

CH 302 – Unit 2 Review 2

LE CHATELIER'S PRINCIPLE; INTRO TO ACID-BASE

NOTES AT THE END

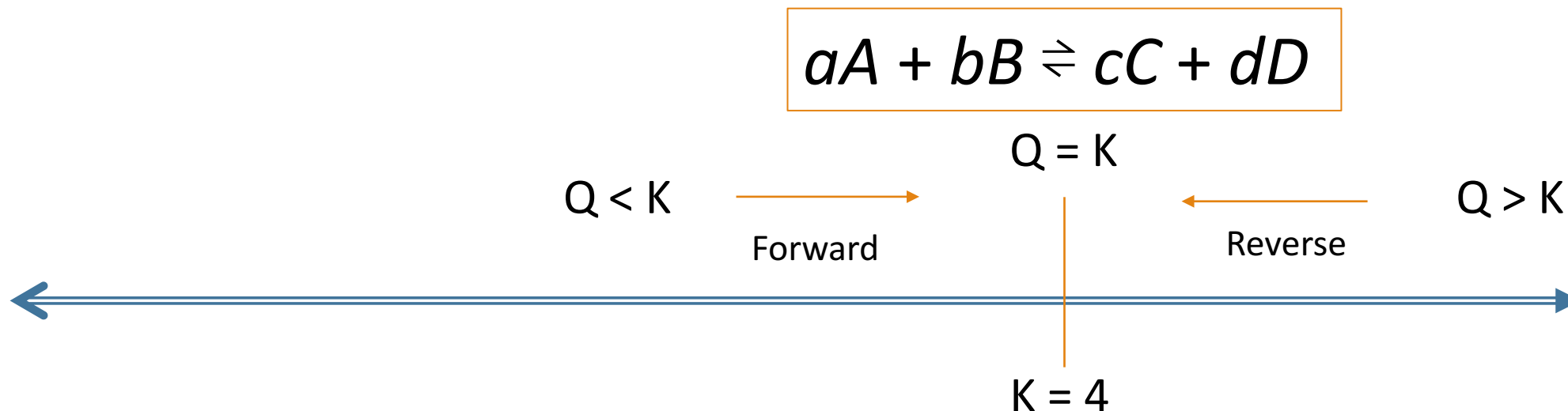
Conceptual Pillars of Equilibrium

1. Many spontaneous chemical reactions reach the lowest free energy state at some point where your reaction mixture is a combination of both products and reactants. This means that many reactions don't just move forward 100%. The amount (concentration or pressure) of products and reactants at the lowest free energy state is quantified using K .
2. **Focus of Today: As written, a reaction can move forward (toward the “products”) or backward (toward the “reactants”), depending on the starting point concentrations (Q) and their relationship to K**
3. Equilibrium is simultaneously the lowest free energy state of a reaction and the point in the extent of the reaction in which ΔG_{rxn} is equal to zero.

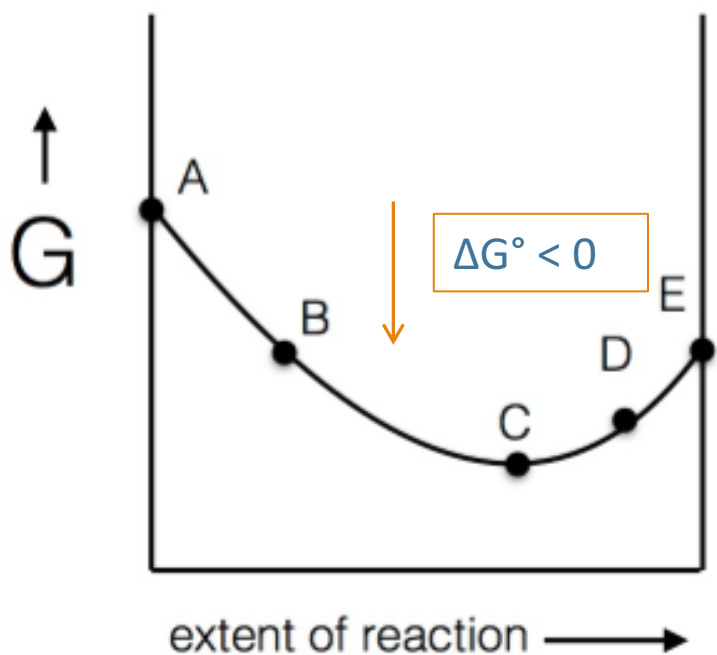
Q vs K: Chemical Equilibrium Terminology

1. $Q < K$: reaction moves **forward** toward equilibrium
2. $Q = K$: reaction is at equilibrium (lowest energy state)
3. $Q > K$: reaction moves **backward** toward equilibrium

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$



Visualizing Free Energy, K, and Q



- A. Q is equal to 0. No matter what K is, Q will be less than K. Reaction will move forward toward equilibrium. $\Delta G_{\text{rxn}} < 0$
- B. Q is less than K. Reaction will move forward. $\Delta G_{\text{rxn}} < 0$
- C. Q is equal to K. Reaction is at equilibrium. $\Delta G_{\text{rxn}} = 0$
- D. Q is greater than K. Reaction will slope back toward the reactants. $\Delta G_{\text{rxn}} > 0$
- E. Q is infinity. No matter what K is, Q will be greater than K. Reaction will move backward toward equilibrium. $\Delta G_{\text{rxn}} > 0$

Quantifying Free Energy, K, Q

Free Energy, K, and Q are all related based on the following formulas:

$$\Delta G_r = \Delta G_r^\circ + RT \ln Q \longrightarrow$$

The free energy of a reaction under any measurable initial conditions

$$\Delta G_r^\circ = -RT \ln K \longrightarrow$$

At equilibrium, $\Delta G_r = 0$. Also, $Q = K$. Therefore, we get a new equation for the relationship between standard free energy and K.

$$K = e^{\frac{-\Delta G_r^\circ}{RT}} \longrightarrow$$

We can rearrange this equation to solve directly for a K value at a given temperature given the standard free energy change.

Le Chatelier's Principle

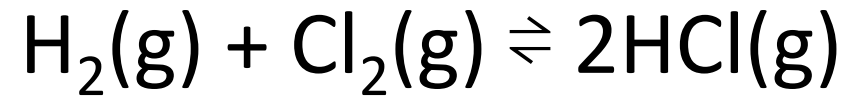
- Le Chatelier's Principle creates the guidelines for how a system responds to any disruption of equilibrium
- In other words, a system at equilibrium will respond to stress by directly opposing the stress.
- Factors that might disrupt equilibrium include:
 - Adding or removing species involved in a 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

1. Adding or removing species:
 - Adding: reaction shifts toward the opposite side of the addition
 - Removing: reaction shifts toward the same side as the removal
2. Increasing or decreasing the volume (gases):
 - Increasing volume (decreasing pressure): shifts toward the side with the most gas moles
 - Decreasing volume (increasing pressure): shifts toward the side with the least gas moles
3. Diluting or concentration a solution (aqueous):
 - Diluting: shifts toward the side of the most aqueous moles
 - Concentration: shifts toward the side of least aqueous moles
4. Changing the temperature:
 - Endothermic: increasing T shifts toward products ; decreasing T shifts toward reactants
 - Exothermic: increasing T shifts toward reactants ; increasing T shifts toward products

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



$$K_p = \frac{(P_{\text{HCl}})^2}{P_{\text{H}_2} P_{\text{Cl}_2}}$$

Add product

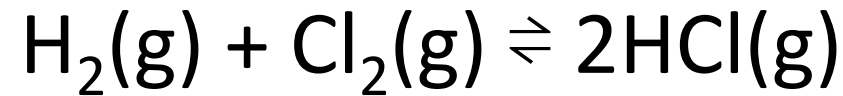
Q becomes greater than K, reaction shifts toward the reactants

Add reactant

Q becomes less than K, reaction shifts toward the products

Le Chatelier's Principle: Adding/Removing Stuff

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



$$K_p = \frac{(P_{\text{HCl}})^2}{P_{\text{H}_2} P_{\text{Cl}_2}}$$

Remove product

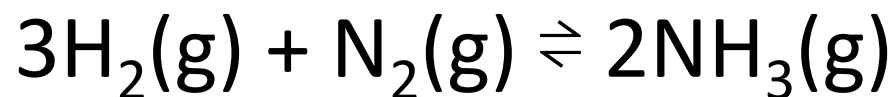
Q becomes less than K, reaction shifts toward the products

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



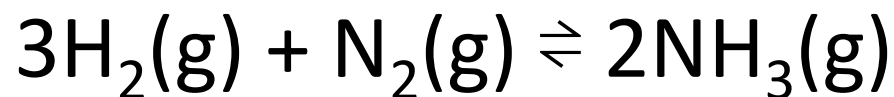
$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 P_{\text{N}_2}}$$

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.**

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



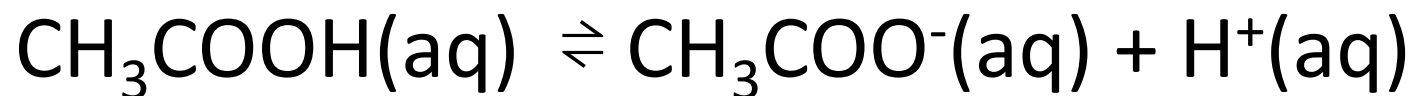
$$K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{H}_2})^3 P_{\text{N}_2}}$$

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



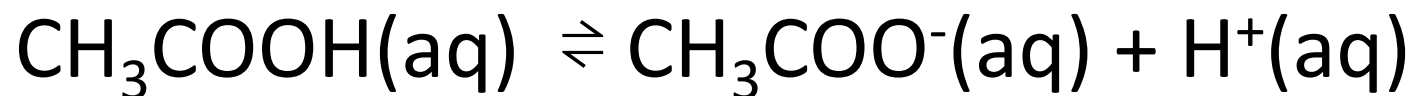
$$K_A = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

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.**

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



$$K_A = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

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

- One incredibly important (and sometimes overlooked) relationship is K and Temperature.
- K's dependence on temperature depends on whether the reaction is endothermic or exothermic. The van't Hoff Equation is:

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

When you do the math, you will see that for endothermic reactions, increasing temperature increases K. For exothermic reactions, increasing temperature decreases K. It all depends on the sign of ΔH_{rxn}

Play with some values to prove this relationship, then next week I will give you an easier way to figure this out.

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 like a reactant. Increasing the heat is like adding a reactant. This shifts the equilibrium toward the products.

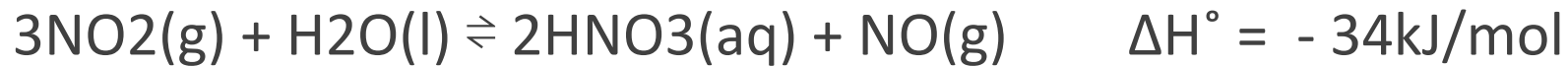


- **Exothermic reactions** have an output of heat; therefore, heat is like a product. Increasing the heat is like adding a product. This shifts the equilibrium toward the reactants.



Questions

Consider the reaction below when it is at equilibrium:



In which direction will the reaction shift when:

- a. 3 moles of $\text{NO}(\text{g})$ are added
- b. The temperature is raised to 320K
- c. The total pressure is increased (by compression)
- d. Remove 0.5L of pure water (just a conceptual example)

Intro to Acids and Bases

Acids and Bases Fundamentals

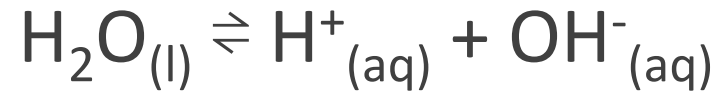
- The study of acids and bases revolves around understanding the chemical environment of aqueous solutions associated with proton and hydroxide concentrations.
- The standard units of measurement for acids and bases are pH and pOH

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

- **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:



$$K_w = 1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$$

- **K_w represents the standard for our pH scale at room temperature**
- 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 1.0×10^{-7}

Quantifying Acids and Bases

- The standard units of measurement for acids and bases are pH and pOH

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

- In a strong acid or strong base solution, we can use this relationship:

$$\text{pH} = -\log[C_A] \qquad \text{pOH} = -\log[C_B]^*$$

- pH and pOH can be interconverted using the relationship based on $\text{p}K_w$ (14):

$$\text{pH} = 14 - \text{pOH} \qquad \text{pOH} = 14 - \text{pH}$$

Quantifying Weak Acids and Bases

- For a weak acid, we are dealing with a more interesting equilibrium (additional steps). The approximation formulas are below:

$$[H^+] = \sqrt{C_{HA} \cdot K_a} \qquad [OH^-] = \sqrt{C_B \cdot K_b}$$

- Don't forget that at any time you can convert between different terms:

$$K_w = 1 \cdot 10^{-14} = [H^+][OH^-]$$

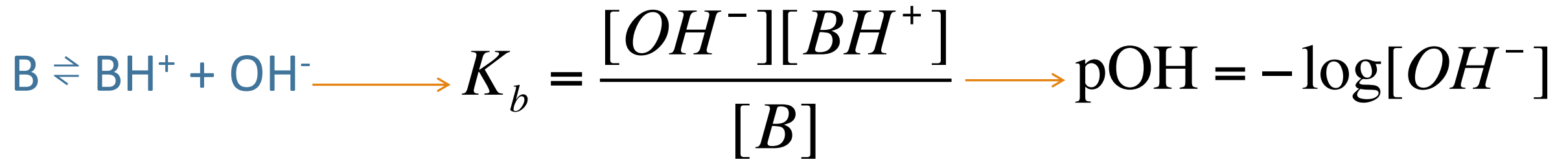
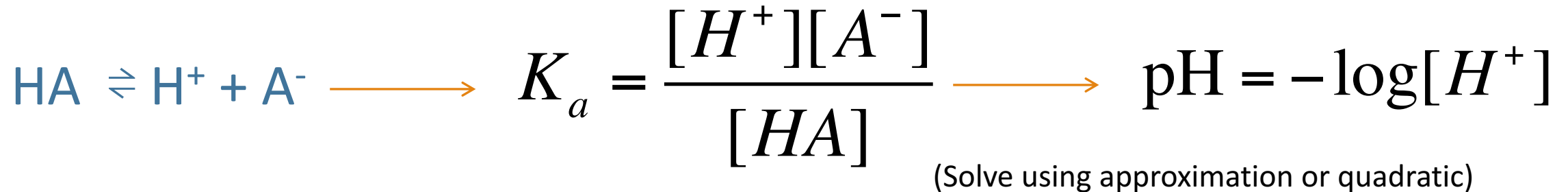
$$K_w = K_a K_b$$

$$\frac{K_w}{K_a} = K_b$$

$$\frac{K_w}{K_b} = K_a$$

Quantifying Weak Acids and Bases

- Important Reminder: K_a will get you $[H^+]$, K_b will get you $[OH^-]$. Therefore, K_a corresponds to a weak acid reaction and K_b corresponds to a weak base reaction.



Warm-Up Question

What is the pH of a 0.5M HNO₃ solution?

Warm-Up Question

What is the pOH of a 0.5M HNO₃ 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. $1.0 \times 10^{-14} = [\text{H}^+][\text{OH}^-]$
- c. $[\text{H}^+] = [\text{OH}^-]$
- d. $[\text{H}^+]$ and $[\text{OH}^-]$ aren't always equal
- e. $\text{pH} = 14 - \text{pOH}$
- f. $\text{pH} = 7$

Final Question (Conceptual)

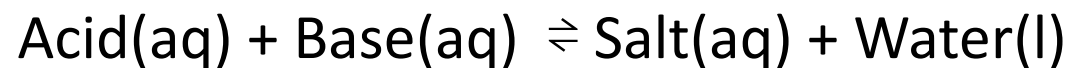
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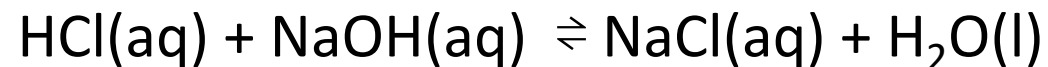
Neutralization Reactions: Salts

- The product of a neutralization reaction is a salt. In acid/base chemistry, your salt can be neutral, acidic, or basic depending on the reaction:

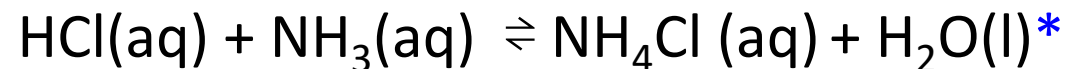
1. **GENERIC REACTION** (very helpful):



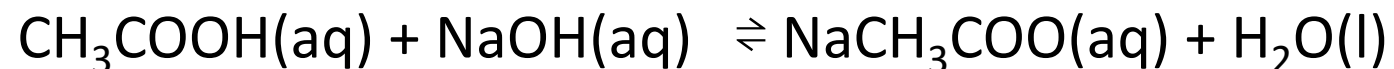
2. **Strong Acid, Strong Base: results in a neutral salt**

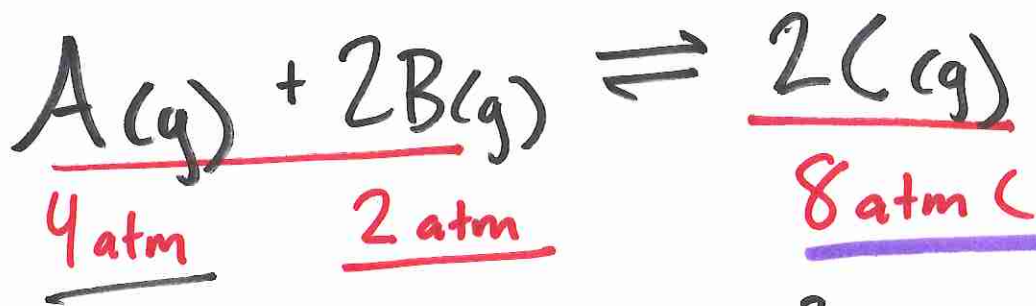


3. **Strong Acid to weak base: results in an acidic salt**

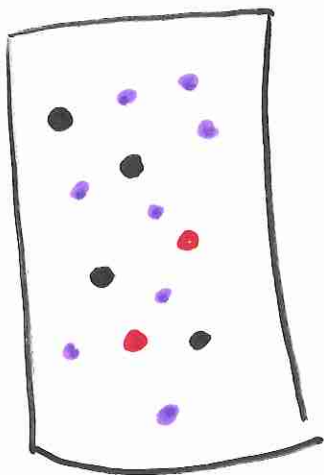


4. **Strong base to weak acid: results in a basic salt**



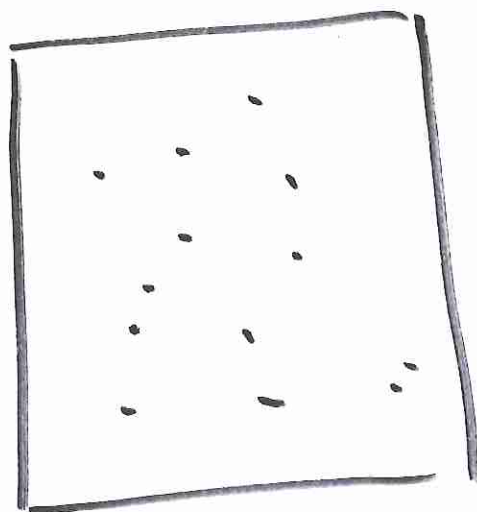


$$K_P = \frac{P_C^2}{P_A \cdot P_B^2} = \frac{8^2}{4 \cdot 2^2} = \cancel{4}$$



10L

expand
x2

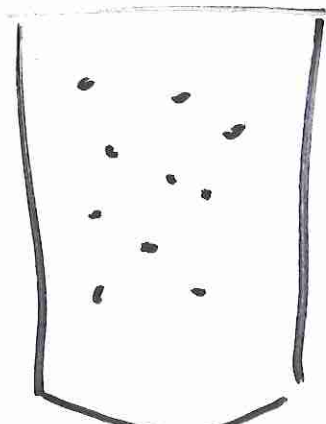


$$Q = \frac{4^2}{2 \cdot 1^2} = 8$$

$Q > K$

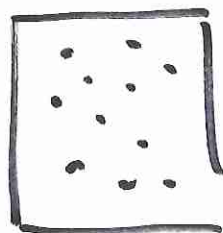
← move toward most gas moles

Add 2 atm
A



$$Q = \frac{8^2}{6 \cdot 2^2} = 2.67 \quad Q < K \rightarrow$$

compress
x2



5L

$$Q = \frac{16^2}{8 \cdot 4^2} = 2$$

$Q < K$

→
✓ move away from most gas moles



a)

← stress

b)

← + heat (smaller K)

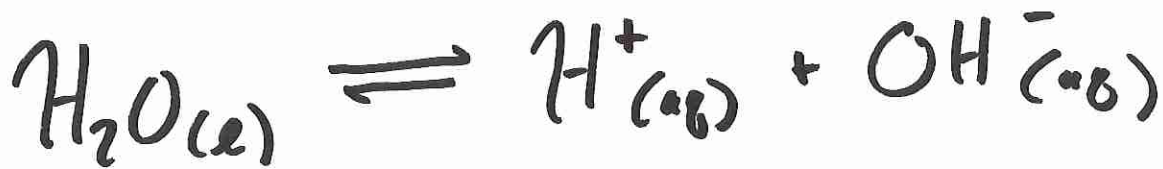
c)

stress →

d)

no effect of H₂O ...
← stress (aq)

Acid / Base



$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$$

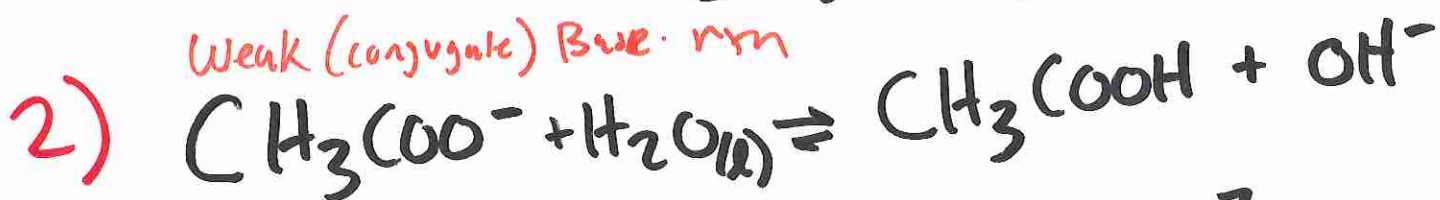
$$-\log \quad \underbrace{10^{-7} \cdot 10^{-7}}_{7 + 7 = 14} = 10^{-14}$$

Weak acid rxn:



$$\text{Weak} \Rightarrow K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

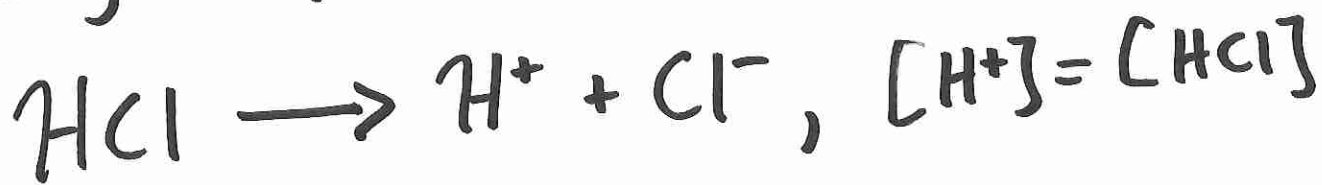
Weak (conjugate) Base rxn



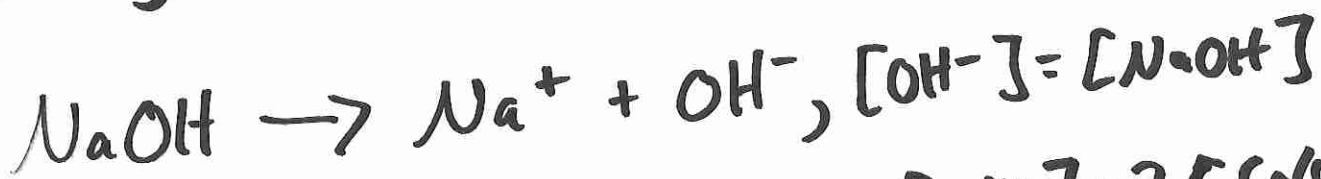
$$\text{weak} \Rightarrow K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_w = K_a \cdot K_b = [\text{H}^+][\text{OH}^-]$$

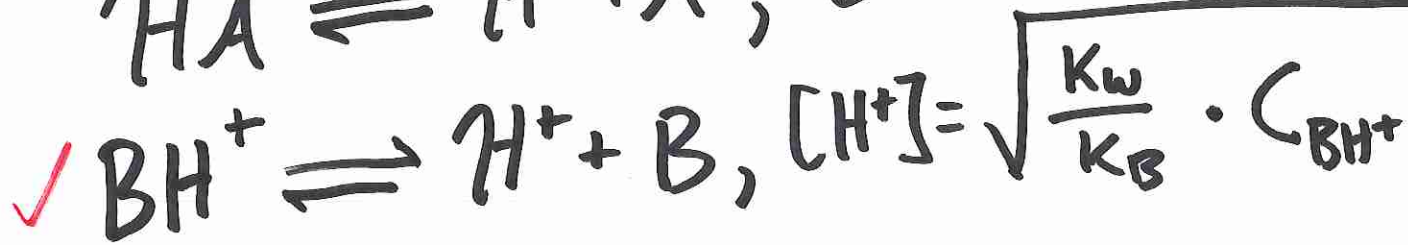
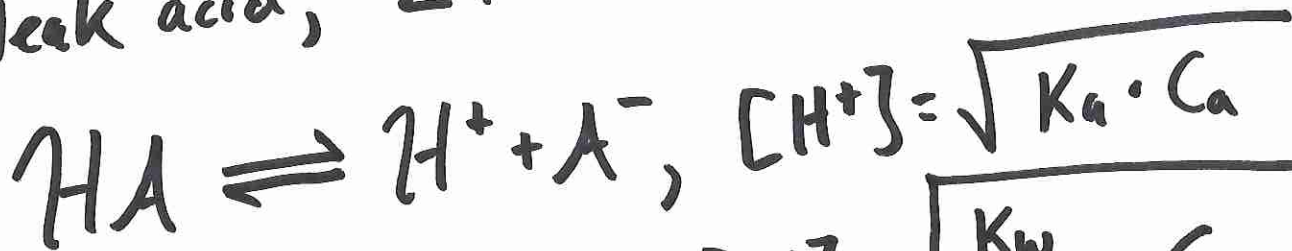
1) Strong Acid, 100% dissociation



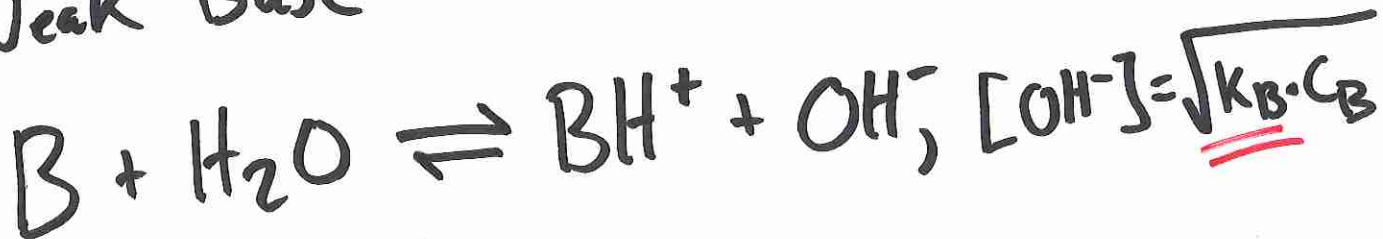
2) Strong Base,



3) Weak acid, $< 1\%$



4) Weak Base



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

$$K_w = 10^{-14} = [H^+][OH^-]$$

$$10^{-14} = (x) \left(\frac{x}{630} \right)$$

$$10^{-14} = \frac{x^2}{630}$$

$$x = 2.51 \times 10^{-6} = [H^+]$$

$$-\log(x) = \text{pH} = 5.60$$

pH of 0.5M HNO_3



$$[\text{H}^+] = 0.5\text{M}$$

$$\text{pH} = -\log(0.5) = 0.301$$

$$14 - \text{pH} = \text{pOH} = 13.70$$

$[\text{H}^+]$ in 0.3M $\text{Ca}(\text{OH})_2$

$$\rightarrow [\text{OH}^-] = 2 \times 0.3\text{M} = 0.6\text{M}$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\frac{10^{-14}}{0.6} = [\text{H}^+] = 1.67 \times 10^{-14}$$

$$\uparrow [\text{H}^+] = 10^{-13.778}$$

↓

$$\text{pOH} = -\log 0.6$$
$$= 0.222$$

$$\text{pH} = 13.778$$