# CH 302 – Unit 2 Review 2

LE CHATELIER'S PRINCIPLE, INTRODUCTION TO ACIDS & BASES

# Brief overview of Equilibrium Terminology

- We use K and $\Delta G^\circ$ to express which side of a reaction is "favored"
  - If $K > 1$ , the products are favored ($\Delta G^\circ$ is negative)
  - If $K < 1$ , the reactants are favored ($\Delta G^\circ$ is positive)
- We use the relationship between Q and K to explain which way a reaction will progress toward equilibrium
  - If the starting point of a reaction is $Q < K$, the reaction moves forward toward equilibrium
  - If the starting point of a reaction is $Q > K$, the reaction moves backward toward equilibrium.
- We stress a system at equilibrium to examine how a reaction will "shift" to oppose the stress
  - This is what we will look at today with Le Chatelier's Principle

# Le Chatelier’s Principle

# Le Chatelier’s Principle

- Le Chatelier’s Principle creates the guidelines for how a system responds to any disruption of equilibrium
- In other words, a system at equilibrium will respond to stress by directly opposing the stress.
- Factors that might disrupt equilibrium include:
  - Adding or removing species involved in a reaction
  - A change in the volume or pressure
  - A change in temperature
  - Dilution or concentration of the system
- Note: the “why” of Le Chatelier’s Principle will be just as important on the test as predicting the outcome of the stress

# Le Chatelier's Principle: Adding/Removing Stuff

- By adding or removing product or reactant, you are manipulating Q
- When you manipulate Q, the reaction "shifts" to get you back to K

$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K_p = \frac{(P_{HCl})^2}{P_{H_2} P_{Cl_2}}$$

Add product → Q becomes greater than K, reaction shifts toward the reactants

Add reactant → Q becomes less than K, reaction shifts toward the products

# Le Chatelier's Principle: Adding/Removing Stuff

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$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

$$K_p = \frac{(P_{HCl})^2}{P_{H_2} P_{Cl_2}}$$

Remove product → Q becomes less than K, reaction shifts toward the products

Remove reactant → Q becomes greater than K, reaction shifts toward the reactants

# Le Chatelier's Principle: Volume and Pressure

- By changing the volume or pressure, you can manipulate Q for a gaseous system.
- The reaction shifts based on the number of gas species in the products or reactants

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

$$K_p = \frac{(P_{NH_3})^2}{(P_{H_2})^3 P_{N_2}}$$

Reduce the volume → Increase the pressure

If you increase the pressure, you are causing the most stress on the side of the reaction with the most gas species. **The reaction will shift toward the side of the least gas species.**

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Increase the volume → Decrease the pressure

If you decrease the pressure, you are causing the most stress on the side of the reaction with the least gas species. **The reaction will shift toward the side of the most gas species.**

# Le Chatelier's Principle: Concentration

- Based on the same principle, changing the concentration is changing the volume of the solvent (as opposed to the volume of the container in the previous example).
- The reaction shifts based on the number of aqueous species in the products or reactants

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

$$K_A = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Concentrate the solution →

If you concentrate the solution, you are causing the most stress on the side with the most aqueous species. **The reaction will shift in toward the side with the least aqueous species.**

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

$$K_A = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

Dilute the solution →

If you dilute the solution, you are causing the most stress on the side with the least aqueous species. **The reaction will shift toward the side of the most aqueous species.**

# Temperature Dependence of K

- All previous examples of Le Chatelier's principle involve manipulating Q to cause stress on a system at equilibrium.
- By changing temperature, you are actually able to change K.

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

By increasing K, you are shifting toward the products.

By decreasing K, you are shifting toward the products.

# Le Chatelier's Principle: Temperature

- To simplify the relationship between K and temperature, we can think of temperature like a product or a reactant of a chemical reaction depending on whether the reaction is exothermic or endothermic.
- Endothermic reactions are driven by an input of heat; therefore, heat is a reactant. Increasing the heat is like adding a reactant. This shifts the equilibrium toward the products.

$$\text{Heat} + \text{Reactants} \rightleftharpoons \text{Products}$$

- Exothermic reactions have an output of heat; therefore, heat is a product. Increasing the heat is like adding a product. This shifts the equilibrium toward the reactants.

$$\text{Reactants} \rightleftharpoons \text{Products} + \text{Heat}$$

# Questions

Consider the reaction below when it is at equilibrium:

$3NO_2(g) + H_2O(l) \rightleftharpoons 2HNO_3(aq) + NO(g)$ $\Delta H^\circ = -34 kJ/mol$

In which direction will the reaction shift when:

a. 3 moles of NO(g) are added
b. The temperature is raised to 320K
c. The total pressure is increased (by compression)
d. Remove 0.5L of water

# Intro to Acids and Bases

# Acids and Bases Fundamentals

- How we go from neutral to an acidic or basic solution depends on what we throw in water. We categorize these chemicals based on their behavior in water (acid or base) and their relative strength.
- Arrhenius Definition:
  - Acids produce $H_3O^+_{(aq)}$ in solution
  - Bases produce $OH^-_{(aq)}$ in solution
- Lowry-Bronsted Definition:
  - Acids are proton **donors**
  - Bases are proton **acceptors**

# Acids and Bases Fundamentals

- The study of acids and bases revolves around understanding the chemical environment of aqueous solutions associated with proton and hydroxide concentrations.
- The standard units of measurement for acids and bases are pH and pOH

$$pH = -\log[H^+] \qquad pOH = -\log[OH^-]$$

- Some things to note about this relationship:
  - Because this relationship is based on the negative log, **a high value of $[H^+]$ will have a low pH value**.
  - By using a logarithmic scale, you should understand that a difference between pH = 2 and pH = 7 is not a difference of 5, **but 5 orders of magnitude**.

# A particularly important K value

$K_w$ represents the auto-ionization of water; that is, it is the equilibrium constant for the following reaction at 298.15K:

- $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$
- $K_w = 1.0 \times 10^{-14} = [H^+][OH^-]$
- **$K_w$ represents the standard for our pH scale**
  - For a neutral solution, pH = 7
    - **Acidic solutions** have pH < 7
    - **Basic solutions** have pH > 7
  - Therefore, at $K_w$ for a neutral solution the $H^+$ and $OH^-$ concentrations are equal to $1.0 \times 10^{-7}$
  - $K_w$ for a basic or acidic solution will have different values of $H^+$ and $OH^-$, but their product will still = $1.0 \times 10^{-14}$
- **$K_w$ is important to our discussion because it holds its value no matter the pH**
  - **If we want to switch between pH and pOH, we can simply insert values into our $K_w$ expression.**

# Warm-Up Question

What is the pH of a 0.5M $HNO_3$ solution?

# Warm-Up Question

What is the pOH of a 0.5M $HNO_3$ solution?

# Warm-Up Question

What is the hydronium ion concentration of a 0.3M calcium hydroxide solution?

# Challenging Question

The hydrogen ion concentration in a 25˚C solution is 630 times the concentration of the hydroxide ion. What is the pH of this solution?

# Final Question (Conceptual)

Which of the following is true for a neutral pure water solution at any temperature?

a. $K_w = 1.0 \times 10^{-14}$
b. $1.0 \times 10^{-14} = [H^+][OH^-]$
c. $[H^+]=[OH^-]$
d. $[H^+]$ and $[OH^-]$ aren't always equal

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

$$[H^+] = 630[OH^-]$$

$$K_w = [H^+][OH^-] = 1\times10^{-14}$$

$$x = [H^+]$$

$$\frac{x}{630} = [OH^-]$$

$$1\times10^{-14} = (x)\left(\frac{x}{630}\right)$$

$$\sqrt{6.3\times10^{-12}} = \sqrt{x^2}$$

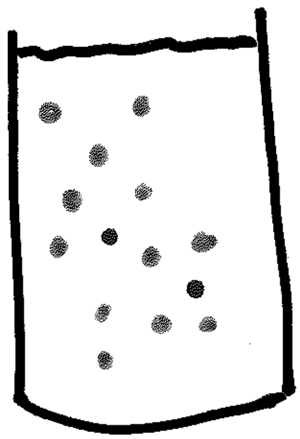
$$2.51\times10^{-6} = x = [H^+]$$

$$pH = -\log(x)$$

$$= 5.6$$

$$A_{(aq)} + 2B_{(aq)} \rightleftharpoons 2C_{(aq)}$$

4M 2M 8M @ equil



$$K_c = \frac{[C]^2}{[A][B]^2}$$

$$K_c = \frac{8^2}{4 \cdot 2^2} = 4$$

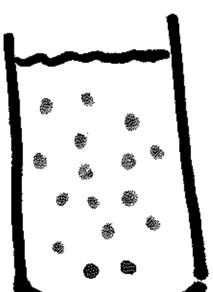
1L

+ 2 moles A

concentrate ×2

dilute ×2

1)

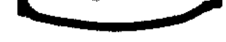


1L

$$A + 2B \rightleftharpoons 2C$$

$$Q = \frac{8^2}{6 \times 2^2} = 2.67$$

2)



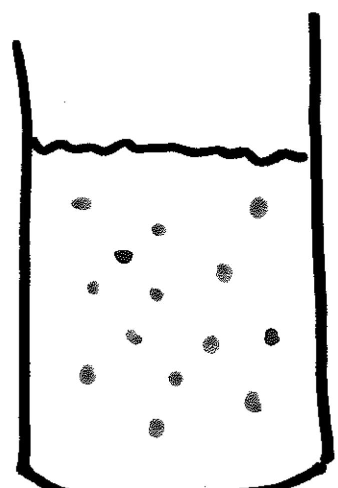
0.5L

$$\frac{16^2}{8 \times 4^2} = 2$$

$Q < K$

→

3)



2L

$$\frac{4^2}{2 \times 1} = 8$$

$Q > K$

←

$$3NO_{2}(g) + H_2O(l) \rightleftharpoons 2HNO_3(aq) + NO(g)$$

a) ⟵ stress

b) ⟵ (+ heat) stress

c) stress ⟶

d) no effect of $H_2O$ BUT → $HNO_3$ becomes more concentrated

⟵ shifts

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Adding, shifts opposite

Removing, shifts toward

# Arrhenius

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

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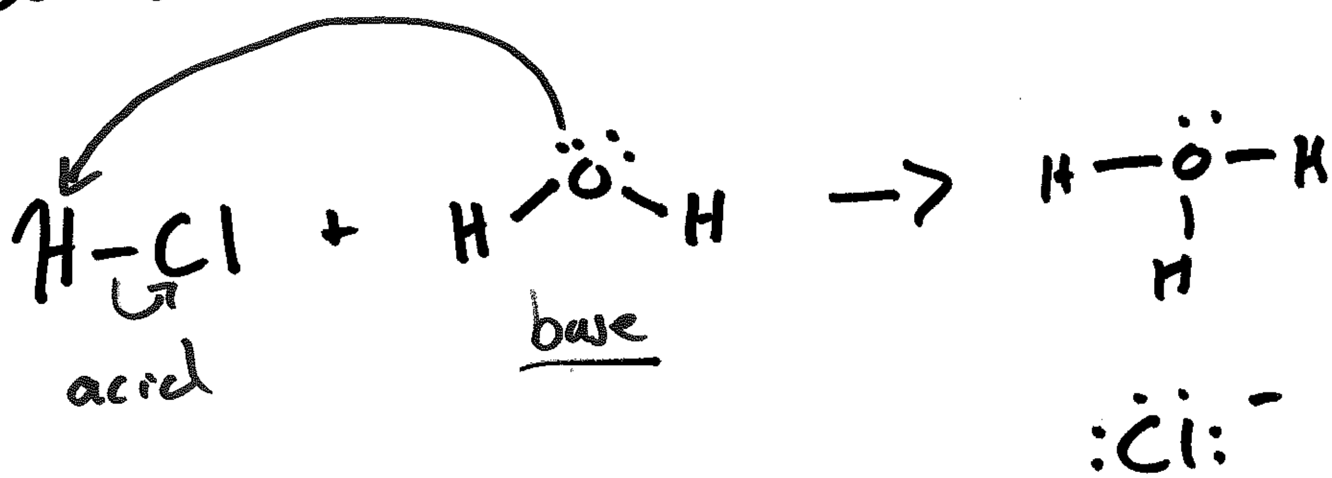
Lowry - Bronsted




[ Both deal with **Protons** & hydroxide ions ]

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$K_w = [H^+][OH^-] = 1\times10^{-14}$$

$$(1\times10^{-7})(1\times10^{-7}) = 1\times10^{-14}$$

$-\log$ $\qquad$ $-\log(\ )$

$$pH + pOH = pK_w$$

$$7 + 7 = 14$$

$$pOH = 14 - pH$$

$$pH = 14 - pOH$$

$$K_w = 1\times10^{-14} = [H^+][OH^-]$$

$HNO_3$, $H_2SO_4$, $HClO_4$, $HClO_3$

1) $0.5 M \; HNO_3 \Rightarrow 0.5 M \; [H^+]$

$$pH = -\log[HNO_3]$$
$$-\log(0.5)$$
$$= 0.3$$

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2) $$K_w = [H^+][OH^-]$$

$$pOH = 14 - pH$$
$$14 - 0.3$$
$$pOH = 13.7$$

✓

#3) $\overset{0.3M}{Ca(OH)_2} \rightarrow Ca^{2+} + \underline{2OH^-}$

$\underline{0.6M\ OH^-}$

$H^+$?

$pOH = -\log(0.6M)$

$= 0.22$

$pH = 14 - 0.22$

$pH = 13.78$

$[H_3O^+] = 10^{-pH}$

$= 10^{-13.78}$

$= \underline{1.7 \times 10^{-14}}$

$K_w = (0.6)(1.7 \times 10^{-14})$