CH 302 EXAM REVIEW

CHEMICAL, ACID, BASE EQUILIBRIUM

Chemical and Aqueous Equilibrium Exam Breakdown

Exam 2 $\rightarrow$ 20 Q's

~7 chem eq   ~13 acid/base

~50/50   calc + concept

Provided on exam } K_a, pK_a, K_b, pK_b
neutral species

Cinematic Study

SHUFFLE PLAY

Downloaded

Extra Practice Skip:
Chem Eq: 13 (good question, just too long/waste of time)
AB I: 37, 44
AB II: 6, 28

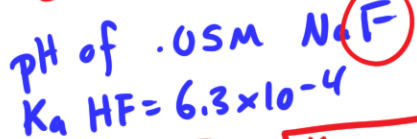# Chemical and Aqueous Equilibrium Exam Breakdown

- Describe the relationship between free energy and equilibrium
- Convert ΔG to Q, as well as $\Delta G°$ to K and vice versa.
- Determine if a system is at equilibrium and if not which direction the reaction will shift to achieve equilibrium.
- Set up and solve a RICE table for a multitude of various reaction types.
- Calculate the concentration/pressure of all species at equilibrium.
- Show a complete understanding of Le Chatelier's principle.
- Predict the response of a reaction to an applied stress (concentration, pressure, volume, temperature) both qualitatively and quantitatively.
- Calculate the new value of K when the temperature changes to a new value.

- Understand the strength of an acid (or base) as determined by the percent of ionization in solution.
- Identify strong and weak acids and bases.
- Identify acid/base conjugate pairs and their relative strengths.
- Understand the process of auto-ionization of water and what is meant by acidic, basic, and neutral.
- Know the value of K_w at 25°C, and the relationship between K_a and K_b for a conjugate pair.
- Convert between hydronium ion concentration, hydroxide ion concentration, pH and pOH for a given solution.
- Determine the pH of a strong acid or base solution.
- Determine the pH of a weak acid or weak base solution.
- Determine the pH of the solution made from the salt of a weak acid or the salt of a weak base.
- Recognize and predict the components of a buffer solution.
- Calculate the pH of a buffer solution, and a buffer

- solution after the addition of strong acid or strong base.
- Balance a reaction for the neutralization of an acid or base and calculate stoichiometric quantities throughout the reaction (titration).
- Determine the majority species for acid/base solutions as well as the pH following neutralization.
- Interpret a titration curve plot including calculating the concentration and K_a or K_b for the analyte.
- Understand the concept of an acid/base indicator, and determine which indicators are appropriate for a given titration.
- Determine the protonation state (or overall charge) for a polyprotic species at a particular pH.
- Apply concepts from equilibria to acid/base problems

Common Mistakes Stem from the Following…

1. The [OH$^-$] is two times the stated concentration for the strong bases $Ca(OH)_2$, $Sr(OH)_2$, and $Ba(OH)_2$

2. Proper use of K_a, K_b, pK_a, and pK_b
   - K_a and pK_a refer to weak acid reactions and will help you find [H$^+$]
   - K_b and pK_b refer to weak base reactions and will help you find [OH$^-$]

3. Stoichiometry counts, use the coefficients of your chemical reaction properly

4. A buffer is the result of a **partial** neutralization reaction not a **full** neutralization

$$.05 \text{ M } Ca(OH)_2$$
$$[OH^-] = .1 \text{ M}$$

$$pH \text{ of } .05M \text{ NaF}$$
$$K_a \text{ HF} = 6.3 \times 10^{-4}$$
$$[OH^-] = \sqrt{\frac{K_w}{K_a} \times .05}$$

$\rightarrow$ 0.5 moles HF + 0.5 moles NaOH
NOT buffer

$\hookrightarrow$ 0.5 moles HF + 0.4 moles NaOH ✓

Chemical Equilibrium

~7 QUESTIONS, CONCEPT HEAVY

Conceptual - ΔG, $\Delta G°$, K, and Q

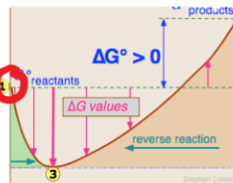$-\Delta G° \propto K$

ΔG, Q

- 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.

When the reactant is favored, the $\Delta G°$ is positive.
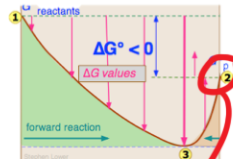
$G = 0$
$Q < K$
$\Delta G < 0$

- 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.
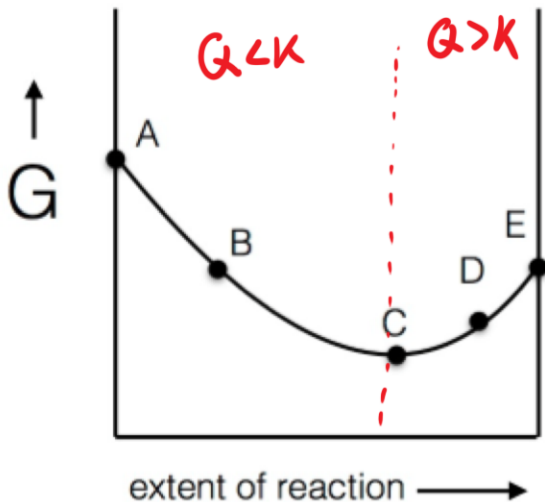
When the product is favored, the $\Delta G°$ is negative.
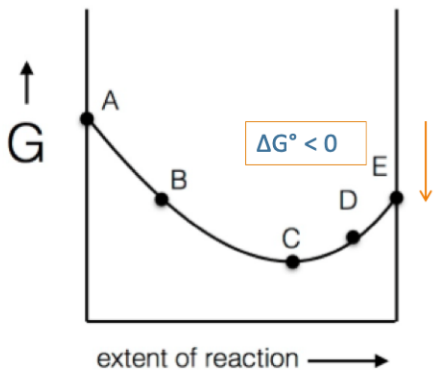

$G = Q > K$
$\Delta G > 0$

Visualizing Free Energy, K, and Q (Checklist)

- Identify the relationship between Q and K at any given point on the graph → A–C
- Determine which points the reaction is spontaneous and nonspontaneous → C–E
- Determine whether the reaction is reactant-favored or product-favored
- Is ΔG° positive or negative for the reaction?
- Is K greater than or less than 1 on the graph? K>1
- Where is ΔG = 0? C

Graph annotations: Q<K, Q>K; G (vertical axis); points A, B, C, D, E; extent of reaction →

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. $\Delta G_{rxn} > 0$

Q vs K: Chemical Equilibrium Terminology

1. Q < K : reaction moves forward toward equilibrium +X products

2. Q = K : reaction is at equilibrium (lowest energy state)

3. Q > K : reaction moves backward toward equilibrium +X reactants

Q = K

Q < K   Forward →   ← Reverse   Q > K

K = 4
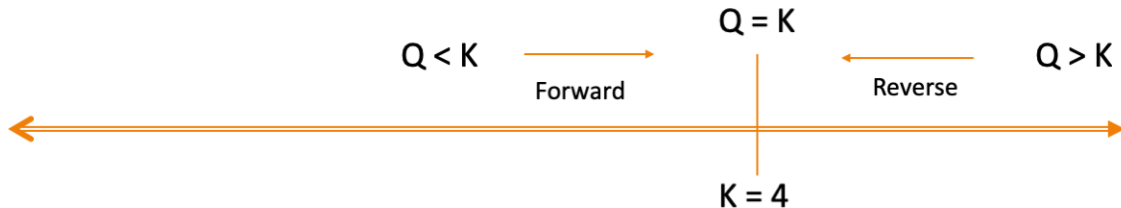
Quantifying Free Energy, K, Q

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.

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

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

Le Chatelier's Principle

"add away"
"take toward"

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):
   - Decreasing Pressure (increasing volume): shifts toward the side with the most gas moles
   - Increasing Pressure (decreasing volume): shifts toward the side with the least gas moles

   } Q

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**

   } K

Temperature Dependence of K

Changing the temperature shifts K, not Q

- K's dependence on temperature depends on whether the reaction is endothermic or exothermic. The van't Hoff Equation is:
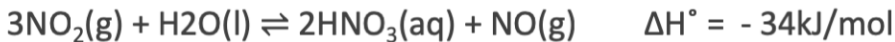
$$\ln(\frac{K_2}{K_1}) = \frac{\Delta H_{rxn}}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$\Delta H > 0 \quad T\uparrow \quad K\uparrow$

$\Delta H < 0 \quad T\uparrow \quad K\downarrow$

Le Chatelier's Questions

Consider the reaction below when it is at equilibrium:

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

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

a. You add 3 moles HNO_3 $Q > K$ ←

b. The total volume is decreased $P\uparrow$ →

c. An inert gas is added at constant volume   X

d. An inert gas is added at constant pressure $P_i \downarrow$ ←

e. You remove 3 moles NO $Q < K$ →

f. You increase the temperature $K \downarrow$ ←

pH Calculations

Can you calculate the pH (or pOH, [H⁺], [OH⁻]) of...

1. A strong acid
$$pH = -\log C_A$$

2. A strong base
$$pOH = -\log C_B \quad *$$
$$* \text{ maybe } \times 2$$

3. A weak acid
$$[H^+] = \sqrt{K_a \cdot C_A}$$

4. A weak base
$$[OH^-] = \sqrt{K_b \cdot C_B}$$

5. The salt of a weak acid $\rightarrow$ base
$$[OH^-] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}}$$

6. The salt of a weak base
$$[H^+] = \sqrt{\frac{K_w}{K_b} \cdot C_{BH^+}}$$

7. A weak acid buffer
$$pH = pK_a + \log \frac{A^-}{HA}$$

8. A weak base buffer
$$pK_a = 14 - pK_b \qquad pH = pK_a + \log \frac{base}{acid}$$

Quantifying Acids and Bases

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

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

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

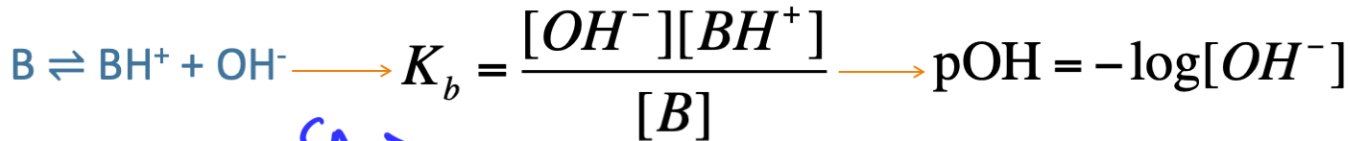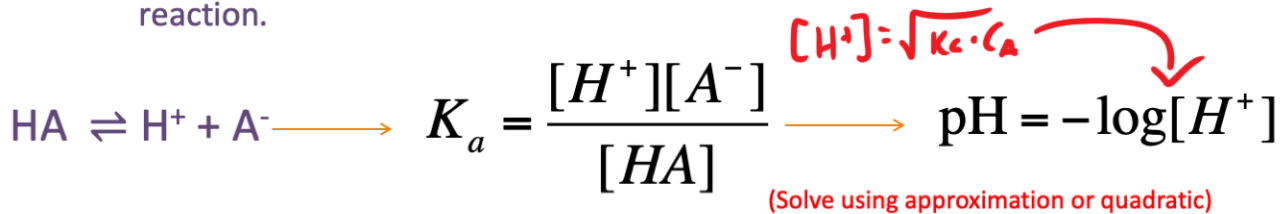$$pH = -\log[C_A] \qquad pOH = -\log[C_B]_*$$

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

$$pH = 14 - pOH \qquad pOH = 14 - pH$$

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.

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

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

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

(Solve using approximation or quadratic)

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

Ignore x when $\dfrac{C_A}{K_A} \geq 1000$

Quantifying Weak Acids and Bases

- It is far to say that most questions will use the approximations:
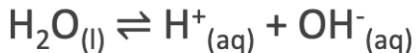
$$[H^+] = \sqrt{C_{HA} \cdot K_a} \qquad [OH^-] = \sqrt{C_B \cdot K_b}$$

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

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

$$K_w = K_a K_b$$

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

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

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**:

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

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

◦ **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}

Handwritten annotations:
$\rightarrow pH = 12$
$[H_3O^+] = 10^{-12}$

Base, pOH = 2
$[H_3O^+]?$
$[OH^-] = 10^{-2}$
$10^{-14} = [H_3O^+] \cdot 10^{-12}$
$[H_3O^+] = 10^{-12}$

Percent Ionization to K_a

Percent ionization is an important way of depicting electrolyte strength.

K_a is, of course, the more formal way of depicting acid/base strength.

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

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

Example: Consider a weak acid, HA, with a % ionization equal to 10% at a 0.1 M concentration. What is K_a?

	$HA \rightleftharpoons H^+ + A^-$		
R			
I	0.1M	$\emptyset$	$\emptyset$
C	-.01	+.01	+.01
E	.09	.01	.01

$$K_a = \frac{(.01)^2}{.09} = 1.11 \times 10^{-3}$$

Comparing Acid Strength: pK_a

Conceptual comparisons of acid strength can use K_a but it is best to use pK_a

A **smaller pKₐ** will be a **stronger acid**

Consider the following information:

HF, pK_a = 3.2   HIO, pK_a = 10.7 $C_6H_5NH_2$, pK_b = 9.37

What is the stronger acid?

- HF or HIO?   **HF**
- HIO or $C_6H_5NH_3^+$
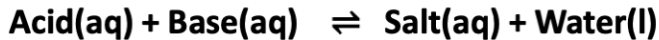
$$\rightarrow 14 - 9.37$$
$$= 4.63$$

pKa of $C_6H_5NH_3^+$

Buffers and Titrations

Neutralization Reactions: Salts

$$C_6H_5NH_3I$$

$$C_6H_5NH_2 \quad K_b \quad pK_b$$

$$+ HI$$
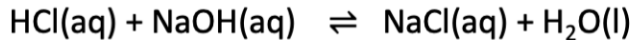
- The product of a neutralization reaction is a salt. In acid/base chemistry, your salt can be neutral, acidic, or basic depending on the reaction.
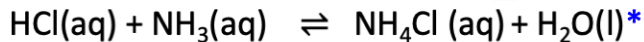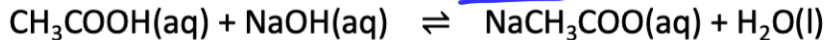
1. **GENERIC REACTION (very helpful):**

   Acid(aq) + Base(aq) $\rightleftharpoons$ 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**

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

Buffers: Conceptual, Calculation

- **The purpose of a buffer is to resist changes in pH.**

- By definition, a buffer is made of:
  - A weak acid and its salt (conjugate base)
  - A weak base and its salt (conjugate acid)

- **By definition, a buffer is effective when:**
  - **The pH is within about +/- 1 of the pK_a or pK_b**
  - **This favorable ratio of the weak acid : salt (or weak base : salt) is known as the "Buffer Zone"**

$$\text{moles}$$
$$\text{OR}$$
$$\text{concentration}$$

$$pH = pK_a + \log\left(\frac{A^-}{HA}\right)$$

$$pH = 14 - pK_b + \log\frac{\text{base}}{\text{acid}}$$

$$= pK_a$$

Buffer Calculation

A buffer is prepared by combining 300 mL 0.850 M butanoic acid (C_3H_7COOH) to 300 mL 0.640 M sodium hydroxide (NaOH). What is the pH of this solution? pKa = 4.82

moles →

R	C_3H_7COOH + NaOH ⇌ NaC_3H_7COO + H_2O

	C_3H_7COOH	NaOH	NaC_3H_7COO
I	.255	.192	∅
C	−.192	−.192	+.192
E	.063	∅	.192

$$pH = 4.82 + \log \frac{.192}{.063}$$

$$= 5.30$$

What is a buffer and what is not:

- **A buffer is made of:**
  - A weak acid and its salt (conjugate base)
  - A weak base and its salt (conjugate acid)

- **A buffer is made by a partial neutralization:**
 - Weak acid + strong base
  - Weak base + strong acid

$$HA : A^-$$
$$\rightarrow 1:1$$
$$\rightarrow pH = pKa + \cancel{log\frac{1}{1}}$$
$$= 0$$
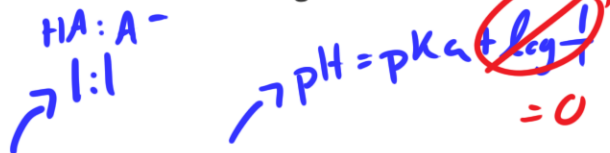
Example Question: Which of the following will form an ideal buffer at pH = 6.37?

a. 0.1 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, pKa_1 = 6.37   *Not buffer* <u>A^-</u>

b. 0.05 M, 100 mL NaOH + 0.1 M, 100 mL Hydrofluoric Acid, pKa = 3.20   *wrong pH*

c. 0.05 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, pKa_1 = 6.37

d. 0.06 M, 100 mL NaOH + 0.1 M, 100 mL Carbonic Acid, pKa_1 = 6.37   *buffer, not ideal, not 1:1 pH ≠ 6.37*

Titrations of Buffered Solutions Calculations

100 mL HA titrated with 0.2 M NaOH
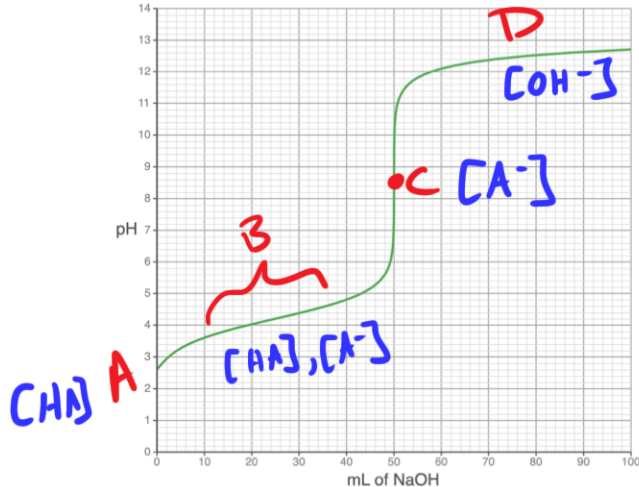
A) Before you have started:
Calculate pH using the approximation formula or using $K_a = [H^+][A^-] / [HA]$.

B) Within the buffer zone:
pH = pKa + log ([A⁻]/[HA])
RICE table in moles (partial neutralization)
Also: when pKa = pH (middle of the buffer zone)

C) At the equivalence point:
You only have the salt of your weak acid in solution. Use $K_w = K_aK_b$, then solve for [OH⁻], pOH, then convert to pH. Use a RICE table in moles then get concentration with the **final** volume
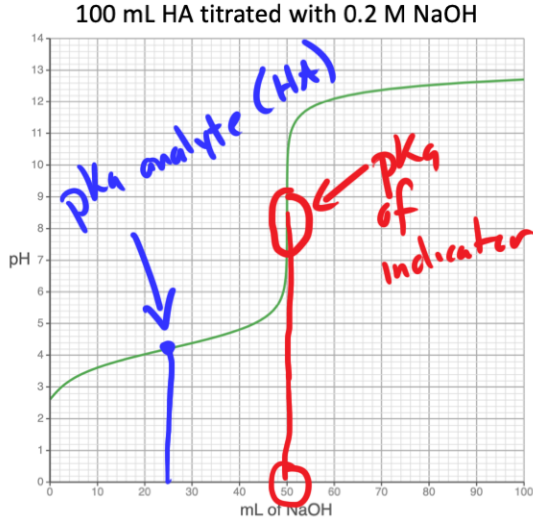
D) After the equivalence point:
Find the pH using the excess base in solution
pOH = -log ([excess base]). Again use the **final** volume
pH = 14- pOH

Titrations of Buffered Solutions Conclusions

100 mL HA titrated with 0.2 M NaOH

1) eq point
   moles HA = moles OH$^-$

$$(\underline{0.1\ M})(100\ mL) = (\underline{0.2\ M})(50\ mL)$$

$$C_1 V_1 = C_2 V_2$$

2) ½ eq pt, pH = pKa
   pH = 4.20
   $\hookrightarrow$ benzoic acid
   pKa ≈ 4.20

3) end point, indicator of
   $\hookrightarrow$ pKa of indicator
   matches pH @
   eq pt.

Titration Curve: Points to Know Summary
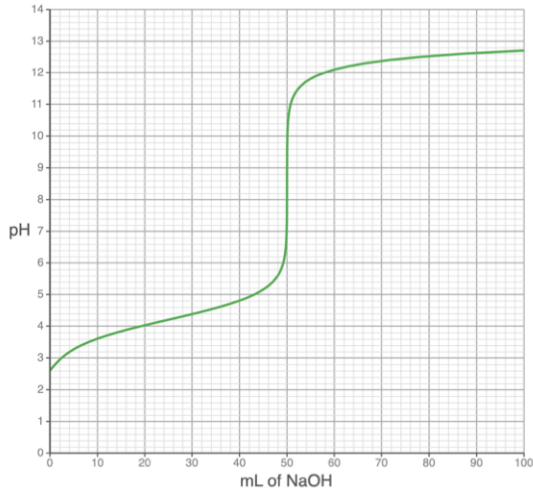
1) Equivalence Point
Full neutralization:
moles titrant = moles analyte
Ex: 100% conjugate base (A⁻)

2) Half-Equivalence Point
pH = pKa
moles HA = moles A⁻
Ex: HALF neutralized (1:1, HA:A⁻)
Ideal Buffer

3) End Point
Where you indicator changes color
OBSERVATIONAL depiction of equivalent point
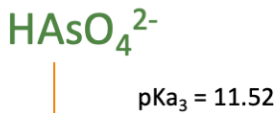
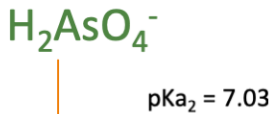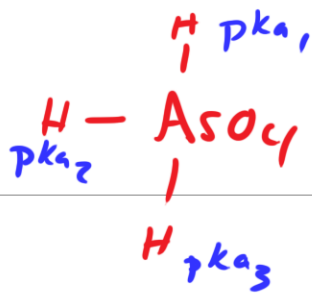**4) Buffer Zone**
+/- 1 pH unit of the pKa

Conceptualizing Protonation States

- For weak acids, especially for organic compounds and polyprotic acids, you can determine the protonation state of your molecule at any given pH.

- A few simple rules go a long way with answering these types of questions:

1. If pH < pK_a ; you have too many hydrogen ions in solution for it to be favorable for a hydrogen ion on your molecule to "pop off"

   ○ **Think about it: when the environment is more acidic, it is more "proton-donating,"**

   } protonated

2. If pH > pK_a ; the environment around your molecule is thirsty for hydrogen ions, so it is favorable for a hydrogen ion on your molecule to pop off

   ○ **Think about it: when the environment is more basic, it is more "proton-accepting."**

   } deprotonated

Fraction of Species Example

$H - AsO_4$ with H at top labeled pKa_1, pKa_2 on left, H at bottom labeled pKa_3

H_3AsO_4

↓ $pKa_1 = 2.30$

$H_2AsO_4^-$

↓ $pKa_2 = 7.03$

$HAsO_4^{2-}$

↓ $pKa_3 = 11.52$

AsO_4^{3-}

What is the dominant species if...

1. pH = 1 H_3AsO_4
2. pH = 5 $H_2AsO_4^-$
3. pH = 9 $HAsO_4^{2-}$
4. pH = 13 AsO_4^{3-}

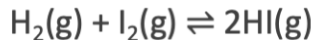# Extra Practice (answers and work in previous reviews)

Application Question

Consider the reaction: $A(g) \rightleftharpoons 2B(g)$

3 atm of A is added to an empty chamber. Once the reaction reaches equilibrium, there is 5 atm in total. What is the K_p for this reaction?

Application Question

The system

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

is at equilibrium at a fixed temperature with a partial pressure of H_2 of 0.200 atm, a partial pressure of I_2 of 0.200 atm, and a partial pressure of HI of 0.100 atm. An additional 0.26 atm pressure of HI is admitted to the container, and it is allowed to come to equilibrium again. What is the new partial pressure of HI?
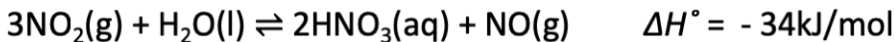
Exam Question

Consider the following generic reaction:

$$A(g) \rightleftharpoons 2B(g)$$

4.18 atm of reactant A and 8.23 atm of product B are introduced to a vacuum chamber. 1/2 of B reacts to reach equilibrium. What is the value of K for this reaction?

Le Chatelier's Principle - Questions

Consider the reaction below when it is at equilibrium:

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

In which direction will the reaction shift when:

a. 3 moles of NO(g) are added

b. The temperature is raised to 320 K

c. The total pressure is increased (by compression)

d. An inert gas is added at constant volume

e. An inert gas is added at constant pressure (in a piston system)

Warm-Up Question

What is the pH of a 0.50 M HNO_3 solution?

Warm-Up Question

What is the hydrogen ion concentration of a 0.30 M calcium hydroxide solution?

Challenge Question I

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?

Challenge Question II

Trichloroacetic acid is a harsh chemical, typically used for cosmetic treatments such as tattoo removal. What is the pH of a .0100 M trichloroacetic acid solution (CCl_3COOH)?

K_a = 2.1 x 10^{-1}

Neutralization Reactions: Salts

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

0.3 M LiCN

0.05 M $CH_3CH_2NH_3^+Cl^-$

0.08 M $KClO_4$

0.1 M KF

One step harder…

An ammonium perchlorate solution is made by combining 200 mL 1.0 M perchloric acid ($HClO_4$) and 200 mL 1.0 M ammonia (NH_3) . What is the pH?

R

I

C

E
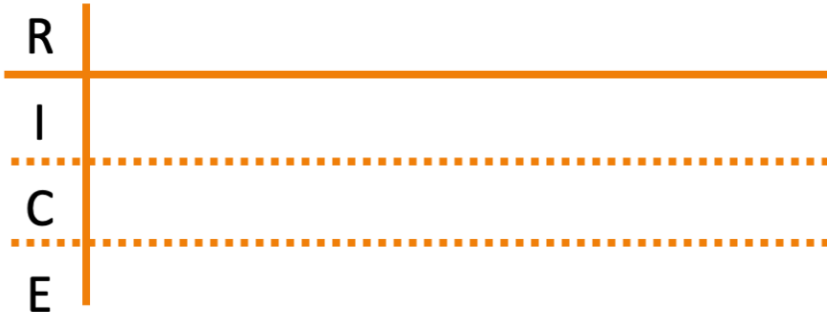
Future note: this question is identical to calculating the buffer zone of a titration experiment

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

And even harder…

An ammonium perchlorate solution is made by combining 100 mL 1.1 M perchloric acid ($HClO_4$) and 100 mL 2.0 M ammonia (NH_3) . What is the pH?

R

I

C

E

Future note: this question is identical to calculating the pH at the equivalence point of a titration

Exam Question

A buffer was prepared by mixing 0.200 mole of ammonia (pK_b = 4.76) and 0.200 mole of ammonium chloride to form an aqueous solution with a total volume of 500 mL.

50.0 mL of 1.00 M HCl was added to 250 mL of this solution.

What is the pH of this solution?