CH 302 Unit 2 Exam Review

CHEMICAL EQUILIBRIUM, ACID/BASE CHEMISTRY

http://mccord.cm.utexas.edu/courses/spring2018/ch302/exam2.php

Secret Formula for Success

1. Focus on Canvas Extra Practice and old McCord homeworks. Be done with Sapling. Do ALL the problems honestly to gauge your knowledge.
2. Make an outline that simplifies the material. For Acids/Bases, write out the RICE tables to visualize the reactions; then explain to yourself and/or your study group why they are unnecessary.
3. Dr. McCord worked a few problems in class that he specifically wanted tested on the exam. It's a very good idea to re-work clicker questions from class.
4. Do not go to bed uncertain about the material. This is the difference between an 80+ and a sub-60 grade for this exam.

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.

   ΔG°_{rxn} vs K

2. 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

   Q vs 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.

   $\Delta G_{rxn} = \varnothing$

Introduction to Chemical Equilibrium

- A working definition for equilibrium is the state of a chemical reaction when the rate of the forward reaction and the reverse reaction are equal.
- At this point, there is no net change in the concentrations of your reaction ($\Delta G_{rxn} = 0$)
- We use the equilibrium constant, K, to calculate these exact amounts at equilibrium:

$$aA + bB \rightleftharpoons cC + dD$$

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

Mathematically, K is equal to the ratio of the action of the products raised to the power of their coefficients divided by the action of the reactants raised to the power of their coefficients.
Conceptually, K is a description of the equilibrium state. Not just that a reaction is "spontaneous"/"non-spontaneous", but what the actual concentrations of the products/reactants are at equilibrium

Introduction to Chemical Equilibrium

- We can directly correlate "activity" to pressure and concentration to create a relationship more suitable to test questions.

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

$$a_i = \frac{[i]}{[i]^\circ} \rightarrow K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$a_i = \frac{P_i}{P_i^\circ} \rightarrow K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

REMEMBER: the action of any LIQUID or SOLID is 1. These terms will drop out of the mass action expression.

$$aA + bB \rightleftharpoons cC + dD$$

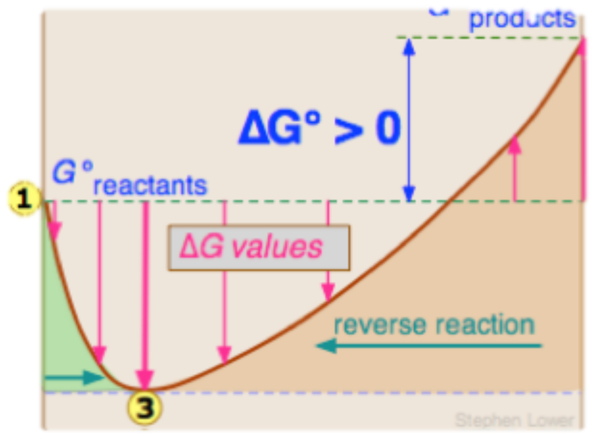
$$K = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$$

Q vs K: Chemical Equilibrium Terminology

1. Q < K : reaction moves forward toward equilibrium ⟹ −x, reactant side; +x, product side
2. Q = K : reaction is at equilibrium (lowest energy state)
3. Q > K : reaction moves backward toward equilibrium ⟹ +x, reactant side; −x, product side

Free Energy vs K

- When K is small (less than 1), only a small fraction of your reactants becomes products. A reaction with a small K reacts to a small extent.



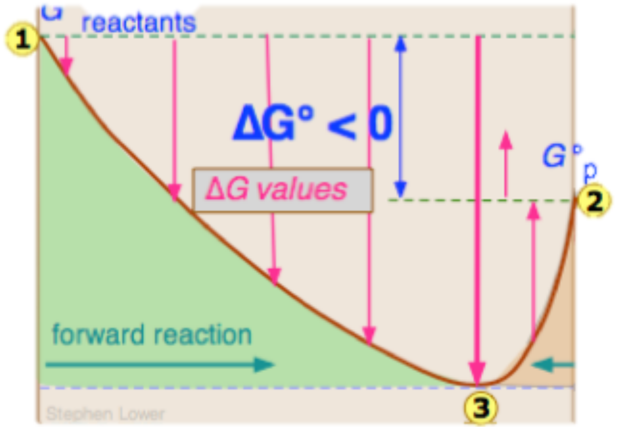
$K < 1$, $\Delta G°_{rxn} > 0$

non-spontaneous, reactant favored

- When K is large (greater than 1), a greater amount of products are formed than reactants remain. A reaction with a large K reacts to a large extent.

$K > 1$, $\Delta G°_{rxn} < 0$

Spontaneous product favored



3 Ways to Manipulate K

1. Reverse the reaction

$$2A + B \rightleftharpoons 3C + 2D \text{ , K} = 4$$

2. Multiply the coefficients by a factor, x

$$2A + B \rightleftharpoons 3C + 2D \text{ , K} = 4$$

3. Modify the temperature

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

$$K' = K^{-1}$$

$$3C + 2D \rightleftharpoons 2A + B \text{ , K} = 0.25$$

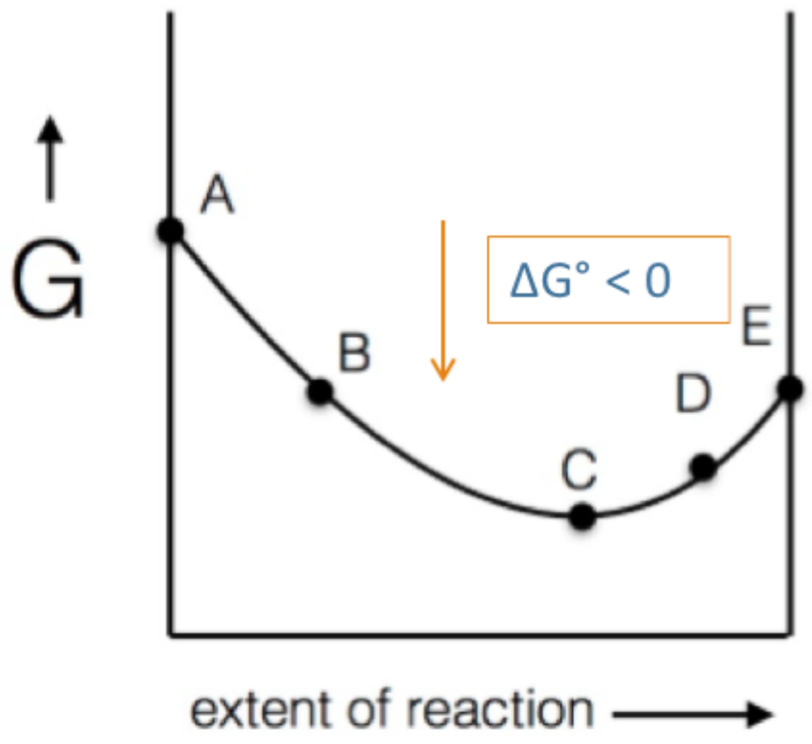
$$4A + 2B \rightleftharpoons 6C + 4D \text{ , K} = 16$$

$$K' = K^{x}$$

Brief overview of Equilibrium Terminology

- We use K and ΔG° to express which side of a reaction is "favored"
  - If $K > 1$, the products are favored (ΔG° is negative)
  - If $K < 1$, the reactants are favored (ΔG° 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
  - Stressing equilibrium can either change Q or K, resulting in more products or reactants formed

Visualizing Free Energy, K, and Q (Checklist)

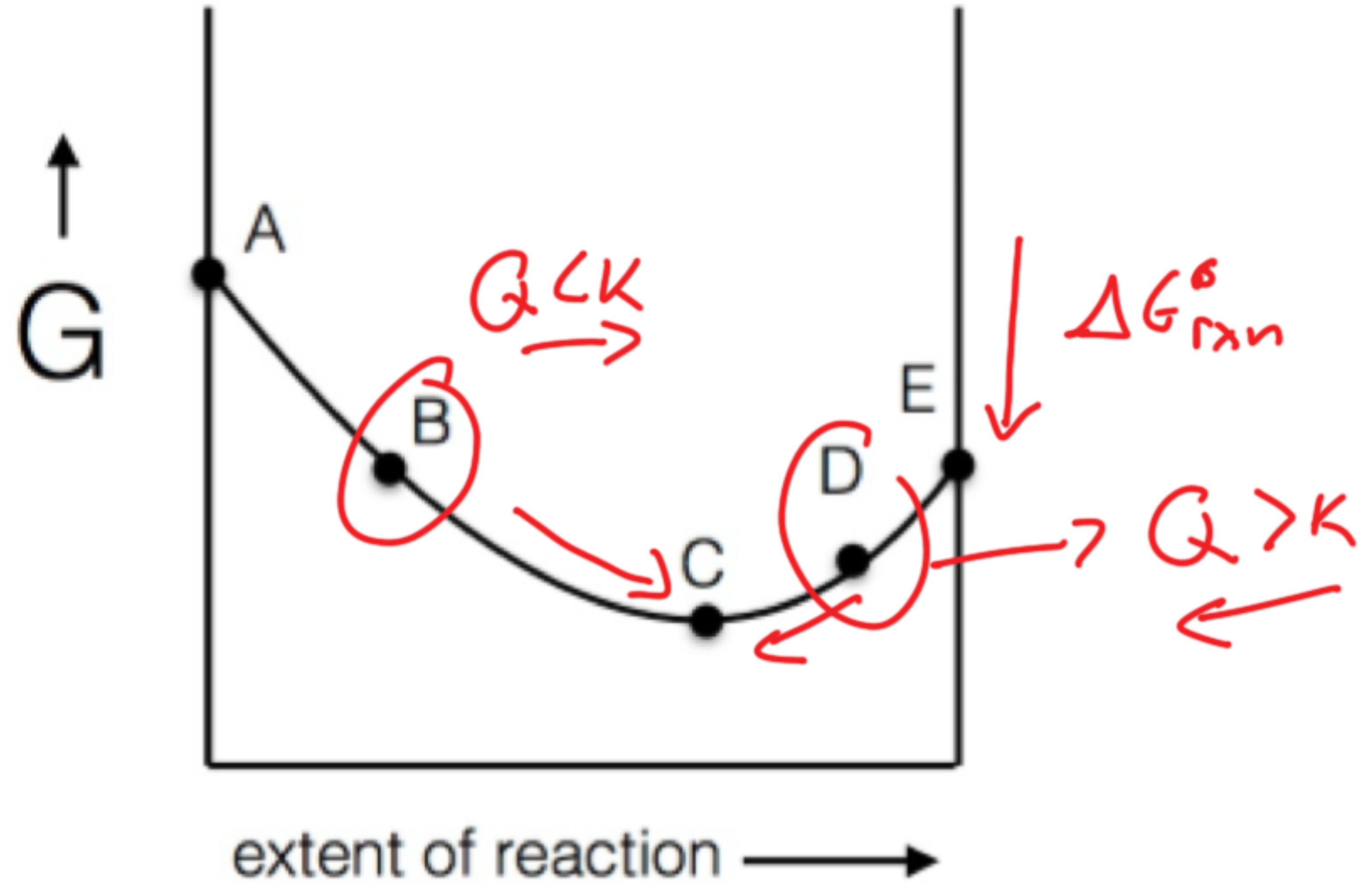


- Identify the relationship between Q and K at any given point on the graph
- Determine whether the reaction is spontaneous or non-spontaneous
- Is $\Delta G°$ positive or negative for the reaction?
- Is K greater than or less than 1 on the graph?
- Is ΔG positive or negative at any given point?

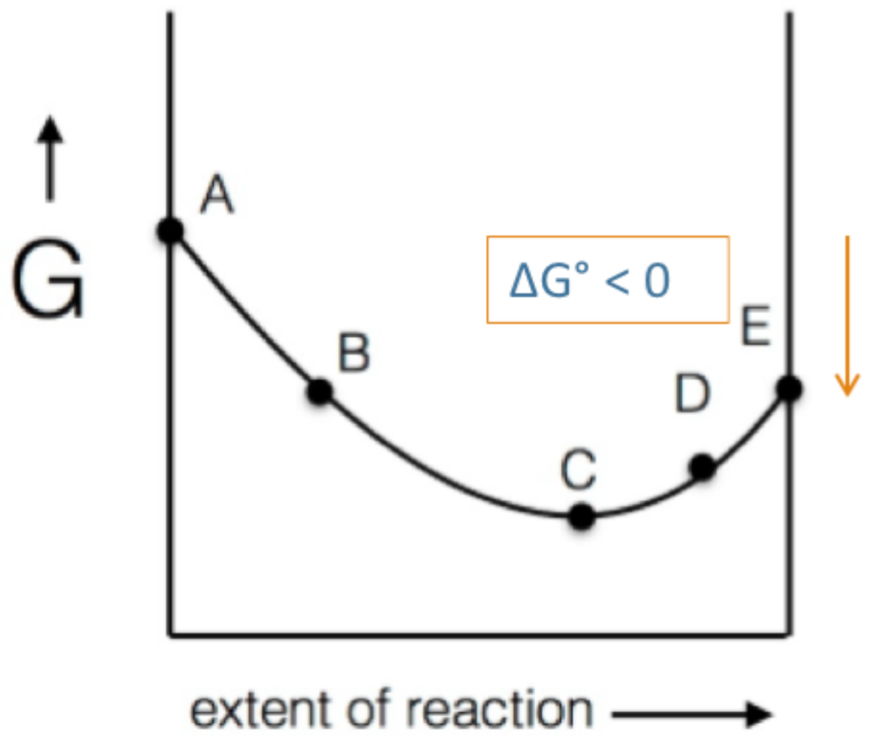
Advanced:

- How will the graph change if you compared to another reaction with a $\Delta G°$ of greater magnitude?
- How will the graph change if you increase K?

Visualizing Free Energy, K, and Q (Checklist)



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

Quantifying Free Energy, K, Q

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

$$\Delta G_r = \Delta G_r{}^\circ + RT\ln Q$$

The free energy of a reaction under any measurable initial conditions

$$\Delta G_r{}^\circ = -RT\ln K$$

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

Calculations

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

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

Strong Acid, Dilute it $[H^+]\downarrow$ $pH\uparrow$, Concentrate $[H^+]\uparrow$ $pH\downarrow$

Strong Base Dilute $[OH^-]\downarrow$ $pH\downarrow$, Concentrate $[OH^-]\uparrow$ $pH\uparrow$

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 ; decreasing T shifts toward products

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:

+ , T ↑ , k ↑

− , T ↑ , K ↓

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

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.

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

- 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.

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

Questions

Consider the reaction below when it is at equilibrium:

$3NO_2(g) + H2O(l) \rightleftharpoons 2HNO_3(aq) + NO(g)$ $\Delta H^\circ = -34 kJ/mol$

In which direction will the reaction shift when (and why):

a. 5 moles of $NO_2(g)$ are added — reactant; $Q < K$ ⟶
b. The temperature is decreased to 100 K — $\Delta H = (-)$, $T\downarrow$, $K\uparrow$ ⟶
c. The total pressure is decreased (by volume expansion) — $P\downarrow$ ⟵
d. An inert gas is added at constant volume and temperature

Nothing happens

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**.

• Be able to identify conjugates, • Weak acids have weak base conjugates

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**:

Endothermic reaction
$\Delta H \approx 56$ kJ/mol
T↑, k↑

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

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

- **K_w represents the following 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

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

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

0.5 M $Ca(OH)_2$ → $[OH^-] = 1.0$ M

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

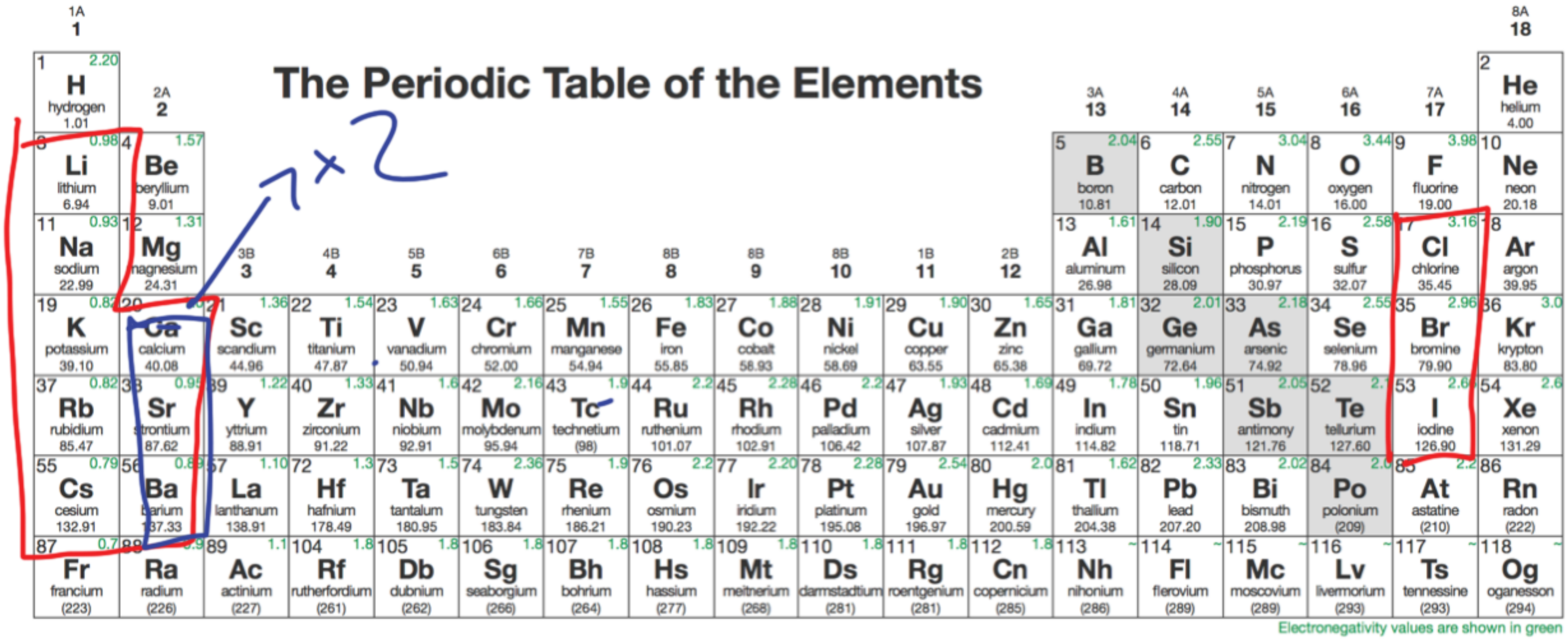
- pH and pOH can be interconverted using the relationship based on pK_w (14):

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

HNO_3, H_2SO_4, $HClO_3$

$HClO_4$

Strong Acids and Bases



Quantifying Weak Acids and Bases

$HA \rightleftharpoons H^+ + A^-$

$B + H_2O \rightleftharpoons BH^+ + OH^-$

$$[H^+] = \sqrt{C_{HA} \cdot K_a}$$

$$[OH^-] = \sqrt{C_B \cdot K_b}$$

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.

$BH^+ \rightleftharpoons H^+ + B$

$HA \rightleftharpoons H^+ + A^-$ → $$K_a = \frac{[H^+][A^-]}{[HA]}$$ → $$pH = -\log[H^+]$$

(Solve using approximation or quadratic)

$B \rightleftharpoons BH^+ + OH^-$ → $$K_b = \frac{[OH^-][BH^+]}{[B]}$$ → $$pOH = -\log[OH^-]$$

$A^- \rightleftharpoons HA + OH^-$

Percent Ionization

- Another way of explaining how much a weak acid or base dissolves is percent ionization. You can memorize the formula:

$$[H^+] = (\%\ \text{ionization})(C_{HA})$$

$[H^+]$ can be solved for using the approximation or quadratic formula. Rearrange to solve for % ionization.

If you have the % ionization, you can multiply by the concentration of your weak acid to get $[H^+]$.

$$[OH^-] = (\%\ \text{ionization})(C_B)$$

→ protonation

Note that these are fractions, 0-1, so you need to multiply by 100 to get the "percent" value

Percent Ionization to K_a

Percent ionization is a very quick, easy way of depicting electrolyte strength. K_a is, of course, the more formal way of depicting acid/base strength. The two can be converted between each other.

$$[H^+] = (\%\ \text{ionization})(C_{HA}) = x$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{C_A - x} = K_a$$

The Continuous Story (Chem Eq vs. Acid/Base)

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

e. $pH = 14 - pOH$

f. $pH = 7$

a, b, e, f

TRUE @ RT

T↑, K↑

Acid/Base Reactions

1) Strong Acid Reaction: $-\log C_A = pH$

2) Strong Base: $-\log C_B = pOH$ // $-\log(2 \times C_B) = pOH$

3) Weak acid: $[H^+] = \sqrt{K_a \cdot C_A}$ OR $[H^+] = x$ when $K_a = \frac{x^2}{C_A - x}$

4) Weak Base: $[OH^-] = \sqrt{K_B \cdot C_B}$ OR $[OH^-] = x$ when $K_B = \frac{x^2}{C_B - x}$

Approximate when

$$\frac{C_A}{K_A} > 1000$$

$$\frac{C_B}{K_B} > 1000$$

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):

   Acid(aq) + Base(aq) ⇌ Salt(aq) + Water(l)

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

   $HCl(aq) + NaOH(aq) \rightleftharpoons NaCl(aq) + H_2O(l)$

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

   $HCl(aq) + NH_3(aq) \rightleftharpoons NH_4Cl(aq) + H_2O(l)$*

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

   $CH_3COOH(aq) + NaOH(aq) \rightleftharpoons NaCH_3COO(aq) + H_2O(l)$

Neutralization Reactions: Salts

Identify whether the following solutions will be acidic, basic, or neutral. How would you solve for the pH?

Basic

0.3 M $LiCN$

Acidic

0.05 M $CH_3CH_2NH_3^+Cl^-$

Neutral

0.08 M $KClO_4$

Basic

0.1 M KF

$NH_4^+ \rightleftharpoons H^+ + A^-$

$K_b\ NH_3 = 1.8 \times 10^{-5}$

Neutralization Reactions

What is important about neutralization reactions on the test is the experimental process.
You can simplify the question below to just be a weak acid problem, but what is the concentration you use for your weak acid approximation? What is your K value?

$HClO_4(aq) + NH_3(aq) \rightleftharpoons NH_4ClO_4(aq) + H_2O(l)$

An ammonium perchlorate solution is made by combining 100 mL 0.2 M perchloric acid and 100 mL 0.2 M ammonia. What is the [H⁺]? pH? pOH?

$[H^+] = \sqrt{K_a \cdot C_a}$

$M_1V_1 = M_2V_2$

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

2) $C_1V_1 = C_2V_2$

$V_2 = 100mL + 100mL$

$$[H^+] = \sqrt{\frac{K_w}{K_b} \times \frac{C_1V_1}{V_2}}$$

Strong Base to Acid

$$[OH^-] = \sqrt{\frac{K_w}{K_a} \times \frac{C_1V_1}{V_2}}$$

CH 302 – Exam Review

ADDITIONAL SLIDES

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

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

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

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

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.**

Le Chatelier's Principle: Volume and Pressure

- By changing the volume or pressure, you can manipulate Q for a gaseous system.
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$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$$

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

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

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

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

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.**

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

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

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

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.**