

Chapter 4

Reactions In Aqueous Solution

I) General Properties of Aqueous Solutions

Homogeneous mixture on a molecular level

- prop. same throughout
- separable by physical means
- variable composition

Has at least 2 components:

Solvent : component present in greatest amount
- same phase as soln.

Solute(s) : other component(s)

A) Dissolution

Process of dissolving

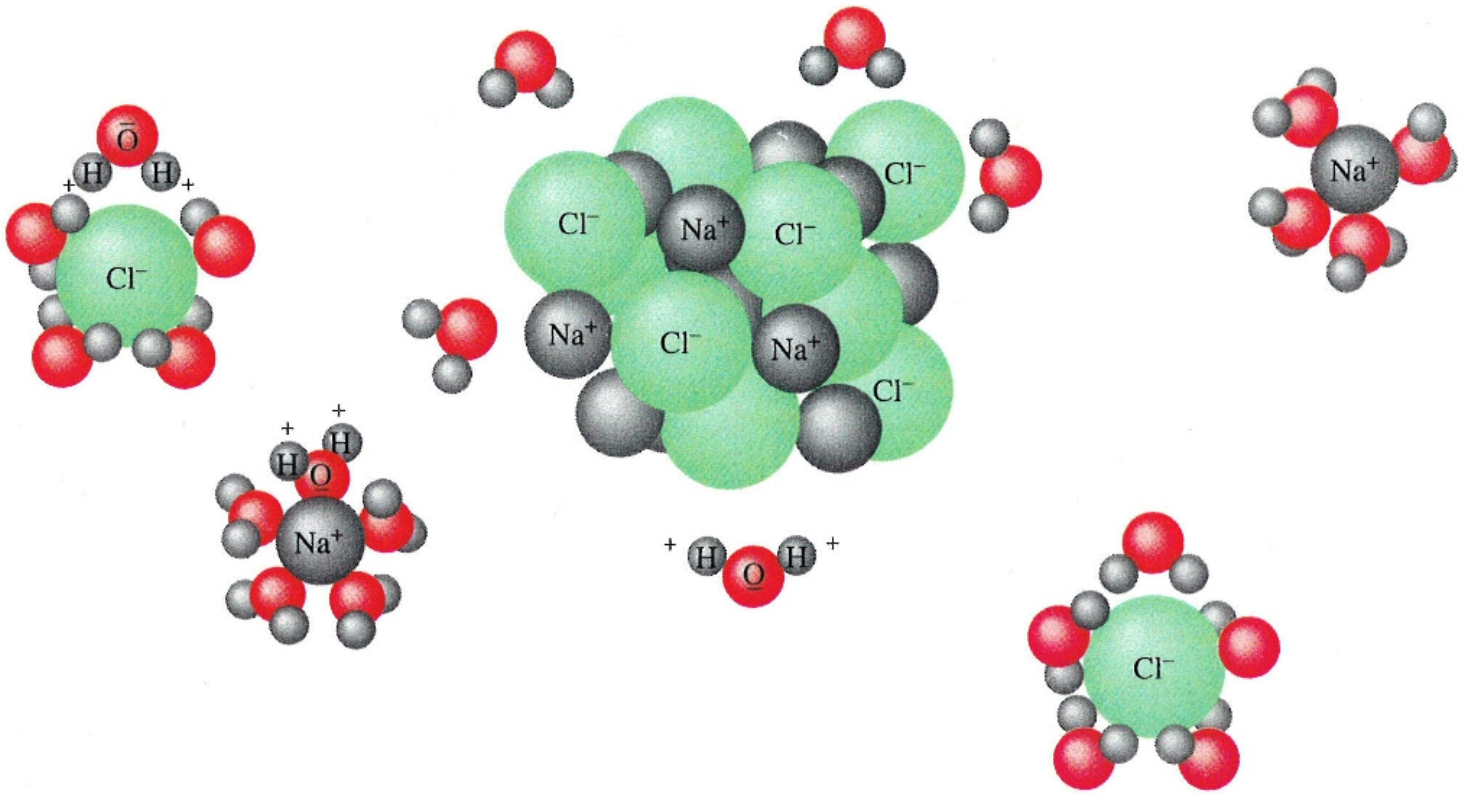
Solute is solvated by solvent

Solvent surrounds solute

Solvation

1) Aqueous

H₂O as solvent



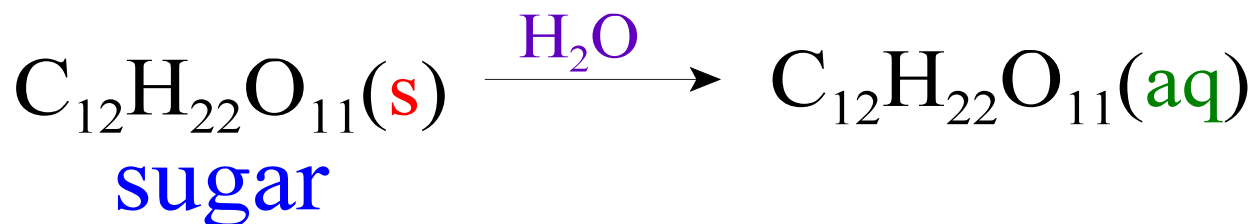
B) Nonelectrolytes

Substances which dissolve
in **molecular** form

- Present in **both solid & soln.**
as **molecules**

do **NOT conduct** electricity

Pure H₂O



C) Electrolytes

Substance whose aqueous soln. **conducts electricity**

- due to **ions** in the soln.

1) Dissociation

Ionic solutes dissolve as **ions**



Dissociation

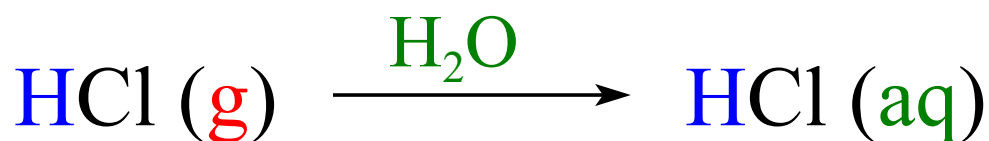
All **soluble ionic** substances **dissociate completely**

- **strong electrolytes**

2) Ionization

Some polar covalent molecules dissolve w. formation of ions.

1) Strong Acids



Ionization

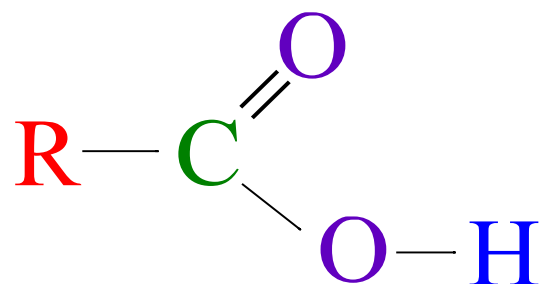
HCl - strong electrolyte
(completely ionizes)

2) Weak Electrolytes

Weak conductors

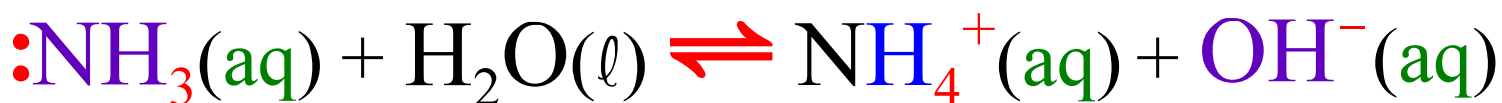
- Partial ionization

a) Weak Acids & Bases



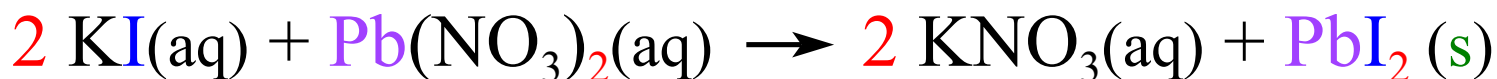
Chemical Equilibrium

- some molecular form remains



II) Precipitation Reactions

Precipitate \equiv insoluble solid formed



A) Solubility Rules

Which ionic cmpds. are soluble or insoluble in H_2O

1) Solubility

amt. of solid that dissolves in a given amt. of H_2O at a given temp.

NOTE: ALL ionic cmpds. of group IA & NH_4^+ are soluble

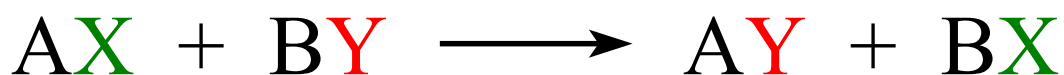
EMPIRICAL RULES FOR THE SOLUBILITY OF IONIC SOLIDS IN H₂O

COMPOUNDS CONTAINING	SOLUBILITY	IMPORTANT EXCEPTIONS
alkali metal (grp 1A) ammonium (NH ₄ ⁺)	Soluble	None
nitrates (NO ₃ ⁻), acetates (C ₂ H ₃ O ₂ ⁻), chlorates (ClO ₃ ⁻), perchlorates (ClO ₄ ⁻), permanganates (MnO ₄ ²⁻)	Soluble	None
chlorides (Cl ⁻), bromides (Br ⁻), iodides (I ⁻)	Soluble	Cmpds of Ag ⁺ , Hg ₂ ²⁺ , Pb ²⁺ , Hg ²⁺ iodide and Hg ²⁺ bromide
sulfates (SO ₄ ²⁻)	Soluble	Cmpds of Sr ²⁺ , Ba ²⁺ , Hg ₂ ²⁺ , Pb ²⁺
hydroxides (OH ⁻), oxides (O ²⁻), sulfides (S ²⁻)	Insoluble	Cmpds of alkali metals (grp 1A), NH ₄ ⁺ , Ca ²⁺ , Sr ²⁺ , Ba ²⁺
sulfites (SO ₃ ²⁻), carbonates (CO ₃ ²⁻), phosphates (PO ₄ ³⁻), chromates (CrO ₄ ²⁻)	Insoluble	Cmpds of alkali metals (grp 1A), NH ₄ ⁺

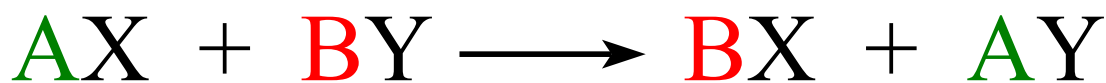
B) Exchange (Metathesis) Reactions

Also called, **Double-Replacement** Rx's

Cations & **Anions** **exchange** partners



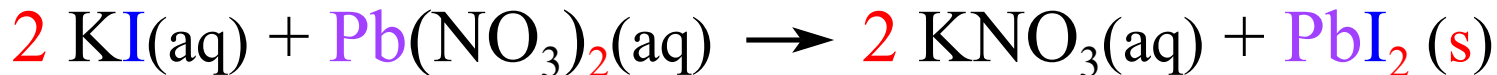
or



Must be a **driving force** for a rx. to occur (**remove ions**)

- formation of **precipitate**
- formation of **gas**
- formation of **weak** or **nonelectrolyte**

1) Precipitation Reactions



a) Molecular Eqn:

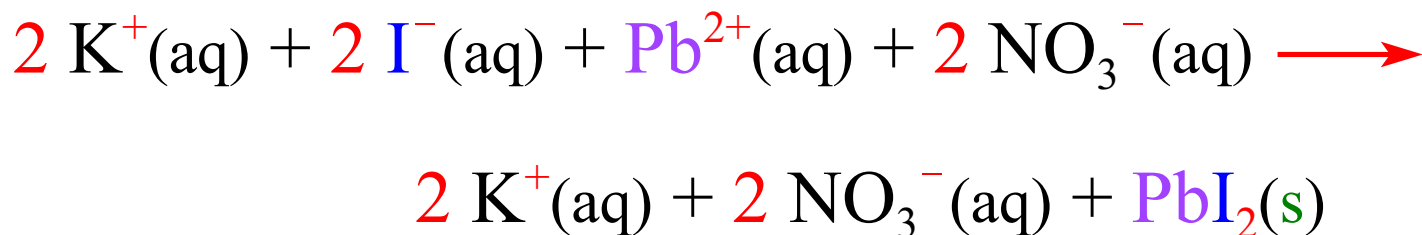
written as if all substances were
molecules

- tells what soln's are combined

- **must use** for **quantitative calc.**

b) Ionic Eqn:

shows each substance as it
exist in **soln.**



1) **soluble** ionic substances
written as **ions(aq)**



2) **insoluble** ionic substances
written as **formula(s) \Rightarrow XY(s)**



3) **molecular** subst. that are
strong electrolytes \Rightarrow ions(aq)



4) **molecular weak electrolytes**
or **nonelectrolytes \Rightarrow**
molecular formula (phase)



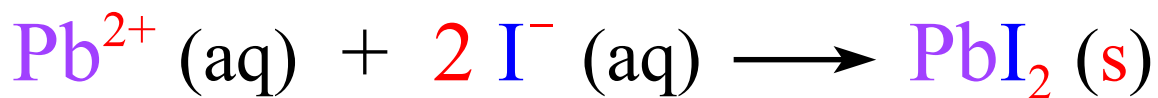
b) Net Ionic Eqn:

Note : K^+ & NO_3^- do **not** undergo **change** & appear on **both sides** of arrow

Spectator Ions

Eliminate spectator Ions \Rightarrow

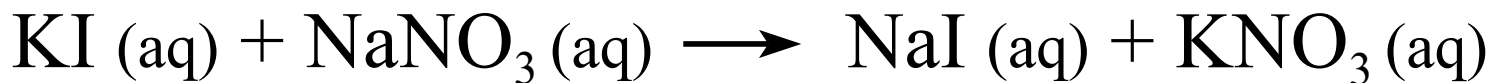
Net Ionic Eqn.



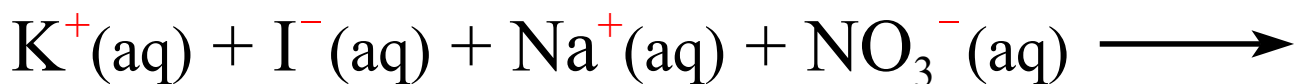
2 Advantages

- 1) focuses **attention** on **change** that is **occurring**
- 2) more **general**: **Any** subst. that produces $Pb^{2+} + I^-$ in soln. will produce a **ppt.** of $PbI_2 (s)$

2) Ex: Mix KI (aq) & NaNO₃ (aq) soln's.



Ionic Eqn:



Eliminate ALL spectator ions

- nothing left

No driving force

∴ If we know solubilities of cmpds then we can predict when a ppt. will occur.

III) Acids, Bases & Neutralization Rxns.

A) Acids

Ionize in water to form $\text{H}^+(\text{aq})$

- **Proton donors**

HCl , H_2SO_4 , $\text{HC}_2\text{H}_3\text{O}_2$ ($\text{CH}_3\text{CO}_2\text{H}$)

1) 7 Strong Acids

Ionize Completely

HCl , HBr , HI , HNO_3 , HClO_3 , HClO_4 ,
 H_2SO_4 (**1st H^+ only**)



2) Weak Acids

Partial ionization

- weak electrolyte



Chemical Equilibrium

Acid that's NOT a strong acid



B) Bases

Produce OH^- (aq) in water

- Proton acceptors

NaOH , $\text{Ca}(\text{OH})_2$, NH_3

1) Strong Bases

soluble ionic cmpds. which
dissolve to give OH^-



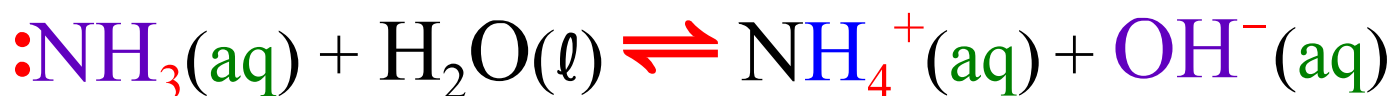
Dissociate completely

Hydroxides & Oxides of Groups
IA & IIA (except Be, Mg)

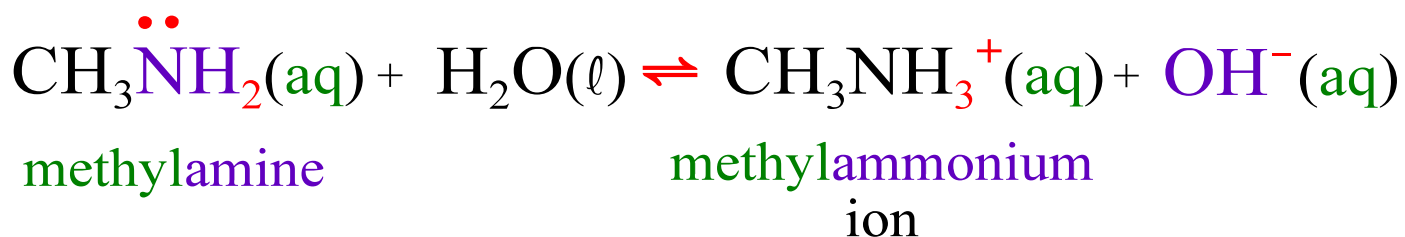
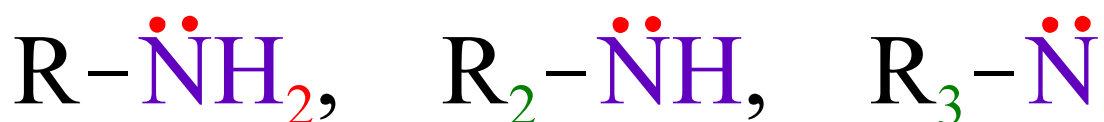
2) Weak Bases

Partially ionized

a) Ammonia, NH₃



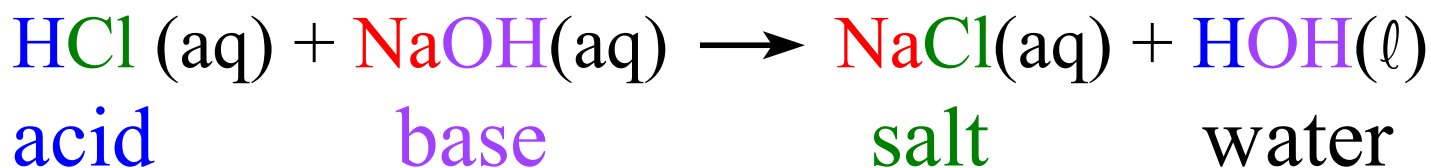
b) Amines



C) Neutralization Rx's

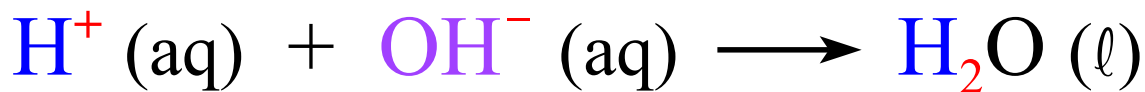
Formation of Weak or Nonelectrolyte

1) Strong Acid & Strong Base



Driving Force \Rightarrow formation of H_2O

Net Ionic Eq.

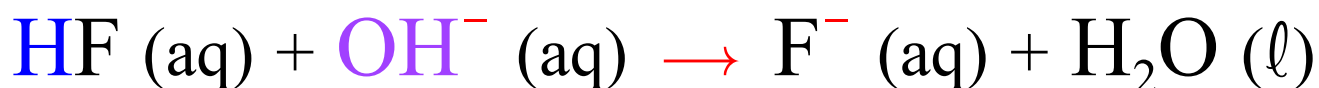


True for rx. between
any strong acid & strong base

2) Weak Acid & Strong Base

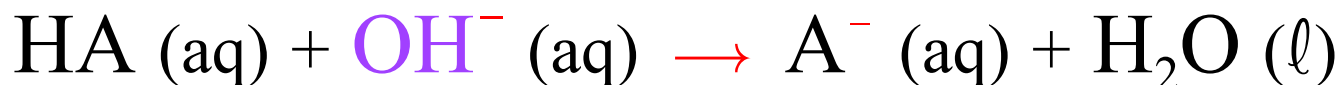


Net :



Generally,

Rx. of weak monoprotic acid
w. strong soluble base



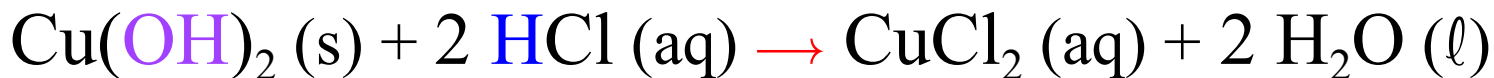
3) Weak Base & Strong Acid



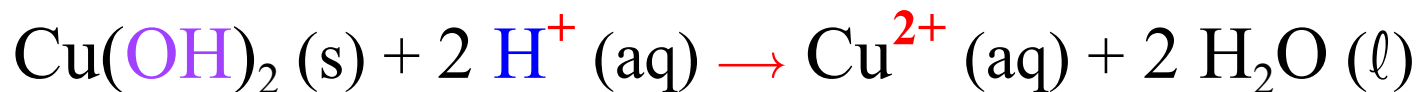
Net :



4) Insoluble Hydroxides & Acids



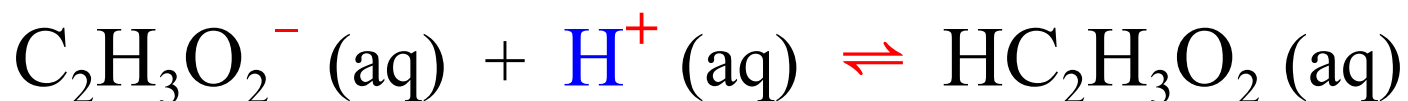
Net:



5) Formation of Weak Electrolyte



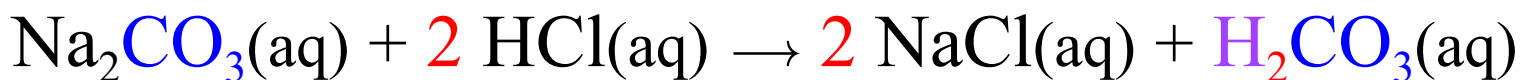
Net:



formation of $\text{HC}_2\text{H}_3\text{O}_2$ removes
ions from soln.

D) Neutralization Rx's w. Gas Formation
Gaseous product which escapes
from the soln.

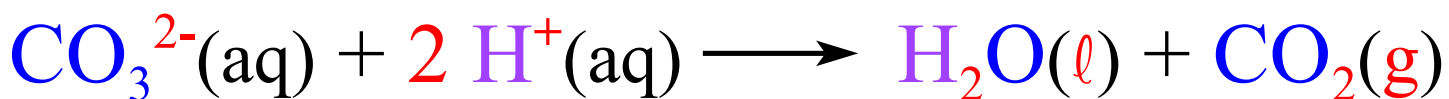
1) Carbonates & Bicarbonates



Carbonic acid decomposes:



Net:

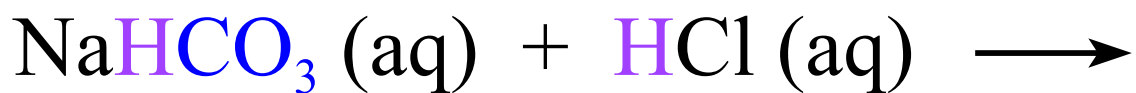


Insoluble Carbonates also work:

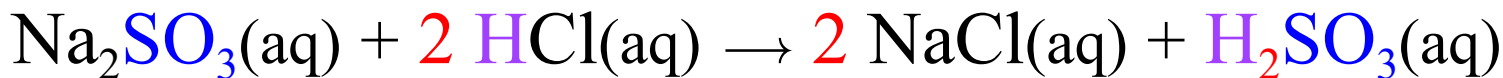
Net:



Bicarbonates



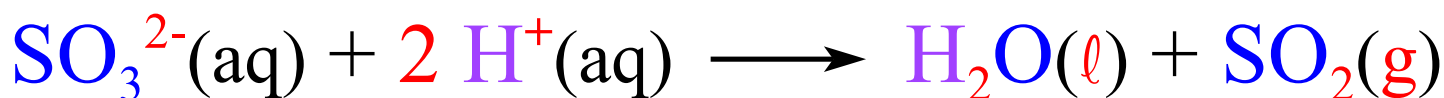
2) Sulfites & Bisulfites



Sulfurous acid decomposes:



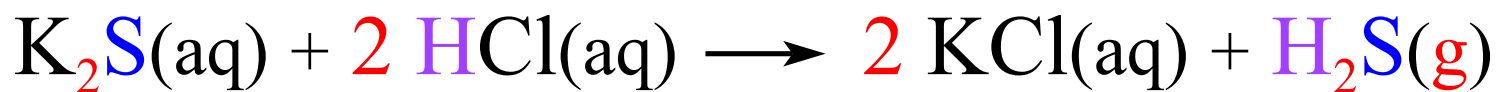
Net:



Bisulfites



3) Sulfides



Net :



IV) Oxidation - Reduction Rx's (Redox)

Involves **loss** of e^- by one element & **gain** of e^- by another element

Oxidation: lose e^-
(inc. in **oxidation #**)

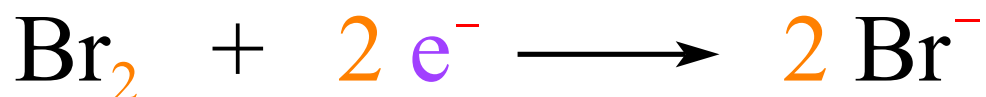
Reduction: gain e^-
(dec. in **oxidation #**)

Oxidizing agent: substance that
is **reduced**

Reducing agent: substance that
is **oxidized**



Zn lost $\text{e}^- \Rightarrow$ oxidized

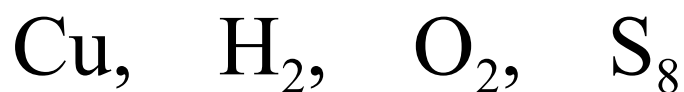


Br gained $\text{e}^- \Rightarrow$ reduced

A) Oxidation Numbers

Charge that an atom **would have** if e^- in cmpds. are **assigned** in a certain way.

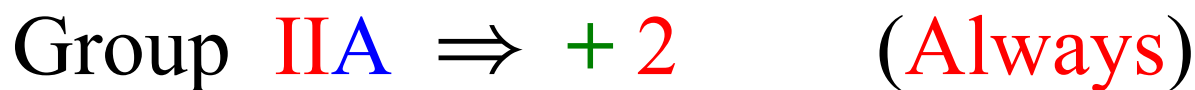
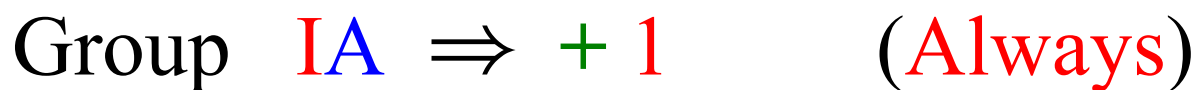
1) Elemental Form



$$\text{ox. \#} = 0 \quad (\text{zero})$$

2) Monatomic Ion

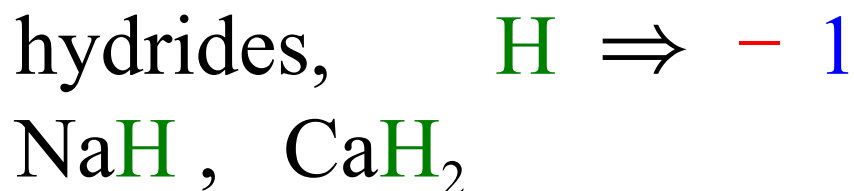
$$\text{ox. \#} = \text{charge}$$



3) Hydrogen



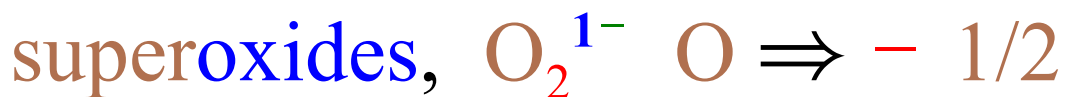
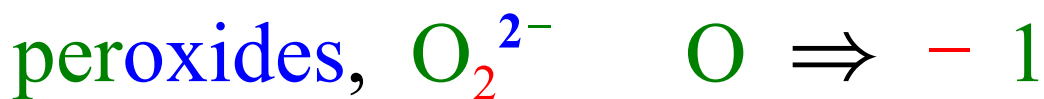
exceptions



4) Oxygen



exceptions



5) Fluorine

F \Rightarrow - 1 Always

6) Halogens: Cl, Br, I

- 1 except when combined
w. a more E.N. element

CBr_4 : Br \Rightarrow - 1

can be : +1, +3, +5, +7

ClO_4^- : +7

7) **Sum** of **ox. no.'s** of atoms
in **neutral** cmpds. =

0 (zero)

8) **Sum** of **ox. no.'s** of atoms
in a **polyatomic ion** =

charge

9) **Ox. no.** can't be:

more **positive** than the **group #**

or

more **negative** than (**group # - 8**)

B) Examples

1) Ex 1: What is **ox. #** of **N** in **NH₃** ?

$$\# x_{\text{N}} + 3(+1) = 0$$

$$\# x_{\text{N}} = -3$$

2) Ex 2: What is **ox. #** of **N** in **NO₃⁻** ?

3) Ex 3: What is **ox. #** of **N** in **NO₂⁻** ?

4) Ex 4: What is **ox. #** of **Xe**
in **XeOF₄**?

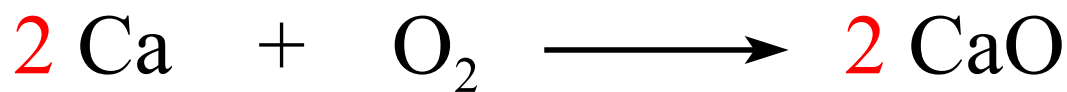
5) Ex 5: What is **ox. #** of **Cr**
in **K₂Cr₂O₇**?

C) Redox Reactions

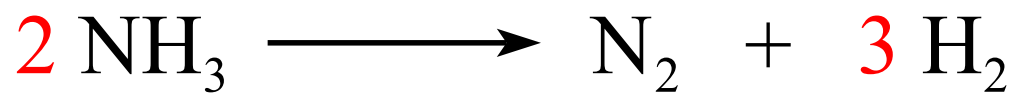
Oxidation: inc. in ox. #
 (lose e⁻)

Reduction: dec. in ox. #
 (gain e⁻)

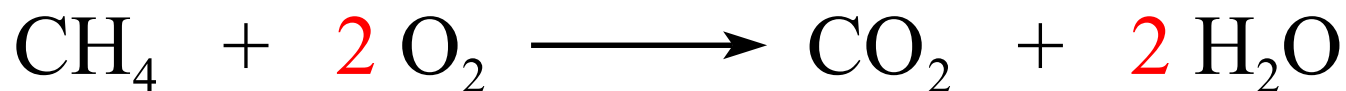
1) Combination



2) Decomposition



3) Combustion



4) Displacement Rxs.

Single – Replacement Rxs

one element replaces another
element in a compd.

Active metals displace
less active metals or hydrogen

the most active metals lose
their e^- most easily

– most easily oxidized

(strongest reducing agent)

a) Metals

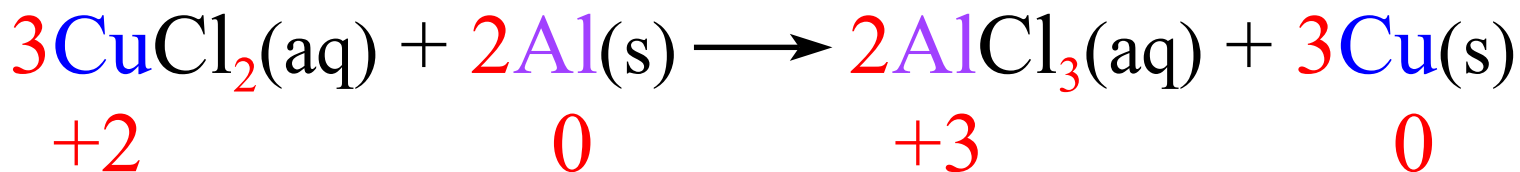
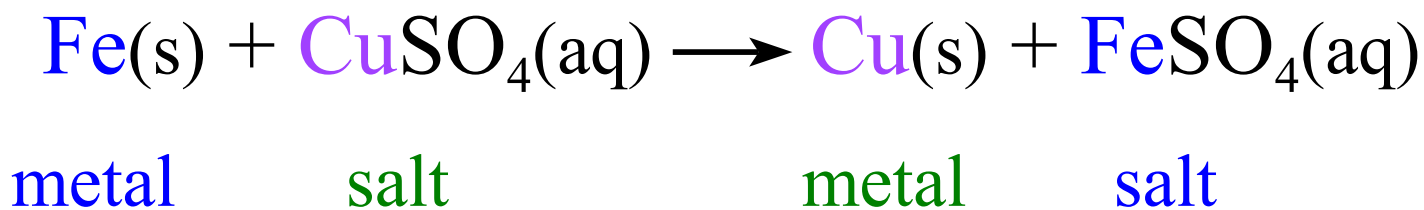
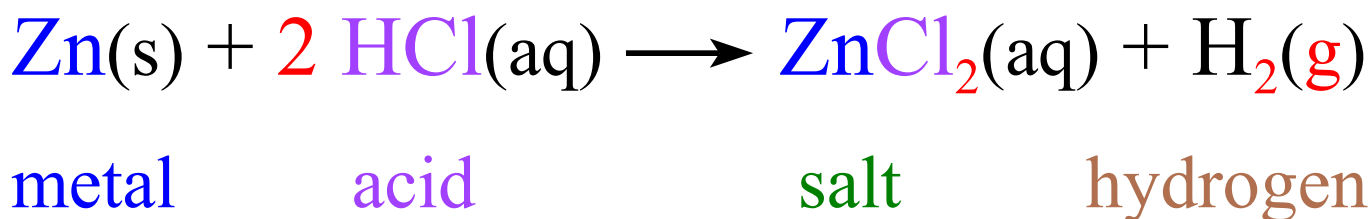
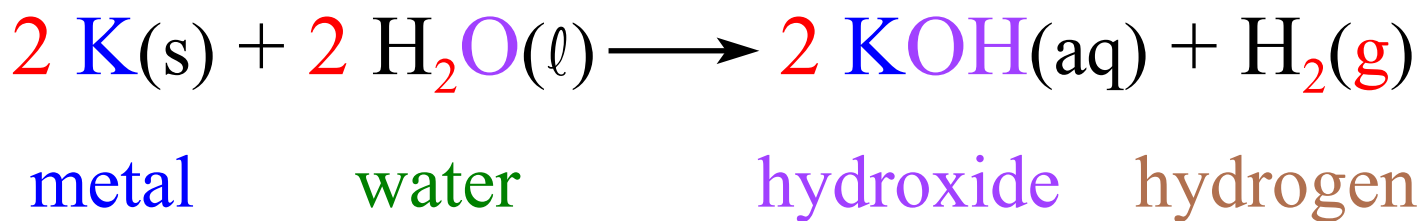


TABLE 4.5 • Activity Series of Metals in Aqueous Solution

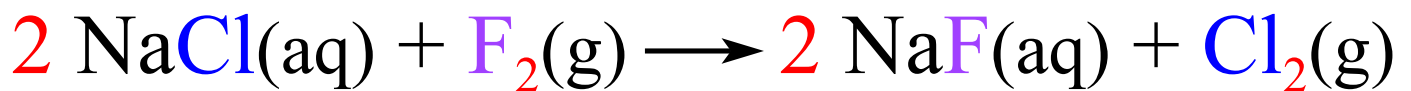
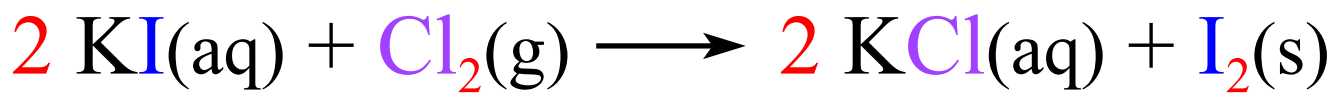
Metal	Oxidation Reaction
Lithium	$\text{Li}(s) \longrightarrow \text{Li}^+(aq) + e^-$
Potassium	$\text{K}(s) \longrightarrow \text{K}^+(aq) + e^-$
Barium	$\text{Ba}(s) \longrightarrow \text{Ba}^{2+}(aq) + 2e^-$
Calcium	$\text{Ca}(s) \longrightarrow \text{Ca}^{2+}(aq) + 2e^-$
Sodium	$\text{Na}(s) \longrightarrow \text{Na}^+(aq) + e^-$
Magnesium	$\text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + 2e^-$
Aluminum	$\text{Al}(s) \longrightarrow \text{Al}^{3+}(aq) + 3e^-$
Manganese	$\text{Mn}(s) \longrightarrow \text{Mn}^{2+}(aq) + 2e^-$
Zinc	$\text{Zn}(s) \longrightarrow \text{Zn}^{2+}(aq) + 2e^-$
Chromium	$\text{Cr}(s) \longrightarrow \text{Cr}^{3+}(aq) + 3e^-$
Iron	$\text{Fe}(s) \longrightarrow \text{Fe}^{2+}(aq) + 2e^-$
Cobalt	$\text{Co}(s) \longrightarrow \text{Co}^{2+}(aq) + 2e^-$
Nickel	$\text{Ni}(s) \longrightarrow \text{Ni}^{2+}(aq) + 2e^-$
Tin	$\text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + 2e^-$
Lead	$\text{Pb}(s) \longrightarrow \text{Pb}^{2+}(aq) + 2e^-$
Hydrogen	$\text{H}_2(g) \longrightarrow 2\text{H}^+(aq) + 2e^-$
Copper	$\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2e^-$
Silver	$\text{Ag}(s) \longrightarrow \text{Ag}^+(aq) + e^-$
Mercury	$\text{Hg}(l) \longrightarrow \text{Hg}^{2+}(aq) + 2e^-$
Platinum	$\text{Pt}(s) \longrightarrow \text{Pt}^{2+}(aq) + 2e^-$
Gold	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$



b) Nonmetals

Halogens

order
of
activity

$$F > Cl > Br > I$$


c) Metal Salt & Hydrogen or Carbon



f) Ex : If iron is placed in a soln. of silver nitrate will silver plate out?

V) Concentration of Solutions

amount of solute dissolved in a given quantity of solvent or solution

A) Molarity (M)

$$M = \frac{\text{moles solute}}{\text{L soln}}$$

Conversion factor between moles solute & L soln.

1) Ex 1: How many moles of CaCl_2 are present in 200.0 mL of 2.0 M CaCl_2 ?

2) Ex 2: A rx. req. 1.94 g Ca^{2+} ions.
What vol. of 2.00 M CaCl_2 is
req. to provide this amt. of
 Ca^{2+} ?

B) Dilution

Add more solvent & get
a more dilute soln.

$$\text{moles solute} = \frac{\text{moles}}{L} \times L = M \times V$$

moles solute
before dilution = moles solute
after dilution

$$M_1 V_1 = M_2 V_2$$

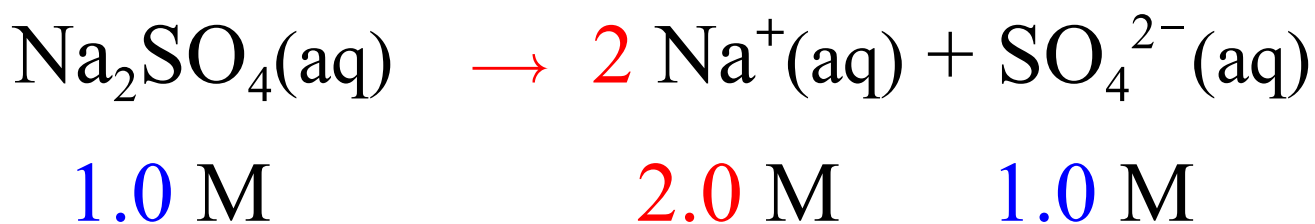
1) Ex 1: A 100.0 mL sample of 0.200 M sucrose was diluted to 500.0 mL. Calc. the new molarity.

2) Ex 2: How much water must be added to 100.0 mL of 0.300 M NaCl to prepare a 0.0500 M NaCl soln?

VI) Solution Stoichiometry

When working w. solutions “How much” may refer to either **volume required** or **concentration**.

A) Ions and Ionic Compounds



Use **stoichiometry** of **balanced eqn.** to determine **molarity** of **ions** in soln.

1) Ex : What is the molarity of OH^- in a 0.20 M $\text{Ba}(\text{OH})_2$ soln.?

a) Use dimensional analysis

$$\begin{aligned} ? \frac{\text{mol } \text{OH}^-}{\text{L soln}} &= \frac{0.20 \text{ mol Ba}(\text{OH})_2}{\text{L soln}} \times \frac{2 \text{ mol } \text{OH}^-}{1 \text{ mol Ba}(\text{OH})_2} \\ &= 0.40 \text{ M } \text{OH}^- \end{aligned}$$

b) Use “ICE” table in Molarity

	$1 \text{ Ba}(\text{OH})_2$	\rightarrow	1 Ba^{2+}	$+ 2 \text{ OH}^-$
Initial	0.20		0	0
Change	- 0.20		+ 0.20	+ 0.40
Equilibrium	0		0.20	0.40

B) Reaction Stoichiometry

Stoichiometry problems involving solns

- 1) Ex : What **volume (mL)** of 0.215 M HCl is req. to completely react w. 10.00 mL of 0.400 M Ba(OH)₂?



$$\begin{aligned} ? \text{ L} &= 0.01000 \text{ L} \times \frac{0.400 \text{ mol Ba(OH)}_2}{1 \text{ L soln}} \times \frac{2 \text{ mol HCl}}{1 \text{ mol Ba(OH)}_2} \times \frac{1 \text{ L soln}}{0.215 \text{ mol HCl}} \\ &= 0.0372 \text{ L} = 37.2 \text{ mL} \end{aligned}$$

Could also calc. moles of Ba(OH)₂ first by using M*V and then do a mole-to-mole stoich. problem to find moles of HCl and then use M*V to solve for the volume of HCl.

C) Titration (Volumetric Analysis)

neutralization, precipitation, redox

1) Titration

Method for determining **conc.** of a substance, **A**, by adding a measured volume of a soln. of **known** conc., **S**, (**standard** soln.).

Rxn. between **A** and **S**
must go to **completion**.

a) Equivalence Point

Point in titration at which stoichiometrically equivalent amounts of reactants have reacted.

b) Endpoint

Point at which an indicator changes color

1) Indicator

Substance which changes color as close as possible to the eq. pt.

Want endpoint and eq. pt. to be close to each other

2) Acid-Base Titration

At eq. pt.:

mol Acid = mol Base

$$M_a * V_a = M_b * V_b$$

In this eqn. the **molarities** are the **molarities** of H^+ and OH^- .

The **volumes** can be left in **mL**.

a) Ex : It takes 60.00 mL of 0.1000 M NaOH to titrate 20.00 mL of HCl to the eq. pt. What is the conc. of the original HCl solution?



$$\begin{aligned} ? \text{ mol HCl} &= 0.06000 \text{ L NaOH} \times \frac{0.1000 \text{ mol NaOH}}{1 \text{ L soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \\ &= 0.006000 \text{ mol HCl} \end{aligned}$$

$$M(\text{HCl}) = \frac{0.006000 \text{ mol HCl}}{0.02000 \text{ L soln}} = 0.3000 \text{ M HCl}$$

Could use $M_a * V_a = M_b * V_b$

$$M_a = \frac{M_b * V_b}{V_a} = \frac{(0.1000 \text{ M})(60.00 \text{ mL})}{20.00 \text{ mL}} = 0.3000 \text{ M}$$