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Topic 8.5: Acid-Base Titrations

Worksheet · AP Chemistry

UNIT 8 · ACIDS AND BASES

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How to Use This Worksheet

Work in order. Section A checks the ideas: titration vocabulary, equivalence pH for the three pairings, what the flask holds region by region, indicator choice, and the species at equivalence. Section B practises the skills: points along strong and weak curves, a weak base's equivalence, buffer region points, an unknown concentration, and the excess region. Section C is exam style: an HF curve point by point, an unknown acid read from its curve, and a diprotic acid's two equivalence points.

Conventions: 25 °C throughout, Kw = 1.0×10^{-14}, concentrations in mol L^{-1}, pH and pOH to two decimal places. Constants that recur: Ka of CH_3COOH = 1.8×10^{-5} (pKa 4.74), Kb of NH_3 = 1.8×10^{-5} (pKb 4.74), Ka of HF = 6.8×10^{-4} (pKa 3.17), and the conjugates Ka of NH_4^+ = Kb of CH_3COO^- = 5.6×10^{-10} and Kb of F^- = 1.47×10^{-11} from Kw.

One working habit ties the sheet together: moles first, region second. Compare moles of titrant added with moles of analyte; the comparison names the region (analyte left over, exactly matched, titrant in excess), and the region names the calculation: leftover analyte equilibrium, salt hydrolysis, buffer ratio, or excess titrant.

Two checks run through the sheet. The volume check: every post-mixing concentration uses the total volume. The direction check: adding base to an acid never lowers pH, nor acid to a base raises it; a wrong-way result exposes a mole error.

The answer key shows every mole comparison, volume and equilibrium step in full. Do not look at it until you have attempted every question.

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Section A: Recall and Concepts

A1. Define each term, and how the last two are related: (a) analyte; (b) titrant; (c) equivalence point; (d) endpoint. (e) A student's indicator changes color 3.0 mL before the true equivalence volume (analyte in flask, titrant in burette). State whether the calculated analyte concentration comes out high, low or correct, and explain why.

A2. For each titration, state whether the equivalence pH is below, equal to or above 7, naming the species responsible: (a) HCl titrated with NaOH; (b) CH_3COOH titrated with NaOH; (c) NH_3 titrated with HCl; (d) HNO_3 titrated with KOH.

A3. A weak acid is titrated with a strong base. For each stage, state what the solution mainly contains and what sets the pH: (a) before any titrant is added; (b) halfway to equivalence; (c) at equivalence; (d) past equivalence. (e) State the one point on this curve at which the acid's Ka can be read directly, and how.

A4. Two indicators are available: methyl orange (changes over pH 3 to 4) and phenolphthalein (pH 8 to 10). Choose the suitable one, or state that either works, for each titration, justifying every choice by the steep section's pH region: (a) HCl with NaOH; (b) CH_3COOH with NaOH; (c) NH_3 with HCl.

A5. At the equivalence point of each titration, list the major species in the flask and name the one that sets the pH: (a) 25.0 mL of 0.100 mol L^{-1} HCl with 0.100 mol L^{-1} NaOH; (b) 25.0 mL of 0.100 mol L^{-1} CH_3COOH with 0.100 mol L^{-1} NaOH; (c) 25.0 mL of 0.100 mol L^{-1} NH_3 with 0.100 mol L^{-1} HCl.

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Section B: Core Practice

B1. 40.0 mL of 0.100 mol L^{-1} HCl is titrated with 0.100 mol L^{-1} NaOH. Calculate the pH: (a) before any NaOH is added; (b) after 15.0 mL of NaOH has been added; (c) at the equivalence point, stating its volume; (d) after 50.0 mL of NaOH in total has been added.

B2. 25.0 mL of 0.100 mol L^{-1} CH_3COOH, Ka = 1.8×10^{-5}, is titrated with 0.100 mol L^{-1} NaOH. (a) Calculate the initial pH, solving the quadratic or checking the square root approximation against percent ionization. (b) State the equivalence volume, and the volume and pH at half-equivalence. (c) Calculate $[CH_3COO^-]$ at the equivalence point, and the pH there.

B3. 25.0 mL of 0.100 mol L^{-1} NH_3, Kb = 1.8×10^{-5}, is titrated with 0.100 mol L^{-1} HCl. (a) State the equivalence volume. (b) Calculate the concentration of NH_4^+ at the equivalence point. (c) Calculate the pH at the equivalence point, showing where its Ka comes from. (d) Calculate the pH at half-equivalence.

B4. 50.0 mL of 0.100 mol L^{-1} CH_3COOH, Ka = 1.8×10^{-5}, is titrated with 0.100 mol L^{-1} NaOH. After 20.0 mL of NaOH, recount moles of CH_3COOH and CH_3COO^- and calculate the pH.

B5. (a) A 20.0 mL sample of HNO_3 is titrated with 0.150 mol L^{-1} NaOH, and the equivalence point comes at 24.0 mL. Calculate the concentration of the HNO_3. (b) A 25.0 mL sample of a diprotic acid H_2A is fully neutralized by 40.0 mL of 0.100 mol L^{-1} NaOH. Calculate the concentration of the H_2A, stating the mole ratio your calculation uses.

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B6. 25.0 mL of 0.100 mol L^{-1} CH_3COOH is titrated with 0.100 mol L^{-1} NaOH, and 30.0 mL of the NaOH has now been added. (a) Show by moles that this point is past equivalence. (b) Calculate the pH. (c) Explain why CH_3COO^- contributes negligibly to the pH here.

Section C: Exam Style

C1. 50.0 mL of 0.100 mol L^{-1} HF, Ka = 6.8×10^{-4}, is titrated with 0.100 mol L^{-1} NaOH. (a) Calculate the initial pH twice: with the square root approximation, and by solving the quadratic. Give the percent ionization for each, and state which pH stands. (b) State the volume at half-equivalence and the pH there. (c) Calculate $[F^-]$ at the equivalence point and the pH there, showing where your Kb comes from. (d) Calculate the pH after 60.0 mL of NaOH has been added.

C2. An unknown weak acid HA is investigated by titrating 25.0 mL of it with 0.100 mol L^{-1} NaOH. The recorded curve gives: volume of NaOH 0.0 mL, pH 2.70; 10.0 mL, pH 4.30; 15.0 mL, pH 4.78; 20.0 mL, pH 8.47; 30.0 mL, pH 12.26. (a) Identify the equivalence volume, and hence calculate the moles and concentration of HA. (b) Determine the pKa and Ka of HA. (c) Explain why the equivalence pH is 8.47 rather than 7. (d) Choose between methyl orange (changes over pH 3 to 4) and phenolphthalein (pH 8 to 10), and justify the choice. (e) Use your Ka and concentration to calculate the initial pH, and state whether it agrees with the recorded 2.70.

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C3. A 25.0 mL sample of 0.100 mol L^{-1} H_2A is titrated with 0.100 mol L^{-1} NaOH, and the curve shows two steep rises. (a) State the volume of NaOH at the first equivalence point, and the species that dominates the flask there. (b) State the total NaOH volume at the second equivalence point, and the moles of OH^- consumed per mole of H_2A. (c) A classmate claims the curve should show only one equivalence point, because the same base removes both protons. Correct the claim. (d) State what happens to the two rises if Ka1 and Ka2 are very close.

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Answer Key

A1. (a) The analyte is the solution of unknown concentration in the flask, in a measured volume. (b) The titrant is the solution of known concentration in the burette, added in measured volumes. (c) The equivalence point is the stoichiometric stage: moles of titrant added are exactly what the balanced equation demands for complete reaction with the analyte. (d) The endpoint is the volume at which the indicator changes color. It is the experimental estimate of the equivalence point, coinciding with it only if the color change falls at the equivalence stage. (e) Low. The recorded volume is smaller than the true equivalence volume, so the moles of analyte calculated from it are too small, and dividing by the same flask volume gives too low a concentration.

A2. (a) Equal to 7. The flask holds Na^+, Cl^- and water; neither ion reacts with water. (b) Above 7. CH_3COOH has all become CH_3COO^-, which hydrolyzes: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$, making the solution basic. (c) Below 7. NH_3 has all become NH_4^+, which donates a proton to water: $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$, making the solution acidic. (d) Equal to 7. HNO_3 and KOH are both strong; K^+ and NO_3^- are spectators and the salt is neutral.

A3. (a) Only the weak acid, partly ionized: HA with a trace of H_3O^+ and A^-. The acid's own Ka equilibrium sets the pH. (b) Equal amounts of HA and A^-. The pair is a buffer, and the ratio sets the pH through the Ka expression of Topic 8.4. (c) Essentially all A^- (initial moles over total volume) plus spectator Na^+. Hydrolysis of A^-, governed by Kb = Kw / Ka, sets the pH, above 7. (d) A^- plus excess OH^-. The free OH^- dwarfs anything hydrolysis supplies, so excess titrant over total volume sets the pH. (e) The half-equivalence point: at half the equivalence volume, [HA] = [A^-], so pH equals pKa, and Ka = 10 raised to minus that pH.

A4. (a) Either works. The strong/strong steep section spans many units, roughly pH 4 to 10 and beyond, so both ranges fall inside it. (b) Phenolphthalein. The equivalence pH is above 7 and the steep section sits on the basic side, inside phenolphthalein's range. Methyl orange would change inside the buffer region, well before equivalence. (c) Methyl orange. The equivalence pH is below 7 and the steep section is acidic; phenolphthalein fades during the buffer region, well before equivalence.

A5. (a) Na^+, Cl^- and H_2O. No species present reacts with water, so water's own equilibrium sets the pH at 7.00. (b) CH_3COO^- at 0.0500 mol L^{-1} (0.00250 mol in the 50.0 mL total), Na^+ and H_2O. The pH is set by CH_3COO^- through its hydrolysis. (c) NH_4^+ at 0.0500 mol L^{-1} (0.00250 mol in 50.0 mL), Cl^- and H_2O. The pH is set by NH_4^+ through its proton donation to water.

B1. The flask starts with 0.0400 L × 0.100 mol L^{-1} = 0.00400 mol of H_3O^+. (a) No titrant yet: [H_3O^+] = 0.100 mol L^{-1}, pH = 1.00. (b) NaOH added: 0.0150 L × 0.100 = 0.00150 mol of OH^-, consuming H_3O^+ mole for mole: $H_3O^+ + OH^- \rightarrow 2H_2O$. Left over: 0.00400 − 0.00150 = 0.00250 mol in 55.0 mL, so [H_3O^+] = 0.00250 / 0.0550 = 0.0455 mol L^{-1}, pH = 1.34. (c) Equivalence needs 0.00400 mol of OH^-,

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which is 40.0 mL of the 0.100 mol L^{-1} NaOH. The flask holds only Na^+, Cl^- and water, so pH = 7.00. (d) OH^- added in total: 0.0500 × 0.100 = 0.00500 mol. Excess over the 0.00400 mol consumed: 0.00100 mol in 90.0 mL, so $[OH^-]$ = 0.00100 / 0.0900 = 0.0111 mol L^{-1}, pOH = 1.95, pH = 14.00 − 1.95 = 12.05.

B2. (a) For $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$, the quadratic on $Ka = x^2 / (0.100 - x) = 1.8 \times 10^{-5}$ gives $x = [H_3O^+] = 1.33 \times 10^{-3}$ mol L^{-1}, pH = 2.88. The square root approximation gives $x = \sqrt{(1.8 \times 10^{-5} \times 0.100)} = 1.34 \times 10^{-3}$ mol L^{-1}, pH = 2.87; percent ionization is $1.33 \times 10^{-3} / 0.100 \times 100 = 1.3$ percent, well under 5 percent, so the approximation is justified. (b) Equivalence needs 0.00250 mol of OH^-, which is 25.0 mL of the 0.100 mol L^{-1} NaOH. Half-equivalence is at 12.5 mL, where $[CH_3COOH] = [CH_3COO^-]$ and pH = pKa = 4.74. (c) At equivalence all 0.00250 mol of acid has become CH_3COO^- in 50.0 mL, so $[CH_3COO^-]$ = 0.00250 / 0.0500 = 0.0500 mol L^{-1}. Its $Kb = Kw / Ka = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. Hydrolysis gives $[OH^-] = \sqrt{(5.6 \times 10^{-10} \times 0.0500)} = 5.3 \times 10^{-6}$ mol L^{-1}, pOH = 5.28, pH = 14.00 − 5.28 = 8.72.

B3. (a) The flask holds 0.0250 × 0.100 = 0.00250 mol of NH_3, so equivalence needs 0.00250 mol of H_3O^+: 25.0 mL of the 0.100 mol L^{-1} HCl. (b) All the NH_3 becomes NH_4^+: 0.00250 mol in 50.0 mL, so $[NH_4^+]$ = 0.0500 mol L^{-1}. (c) NH_4^+ is the conjugate acid of NH_3, so its Ka comes from the pair relation: $Ka = Kw / Kb = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. For $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$, $[H_3O^+] = \sqrt{(5.6 \times 10^{-10} \times 0.0500)} = 5.3 \times 10^{-6}$ mol L^{-1}, so pH = 5.28. (d) At half-equivalence (12.5 mL), $[NH_3] = [NH_4^+]$, so pOH = pKb = 4.74 and pH = 14.00 − 4.74 = 9.26.

B4. The flask starts with 0.0500 L × 0.100 = 0.00500 mol of CH_3COOH. OH^- added: 0.0200 × 0.100 = 0.00200 mol. It converts acid to acetate mole for mole through $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$: CH_3COOH falls to 0.00300 mol and CH_3COO^- rises to 0.00200 mol. The pair shares one volume, so the ratio uses moles directly: $pH = pKa + \log([CH_3COO^-] / [CH_3COOH]) = 4.74 + \log(0.00200 / 0.00300) = 4.74 - 0.18 = 4.57$.

B5. (a) Moles match 1:1 at equivalence. Moles of OH^- used: 0.0240 L × 0.150 mol L^{-1} = 0.00360 mol, so the sample held 0.00360 mol of HNO_3 in 0.0200 L: concentration = 0.00360 / 0.0200 = 0.180 mol L^{-1}. (b) Moles of OH^- used: 0.0400 × 0.100 = 0.00400 mol. Full neutralization of a diprotic acid takes 2 mol OH^- per mole H_2A, one per proton, so moles of H_2A = 0.00400 / 2 = 0.00200 mol in 0.0250 L: concentration = 0.00200 / 0.0250 = 0.0800 mol L^{-1}.

B6. (a) Acid in the flask: 0.0250 × 0.100 = 0.00250 mol. OH^- added: 0.0300 × 0.100 = 0.00300 mol, which exceeds 0.00250 mol: past equivalence, by 5.0 mL. (b) Excess OH^-: 0.00300 − 0.00250 = 0.000500 mol in 55.0 mL: $[OH^-] = 0.000500 / 0.0550 = 9.09 \times 10^{-3}$ mol L^{-1}. pOH = 2.04, so pH = 14.00 − 2.04 = 11.96. (c) Acetate hydrolysis, $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$, has Kb of only 5.6×10^{-10} and would supply OH^- of order 10^{-6} mol L^{-1} alone; beside 9.09×10^{-3} mol L^{-1} of free OH^- it changes nothing at this precision.

C1. (a) Approximation: $[H_3O^+] \approx \sqrt{(Ka \times 0.100)} = \sqrt{(6.8 \times 10^{-4} \times 0.100)} = 8.2 \times 10^{-3}$ mol L^{-1}, pH = 2.08, percent ionization 8.2 percent. Above the 5 percent limit, the approximation cannot be trusted.

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Quadratic: solving $K_a = x^2 / (0.100 - x) = 6.8 \times 10^{-4}$ gives $x = 7.9 \times 10^{-3}$ mol L^{-1}, pH = 2.10, percent ionization 7.9 percent. The quadratic value, pH 2.10, stands. (b) Half-equivalence: 25.0 mL, half the equivalence volume, where $[HF] = [F^-]$ and pH = pKa = 3.17. (c) At equivalence the 0.00500 mol of HF has become 0.00500 mol of F^- in 100.0 mL, so $[F^-] = 0.0500$ mol L^{-1}. F^- is HF's conjugate base, so its Kb comes from Kw: $K_b = 1.0 \times 10^{-14} / 6.8 \times 10^{-4} = 1.47 \times 10^{-11}$. Hydrolysis through $F^- + H_2O \rightleftharpoons HF + OH^-$ gives $[OH^-] = \sqrt{(1.47 \times 10^{-11} \times 0.0500)} = 8.6 \times 10^{-7}$ mol L^{-1}, pOH = 6.07, pH = 14.00 − 6.07 = 7.93. (d) OH^- added: 0.0600 × 0.100 = 0.00600 mol, against 0.00500 mol of HF. Excess: 0.00100 mol in 110 mL, so $[OH^-] = 0.00100 / 0.110 = 9.09 \times 10^{-3}$ mol L^{-1}, pOH = 2.04, pH = 11.96.

C2. (a) The steep rise is centered on 20.0 mL: pH jumps from 4.78 at 15.0 mL to 8.47 at 20.0 mL and on to 12.26 at 30.0 mL, so the equivalence volume is 20.0 mL. Moles of OH^- used: 0.0200 L × 0.100 = 0.00200 mol, matching HA 1:1. Concentration: 0.00200 mol / 0.0250 L = 0.0800 mol L^{-1}. (b) Half-equivalence is at 10.0 mL, where the recorded pH is 4.30. There $[HA] = [A^-]$, so pKa = 4.30 and Ka = 10 raised to minus 4.30 = 5.0×10^{-5}. (c) At equivalence every HA has become A^-, and A^- hydrolyzes, $A^- + H_2O \rightleftharpoons HA + OH^-$, producing OH^-. The equivalence solution is therefore basic, which is why its pH is 8.47. (d) Phenolphthalein. The steep section passes through the equivalence pH of 8.47, inside phenolphthalein's 8 to 10 range, so its color change lands on the jump. Methyl orange finishes changing by pH 4, reached in the buffer region at roughly 7 mL, long before equivalence. (e) With $K_a = 5.0 \times 10^{-5}$ and 0.0800 mol L^{-1}, the quadratic on $K_a = x^2 / (0.0800 - x)$ gives $x = [H_3O^+] = 2.0 \times 10^{-3}$ mol L^{-1}, pH = 2.70, agreeing with the recorded initial pH.

C3. (a) The flask holds 0.0250 × 0.100 = 0.00250 mol of H_2A. The first proton takes one mole of OH^- per mole of acid, so the first equivalence point comes at 0.00250 mol of OH^-: 25.0 mL. The flask there is dominated by HA^-, product of the first step, $H_2A + OH^- \rightarrow HA^- + H_2O$, alongside Na^+. (b) The second proton takes a second 0.00250 mol of OH^-, through $HA^- + OH^- \rightarrow A^{2-} + H_2O$, so the second equivalence point comes at 50.0 mL in total: 0.00500 mol of OH^- for 0.00250 mol of H_2A, which is 2 mol of OH^- per mole of H_2A. (c) The protons do not leave together. They are removed in two separate stoichiometric steps, H_2A to HA^- then HA^- to A^{2-}, each with its own equivalence point where that step's mole condition is exactly met. (d) The two rises merge into one broad step: the second proton starts leaving before the first step is cleanly finished, so no separate endpoints can be read.

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