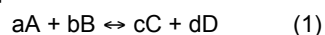


## Chemical Equilibrium

### Equilibrium Constants

- For a generic chemical reaction, the equilibrium constant is defined as:

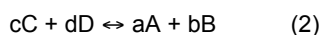


$$K_{\text{eq1}} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

- The "equilibrium constant",  $K_{\text{eq}}$ , for a chemical reaction indicates whether the reactants or the products will be favored in an equilibrium process

### Equilibrium Constants

- For the reverse reaction

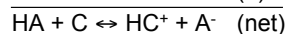
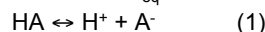


the equilibrium constant is the inverse of the forward reaction:

$$K_{\text{eq2}} = \frac{1}{K_{\text{eq1}}} = \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

### Equilibrium Constants

- When reactions are added to produce a net reaction, the net equilibrium constant is the product of the  $K_{\text{eq}}$ s for each reaction:

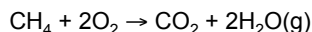


$$K_1 = \frac{[H^+][A^-]}{[HA]} \quad K_2 = \frac{[HC^+]}{[H^+][C]}$$

$$K_{\text{net}} = K_1 K_2 = \frac{[HC^+][A^-]}{[HA][C]}$$

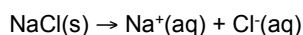
### Thermodynamics

- Enthalpy,  $\Delta H$ , is a measure of the change in heat content between reactants and products



$$\Delta H_{\text{rxn}}^{\circ} = -802.34 \text{ kJ}$$

- Methane releases heat to surrounding when combusted

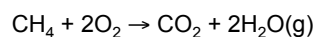


$$\Delta H_{\text{rxn}}^{\circ} = 3.87 \text{ kJ}$$

- Sodium chloride takes heat from surroundings when dissolved

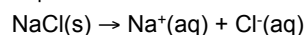
### Thermodynamics

- Entropy,  $\Delta S$ , is a measure of the change of disorder when going from reactants to products



$$\Delta S_{\text{rxn}}^{\circ} = -5.14 \text{ J/K}$$

- The products are more ordered than the reactants



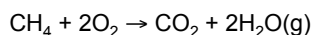
$$\Delta S_{\text{rxn}}^{\circ} = 43.4 \text{ J/K}$$

- The products are more disordered than the reactants—more space between ions in solution

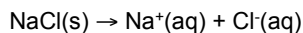
### Thermodynamics

- Gibb's Free Energy,  $\Delta G$ , is a measure of the energy available to do work following reaction

- Definition:  $\Delta G = \Delta H - T\Delta S$



$$\Delta G^\circ_{\text{rxn}} = -800.78 \text{ kJ}$$



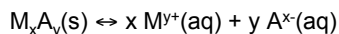
$$\Delta G^\circ_{\text{rxn}} = -9.00 \text{ kJ}$$

### Thermodynamics

- $\Delta G$  is also a measure of where the equilibrium for a reaction will lie:
  - If  $\Delta G_{\text{rxn}} < 0$ , the reaction is product favored
  - If  $\Delta G_{\text{rxn}} > 0$ , the reaction is reactant favored
  - If  $\Delta G_{\text{rxn}} = 0$ , the reaction is in equilibrium
- The equilibrium constant is related to the Gibb's Free Energy:
  - $K_{\text{eq}} = \exp\{-\Delta G^\circ_{\text{rxn}}/RT\}$
  - R = gas constant = 8.314 J/mol·K
  - T = temperature (in K)

### Solubility Products

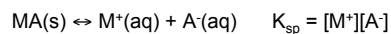
- The solubility product,  $K_{\text{sp}}$ , for a salt is a specific type of equilibrium constant
- Given an excess of salt,  $K_{\text{sp}}$  for the salt will determine how much of the salt will dissolve in water:



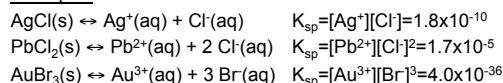
$$K_{\text{sp}} = [\text{M}^{y+}]^x [\text{A}^{x-}]^y$$

### Solubility Products

- Many salts are only slightly soluble
- The solubility product is a measure of the concentration of ions in a solution saturated with the salt



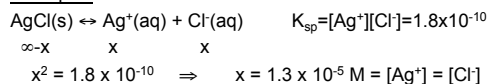
#### Examples



### Solubility Products

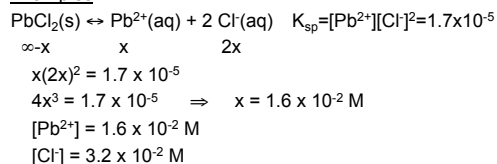
- Knowing the  $K_{\text{sp}}$ , we can calculate the concentration of ions in solution

#### Examples



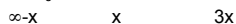
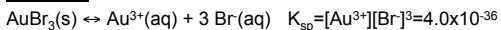
### Solubility Products

#### Examples



## Solubility Products

### Examples



$$x(3x)^3 = 4.0 \times 10^{-36}$$

$$27x^4 = 4.0 \times 10^{-36} \Rightarrow x = 6.2 \times 10^{-10} \text{ M}$$

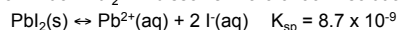
$$[\text{Au}^{3+}] = 6.2 \times 10^{-10} \text{ M}$$

$$[\text{Br}^-] = 1.9 \times 10^{-9} \text{ M}$$

## Solubility Products

### Examples—Common ion effect

How much  $\text{PbI}_2$  will dissolve in a 0.0100 M solution of  $\text{NaI}$ ?



$$x(2x + .0100)^2 = 8.7 \times 10^{-9}$$

$$x(4x^2 + 0.0400x + 1.0 \times 10^{-4}) = 8.7 \times 10^{-9}$$

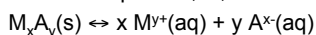
$$4x^3 + .0400x^2 + 1.0 \times 10^{-4}x - 8.7 \times 10^{-9} = 0$$

$$x = 8.4 \times 10^{-5} \text{ M}$$

vs  $1.3 \times 10^{-3} \text{ M}$  if no  $\text{I}^-(\text{aq})$  were present initially

## Precipitation

- Define ion quotient,  $Q$ , as:



$$Q = [\text{M}^{y+}]^x [\text{A}^{x-}]^y$$

$Q$  looks just like  $K_{\text{eq}}$ , but the system is not in equilibrium

- A precipitate will form only when  $Q$  exceeds  $K_{\text{sp}}$ 
  - $Q < K_{\text{sp}}$ : solution is unsaturated—no precipitate
  - $Q > K_{\text{sp}}$ : solution is saturated—precipitate forms
  - $Q = K_{\text{sp}}$ : solution at saturation point

## Precipitation

Example: a solution contain 0.0200 M  $\text{Pb}^{2+}$  and 0.0500M  $\text{Ag}^+$ . You want to remove one of the ions from solution by adding  $\text{Cl}^-$  without precipitating the other ion.

- Which metal will precipitate first?

$$K_{\text{sp}}(\text{AgCl}) = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

$$K_{\text{sp}}(\text{PbCl}_2) = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.7 \times 10^{-5}$$

## Precipitation

### Example:

- How much  $\text{Cl}^-$  must be added before each metal begins to precipitate?

$$\text{Silver: } [\text{Cl}^-] = K_{\text{sp}}/[\text{Ag}^+] = 1.8 \times 10^{-10}/0.0500 \\ = 3.6 \times 10^{-9} \text{ M}$$

$$\text{Lead: } [\text{Cl}^-] = \{K_{\text{sp}}/[\text{Pb}^{2+}]\}^{1/2} \\ = \{1.7 \times 10^{-5}/0.0200\} \\ = 0.029 \text{ M}$$

## Precipitation

### Example:

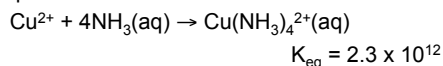
- How much  $\text{Ag}^+$  will remain in solution when lead begins to precipitate?

$$[\text{Cl}^-] = 0.029 \text{ M when lead begins to precipitate} \\ [\text{Ag}^+] = K_{\text{sp}}/[\text{Cl}^-] = 1.8 \times 10^{-10}/0.029 \\ = 6.2 \times 10^{-9} \text{ M}$$

$$\% \text{Ag remaining} = 6.2 \times 10^{-9}/0.0500 \times 100\% \\ = .0000124\%$$

### Complex Formation

- Frequently, a metal may combine with one or more simple anions or neutral species to form an ion soluble in water. The resulting ion is called a complex ion:



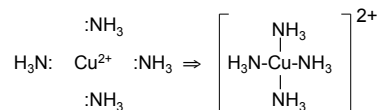
Copper acts as a Lewis Acid (accepts pair of electrons) and ammonia acts as a Lewis Base (donates pair of electrons)

### Complex Formation

$\text{Cu}^{2+}$  electron configuration:  $[\text{Ar}] 4s^2 3d^7$

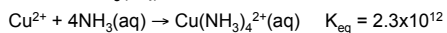
$\text{Cu}^{2+}$  hybridizes to  $sp^3d^2$  which leaves unoccupied hybrid orbitals

Each  $\text{NH}_3$  has an electron lone pair on the nitrogen atom which fills the hybrid orbitals to make a complex ion:



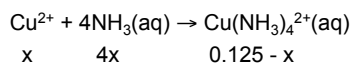
### Complex Formation

Example: Determine the concentration of  $\text{Cu}^{2+}$  in a 0.50 M  $\text{NH}_3(\text{aq})$  solution



because the equilibrium constant is large, the reaction will strongly favor the product

$\therefore$  let reaction go completely to right, and then allow some dissociation back to reactants



### Complex Formation

Example: Determine the concentration of  $\text{Cu}^{2+}$  in a 0.50 M  $\text{NH}_3(\text{aq})$  solution

$$K_{\text{eq}} = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 2.3 \times 10^{12}$$

$$= \frac{(0.125 - x)}{x(4x)^4} = 2.3 \times 10^{12} \quad \text{assume } x \text{ is negligible}$$

$$\text{rearranging gives: } 256x^5 = \frac{0.125}{2.3 \times 10^{12}}$$

$$x = 7.3 \times 10^{-4} \text{ M} = [\text{Cu}^{2+}]$$

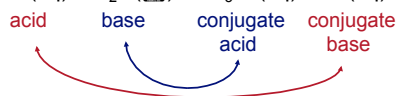
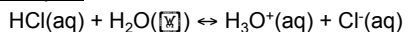
### Acids and Bases

- Brønsted-Lowry acids and base
  - Acid:  $\text{H}^+$  ion donor
  - Base:  $\text{H}^+$  ion acceptor
- Brønsted-Lowry acids are also called protic acids because they donate protons ( $\text{H}^+$ )

### Conjugate Acids & Bases

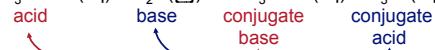
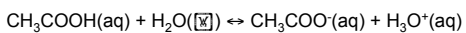
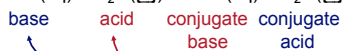
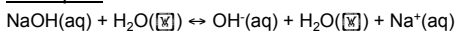
- Acids react with bases and *vice versa*
- All acids and bases come with a *conjugate* pair—a base or acid, respectively, that is formed in conjunction with the original species

Examples



## Conjugate Acids & Bases

### Examples



## Strengths of Acids and Bases

- Strong acids donate  $\text{H}^+$  ions more easily
  - The stronger the acid, the weaker the conjugate base associated with that acid
- Strong bases accept  $\text{H}^+$  ions more easily
  - The stronger the base, the weaker the conjugate acid associated with that base

Strong 100% ionized ( $\text{H}^+$ completely donated to water)	Conjugate acid	Conjugate base	Extremely weak (negligible $\text{H}^+$ acceptance from water)
	$\text{H}_2\text{SO}_4$	$\text{HSO}_4^-$	
	$\text{HBr}$	$\text{Br}^-$	
	$\text{HCl}$	$\text{Cl}^-$	
	$\text{HNO}_3$	$\text{NO}_3^-$	
	$\text{H}_2\text{O}^+$	$\text{H}_2\text{O}$	
	$\text{H}_2\text{SO}_3$ (sulfurous)	$\text{HSO}_3^-$	
	$\text{HSO}_4^-$	$\text{SO}_4^{2-}$	
	$\text{H}_3\text{PO}_4$ (phosphoric)	$\text{H}_2\text{PO}_4^-$	
	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$	
	$\text{HF}$ (hydrofluoric)	$\text{F}^-$	
	$\text{HNO}_2$ (nitrous)	$\text{NO}_2^-$	
	$\text{CH}_3\text{COOH}$ (acetic)	$\text{CH}_3\text{COO}^-$	
	$\text{H}_2\text{CO}_3$ (carbonic)	$\text{HCO}_3^-$	
	$\text{H}_2\text{S}$ (hydrosulfuric)	$\text{HS}^-$	
	$\text{H}_2\text{PO}_4^-$	$\text{HPO}_4^{2-}$	
	$\text{NH}_4^+$	$\text{NH}_3$	
	$\text{HCN}$	$\text{CN}^-$	
	$\text{HCO}_3^-$	$\text{CO}_3^{2-}$	
	$\text{H}_2\text{O}$	$\text{OH}^-$	
	$\text{OH}^-$	$\text{O}^{2-}$	
	$\text{H}_2$	$\text{H}^-$	
	$\text{CH}_4$	$\text{CH}_3^-$	
Extremely weak (negligible $\text{H}^+$ donation to water)			100% reacted with $\text{H}^+$ from water

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## The pH Scale

- pH is a measure of the hydronium ion content of a solution
- pH is defined as:
 
$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$
 log is log base 10, not ln (natural log)  
 $[\text{H}_3\text{O}^+]$  is given in molar units (M)
- pH of pure water ( $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-7} \text{ M}$ ):
 
$$\text{pH} = -\log(1.0 \times 10^{-7}) = 7.0$$

## The pH Scale

- Neutral is defined as the pH of pure water:
 
$$\text{pH} = 7$$
- Acidic solutions have pH lower than 7:
 
$$\text{pH} < 7 \Rightarrow \text{acidic}$$
- Basic solutions have pH larger than 7:
 
$$\text{pH} > 7 \Rightarrow \text{basic}$$

## The pH Scale

- We can also use pOH to describe a solution
- pOH is defined as:
 
$$\text{pOH} = -\log[\text{OH}^-]$$
- The sum of pH and pOH must equal 14
 
$$\text{pH} + \text{pOH} = 14$$
 assuming room temperature (25 °C)

## The pH Scale

### Example

Find  $[H_3O^+]$  of a solution that has  $pOH = 9.37$

**Method 1:** Calculate pH, then  $[H_3O^+]$

**Step 1:** Determine pH

$$pH = 14 - pOH = 14.00 - 9.37 = 4.63$$

**Step 2:** Determine  $[H_3O^+]$

$$[H_3O^+] = 10^{-pH} = 10^{-4.63} = 2.34 \times 10^{-5} \text{ M}$$

## The pH Scale

### Example (con't.)

Find  $[H_3O^+]$  of a solution that has  $pOH = 9.37$

**Method 2:** Calculate  $[OH^-]$ , then  $[H_3O^+]$  using  $K_w$

**Step 1:** Determine  $[OH^-]$

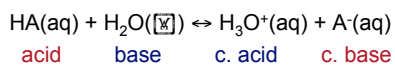
$$[OH^-] = 10^{-pOH} = 10^{-9.37} = 4.27 \times 10^{-10} \text{ M}$$

**Step 2:** Determine  $[H_3O^+]$  using  $K_w$

$$[H_3O^+] = K_w/[OH^-] = (1.0 \times 10^{-14})/(4.27 \times 10^{-10}) \\ = 2.34 \times 10^{-5} \text{ M}$$

## Ionization Constants

- The extent of dissociation of an acid or base in  $H_2O$  can be quantified using its *ionization constant*— $K_a$  is a specific type of equilibrium constant



$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[H_3O^+][\text{conjugate base}]}{[\text{acid}]}$$

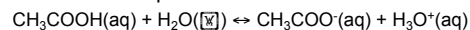
$[HA]$  = undissociated acid in solution

## Ionization Constants

### Example:

Acetic acid has a  $K_a = 1.8 \times 10^{-5}$

Determine the pH of a 0.2 M acetic acid solution



	$CH_3COOH$	$CH_3COO^-$	$H_3O^+$
initial	0.2	0	0
$\Delta$	-x	x	x
equil	.2 - x	x	x

## Ionization Constants

**Example (con't.):** Determine the pH of a 0.2 M acetic acid solution

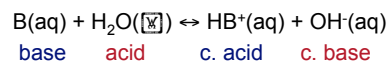
$$K_a = 1.8 \times 10^{-5} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{x^2}{.2 - x} \Rightarrow x = 0.0019 \text{ M}$$

$$pH = -\log[H_3O^+] = -\log(.0019) = 2.7$$

## Ionization Constants

- $K_b$  is a specific equilibrium constant for bases



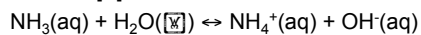
$$K_b = \frac{[HB^+][OH^-]}{[B]} = \frac{[OH^-][\text{conjugate acid}]}{[\text{base}]}$$

$[B]$  = undissociated base in solution

### Ionization Constants

#### Example:

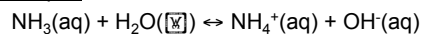
Determine [B] in a  $1.82 \times 10^{-3}$  M solution of  $\text{NH}_3$



	$\text{NH}_3$	$\text{NH}_4^+$	$\text{OH}^-$
initial	$1.82 \times 10^{-3}$	0	0
$\Delta$	-x	x	x
equil	$1.82 \times 10^{-3} - x$	x	x

### Ionization Constants

#### Example:



$$K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{1.82 \times 10^{-3} - x}$$

$$x = 1.72 \times 10^{-4} \text{ M} = [\text{NH}_4^+] = [\text{OH}^-]$$

$$\begin{aligned} [\text{NH}_3] &= 1.82 \times 10^{-3} \text{ M} - 1.72 \times 10^{-4} \text{ M} \\ &= 1.65 \times 10^{-3} \text{ M} \end{aligned}$$

### Ionization Constants

- $K_a$  and  $K_b$  are related through  $K_w$  (autoionization constant of water):

$$K_a \cdot K_b = K_w$$

$$K_a = K_w / K_b$$

$$K_b = K_w / K_a$$

- Example: Acetic acid has  $K_a = 1.8 \times 10^{-5}$ . what is  $K_b$  for acetate ion ( $\text{CH}_3\text{COO}^-$ )?

$$K_b = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$$