

# 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

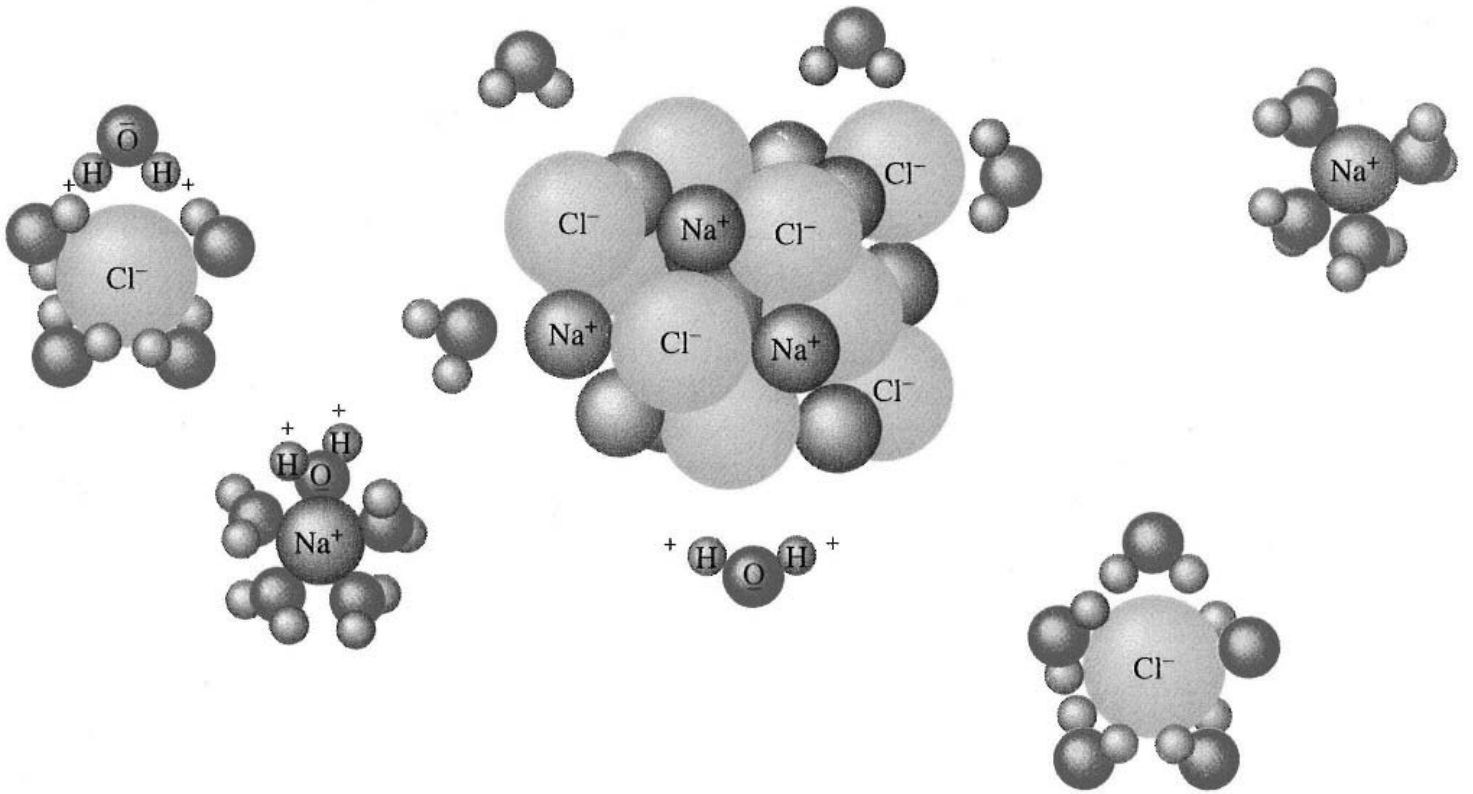
Solute is solvated by solvent

Solvent surrounds solute

Solvation

1) Aqueous

H<sub>2</sub>O as solvent



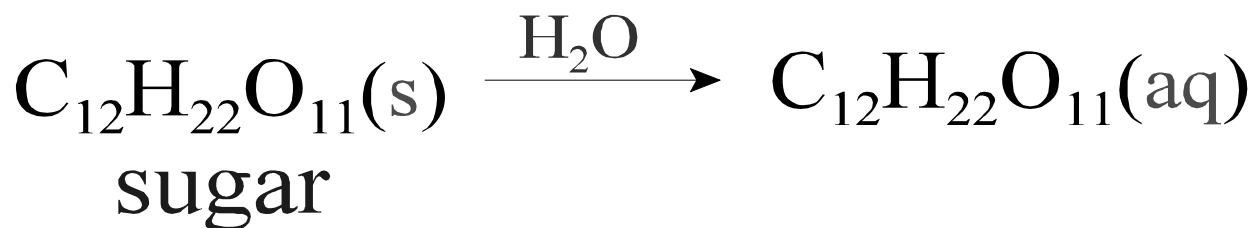
## B) Nonelectrolytes

Substances which dissolve  
in molecular form

- Present as molecules in solid, liquid & gas states and in soln.
- do NOT form ions in soln.

Soln. does NOT conduct electricity

Pure H<sub>2</sub>O



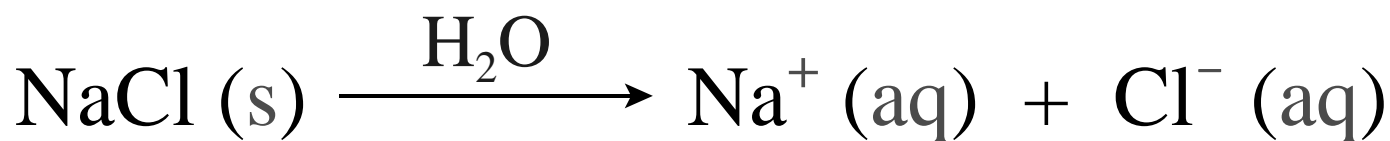
## C) Electrolytes

Substance whose aqueous soln. conducts electricity

- due to ions in the soln.

### 1) Dissociation

Ionic solutes dissolve as ions



### Dissociation

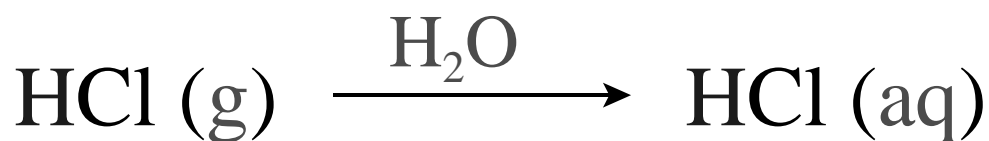
All soluble ionic substances dissociate completely

- strong electrolytes

## 2) Ionization

Some polar covalent molecules dissolve w. formation of ions.

### 1) Strong Acids



### Ionization

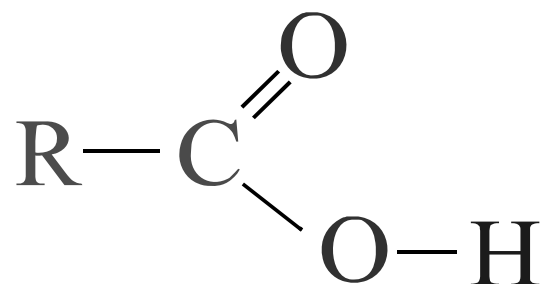
HCl - strong electrolyte  
(completely ionizes)

## 2) Weak Electrolytes

Weak conductors

- Partial ionization

### a) Weak Acids & Bases



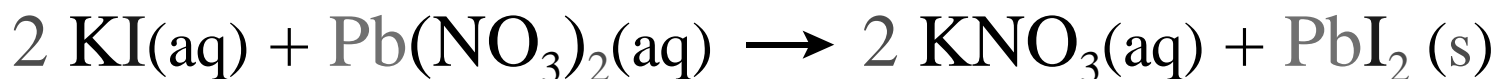
Chemical Equilibrium

- some molecular form remains



## II) Precipitation Reactions

Precipitate  $\equiv$  insoluble solid formed



### A) Solubility Rules

Which ionic cmpds. are soluble or insoluble in  $\text{H}_2\text{O}$

#### 1) Solubility

amt. of solid that dissolves in a given amt. of  $\text{H}_2\text{O}$  at a given temp.

**NOTE:** ALL ionic cmpds. of group IA &  $\text{NH}_4^+$  are soluble



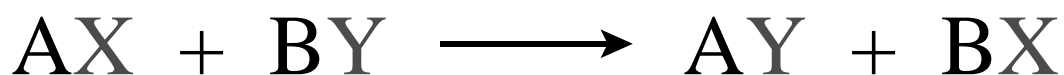
## EMPIRICAL RULES FOR THE SOLUBILITY OF IONIC SOLIDS IN H<sub>2</sub>O

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

## 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



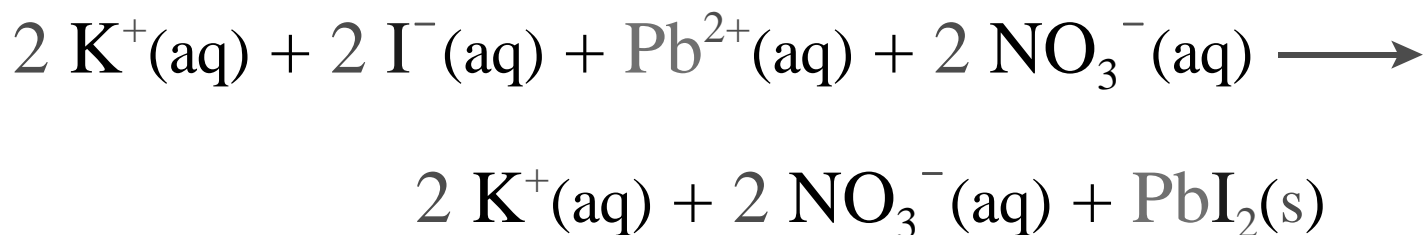
## a) Molecular Eqn:

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)



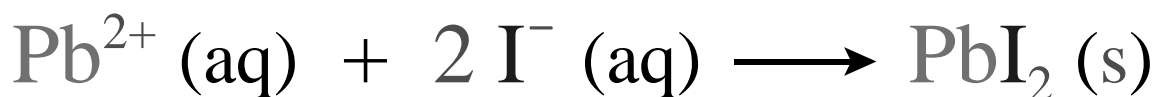
## b) Net Ionic Eqn:

Note :  $\text{K}^+$  &  $\text{NO}_3^-$  do not undergo change & appear on both sides of arrow

Spectator Ions

Eliminate spectator Ions  $\Rightarrow$

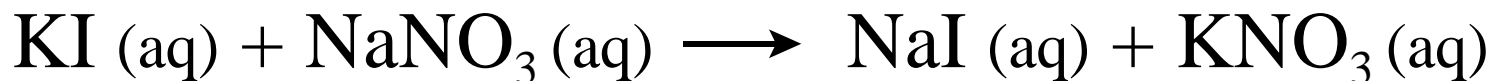
Net Ionic Eqn.



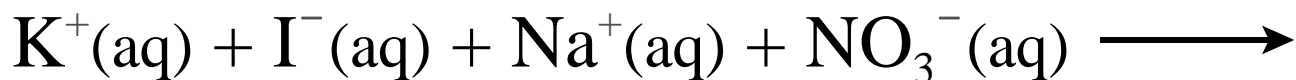
## 2 Advantages

- 1) focuses attention on change that is occurring
- 2) more general: Any subst. that produces  $\text{Pb}^{2+} + \text{I}^-$  in soln. will produce a ppt. of  $\text{PbI}_2 (\text{s})$

2) Ex: Mix KI (aq) & NaNO<sub>3</sub> (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

$\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HC}_2\text{H}_3\text{O}_2$  ( $\text{CH}_3\text{CO}_2\text{H}$ )

#### 1) 7 Strong Acids

Ionize Completely

$\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$ ,  
 $\text{H}_2\text{SO}_4$  ( $1^{\text{st}} \text{H}^+$  only)



## 2) Weak Acids

Partial ionization

- weak electrolyte



Chemical Equilibrium

Acid that's NOT a strong acid





## B) Bases

Produce  $\text{OH}^-$  (aq) in water

- Proton acceptors

$\text{NaOH}$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{NH}_3$

### 1) Strong Bases

soluble ionic cmpds. which  
dissolve to give  $\text{OH}^-$



Dissociate completely

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

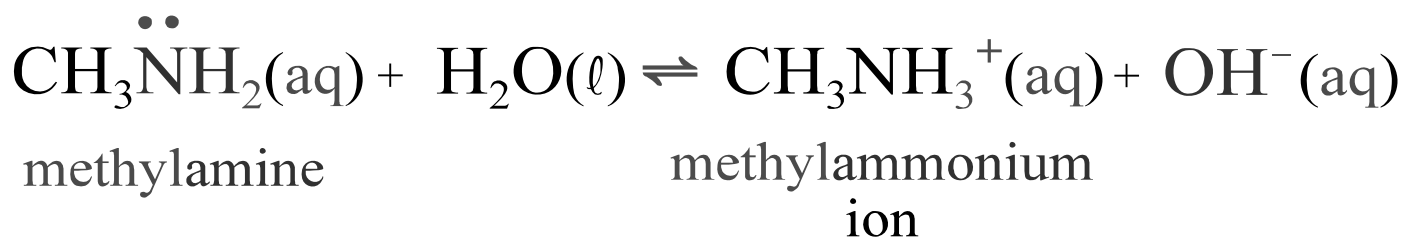
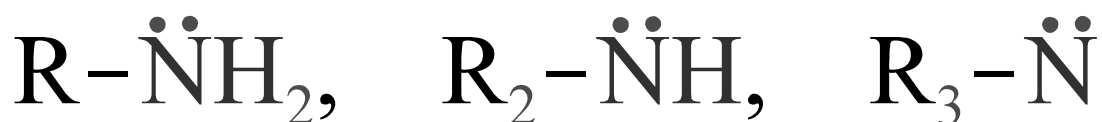
## 2) Weak Bases

Partially ionized

a) Ammonia, NH<sub>3</sub>



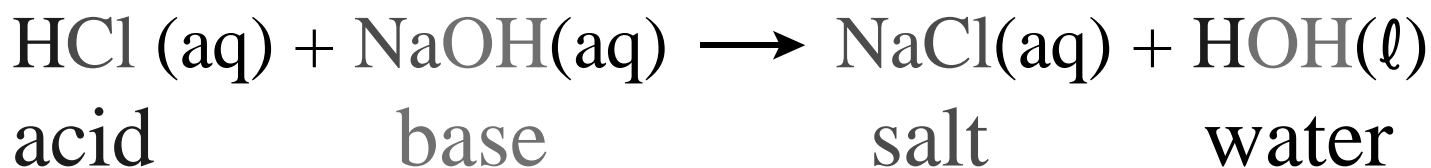
b) Amines



## C) Neutralization Rx's

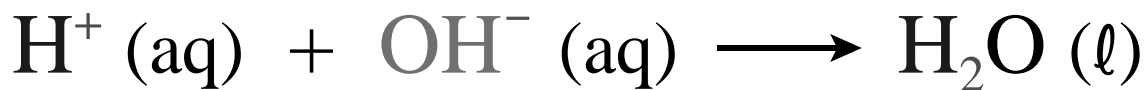
### Formation of Weak or Nonelectrolyte

#### 1) Strong Acid & Strong Base



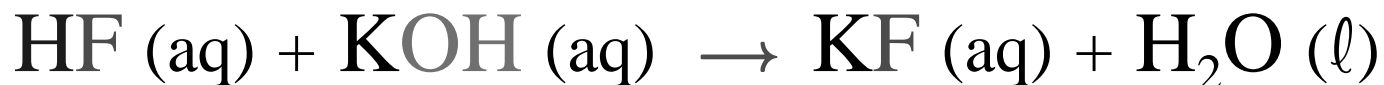
Driving Force  $\Rightarrow$  formation of  $\text{H}_2\text{O}$

Net Ionic Eq.

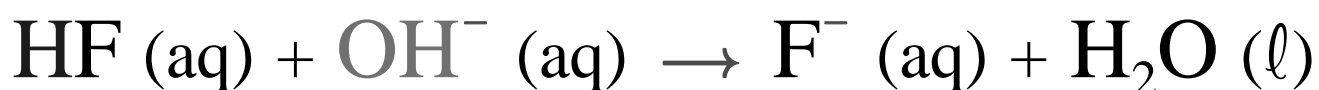


True for rx. between  
any strong acid & strong base

## 2) Weak Acid & Strong Base

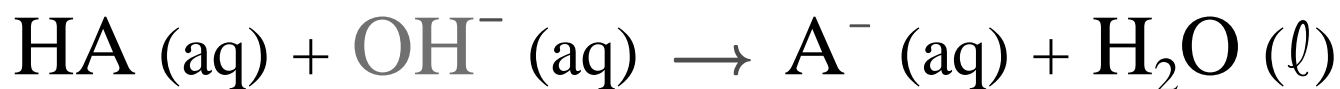


Net :



Generally,

Rx. of weak monoprotic acid  
w. strong soluble base



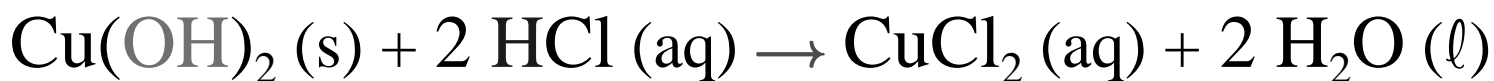
### 3) Weak Base & Strong Acid



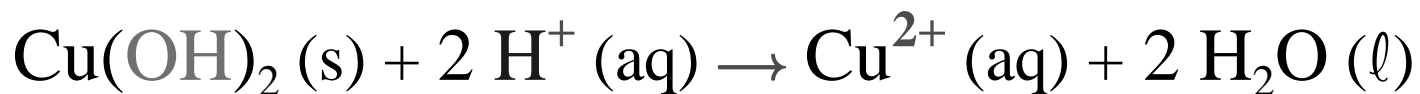
Net :



### 4) Insoluble Hydroxides & Acids



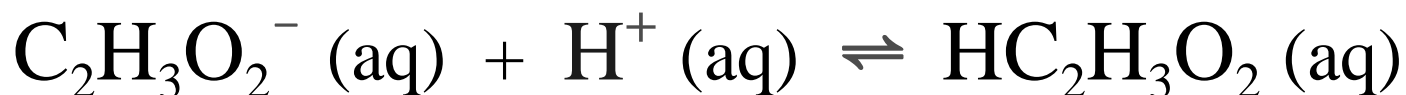
Net:



## 5) Formation of Weak Electrolyte



Net:

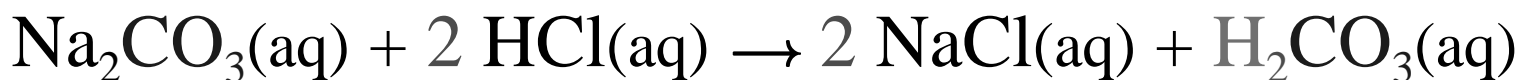


formation of  $\text{HC}_2\text{H}_3\text{O}_2$  removes  
ions from soln.

## D) Neutralization Rx's w. Gas Formation

Gaseous product which escapes from the soln.

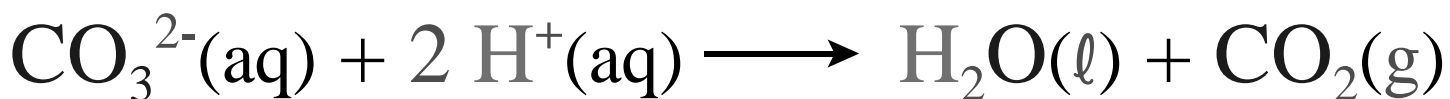
### 1) Carbonates & Bicarbonates



Carbonic acid decomposes:



Net:



Insoluble Carbonates also work:

Net:

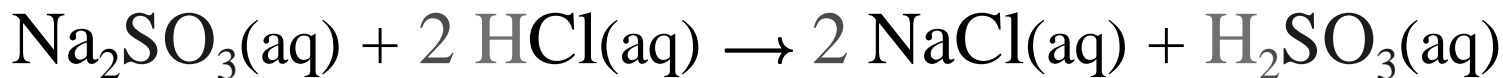


Bicarbonates





## 2) Sulfites & Bisulfites



Sulfurous acid decomposes:



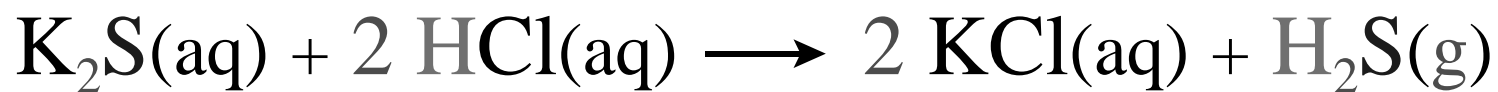
Net:



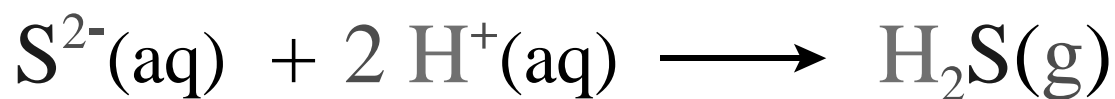
Bisulfites



### 3) Sulfides



Net :



## IV) Oxidation - Reduction Rx's (Redox)

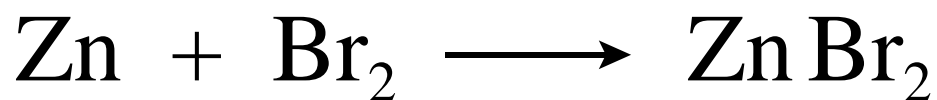
Involves loss of  $e^-$  by one element & gain of  $e^-$  by another element

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

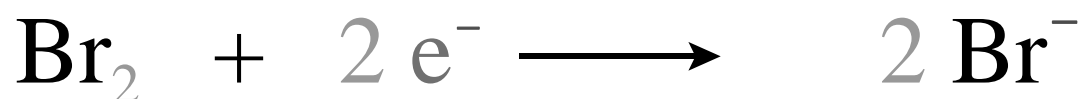
Reduction: gain  $e^-$   
(dec. in oxidation #)

Oxidizing agent: substance that  
is reduced

Reducing agent: substance that  
is oxidized



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

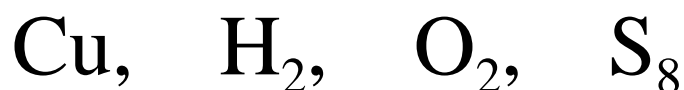


Br gained  $\text{e}^- \Rightarrow$  reduced

## A) Oxidation Numbers

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

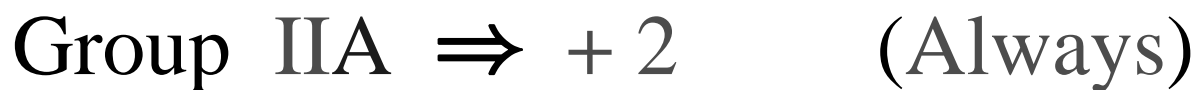
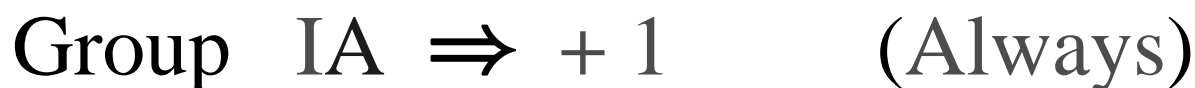
### 1) Elemental Form



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

### 2) Monatomic Ion

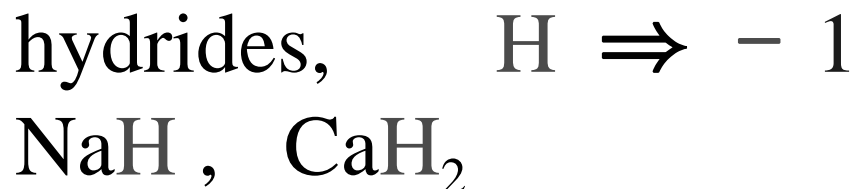
$$\text{ox. \#} = \text{charge}$$



### 3) Hydrogen



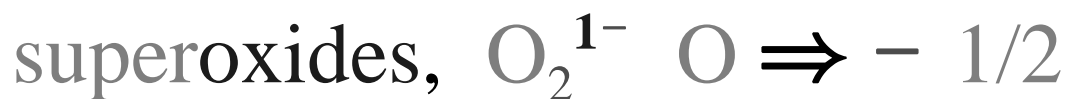
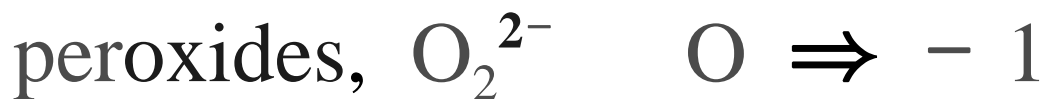
exceptions



### 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  $\text{NH}_3$  ?

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

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

2) Ex 2: What is ox. # of N in  $\text{NO}_3^-$  ?

3) Ex 3: What is ox. # of N in  $\text{NO}_2^-$  ?

4) Ex 4: What is ox. # of Xe  
in  $\text{XeOF}_4$ ?

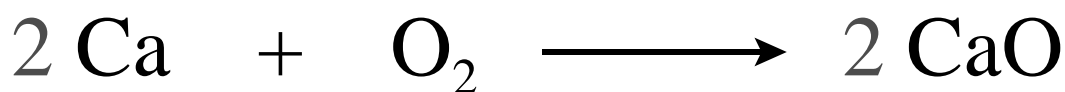
5) Ex 5: What is ox. # of Cr  
in  $\text{K}_2\text{Cr}_2\text{O}_7$ ?

## 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)

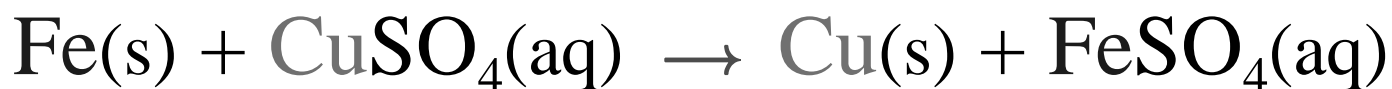
## a) Metals



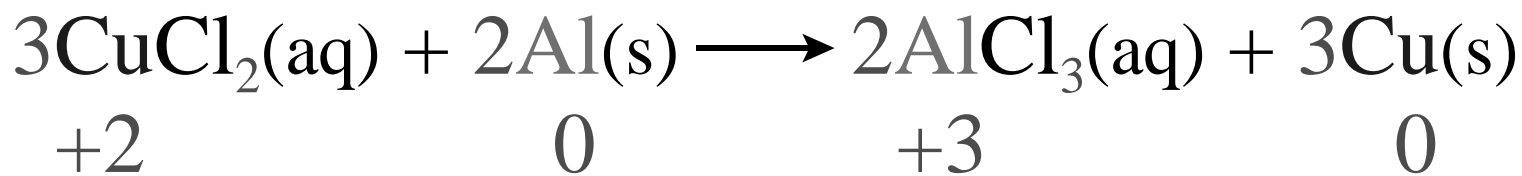
metal            water            hydroxide    hydrogen



metal            acid            salt            hydrogen



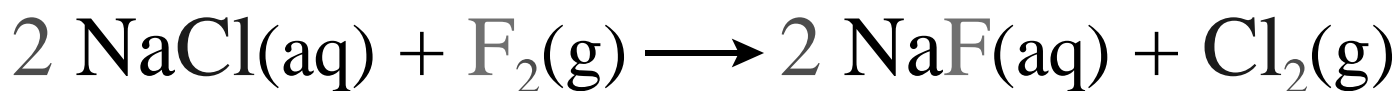
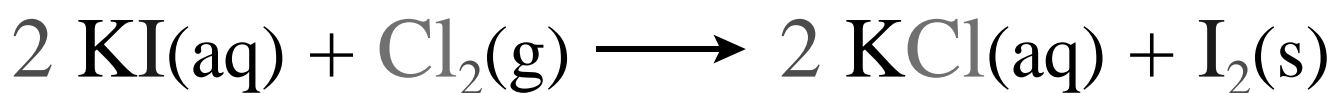
metal            salt            metal            salt



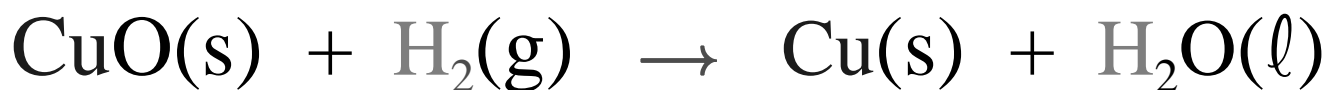
## b) Nonmetals

### Halogens

order  
of  
activity



## c) Metal Salt & Hydrogen or Carbon



**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	$\text{Au}(s) \longrightarrow \text{Au}^{3+}(aq) + 3e^-$



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  $\text{CaCl}_2$  are present in 200.0 mL of 2.0 M  $\text{CaCl}_2$ ?

2) Ex 2: A rx. req. 1.94 g  $\text{Ca}^{2+}$  ions.  
What vol. of 2.00 M  $\text{CaCl}_2$  is  
req. to provide this amt. of  
 $\text{Ca}^{2+}$  ?

## B) Dilution

Add more solvent & get  
a more dilute soln.

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

$$\begin{array}{ccc} \text{moles solute} & & \text{moles solute} \\ \text{before dilution} & = & \text{after dilution} \end{array}$$

$$\boxed{\text{M}_1 \text{V}_1 = \text{M}_2 \text{V}_2}$$

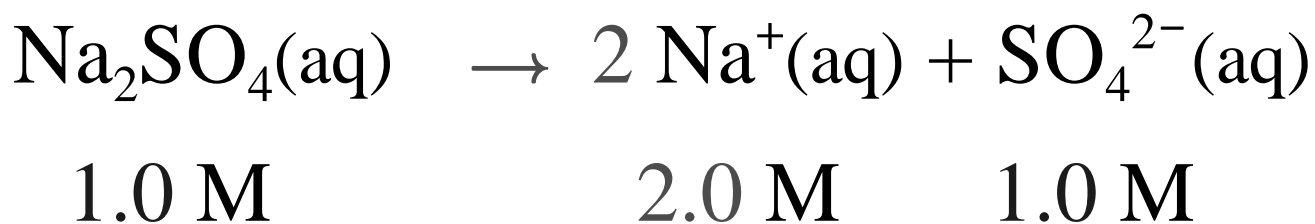
1) Ex 1: A 100.0 mL sample of 0.200 M sucrose was diluted to 500.0 mL. Calc. the new molarity.

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  $\text{OH}^-$  in a 0.20 M  $\text{Ba}(\text{OH})_2$  soln.?

a) Use dimensional analysis

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

b) Use “ICE” table in Molarity

	$1 \text{ Ba}(\text{OH})_2$	$\rightarrow$	$1 \text{ Ba}^{2+}$	$+ 2 \text{ OH}^-$
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)<sub>2</sub>?



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

Could also calc. moles of Ba(OH)<sub>2</sub> 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

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

1) Indicator

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

## 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?



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

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

Could use  $M_a * V_a = M_b * V_b$

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