

# Chapter 5 Chemical Reaction in Aqueous Solution

## Review of Terms in Ch. 3

Solvent, Solute

Concentrated, Dilute

Saturated, unsaturated, Supersaturated (Solubility Curves, p. 430)

Make Supersaturated NaAc Soln. (119g NaAc/100mL H<sub>2</sub>O at 0°C)

Saturate Hot Soln and allow to cool (To 0°C?) Add crystal

Electrolytes - Substances which, when dissolved in H<sub>2</sub>O, conducts electricity

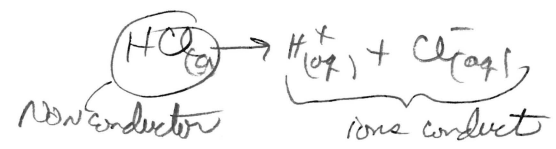
ionic substance is solid with ions held in place, when dissolved they separate and roam

Dissociation - Separation of ions (e.g. NaCl + ionic compound)



after dissociation ions are surrounded by polar water molecules and are said to be hydrated. (aq) indicates hydrated

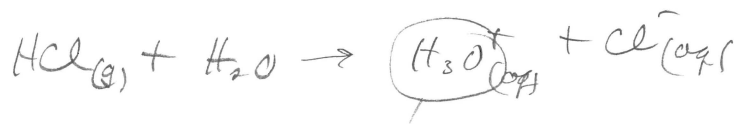
ionization - Formation of ions



Note \* (NaCl conducts in liquid phase HCl does not)

H<sup>+</sup> - hydrogen ion does not really exist in soln because of large charge to radius ratio (same logic for low K for HF)

Rx is more accurately written



hydronium ion

(The hydronium ion is also known to occur in a few crystalline hydrates of acids

such as  $\text{H}_3\text{O}^+, \text{ClO}_4^-$ ;  $\text{H}_3\text{O}^+, \text{Cl}^-$ ;  $\text{H}_3\text{O}^+, \text{NO}_3^-$ ) \*Mortimer, p. 101

Because of its large charge to radius ratio, the unassociated proton ( $\text{H}^+$ ) does not exist in ordinary chemical systems; in pure acids, the hydrogen atom is covalently bonded to the rest of the molecule, and in aqueous solutions the proton is hydrated. There is evidence that the proton bonds to a water molecule by means of a pair of electrons of the oxygen atom to form an ion,  $\text{H}_3\text{O}^+$ , called the **hydronium ion**. The three hydrogen atoms of the  $\text{H}_3\text{O}^+$  ion are equivalent, and the ion is in the form of a trigonal pyramid with the oxygen atom at the apex. The hydronium ion is known to occur in a few crystalline hydrates of acids such as  $\text{H}_3\text{O}^+, \text{ClO}_4^-$ ;  $\text{H}_3\text{O}^+, \text{Cl}^-$ ; and  $\text{H}_3\text{O}^+, \text{NO}_3^-$ .

Thermal and electrical conductivity experiments indicate that the  $\text{H}_3\text{O}^+$  ion is associated with three additional water molecules (by means of hydrogen bonds, Section 8.11) in water solution, and a pyramidal  $\text{H}_9\text{O}_4^+$  ion has been postulated (Figure 3.17). Other types of experimental evidence tend to

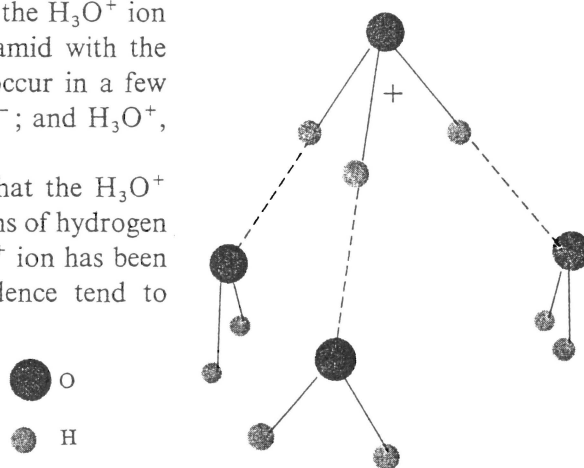


Figure 3.17 Proposed structure of  $\text{H}_9\text{O}_4^+$  ion.

(Mortimer p. 101)

(See Section 9.2 + 9.3 in Mortimer)

Also explains High Conductivity of  $\text{H}^+$   
 Usually just write  $\text{H}^+$  for  $\text{H}_3\text{O}^+$  but understand what is occurring.

Strong electrolytes - completely dissociated

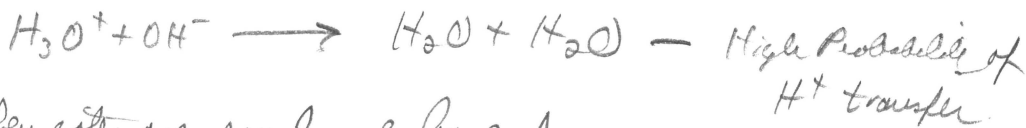
usu. ionic compounds / 100% diss.

Weak Electrolytes - partially dissociated + weakly conduct electricity

e.g. HAc only 0.43% dissociation

Demos { Conductivity depends on # of ions in solution (so do Demos with HCl and HAc)  
 Adding Additional H<sub>2</sub>O to each soln + how HCl soln does not get brighter w extra H<sub>2</sub>O but HAc does due to shift to right of Eq.  
 $HAc \rightleftharpoons H^+ + Ac^-$  More H<sub>2</sub>O shifts to right

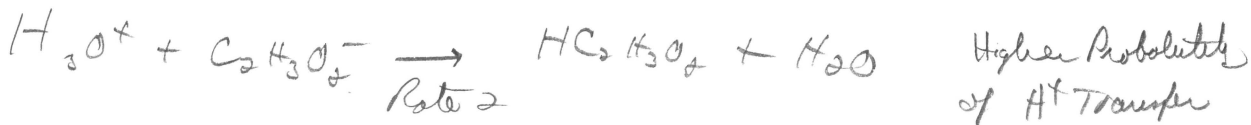
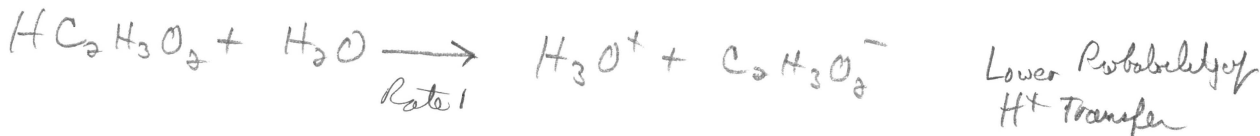
In pure water (or any solution) there are constant collisions. Most have no effect but a small number result in a proton transfer



- Simultaneous Apps + when rates are equal we have Dynamic Eq.

Now add

$HC_2H_3O_2$  to get constant collisions of



When  $\text{rate 1} = \text{rate 2}$  we have Dynamic Eq.

No Net Change



Double Arrows  
 slow both directions  
 + usually same rate

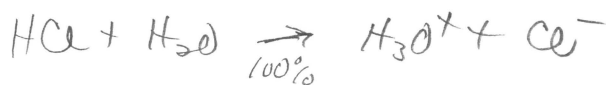
For  $\text{H}_2\text{O}$  Equilibrium occurs after very little ionization has occurred

For  $\text{HAc}$  " " " a bit more " " "

For weak electrolytes, equilibrium lies to the left

i.e. most of species still in molecular form.

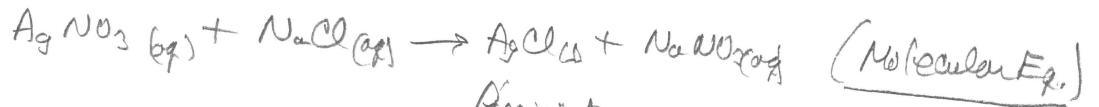
For strong electrolytes



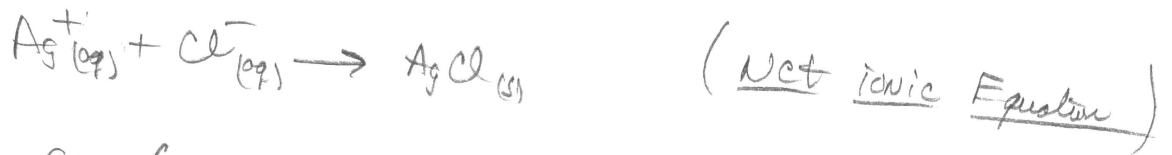
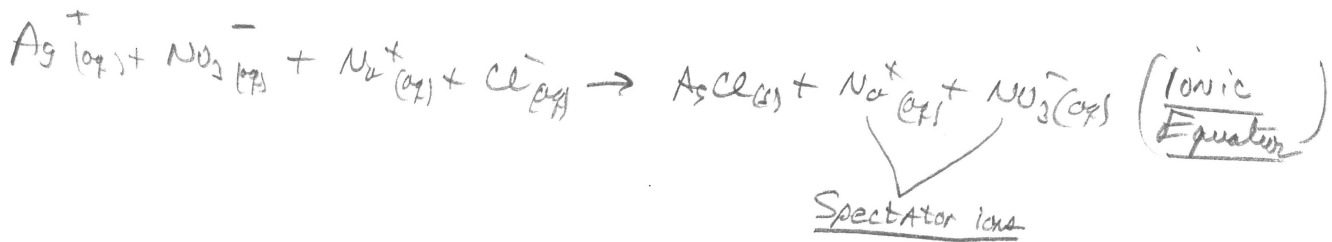
Even if  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  collide, No Rx occurs. (important for later)

No reverse Rx.

Ionic Reaction - occur between ions in solution



Double Replacement (Displacement) for Precipitate or Metathesis Rxn.



(\*Note  $\text{AgF}$  is soluble (100g/100ml) while other silver halides are not.)

$\text{AgCl}(s)$ is white $\text{AgBr}(s)$ cream colored $\text{AgI}(s)$ is yellow	}	Morrison P. 365
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The insolubility of the silver salts of  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  is the basis of a common test for these halide ions;  $\text{AgCl}$  is white,  $\text{AgBr}$  is cream, and  $\text{AgI}$  is yellow. The silver halide precipitates may be formed by the addition of a solution of silver nitrate to a solution containing the appropriate halide ion. Silver iodide is insoluble in excess ammonia; however,  $\text{AgCl}$  readily dissolves to form the  $\text{Ag}(\text{NH}_3)_2^+$  complex ion and  $\text{AgBr}$  dissolves with difficulty. Silver fluoride is soluble; generally,  $\text{MgF}_2$  or  $\text{CaF}_2$  precipitates are used to confirm the presence of the fluoride ion in a solution.

← Demo?

Acids + Properties (See p. 125-126)

Indicators - change color depending on pH (Acidity or Alkalinity)  
(e.g. phenolphthalein, litmus)

Arrhenius Definition -

Acid - Substance that increases  $H_3O^+$  concentration -

Base - " " " "  $OH^-$  concentration

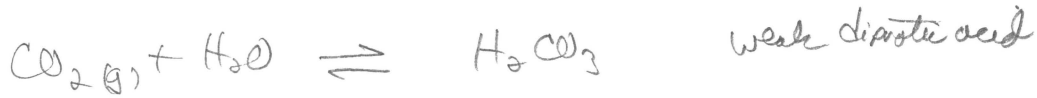
In general Acids are

- ① Molecular
- ② Produce  $H_3O^+$  in water
- ③ Strong + weak acids based on degree of dissociation

Monoprotic versus polyprotic  
diprotic  
triprotic



Show  $H_3PO_4$  dissociation steps and note that all are weak.



\* Note ( Reaction is typical of Non-metal oxides which generally react with water to form Oxoacids  $\text{SO}_3 + \text{SO}_2 + \text{NO}_2$  For Acid rain)

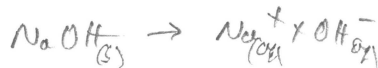
\* (Exceptions NO and CO do not react with  $\text{H}_2\text{O}$ )

Acid Anhydride - Non metal oxide which forms an Oxoacid with  $\text{H}_2\text{O}$



### Bases Two types

(1) ionic hydroxides - consist of metal and hydroxide and are usually strong bases (100%)  
 only  $\text{NH}_4^+$  and Alkali metal ions



(2) Molecular Substances that react with  $\text{H}_2\text{O}$  to produce  $\text{OH}^-$  and are usually weak bases (Eq. lies to left)



\* (Note that  $\text{NH}_4\text{OH}$  does not exist despite of frequent name)

Basic Anhydride - a metal oxide that forms a base when reacted with  $\text{H}_2\text{O}$ .



It is the  $\text{O}^{2-}$  that drives this rxn, Na is fairly inactive.

Neutralization

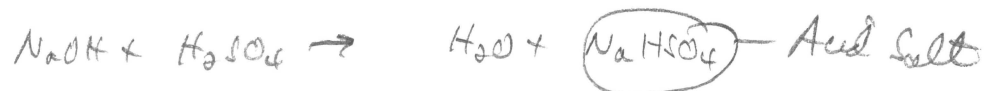
Insoluble Acids + bases will be dissolved by soluble bases and acids, respectively, to make  
 H<sub>2</sub>O + Very Exothermic R<sub>xn</sub>

Rust removal



Driven by desire to be Neutralization R<sub>xn</sub>.

Acid Salts - result from the partial Neutralization of Polyprotic Acids and  
 can undergo further Neutralization



### Driving Force Behind Metathesis R<sub>xn</sub>'s

#### ① Precipitation Reaction

Are All ion pairs present Soluble?

Solubility Rules (P. 132) (P. 184 (KOTZ))





Always Soluble

- Alkali Metal Salts
- Ammonium Salts
- Nitrates
- Chlorates
- Perchlorates
- Acetates

Generally Soluble

ch 5 (9)

- Chlorides
  - Bromides
  - Iodides
- } Except  $Ag^{1+}$ ,  $Pb^{2+}$ ,  $Hg_2^{2+}$

- Sulfates
- Except  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$ ,  $Pb^{2+}$

Generally Insoluble

Metal Oxides - except Alkali Metals,  $Ca^{2+}$ ,  $Sr^{2+}$ ,  $Ba^{2+}$   
(React with  $H_2O$  to form hydroxides)

Hydroxides - (except for those above)

- Carbonates
  - Phosphates
  - Sulfides
  - Sulfites
- } Except for Above Exceptions

See Kotz P. 184  
for Table