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AP Chemistry Unit 8 - Advanced FRQ Practice

Unit 8: Acids and Bases

Challenging **Time: 150 minutes (15 min/question)**

From "I Don't Get It" to "I Ace It" - Master Acid-Base Chemistry for AP Success! 🎯

📋 Instructions:

- Show ALL work clearly for full credit consideration
- Include proper units in all calculations and final answers
- Use appropriate significant figures (pH typically 2 decimal places)
- Explain reasoning for conceptual questions using complete sentences
- Reference the provided constants and equations when applicable
- Set up ICE tables where equilibrium calculations are required
- Justify use of approximations (e.g., "x is small" for weak acids)

📊 Reference Information & Constants:

Water ionization constant: $K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

pH and pOH: $pH = -\log[H_3O^+]$; $pOH = -\log[OH^-]$; $pH + pOH = 14.00$ at 25°C

pKa and pKb: $pKa = -\log(Ka)$; $pKb = -\log(Kb)$; $pKa + pKb = 14.00$

Henderson-Hasselbalch: $pH = pKa + \log([A^-]/[HA])$ for buffers

Percent ionization: % ionization = $([H_3O^+]_{eq}/[HA]_{initial}) \times 100\%$

Gas Constant: $R = 8.314$ J/(mol·K)

Question 1: Weak Acid Equilibrium and pH Calculations (15 points)

Acetic acid (CH_3COOH) is a weak acid commonly found in vinegar. The acid dissociation constant Ka for acetic acid is 1.8×10^{-5} at 25°C.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Given Information:

- Ka for $CH_3COOH = 1.8 \times 10^{-5}$ at 25°C
- A solution is prepared by dissolving 0.500 mol of pure acetic acid in water to make 1.00 L of solution
- Temperature = 25°C

(a) Write the equilibrium constant expression Ka for the dissociation of acetic acid. (1 point)

(b) Set up a complete ICE table for this equilibrium system. (2 points)

(c) Calculate the equilibrium concentration of H_3O^+ ions in the solution. Show that the "x is small" approximation is valid. (4 points)

(d) Calculate the pH of the solution. (2 points)

(e) Calculate the percent ionization of acetic acid in this solution. (2 points)

(f) If the initial concentration of acetic acid were increased to 1.00 M (instead of 0.500 M), predict whether the percent ionization would increase, decrease, or remain the same. Justify your answer using Le Châtelier's principle. (2 points)

(g) Calculate the pOH and the hydroxide ion concentration $[OH^-]$ in the original 0.500 M acetic acid solution. (2 points)

Question 2: Buffer Systems and Henderson-Hasselbalch Equation (16 points)

A buffer solution is prepared to maintain a specific pH for a biochemical experiment.

Buffer Composition:

- 250.0 mL of 0.400 M NH_3 (ammonia, Kb = 1.8×10^{-5})
- 250.0 mL of 0.300 M NH_4Cl (ammonium chloride)
- Final volume after mixing = 500.0 mL
- Temperature = 25°C

(a) Identify the conjugate acid-base pair in this buffer system and write the equilibrium equation for the base (NH_3) in water. (2 points)

(b) Calculate the concentrations of NH_3 and NH_4^+ after mixing but before any equilibrium is established. (2 points)

(c) Calculate the pKb of ammonia and use the relationship pKa + pKb = 14.00 to find the pKa of the ammonium ion (NH_4^+). (2 points)

(d) Use the Henderson-Hasselbalch equation to calculate the pH of the buffer solution. (3 points)

(e) If 0.010 mol of solid NaOH is added to the 500.0 mL buffer solution (assume no volume change), calculate the new pH of the solution. Show your reasoning clearly. (4 points)

(f) Explain at the molecular level how this buffer resists pH changes when a small amount of strong acid is added. (3 points)

Question 3: Strong Acid-Weak Base Titration (14 points)

A titration is performed in which 25.00 mL of 0.100 M ammonia (NH_3, Kb = 1.8×10^{-5}) is titrated with 0.100 M HCl.

Titration Setup:

- Initial: 25.00 mL of 0.100 M NH_3
- Titrant: 0.100 M HCl added from buret
- Kb for NH_3 = 1.8×10^{-5}
- Temperature = 25°C

(a) Write the net ionic equation for the reaction that occurs during the titration. (1 point)

(b) Calculate the volume of HCl required to reach the equivalence point. (2 points)

(c) At the equivalence point, identify the major species present in solution (excluding water). Determine whether the solution at the equivalence point is acidic, basic, or neutral, and explain your reasoning. (3 points)

(d) Calculate the pH at the equivalence point. (4 points)

(e) Calculate the pH after 12.50 mL of HCl has been added (half-equivalence point). (3 points)

(f) Sketch the general shape of the titration curve (pH vs. volume of HCl added), labeling the initial pH, equivalence point, and buffer region. (1 point)

Question 4: Polyprotic Acid Equilibria (15 points)

Phosphoric acid (H_3PO_4) is a triprotic acid with three successive ionization equilibria.

Ionization Constants at 25°C:

- $Ka_1 = 7.5 \times 10^{-3}$
- $Ka_2 = 6.2 \times 10^{-8}$
- $Ka_3 = 4.8 \times 10^{-13}$
- A solution contains 0.100 M H_3PO_4

(a) Write the three successive ionization equations for phosphoric acid in water. (3 points)

(b) Explain why $Ka_1 >> Ka_2 >> Ka_3$ for polyprotic acids. Include discussion of charge and molecular structure. (2 points)

(c) Calculate the pH of the 0.100 M H_3PO_4 solution. You may assume that only the first ionization contributes significantly to the H_3O^+ concentration. (4 points)

(d) Calculate the equilibrium concentration of PO_4^{3-} (the fully deprotonated form) in the 0.100 M H_3PO_4 solution. (3 points)

(e) At what approximate pH would you expect $H_2PO_4^-$ to be the predominant phosphate species in solution? Explain your reasoning using the pKa values. (3 points)

Question 5: Salt Hydrolysis and pH (13 points)

Several salt solutions are prepared by dissolving different ionic compounds in water.

Salts to Consider:
- NaCl (sodium chloride)
- NH_4Cl (ammonium chloride, Ka of $NH_4^+ = 5.6 \times 10^{-10}$)
- $NaCH_3COO$ (sodium acetate, Kb of $CH_3COO^- = 5.6 \times 10^{-10}$)
- $Al(NO_3)_3$ (aluminum nitrate, Ka of $Al(H_2O)_6^{3+} = 1.4 \times 10^{-5}$)

(a) For each salt listed above, predict whether its aqueous solution will be acidic, basic, or neutral. Provide a brief explanation for each prediction. (4 points)

(b) Write the net ionic equation showing how NH_4Cl produces an acidic solution when dissolved in water. (2 points)

(c) Calculate the pH of a 0.200 M NH_4Cl solution. (4 points)

(d) A solution is prepared by dissolving 0.100 mol of $NaCH_3COO$ in water to make 1.00 L of solution. Calculate the pH of this solution. (3 points)

Question 6: Weak Acid-Strong Base Titration Curve Analysis (14 points)

Consider the titration of 50.0 mL of 0.100 M HF (hydrofluoric acid, Ka = 7.2×10^{-4}) with 0.100 M NaOH.

Titration Information:

- Sample: 50.0 mL of 0.100 M HF
- Titrant: 0.100 M NaOH
- Ka for HF = 7.2×10^{-4}
- Temperature = 25°C

(a) Calculate the initial pH of the HF solution before any NaOH is added. (3 points)

(b) Write the net ionic equation for the neutralization reaction. (1 point)

(c) Calculate the volume of NaOH required to reach the equivalence point. (1 point)

(d) Calculate the pH at the half-equivalence point. Explain why pH = pKa at this point. (3 points)

(e) At the equivalence point, identify the major species in solution and determine whether the pH will be less than 7, equal to 7, or greater than 7. Justify your answer. (2 points)

(f) Calculate the pH at the equivalence point. (4 points)

Question 7: Buffer Capacity and Preparation (13 points)

A biochemistry laboratory needs to prepare a buffer solution with specific properties.

Buffer Requirements:

- Target pH = 4.50
- Total volume = 1.00 L
- Available reagents: acetic acid (CH_3COOH, Ka = 1.8×10^{-5}), sodium acetate ($NaCH_3COO$), and solid NaOH
- Temperature = 25°C

(a) Calculate the pKa of acetic acid and explain why acetic acid/acetate is an appropriate buffer system for pH 4.50. (2 points)

(b) Using the Henderson-Hasselbalch equation, calculate the ratio $[CH_3COO^-]/[CH_3COOH]$ required to achieve pH 4.50. (2 points)

(c) If the buffer is prepared with a total concentration of 0.500 M (combined $[CH_3COOH] + [CH_3COO^-] = 0.500$ M), calculate the individual concentrations of CH_3COOH and CH_3COO^- needed. (3 points)

(d) Describe two different methods to prepare this buffer solution, specifying the masses or volumes of reagents required for Method 1: mixing acetic acid and sodium acetate; Method 2: partial neutralization of acetic acid with NaOH. (4 points)

(e) Explain why a buffer with $[CH_3COOH] = [CH_3COO^-] = 0.50$ M has greater buffer capacity than one with $[CH_3COOH] = [CH_3COO^-] = 0.05$ M, even though both have the same pH. (2 points)

Question 8: Molecular Structure and Acid Strength (12 points)

Consider the following series of acids and their Ka values at 25°C:

Acid	Formula	Ka
Acetic acid	CH_3COOH	1.8×10^{-5}
Chloroacetic acid	$ClCH_2COOH$	1.4×10^{-3}
Dichloroacetic acid	$Cl_2CHCOOH$	5.0×10^{-2}
Trichloroacetic acid	Cl_3CCOOH	3.0×10^{-1}

(a) Rank these acids in order of increasing acid strength and explain the trend you observe. (2 points)

(b) Explain how the presence of chlorine atoms affects the acidity of these carboxylic acids. Include discussion of electronegativity and the inductive effect. (3 points)

(c) Draw the Lewis structure of the acetate ion (CH_3COO^-). Explain how resonance stabilization of the conjugate base contributes to the acidity of carboxylic acids. (3 points)

(d) Predict which would be more acidic: phenol (C_6H_5OH) or ethanol (CH_3CH_2OH). Justify your prediction based on the stability of the conjugate base. (2 points)

(e) Calculate the pH of a 0.100 M solution of chloroacetic acid (Ka = 1.4×10^{-3}). (2 points)

Question 9: Acid-Base Indicators and Titration

(14 points)

Acid-base indicators are weak acids that change color depending on the pH of the solution.

Indicator Properties:

- Methyl red: pKa = 5.1, changes from red (acidic) to yellow (basic)
- Bromothymol blue: pKa = 7.0, changes from yellow (acidic) to blue (basic)
- Phenolphthalein: pKa = 9.4, changes from colorless (acidic) to pink (basic)

(a) For a generic indicator HIn that dissociates according to HIn $\rightleftharpoons H^+ + In^-$, write the Henderson-Hasselbalch equation in terms of [HIn] and $[In^-]$. (1 point)

(b) Explain why the color change for an indicator occurs over a pH range of approximately pKa ± 1. (2 points)

(c) Which indicator (methyl red, bromothymol blue, or phenolphthalein) would be most appropriate for the titration of 25.0 mL of 0.100 M HCl with 0.100 M NaOH? Justify your choice by calculating the pH at the equivalence point. (3 points)

(d) Which indicator would be most appropriate for the titration of 25.0 mL of 0.100 M acetic acid ($K_a = 1.8 \times 10^{-5}$) with 0.100 M NaOH? Justify your choice by calculating the pH at the equivalence point. (4 points)

(e) Explain why phenolphthalein would NOT be a good choice for the titration of ammonia with hydrochloric acid. (2 points)

(f) At what pH would methyl red (pKa = 5.1) show equal amounts of its red and yellow forms? (2 points)

Question 10: Comprehensive Acid-Base Integration (16 points)

A chemist is investigating the buffering capacity of human blood, which maintains a pH of approximately 7.40 through the carbonic acid-bicarbonate buffer system.

Blood Buffer System:

- $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$
- Ka for $H_2CO_3 = 4.3 \times 10^{-7}$
- Normal blood pH = 7.40
- Typical concentrations: $[HCO_3^-] = 0.024$ M, $[H_2CO_3] = 0.0012$ M

(a) Calculate the pKa of carbonic acid. (1 point)

(b) Using the Henderson-Hasselbalch equation, verify that the given concentrations produce a pH of 7.40. (2 points)

(c) Calculate the ratio $[HCO_3^-]/[H_2CO_3]$ in normal blood. (1 point)

(d) During strenuous exercise, lactic acid ($HC_3H_5O_3$) is produced in muscle tissue and enters the bloodstream. If 0.0020 mol of lactic acid is added to 1.0 L of blood (assume the buffer concentrations given above), calculate the new pH of the blood. (4 points)

(e) Explain why the bicarbonate buffer system is effective at maintaining pH near 7.40, even though the pKa of carbonic acid (6.37) is not exactly equal to 7.40. (2 points)

(f) The condition known as acidosis occurs when blood pH falls below 7.35. Calculate the $[HCO_3^-]/[H_2CO_3]$ ratio that would correspond to a pH of 7.35. (2 points)

(g) The body can regulate blood pH by controlling the concentration of H_2CO_3 through respiration (exhaling CO_2 decreases $[H_2CO_3]$). If the $[HCO_3^-]$ remains at 0.024 M, what concentration of H_2CO_3 would be required to restore pH to 7.40 from the acidotic state (pH 7.35)? (2 points)

(h) Explain why the blood buffer system is an example of a coupled equilibrium involving both chemical and physiological processes. (2 points)

💡 Unit 8 Acid-Base Mastery Tips:

- **ICE Tables for Weak Acids/Bases:** Always set up complete ICE tables; check "x is small" approximation by verifying $K_a < 10^{-4}$ and $[HA] > 100\times K_a$
- **Henderson-Hasselbalch Validity:** Use only for buffers; requires both acid and conjugate base present in significant amounts (ratio between 0.1 and 10)
- **pH Decimal Places:** pH values should have as many decimal places as there are significant figures in $[H_3O^+]$ (e.g., $[H^+] = 3.2 \times 10^{-5} \rightarrow pH = 4.49$)
- **Titration Equivalence Points:** Strong acid-strong base: pH = 7; weak acid-strong base: pH > 7; weak base-strong acid: pH < 7
- **Half-Equivalence Point:** pH = pKa for weak acid titrations; pOH = pKb for weak base titrations; occurs at 50% neutralization
- **Salt Hydrolysis Rules:** Cation from weak base → acidic; anion from weak acid → basic; strong acid/base ions → neutral
- **Buffer Preparation:** Mix weak acid + conjugate base, OR partially neutralize weak acid with strong base (or weak base with strong acid)
- **Polyprotic Acids:** Usually only first ionization contributes significantly to pH when $K_{a1} \gg K_{a2}$ (factor of 10^3 or more)
- **pKa + pKb = 14:** For conjugate acid-base pairs at 25°C; use to convert between Ka and Kb when working with buffers
- **Molecular Structure → Acidity:** Stronger acids have more stable conjugate bases (resonance, electronegativity, inductive effects)

🎯 ANSWER KEY & DETAILED SOLUTIONS

Question 1: Weak Acid Equilibrium - Complete Solution (15 points)

(a) Equilibrium constant expression (1 point)

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

Scoring (1 point): Correct Ka expression with proper notation

(b) ICE table (2 points)

	CH_3COOH	H_3O^+	CH_3COO^-
I	0.500 M	≈0	0
C	−x	+x	+x
E	0.500 − x	x	x

Scoring (2 points): 1 point for correct initial concentrations; 1 point for correct change and equilibrium expressions

(c) Calculate [H_3O^+] and verify approximation (4 points)

Step 1: Write Ka expression with equilibrium values

$$K_a = \frac{x \cdot x}{0.500 - x} = 1.8 \times 10^{-5}$$

Step 2: Check if "x is small" approximation is valid
For the approximation to be valid, we need Ka < 10^{-4} and [HA]initial/Ka > 100
Check: 0.500 / (1.8 × 10^{-5}) = 27,778 >> 100 ✓
Ka = 1.8 × 10^{-5} < 10^{-4} ✓
Therefore, approximation is VALID.

Step 3: Solve using approximation (0.500 − x ≈ 0.500)

$$\frac{x^2}{0.500} = 1.8 \times 10^{-5}$$

$$x^2 = (1.8 \times 10^{-5})(0.500) = 9.0 \times 10^{-6}$$

$$x = \sqrt{9.0 \times 10^{-6}} = 3.0 \times 10^{-3} \text{ M}$$

Step 4: Verify approximation
Percent error = (3.0 × 10^{-3} / 0.500) × 100% = 0.60% < 5% ✓

Answer: $[H_3O^+]$ = 3.0 × 10^{-3} M

Scoring (4 points): 1 point for Ka expression; 1 point for verifying approximation validity; 1 point for correct calculation; 1 point for checking approximation

(d) Calculate pH (2 points)

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.0 \times 10^{-3})$$

$$\text{pH} = -(-2.52) = 2.52$$

Answer: pH = 2.52

Scoring (2 points): 1 point for correct formula; 1 point for correct answer with 2 decimal places

(e) Calculate percent ionization (2 points)

$$\text{Percent ionization} = \frac{[\text{H}_3\text{O}^+]_{\text{eq}}}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\%$$

$$\text{Percent ionization} = \frac{3.0 \times 10^{-3}}{0.500} \times 100\% = 0.60\%$$

Answer: 0.60% ionization

Scoring (2 points): 1 point for correct formula; 1 point for correct calculation

(f) Effect of concentration on percent ionization (2 points)

Prediction: Percent ionization would DECREASE if initial concentration increased to 1.00 M.

Justification: According to Le Châtelier's principle, increasing the concentration of acetic acid shifts the equilibrium toward products (H_3O^+ and CH_3COO^-), BUT the percent ionization decreases because the absolute increase in $[H_3O^+]$ is proportionally smaller than the increase in initial $[CH_3COOH]$.

Mathematically: For weak acids, % ionization $\propto$ 1/√[HA]initial
At higher concentrations, a smaller fraction ionizes even though more ions form in absolute terms.

Scoring (2 points): 1 point for correct prediction (decrease); 1 point for proper Le Châtelier justification

(g) Calculate pOH and $[OH^-]$ (2 points)

Step 1: Calculate pOH

pH + pOH = 14.00

pOH = 14.00 − 2.52 = 11.48

Step 2: Calculate $[OH^-]$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-11.48} = 3.3 \times 10^{-12} \text{ M}$$

Alternative calculation:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-3}} = 3.3 \times 10^{-12} \text{ M}$$

Answers: pOH = 11.48; $[OH^-] = 3.3 \times 10^{-12}$ M

Scoring (2 points): 1 point for pOH; 1 point for $[OH^-]$

Question 2: Buffer Systems - Complete Solution (16 points)

(a) Conjugate acid-base pair and equilibrium (2 points)

Conjugate pair: NH_3 (base) and NH_4^+ (conjugate acid)

Equilibrium for NH_3 in water:

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Scoring (2 points): 1 point for identifying conjugate pair; 1 point for correct equilibrium equation

(b) Calculate concentrations after mixing (2 points)

For NH_3:

Moles NH_3 = (0.400 M)(0.250 L) = 0.100 mol
$[NH_3]$ = 0.100 mol / 0.500 L = **0.200 M**

For NH_4^+:

Moles NH_4^+ = (0.300 M)(0.250 L) = 0.0750 mol
$[NH_4^+]$ = 0.0750 mol / 0.500 L = **0.150 M**

Scoring (2 points): 1 point for correct $[NH_3]$; 1 point for correct $[NH_4^+]$

(c) Calculate pKb and pKa (2 points)

pKb of NH_3:

pKb = −log(Kb) = −log(1.8×10^{-5}) = 4.74

pKa of NH_4^+:

pKa + pKb = 14.00
pKa = 14.00 − 4.74 = **9.26**

Scoring (2 points): 1 point for pKb; 1 point for pKa

(d) Calculate pH using Henderson-Hasselbalch (3 points)

For a buffer system with weak acid NH_4^+ and conjugate base NH_3:

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$\text{pH} = 9.26 + \log\left(\frac{0.200}{0.150}\right)$$

$$\text{pH} = 9.26 + \log(1.333)$$

$$\text{pH} = 9.26 + 0.12 = 9.38$$

Answer: pH = 9.38

Scoring (3 points): 1 point for correct equation; 1 point for correct substitution; 1 point for correct answer

(e) Calculate new pH after adding NaOH (4 points)

Step 1: Determine reaction
NaOH (strong base) reacts with NH_4^+ (weak acid):
$NH_4^+ + OH^- \rightarrow NH_3 + H_2O$

Step 2: Calculate moles before reaction
- Moles NH_3 = (0.200 M)(0.500 L) = 0.100 mol
- Moles NH_4^+ = (0.150 M)(0.500 L) = 0.0750 mol
- Moles OH^- added = 0.010 mol

Step 3: Reaction stoichiometry
NH_4^+ consumed: 0.010 mol
NH_3 produced: 0.010 mol

Step 4: Calculate new moles and concentrations
- New moles NH_3 = 0.100 + 0.010 = 0.110 mol → $[NH_3]$ = 0.110/0.500 = 0.220 M
- New moles NH_4^+ = 0.0750 − 0.010 = 0.0650 mol → $[NH_4^+]$ = 0.0650/0.500 = 0.130 M

Step 5: Calculate new pH

$$\text{pH} = 9.26 + \log\left(\frac{0.220}{0.130}\right)$$

$$\text{pH} = 9.26 + \log(1.692) = 9.26 + 0.23 = 9.49$$

Answer: pH = 9.49
pH change = 9.49 − 9.38 = 0.11 (small change demonstrates buffer action)

Scoring (4 points): 1 point for reaction equation; 1 point for stoichiometry; 1 point for new concentrations; 1 point for correct pH

(f) Molecular-level explanation of buffer action (3 points)

When a strong acid (H_3O^+) is added to this buffer:

1. Neutralization: The weak base NH_3 reacts with the added H_3O^+:
$NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) + H_2O(l)$

2. Buffer Component Shift: The added H_3O^+ is consumed by NH_3, converting it to NH_4^+. This decreases $[NH_3]$ and increases $[NH_4^+]$ slightly, but both components remain in significant amounts.

3. pH Resistance: Because the ratio $[NH_3]/[NH_4^+]$ changes only slightly (since both are present in relatively large amounts), the pH change is minimal according to the Henderson-Hasselbalch equation. The weak base "absorbs" the strong acid, preventing a large pH drop that would occur in an unbuffered solution.

Scoring (3 points): 1 point for reaction equation; 1 point for explaining consumption of H_3O^+; 1 point for explaining why pH change is small

Question 3: Strong Acid-Weak Base Titration - Solutions Summary (14 points)

(a) Net ionic equation: $NH_3(aq) + H_3O^+(aq) \rightarrow NH_4^+(aq) +$

$H_2O(l)$
(OR: $NH_3(aq) + H^+(aq) \rightarrow NH_4^+(aq)$)

(b) Volume at equivalence point:
Moles NH_3 = (0.100 M)(0.02500 L) = 0.00250 mol
Volume HCl = 0.00250 mol / 0.100 M = 0.0250 L = **25.00 mL**

(c) At equivalence point:
- Major species: NH_4^+, Cl^-, H_2O
- NH_4^+ is a weak acid (conjugate acid of weak base NH_3)
- Cl^- is neutral (from strong acid HCl)
- Solution is ACIDIC due to NH_4^+ hydrolysis

(d) pH at equivalence point:
Total volume = 50.00 mL; $[NH_4^+]$ = 0.00250 mol / 0.0500 L = 0.0500 M
Ka of NH_4^+ = Kw/Kb = $(1.0 \times 10^{-14})/(1.8 \times 10^{-5}) = 5.6 \times 10^{-10}$
Using ICE table: $[H_3O^+] = \sqrt{}(Ka \times [NH_4^+]) = \sqrt{}(5.6 \times 10^{-10} \times 0.0500) = 5.3 \times 10^{-6}$ M
pH = $-\log(5.3 \times 10^{-6})$ = **5.28**

(e) pH at half-equivalence point (12.50 mL added):
At half-equivalence: $[NH_3] = [NH_4^+]$ (buffer with equal concentrations)
pOH = pKb = $-\log(1.8 \times 10^{-5})$ = 4.74
pH = 14.00 − 4.74 = **9.26**

(f) Titration curve should show:
- Initial pH ≈ 11 (weak base)
- Buffer region from 0-25 mL with gradual pH decrease
- Half-equivalence at 12.5 mL where pH = 9.26
- Steep drop near equivalence point at 25 mL
- Equivalence point pH = 5.28 (< 7, acidic)
- pH continues to decrease slightly after equivalence point

Question 4: Polyprotic Acid Equilibria - Solutions Summary (15 points)

(a) Three ionization equations:
1st: $H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$ $Ka_1 = 7.5 \times 10^{-3}$
2nd: $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HPO_4^{2-}(aq)$ $Ka_2 = 6.2 \times 10^{-8}$
3rd: $HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PO_4^{3-}(aq)$ $Ka_3 = 4.8 \times 10^{-13}$

(b) Explanation of $Ka_1 >> Ka_2 >> Ka_3$:
• First ionization: Removing H^+ from neutral H_3PO_4 is easiest
• Second ionization: Removing H^+ from negatively charged $H_2PO_4^-$ is harder (electrostatic repulsion)
• Third ionization: Removing H^+ from doubly negative HPO_4^{2-} is much harder
• Each successive ionization requires removing a proton from an increasingly negative species

(c) pH of 0.100 M H_3PO_4:
Using only first ionization ($Ka_1 = 7.5 \times 10^{-3}$):
$Ka_1 = x^2/(0.100 - x) = 7.5 \times 10^{-3}$
Check approximation: $0.100/7.5\times10^{-3} = 13.3 < 100$, so must use quadratic
$x^2 + 0.0075x - 0.00075 = 0$
$x = 0.024$ M $= [H_3O^+]$
pH $= -\log(0.024) =$ **1.62**

(d) Concentration of PO_4^{3-}:
For polyprotic acids: $[PO_4^{3-}] = Ka_2 \times Ka_3 / [H_3O^+]$
$[PO_4^{3-}] = (6.2 \times 10^{-8})(4.8 \times 10^{-13}) / 0.024 =$ **1.2×10^{-18} M**
(Extremely small concentration, as expected for triply deprotonated form)

(e) Predominance of $H_2PO_4^-$:

$H_2PO_4^-$ predominates when pH is between pKa_1 and pKa_2
$pKa_1 = -\log(7.5 \times 10^{-3}) = 2.12$
$pKa_2 = -\log(6.2 \times 10^{-8}) = 7.21$
$H_2PO_4^-$ is dominant in the range **pH ≈ 2-7**, with maximum at around pH ≈ 4.7 (midpoint)

Question 5: Salt Hydrolysis - Solutions Summary (13 points)

(a) pH predictions:
- NaCl: NEUTRAL (Na^+ from strong base, Cl^- from strong acid → neither hydrolyzes)
- NH_4Cl: ACIDIC (NH_4^+ is weak acid, Cl^- is neutral)
- $NaCH_3COO$: BASIC (Na^+ is neutral, CH_3COO^- is weak base)
- $Al(NO_3)_3$: ACIDIC (Al^{3+} forms $Al(H_2O)_6^{3+}$ which acts as weak acid; NO_3^- is neutral)

(b) NH_4Cl produces acidic solution:
$NH_4^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

(c) pH of 0.200 M NH_4Cl:
Ka of $NH_4^+ = 5.6 \times 10^{-10}$
$[H_3O^+] = \sqrt{(Ka \times [NH_4^+])} = \sqrt{(5.6 \times 10^{-10} \times 0.200)} = 1.06 \times 10^{-5}$ M
$pH = -\log(1.06 \times 10^{-5}) =$ **4.97**

(d) pH of 0.100 M $NaCH_3COO$:
Kb of $CH_3COO^- = 5.6 \times 10^{-10}$
$[OH^-] = \sqrt{(Kb \times [CH_3COO^-])} = \sqrt{(5.6 \times 10^{-10} \times 0.100)} = 7.48 \times 10^{-6}$ M
$pOH = -\log(7.48 \times 10^{-6}) = 5.13$
$pH = 14.00 - 5.13 =$ **8.87**

Question 6: Weak Acid-Strong Base Titration - Solutions Summary (14 points)

(a) Initial pH of 0.100 M HF:
Ka = 7.2 × 10^{-4}
$[H_3O^+] = \sqrt{(Ka \times [HF])} = \sqrt{(7.2 \times 10^{-4} \times 0.100)} = 8.49 \times 10^{-3}$ M
pH = **2.07**

(b) Net ionic equation: $HF(aq) + OH^-(aq) \rightarrow F^-(aq) + H_2O(l)$

(c) Volume to equivalence point:
Moles HF = (0.100 M)(0.0500 L) = 0.00500 mol
Volume NaOH = 0.00500 mol / 0.100 M = **50.0 mL**

(d) pH at half-equivalence (25.0 mL added):
At half-equivalence: $[HF] = [F^-]$, so pH = pKa
pKa = $-\log(7.2 \times 10^{-4})$ = **3.14**
Explanation: Henderson-Hasselbalch equation shows pH = pKa + log(1) = pKa when acid and conjugate base concentrations are equal.

(e) At equivalence point:
- Major species: F^- (conjugate base), Na^+, H_2O
- F^- is a weak base, so solution is BASIC (pH > 7)

(f) pH at equivalence point:
Total volume = 100.0 mL; $[F^-]$ = 0.00500 mol / 0.100 L = 0.0500 M
Kb of F^- = $Kw/Ka = (1.0 \times 10^{-14})/(7.2 \times 10^{-4}) = 1.39 \times 10^{-11}$
$[OH^-] = \sqrt{(Kb \times [F^-])} = \sqrt{(1.39 \times 10^{-11} \times 0.0500)} = 8.34 \times 10^{-7}$ M
pOH = 6.08; pH = 14.00 − 6.08 = **7.92**

Question 7: Buffer Capacity and Preparation - Solutions Summary (13 points)

(a) pKa and buffer appropriateness:
$pKa = -\log(1.8 \times 10^{-5}) = 4.74$
Appropriate because target pH (4.50) is within ±1 of pKa (4.74), the effective buffering range.

(b) Calculate ratio:
$pH = pKa + \log([A^-]/[HA])$
$4.50 = 4.74 + \log([CH_3COO^-]/[CH_3COOH])$
$\log([CH_3COO^-]/[CH_3COOH]) = -0.24$
$[CH_3COO^-]/[CH_3COOH] = 10^{-0.24} = \mathbf{0.575}$

(c) Individual concentrations:
Let $x = [CH_3COO^-]$ and $y = [CH_3COOH]$
$x + y = 0.500$ M
$x/y = 0.575$
Solving: $y = 0.318$ M (CH_3COOH); $x = 0.182$ M (CH_3COO^-)

(d) Preparation methods:
Method 1: Mix acetic acid and sodium acetate
- Dissolve 0.318 mol CH_3COOH (19.1 g) and 0.182 mol $NaCH_3COO$ (14.9 g) in water to make 1.00 L

Method 2: Partial neutralization
- Dissolve 0.500 mol CH_3COOH (30.0 g) in water
- Add 0.182 mol NaOH (7.28 g solid) to neutralize portion to acetate
- Dilute to 1.00 L

(e) Buffer capacity explanation:
Higher concentration buffer (0.50 M each) has more moles of acid and conjugate base available to neutralize added acid/base. Though pH is the same (ratio is identical), the 0.50 M buffer can absorb 10× more added acid/base before pH

changes significantly compared to 0.05 M buffer.

Question 8: Molecular Structure and Acid Strength - Solutions Summary (12 points)

(a) Ranking (increasing acid strength):
$CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$
(Ka increases from 1.8×10^{-5} to 3.0×10^{-1})

(b) Effect of chlorine atoms:
- Chlorine is highly electronegative
- Withdraws electron density from carboxyl group via inductive effect
- This weakens O−H bond, making H^+ easier to remove
- More importantly, electron withdrawal stabilizes the conjugate base (COO^-) by delocalizing negative charge
- More Cl atoms → stronger electron withdrawal → stronger acid

(c) Lewis structure and resonance:
Acetate ion: $CH_3{-}C(=O){-}O^-$ has resonance between two equivalent structures where the negative charge is delocalized over both oxygen atoms. This resonance stabilization of the conjugate base makes carboxylic acids more acidic than alcohols (where conjugate base RO^- has no resonance stabilization).

(d) Phenol vs ethanol:
Phenol is MORE acidic because the phenoxide ion ($C_6H_5O^-$) is stabilized by resonance with the benzene ring (negative charge delocalizes into aromatic system). Ethoxide ion ($CH_3CH_2O^-$) has no such stabilization.

(e) pH of 0.100 M chloroacetic acid:
$Ka = 1.4 \times 10^{-3}$; check: $0.100/(1.4\times10^{-3}) = 71 < 100$, use

quadratic
$x^2 + 0.0014x - 0.00014 = 0$
$x = 0.0109$ M = $[H_3O^+]$
pH = **1.96**

Question 9: Acid-Base Indicators - Solutions Summary (14 points)

(a) Henderson-Hasselbalch for indicator:
pH = pKa(indicator) + log($[In^-]/[HIn]$)

(b) Color change range explanation:
When pH = pKa − 1: log($[In^-]/[HIn]$) = −1, so $[In^-]/[HIn]$ = 0.1 (10:1 acid:base, acid color dominates)
When pH = pKa + 1: log($[In^-]/[HIn]$) = +1, so $[In^-]/[HIn]$ = 10 (1:10 acid:base, base color dominates)
Human eye perceives color change when ratio changes from 1:10 to 10:1 (pKa ± 1 range).

(c) Indicator for HCl/NaOH titration:
Strong acid-strong base equivalence point: pH = 7.00
Best choice: Bromothymol blue (pKa = 7.0, range 6-8)
Changes color right at equivalence point.

(d) Indicator for acetic acid/NaOH titration:
At equivalence: all acetic acid converted to acetate (weak base)
$[CH_3COO^-]$ = 0.0500 M (similar calculation to previous problems)
$K_b = 5.6 \times 10^{-10}$; $[OH^-] = 5.3 \times 10^{-6}$ M; pOH = 5.28; pH ≈ 8.72
Best choice: Phenolphthalein (pKa = 9.4, range 8.3-10.0)
Bromothymol blue would also work (upper end of range).

(e) Why phenolphthalein is inappropriate for NH_3/HCl:

Weak base-strong acid titration has acidic equivalence point (pH ≈ 5-6, as calculated earlier). Phenolphthalein range (8.3-10) is far too high; indicator would never change color at equivalence point.

(f) pH for equal red/yellow forms of methyl red:
When $[HIn] = [In^-]$, pH = pKa = **5.1**

Question 10: Blood Buffer System - Solutions Summary (16 points)

(a) $pKa = -\log(4.3 \times 10^{-7})$ = **6.37**

(b) Verify pH = 7.40:
$pH = 6.37 + \log(0.024/0.0012) = 6.37 + \log(20) = 6.37 + 1.30 = 7.67$
Note: Discrepancy suggests given concentrations may be approximate or other equilibria involved
Using pH = 7.40 works if ratio is: $7.40 = 6.37 + \log(\text{ratio}) \rightarrow$ ratio ≈ 10.7:1

(c) Ratio $[HCO_3^-]/[H_2CO_3] = 0.024/0.0012$ = **20:1**

(d) pH after adding lactic acid:
Lactic acid (strong enough to be treated as fully ionized in this context) reacts with HCO_3^-:
$HC_3H_5O_3 + HCO_3^- \rightarrow C_3H_5O_3^- + H_2CO_3$
New $[HCO_3^-] = 0.024 - 0.0020 = 0.022$ M
New $[H_2CO_3] = 0.0012 + 0.0020 = 0.0032$ M
New $pH = 6.37 + \log(0.022/0.0032) = 6.37 + 0.84$ = **7.21**
(pH drops from 7.40 to 7.21, but remains in physiological range due to buffering)

(e) Effectiveness despite pKa ≠ pH:
Buffer is effective because:

- pH (7.40) is within ±1 of pKa (6.37), the effective buffering range
- High $[HCO_3^-]/[H_2CO_3]$ ratio (20:1) provides large reservoir of HCO_3^- to neutralize acids (which are more commonly produced in metabolism)
- Body can adjust $[H_2CO_3]$ via respiration, adding dynamic control

(f) Ratio for pH 7.35 (acidosis):
$7.35 = 6.37 + \log(\text{ratio})$
$\log(\text{ratio}) = 0.98$
ratio = $10^{0.98}$ = **9.5:1**

(g) $[H_2CO_3]$ needed to restore pH to 7.40:
$7.40 = 6.37 + \log(0.024/[H_2CO_3])$
$\log(0.024/[H_2CO_3]) = 1.03$
$0.024/[H_2CO_3] = 10.7$
$[H_2CO_3] = 0.024/10.7 =$ **0.0022 M**
(Decrease from 0.0032 M by exhaling CO_2)

(h) Coupled equilibrium explanation:
The blood buffer involves:
- Chemical equilibrium: $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
- Gas-solution equilibrium: $CO_2(g) + H_2O \rightleftharpoons H_2CO_3(aq)$
- Physiological control: Respiratory rate controls CO_2 elimination, adjusting $[H_2CO_3]$
- Renal control: Kidneys adjust HCO_3^- reabsorption/excretion

This coupling allows both immediate chemical buffering and longer-term physiological pH regulation.
