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Topic 8.4: Acid-Base Reactions and Buffers

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: net ionic equations, which mixtures genuinely buffer, reading a salt ion by ion, a buffer's two defense reactions, and choosing a pair for a target pH. Section B practises the skills: buffer pH for acid and base pairs, half-neutralization, buffers under attack, and a neutralization landing on an acidic salt. Section C is exam style: a buffer built, used and destroyed; two buffers with one pair at different ratios; and a mixing recipe that looks like a buffer and is not.

Conventions: 25 °C throughout, $K_w = 1.0 \times 10^{-14}$, concentrations in mol L^{-1}, pH and pOH to two decimal places. Each question supplies the constant it needs. Constants that recur: Ka of $CH_3COOH = 1.8 \times 10^{-5}$ (pKa 4.74), Ka of $HF = 6.8 \times 10^{-4}$ (pKa 3.17), Kb of $NH_3 = 1.8 \times 10^{-5}$, and the conjugates Ka of NH_4^+ = Kb of CH_3COO^- = 5.6×10^{-10} from Kw.

One working habit ties the sheet together: stoichiometry first, ratio second. When strong acid or base is added to a buffer, the added ion reacts completely with one member first. Recount both members' moles, confirm both still stand, and only then use the ratio:

$[H_3O^+] = K_a \times [HA] / [A^-]$

The base-pair form works the same way. In mixtures, take the moles from the volumes first; a product's own concentration uses the total volume, while a shared volume cancels.

Two checks run through the whole sheet. The midpoint check: equal amounts of the two members must return pH = pKa (or pOH = pKb). The round-trip check: your $[H_3O^+]$,

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substituted back into the Ka expression with the equilibrium amounts, returns the constant you were given. If a check fails, the error is in the working, never in the check.

The answer key shows every mole recount, ratio and logarithm step in full. Do not look at the answer key until you have attempted every question in Sections A, B and C.

Section A: Recall and Concepts

A1. Write the net ionic equation for each neutralization, naming the spectator ions and stating which species you split, which you kept whole, and why: (a) HCl(aq) + NaOH(aq); (b) CH_3COOH(aq) + KOH(aq); (c) HNO_3(aq) + NH_3(aq).

A2. State which of these mixtures are buffers, justifying every verdict: (a) 0.10 M HF with 0.10 M NaF; (b) 0.10 M HCl with 0.10 M NaCl; (c) 0.10 M NH_3 with 0.10 M NH_4Cl; (d) 0.10 M NaOH with 0.10 M NaCl; (e) 0.10 M CH_3COOH on its own; (f) H_2CO_3 with $NaHCO_3$ dissolved in the same solution.

A3. Predict whether each solution is acidic, basic or neutral, justifying each answer by naming the ion that reacts with water, if any. Where both ions come from weak parents, compare their constants: (a) $NaCH_3COO$; (b) NH_4Cl; (c) NaCl; (d) NH_4CH_3COO, given Ka of $NH_4^+ = 5.6 \times 10^{-10}$ and Kb of $CH_3COO^- = 5.6 \times 10^{-10}$.

A4. An acetate buffer, CH_3COOH / CH_3COO^-: (a) write the equation for what happens when a small amount of HCl is added; (b) write the equation for what happens when a small amount of NaOH is added; (c) explain, in terms of the ratio $[CH_3COO^-]$ / $[CH_3COOH]$, why the pH moves only slightly in each case; (d) state the condition under which the buffer stops working.

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A5. Four conjugate pairs and the pKa of the acid member: HF / F^- 3.17, CH_3COOH / CH_3COO^- 4.74, $H_2PO_4^-$ / HPO_4^{2-} 7.21, NH_4^+ / NH_3 9.26. (a) Choose the best pair for holding pH 7.0 and justify the choice. (b) Choose the best pair for holding pH 4.7. (c) A student proposes the NH_4^+ / NH_3 pair for pH 7.0. Calculate the ratio $[NH_3]$ / $[NH_4^+]$ needed, and use it to explain the poor performance.

Section B: Core Practice

B1. A buffer contains 0.40 mol L^{-1} HF and 0.20 mol L^{-1} NaF, with Ka of HF = 6.8×10^{-4}. (a) Calculate $[H_3O^+]$ using the ratio form of the Ka expression. (b) Calculate the pH. (c) Solving the full equilibrium gives $[H_3O^+] = 1.3 \times 10^{-3}$ mol L^{-1}. State the percentage by which the ionization shifts the smaller stock, and comment on whether the ratio answer stands.

B2. A buffer contains 0.20 mol L^{-1} NH_3 and 0.30 mol L^{-1} NH_4Cl, with Kb of NH_3 = 1.8×10^{-5}. (a) Calculate $[OH^-]$. (b) Calculate the pOH and the pH. (c) Both concentrations are doubled at the same ratio. State the new pH and justify the answer in one sentence.

B3. A buffer is made by mixing 200 mL of 0.30 mol L^{-1} CH_3COOH with 100 mL of 0.30 mol L^{-1} NaOH. Ka of CH_3COOH = 1.8×10^{-5}. (a) Calculate the moles of CH_3COOH and of OH^- before mixing. (b) Calculate the moles of CH_3COOH and of CH_3COO^- after the reaction, and their concentrations in the 300 mL mixture. (c) Calculate the pH. (d) State why this mixture is a buffer even though no acetate salt was ever weighed out.

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B4. A 1.0 L acetate buffer contains 0.15 mol CH_3COOH and 0.15 mol CH_3COO^-, with Ka = 1.8×10^{-5}. Then 0.020 mol of HCl is added. (a) Recount the moles of each member after the addition. (b) Calculate the new pH and its change. (c) Calculate the pH if the same 0.020 mol of HCl were added to 1.0 L of plain water, and comment.

B5. A 500 mL buffer contains 0.20 mol L^{-1} NH_3 and 0.20 mol L^{-1} NH_4Cl, with Kb of NH_3 = 1.8×10^{-5}. Then 0.010 mol of NaOH is added, with negligible volume change. (a) Calculate the moles of each member before the addition. (b) Recount the moles after the addition, stating which member the OH^- attacks. (c) Calculate the new pH and the change.

B6. 50 mL of 0.40 mol L^{-1} HCl is mixed with 50 mL of 0.40 mol L^{-1} NH_3. Kb of NH_3 = 1.8×10^{-5}. (a) Write the net ionic equation for the reaction. (b) Calculate the moles of each reactant, and the salt formed and its concentration. (c) Predict whether the resulting solution is acidic, basic or neutral, naming the ion responsible. (d) Calculate the pH of the resulting solution, showing where its Ka comes from and checking your approximation.

Section C: Exam Style

C1. A buffer is prepared by mixing 250 mL of 0.40 mol L^{-1} HF with 250 mL of 0.20 mol L^{-1} NaOH. Ka of HF = 6.8×10^{-4}. (a) Calculate the moles of HF and of F^- in the mixture and their concentrations. (b) Calculate the pH of the buffer. (c) Now 0.010 mol of HCl is added to the 500 mL mixture, volume change negligible. Recount the members and calculate the new pH. (d) A second student adds 0.060 mol of HCl to a fresh 500 mL portion of the same buffer instead. Explain why no buffer calculation applies, and calculate the pH.

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C2. Two acetate buffers use Ka = 1.8×10^{-5}. Buffer X holds 0.10 mol L^{-1} CH_3COOH and 0.10 mol L^{-1} CH_3COO^-. Buffer Y holds 0.10 mol L^{-1} CH_3COOH and 0.010 mol L^{-1} CH_3COO^-. (a) Calculate the pH of each buffer. (b) 0.0050 mol of NaOH is added to each litre of each buffer. Calculate the new pH of each, and the size of each change. (c) Explain why the same addition moves Y so much further than X, and state which attack, acid or base, Y is worst equipped to survive, and why.

C3. A student mixes 100 mL of 0.10 mol L^{-1} HCl with 100 mL of 0.10 mol L^{-1} $NaCH_3COO$ and labels the result an acetate buffer. Ka of CH_3COOH = 1.8×10^{-5}. (a) Calculate the moles of H_3O^+ and of CH_3COO^- mixed, and the composition of the resulting solution, including the concentration of the main solute. (b) Explain why the label is wrong. (c) Calculate the pH of the resulting solution, solving the quadratic rather than assuming the approximation, and give the percent ionization. (d) What volume of the 0.10 mol L^{-1} HCl would have made a genuine buffer from the same 100 mL of $NaCH_3COO$ solution, and at what pH?

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Answer Key

A1. (a) Split both strong electrolytes and the soluble salt: $H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O$. Na^+ and Cl^- cancel as spectators. Net ionic: $H_3O^+ + OH^- \rightarrow 2H_2O$, equivalently $H^+ + OH^- \rightarrow H_2O$. (b) KOH and the salt are split, but weak CH_3COOH stays whole: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. Spectator: K^+. (c) HNO_3 is split, NH_3 stays whole as a weak base: $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$. Spectator: NO_3^-.

A2. (a) Buffer: HF weak acid, F^- its conjugate base, both in full concentration. (b) Not a buffer: HCl is strong, and Cl^- never accepts a proton in water. (c) Buffer: NH_3 weak base, NH_4^+ its conjugate acid, both appreciable. (d) Not a buffer: NaOH is a strong base and NaCl gives only spectators. (e) Not a buffer: alone, the acid holds only the trace of CH_3COO^- from its own ionization. (f) Buffer: H_2CO_3 weak acid, HCO_3^- its conjugate base.

A3. (a) Basic: CH_3COO^-, conjugate base of a weak acid, reacts with water to give OH^-; Na^+ is a spectator. (b) Acidic: NH_4^+, conjugate acid of the weak base NH_3, donates a proton to water; Cl^- is a spectator. (c) Neutral: Na^+ from strong NaOH, Cl^- from strong HCl; neither reacts with water. (d) Approximately neutral. Both ions react with water, but their constants are equal at 5.6×10^{-10}, so proton donation and acceptance balance.

A4. (a) $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$: the base member consumes the added acid, becoming the acid member. (b) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$: the acid member consumes the added base, becoming the base member. (c) Through $pH = pKa + \log([CH_3COO^-] / [CH_3COOH])$, each addition converts a little of one member into the other, so the ratio and its logarithm barely move. (d) The buffer stops working once an addition exhausts the member it attacks, more H_3O^+ than there is CH_3COO^- or more OH^- than there is CH_3COOH; after that the excess is unopposed.

A5. (a) $H_2PO_4^-$ / HPO_4^{2-}: pKa 7.21 is closest to 7.0, only 0.21 away. (b) CH_3COOH / CH_3COO^-, pKa 4.74, within 0.04 of the target. (c) The log form requires $\log([NH_3] / [NH_4^+]) = 7.00 - 9.26 = -2.26$, so $[NH_3] / [NH_4^+] = 5.6 \times 10^{-3}$: barely one NH_3 for every 180 NH_4^+ ions. Almost no NH_3 is present, so the first small acid attack exhausts it and the pH collapses.

B1. (a) $[H_3O^+] = Ka \times [HF] / [F^-] = 6.8 \times 10^{-4} \times 0.40 / 0.20 = 1.4 \times 10^{-3}$ mol L^{-1} (1.36×10^{-3} before rounding). (b) $pH = -\log(1.36 \times 10^{-3}) = 2.87$. (c) The smaller stock is F^- at 0.20 mol L^{-1}; the shift of about 1.3×10^{-3} mol L^{-1} is roughly 0.7 percent of it. Exact and ratio values agree at the precision quoted and both give pH 2.87, so the ratio answer stands; the round trip returns 6.8×10^{-4}.

B2. (a) The same rearrangement on Kb: $[OH^-] = Kb \times [NH_3] / [NH_4^+] = 1.8 \times 10^{-5} \times 0.20 / 0.30 = 1.2 \times 10^{-5}$ mol L^{-1}. (b) $pOH = -\log(1.2 \times 10^{-5}) = 4.92$, and $pH = 14.00 - 4.92 = 9.08$. (c) Unchanged at 9.08: only the ratio enters, and doubling both leaves it at 0.20 / 0.30.

B3. (a) CH_3COOH: 0.200 L × 0.30 mol L^{-1} = 0.060 mol. OH^-: 0.100 L × 0.30 mol L^{-1} = 0.030 mol. (b) The OH^- converts CH_3COOH to CH_3COO^- mole for mole: CH_3COOH falls to $0.060 - 0.030 = 0.030$ mol,

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and CH_3COO^- rises from zero to 0.030 mol. In the 300 mL mixture each is 0.030 / 0.300 = 0.10 mol L^{-1}. (c) Equal members trigger the midpoint check: pH = pKa = $-\log(1.8 \times 10^{-5})$ = 4.74. (d) Partial neutralization manufactures the conjugate base in place; a buffer needs the pair in appreciable amounts.

B4. (a) The added H_3O^+ attacks the base member: $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$. CH_3COO^- falls to 0.15 − 0.020 = 0.13 mol and CH_3COOH rises to 0.15 + 0.020 = 0.17 mol. (b) pH = pKa + log([CH_3COO^-] / [CH_3COOH]) = 4.74 + log(0.13 / 0.17) = 4.63. The pH fell by 0.11. (c) In plain water the 0.020 mol of HCl simply stands as 0.020 mol L^{-1} H_3O^+: pH = $-\log(0.020)$ = 1.70, a fall of 5.30 from 7.00. The buffer turned a five-unit crash into a tenth of a unit, because the acid was spent converting CH_3COO^- rather than accumulating as free H_3O^+.

B5. (a) In 0.500 L: NH_3 = 0.500 × 0.20 = 0.10 mol, and NH_4^+ = 0.10 mol. (b) OH^- attacks the acid member: $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$. NH_4^+ falls to 0.10 − 0.010 = 0.090 mol and NH_3 rises to 0.10 + 0.010 = 0.11 mol. (c) $[OH^-] = K_b \times [NH_3] / [NH_4^+] = 1.8 \times 10^{-5} \times 0.11 / 0.090 = 2.2 \times 10^{-5}$ mol L^{-1}. pOH = $-\log(2.2 \times 10^{-5})$ = 4.66, so pH = 14.00 − 4.66 = 9.34. The buffer started at the midpoint value 9.26, so the pH rose by 0.08.

B6. (a) $H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$, with Cl^- as the only spectator. (b) HCl: 0.050 L × 0.40 mol L^{-1} = 0.020 mol. NH_3: 0.050 L × 0.40 = 0.020 mol. Neither is in excess, so 0.020 mol of NH_4Cl forms in 0.100 L: 0.20 mol L^{-1}. (c) Acidic: NH_4^+, conjugate acid of weak NH_3, donates protons to water; Cl^- does not react. (d) The salt's acidity runs on Ka of NH_4^+ from the pair relation: $K_a = K_w / K_b = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. For $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$, $x = [H_3O^+] \approx \sqrt{(5.6 \times 10^{-10} \times 0.20)} = 1.1 \times 10^{-5}$ mol L^{-1} (the quadratic agrees). Percent ionization is 0.0053 percent, fully justifying the approximation. pH = $-\log(1.1 \times 10^{-5})$ = 4.98.

C1. (a) HF mixed: 0.250 L × 0.40 mol L^{-1} = 0.100 mol. OH^- mixed: 0.250 L × 0.20 = 0.050 mol. The neutralization $HF + OH^- \rightarrow F^- + H_2O$ leaves HF = 0.100 − 0.050 = 0.050 mol and creates F^- = 0.050 mol. In 500 mL, [HF] = [F^-] = 0.050 / 0.500 = 0.10 mol L^{-1}. (b) Equal members: pH = pKa = $-\log(6.8 \times 10^{-4})$ = 3.17. (c) The added H_3O^+ converts F^- to HF: F^- falls to 0.050 − 0.010 = 0.040 mol (0.080 mol L^{-1}) and HF rises to 0.050 + 0.010 = 0.060 mol (0.120 mol L^{-1}). Then $[H_3O^+] = K_a \times [HF] / [F^-] = 6.8 \times 10^{-4} \times 0.120 / 0.080 = 1.0 \times 10^{-3}$ mol L^{-1}, and pH = 2.99. The full equilibrium gives $[H_3O^+] = 1.0 \times 10^{-3}$ mol L^{-1} and pH 3.00, confirming the ratio result. (d) The buffer holds only 0.050 mol of F^-, but 0.060 mol of H_3O^+ arrives. The first 0.050 mol is absorbed converting F^- to HF; the remaining 0.010 mol has no partner left and stands as free strong acid in 0.500 L: 0.020 mol L^{-1}, so pH = $-\log(0.020)$ = 1.70. (The HF present adds negligibly; the strong acid suppresses its ionization.)

C2. (a) Buffer X: equal members, so pH = pKa = 4.74. Buffer Y: $[H_3O^+] = K_a \times [HA] / [A^-] = 1.8 \times 10^{-5} \times 0.10 / 0.010 = 1.8 \times 10^{-4}$ mol L^{-1}, so pH = 3.74. (The full equilibrium gives 3.75 for Y; the ratio value stands at the quoted precision.) (b) The OH^- converts HA to A^- mole for mole. Buffer X: HA falls to 0.095 and A^- rises to 0.105 mol L^{-1}, so pH = 4.74 + log(0.105 / 0.095) = 4.79, a rise of 0.04. Buffer Y: HA falls to 0.095 and A^- rises to 0.015 mol L^{-1}, so pH = 4.74 + log(0.015 / 0.095) = 3.94, a rise of 0.20,

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five times X's movement. (c) Because pH reads the ratio through a logarithm, it answers to percentage changes in the members, not absolute ones. The same 0.0050 mol is 5 percent of X's A^- stock but 50 percent of Y's, so Y's ratio swings far harder. Against acid, Y is worst equipped: its entire A^- stock is 0.010 mol per litre, so just over 0.010 mol of added H_3O^+ exhausts it.

C3. (a) H_3O^+ mixed: 0.100 L × 0.10 mol L^{-1} = 0.010 mol. CH_3COO^- mixed: 0.010 mol. They react completely, $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$, leaving 0.010 mol of CH_3COOH in 200 mL (0.050 mol L^{-1}), with Na^+ and Cl^- as spectators. (b) The strong acid consumed the entire CH_3COO^- stock, so the base member a buffer needs exists only at the trace level the acid's own ionization supplies. The mixture is a plain weak acid solution, with nothing ready to absorb added acid. (c) For $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$, $K_a = x^2 / (0.050 - x) = 1.8 \times 10^{-5}$. The quadratic $x^2 + (1.8 \times 10^{-5})x - 9.0 \times 10^{-7} = 0$ gives $x = 9.4 \times 10^{-4}$ mol L^{-1}. (The unchecked approximation gives 9.5×10^{-4} mol L^{-1}, close here.) pH = $-\log(9.4 \times 10^{-4})$ = 3.03, and percent ionization = $9.4 \times 10^{-4} / 0.050 \times 100$ = 1.9 percent. (d) Half as much: 50 mL of the 0.10 mol L^{-1} HCl supplies 0.0050 mol of H_3O^+, converting exactly half of the 0.010 mol of CH_3COO^- and leaving CH_3COOH and CH_3COO^- in equal amounts. That mixture is a genuine buffer at pH = pKa = 4.74.

Continue Revising

Topic 8.4 Revision Notes

Topic 8.4 Quiz: Acid-Base Reactions and Buffers

Previous Worksheet: Topic 8.3 Weak Acid and Base Equilibria

Next Worksheet: Topic 8.5 Acid-Base Titrations

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