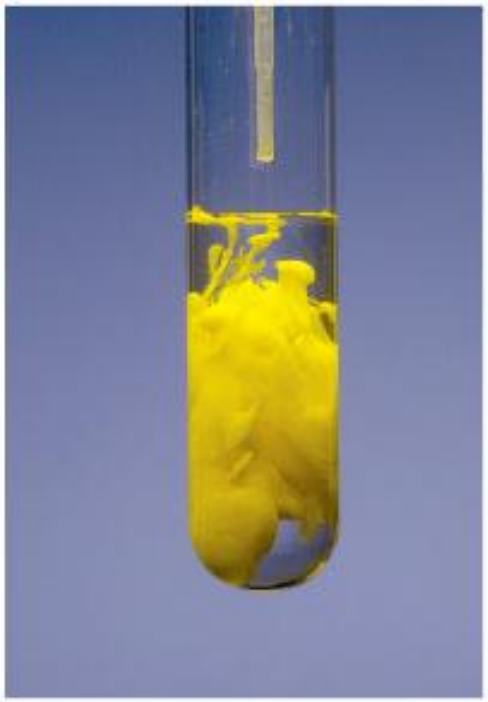
$$Pb^{2+} + 2I^- \longrightarrow PbI_2\ (s)$$

net ionic equation

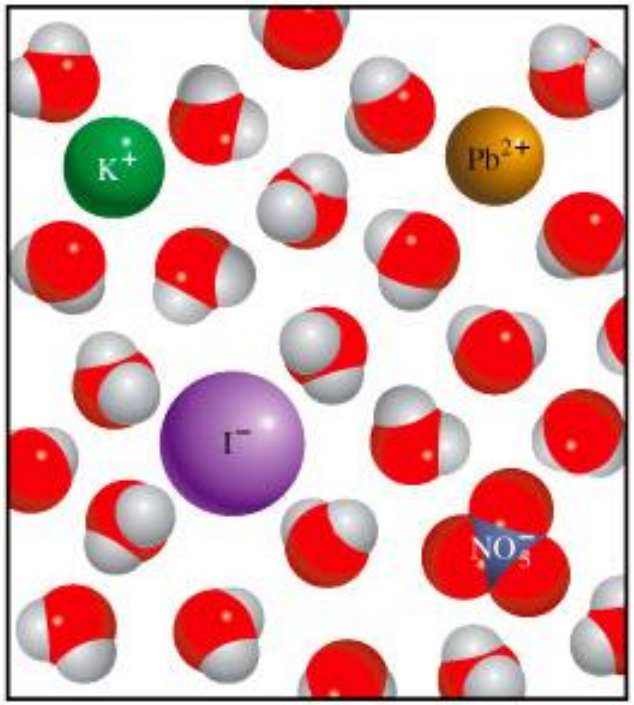
Na^+ and NO_3^- are ***spectator*** ions

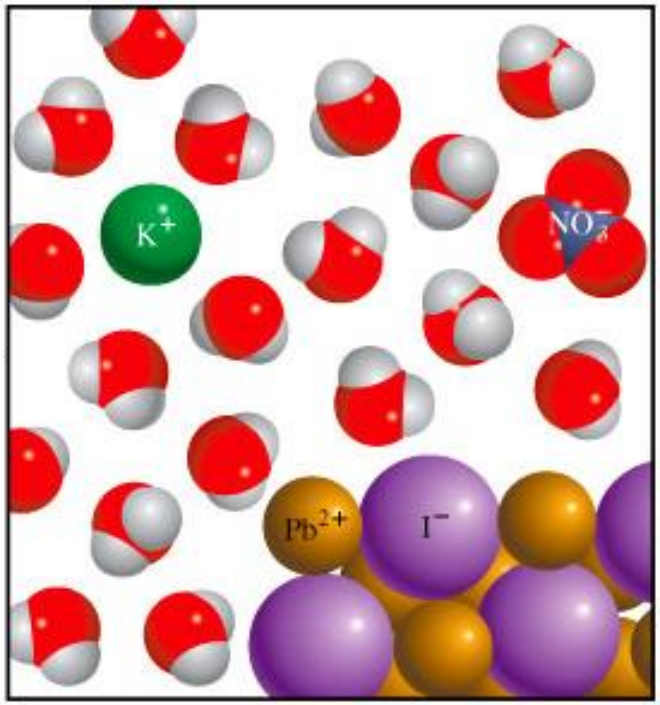
Precipitation of Lead Iodide

$$Pb^{2+} + 2I^{-} \longrightarrow PbI_2\,(s)$$



PbI_2





Solubility is the maximum amount of solute that will dissolve in a given quantity of solvent at a specific temperature.

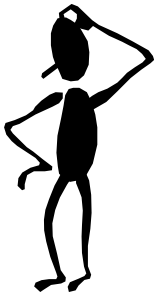
TABLE 4.2 Solubility Rules for Common Ionic Compounds in Water at 25°C

Soluble Compounds	Exceptions
Compounds containing alkali metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+) and the ammonium ion (NH_4^+)	
Nitrates (NO_3^-), bicarbonates (HCO_3^-), and chlorates (ClO_3^-)	
Halides (Cl^-, Br^-, I^-)	Halides of Ag^+, Hg_2^{2+}, and Pb^{2+}
Sulfates (SO_4^{2-})	Sulfates of Ag^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg_2^{2+}, and Pb^{2+}

Insoluble Compounds	Exceptions
Carbonates (CO_3^{2-}), phosphates (PO_4^{3-}), chromates (CrO_4^{2-}), sulfides (S^{2-})	Compounds containing alkali metal ions and the ammonium ion
Hydroxides (OH^-)	Compounds containing alkali metal ions and the Ba^{2+} ion

Writing Net Ionic Equations

1. Write the balanced molecular equation.
2. Write the ionic equation showing the strong electrolytes completely dissociated into cations and anions.
3. Cancel the spectator ions on both sides of the ionic equation
4. Check that charges and number of atoms are balanced in the net ionic equation



Write the net ionic equation for the reaction of silver nitrate with sodium chloride.

$$AgNO_3\,(aq) + NaCl\,(aq) \longrightarrow AgCl\,(s) + NaNO_3\,(aq)$$

$$Ag^+ + \cancel{NO_3^-} + \cancel{Na^+} + Cl^- \longrightarrow AgCl\,(s) + \cancel{Na^+} + \cancel{NO_3^-}$$

$$Ag^+ + Cl^- \longrightarrow AgCl\,(s)$$

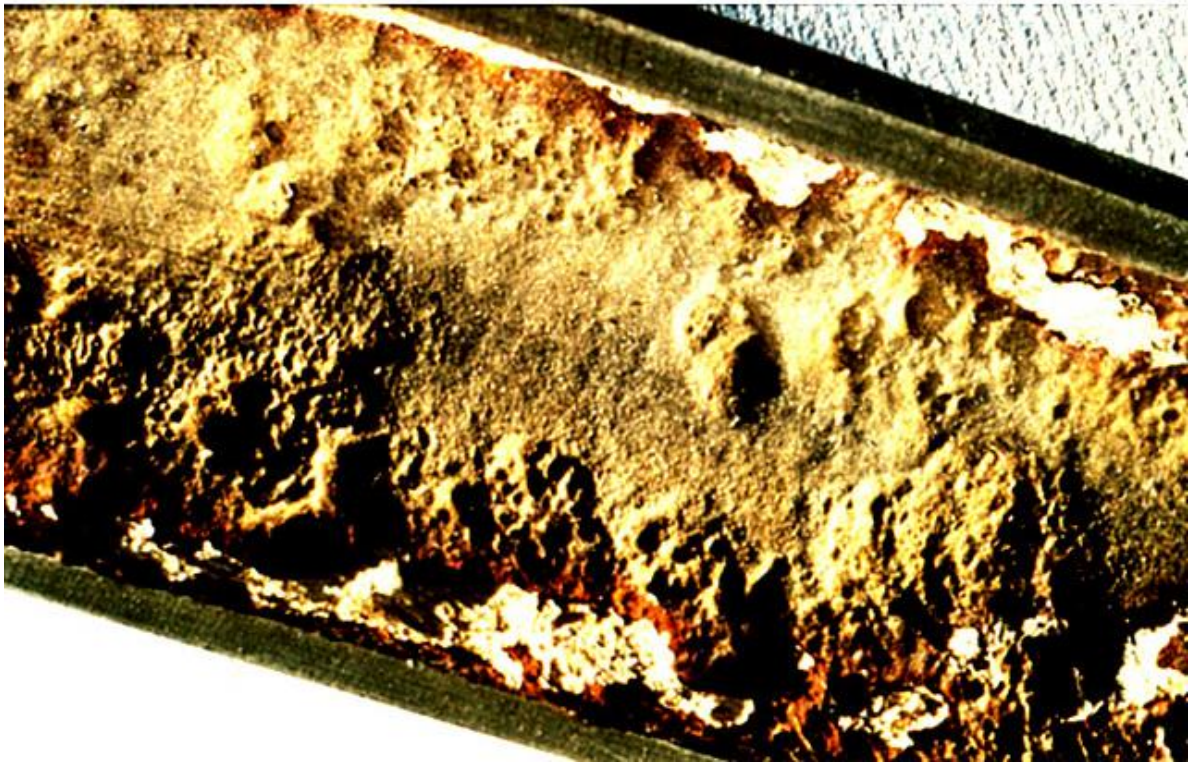
Chemistry In Action:

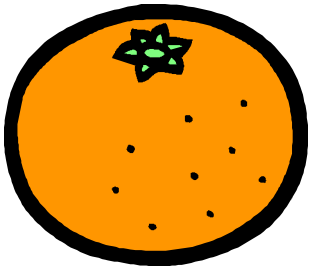
An Undesirable Precipitation Reaction

$$Ca^{2+}\,(aq) + 2HCO_3^-\,(aq) \xrightarrow{\Delta} CaCO_3\,(s) + CO_2\,(aq) + H_2O\,(l)$$

$$CO_2\,(aq) \xrightarrow{\Delta} CO_2\,(g)$$

Boiler Scale Deposits





Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

Cause color changes in plant dyes.

React with certain metals to produce hydrogen gas.

$$2HCl\ (aq) + Mg\ (s) \longrightarrow MgCl_2\ (aq) + H_2\ (g)$$

React with carbonates and bicarbonates to produce carbon dioxide gas

$$2HCl\ (aq) + CaCO_3\ (s) \longrightarrow CaCl_2\ (aq) + CO_2\ (g) + H_2O\ (l)$$

Aqueous acid solutions conduct electricity.

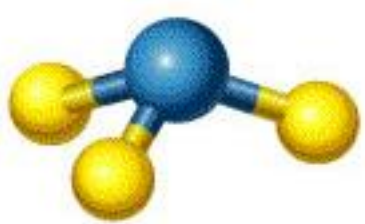
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

Cause color changes in plant dyes.

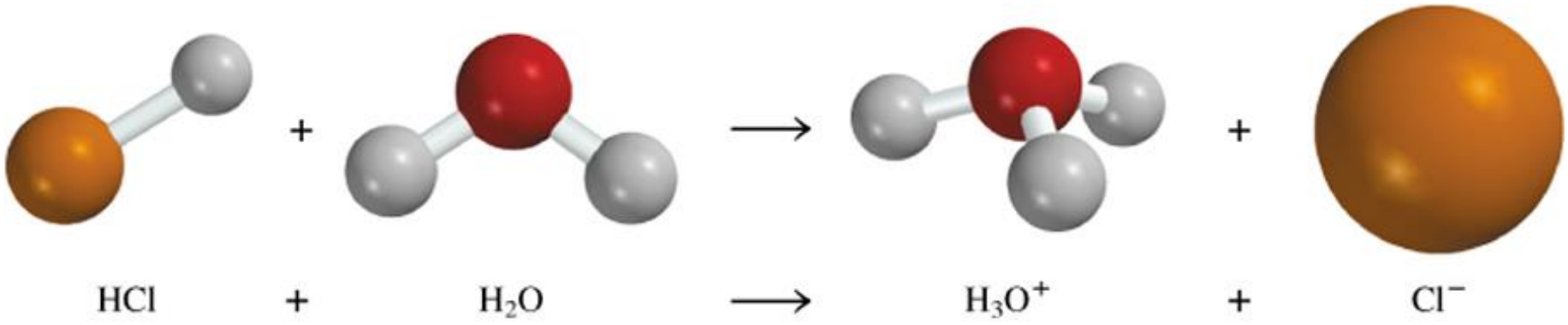
Aqueous base solutions conduct electricity.



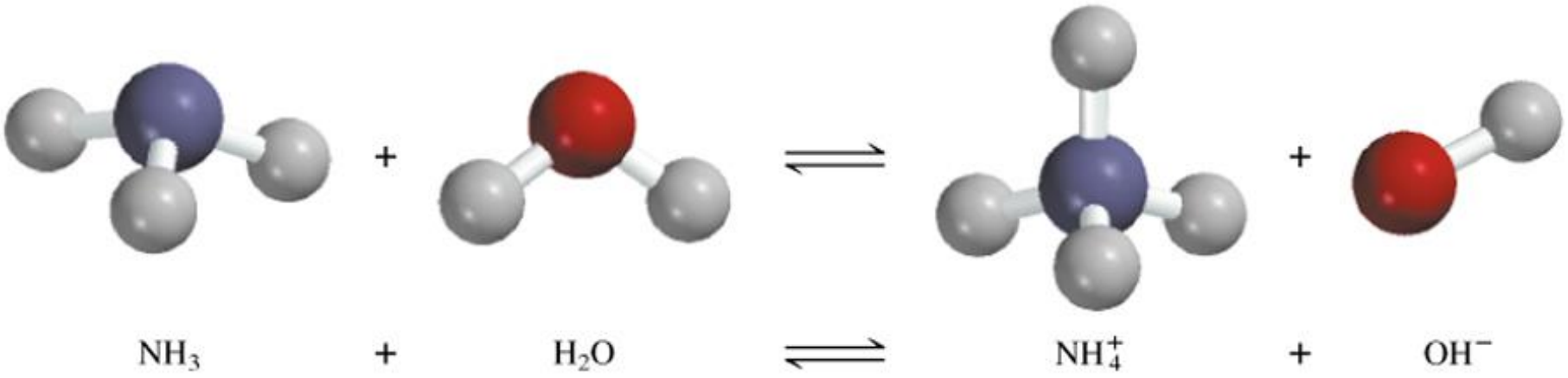
NH_3

OH^-

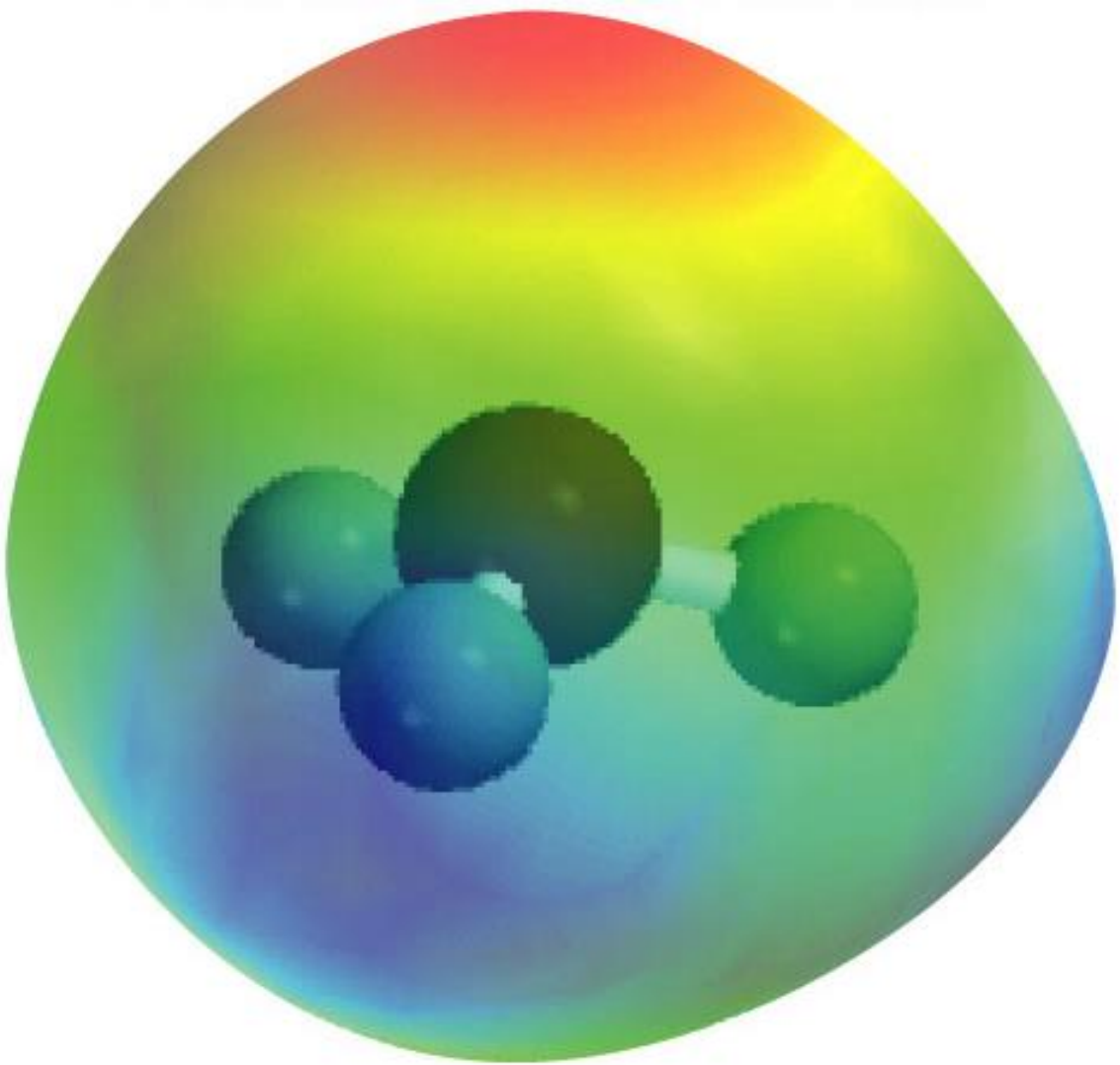
Arrhenius acid is a substance that produces H^+ (H_3O^+) in water



Arrhenius base is a substance that produces OH^- in water

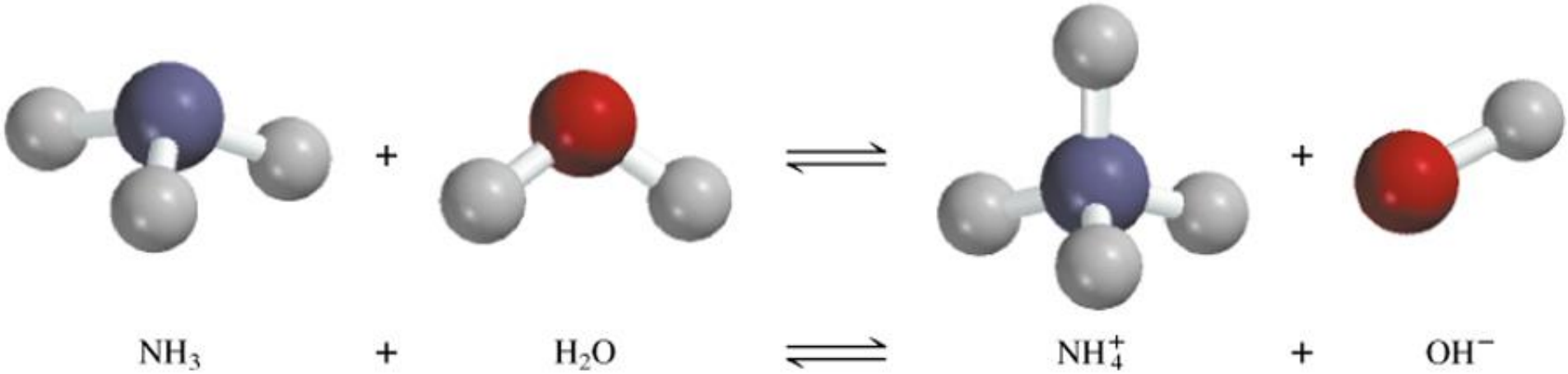


Hydronium ion, hydrated proton, H_3O^+



A ***Brønsted acid*** is a proton donor

A ***Brønsted base*** is a proton acceptor



A Brønsted acid must contain at least one ionizable proton!

Monoprotic acids

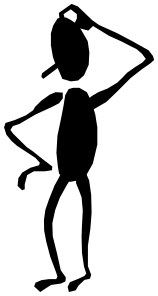
$HCl \longrightarrow H^+ + Cl^-$	Strong electrolyte, strong acid
$HNO_3 \longrightarrow H^+ + NO_3^-$	Strong electrolyte, strong acid
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	Weak electrolyte, weak acid

Diprotic acids

$H_2SO_4 \longrightarrow H^+ + HSO_4^-$	Strong electrolyte, strong acid
$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	Weak electrolyte, weak acid

Triprotic acids

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	Weak electrolyte, weak acid
$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	Weak electrolyte, weak acid
$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	Weak electrolyte, weak acid



Identify each of the following species as a Brønsted acid, base, or both. (a) HI, (b) CH_3COO^-, (c) $H_2PO_4^-$

$HI\ (aq) \longrightarrow H^+\ (aq) + I^-\ (aq)$ Brønsted acid

$CH_3COO^-\ (aq) + H^+\ (aq) \rightleftharpoons CH_3COOH\ (aq)$ Brønsted base

$H_2PO_4^-\ (aq) \rightleftharpoons H^+\ (aq) + HPO_4^{2-}\ (aq)$ Brønsted acid

$H_2PO_4^-\ (aq) + H^+\ (aq) \rightleftharpoons H_3PO_4\ (aq)$ Brønsted base

Neutralization Reaction

acid + base ⟶ salt + water

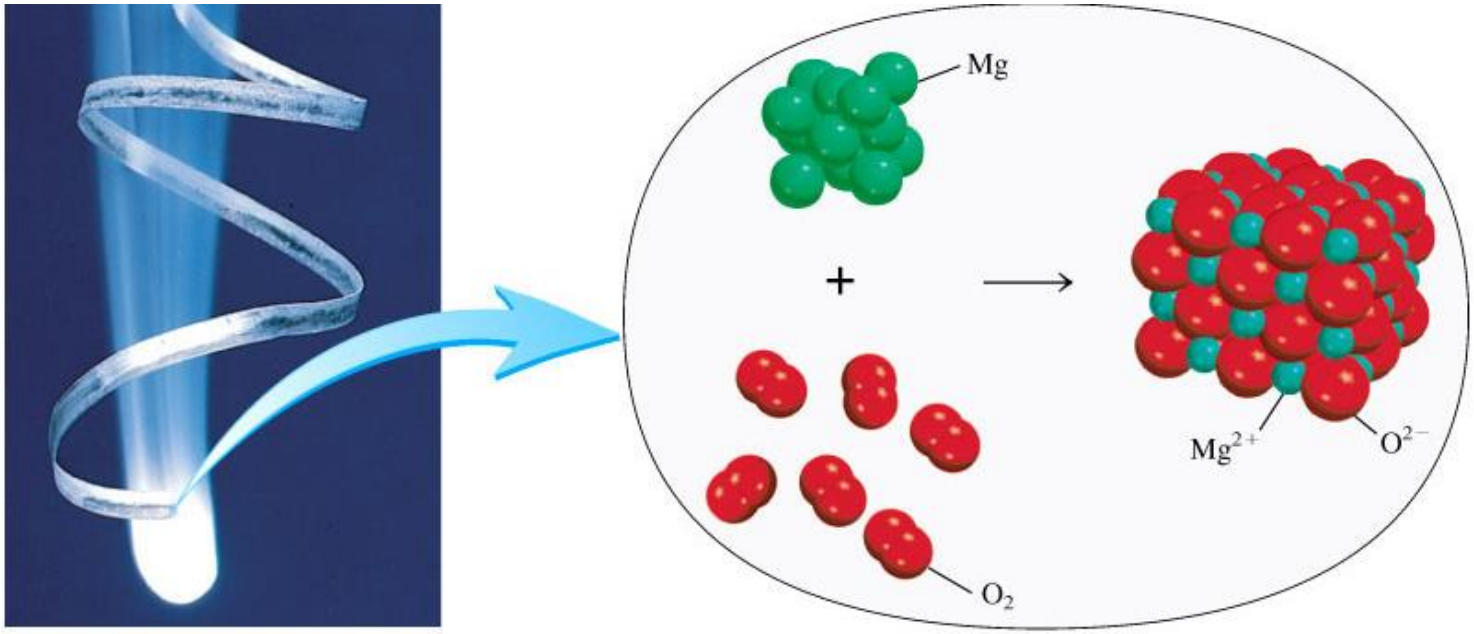
$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O$

$H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \longrightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O$

$H^+ + OH^- \longrightarrow H_2O$

Oxidation-Reduction Reactions

(electron transfer reactions)



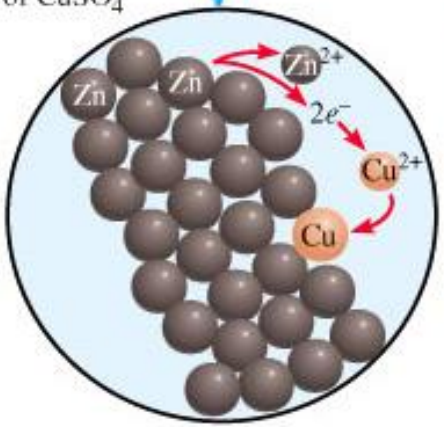
$2Mg \longrightarrow 2Mg^{2+} + 4e^-$ ***Oxidation*** half-reaction (lose e^-)

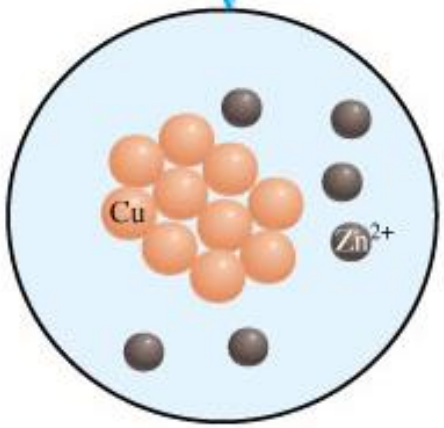
$O_2 + 4e^- \longrightarrow 2O^{2-}$ ***Reduction*** half-reaction (gain e^-)

$$2Mg + O_2 + \cancel{4e^-} \longrightarrow 2Mg^{2+} + 2O^{2-} + \cancel{4e^-}$$

$$2Mg + O_2 \longrightarrow 2MgO$$

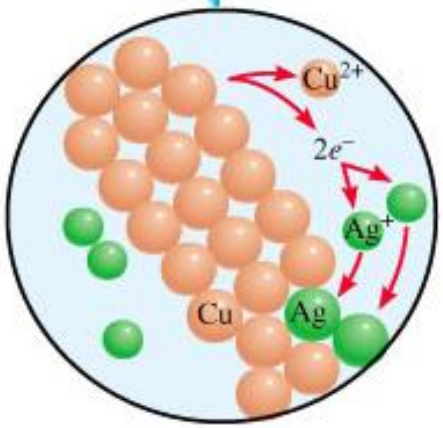
The Zn bar is in aqueous solution of $CuSO_4$

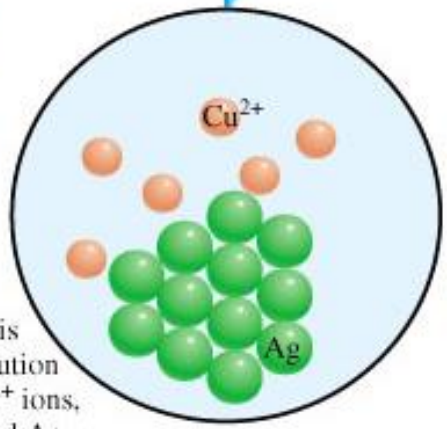




Cu^{2+} ions are converted to Cu atoms. Zn atoms enter the solution as Zn^{2+} ions.

(a)





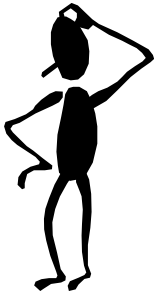
When a piece of copper wire is placed in an aqueous $AgNO_3$ solution Cu atoms enter the solution as Cu^{2+} ions, and Ag^+ ions are converted to solid Ag.

(b)

$$Zn\,(s) + CuSO_4\,(aq) \longrightarrow ZnSO_4\,(aq) + Cu\,(s)$$

$Zn \longrightarrow Zn^{2+} + 2e^-$ Zn is oxidized Zn is the ***reducing agent***

$Cu^{2+} + 2e^- \longrightarrow Cu$ Cu^{2+} is reduced Cu^{2+} is the ***oxidizing agent***



Copper wire reacts with silver nitrate to form silver metal. What is the oxidizing agent in the reaction?

$$Cu\,(s) + 2AgNO_3\,(aq) \longrightarrow Cu(NO_3)_2\,(aq) + 2Ag\,(s)$$

$Cu \longrightarrow Cu^{2+} + 2e^-$

$Ag^+ + 1e^- \longrightarrow Ag$ Ag^+ is reduced Ag^+ is the oxidizing agent

Oxidation number

The charge the atom would have in a molecule (or an ionic compound) if electrons were completely transferred.

1. Free elements (uncombined state) have an oxidation number of zero.

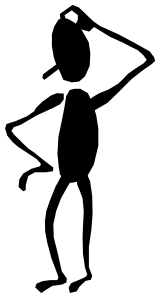
$$Na, Be, K, Pb, H_2, O_2, P_4 = 0$$

2. In monatomic ions, the oxidation number is equal to the charge on the ion.

$$Li^+, Li = +1; Fe^{3+}, Fe = +3; O^{2-}, O = -2$$

3. The oxidation number of oxygen is **usually** –2. In H_2O_2 and O_2^{2-} it is –1.

4. The oxidation number of hydrogen is +1 *except* when it is bonded to metals in binary compounds. In these cases, its oxidation number is –1.
5. Group IA metals are +1, IIA metals are +2 and fluorine is always –1.
6. The sum of the oxidation numbers of all the atoms in a molecule or ion is equal to the charge on the molecule or ion.
7. Oxidation numbers do not have to be integers. Oxidation number of oxygen in the superoxide ion, O_2^-, is -½.



Oxidation numbers of all the elements in HCO_3^- ?

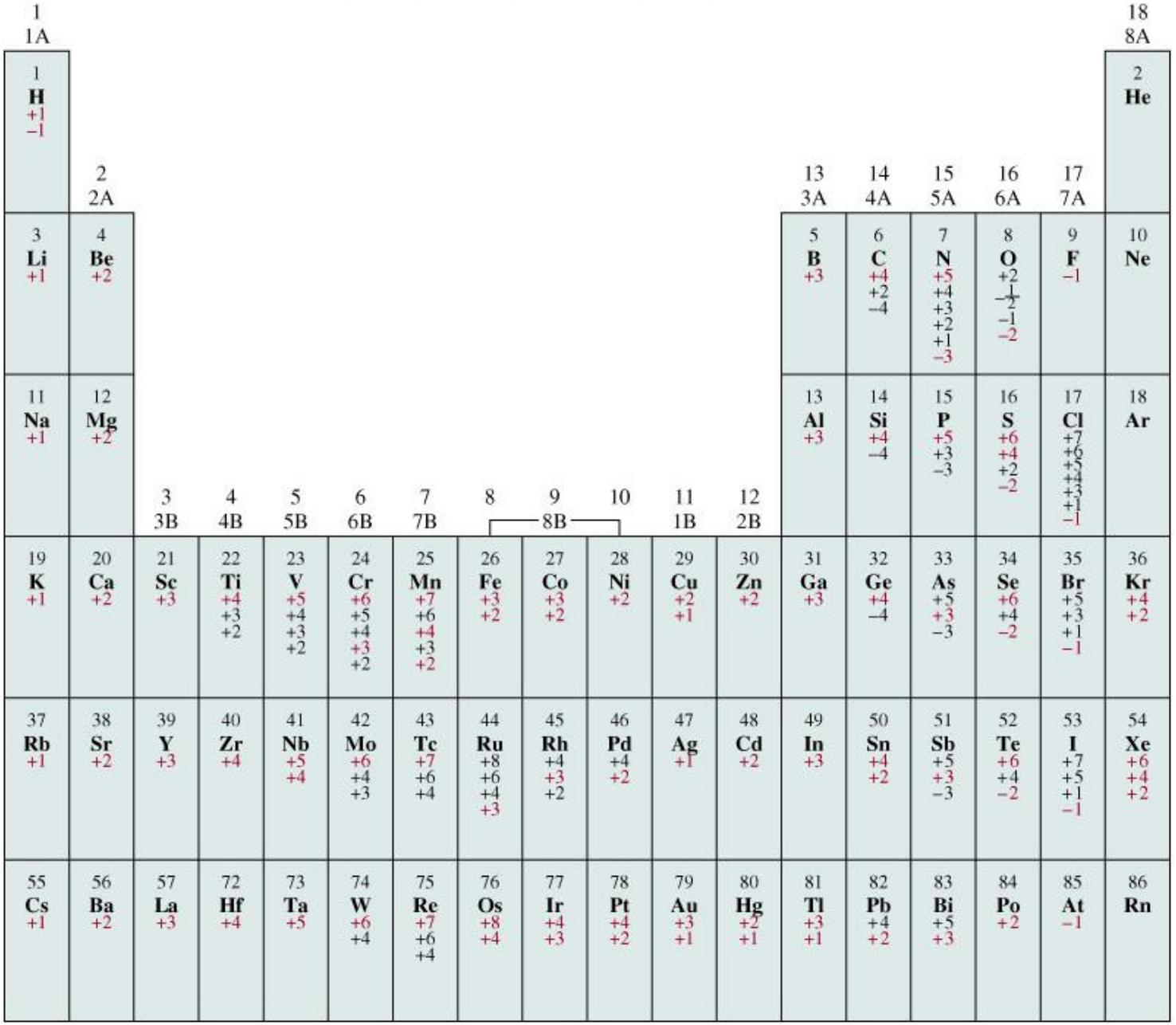
HCO_3^-

O = -2 H = +1

3x(-2) + 1 + ? = -1

C = +4

The oxidation numbers of elements in their compounds



Oxidation numbers of all the elements in the following ?

IF_7

F = -1

7x(-1) + ? = 0

I = +7

$NaIO_3$

Na = +1 O = -2

3x(-2) + 1 + ? = 0

I = +5

$K_2Cr_2O_7$

O = -2 K = +1

7x(-2) + 2x(+1) + 2x(?) = 0

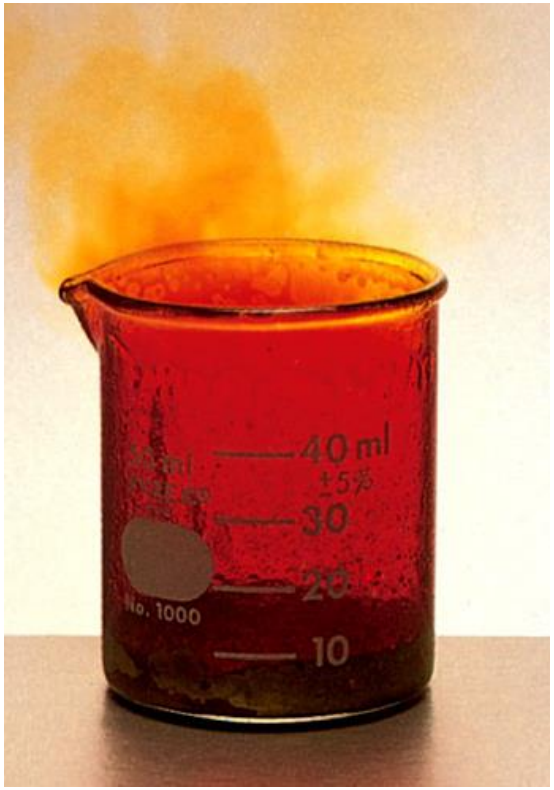
Cr = +6

Types of Oxidation-Reduction Reactions

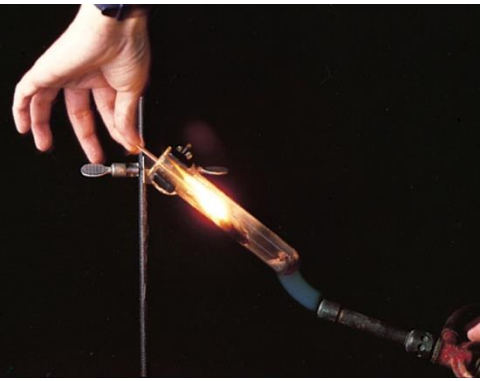
Combination Reaction

$$A + B \longrightarrow C$$

$$\overset{0}{2Al} + \overset{0}{3Br_2} \longrightarrow \overset{+3\ -1}{2AlBr_3}$$



Decomposition Reaction



$$C \longrightarrow A + B$$

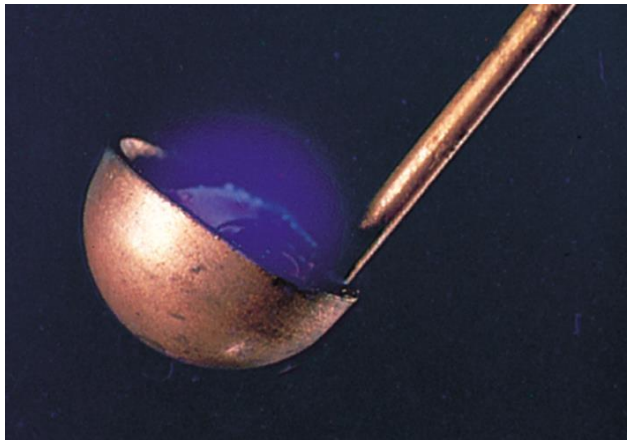
$$\overset{+1\ +5\ -2}{2KClO_3} \longrightarrow \overset{+1\ -1}{2KCl} + \overset{0}{3O_2}$$

Types of Oxidation-Reduction Reactions

Combustion Reaction

$$A + O_2 \longrightarrow B$$

$$\overset{0}{S} + \overset{0}{O_2} \longrightarrow \overset{+4\ -2}{SO_2}$$



$$\overset{0}{2Mg} + \overset{0}{O_2} \longrightarrow \overset{+2\ -2}{2MgO}$$

Types of Oxidation-Reduction Reactions

Displacement Reaction

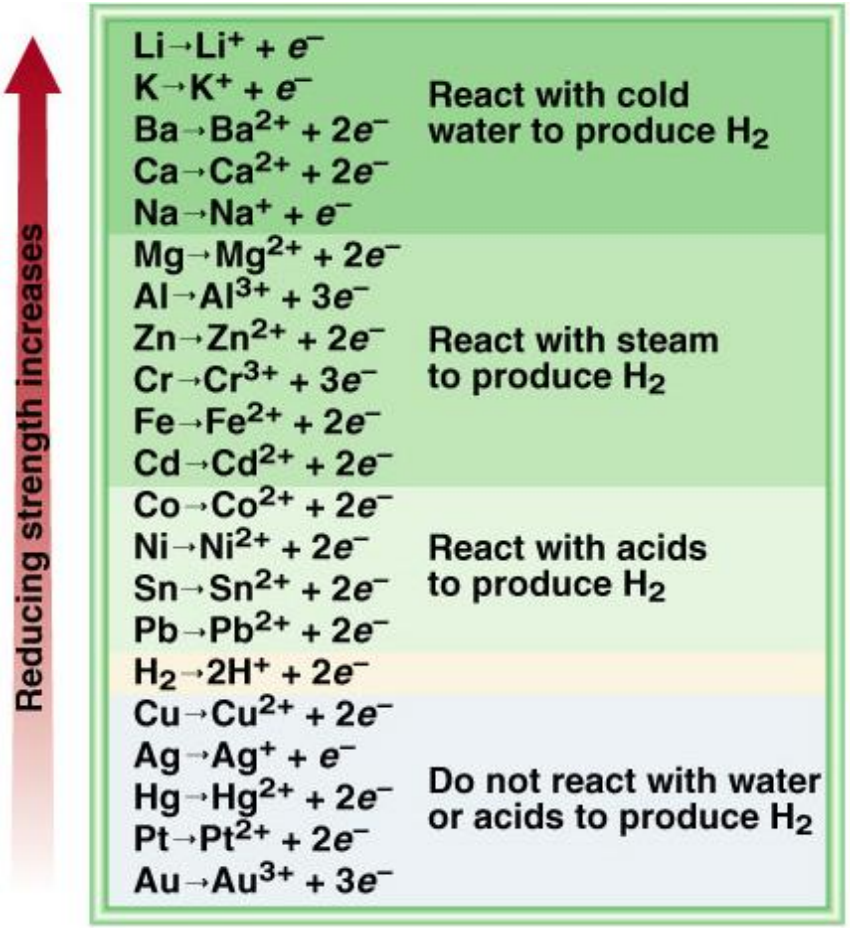
$$A + BC \longrightarrow AC + B$$

$\overset{0}{Sr} + 2\overset{+1}{H_2O} \longrightarrow \overset{+2}{Sr(OH)_2} + \overset{0}{H_2}$ Hydrogen Displacement

$\overset{+4}{TiCl_4} + 2\overset{0}{Mg} \longrightarrow \overset{0}{Ti} + 2\overset{+2}{MgCl_2}$ Metal Displacement

$\overset{0}{Cl_2} + 2\overset{-1}{KBr} \longrightarrow 2\overset{-1}{KCl} + \overset{0}{Br_2}$ Halogen Displacement

The Activity Series for Metals



Hydrogen Displacement Reaction

$$M + BC \longrightarrow AC + B$$

M is metal

BC is acid or H_2O

B is H_2

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + H_2$$

~~$$Pb + 2H_2O \longrightarrow Pb(OH)_2 + H_2$$~~

The Activity Series for Halogens

$$F_2 > Cl_2 > Br_2 > I_2$$

Halogen Displacement Reaction

$$\overset{0}{Cl_2} + 2K\overset{-1}{Br} \longrightarrow 2K\overset{-1}{Cl} + \overset{0}{Br_2}$$

~~$I_2 + 2KBr \longrightarrow 2KI + Br_2$~~

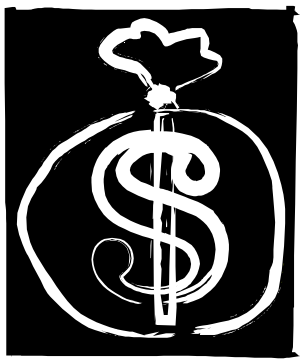
Types of Oxidation-Reduction Reactions

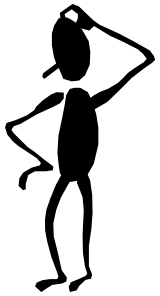
Disproportionation Reaction

Element is simultaneously oxidized and reduced.

$$\overset{0}{Cl_2} + 2OH^- \longrightarrow \overset{+1}{ClO^-} + \overset{-1}{Cl^-} + H_2O$$

Chlorine Chemistry





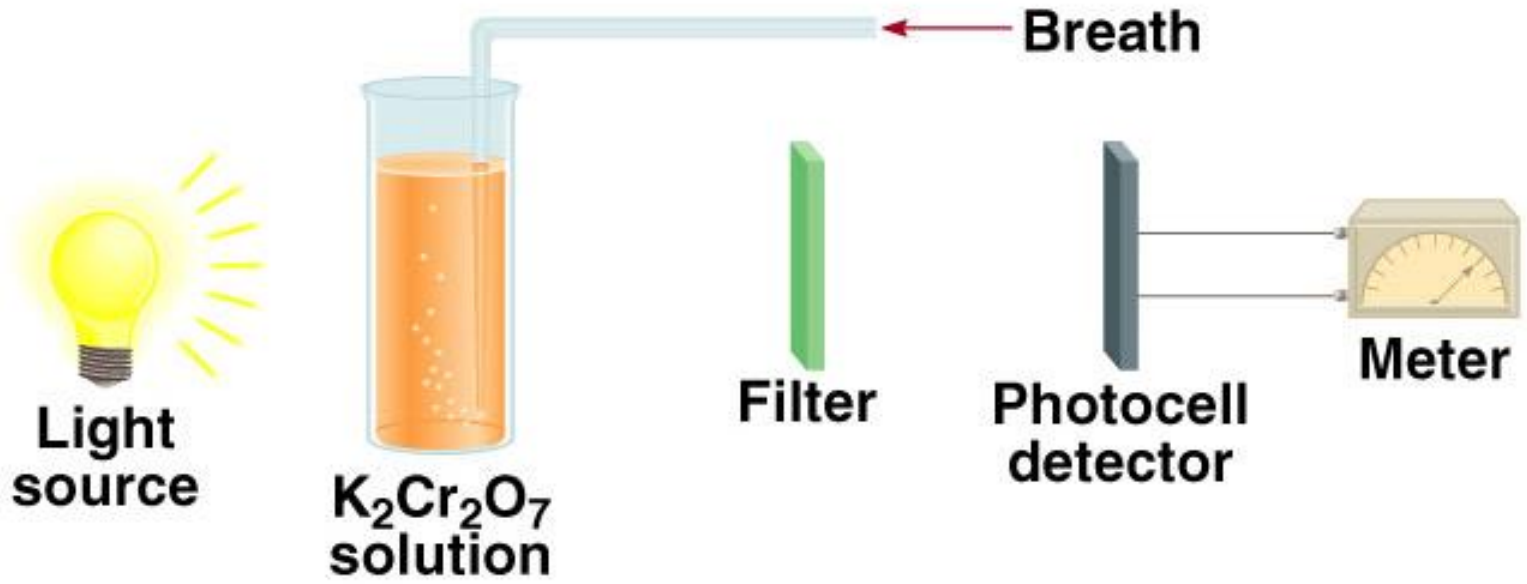
Classify the following reactions.

$Ca^{2+} + CO_3^{2-} \longrightarrow CaCO_3$	Precipitation
$NH_3 + H^+ \longrightarrow NH_4^+$	Acid-Base
$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$	Redox (H_2 Displacement)
$Ca + F_2 \longrightarrow CaF_2$	Redox (Combination)

Chemistry in Action: Breath Analyzer

$$3CH_3CH_2OH + \overset{+6}{2K_2Cr_2O_7} + 8H_2SO_4 \longrightarrow$$

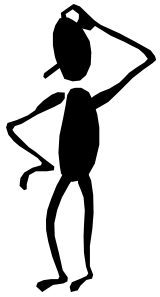
$$3CH_3COOH + \overset{+3}{2Cr_2(SO_4)_3} + 2K_2SO_4 + 11H_2O$$



Solution Stoichiometry

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

$$M = \textbf{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

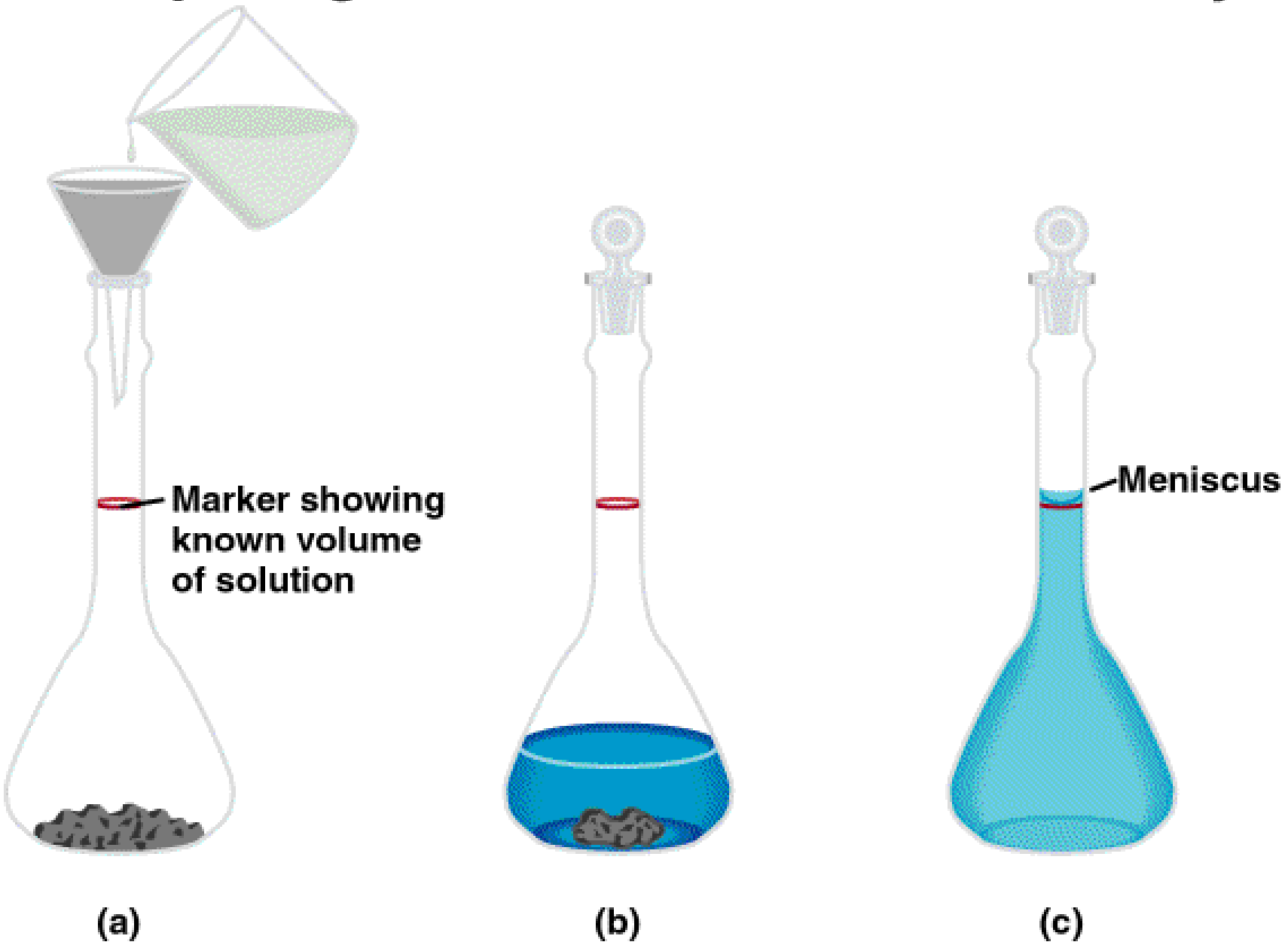


What mass of KI is required to make 500. mL of a 2.80 *M* KI solution?

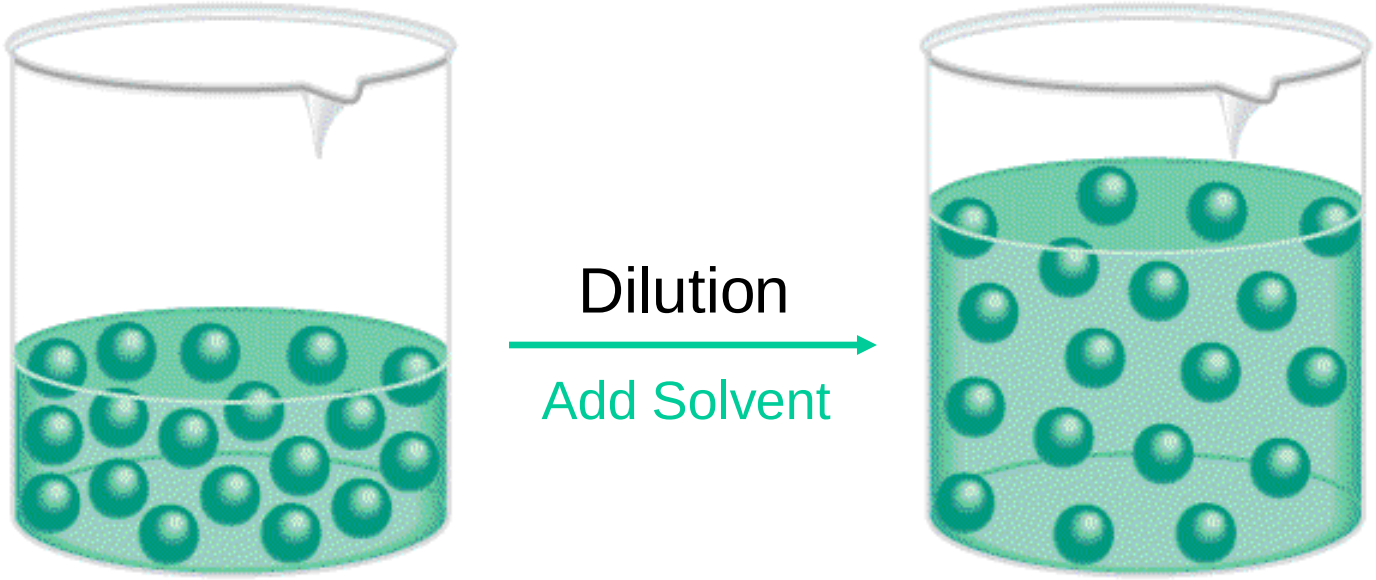
volume of KI solution $\xrightarrow{M\ \text{KI}}$ moles KI $\xrightarrow{\mathcal{M}\ \text{KI}}$ grams KI

$$500.\ \text{mL} \times \frac{1\ \text{L}}{1000\ \text{mL}} \times \frac{2.80\ \text{mol KI}}{1\ \text{L soln}} \times \frac{166\ \text{g KI}}{1\ \text{mol KI}} = 232\ \text{g KI}$$

Preparing a Solution of Known Molarity

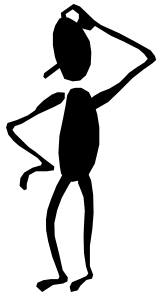


Dilution is the procedure for preparing a less concentrated solution from a more concentrated solution.



Moles of solute before dilution (i) = Moles of solute after dilution (f)

$M_i V_i = M_f V_f$



How would you prepare 60.0 mL of 0.200 *M* HNO_3 from a stock solution of 4.00 *M* HNO_3?

$$M_i V_i = M_f V_f$$

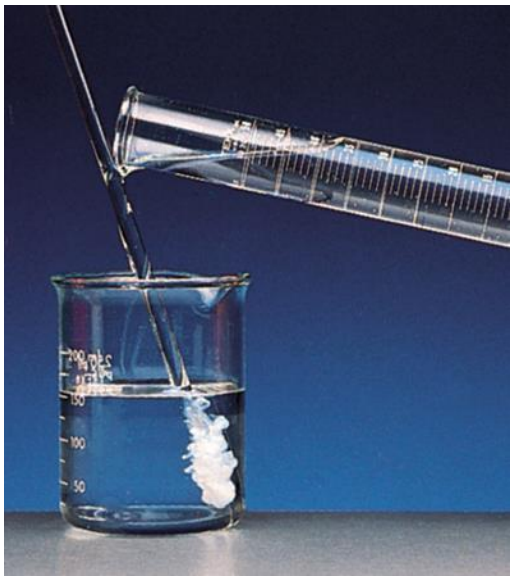
$M_i = 4.00$ $M_f = 0.200$ $V_f = 0.06$ L $V_i = ?$ L

$$V_i = \frac{M_f V_f}{M_i} = \frac{0.200 \times 0.06}{4.00} = 0.003 \text{ L} = 3 \text{ mL}$$

3 mL of acid + 57 mL of water = 60 mL of solution

Gravimetric Analysis

1. Dissolve unknown substance in water
2. React unknown with known substance to form a precipitate
3. Filter and dry precipitate
4. Weigh precipitate
5. Use chemical formula and mass of precipitate to determine amount of unknown ion

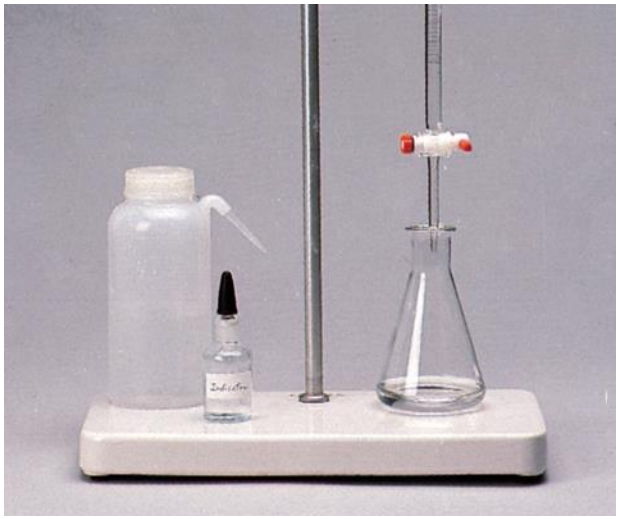


Titrations

In a ***titration*** a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

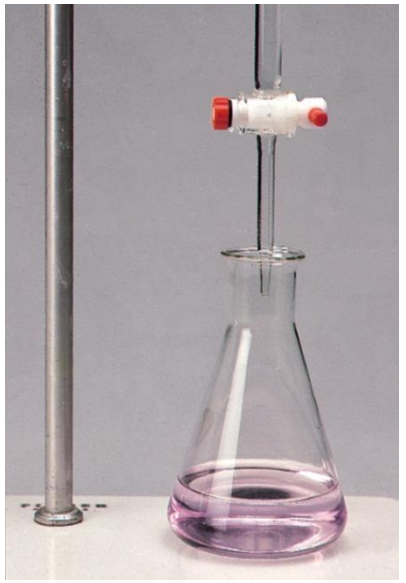
Equivalence point – the point at which the reaction is complete

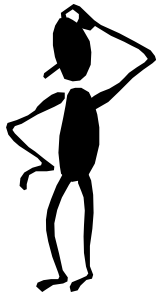
Indicator – substance that changes color at (or near) the equivalence point



Slowly add base to unknown acid UNTIL

the indicator changes color





What volume of a 1.420 *M* NaOH solution is Required to titrate 25.00 mL of a 4.50 *M* H_2SO_4 solution?

WRITE THE CHEMICAL EQUATION!

$$H_2SO_4 + 2NaOH \longrightarrow 2H_2O + Na_2SO_4$$

volume acid $\xrightarrow[\text{acid}]{M}$ moles acid $\xrightarrow[\text{coef.}]{\text{rx}}$ moles base $\xrightarrow[\text{base}]{M}$ volume base

$$25.00\ \cancel{mL} \times \frac{4.50\ \cancel{mol\ H_2SO_4}}{1000\ \cancel{mL\ soln}} \times \frac{2\ \cancel{mol\ NaOH}}{1\ \cancel{mol\ H_2SO_4}} \times \frac{1000\ ml\ soln}{1.420\ \cancel{mol\ NaOH}} = 158\ mL$$

Chemistry in Action: Metals from the Sea

$$CaCO_3\,(s) \xrightarrow{\Delta} CaO\,(s) + CO_2\,(g)$$

$$CaO\,(s) + H_2O\,(l) \longrightarrow Ca^{2+}\,(aq) + 2OH^-\,(aq)$$

$$Mg^{2+}\,(aq) + 2OH^-\,(aq) \longrightarrow Mg(OH)_2\,(s)$$

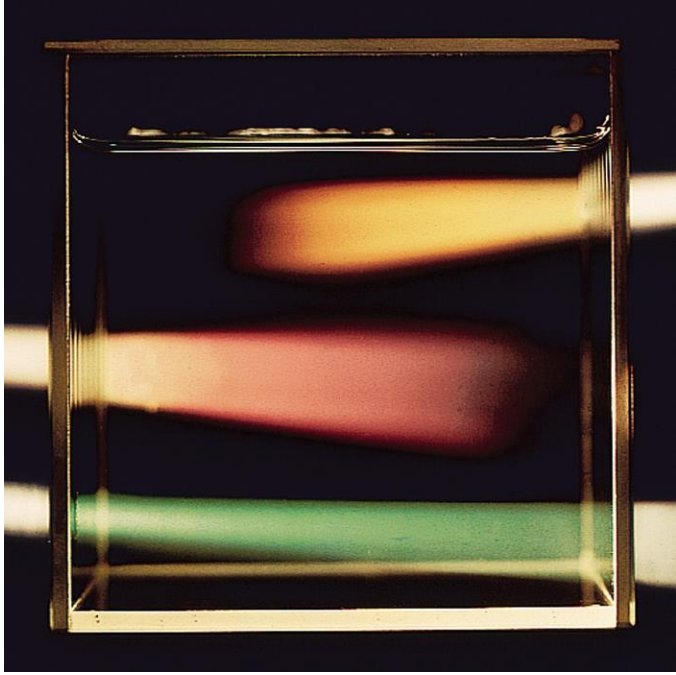
$$Mg(OH)_2\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + 2H_2O\,(l)$$

Magnesium Hydroxide

$$Mg^{2+} + 2e^- \longrightarrow Mg$$

$$2Cl^- \longrightarrow Cl_2 + 2e^-$$

$$MgCl_2\,(aq) \longrightarrow Mg\,(s) + Cl_2\,(g)$$



Physical Properties of Solutions

Chapter 12

A ***solution*** is a homogenous mixture of 2 or more substances

The ***solute*** is(are) the substance(s) present in the smaller amount(s)

The ***solvent*** is the substance present in the larger amount

TABLE 12.1 Types of Solutions

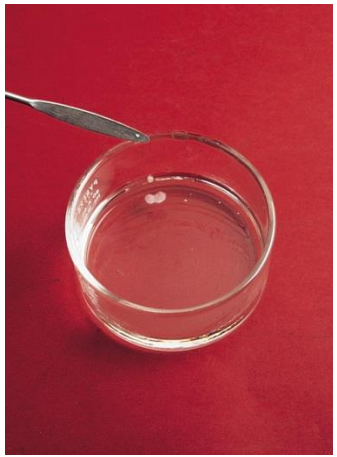
Component 1	Component 2	State of Resulting Solution	Examples
Gas	Gas	Gas	Air
Gas	Liquid	Liquid	Soda water (CO_2 in water)
Gas	Solid	Solid	H_2 gas in palladium
Liquid	Liquid	Liquid	Ethanol in water
Solid	Liquid	Liquid	NaCl in water
Solid	Solid	Solid	Brass (Cu/Zn), solder (Sn/Pb)

A ***saturated solution*** contains the maximum amount of a solute that will dissolve in a given solvent at a specific temperature.

An ***unsaturated solution*** contains less solute than the solvent has the capacity to dissolve at a specific temperature.

A ***supersaturated solution*** contains more solute than is present in a saturated solution at a specific temperature.

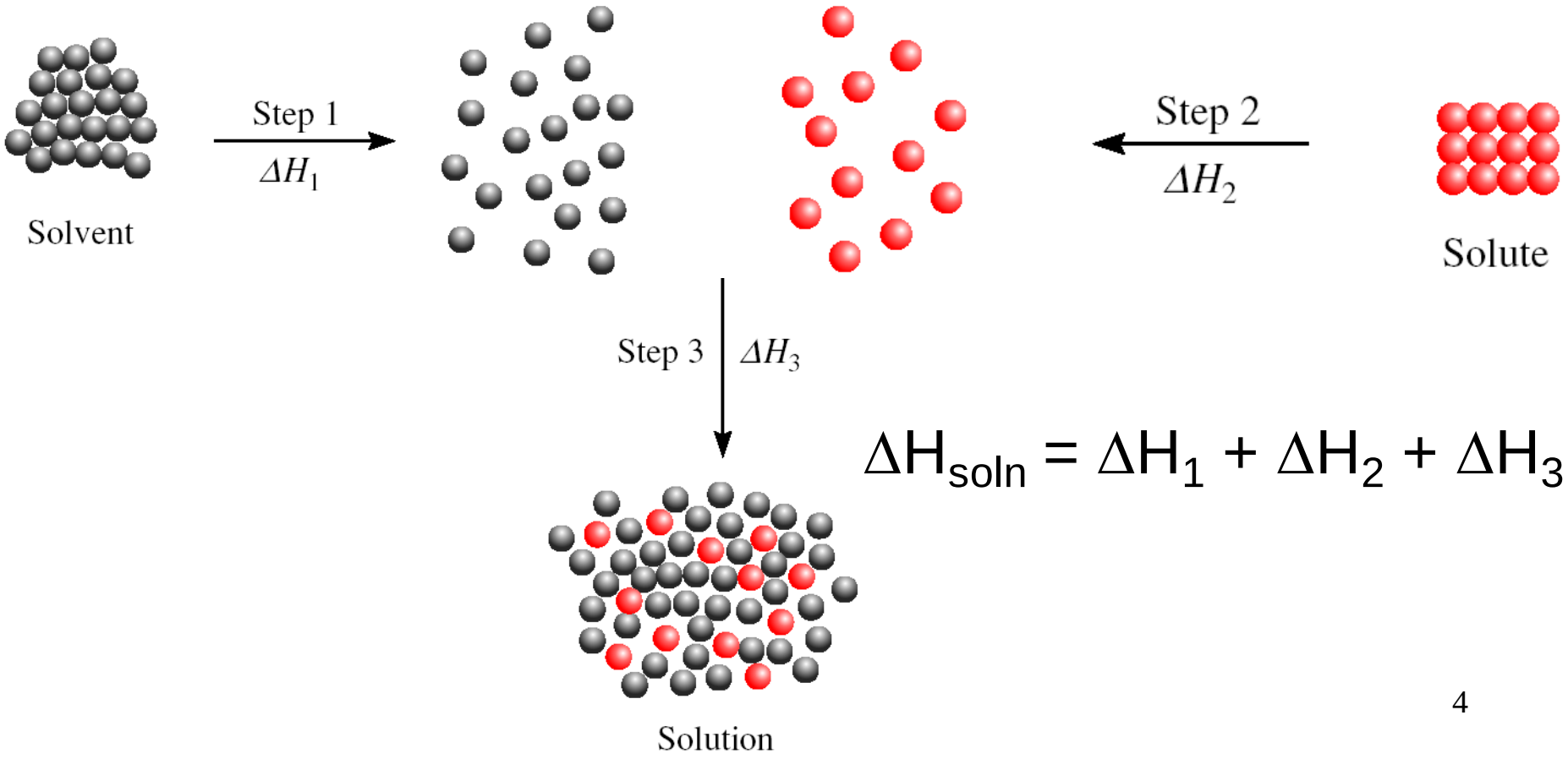
Sodium acetate crystals rapidly form when a seed crystal is added to a supersaturated solution of sodium acetate.



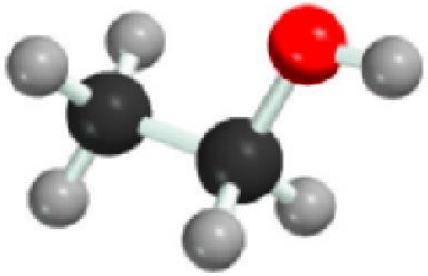
Three types of interactions in the solution process:

- solvent-solvent interaction
- solute-solute interaction
- solvent-solute interaction

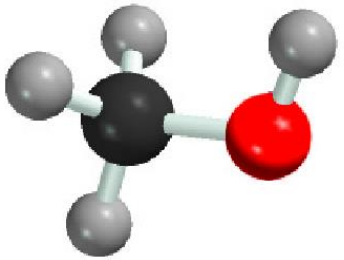
Molecular view of the formation of solution



$$\Delta H_{soln} = \Delta H_1 + \Delta H_2 + \Delta H_3$$



"**like dissolves like**"



Two substances with similar ***intermolecular*** forces are likely to be soluble in each other.

- non-polar molecules are soluble in non-polar solvents

  CCl_4 in C_6H_6

- polar molecules are soluble in polar solvents

  C_2H_5OH in H_2O

- ionic compounds are more soluble in polar solvents

  NaCl in H_2O or NH_3 (*l*)

Concentration Units

The ***concentration*** of a solution is the amount of solute present in a given quantity of solvent or solution.

Percent by Mass

$$\% \text{ by mass} = \frac{\text{mass of solute}}{\text{mass of solute} + \text{mass of solvent}} \times 100\%$$

$$= \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

Mole Fraction *(X)*

$$X_A = \frac{\text{moles of A}}{\text{sum of moles of all components}}$$

Concentration Units Continued

Molarity ***(M)***

$$M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Molality ***(m)***

$$m = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$$

What is the molality of a 5.86 *M* ethanol (C_2H_5OH) solution whose density is 0.927 g/mL?

$$\boldsymbol{m} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} \qquad \boldsymbol{M} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Assume 1 L of solution:

5.86 moles ethanol = 270 g ethanol

927 g of solution (1000 mL x 0.927 g/mL)

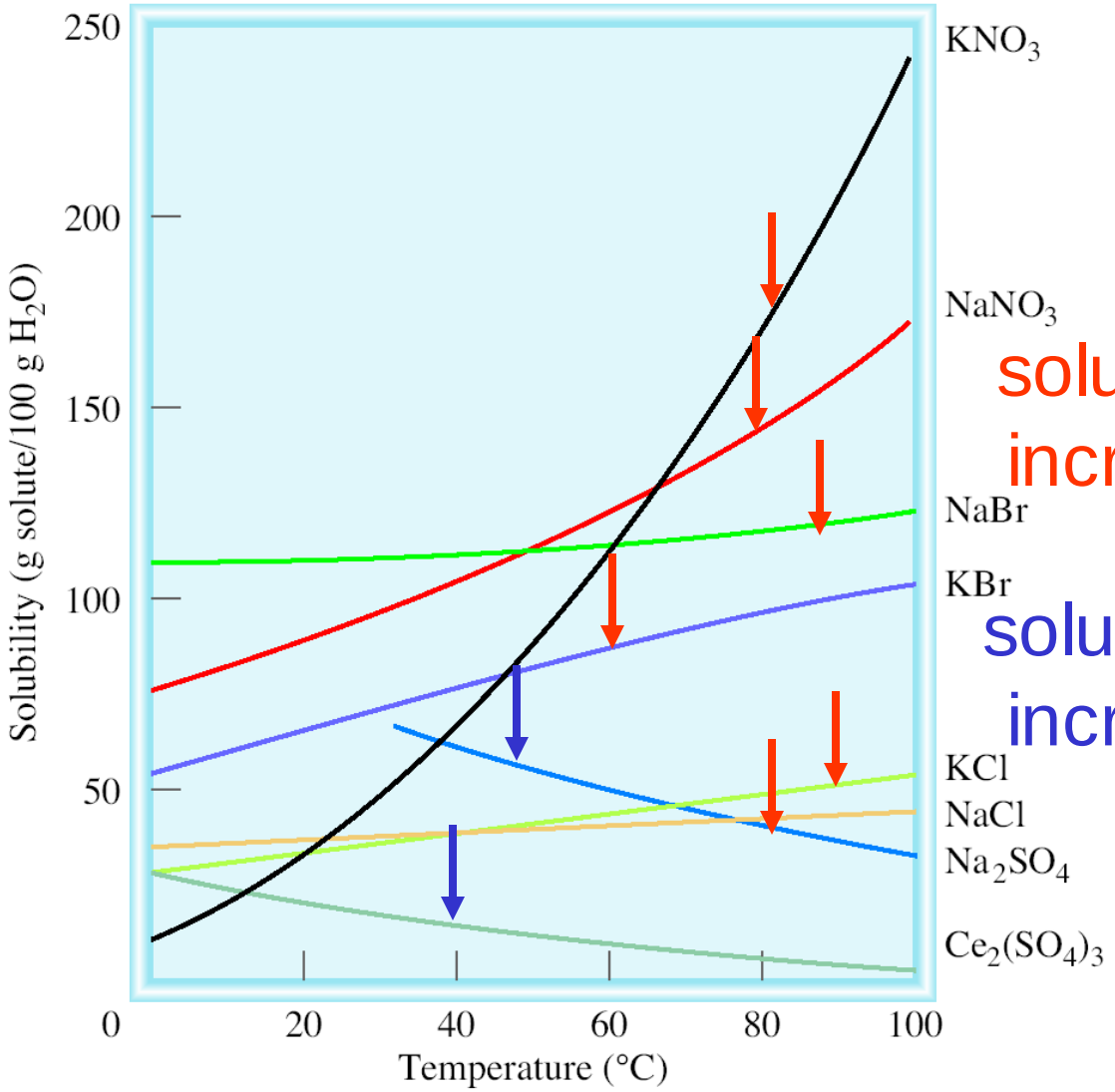
mass of solvent = mass of solution – mass of solute

= 927 g – 270 g = 657 g = 0.657 kg

$$\boldsymbol{m} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{5.86 \text{ moles } C_2H_5OH}{0.657 \text{ kg solvent}} = 8.92\ m$$

Temperature and Solubility

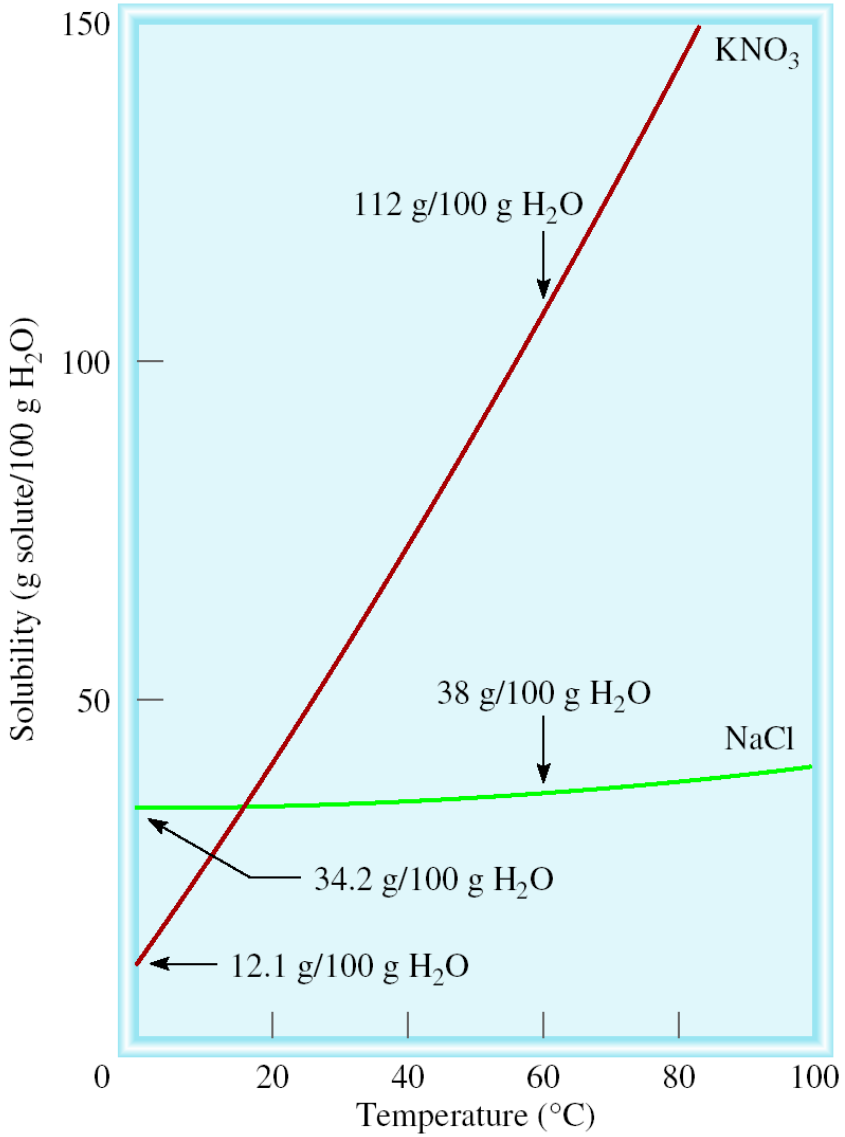
Solid solubility and temperature



solubility increases with increasing temperature

solubility decreases with increasing temperature

Fractional crystallization is the separation of a mixture of substances into pure components on the basis of their differing solubilities.



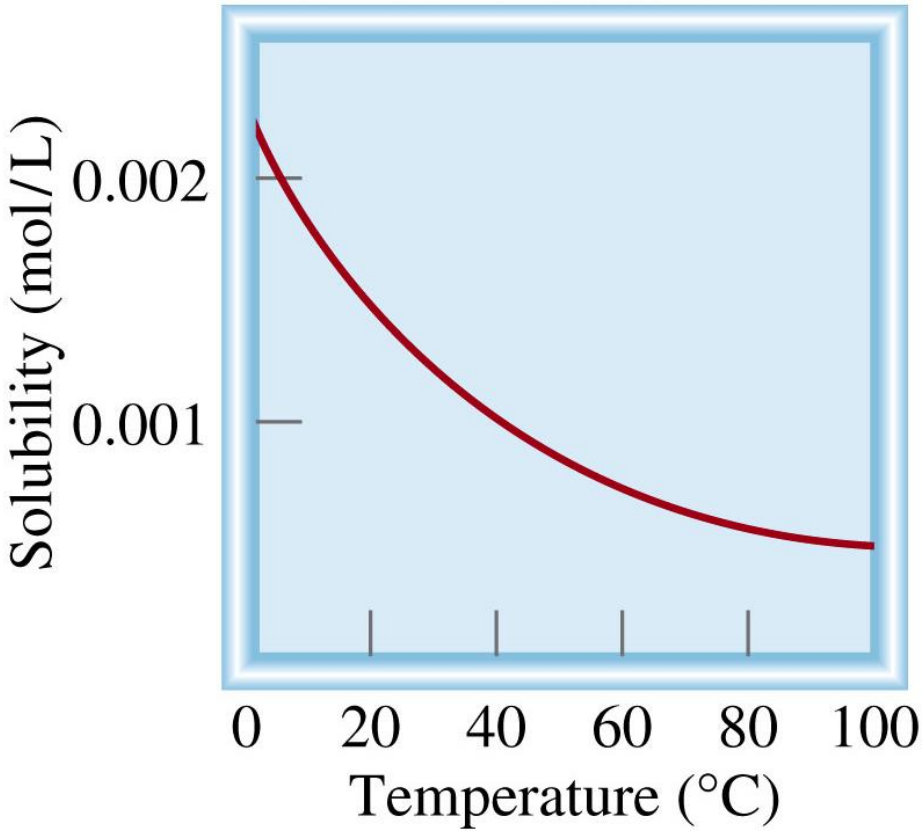
Suppose you have 90 g KNO_3 contaminated with 10 g NaCl.

<u>Fractional crystallization:</u>

1. Dissolve sample in 100 mL of water at 60^0C
2. Cool solution to 0^0C
3. All NaCl will stay in solution (s = 34.2g/100g)
4. 78 g of PURE KNO_3 will precipitate (s = 12 g/100g). 90 g – 12 g = 78 g

Temperature and Solubility

O_2 gas solubility and temperature



solubility usually decreases with increasing temperature

Pressure and Solubility of Gases

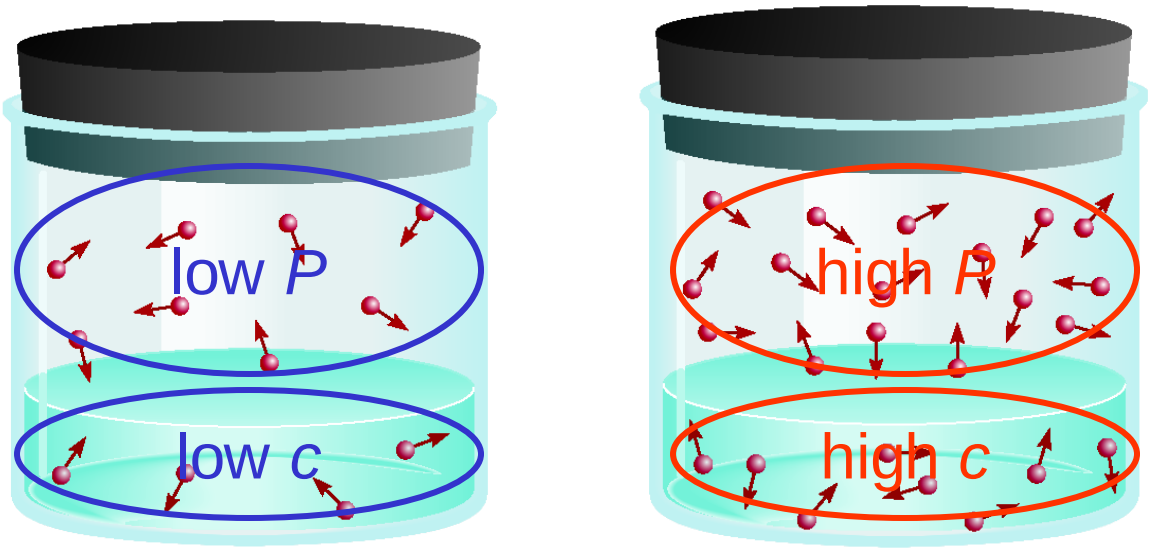
The solubility of a gas in a liquid is proportional to the pressure of the gas over the solution (***Henry's law***).

$$c = kP$$

c is the concentration (*M*) of the dissolved gas

P is the pressure of the gas over the solution

k is a constant for each gas (mol/L•atm) that depends only on temperature



Chemistry In Action: The Killer Lake

8/21/86
CO_2 Cloud Released
1700 Casualties

Lake Nyos, West Africa

Trigger?

- **earthquake**
- **landslide**
- **strong Winds**

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering

$$P_1 = X_1 P_1^0$$

Raoult's law

P_1^0 = vapor pressure of **pure** solvent

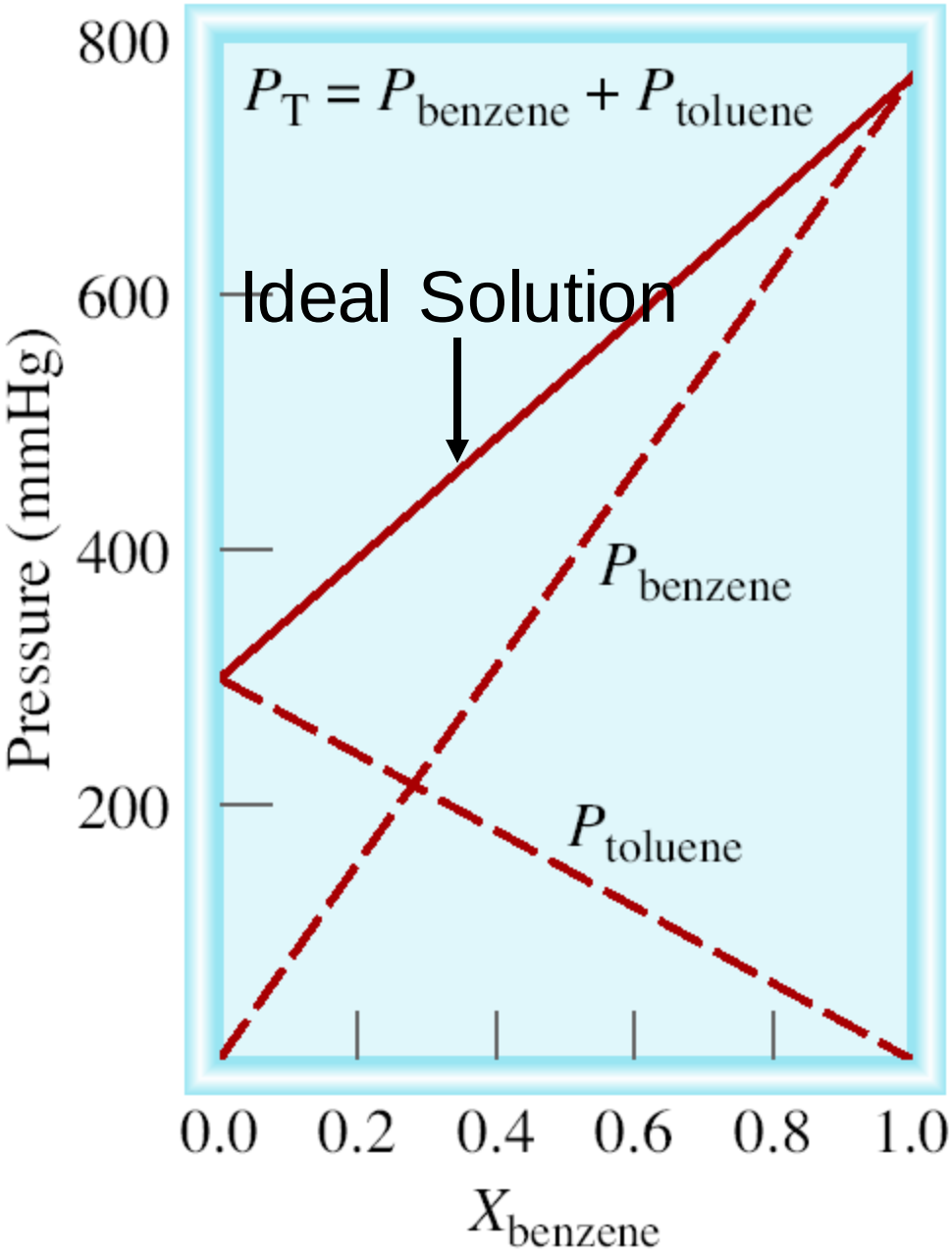
X_1 = mole fraction of the solvent

If the solution contains only one solute:

$$X_1 = 1 - X_2$$

$$P_1^0 - P_1 = \Delta P = X_2 P_1^0$$

X_2 = mole fraction of the solute



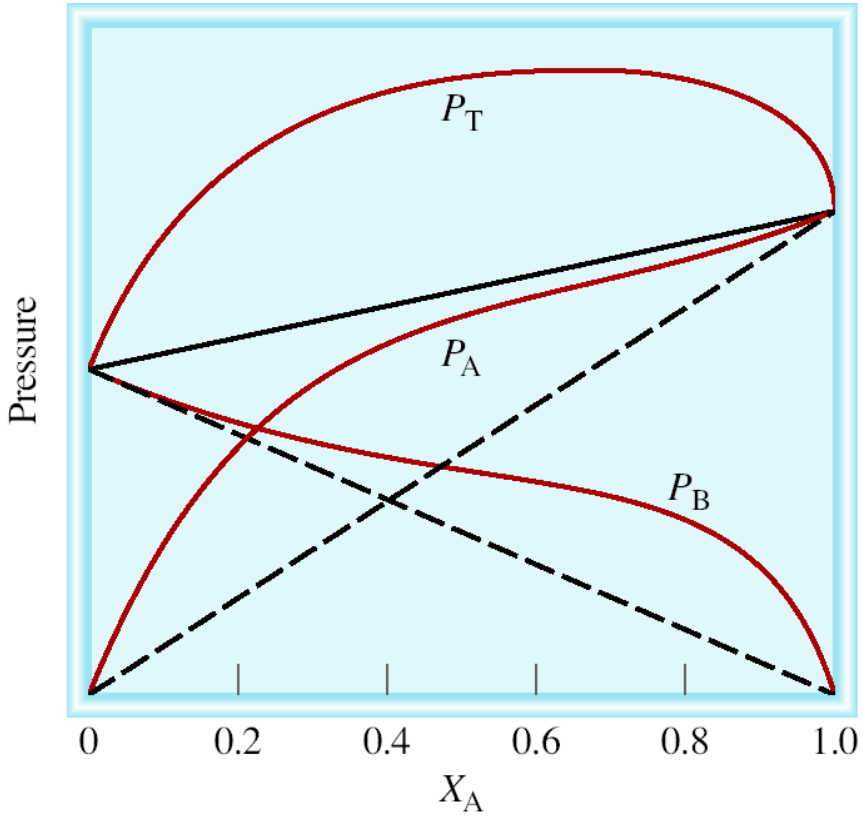
$$P_A = X_A P^0_A$$

$$P_B = X_B P^0_B$$

$$P_T = P_A + P_B$$

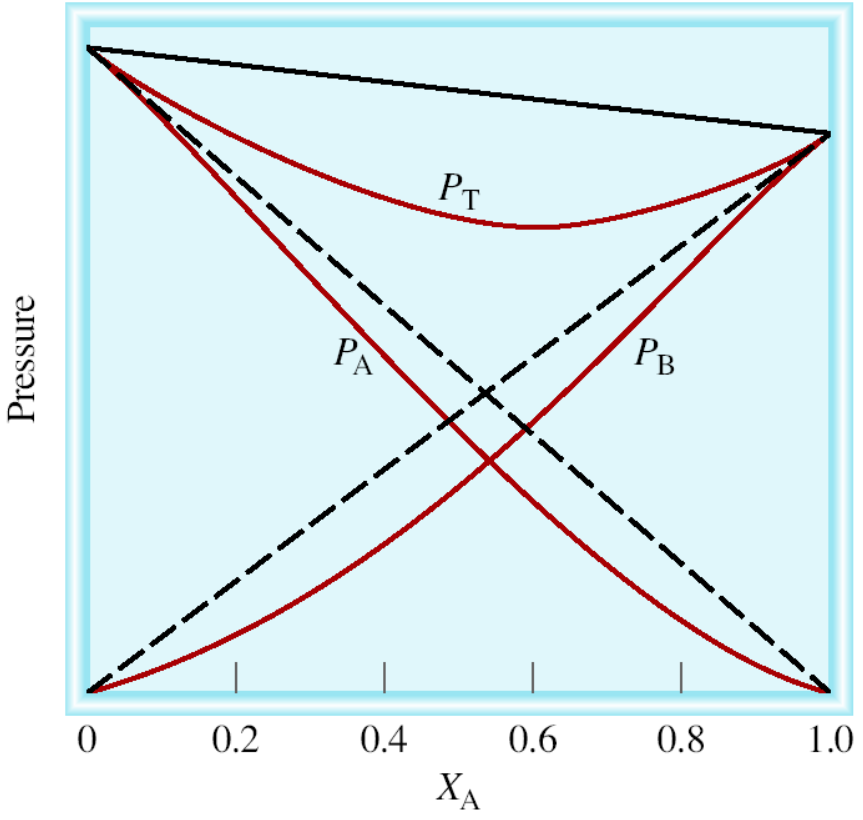
$$P_T = X_A P^0_A + X_B P^0_B$$

P_T is greater than predicted by Raoults's law



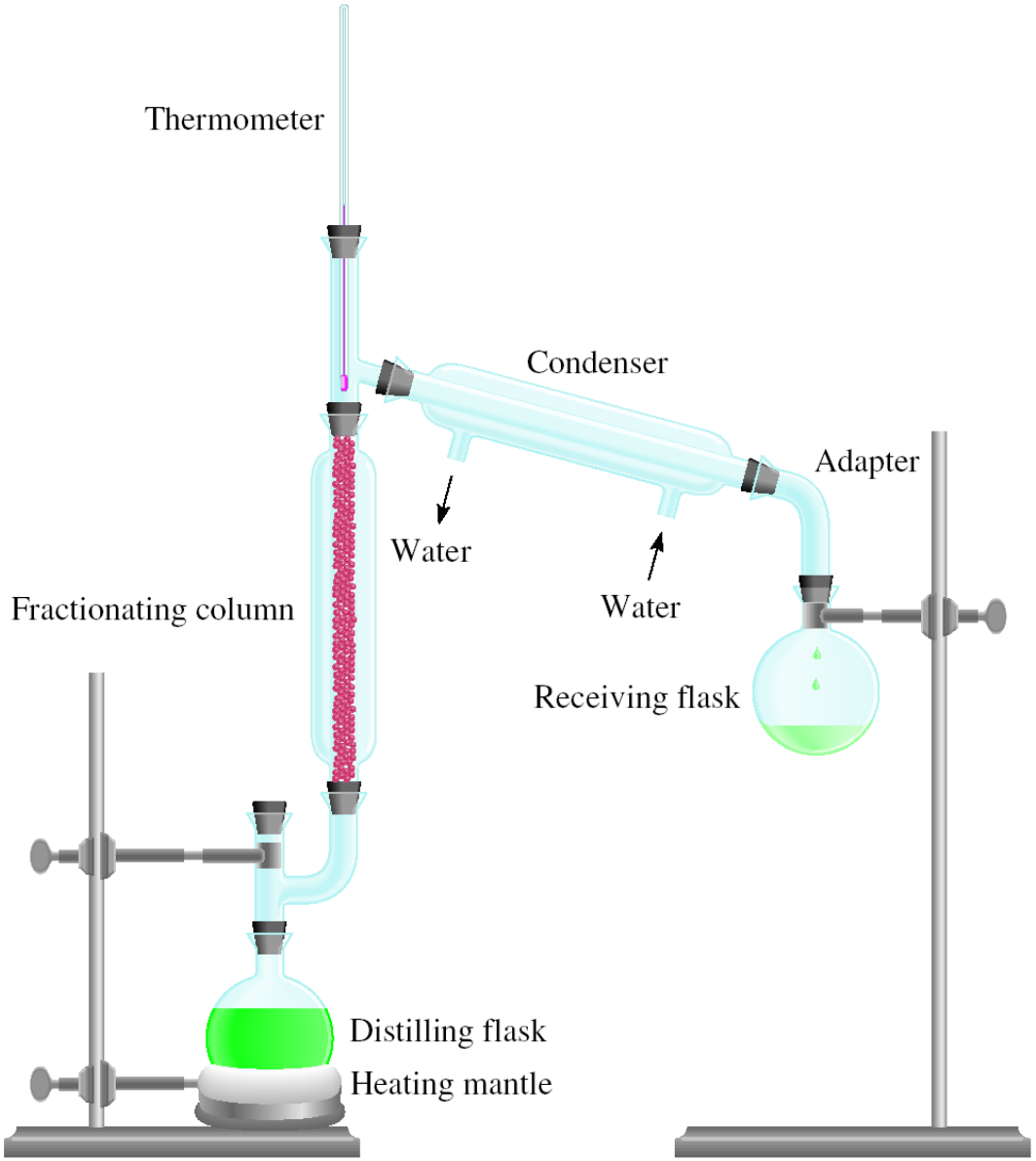
Force A-B < Force A-A & Force B-B

P_T is less than predicted by Raoults's law

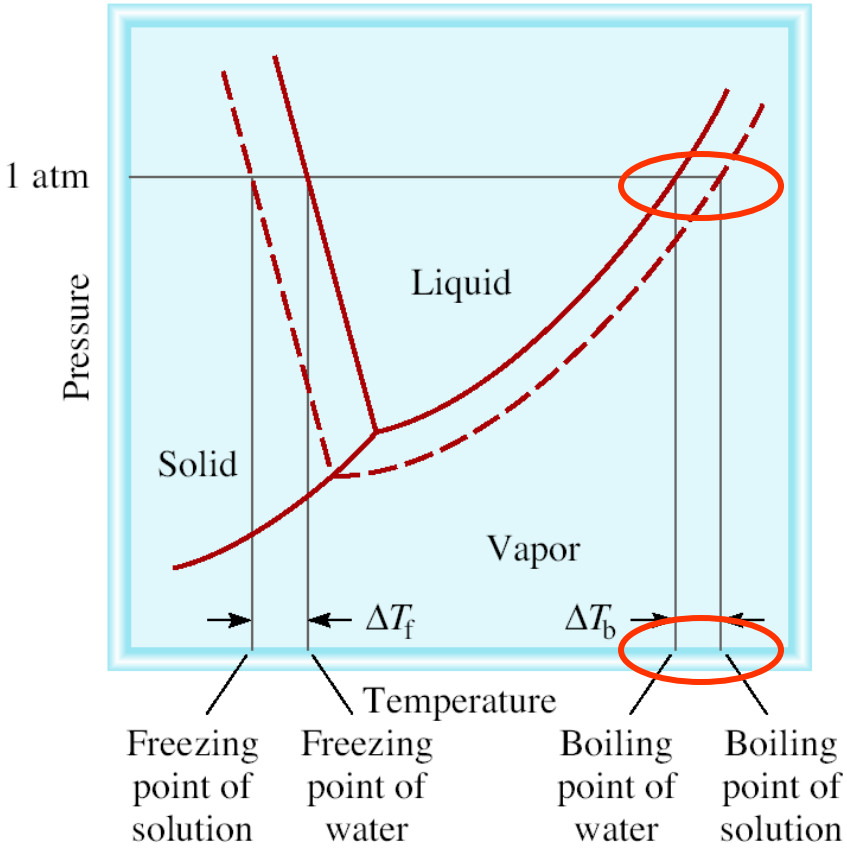


Force A-B > Force A-A & Force B-B

Fractional Distillation Apparatus



Boiling-Point Elevation



$$\Delta T_b = T_b - T_b^0$$

T_b^0 is the boiling point of the pure solvent

T_b is the boiling point of the solution

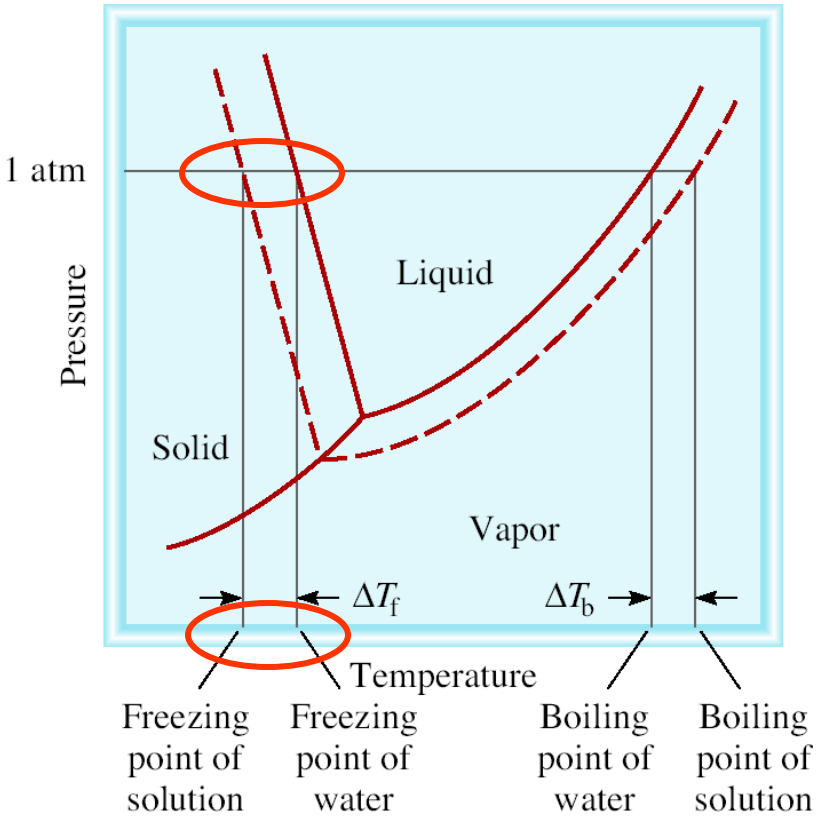
$$T_b > T_b^0 \qquad \Delta T_b > 0$$

$$\boxed{\Delta T_b = K_b\, m}$$

m is the molality of the solution

K_b is the molal boiling-point elevation constant ($^0C/m$) for a given solvent

Freezing-Point Depression



$$\Delta T_f = T_f^0 - T_f$$

T_f^0 is the freezing point of the pure solvent

T_f is the freezing point of the solution

$$T_f^0 > T_f \qquad \Delta T_f > 0$$

$$\boxed{\Delta T_f = K_f\, m}$$

m is the molality of the solution

K_f is the molal freezing-point depression constant ($^0C/m$) for a given solvent

TABLE 12.2 Molal Boiling-Point Elevation and Freezing-Point Depression Constants of Several Common Liquids

Solvent	Normal Freezing Point (°C)*	K_f (°C/*m*)	Normal Boiling Point (°C)*	K_b (°C/*m*)
Water	0	1.86	100	0.52
Benzene	5.5	5.12	80.1	2.53
Ethanol	−117.3	1.99	78.4	1.22
Acetic acid	16.6	3.90	117.9	2.93
Cyclohexane	6.6	20.0	80.7	2.79

*Measured at 1 atm.

What is the freezing point of a solution containing 478 g of ethylene glycol (antifreeze) in 3202 g of water? The molar mass of ethylene glycol is 62.01 g.

$$\Delta T_f = K_f\, m \qquad K_f \text{ water} = 1.86\ ^{o}\text{C}/m$$

$$\boldsymbol{m} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}} = \frac{478\ \text{g} \times \dfrac{1\ \text{mol}}{62.01\ \text{g}}}{3.202\ \text{kg solvent}} = 2.41\ m$$

$$\Delta T_f = K_f\, m = 1.86\ ^{o}\text{C}/m \times 2.41\ m = 4.48\ ^{o}\text{C}$$

$$\Delta T_f = T_f^0 - T_f$$

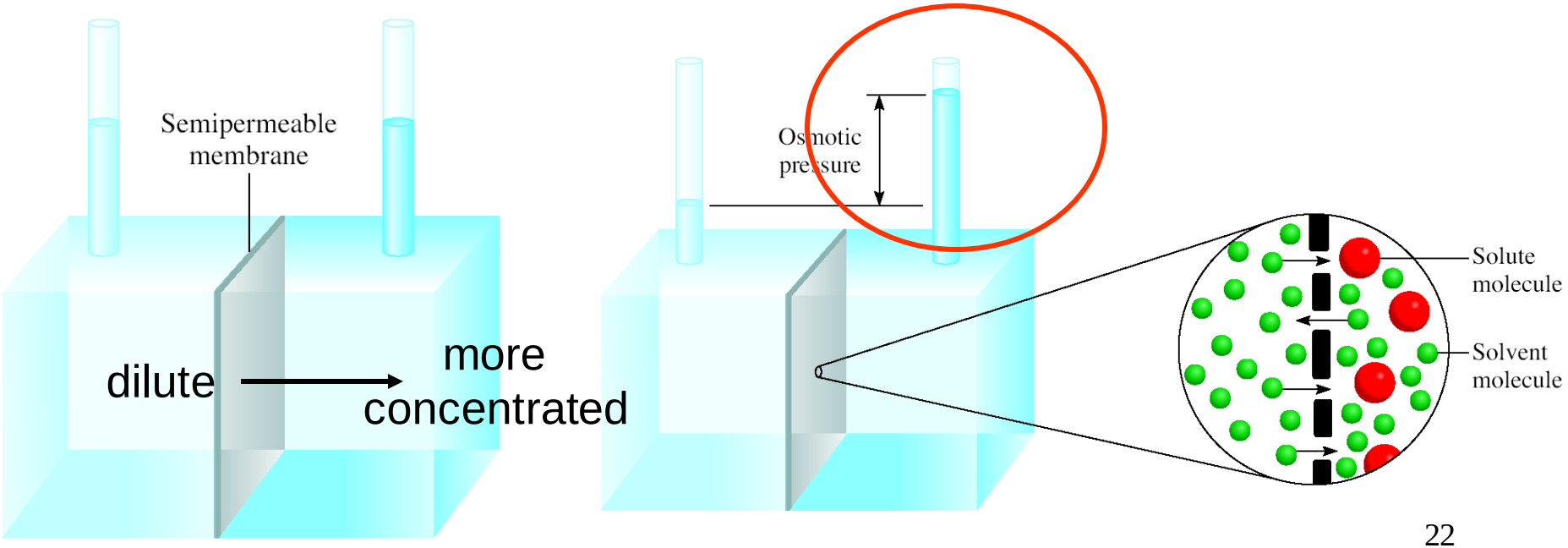
$$T_f = T_f^0 - \Delta T_f = 0.00\ ^{o}\text{C} - 4.48\ ^{o}\text{C} = -4.48\ ^{o}\text{C}$$

Osmotic Pressure (π)

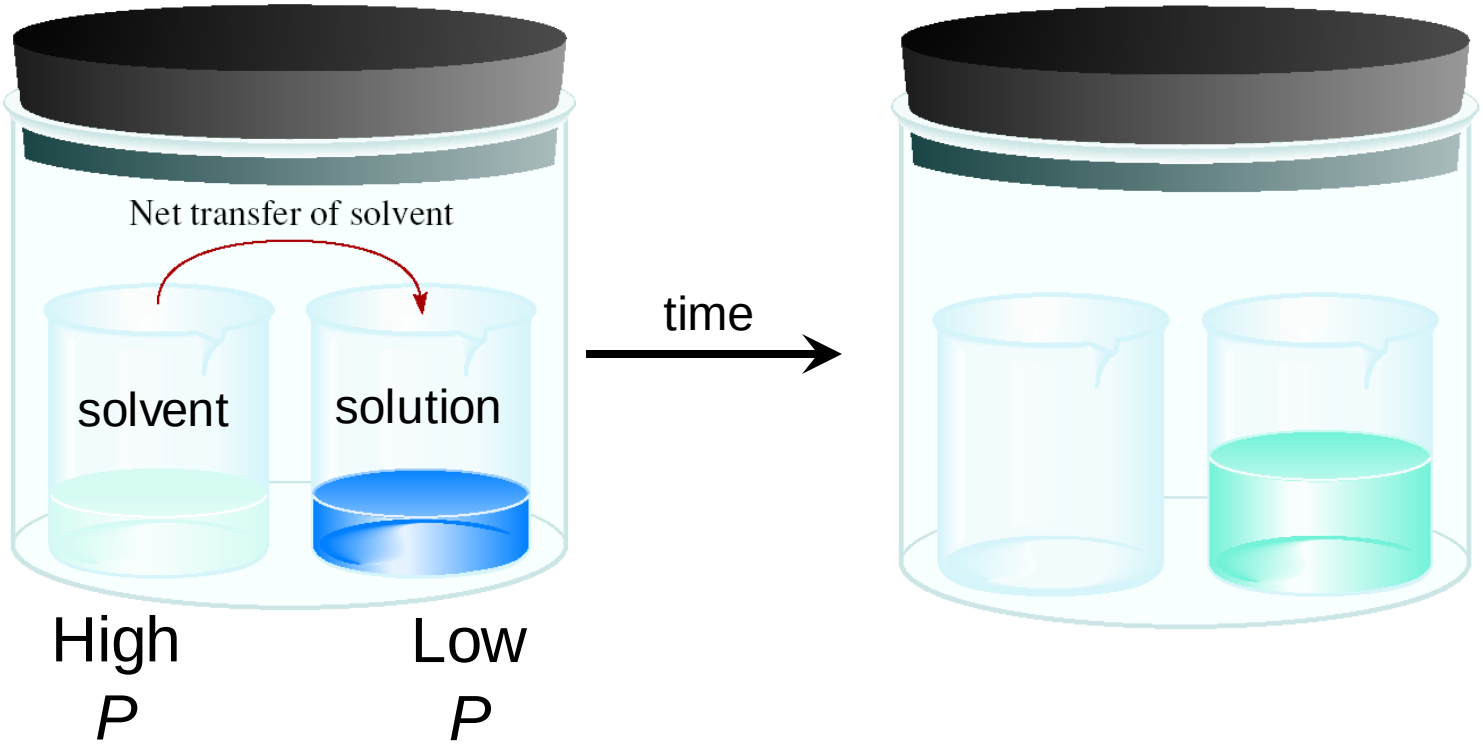
Osmosis is the selective passage of solvent molecules through a porous membrane from a dilute solution to a more concentrated one.

A ***semipermeable membrane*** allows the passage of solvent molecules but blocks the passage of solute molecules.

Osmotic pressure (π) is the pressure required to stop osmosis.



Osmotic Pressure (π)



$$\pi = MRT$$

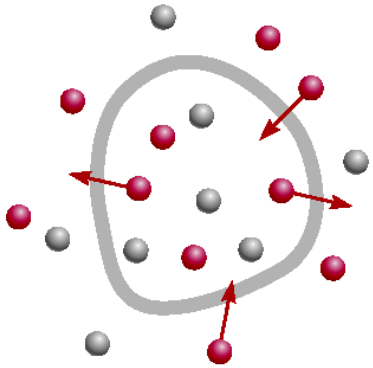
M is the molarity of the solution

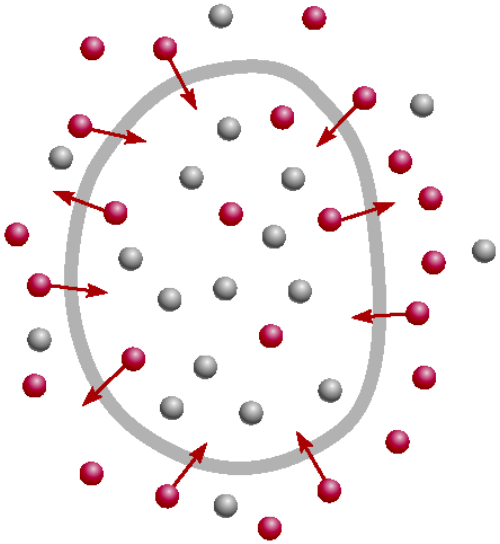
R is the gas constant

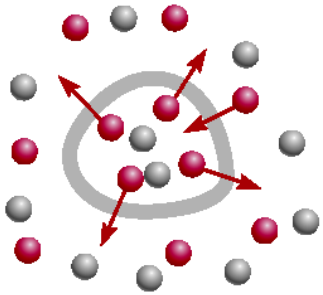
T is the temperature (in K)

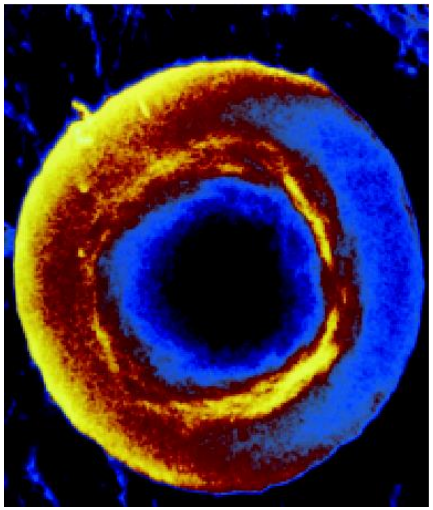
A cell in an:

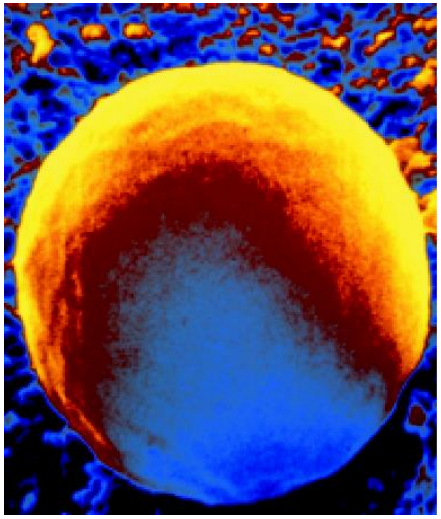
Water molecules
Solute molecules

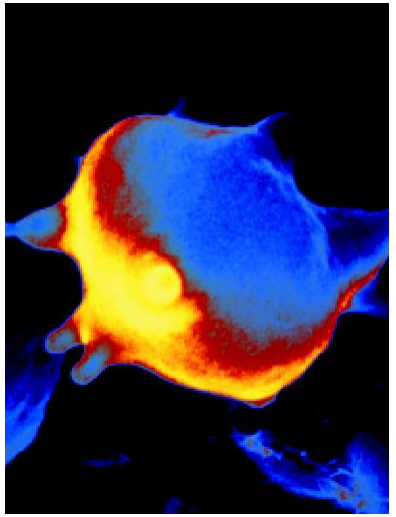












isotonic solution

hypotonic solution

hypertonic solution

Colligative Properties of Nonelectrolyte Solutions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

Vapor-Pressure Lowering $P_1 = X_1 P_1^0$

Boiling-Point Elevation $\Delta T_b = K_b m$

Freezing-Point Depression $\Delta T_f = K_f m$

Osmotic Pressure (π) $\pi = MRT$

Colligative Properties of Electrolyte Solutions

0.1 *m* NaCl solution $\longrightarrow$ 0.1 *m* Na^+ ions & 0.1 *m* Cl^- ions

Colligative properties are properties that depend only on the **number** of solute particles in solution and not on the **nature** of the solute particles.

0.1 *m* NaCl solution $\longrightarrow$ 0.2 *m* ions in solution

$$\textbf{\textit{van't Hoff factor (i)}} = \frac{\text{actual number of particles in soln after dissociation}}{\text{number of formula units initially dissolved in soln}}$$

	i should be
nonelectrolytes	1
NaCl	2
$CaCl_2$	3

Colligative Properties of Electrolyte Solutions

Boiling-Point Elevation $\Delta T_b = i\,K_b\,m$

Freezing-Point Depression $\Delta T_f = i\,K_f\,m$

Osmotic Pressure (π) $\pi = iMRT$

TABLE 12.3 The van't Hoff Factor of 0.0500 *M* Electrolyte Solutions at 25°C

Electrolyte	*i* (Measured)	*i* (Calculated)
Sucrose*	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
$MgSO_4$	1.3	2.0
$MgCl_2$	2.7	3.0
$FeCl_3$	3.4	4.0

*Sucrose is a nonelectrolyte. It is listed here for comparison only.

A ***colloid*** is a dispersion of particles of one substance throughout a dispersing medium of another substance.

Colloid versus solution

- collodial particles are much larger than solute molecules
- collodial suspension is not as homogeneous as a solution
- colloids exhibit the Tyndall effect

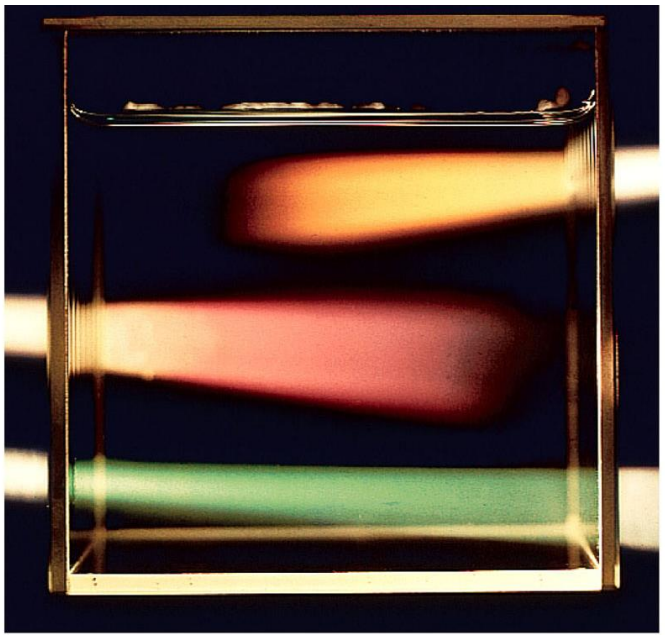
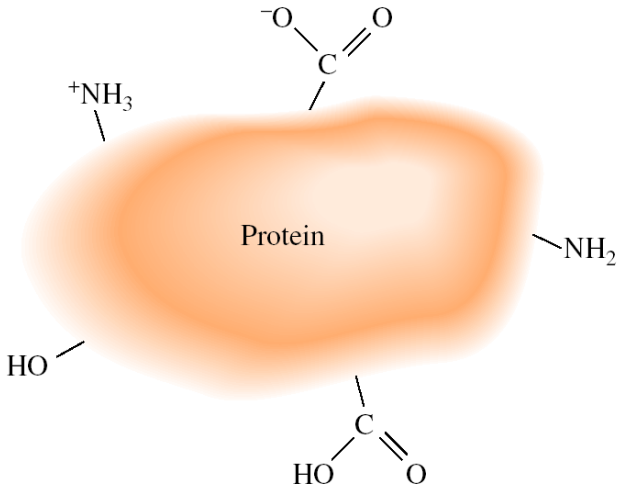


TABLE 12.4 Types of Colloids

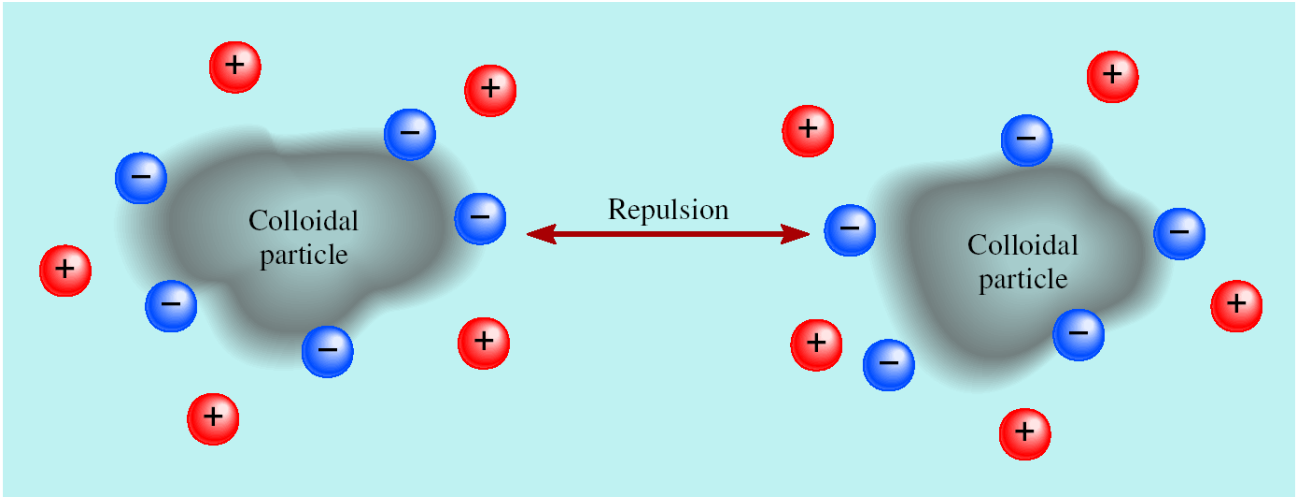
Dispersing Medium	Dispersed Phase	Name	Example
Gas	Liquid	Aerosol	Fog, mist
Gas	Solid	Aerosol	Smoke
Liquid	Gas	Foam	Whipped cream
Liquid	Liquid	Emulsion	Mayonnaise
Liquid	Solid	Sol	Milk of magnesia
Solid	Gas	Foam	Plastic foams
Solid	Liquid	Gel	Jelly, butter
Solid	Solid	Solid sol	Certain alloys (steel), opal

Hydrophilic and Hydrophobic Colloids

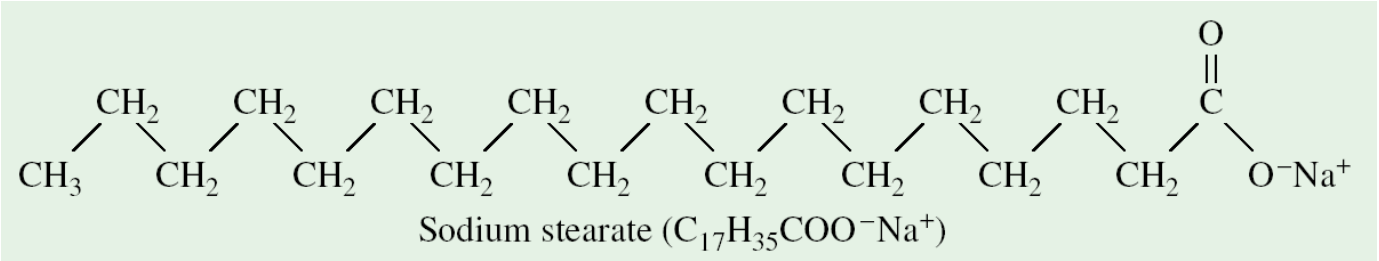
Hydrophilic: water-loving
Hydrophobic: water-fearing



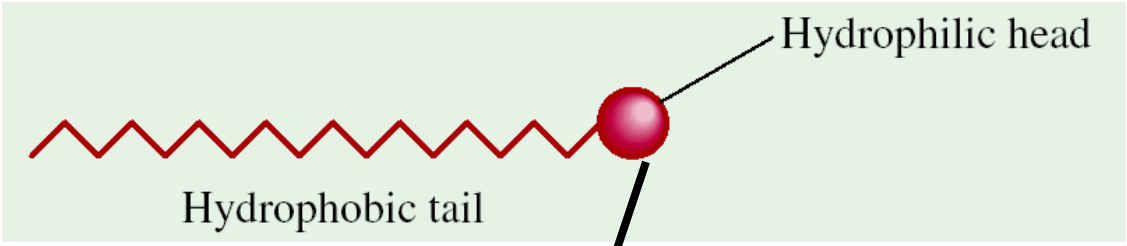
Stabilization of a hydrophobic colloid

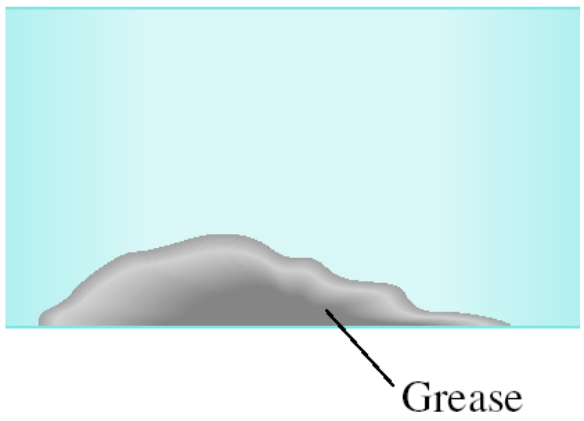


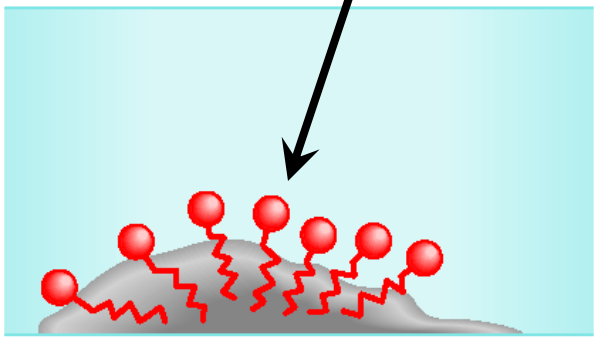
The Cleansing Action of Soap

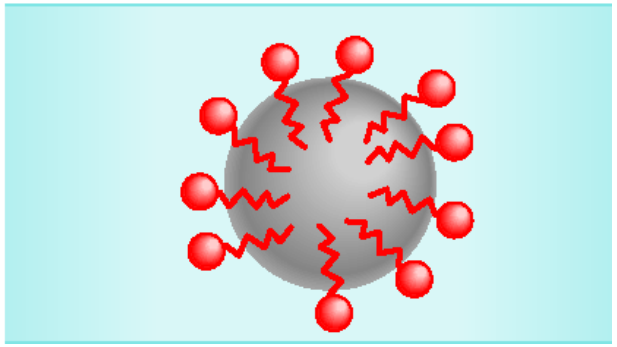


Sodium stearate ($C_{17}H_{35}COO^-Na^+$)





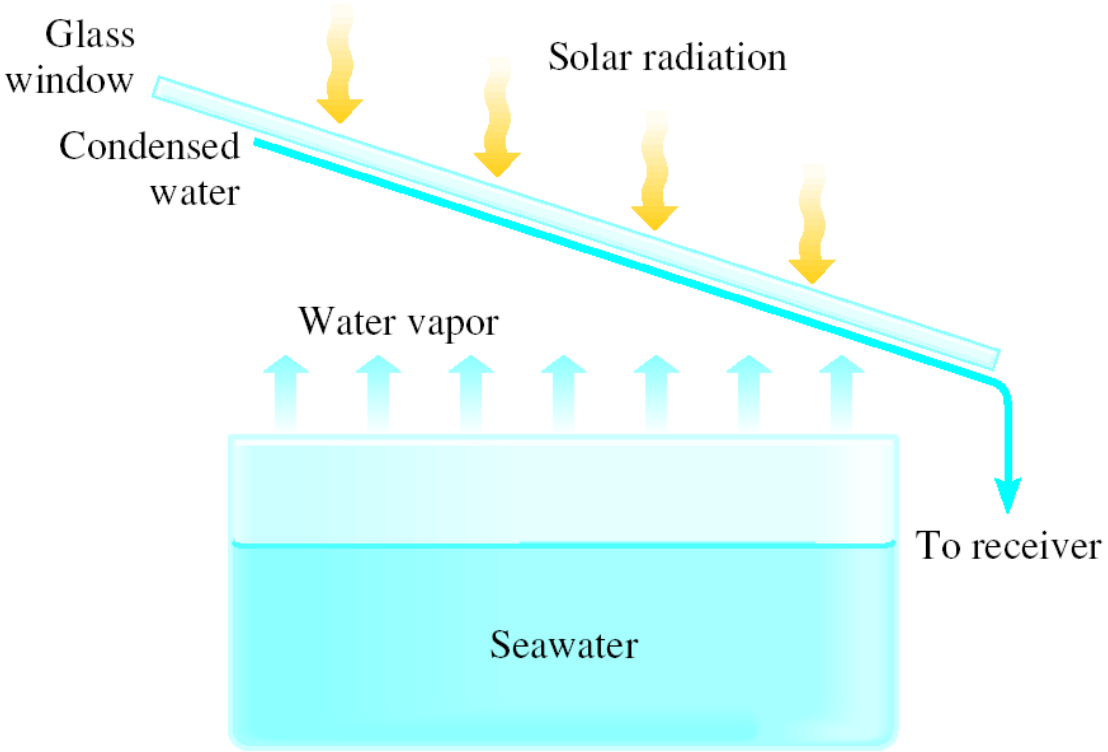




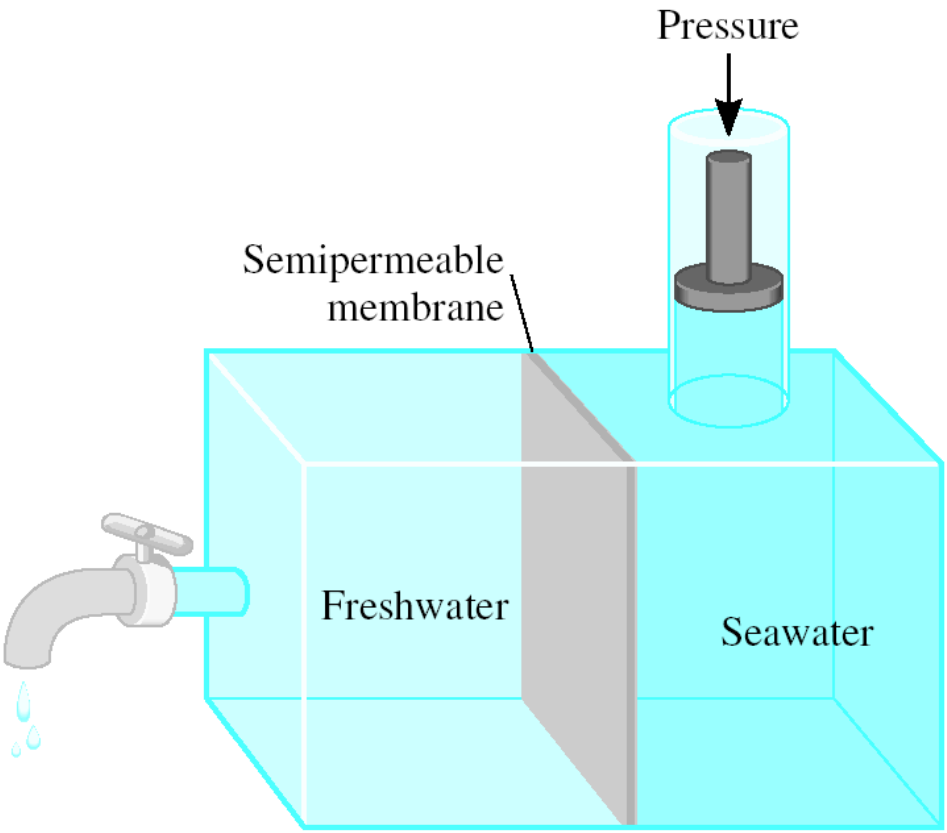
Chemistry In Action:
Desalination

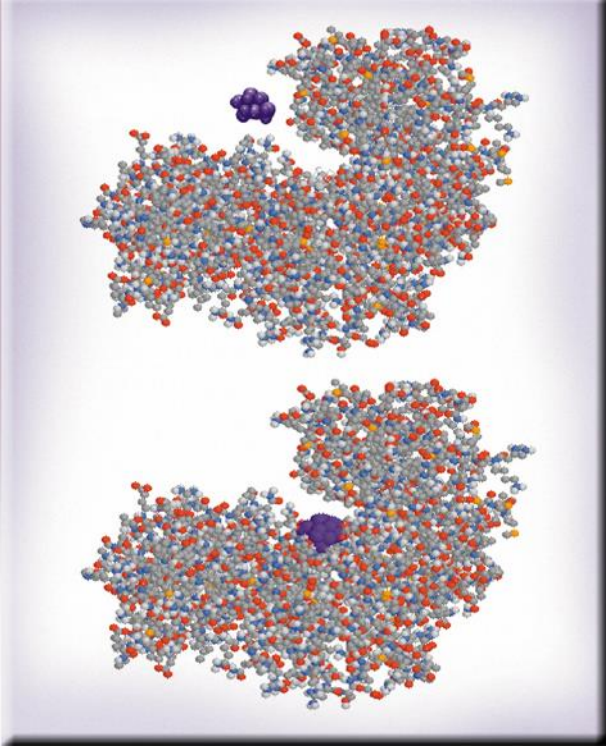
Composition of Seawater

Ions	g/kg of Seawater
Chloride (Cl^-)	19.35
Sodium (Na^+)	10.76
Sulfate (SO_4^{2-})	2.71
Magnesium (Mg^{2+})	1.29
Calcium (Ca^{2+})	0.41
Potassium (K^+)	0.39
Bicarbonate (HCO_3^-)	0.14



Chemistry In Action:
Reverse Osmosis





Chemical Kinetics

Chapter 13

Chemical Kinetics

Thermodynamics – does a reaction take place?

Kinetics – how fast does a reaction proceed?

Reaction rate is the change in the concentration of a reactant or a product with time (*M*/s).

$$A \longrightarrow B$$

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

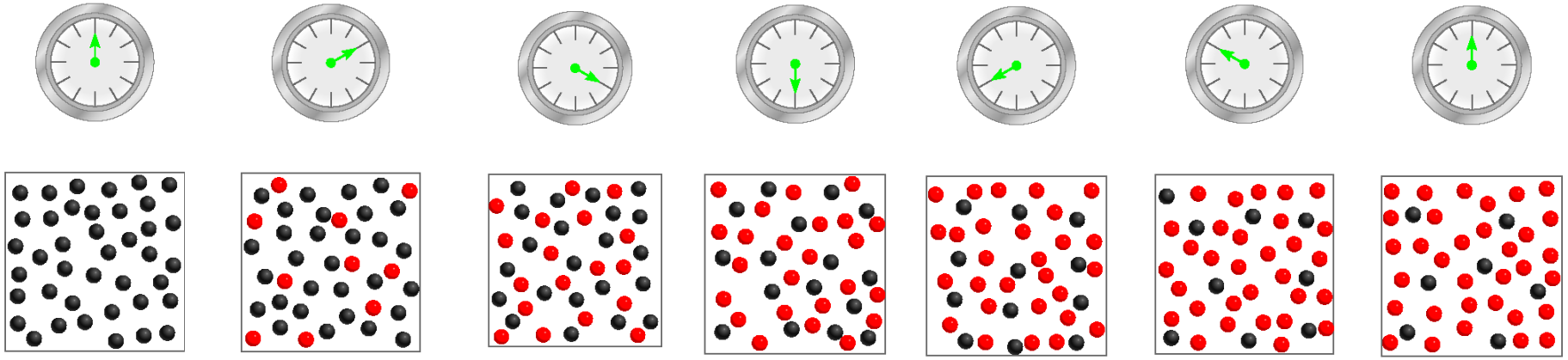
$\Delta[A]$ = change in concentration of A over time period Δt

$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$

$\Delta[B]$ = change in concentration of B over time period Δt

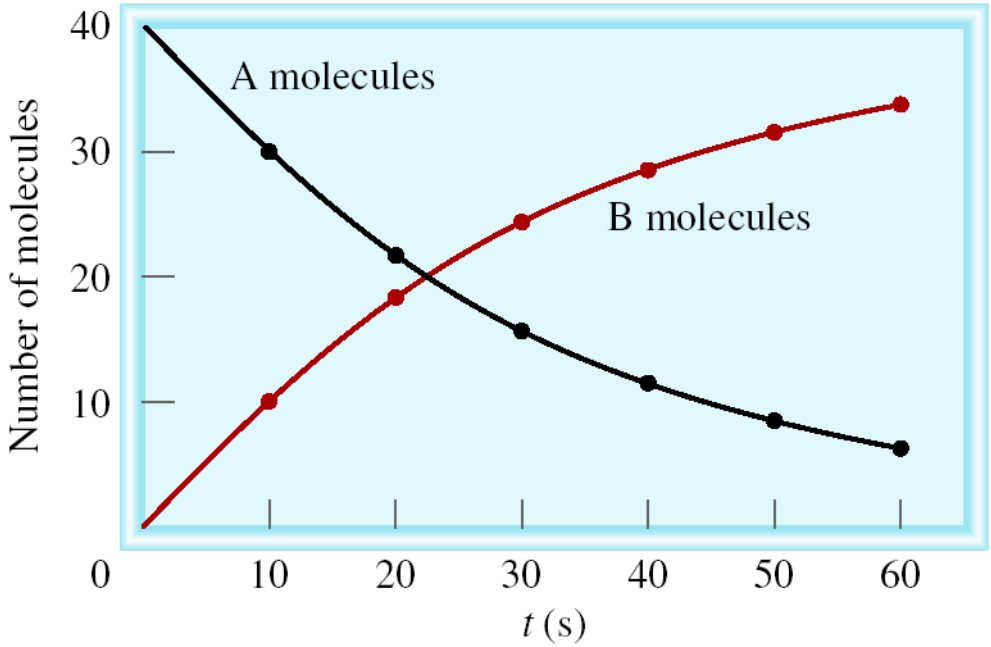
Because [A] decreases with time, $\Delta[A]$ is negative.

A ⟶ B



$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

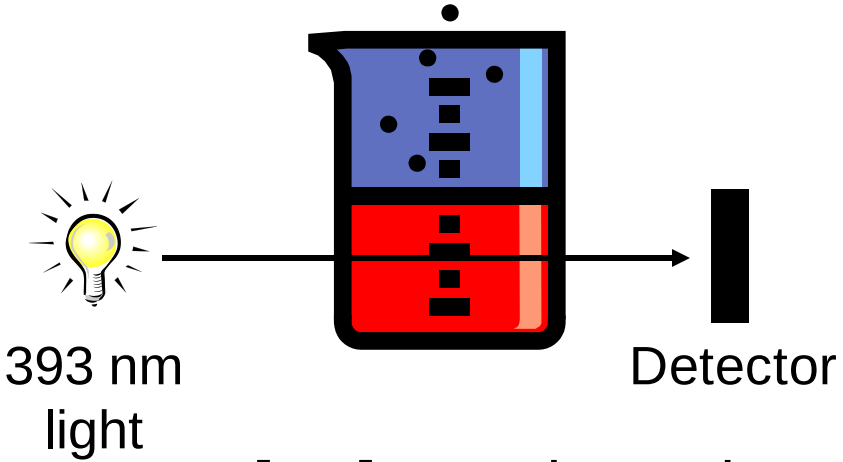
$$\text{rate} = \frac{\Delta[B]}{\Delta t}$$



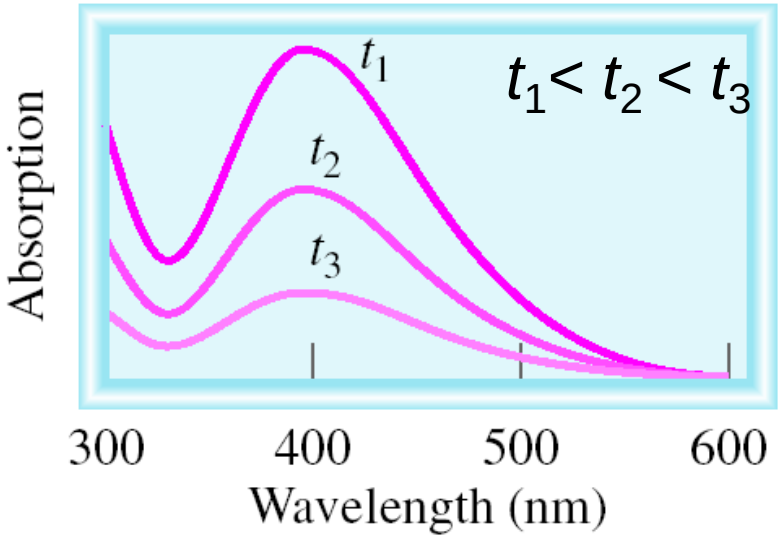
red-brown

$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$

time

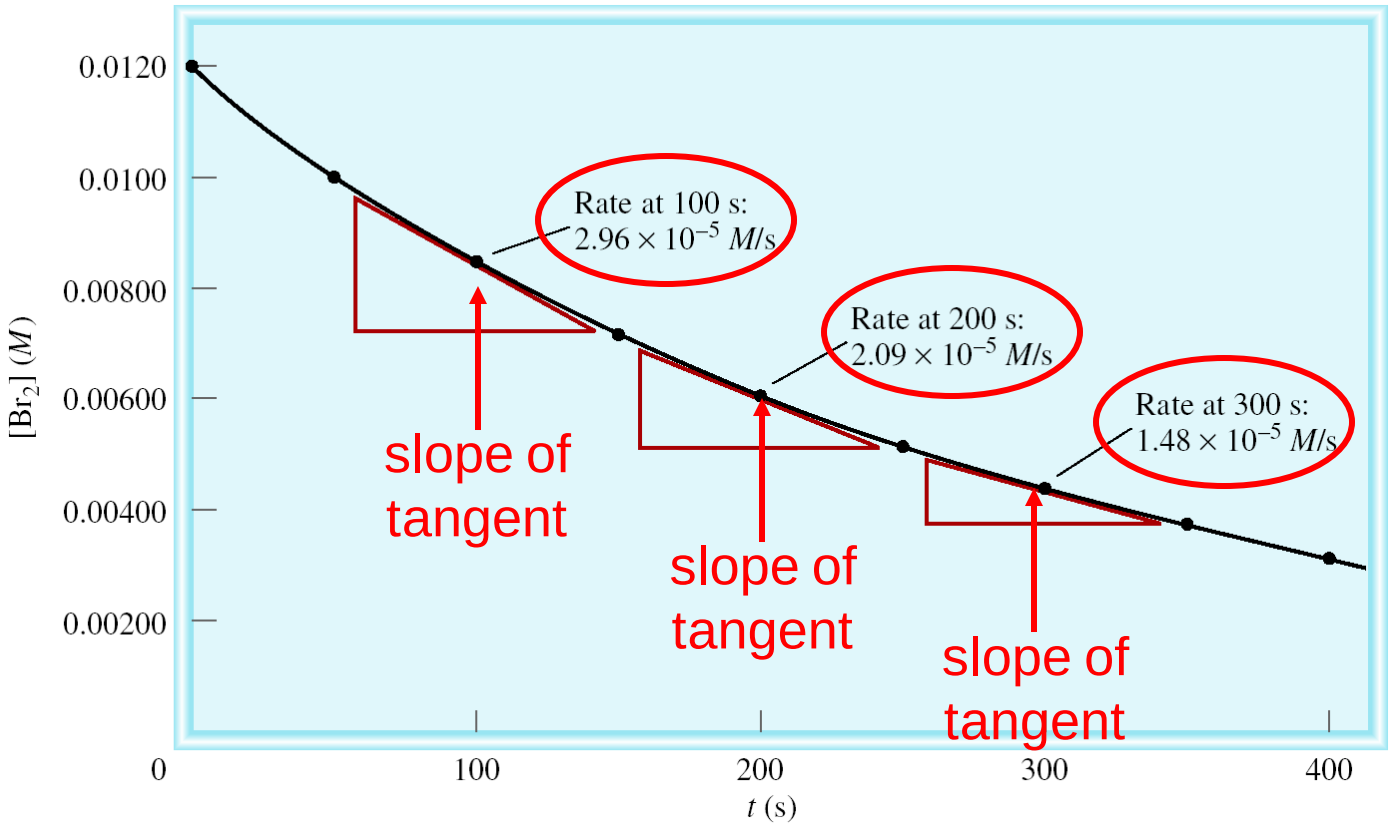


$\Delta[Br_2] \alpha \Delta$ Absorption



$$Br_2\,(aq) + HCOOH\,(aq) \longrightarrow 2Br^-\,(aq) + 2H^+\,(aq) + CO_2\,(g)$$

Time (s)	$[Br_2]$ (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296



$$\textbf{\textit{average rate}} = -\frac{\Delta[Br_2]}{\Delta t} = -\frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

instantaneous rate = rate for specific instance in time

TABLE 13.1 Rates of the Reaction Between Molecular Bromine and Formic Acid at 25°C

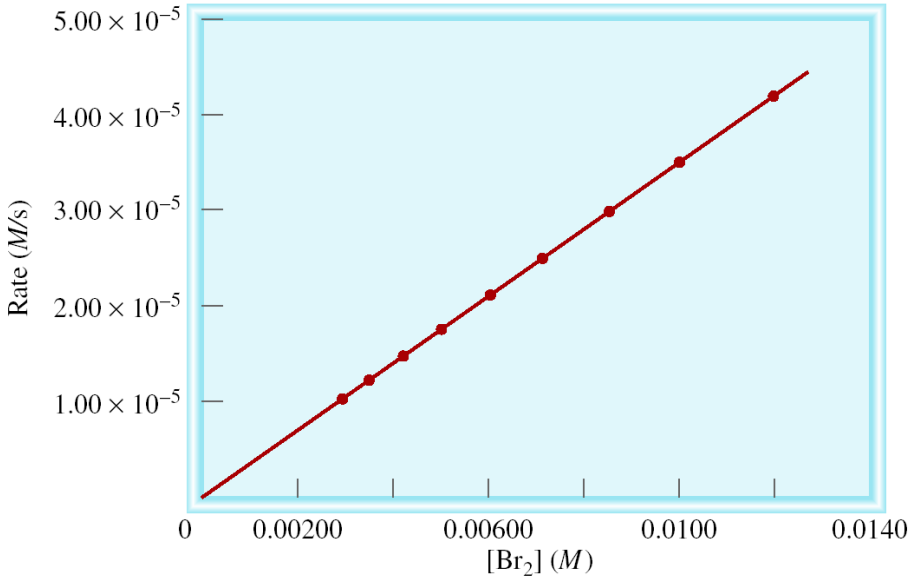
Time (s)	$[Br_2]$ (M)	Rate (M/s)	$k = \frac{\text{rate}}{[Br_2]}$ (s^{-1})
0.0	0.0120	4.20×10^{-5}	3.50×10^{-3}
50.0	0.0101	3.52×10^{-5}	3.49×10^{-3}
100.0	0.00846	2.96×10^{-5}	3.50×10^{-3}
150.0	0.00710	2.49×10^{-5}	3.51×10^{-3}
200.0	0.00596	2.09×10^{-5}	3.51×10^{-3}
250.0	0.00500	1.75×10^{-5}	3.50×10^{-3}
300.0	0.00420	1.48×10^{-5}	3.52×10^{-3}
350.0	0.00353	1.23×10^{-5}	3.48×10^{-3}
400.0	0.00296	1.04×10^{-5}	3.51×10^{-3}

rate α $[Br_2]$

rate = k $[Br_2]$

$$k = \frac{\text{rate}}{[Br_2]} = \textbf{\textit{rate constant}}$$

$= 3.50 \times 10^{-3}\ s^{-1}$



measure ΔP over time

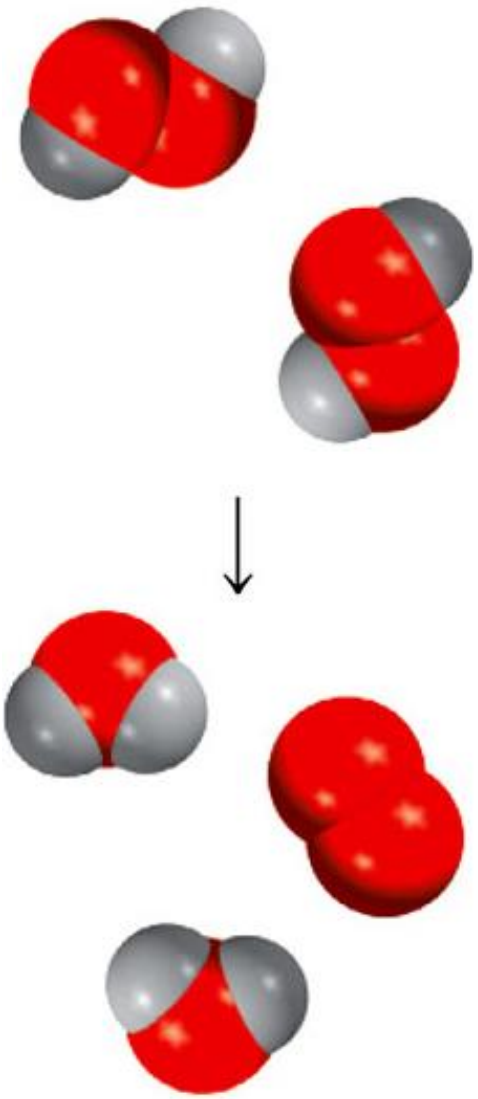
$$2H_2O_2\,(aq) \longrightarrow 2H_2O\,(l) + O_2\,(g)$$

$$PV = nRT$$

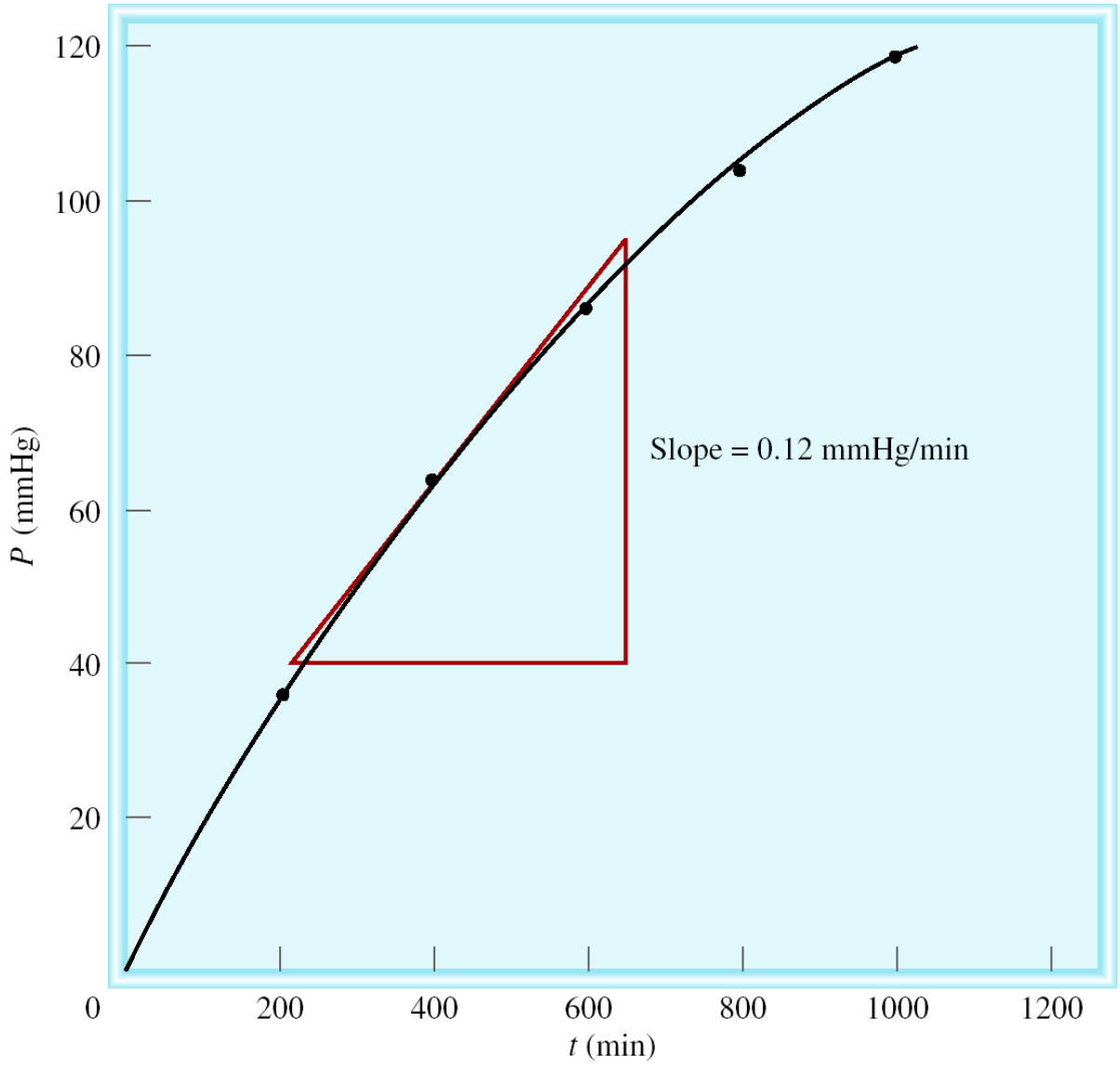
$$P = \frac{n}{V}RT = [O_2]RT$$

$$[O_2] = \frac{1}{RT}P$$

$$\text{rate} = \frac{\Delta[O_2]}{\Delta t} = \frac{1}{RT}\frac{\Delta P}{\Delta t}$$



$$2H_2O_2 \rightarrow 2H_2O + O_2$$



Reaction Rates and Stoichiometry

$$2A \longrightarrow B$$

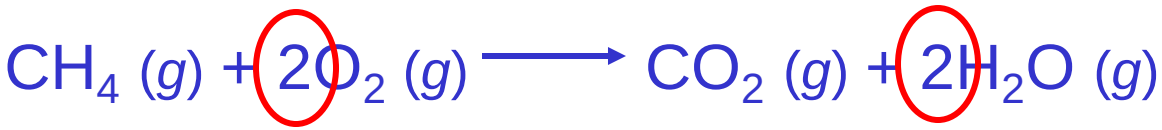
Two moles of A disappear for each mole of B that is formed.

$$\text{rate} = -\frac{1}{2}\frac{\Delta[A]}{\Delta t} \qquad \text{rate} = \frac{\Delta[B]}{\Delta t}$$

$$aA + bB \longrightarrow cC + dD$$

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Write the rate expression for the following reaction:



$$\text{rate} = -\frac{\Delta[CH_4]}{\Delta t} = -\frac{1}{2}\frac{\Delta[O_2]}{\Delta t} = \frac{\Delta[CO_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t}$$

The Rate Law

The ***rate law*** expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = k[A]^x[B]^y$$

Reaction is ***x*th order** in A

Reaction is ***y*th order** in B

Reaction is **(x +y)th order overall**

$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

rate = $k\,[F_2]^x[ClO_2]^y$

TABLE 13.2 Rate Data for the Reaction Between F_2 and ClO_2

$[F_2]$ (M)	$[ClO_2]$ (M)	Initial Rate (M/s)
1. 0.10	0.010	1.2×10^{-3}
2. 0.10	0.040	4.8×10^{-3}
3. 0.20	0.010	2.4×10^{-3}

Double $[F_2]$ with $[ClO_2]$ constant

Rate doubles

$x = 1$

Quadruple $[ClO_2]$ with $[F_2]$ constant

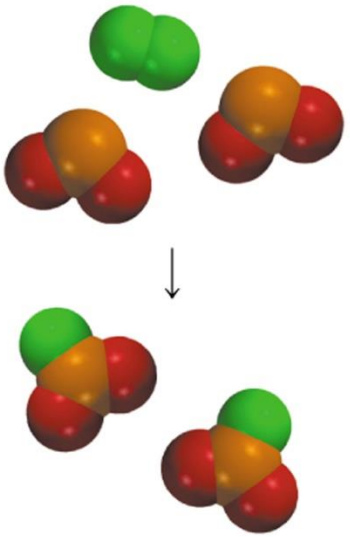
Rate quadruples

$y = 1$

rate = $k\,[F_2][ClO_2]$

Rate Laws

- Rate laws are **always** determined experimentally.
- Reaction order is **always** defined in terms of reactant (not product) concentrations.
- The order of a reactant **is not** related to the stoichiometric coefficient of the reactant in the balanced chemical equation.



$$F_2\,(g) + 2ClO_2\,(g) \longrightarrow 2FClO_2\,(g)$$

$$\text{rate} = k\,[F_2][ClO_2]^{1}$$

Determine the rate law and calculate the rate constant for the following reaction from the following data:

$S_2O_8^{2-}(aq) + 3I^-(aq) \longrightarrow 2SO_4^{2-}(aq) + I_3^-(aq)$

Experiment	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate (M/s)
1	0.08	0.034	2.2×10^{-4}
2	0.08	0.017	1.1×10^{-4}
3	0.16	0.017	2.2×10^{-4}

rate = $k\,[S_2O_8^{2-}]^x[I^-]^y$

$y = 1$

$x = 1$

rate = $k\,[S_2O_8^{2-}][I^-]$

Double $[I^-]$, rate doubles (experiment 1 & 2)

Double $[S_2O_8^{2-}]$, rate doubles (experiment 2 & 3)

$$k = \frac{\text{rate}}{[S_2O_8^{2-}][I^-]} = \frac{2.2 \times 10^{-4}\ M/\text{s}}{(0.08\ M)(0.034\ M)} = 0.08/M\cdot\text{s}$$

First-Order Reactions

A $\longrightarrow$ product

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = k\,[A]$$

$$k = \frac{\text{rate}}{[A]} = \frac{M/s}{M} = 1/s \text{ or } s^{-1}$$

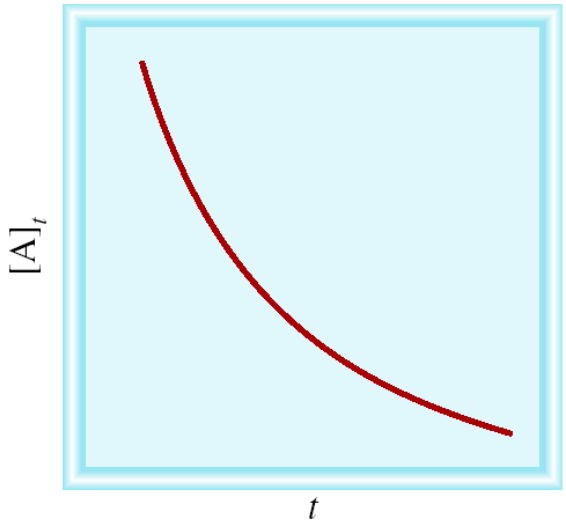
$$-\frac{\Delta[A]}{\Delta t} = k\,[A]$$

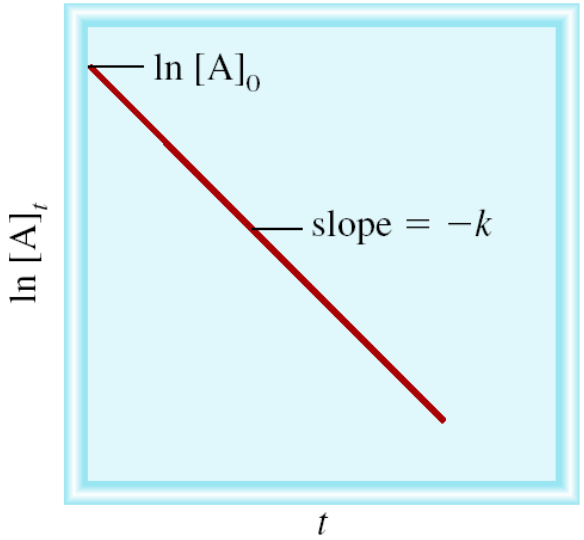
[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time t=0

$$[A] = [A]_0 e^{-kt}$$

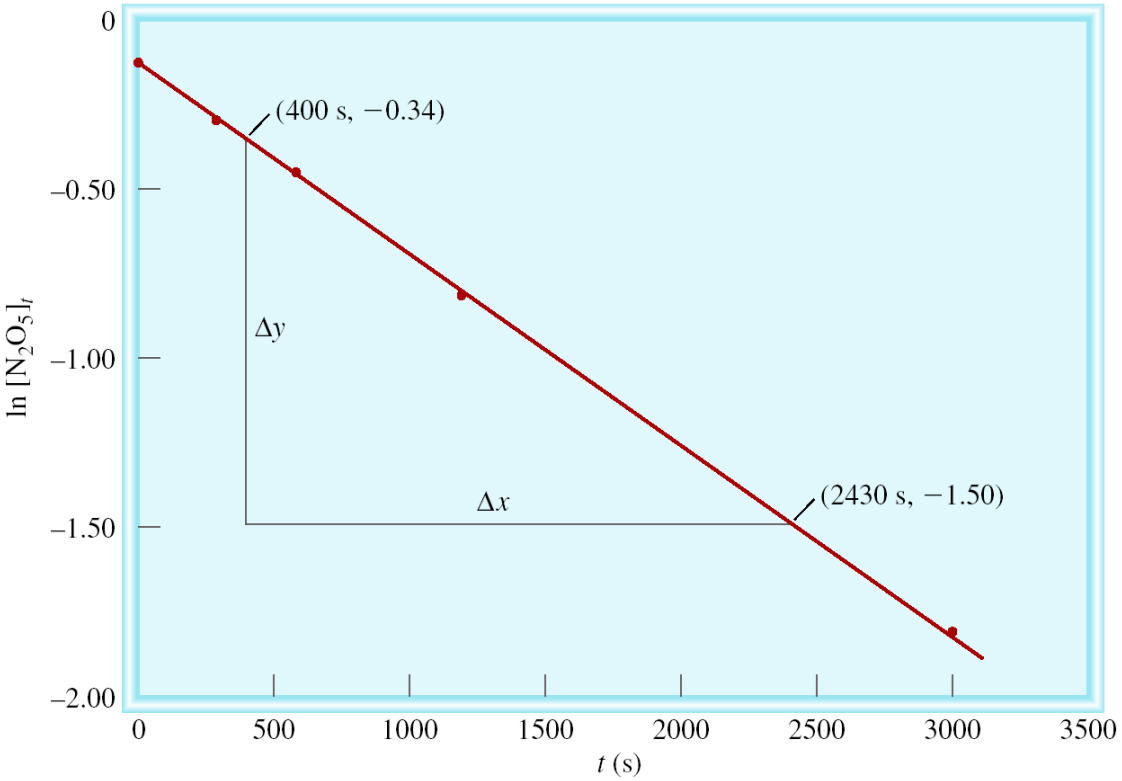
$$\ln[A] = \ln[A]_0 - kt$$





Graphical Determination of *k*

$$2N_2O_5 \longrightarrow 4NO_2\,(g) + O_2\,(g)$$



$$\text{slope } (m) = \frac{\Delta y}{\Delta x}$$

$$= \frac{-1.50 - (-0.34)}{(2430 - 400)\ \text{s}}$$

$$= -5.7 \times 10^{-4}\ \text{s}^{-1}$$

$$m = -k$$

$$k = 5.7 \times 10^{-4}\ \text{s}^{-1}$$

The reaction $2A \longrightarrow B$ is first order in A with a rate constant of $2.8 \times 10^{-2}\ s^{-1}$ at 80^0C. How long will it take for A to decrease from 0.88 *M* to 0.14 *M* ?

$$\ln[A] = \ln[A]_0 - kt$$

$$[A]_0 = 0.88\ M$$

$$[A] = 0.14\ M$$

$$kt = \ln[A]_0 - \ln[A]$$

$$t = \frac{\ln[A]_0 - \ln[A]}{k} = \frac{\ln \dfrac{[A]_0}{[A]}}{k} = \frac{\ln \dfrac{0.88\ \cancel{M}}{0.14\ \cancel{M}}}{2.8 \times 10^{-2}\ s^{-1}} = 66\ s$$

First-Order Reactions

The ***half-life*, $t_{½}$,** is the time required for the concentration of a reactant to decrease to half of its initial concentration.

$$t_{½} = t \text{ when } [A] = [A]_0/2$$

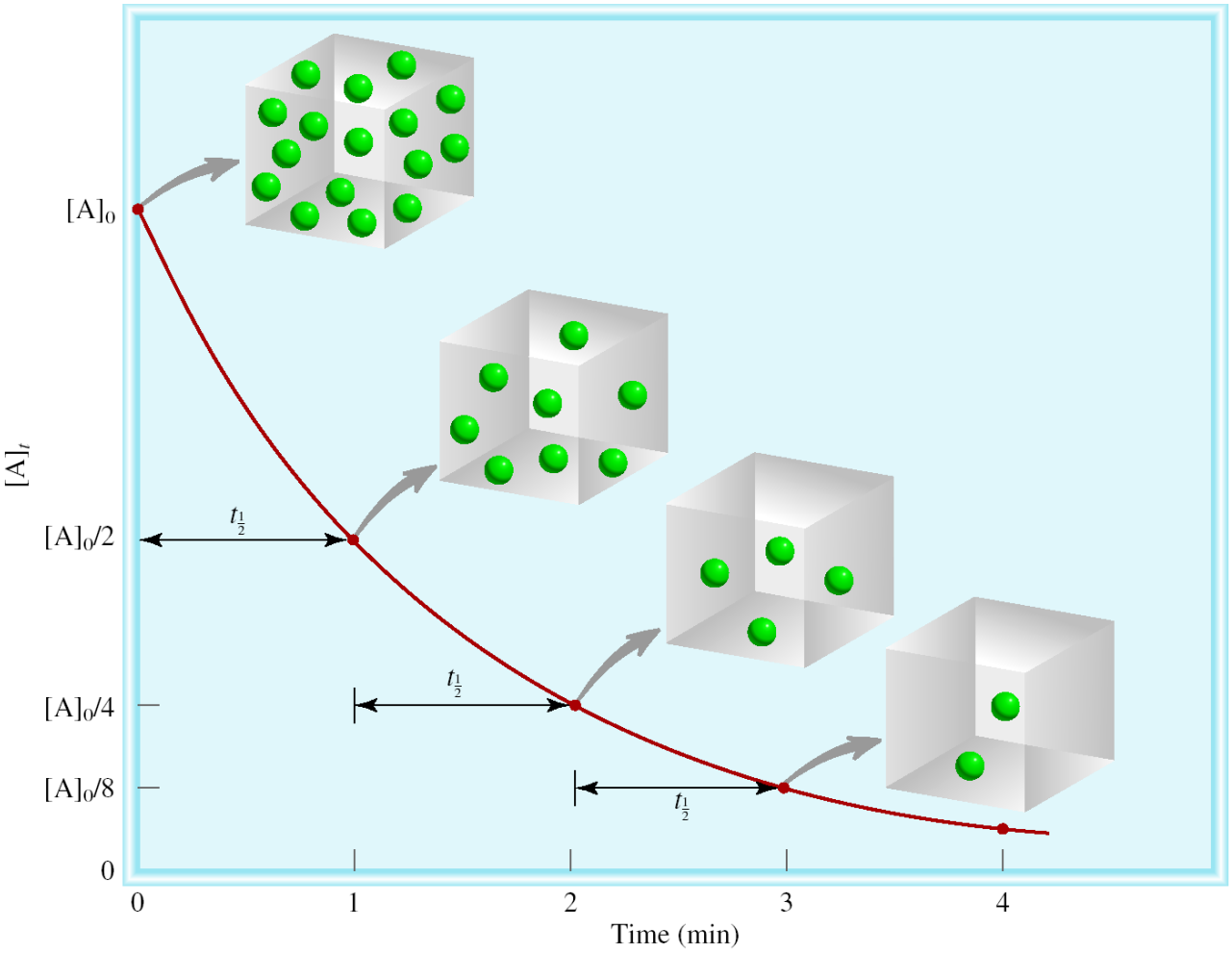
$$t_{½} = \frac{\ln \dfrac{\cancel{[A]_0}}{\cancel{[A]_0}/2}}{k} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

What is the half-life of N_2O_5 if it decomposes with a rate constant of 5.7×10^{-4} s^{-1}?

$$t_{½} = \frac{\ln 2}{k} = \frac{0.693}{5.7 \times 10^{-4}\ s^{-1}} = 1200 \text{ s} = 20 \text{ minutes}$$

How do you know decomposition is first order?

units of k (s^{-1})



First-order reaction

A ⟶ product

# of half-lives	[A] = [A]$_0$/n
1	2
2	4
3	8
4	16

Second-Order Reactions

A $\longrightarrow$ product rate = $-\frac{\Delta[A]}{\Delta t}$ rate = $k\,[A]^2$

$$k = \frac{\text{rate}}{[A]^2} = \frac{M/s}{M^2} = 1/M \cdot s$$

$$-\frac{\Delta[A]}{\Delta t} = k\,[A]^2$$

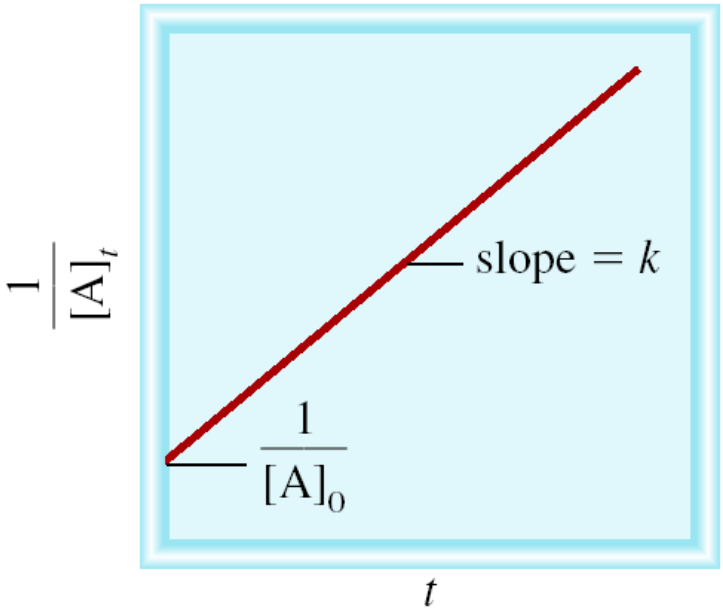
$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$

[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time t=0

$t_{1/2} = t$ when $[A] = [A]_0/2$

$$t_{1/2} = \frac{1}{k[A]_0}$$



Zero-Order Reactions

$A \longrightarrow$ product

$$\text{rate} = -\frac{\Delta[A]}{\Delta t}$$

$$\text{rate} = k\,[A]^0 = k$$

$$k = \frac{\text{rate}}{[A]^0} = M/s$$

$$-\frac{\Delta[A]}{\Delta t} = k$$

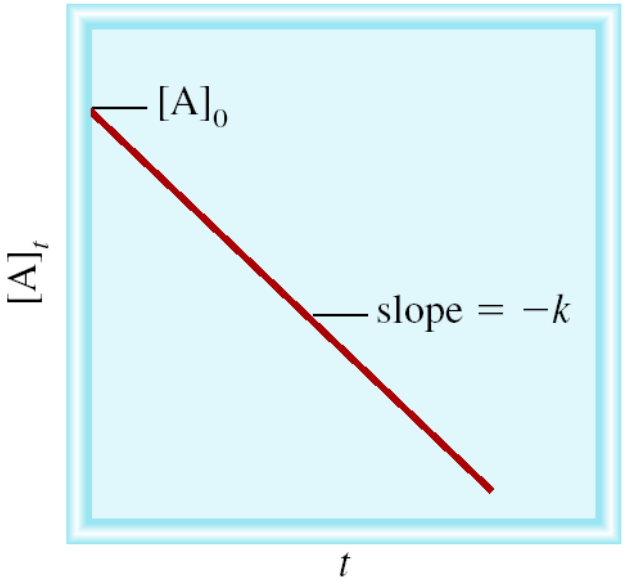
$$[A] = [A]_0 - kt$$

[A] is the concentration of A at any time t

$[A]_0$ is the concentration of A at time $t = 0$

$t_{1/2} = t$ when $[A] = [A]_0/2$

$$t_{1/2} = \frac{[A]_0}{2k}$$

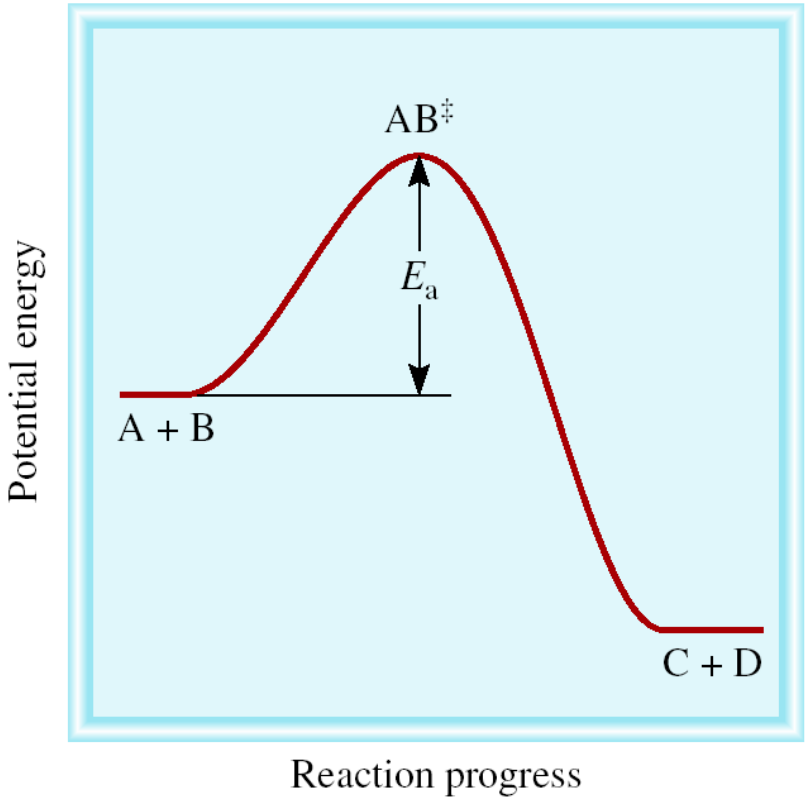


Summary of the Kinetics of Zero-Order, First-Order and Second-Order Reactions

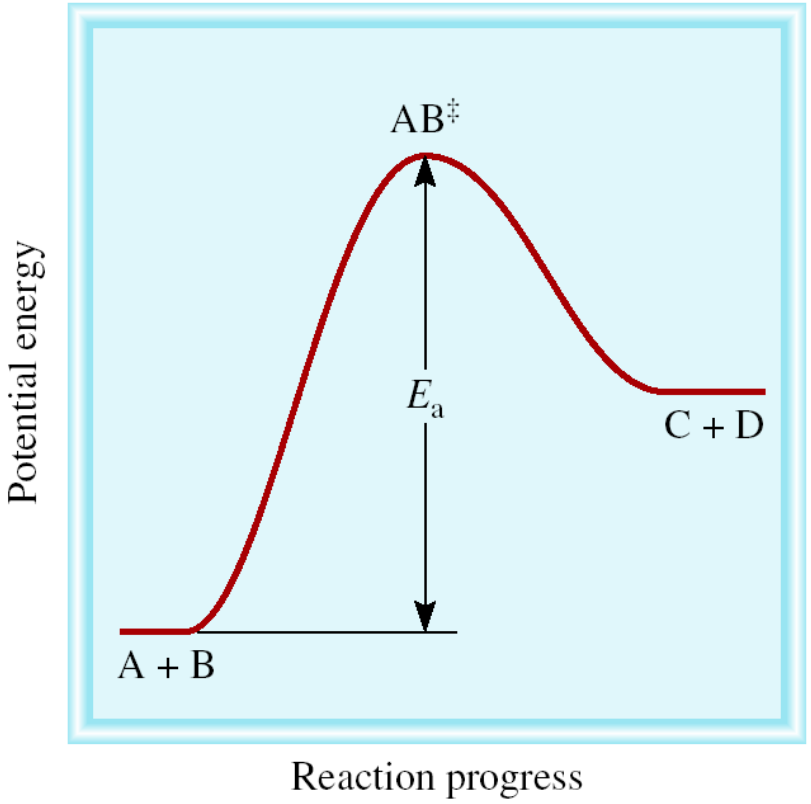
Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \frac{[A]_0}{2k}$
1	rate = k [A]	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}$
2	rate = k $[A]^2$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$	$t_{1/2} = \frac{1}{k[A]_0}$

$$A + B \longrightarrow AB^{\ddagger} \longrightarrow C + D$$

Exothermic Reaction

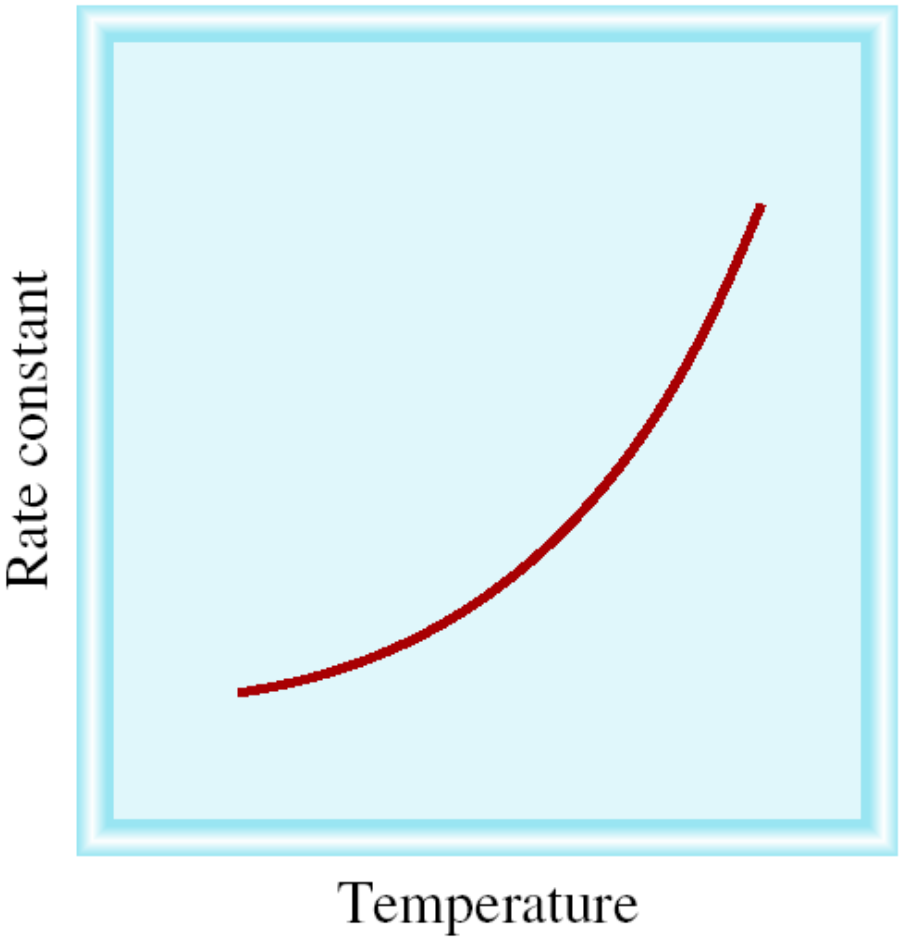


Endothermic Reaction



The ***activation energy (E_a)*** is the minimum amount of energy required to initiate a chemical reaction.

Temperature Dependence of the Rate Constant



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

(Arrhenius equation)

E_a is the activation energy (J/mol)

R is the gas constant (8.314 J/K•mol)

T is the absolute temperature

A is the frequency factor

Alternate format:

$$\ln k = -\frac{E_a}{R}\frac{1}{T} + \ln A$$

Alternate Form of the Arrhenius Equation

At two temperatures, T_1 and T_2

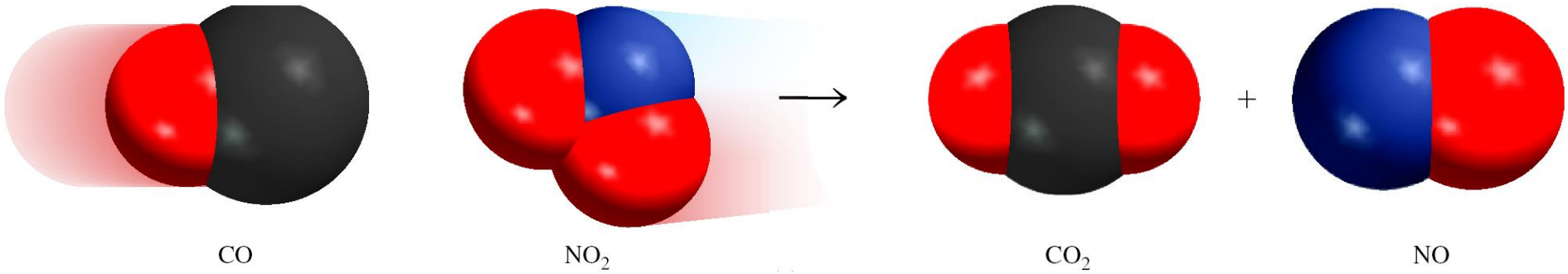
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

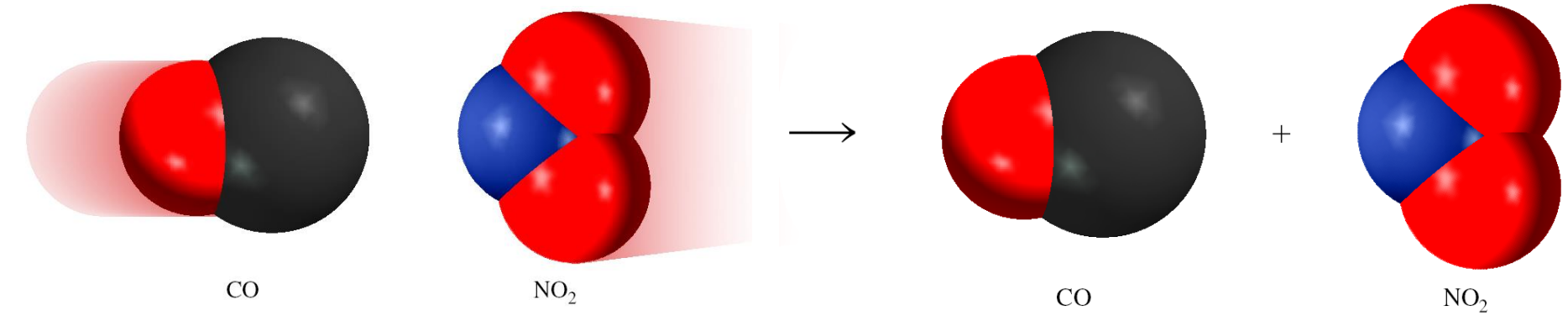
$$\ln \frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

Importance of Molecular Orientation

$$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$$



effective collision



ineffective collision

Reaction Mechanisms

The overall progress of a chemical reaction can be represented at the molecular level by a series of simple ***elementary steps*** or ***elementary reactions.***

The sequence of **elementary steps** that leads to product formation is the ***reaction mechanism***.

$$2NO\ (g) + O_2\ (g) \longrightarrow 2NO_2\ (g)$$

N_2O_2 is detected during the reaction!

Elementary step: $NO + NO \longrightarrow \cancel{N_2O_2}$

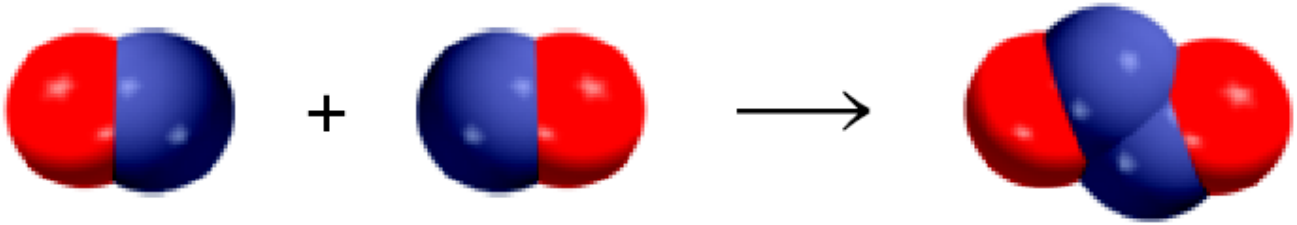
\+ Elementary step: $\cancel{N_2O_2} + O_2 \longrightarrow 2NO_2$

Overall reaction: $2NO + O_2 \longrightarrow 2NO_2$

$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

Mechanism:

$$2NO(g) \longrightarrow N_2O_2(g)$$



$$N_2O_2(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Intermediates are species that appear in a reaction mechanism **but not** in the overall balanced equation.

An **intermediate** is always formed in an early elementary step and consumed in a later elementary step.

Elementary step: $NO + NO \longrightarrow N_2O_2$

\+ Elementary step: $N_2O_2 + O_2 \longrightarrow 2NO_2$

Overall reaction: $2NO + O_2 \longrightarrow 2NO_2$

The ***molecularity of a reaction*** is the number of molecules reacting in an elementary step.

- ***Unimolecular reaction*** – elementary step with 1 molecule
- ***Bimolecular reaction*** – elementary step with 2 molecules
- ***Termolecular reaction*** – elementary step with 3 molecules

Rate Laws and Elementary Steps

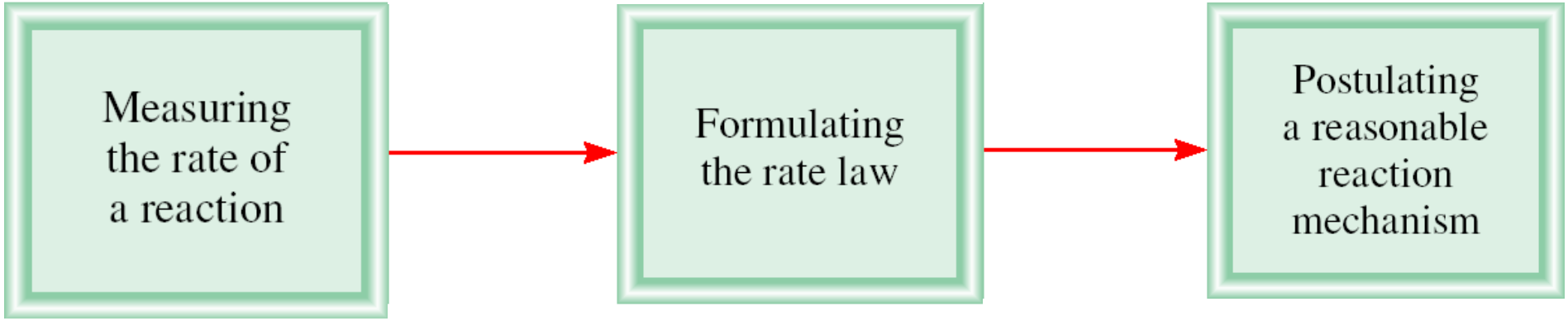
Unimolecular reaction	$A \longrightarrow$ products	rate = k [A]
Bimolecular reaction	$A + B \longrightarrow$ products	rate = k [A][B]
Bimolecular reaction	$A + A \longrightarrow$ products	rate = k [A]^2

Writing plausible reaction mechanisms:

- The sum of the elementary steps **must** give the overall balanced equation for the reaction.
- The rate-determining step should predict the same rate law that is determined experimentally.

The ***rate-determining step*** is the **slowest** step in the sequence of steps leading to product formation.

Sequence of Steps in Studying a Reaction Mechanism



The experimental rate law for the reaction between NO_2 and CO to produce NO and CO_2 is rate = $k[NO_2]^2$. The reaction is believed to occur via two steps:

Step 1: $NO_2 + NO_2 \longrightarrow NO + NO_3$

Step 2: $NO_3 + CO \longrightarrow NO_2 + CO_2$

What is the equation for the overall reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

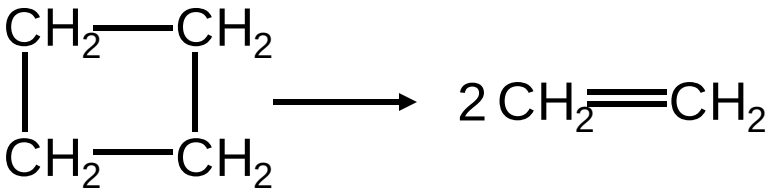
What is the intermediate?

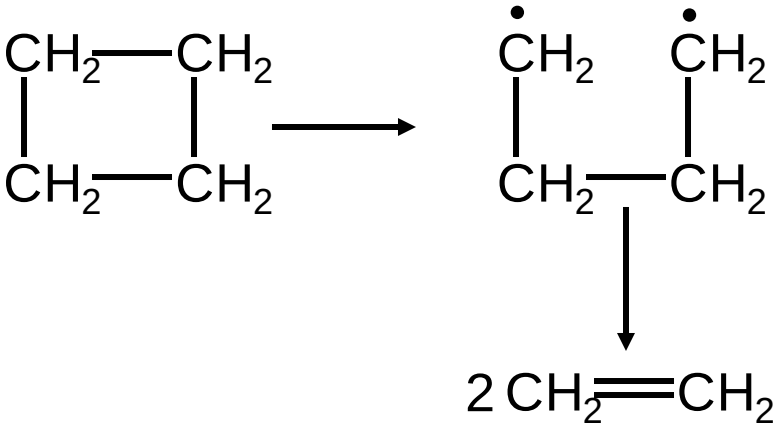
$$NO_3$$

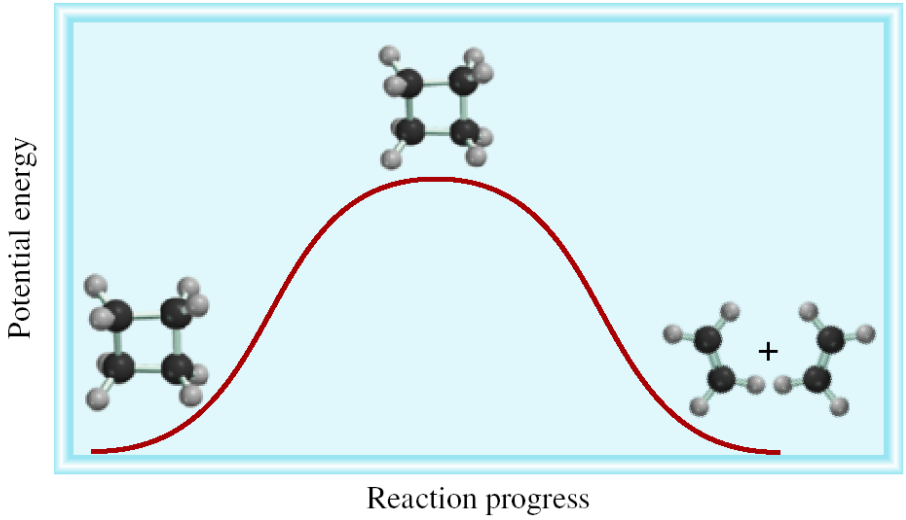
What can you say about the relative rates of steps 1 and 2?

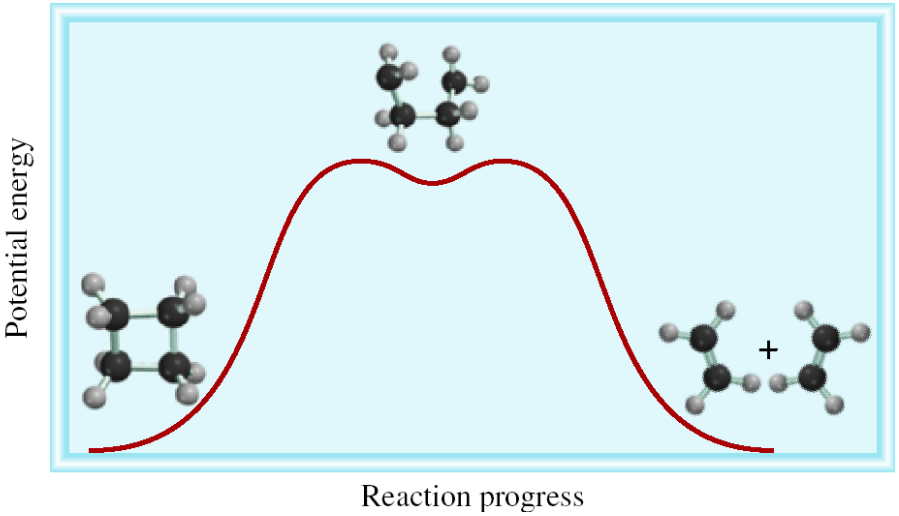
rate = $k[NO_2]^2$ is the rate law for step 1 so step 1 must be slower than step 2

Chemistry In Action: Femtochemistry







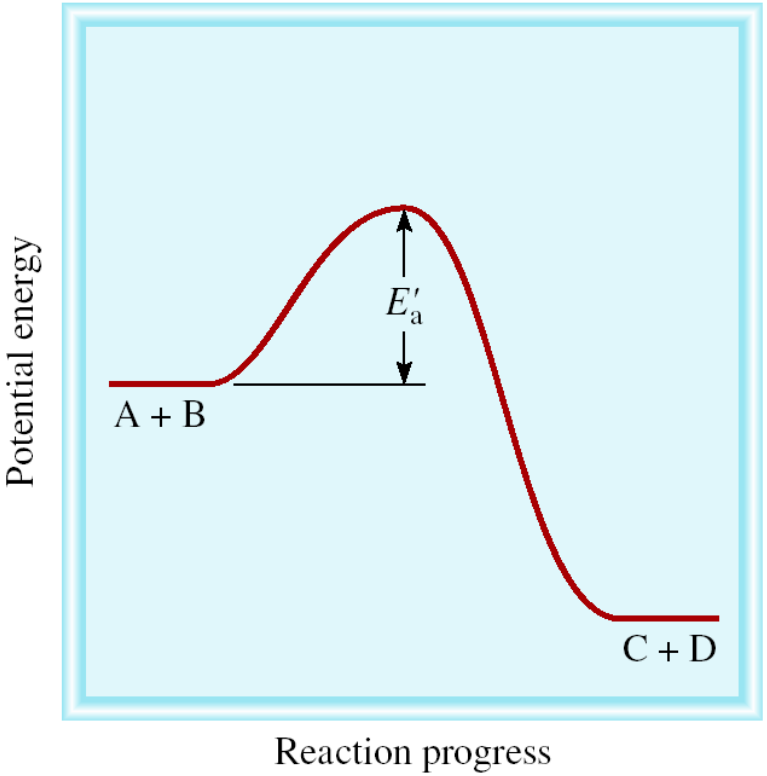


A ***catalyst*** is a substance that increases the rate of a chemical reaction without itself being consumed.

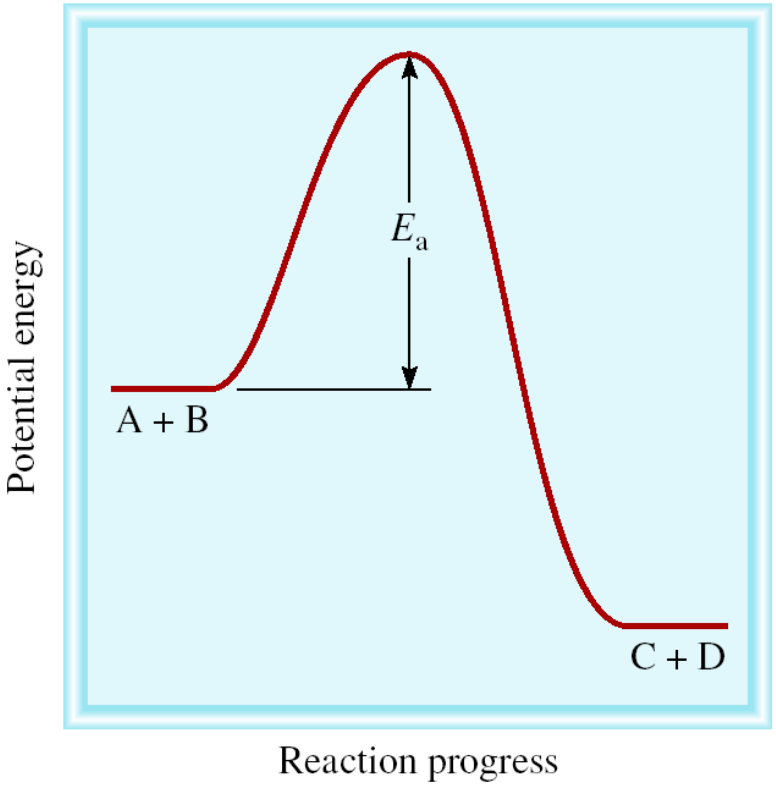
$$k = A \cdot e^{(-E_a / RT)}$$

$E_a \downarrow \quad k \uparrow$

Uncatalyzed



Catalyzed



$\text{rate}_{\text{catalyzed}} > \text{rate}_{\text{uncatalyzed}}$

$E'_a < E_a$

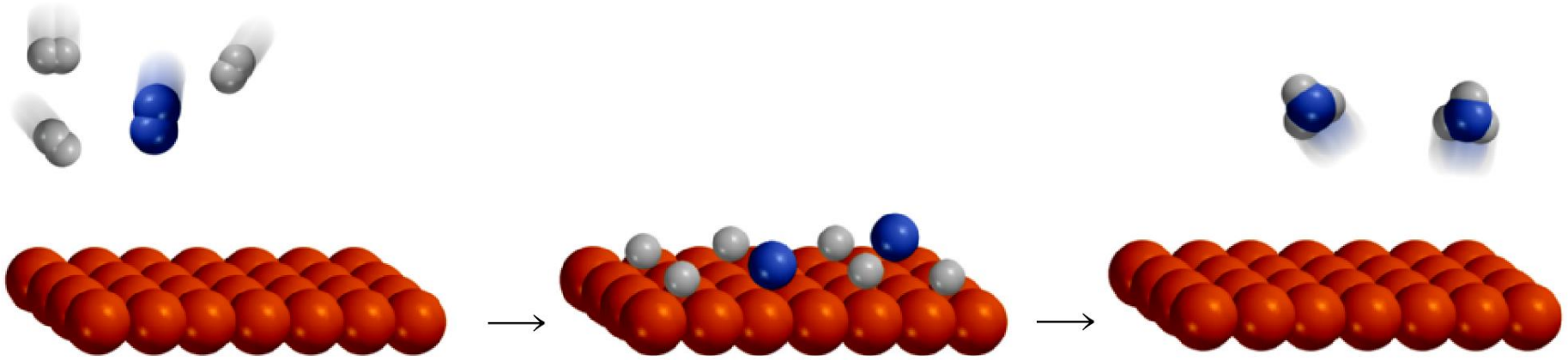
In ***heterogeneous catalysis***, the reactants and the catalysts are in different phases.

- Haber synthesis of ammonia
- Ostwald process for the production of nitric acid
- Catalytic converters

In ***homogeneous catalysis***, the reactants and the catalysts are dispersed in a single phase, usually liquid.

- Acid catalysis
- Base catalysis

Haber Process



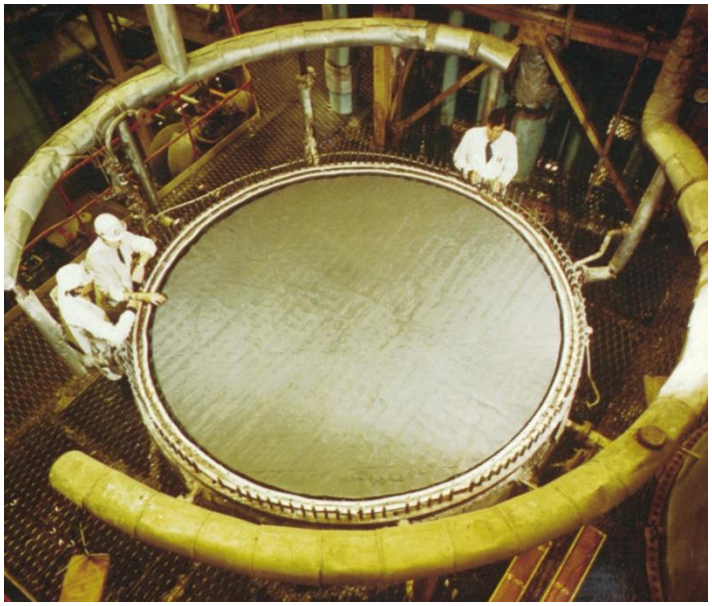
$$N_2\,(g) + 3H_2\,(g) \xrightarrow[\text{catalyst}]{Fe/Al_2O_3/K_2O} 2NH_3\,(g)$$

Ostwald Process

$$4NH_3\,(g) + 5O_2\,(g) \xrightarrow{\text{Pt catalyst}} 4NO\,(g) + 6H_2O\,(g)$$

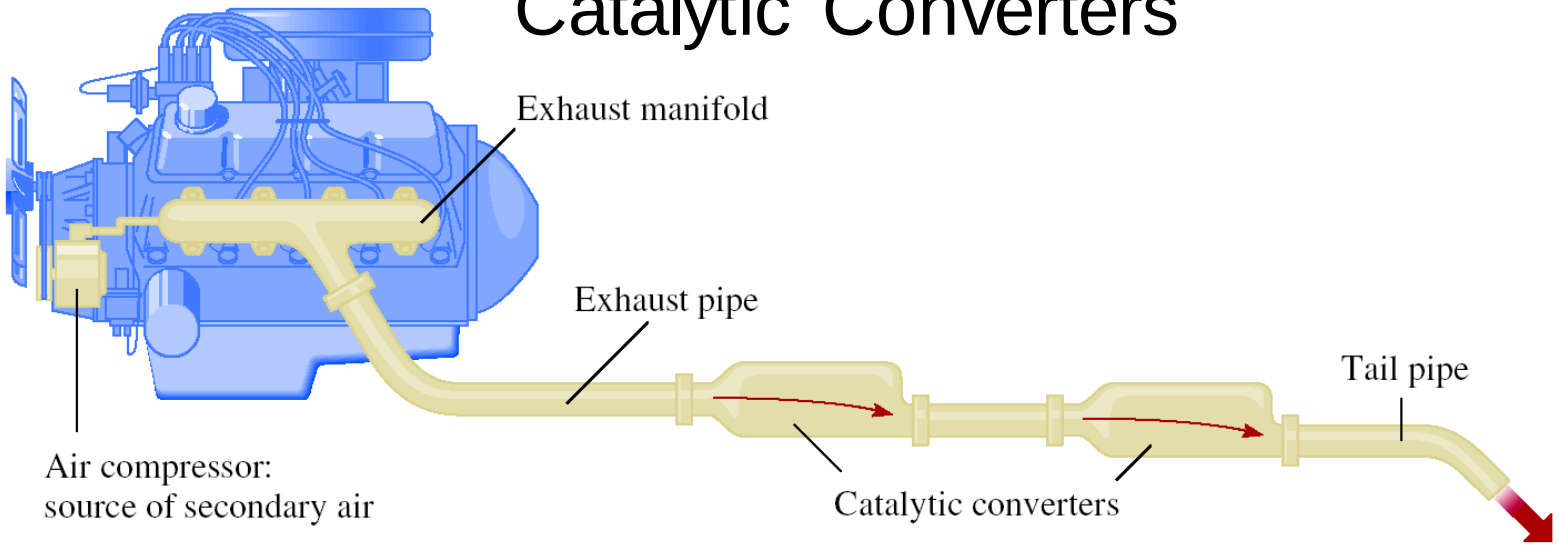
$$2NO\,(g) + O_2\,(g) \longrightarrow 2NO_2\,(g)$$

$$2NO_2\,(g) + H_2O\,(l) \longrightarrow HNO_2\,(aq) + HNO_3\,(aq)$$



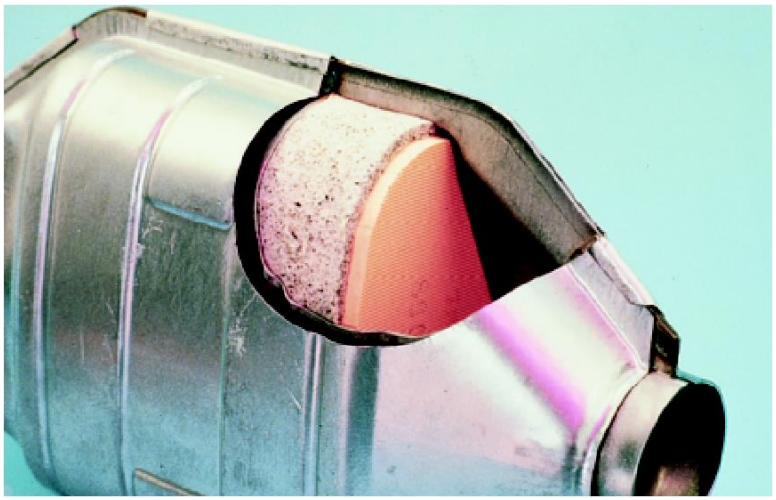
Pt-Rh catalysts used
in Ostwald process

Catalytic Converters

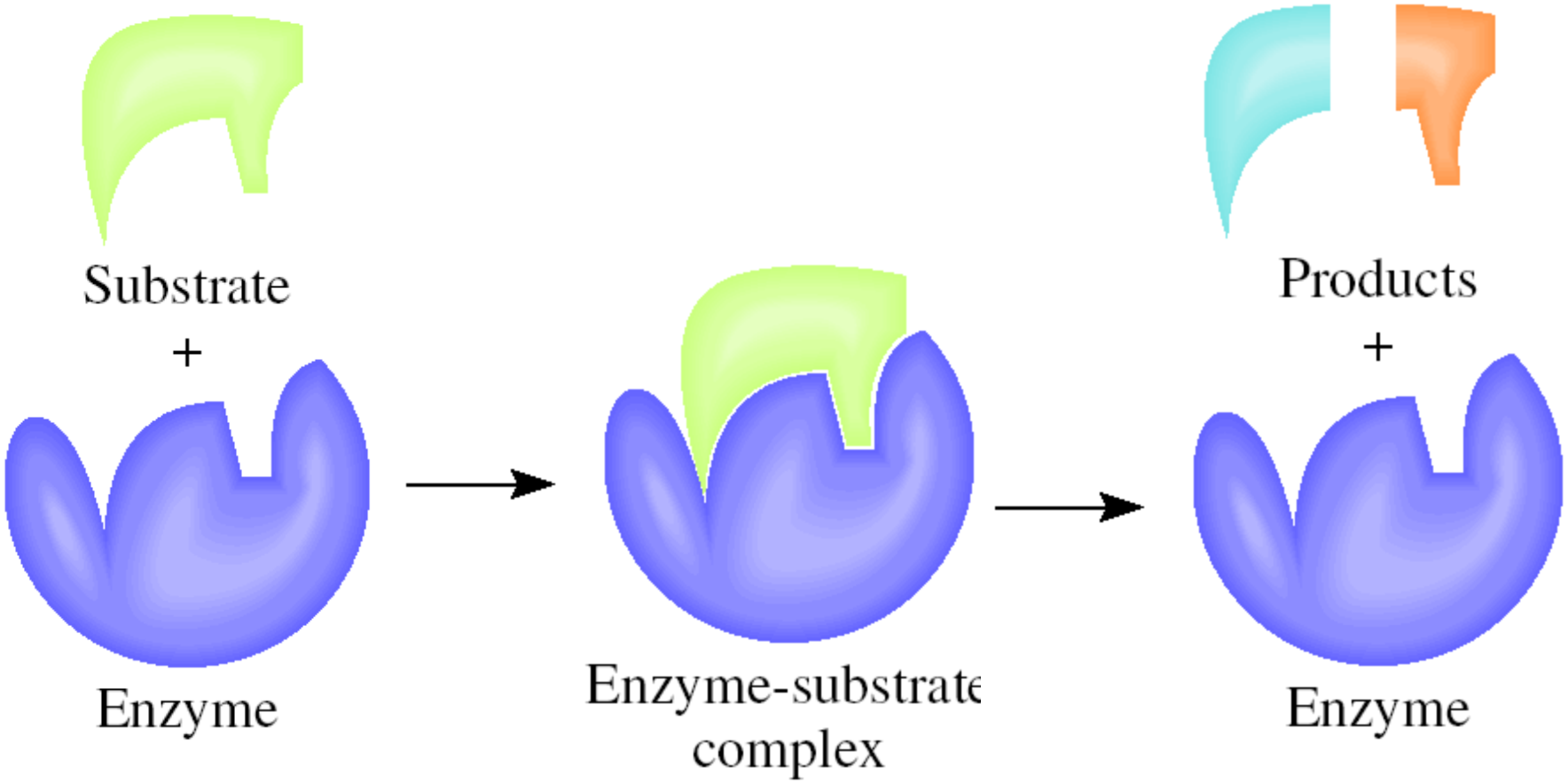


$$\text{CO + Unburned Hydrocarbons} + O_2 \xrightarrow[\text{converter}]{\text{catalytic}} CO_2 + H_2O$$

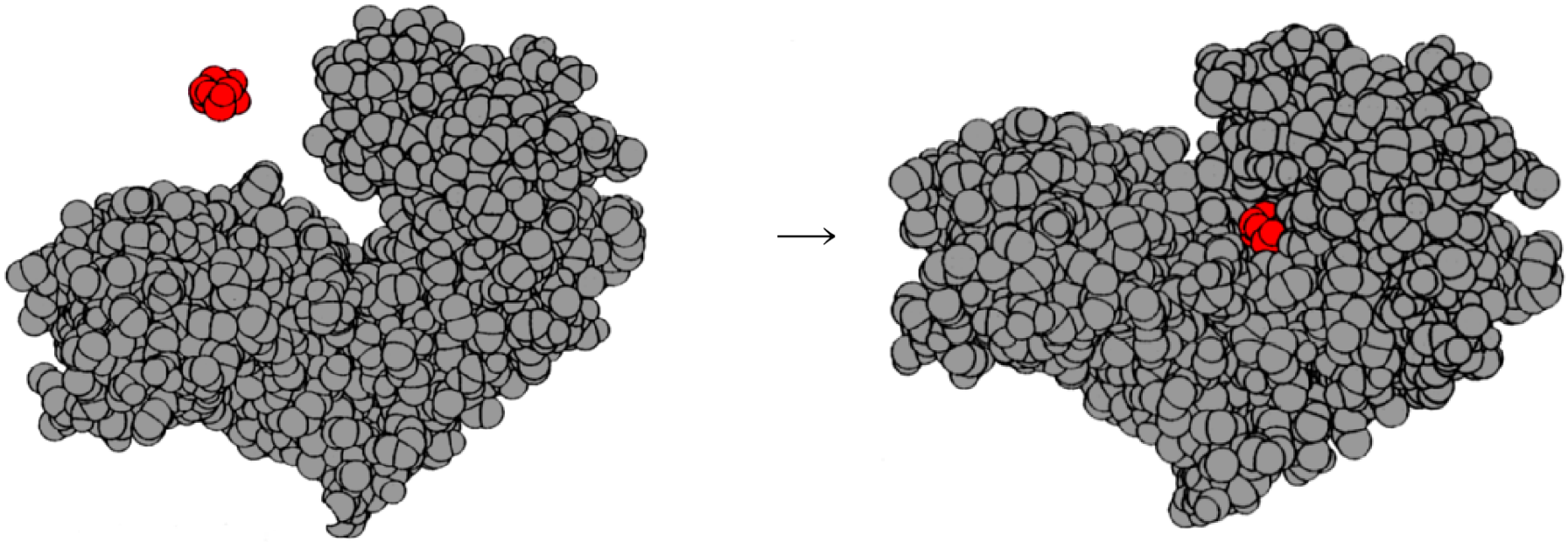
$$2NO + 2NO_2 \xrightarrow[\text{converter}]{\text{catalytic}} 2N_2 + 3O_2$$



Enzyme Catalysis



Binding of Glucose to Hexokinase



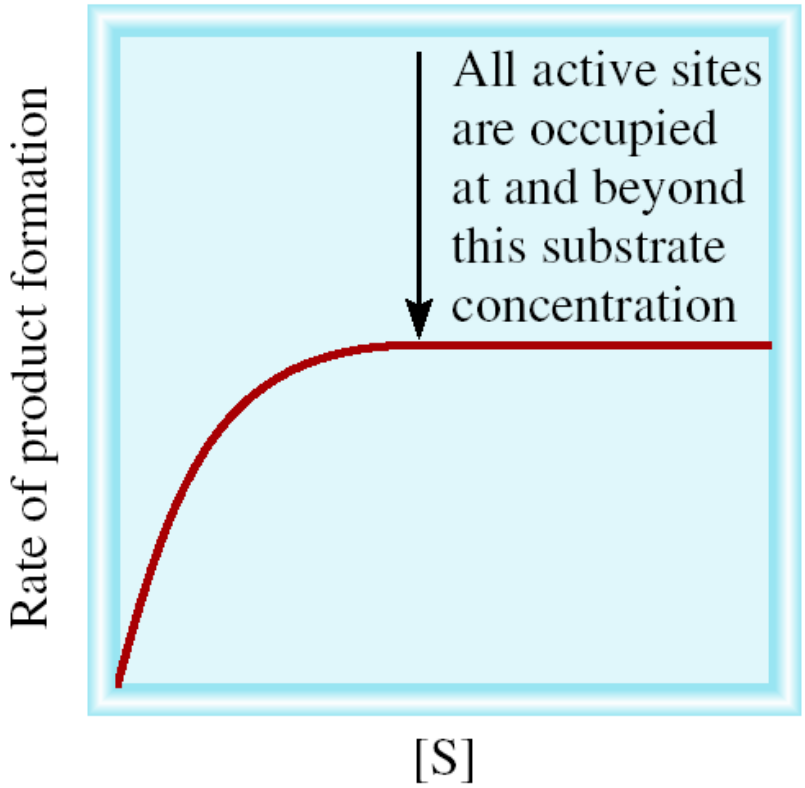
Enzyme Kinetics

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$$

$$ES \xrightarrow{k_2} E + P$$

$$\text{rate} = \frac{\Delta[P]}{\Delta t}$$

$$\text{rate} = k\,[ES]$$



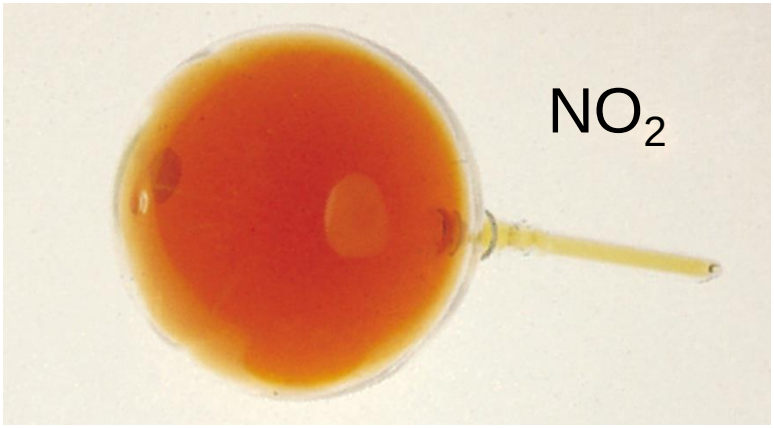
Chemical Equilibrium

Chapter 14

Equilibrium is a state in which there are no observable changes as time goes by.

Chemical equilibrium is achieved when:

- the rates of the forward and reverse reactions are equal and
- the concentrations of the reactants and products remain constant



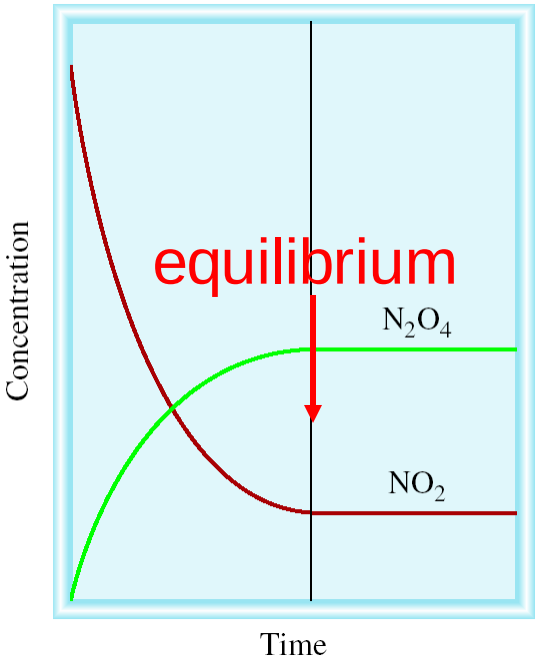
Physical equilibrium

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

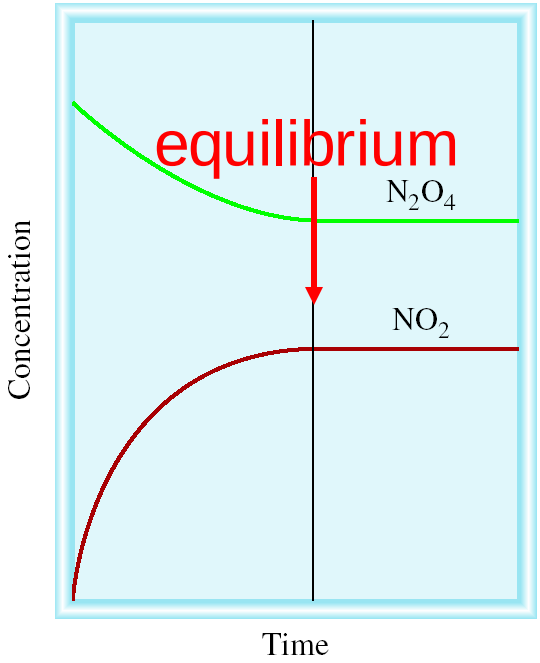
Chemical equilibrium

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

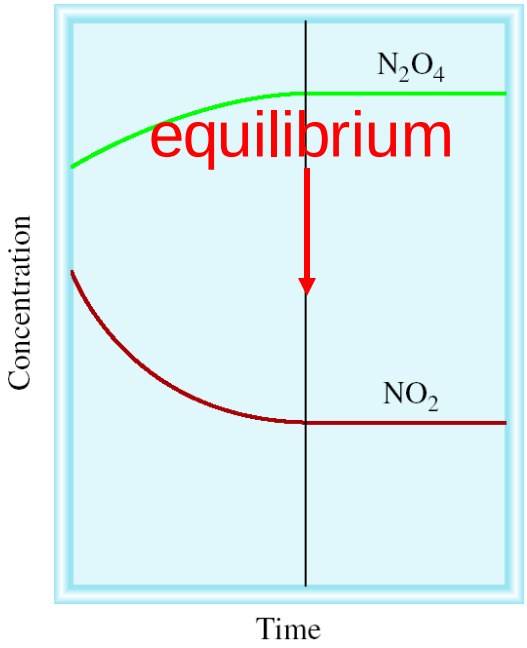
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$



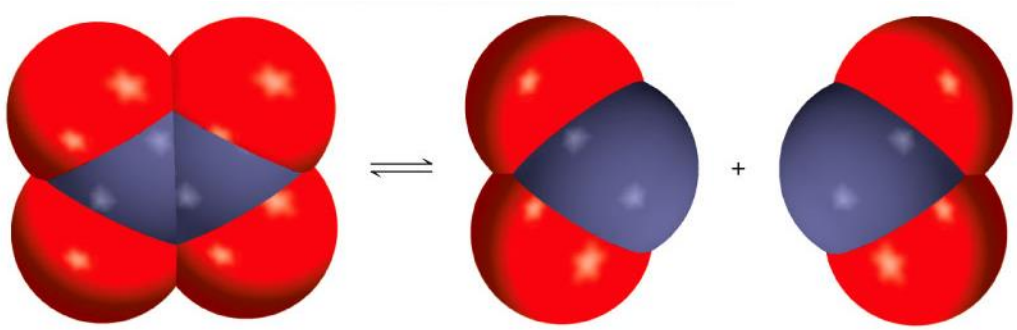
Start with NO_2

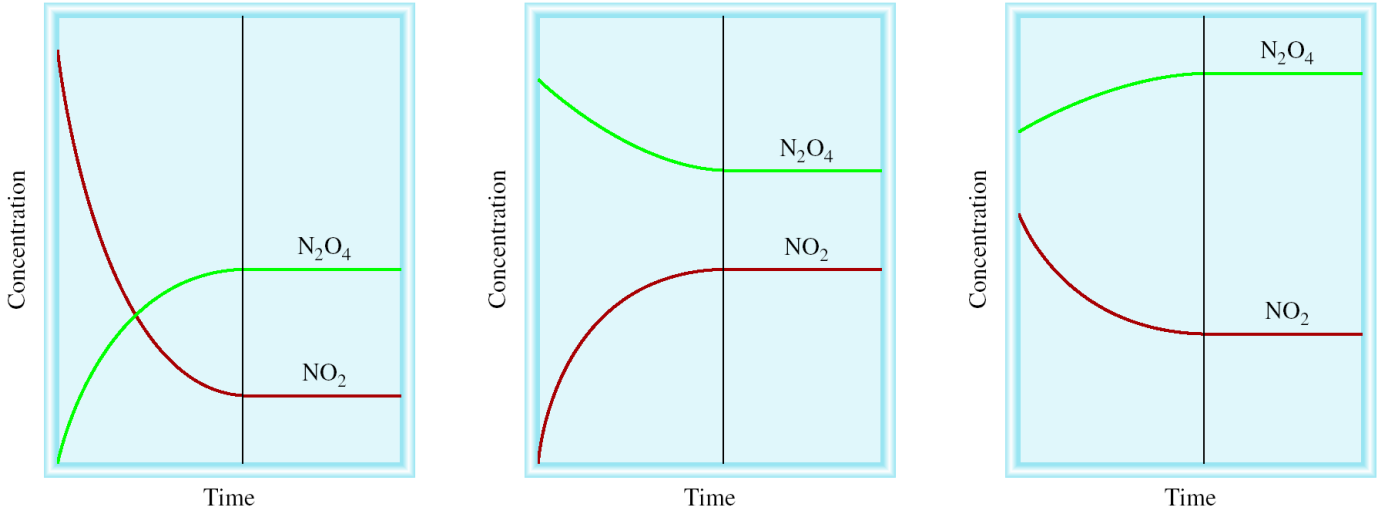


Start with N_2O_4



Start with NO_2 & N_2O_4





constant

TABLE 14.1 The NO_2–N_2O_4 System at 25°C

Initial Concentrations (*M*)		Equilibrium Concentrations (*M*)		Ratio of Concentrations at Equilibrium	
$[NO_2]$	$[N_2O_4]$	$[NO_2]$	$[N_2O_4]$	$\frac{[NO_2]}{[N_2O_4]}$	$\frac{[NO_2]^2}{[N_2O_4]}$
0.000	0.670	0.0547	0.643	0.0851	4.65×10^{-3}
0.0500	0.446	0.0457	0.448	0.102	4.66×10^{-3}
0.0300	0.500	0.0475	0.491	0.0967	4.60×10^{-3}
0.0400	0.600	0.0523	0.594	0.0880	4.60×10^{-3}
0.200	0.000	0.0204	0.0898	0.227	4.63×10^{-3}

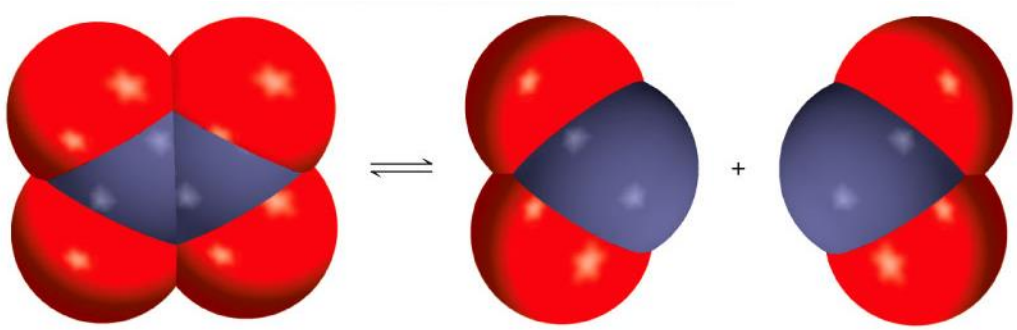
$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$$aA + bB \rightleftharpoons cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Law of Mass Action

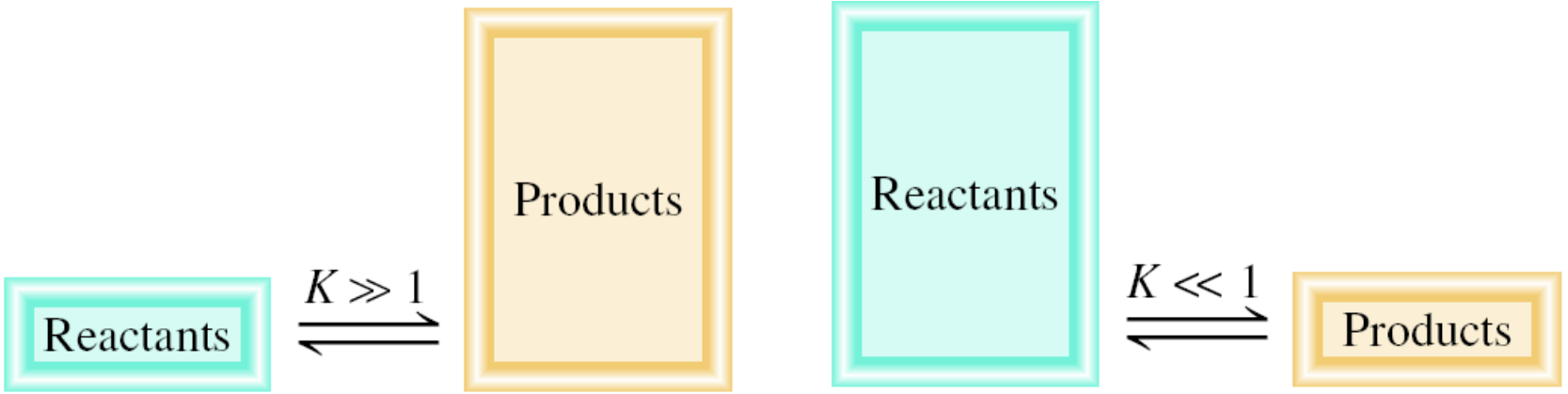


$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$aA + bB \rightleftharpoons cC + dD$$

Equilibrium Will

$K >> 1$	Lie to the right	Favor products
$K << 1$	Lie to the left	Favor reactants



Homogenous equilibrium applies to reactions in which all reacting species **are in the same phase.**

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} \qquad K_p = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

In most cases

$$K_c \neq K_p$$

$$aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)$$

$$K_p = K_c(RT)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$

Homogeneous Equilibrium

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^-\,(aq) + H_3O^+\,(aq)$$

$$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = K_c'\,[H_2O]$$

General practice **not** to include units for the equilibrium constant.

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (*g*) at 74^0C are [CO] = 0.012 *M*, $[Cl_2]$ = 0.054 *M*, and $[COCl_2]$ = 0.14 *M*. Calculate the equilibrium constants K_c and K_p.

$$CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$$

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \times 0.054} = 220$$

$$K_p = K_c(RT)^{\Delta n}$$

$\Delta n = 1 - 2 = -1$ $\quad R = 0.0821$ $\quad T = 273 + 74 = 347$ K

$$K_p = 220 \times (0.0821 \times 347)^{-1} = 7.7$$

The equilibrium constant K_p for the reaction

$$2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$$

is 158 at 1000K. What is the equilibrium pressure of O_2 if the P_{NO_2} = 0.400 atm and P_{NO} = 0.270 atm?

$$K_p = \frac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2}$$

$$P_{O_2} = K_p \frac{P_{NO_2}^2}{P_{NO}^2}$$

$$P_{O_2} = 158 \times (0.400)^2/(0.270)^2 = 347 \text{ atm}$$

Heterogenous equilibrium applies to reactions in which reactants and products **are in different phases.**

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_c' = \frac{[CaO][CO_2]}{[CaCO_3]}$$

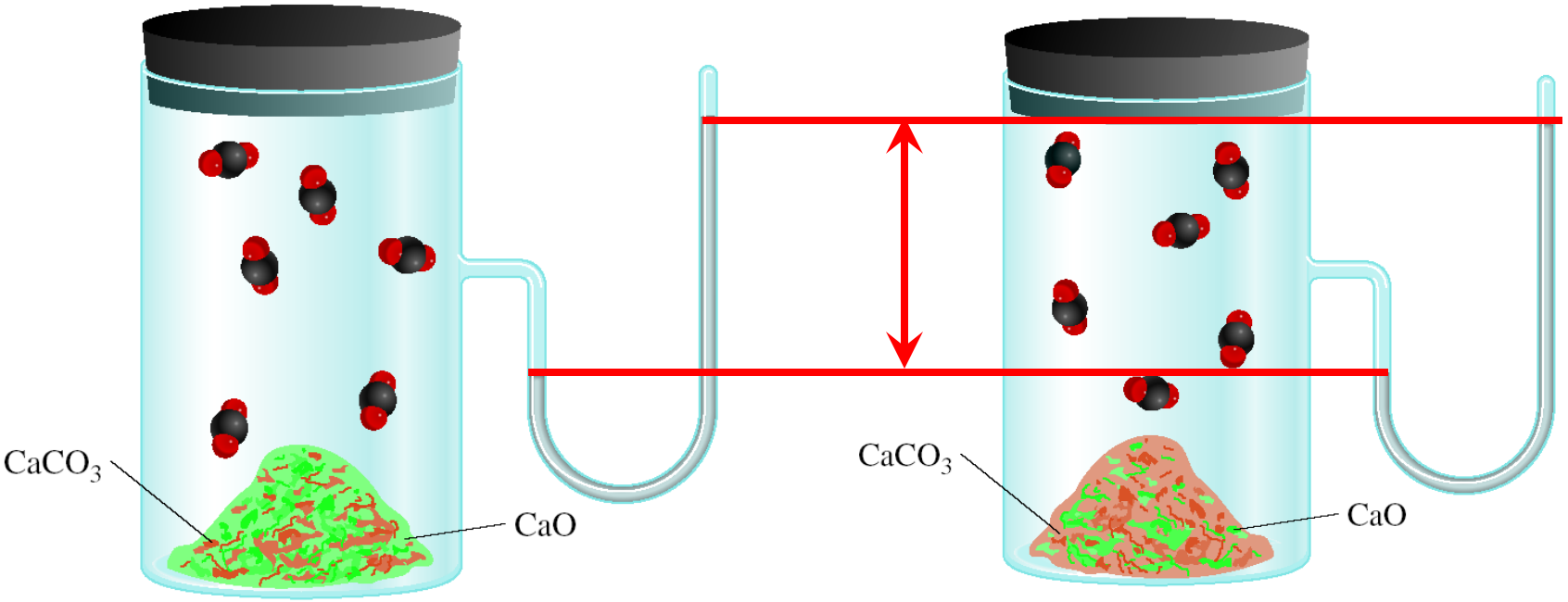
$[CaCO_3]$ = constant
$[CaO]$ = constant

$$K_c = [CO_2] = K_c' \times \frac{[CaCO_3]}{[CaO]}$$

$$K_p = P_{CO_2}$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

$$CaCO_3\ (s) \rightleftharpoons CaO\ (s) + CO_2\ (g)$$



$$P_{CO_2} = K_p$$

P_{CO_2} does not depend on the amount of $CaCO_3$ or CaO

Consider the following equilibrium at 295 K:

$$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$$

The partial pressure of each gas is 0.265 atm. Calculate K_p and K_c for the reaction?

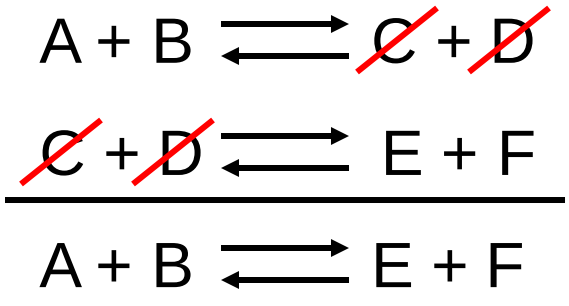
$$K_p = P_{NH_3} P_{H_2S} = 0.265 \times 0.265 = 0.0702$$

$$K_p = K_c(RT)^{\Delta n}$$

$$K_c = K_p(RT)^{-\Delta n}$$

$$\Delta n = 2 - 0 = 2 \qquad T = 295\ K$$

$$K_c = 0.0702 \times (0.0821 \times 295)^{-2} = 1.20 \times 10^{-4}$$



K_c'

K_c''

K_c

$$K_c' = \frac{[C][D]}{[A][B]} \qquad K_c'' = \frac{[E][F]}{[C][D]}$$

$$K_c = \frac{[E][F]}{[A][B]}$$

$$K_c = K_c' \times K_c''$$

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$

$$K = \frac{[NO_2]^2}{[N_2O_4]} = 4.63 \times 10^{-3}$$

$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$

$$K' = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{K} = 216$$

When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

Writing Equilibrium Constant Expressions

1. The concentrations of the reacting species in the condensed phase are expressed in *M*. In the gaseous phase, the concentrations can be expressed in *M* or in atm.
2. The concentrations of pure solids, pure liquids and solvents do not appear in the equilibrium constant expressions.
3. The equilibrium constant is a dimensionless quantity.
4. In quoting a value for the equilibrium constant, you must specify the balanced equation and the temperature.
5. If a reaction can be expressed as a sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

Chemical Kinetics and Chemical Equilibrium

$$A + 2B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} AB_2$$

$$\text{rate}_f = k_f [A][B]^2$$

$$\text{rate}_r = k_r [AB_2]$$

Equilibrium

$$\text{rate}_f = \text{rate}_r$$

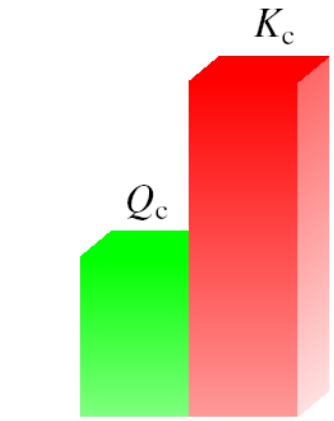
$$k_f [A][B]^2 = k_r [AB_2]$$

$$\frac{k_f}{k_r} = K_c = \frac{[AB_2]}{[A][B]^2}$$

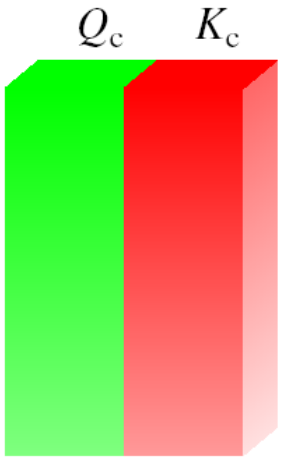
The ***reaction quotient (Q_c)*** is calculated by substituting the initial concentrations of the reactants and products into the equilibrium constant (K_c) expression.

IF

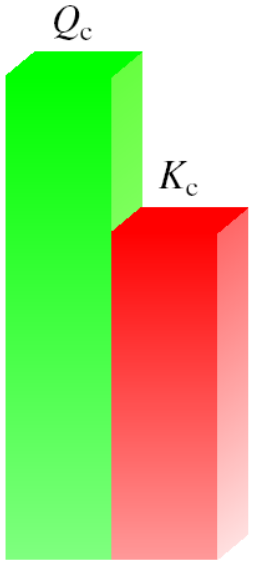
- $Q_c > K_c$ system proceeds from right to left to reach equilibrium
- $Q_c = K_c$ the system is at equilibrium
- $Q_c < K_c$ system proceeds from left to right to reach equilibrium



Reactants → Products



Equilibrium : no net change



Reactants ← Products

Calculating Equilibrium Concentrations

1. Express the equilibrium concentrations of all species in terms of the initial concentrations and a single unknown *x*, which represents the change in concentration.
2. Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for *x*.
3. Having solved for *x*, calculate the equilibrium concentrations of all species.

At 1280°C the equilibrium constant (K_c) for the reaction

$$Br_2\ (g) \rightleftharpoons 2Br\ (g)$$

Is 1.1 x 10^{-3}. If the initial concentrations are $[Br_2]$ = 0.063 *M* and [Br] = 0.012 *M*, calculate the concentrations of these species at equilibrium.

Let *x* be the change in concentration of Br_2

ICE

	$Br_2\ (g) \rightleftharpoons$	$2Br\ (g)$
Initial (*M*)	0.063	0.012
Change (*M*)	-*x*	+2*x*
Equilibrium (*M*)	0.063 - *x*	0.012 + 2*x*

$$K_c = \frac{[Br]^2}{[Br_2]} \qquad K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

Solve for *x*

$$K_c = \frac{(0.012 + 2x)^2}{0.063 - x} = 1.1 \times 10^{-3}$$

$$4x^2 + 0.048x + 0.000144 = 0.0000693 - 0.0011x$$

$$4x^2 + 0.0491x + 0.0000747 = 0$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = -0.0105$ $x = -0.00178$

$Br_2\ (g) \rightleftharpoons 2Br\ (g)$

	Br_2	$2Br$
Initial (M)	0.063	0.012
Change (M)	$-x$	$+2x$
Equilibrium (M)	$0.063 - x$	$0.012 + 2x$

At equilibrium, $[Br] = 0.012 + 2x = -0.009\ M$ or $0.00844\ M$

At equilibrium, $[Br_2] = 0.062 - x = 0.0648\ M$

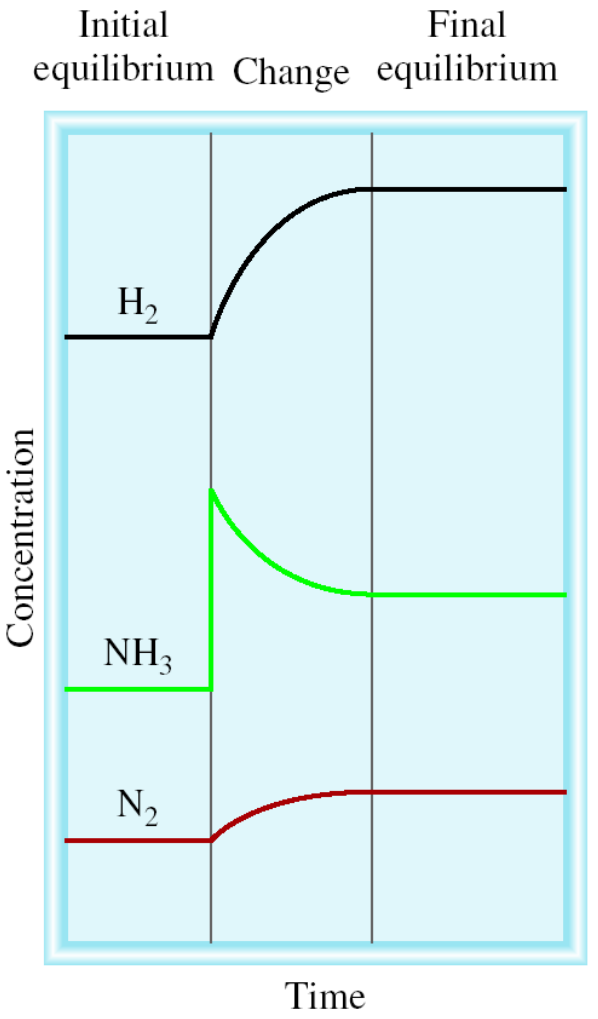
Le Châtelier's Principle

If an external stress is applied to a system at equilibrium, the system adjusts in such a way that the stress is partially offset as the system reaches a new equilibrium position.

- Changes in Concentration

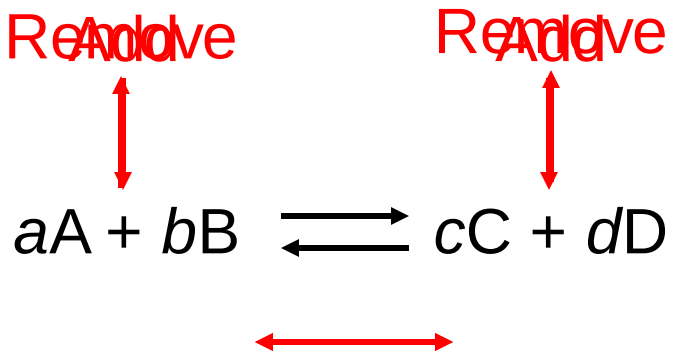
$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

Add NH_3 → Equilibrium shifts left to offset stress



Le Châtelier's Principle

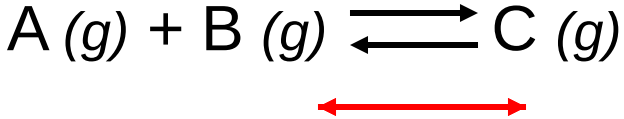
- Changes in Concentration continued



Change	**Shifts the Equilibrium**
Increase concentration of product(s)	left
Decrease concentration of product(s)	right
Increase concentration of reactant(s)	right
Decrease concentration of reactant(s)	left

Le Châtelier's Principle

- Changes in Volume and Pressure



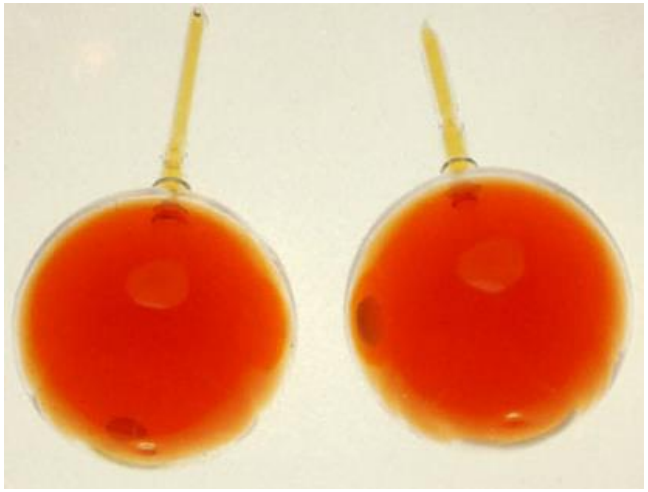
Change	**Shifts the Equilibrium**
Increase pressure	Side with fewest moles of gas
Decrease pressure	Side with most moles of gas
Increase volume	Side with most moles of gas
Decrease volume	Side with fewest moles of gas

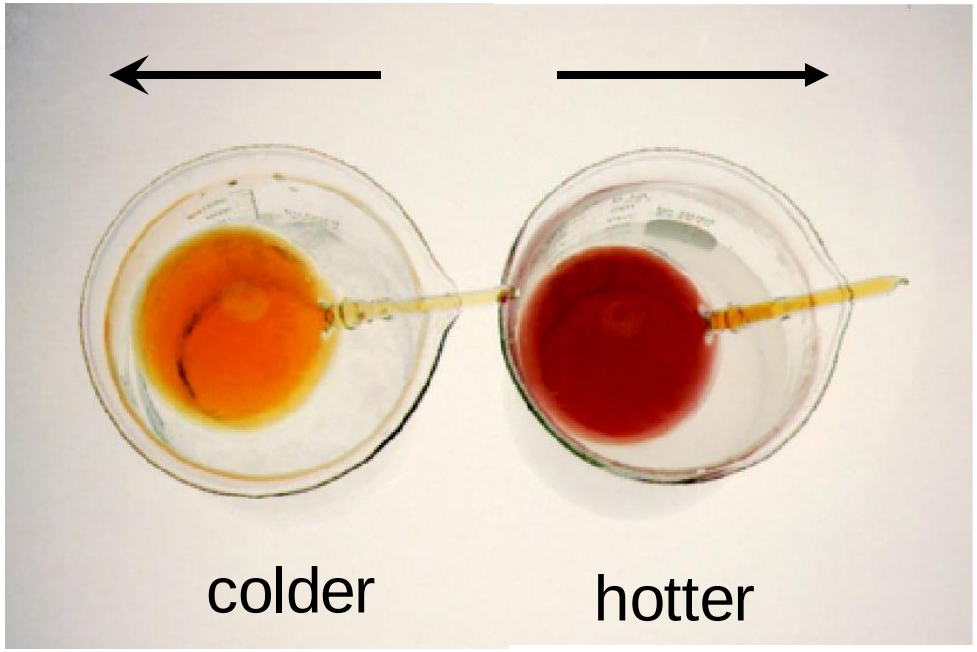
Le Châtelier's Principle

- Changes in Temperature

Change	**Exothermic Rx**	**Endothermic Rx**
Increase temperature	*K* decreases	*K* increases
Decrease temperature	*K* increases	*K* decreases

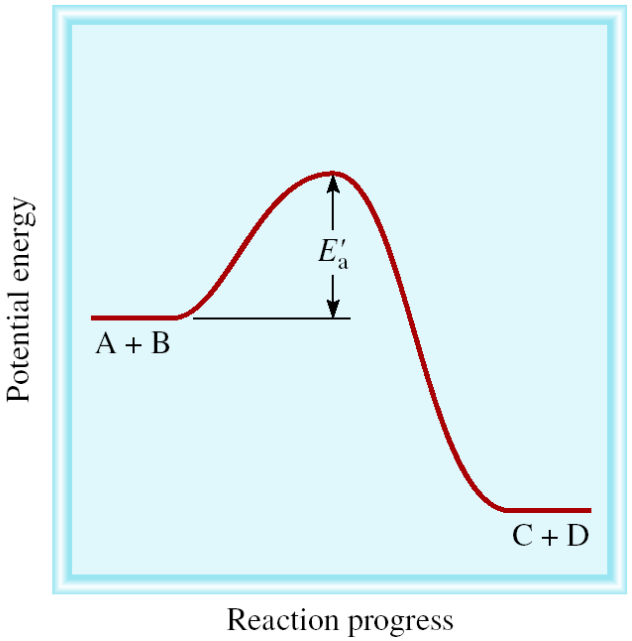
$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$ $\qquad \Delta H^\circ = 58.0\ \text{kJ/mol}$

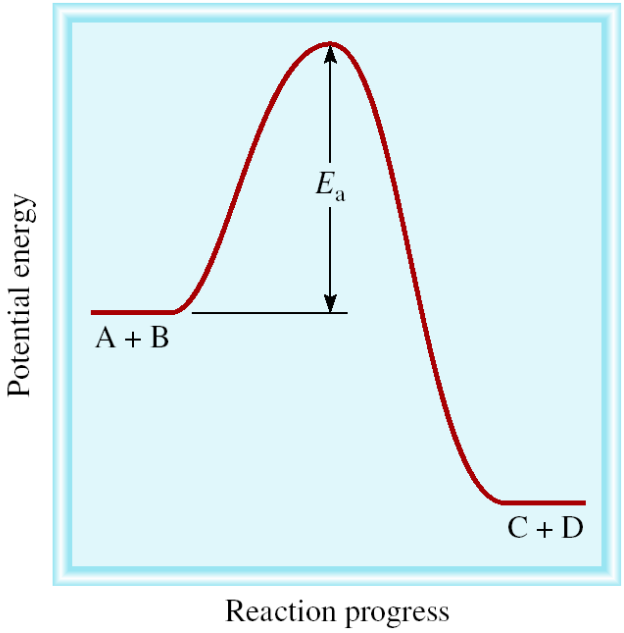




Le Châtelier's Principle

- Adding a Catalyst
  - does not change *K*
  - does not shift the position of an equilibrium system
  - system will reach equilibrium sooner





Catalyst lowers E_a for **both** forward and reverse reactions.

Catalyst does not change equilibrium constant or shift equilibrium.

Chemistry In Action

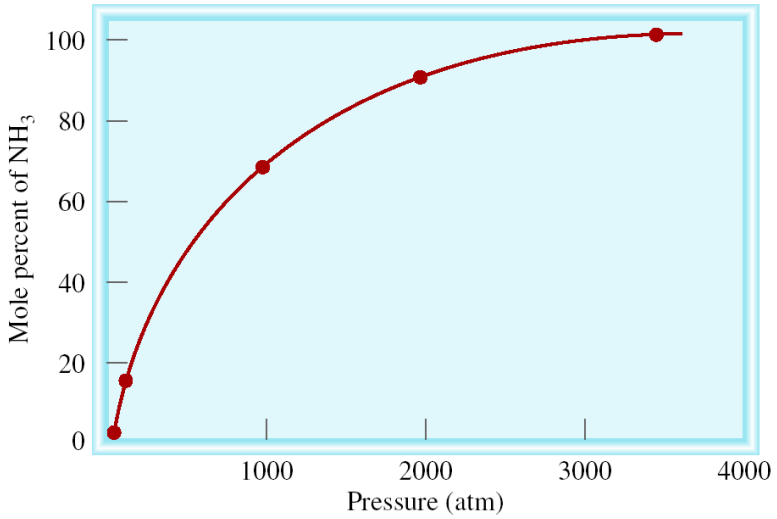
Life at High Altitudes and Hemoglobin Production

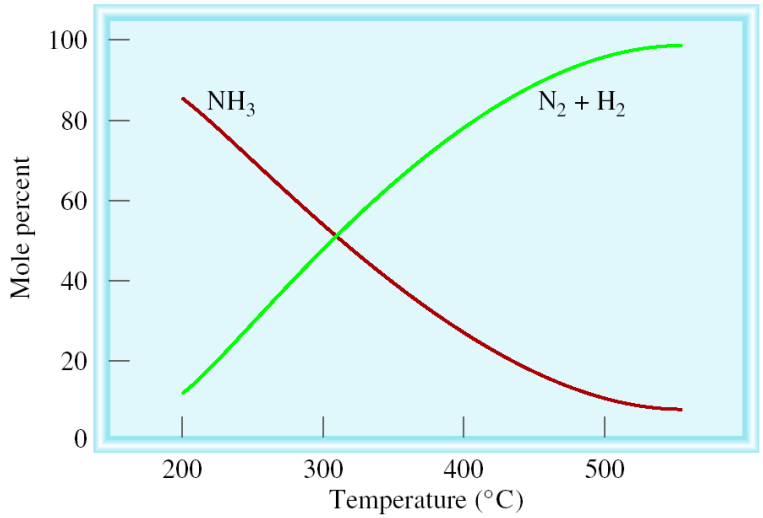
$$Hb\,(aq) + O_2\,(aq) \rightleftharpoons HbO_2\,(aq)$$

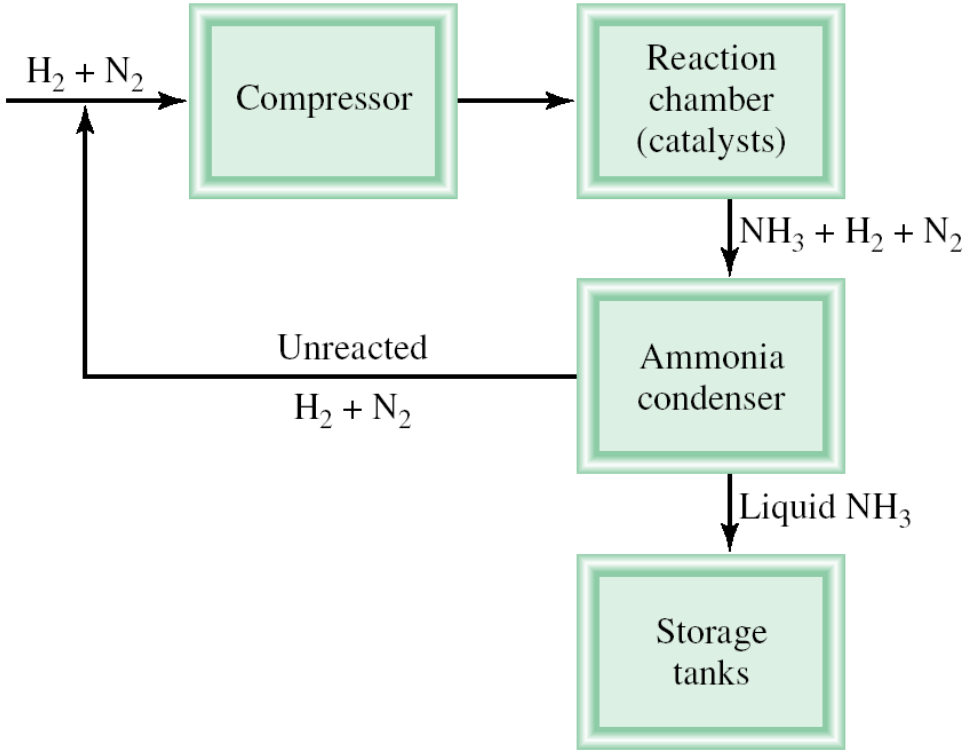
$$K_c = \frac{[HbO_2]}{[Hb][O_2]}$$

Chemistry In Action: The Haber Process

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g) \quad \Delta H^0 = -92.6\ \text{kJ/mol}$$



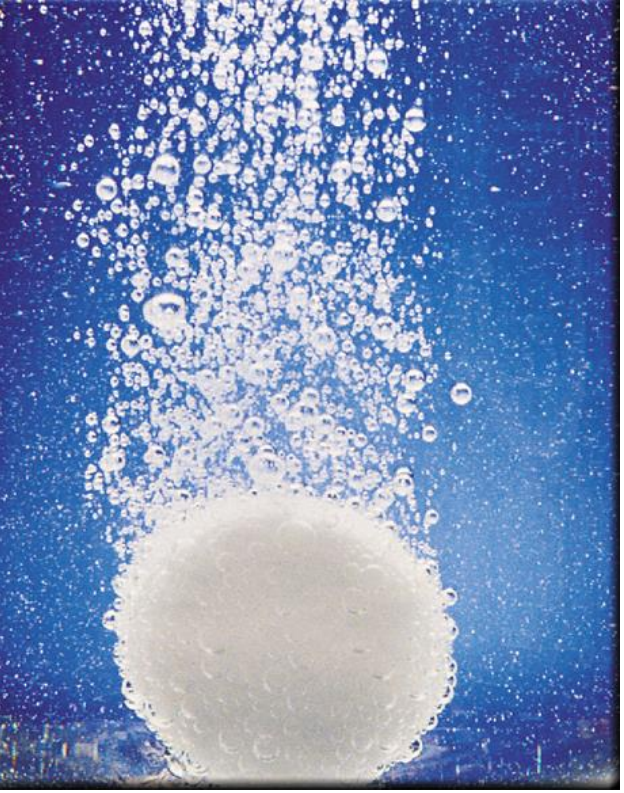




Le Châtelier's Principle - Summary

Change	**Shift Equilibrium**	**Change Equilibrium Constant**
Concentration	yes	no
Pressure	yes*	no
Volume	yes*	no
Temperature	yes	yes
Catalyst	no	no

*Dependent on relative moles of gaseous reactants and products



Acids and Bases

Chapter 15

Acids

Have a sour taste. Vinegar owes its taste to acetic acid. Citrus fruits contain citric acid.

React with certain metals to produce hydrogen gas.

React with carbonates and bicarbonates to produce carbon dioxide gas

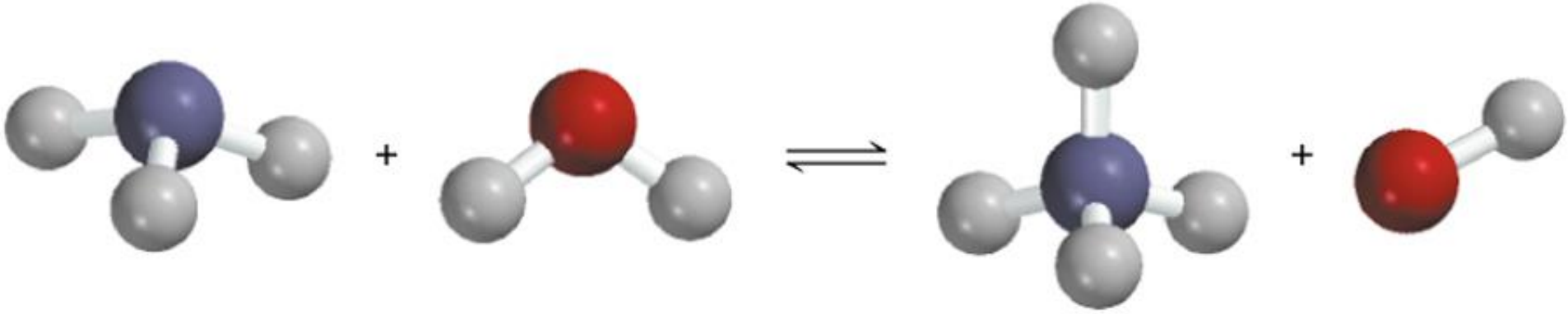
Bases

Have a bitter taste.

Feel slippery. Many soaps contain bases.

A Brønsted acid is a proton donor

A Brønsted base is a proton acceptor



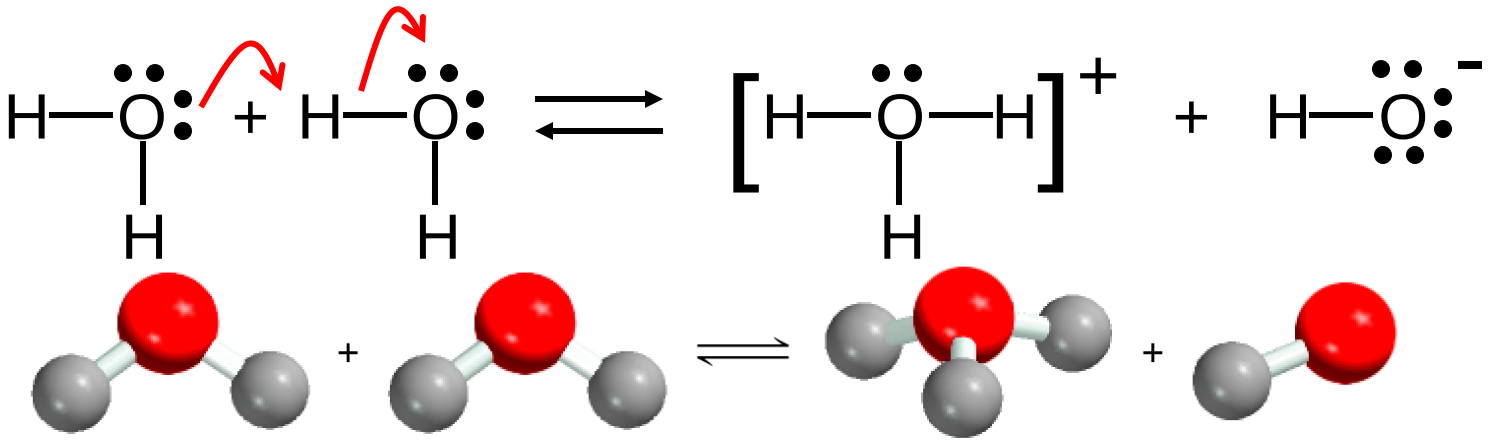
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base	acid		acid	base
base	acid		conjugate acid	conjugate base

Acid-Base Properties of Water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

autoionization of water



base

conjugate acid

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

acid

conjugate base

The Ion Product of Water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq) \qquad K_c = \frac{[H^+][OH^-]}{[H_2O]} \qquad [H_2O] = \text{constant}$$

$$K_c[H_2O] = K_w = [H^+][OH^-]$$

The ***ion-product constant*** (***K_w***) is the product of the molar concentrations of H^+ and OH^- ions **at a particular temperature.**

At 25^0C

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$

	Solution Is
$[H^+] = [OH^-]$	neutral
$[H^+] > [OH^-]$	acidic
$[H^+] < [OH^-]$	basic

What is the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.3 *M*?

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

$$[H^+] = 1.3\ M$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{1.3} = 7.7 \times 10^{-15}\ M$$

pH – A Measure of Acidity

$$pH = -\log [H^+]$$

Solution Is		**At 25^0C**	
neutral	$[H^+] = [OH^-]$	$[H^+] = 1 \times 10^{-7}$	pH = 7
acidic	$[H^+] > [OH^-]$	$[H^+] > 1 \times 10^{-7}$	pH < 7
basic	$[H^+] < [OH^-]$	$[H^+] < 1 \times 10^{-7}$	pH > 7

pH ↑ $[H^+]$ ↓

TABLE 15.1

The pHs of Some Common Fluids

Sample	pH Value
Gastric juice in the stomach	1.0–2.0
Lemon juice	2.4
Vinegar	3.0
Grapefruit juice	3.2
Orange juice	3.5
Urine	4.8–7.5
Water exposed to air*	5.5
Saliva	6.4–6.9
Milk	6.5
Pure water	7.0
Blood	7.35–7.45
Tears	7.4
Milk of magnesia	10.6
Household ammonia	11.5

*Water exposed to air for a long period of time absorbs atmospheric CO_2 to form carbonic acid, H_2CO_3.

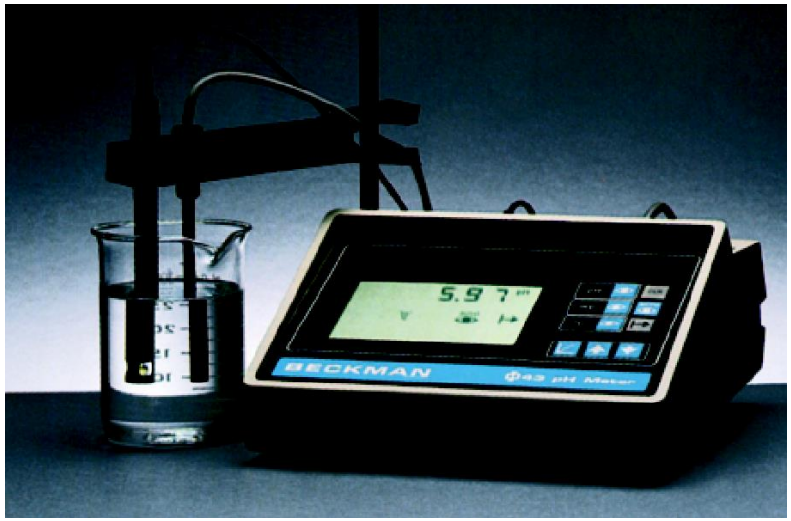
Other important relationships

$$pOH = -\log [OH^-]$$

$$[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$$

$$-\log [H^+] - \log [OH^-] = 14.00$$

$$pH + pOH = 14.00$$



pH Meter

The pH of rainwater collected in a certain region of the northeastern United States on a particular day was 4.82. What is the H^+ ion concentration of the rainwater?

$$pH = -\log [H^+]$$

$$[H^+] = 10^{-pH} = 10^{-4.82} = 1.5 \times 10^{-5}\ M$$

The OH^- ion concentration of a blood sample is $2.5 \times 10^{-7}\ M$. What is the pH of the blood?

$$pH + pOH = 14.00$$

$$pOH = -\log [OH^-] = -\log (2.5 \times 10^{-7}) = 6.60$$

$$pH = 14.00 - pOH = 14.00 - 6.60 = 7.40$$

Strong Electrolyte – 100% dissociation

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Weak Electrolyte – not completely dissociated

$$CH_3COOH \rightleftharpoons CH_3COO^-\ (aq) + H^+\ (aq)$$

Strong Acids are strong electrolytes

$$HCl\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + Cl^-\ (aq)$$

$$HNO_3\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

$$HClO_4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + ClO_4^-\ (aq)$$

$$H_2SO_4\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + HSO_4^-\ (aq)$$

Weak Acids are weak electrolytes

$HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + F^-\ (aq)$

$HNO_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + NO_2^-\ (aq)$

$HSO_4^-\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + SO_4^{2-}\ (aq)$

$H_2O\ (l) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + OH^-\ (aq)$

Strong Bases are strong electrolytes

$NaOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + OH^-\ (aq)$

$KOH\ (s) \xrightarrow{H_2O} K^+\ (aq) + OH^-\ (aq)$

$Ba(OH)_2\ (s) \xrightarrow{H_2O} Ba^{2+}\ (aq) + 2OH^-\ (aq)$

Weak Bases are weak electrolytes

F^- (*aq*) + H_2O (*l*) $\rightleftharpoons$ OH^- (*aq*) + HF (*aq*)

NO_2^- (*aq*) + H_2O (*l*) $\rightleftharpoons$ OH^- (*aq*) + HNO_2 (*aq*)

Conjugate acid-base pairs:

- The conjugate base of a strong acid has no measurable strength.
- H_3O^+ is the strongest acid that can exist in aqueous solution.
- The OH^- ion is the strongest base that can exist in aqeous solution.

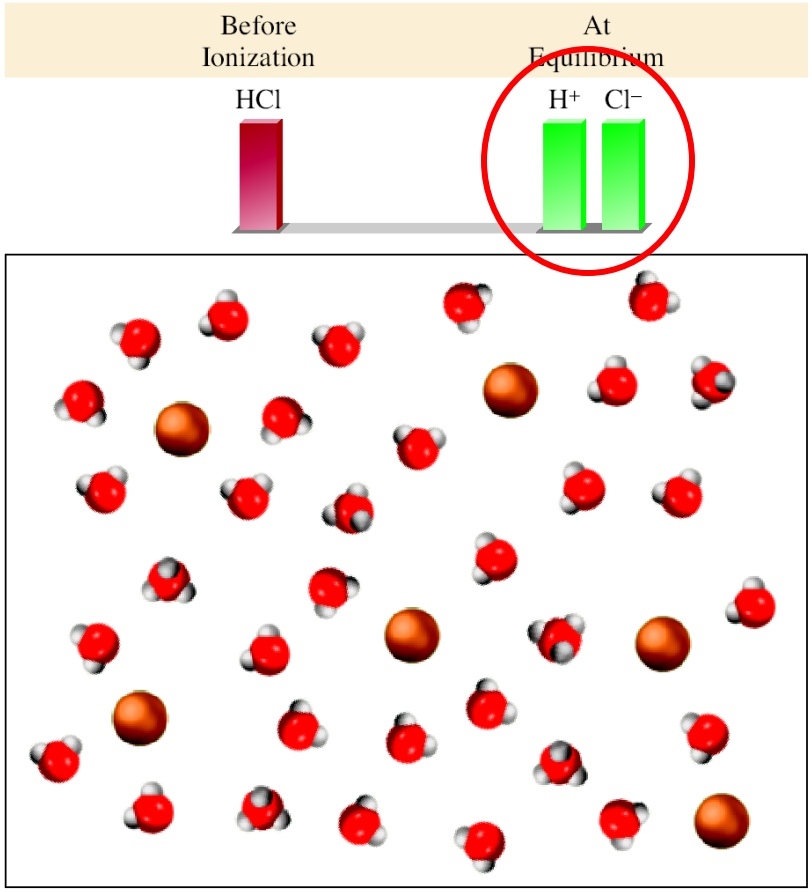
TABLE 15.2 Relative Strengths of Conjugate Acid-Base Pairs

Acid strength increases ↑

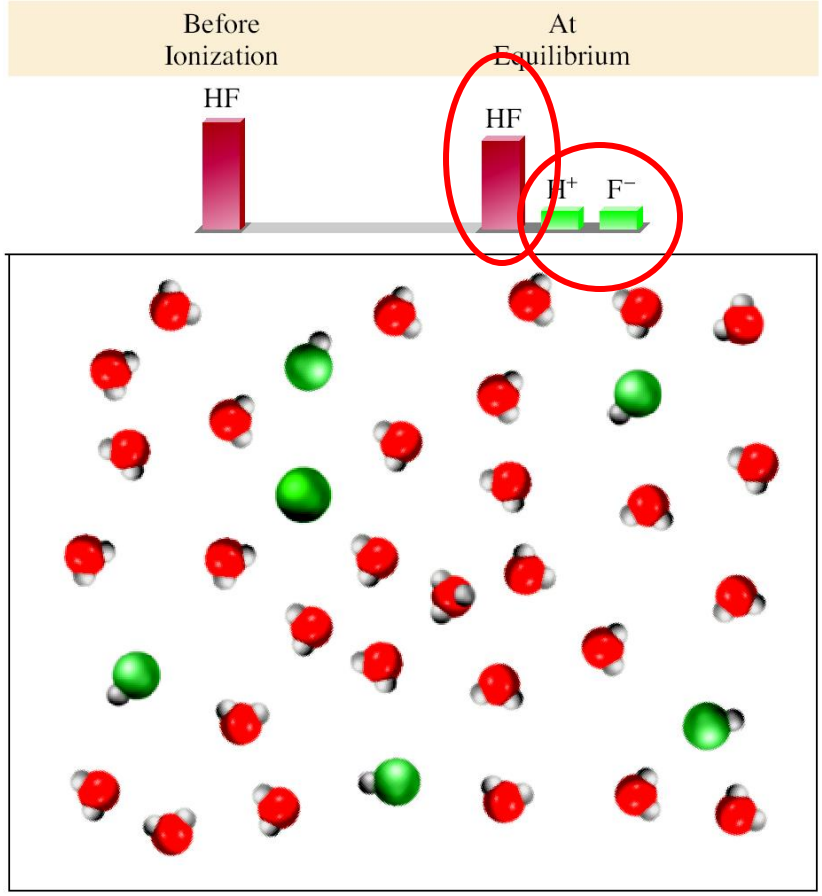
	Acid	Conjugate Base
Strong acids	$HClO_4$ (perchloric acid)	ClO_4^- (perchlorate ion)
	HI (hydroiodic acid)	I^- (iodide ion)
	HBr (hydrobromic acid)	Br^- (bromide ion)
	HCl (hydrochloric acid)	Cl^- (chloride ion)
	H_2SO_4 (sulfuric acid)	HSO_4^- (hydrogen sulfate ion)
	HNO_3 (nitric acid)	NO_3^- (nitrate ion)
	H_3O^+ (hydronium ion)	H_2O (water)
Weak acids	HSO_4^- (hydrogen sulfate ion)	SO_4^{2-} (sulfate ion)
	HF (hydrofluoric acid)	F^- (fluoride ion)
	HNO_2 (nitrous acid)	NO_2^- (nitrite ion)
	HCOOH (formic acid)	$HCOO^-$ (formate ion)
	CH_3COOH (acetic acid)	CH_3COO^- (acetate ion)
	NH_4^+ (ammonium ion)	NH_3 (ammonia)
	HCN (hydrocyanic acid)	CN^- (cyanide ion)
	H_2O (water)	OH^- (hydroxide ion)
	NH_3 (ammonia)	NH_2^- (amide ion)

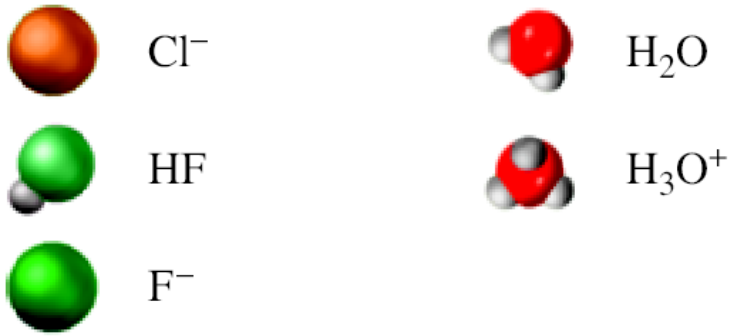
Base strength increases ↓

Strong Acid (HCl)



Weak Acid (HF)





What is the pH of a 2 x 10^{-3} *M* HNO_3 solution?

HNO_3 is a strong acid – 100% dissociation.

Start	0.002 *M*	0.0 *M*	0.0 *M*

$$HNO_3\ (aq) + H_2O\ (l) \longrightarrow H_3O^+\ (aq) + NO_3^-\ (aq)$$

End	0.0 *M*	0.002 *M*	0.002 *M*

$$pH = -\log [H^+] = -\log [H_3O^+] = -\log(0.002) = 2.7$$

What is the pH of a 1.8 x 10^{-2} *M* $Ba(OH)_2$ solution?

$Ba(OH)_2$ is a strong base – 100% dissociation.

Start	0.018 *M*	0.0 *M*	0.0 *M*

$$Ba(OH)_2\ (s) \longrightarrow Ba^{2+}\ (aq) + 2OH^-\ (aq)$$

End	0.0 *M*	0.018 *M*	0.036 *M*

$$pH = 14.00 - pOH = 14.00 + \log(0.036) = 12.6$$

Weak Acids (HA) and Acid Ionization Constants

$$HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

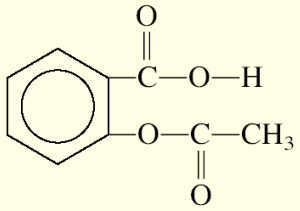
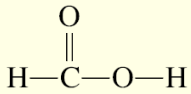
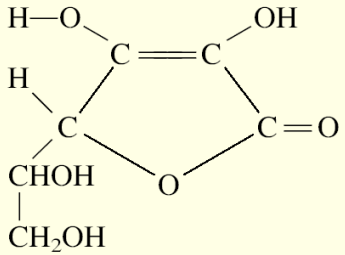
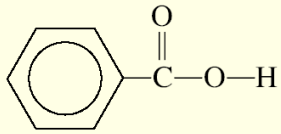
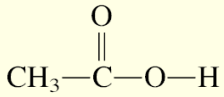
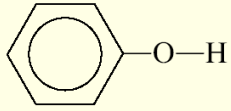
$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq)$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

K_a is the ***acid ionization constant***

K_a ↑ weak acid strength ↑

TABLE 15.3 Ionization Constants of Some Weak Acids and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b†
Hydrofluoric acid	HF	H—F	7.1×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	O=N—O—H	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
Acetylsalicylic acid (aspirin)	$C_9H_8O_4$		3.0×10^{-4}	$C_9H_7O_4^-$	3.3×10^{-11}
Formic acid	HCOOH		1.7×10^{-4}	$HCOO^-$	5.9×10^{-11}
Ascorbic acid*	$C_6H_8O_6$		8.0×10^{-5}	$C_6H_7O_6^-$	1.3×10^{-10}
Benzoic acid	C_6H_5COOH		6.5×10^{-5}	$C_6H_5COO^-$	1.5×10^{-10}
Acetic acid	CH_3COOH		1.8×10^{-5}	CH_3COO^-	5.6×10^{-10}
Hydrocyanic acid	HCN	H—C≡N	4.9×10^{-10}	CN^-	2.0×10^{-5}
Phenol	C_6H_5OH		1.3×10^{-10}	$C_6H_5O^-$	7.7×10^{-5}

*For ascorbic acid it is the upper left hydroxyl group that is associated with this ionization constant.
†The base ionization constant K_b is discussed in Section 15.6.

What is the pH of a 0.5 *M* HF solution (at 25^{0}C)?

$$HF\,(aq) \rightleftharpoons H^+\,(aq) + F^-\,(aq) \qquad K_a = \frac{[H^+][F^-]}{[HF]} = 7.1 \times 10^{-4}$$

$$HF\,(aq) \rightleftharpoons H^+\,(aq) + F^-\,(aq)$$

Initial (*M*)	0.50	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.50 - x$	x	x

$$K_a = \frac{x^2}{0.50 - x} = 7.1 \times 10^{-4} \qquad K_a << 1 \qquad 0.50 - x \approx 0.50$$

$$K_a \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4} \qquad x^2 = 3.55 \times 10^{-4} \qquad x = 0.019\ M$$

$[H^+] = [F^-] = 0.019\ M$ $\qquad$ $pH = -\log [H^+] = 1.72$

$[HF] = 0.50 - x = 0.48\ M$

When can I use the approximation?

$$K_a << 1 \quad 0.50 - x \approx 0.50$$

When x is less than 5% of the value from which it is subtracted.

$x = 0.019$ $\quad \frac{0.019\ M}{0.50\ M} \times 100\% = 3.8\%$ Less than 5%

Approximation ok.

What is the pH of a 0.05 *M* HF solution (at 25^0C)?

$$K_a \approx \frac{x^2}{0.05} = 7.1 \times 10^{-4} \quad x = 0.006\ M$$

$\frac{0.006\ M}{0.05\ M} \times 100\% = 12\%$ More than 5%

Approximation **not** ok.

Must solve for x exactly using quadratic equation or method of successive approximations.

Solving **weak acid** ionization problems:

1. Identify the major species that can affect the pH.
   - In most cases, you can ignore the autoionization of water.
   - Ignore $[OH^-]$ because it is determined by $[H^+]$.
2. Use ICE to express the equilibrium concentrations in terms of single unknown *x*.
3. Write K_a in terms of equilibrium concentrations. Solve for *x* by the approximation method. If approximation is not valid, solve for *x* exactly.
4. Calculate concentrations of all species and/or pH of the solution.

What is the pH of a 0.122 *M* monoprotic acid whose K_a is 5.7 x 10^{-4}?

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

	HA	H^+	A^-
Initial (*M*)	0.122	0.00	0.00
Change (*M*)	-*x*	+*x*	+*x*
Equilibrium (*M*)	0.122 - *x*	*x*	*x*

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4} \qquad K_a << 1 \qquad 0.122 - x \approx 0.122$$

$$K_a \approx \frac{x^2}{0.122} = 5.7 \times 10^{-4} \qquad x^2 = 6.95 \times 10^{-5} \qquad x = 0.0083\ M$$

$$\frac{0.0083\ M}{0.122\ M} \times 100\% = 6.8\%$$

More than 5%

Approximation **not** ok.

$$K_a = \frac{x^2}{0.122 - x} = 5.7 \times 10^{-4} \qquad x^2 + 0.00057x - 6.95 \times 10^{-5} = 0$$

$$ax^2 + bx + c = 0 \qquad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = 0.0081 \qquad x = -0.0081$$

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$$

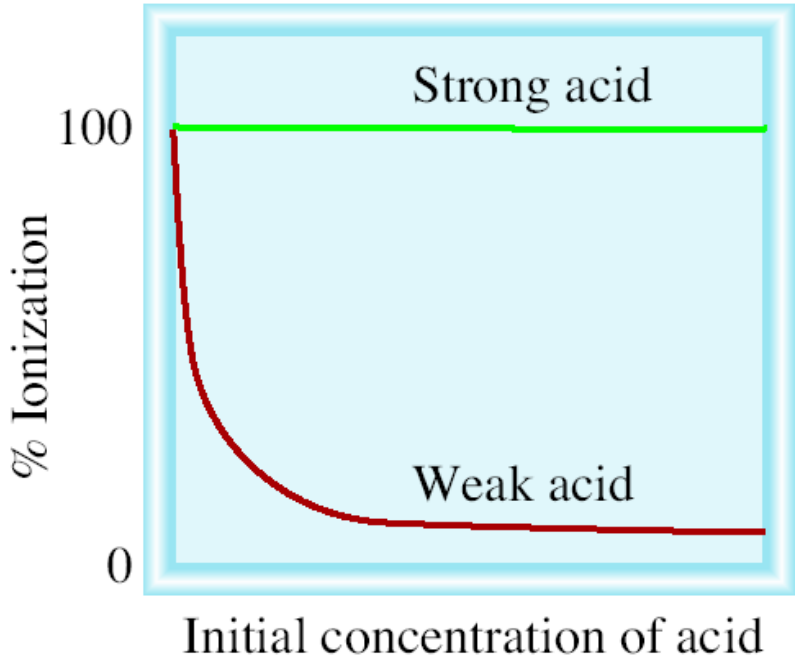
Initial (*M*)	0.122	0.00	0.00
Change (*M*)	-*x*	+*x*	+*x*
Equilibrium (*M*)	0.122 - *x*	*x*	*x*

$$[H^+] = x = 0.0081\ M \qquad pH = -\log[H^+] = 2.09$$

$$\textbf{\textit{percent ionization}} = \frac{\text{Ionized acid concentration at equilibrium}}{\text{Initial concentration of acid}} \times 100\%$$

For a monoprotic acid HA

$$\text{Percent ionization} = \frac{[H^+]}{[HA]_0} \times 100\% \qquad [HA]_0 = \text{initial concentration}$$



Weak Bases and Base Ionization Constants

$$NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

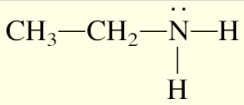
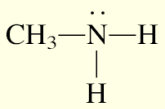
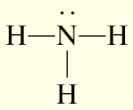
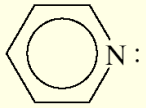
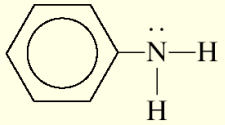
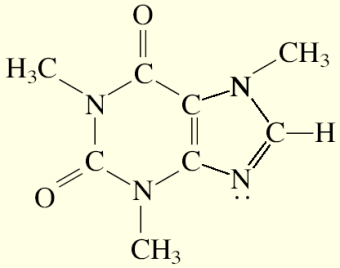
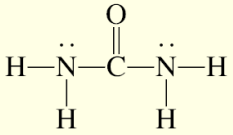
$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b is the ***base ionization constant***

K_b ↑ weak base strength ↑

Solve weak base problems like weak acids ***except*** solve for [OH-] instead of $[H^+]$.

TABLE 15.4 Ionization Constants of Some Weak Bases and Their Conjugate Acids at 25°C

Name of Base	Formula	Structure	K_b*	Conjugate Acid	K_a
Ethylamine	$C_2H_5NH_2$		5.6×10^{-4}	$C_2H_5\overset{+}{N}H_3$	1.8×10^{-11}
Methylamine	CH_3NH_2		4.4×10^{-4}	$CH_3\overset{+}{N}H_3$	2.3×10^{-11}
Ammonia	NH_3		1.8×10^{-5}	NH_4^+	5.6×10^{-10}
Pyridine	C_5H_5N		1.7×10^{-9}	$C_5H_5\overset{+}{N}H$	5.9×10^{-6}
Aniline	$C_6H_5NH_2$		3.8×10^{-10}	$C_6H_5\overset{+}{N}H_3$	2.6×10^{-5}
Caffeine	$C_8H_{10}N_4O_2$		5.3×10^{-14}	$C_8H_{11}\overset{+}{N}_4O_2$	0.19
Urea	$(NH_2)_2CO$		1.5×10^{-14}	$H_2NCO\overset{+}{N}H_3$	0.67

*The nitrogen atom with the lone pair accounts for each compound's basicity. In the case of urea, K_b can be associated with either nitrogen atom.

Ionization Constants of Conjugate Acid-Base Pairs

$$HA\,(aq) \rightleftharpoons H^+\,(aq) + A^-\,(aq) \qquad K_a$$

$$A^-\,(aq) + H_2O\,(l) \rightleftharpoons OH^-\,(aq) + HA\,(aq) \qquad K_b$$

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq) \qquad K_w$$

$$K_aK_b = K_w$$

Weak Acid and Its Conjugate Base

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Diprotic and Triprotic Acids

- May yield more than one hydrogen ion per molecule.
- Ionize in a stepwise manner; that is, they lose one proton at a time.
- An ionization constant expression can be written for each ionization stage.
- Consequently, two or more equilibrium constant expressions must often be used to calculate the concentrations of species in the acid solution.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \qquad K_{a_1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq) \qquad K_{a_2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$$

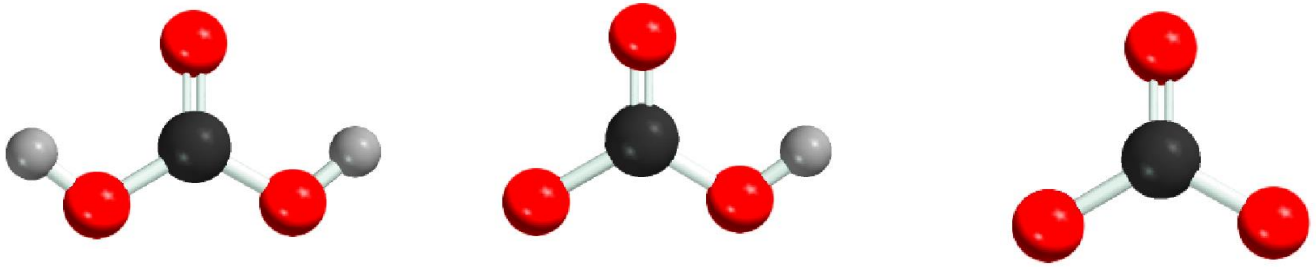
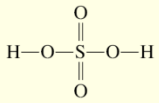
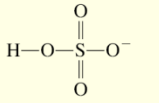
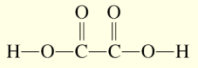
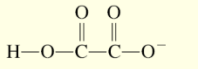
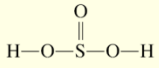
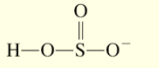
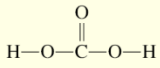
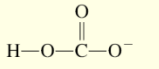
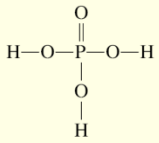
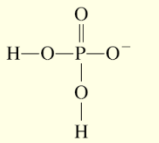
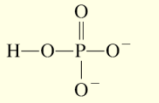


TABLE 15.5 Ionization Constants of Some Diprotic Acids and a Polyprotic Acid and Their Conjugate Bases at 25°C

Name of Acid	Formula	Structure	K_a	Conjugate Base	K_b
Sulfuric acid	H_2SO_4		very large	HSO_4^-	very small
Hydrogen sulfate ion	HSO_4^-		1.3×10^{-2}	SO_4^{2-}	7.7×10^{-13}
Oxalic acid	$H_2C_2O_4$		6.5×10^{-2}	$HC_2O_4^-$	1.5×10^{-13}
Hydrogen oxalate ion	$HC_2O_4^-$		6.1×10^{-5}	$C_2O_4^{2-}$	1.6×10^{-10}
Sulfurous acid*	H_2SO_3		1.3×10^{-2}	HSO_3^-	7.7×10^{-13}
Hydrogen sulfite ion	HSO_3^-		6.3×10^{-8}	SO_3^{2-}	1.6×10^{-7}
Carbonic acid	H_2CO_3		4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
Hydrogen carbonate ion	HCO_3^-		4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrosulfuric acid	H_2S	H—S—H	9.5×10^{-8}	HS^-	1.1×10^{-7}
Hydrogen sulfide ion†	HS^-	H—S^-	1×10^{-19}	S^{2-}	1×10^{5}
Phosphoric acid	H_3PO_4		7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
Dihydrogen phosphate ion	$H_2PO_4^-$		6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen phosphate ion	HPO_4^{2-}		4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}

*H_2SO_3 has never been isolated and exists in only minute concentration in aqueous solution of SO_2. The K_a value here refers to the process $SO_2(g) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$.

†The ionization constant of HS^- is very low and difficult to measure. The value listed here is only an estimate.

Molecular Structure and Acid Strength

$$H{-}X \longrightarrow H^+ + X^-$$

The stronger the bond

The weaker the acid

$$HF << HCl < HBr < HI$$

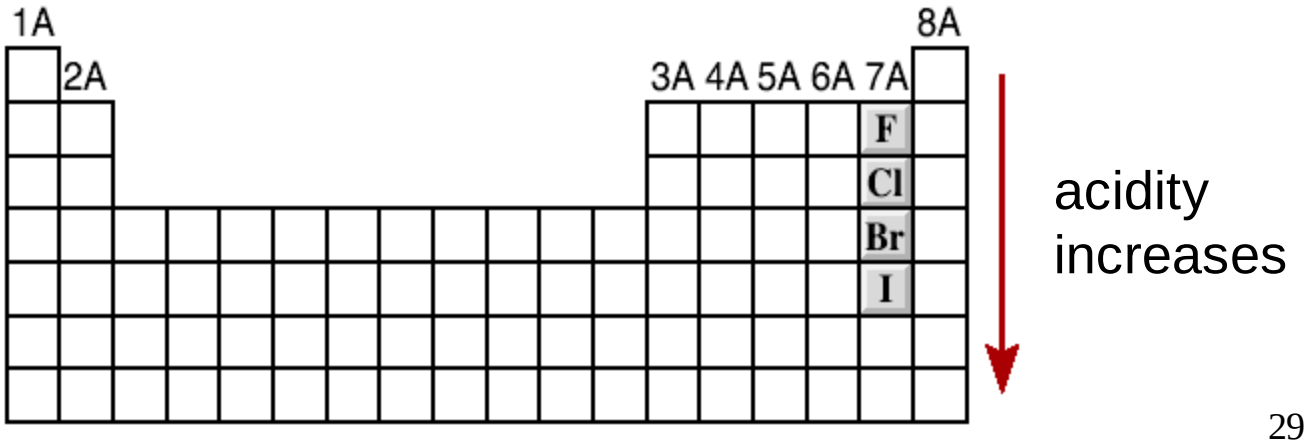
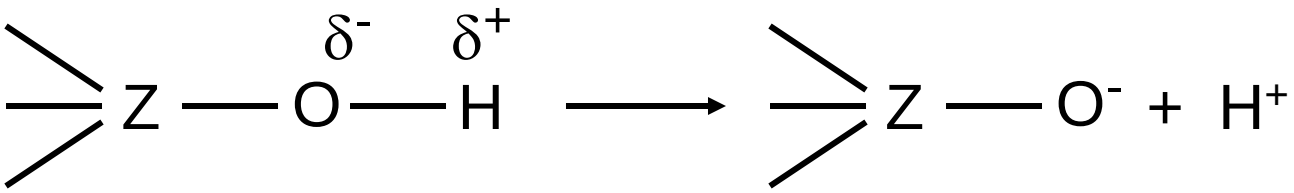


TABLE 15.6 Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids

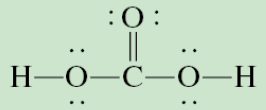
Bond	Bond Enthalpy (kJ/mol)	Acid Strength
H—F	568.2	weak
H—Cl	431.9	strong
H—Br	366.1	strong
H—I	298.3	strong

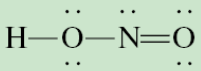
Molecular Structure and Oxoacid Strength

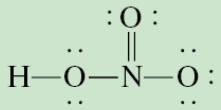


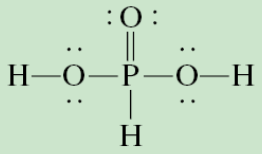
<u>The O-H bond will be more polar and easier to break if:</u>

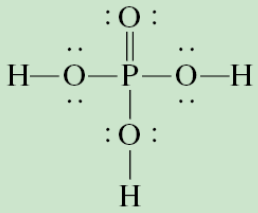
- Z is very electronegative or
- Z is in a high oxidation state

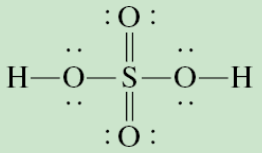

Carbonic acid


Nitrous acid


Nitric acid


Phosphorous acid

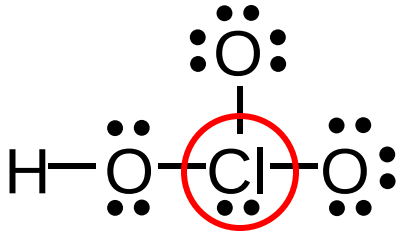

Phosphoric acid

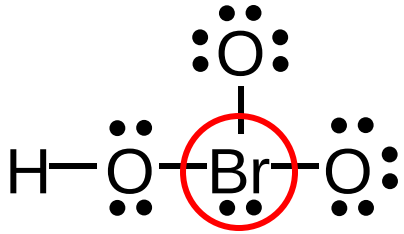

Sulfuric acid

Molecular Structure and Oxoacid Strength

1. Oxoacids having different central atoms (Z) that **are from the same group** and that have the **same oxidation number**.

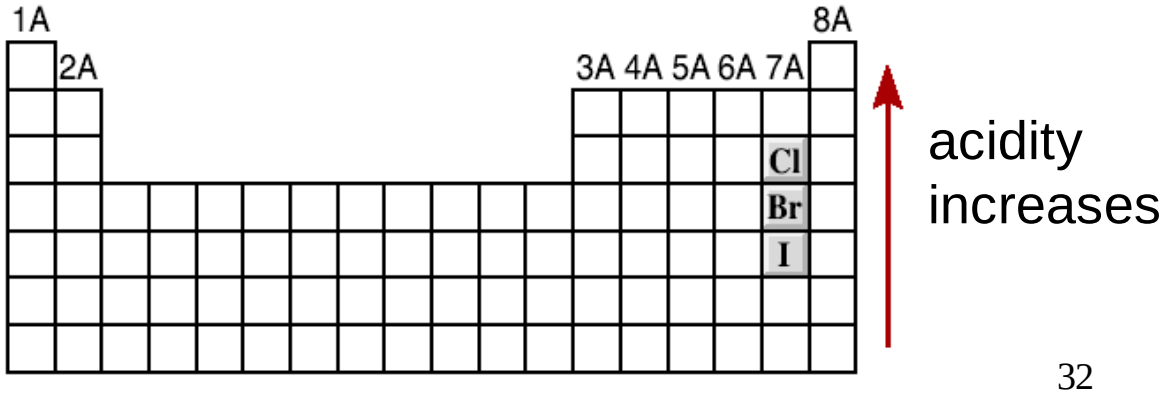
Acid strength increases with increasing electronegativity of Z





Cl is more electronegative than Br

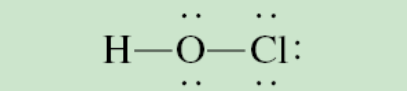
$HClO_3 > HBrO_3$



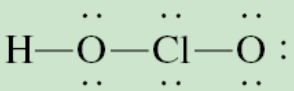
Molecular Structure and Acid Strength

2. Oxoacids having the same central atom (Z) but different numbers of attached groups.

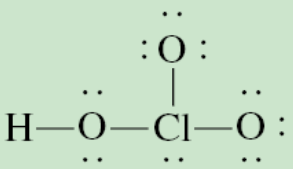
Acid strength increases as the oxidation number of Z increases.



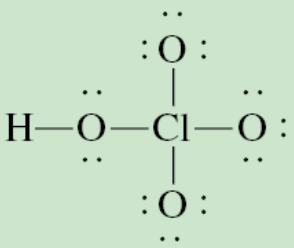
Hypochlorous acid (+1)



Chlorous acid (+3)



Chloric acid (+5)



Perchloric acid (+7)

$HClO_4 > HClO_3 > HClO_2 > HClO$

Acid-Base Properties of Salts

Neutral Solutions:

Salts containing an alkali metal or alkaline earth metal ion (except Be^{2+}) **and** the conjugate base of a **strong** acid (*e.g.* Cl^-, Br^-, and NO_3^-).

$$NaCl\ (s) \xrightarrow{H_2O} Na^+\ (aq) + Cl^-\ (aq)$$

Basic Solutions:

Salts derived from a strong base **and** a **weak** acid.

$$NaCH_3COOH\ (s) \xrightarrow{H_2O} Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

Acid-Base Properties of Salts

Acid Solutions:

Salts derived from a strong acid and a weak base.

$$NH_4Cl\ (s) \xrightarrow{H_2O} NH_4^+\ (aq) + Cl^-\ (aq)$$

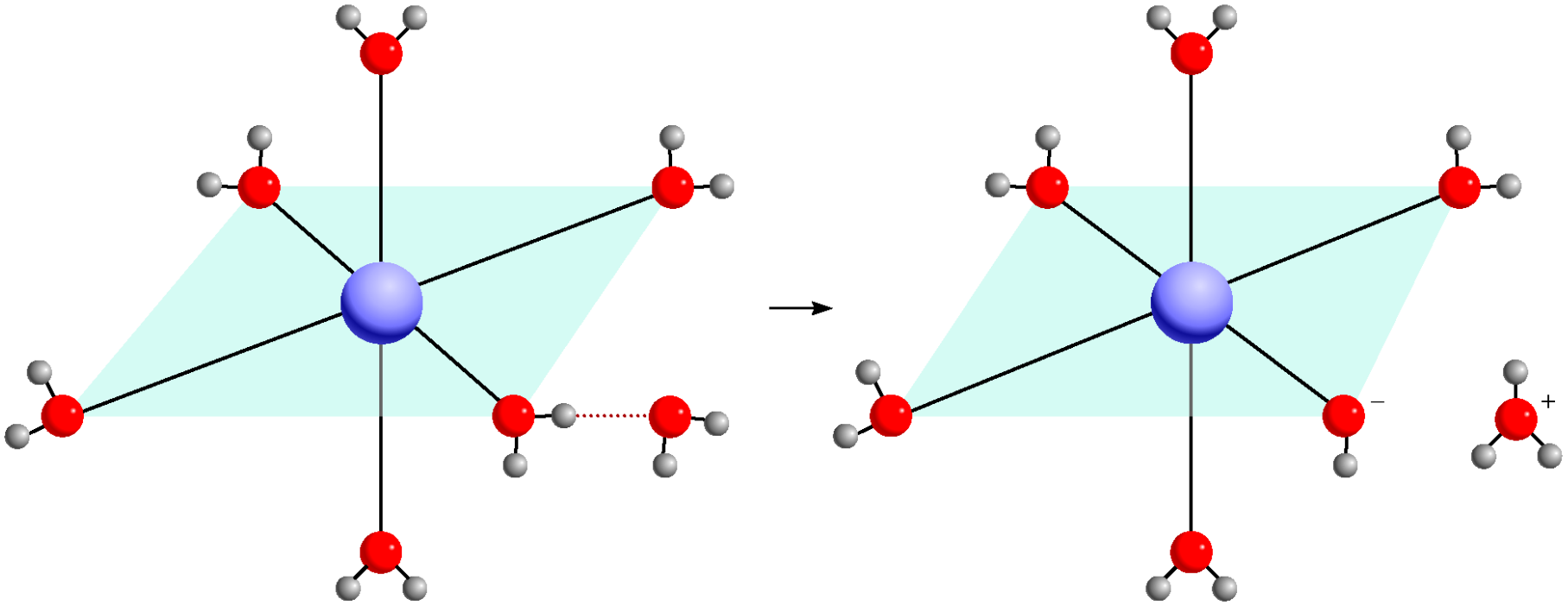
$$NH_4^+\ (aq) \rightleftharpoons NH_3\ (aq) + H^+\ (aq)$$

Salts with small, highly charged metal cations (*e.g.* Al^{3+}, Cr^{3+}, and Be^{2+}) and the conjugate base of a strong acid.

$$Al(H_2O)_6^{3+}(aq) \rightleftharpoons Al(OH)(H_2O)_5^{2+}(aq) + H^+\ (aq)$$

Acid Hydrolysis of Al^{3+}

$Al(H_2O)_6^{3+} + H_2O \longrightarrow Al(OH)(H_2O)_5^{2+} + H_3O^+$



Acid-Base Properties of Salts

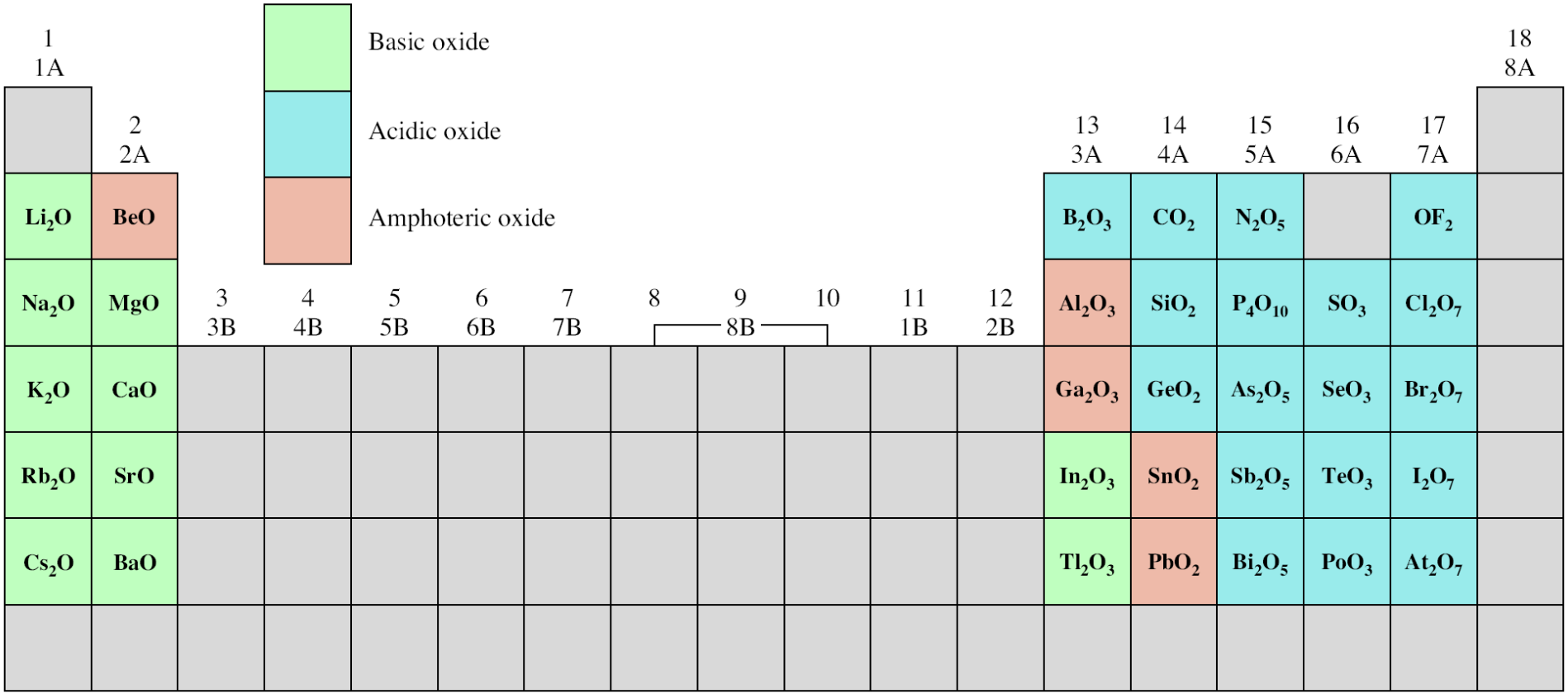
Solutions in which both the cation and the anion hydrolyze:

- K_b for the anion > K_a for the cation, solution will be basic
- K_b for the anion < K_a for the cation, solution will be acidic
- K_b for the anion ≈ K_a for the cation, solution will be neutral

TABLE 15.7 Acid-Base Properties of Salts

Type of Salt	Examples	Ions That Undergo Hydrolysis	pH of Solution
Cation from strong base; anion from strong acid	NaCl, KI, KNO_3, RbBr, $BaCl_2$	None	≈ 7
Cation from strong base; anion from weak acid	CH_3COONa, KNO_2	Anion	> 7
Cation from weak base; anion from strong acid	NH_4Cl, NH_4NO_3	Cation	< 7
Cation from weak base; anion from weak acid	NH_4NO_2, CH_3COONH_4, NH_4CN	Anion and cation	< 7 if $K_b < K_a$ ≈ 7 if $K_b \approx K_a$ > 7 if $K_b > K_a$
Small, highly charged cation; anion from strong acid	$AlCl_3$, $Fe(NO_3)_3$	Hydrated cation	< 7

Oxides of the Representative Elements In Their Highest Oxidation States



$$Na_2O\ (s) + H_2O\ (l) \longrightarrow 2NaOH\ (aq)$$

$$CO_2\ (g) + H_2O\ (l) \rightleftharpoons H_2CO_3\ (aq)$$

$$N_2O_5\ (g) + H_2O\ (l) \rightleftharpoons 2HNO_3\ (aq)$$

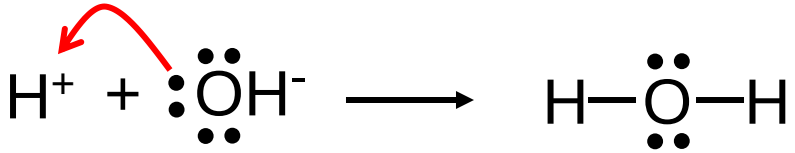
Definition of An Acid

Arrhenius acid is a substance that produces H^+ (H_3O^+) in water

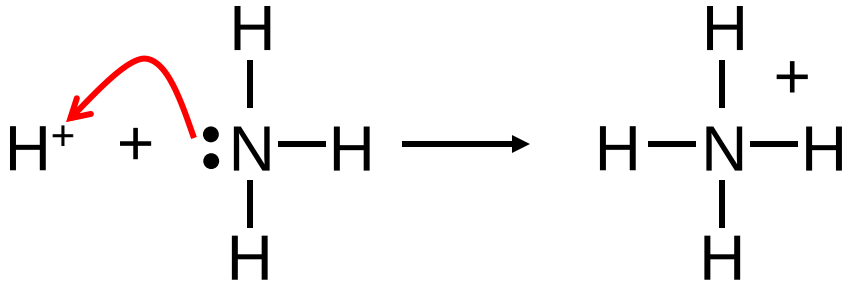
A ***Brønsted acid*** is a proton donor

A ***Lewis acid*** is a substance that can accept a pair of electrons

A ***Lewis base*** is a substance that can donate a pair of electrons

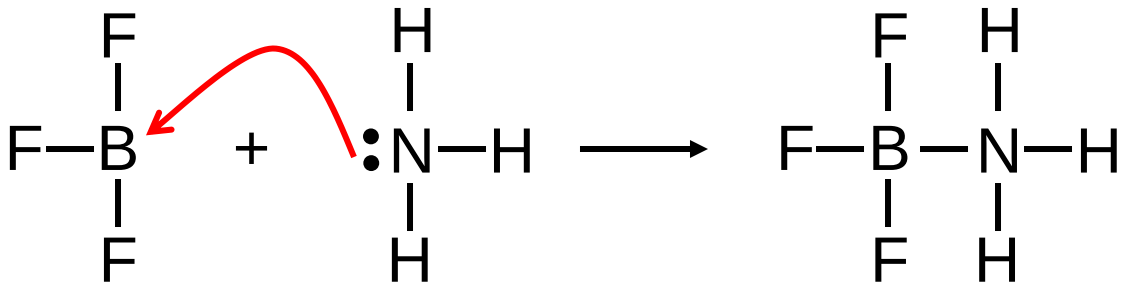


acid base



acid base

Lewis Acids and Bases



acid base

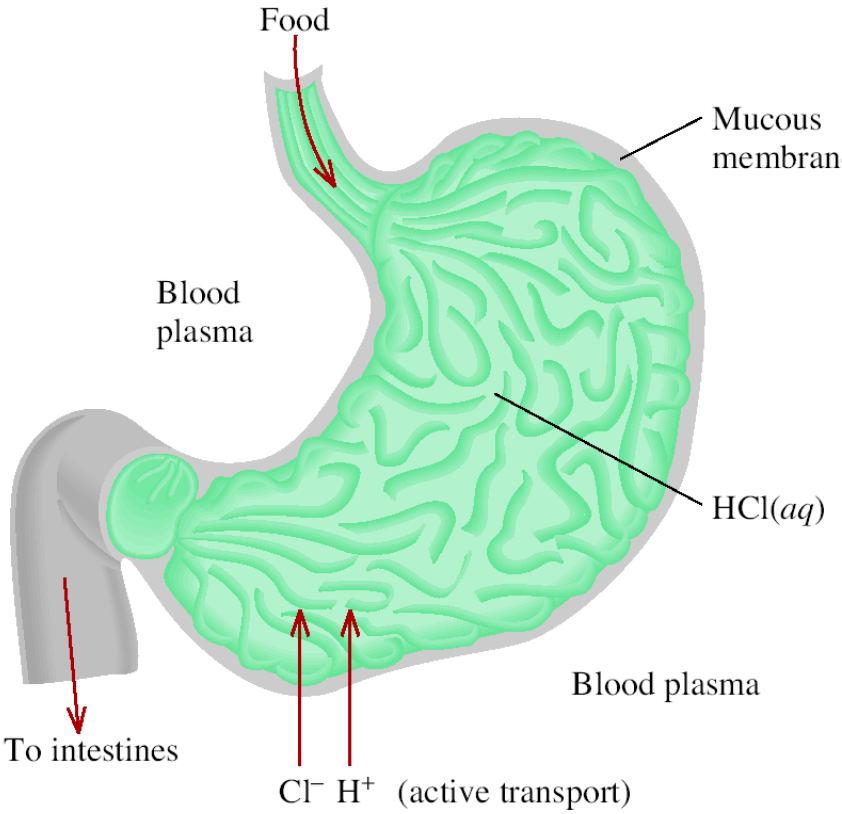
No protons donated or accepted!

Chemistry In Action: Antacids and the Stomach pH Balance

Some Common Commercial Antacid Preparations

Commercial Name	Active Ingredients
Alka-2	Calcium carbonate
Alka-Seltzer	Aspirin, sodium bicarbonate, citric acid
Bufferin	Aspirin, magnesium carbonate, aluminum glycinate
Buffered aspirin	Aspirin, magnesium carbonate, aluminum hydroxide-glycine
Milk of magnesia	Magnesium hydroxide
Rolaids	Dihydroxy aluminum sodium carbonate
Tums	Calcium carbonate

$$NaHCO_3\,(aq) + HCl\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l) + CO_2\,(g)$$



$$Mg(OH)_2\,(s) + 2HCl\,(aq) \longrightarrow MgCl_2\,(aq) + 2H_2O\,(l)$$