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Topic 8.8: Properties of 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 judgements: which mixtures are genuinely effective buffers, which species dominates at a given pH, what dilution really does, choosing a pair for a target pH, and the defence reactions with their limits. Section B practises the working skills: reading pH off a ratio, buffers under attack both ways, both partial neutralization preparations, dilution with the protection counted in moles, and a buffer destroyed. Section C is exam style: one pair at three ratios, the blood buffer quantified, and a buffer designed to a specification.

Conventions: 25 °C throughout, Kw = 1.0×10^{-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 = 1.8×10^{-5} (pKa 4.74), Ka of HF = 6.8×10^{-4} (pKa 3.17), Kb of NH_3 = 1.8×10^{-5} (pKa of NH_4^+ = 9.26), pKa of H_2CO_3 = 6.37, pKa of $H_2PO_4^-$ = 7.21.

One working habit ties the sheet together: moles first, ratio second. An added strong acid or base converts one buffer member into the other completely before any equilibrium is considered. Recount both stocks, confirm both still stand, and only then use pH = pKa + log([A^-] ÷ [HA]) or its base pair equivalent through Kb. Stocks are amounts: each direction is limited by the moles of the member it consumes.

Two checks run through the whole sheet. The range check: an effective buffer holds its ratio between 0.10 and 10, so neither member falls below about 9% of the pair. The survival check: after any addition, both stocks must still be positive.

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

Section A: Recall and Concepts

A1. Judge each mixture: effective buffer, buffer in name only, or not a buffer, justifying every verdict by the members and their amounts: (a) 0.50 mol L^{-1} CH_3COOH with 0.50 mol L^{-1} $NaCH_3COO$; (b) 0.010 mol L^{-1} CH_3COOH with 0.010 mol L^{-1} $NaCH_3COO$; (c) 0.10 mol L^{-1} HCl with 0.10 mol L^{-1} NaCl; (d) 0.10 mol L^{-1} CH_3COOH with 0.0010 mol L^{-1} $NaCH_3COO$; (e) 0.10 mol L^{-1} NH_3 with 0.10 mol L^{-1} NH_4Cl;

A2. An acid HA has pKa = 5.00. For the pair at each pH, state the ratio $[A^-] \div [HA]$, the dominant species, and its approximate percentage of the pair: (a) pH 4.00; (b) pH 5.00; (c) pH 6.00; (d) pH 7.00. (e) State the ratio at pH 3.00 from the pattern, and where pH 3.00 sits relative to the effective range.

A3. A buffer holds 0.20 mol L^{-1} CH_3COOH and 0.20 mol L^{-1} CH_3COO^-, Ka = 1.8×10^{-5}. It is diluted tenfold. (a) State the new concentration of each member. (b) Calculate the pH before and after dilution, showing why they agree. (c) Explain why the pH survives dilution but the protection does not, referring to the moles of CH_3COO^- in one litre of each version.

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A4. Pairs available, with the pKa of the acid member: HF / F^- 3.17, CH_3COOH / CH_3COO^- 4.74, H_2CO_3 / HCO_3^- 6.37, $H_2PO_4^-$ / HPO_4^{2-} 7.21, NH_4^+ / NH_3 9.26. Choose the best pair for each target, justifying with the ratio the target demands: (a) pH 4.0; (b) pH 7.4; (c) pH 9.3. (d) For target (b), name the pair blood uses, its operating ratio there, and how blood escapes the limit that ratio implies.

A5. For an acetate buffer: (a) write the equation when a small amount of HCl is added, naming the member whose stock limits that defence; (b) write the equation when a small amount of NaOH is added, naming the limiting member; (c) state what happens to the pH in each case, and why the change is small rather than zero; (d) state the condition under which each defence fails completely.

Section B: Core Practice

B1. A buffer's acid member has pKa = 4.00. Calculate the pH when $[A^-] \div [HA]$ is: (a) 0.10; (b) 1.0; (c) 10. (d) Calculate the ratio needed for pH 4.50, and state what is true of the scarcer member at the (a) and (c) edges of the range.

B2. A 1.0 L buffer contains 0.20 mol of HF and 0.20 mol of NaF, Ka of HF = 6.8×10^{-4}. Then 0.030 mol of NaOH is added, volume change negligible. (a) Recount the moles of each member, stating which member the OH^- attacks. (b) Calculate the new pH and its change from the starting value.

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B3. A buffer is prepared by mixing 500 mL of 0.40 mol L^{-1} CH_3COOH with 100 mL of 1.0 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 each member after the reaction, and their concentrations in the 600 mL mixture. (c) Calculate the pH. (d) State why this is a buffer even though no acetate salt was weighed out, and what 200 mL of the NaOH would have given instead, with its pH.

B4. A buffer is prepared by adding 0.10 mol of HCl to 1.0 L of 0.30 mol L^{-1} NH_3. Kb of NH_3 = 1.8×10^{-5}. (a) Recount the moles of NH_3 and of NH_4^+ after the reaction. (b) Calculate the pH. (c) State the pKa of NH_4^+ and check (b) against it using the ratio. (d) State what the mixture would be if 0.30 mol of HCl had been added instead.

B5. A student makes 100 mL of an acetate buffer holding 0.040 mol of CH_3COOH and 0.040 mol of CH_3COO^-, then dilutes it to 1.0 L. Ka = 1.8×10^{-5}. (a) Calculate each member's concentration before and after dilution. (b) Calculate the pH after dilution. (c) Calculate the moles of HCl the diluted sample can absorb before its CH_3COO^- is exhausted, and compare with a buffer made directly at the original concentrations in 1.0 L.

B6. A 1.0 L buffer contains 0.10 mol of HF and 0.10 mol of F^-, Ka of HF = 6.8×10^{-4}. A student adds 0.15 mol of HCl. (a) Show the recount at the moment the F^- runs out. (b) Explain why no buffer calculation applies to the final mixture. (c) Calculate the final pH, treating the leftover strong acid as dominant, and state the full solve value for comparison.

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Section C: Exam Style

C1. Three buffers use the pair CH_3COOH / CH_3COO^- (pKa 4.74), each in 1.0 L. Buffer P holds 0.90 mol of CH_3COOH and 0.10 mol of CH_3COO^-; buffer Q holds 0.10 mol and 0.90 mol; buffer R holds 0.50 mol of each. (a) Calculate the pH of each buffer. (b) State which buffer best resists added HCl and which best resists added NaOH, justifying each by the stock it would spend. (c) Now 0.050 mol of HCl is added to Q and to R separately. Calculate each new pH and the size of each change. (d) Explain why R moves less than Q under this attack even though Q holds the larger stock of the member being spent.

C2. Blood plasma is buffered by H_2CO_3 / HCO_3^-, pKa = 6.37, and is held at pH 7.40. (a) Calculate the ratio $[HCO_3^-] \div [H_2CO_3]$ in blood. (b) Plasma holds $[HCO_3^-] = 0.024$ mol L^{-1}. Calculate $[H_2CO_3]$. (c) In a sealed sample of this plasma, metabolic acid consumes 0.0020 mol L^{-1} of HCO_3^-, converting it to H_2CO_3. Calculate the new ratio and pH, and the size of the change. (d) State which member is scarce in blood, and which direction of attack the system is therefore least stocked against.

C3. Design a 1.0 L acetate buffer of pH 5.00 whose two members total 0.20 mol L^{-1}. Ka of CH_3COOH = 1.8×10^{-5}. (a) Calculate the ratio $[CH_3COO^-] \div [CH_3COOH]$ required. (b) Calculate each member's concentration. (c) Give a partial neutralization preparation: moles of CH_3COOH to start with and of NaOH to add. (d) Verify the design by calculating the pH from your concentrations, and confirm that the scarcer member clears the 9% edge of the effective range.

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Answer Key

A1. (a) Effective buffer: weak acid and conjugate base, both 0.50 mol L^{-1}, comparable and concentrated, so both directions are well stocked. (b) Buffer in name only: right pair and ratio, and pH 4.74, but at 0.010 mol L^{-1} the stocks are too small to absorb any real attack. (c) Not a buffer: HCl is a strong acid and Cl^- never accepts a proton, so there is no base member to spend. (d) Buffer in name only: the ratio $[CH_3COO^-] \div [CH_3COOH] = 0.0010 \div 0.10 = 0.010$ sits far outside the 0.10 to 10 range; the base member is about 1% of the pair. (e) Effective buffer: NH_3 with its conjugate acid NH_4^+, both appreciable and equal.

A2. The ratio is $[A^-] \div [HA] = 10^{(pH - pKa)}$. (a) pH 4.00: ratio 0.10, HA dominant, about 91% of the pair. (b) pH 5.00: ratio 1.0, neither dominant, 50% each. (c) pH 6.00: ratio 10, A^- dominant, about 91%. (d) pH 7.00: ratio 100, A^- dominant, about 99%. (e) At pH 3.00 the ratio is 0.010, HA about 99%; that pH lies outside the effective range, which ends at pKa − 1 = 4.00.

A3. (a) Each member falls tenfold: 0.020 mol L^{-1} of each. (b) Before: equal members, so pH = pKa = $-\log(1.8 \times 10^{-5}) = 4.74$. After: the ratio is still $0.020 \div 0.020 = 1$, so pH = 4.74 + log(1) = 4.74. Dilution divides both members by the same factor, leaving the ratio the pH reads untouched. (c) The pH is a ratio property and survives because both members shrink together. The protection is an amount property: one litre held 0.20 mol of CH_3COO^-; after dilution it holds 0.020 mol, ready for a tenth as much.

A4. The target demands a ratio of $10^{(target - pKa)}$; the best pair keeps that ratio between 0.10 and 10, ideally near 1. (a) pH 4.0: CH_3COOH / CH_3COO^-, ratio $10^{(4.0 - 4.74)} = 0.18$, the only candidate in range. (b) pH 7.4: $H_2PO_4^-$ / HPO_4^{2-}, ratio $10^{(7.4 - 7.21)} = 1.5$. (c) pH 9.3: NH_4^+ / NH_3, ratio $10^{(9.3 - 9.26)} = 1.1$. (d) Blood uses H_2CO_3 / HCO_3^- at a ratio of $10^{(7.4 - 6.37)} = 10.7$, just past the range's upper edge; it escapes the limit because the system is open, breathing regulating CO_2 and so the H_2CO_3 supply.

A5. (a) $CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$. The defence is limited by the CH_3COO^- stock, the member consumed. (b) $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. The defence is limited by the CH_3COOH stock. (c) Added acid lowers the pH slightly and added base raises it slightly. Each addition converts a little of one member into the other, so the ratio shifts by a small percentage and its logarithm moves only a little; the change is not zero because the ratio genuinely changes. (d) Each defence fails once an addition exceeds the stock it consumes: more H_3O^+ than there is CH_3COO^-, or more OH^- than there is CH_3COOH. Past that point the excess is unopposed and sets the pH itself.

B1. pH = pKa + log(ratio). (a) 4.00 + log(0.10) = 3.00. (b) 4.00 + log(1.0) = 4.00. (c) 4.00 + log(10) = 5.00. (d) The ratio is $10^{(4.50 - 4.00)} = 10^{0.50} = 3.2$. At the (a) edge the base member is about 9% of the pair, and at the (c) edge the acid member is about 9%; beyond either edge the scarcer member is too small a stock to absorb an attack aimed at it.

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B2. (a) OH^- attacks the acid member: $HF + OH^- \rightarrow F^- + H_2O$. HF falls to 0.17 mol and F^- rises to 0.23 mol. (b) Equal members at the start, so the buffer starts at pH = pKa = $-\log(6.8 \times 10^{-4})$ = 3.17. The new pH = 3.17 + log(0.23 ÷ 0.17) = 3.17 + 0.13 = 3.30, a rise of 0.13. (The full equilibrium solve also returns 3.30: the shift is tiny next to stocks of 0.17 and 0.23 mol.)

B3. (a) CH_3COOH: 0.500 L × 0.40 mol L^{-1} = 0.20 mol. OH^-: 0.100 L × 1.0 mol L^{-1} = 0.10 mol. (b) The OH^- converts CH_3COOH into CH_3COO^- mole for mole and runs out first: CH_3COOH falls to 0.10 mol and CH_3COO^- rises from zero to 0.10 mol. In the 600 mL mixture each is 0.10 ÷ 0.600 = 0.17 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 standing in appreciable amounts, and how the CH_3COO^- arrived is irrelevant. At 200 mL the OH^- would be 0.20 mol, exactly one equivalent: all the CH_3COOH becomes CH_3COO^-, 0.29 mol L^{-1} of a basic salt solution, not a buffer; its pH is 9.10, from Kb of CH_3COO^- = 5.6×10^{-10}.

B4. (a) The H_3O^+ converts NH_3 into NH_4^+ mole for mole and runs out first: NH_3 falls to 0.20 mol and NH_4^+ rises from zero to 0.10 mol. (b) Through the base pair: $[OH^-] = Kb \times [NH_3] \div [NH_4^+] = 1.8 \times 10^{-5} \times 0.20 \div 0.10 = 3.6 \times 10^{-5}$ mol L^{-1}. pOH = $-\log(3.6 \times 10^{-5})$ = 4.44, so pH = 14.00 − 4.44 = 9.56; the full solve returns the same 9.56. (c) pKa of NH_4^+ = 14.00 − pKb of NH_3 = 9.26. Check through the acid member: pH = 9.26 + log(0.20 ÷ 0.10) = 9.26 + 0.30 = 9.56, agreeing with (b). (d) At 0.30 mol of HCl every NH_3 is converted: 0.30 mol L^{-1} NH_4Cl, an acidic salt solution with no NH_3 member standing, not a buffer.

B5. (a) Before dilution, in 0.100 L: each member is 0.040 ÷ 0.100 = 0.40 mol L^{-1}. After dilution to 1.0 L: each is 0.040 mol L^{-1}. (b) The ratio is still 1, so pH = pKa = 4.74, unchanged. (c) The diluted sample holds 0.040 mol of CH_3COO^- in total, so it absorbs 0.040 mol of HCl. A buffer made directly at 0.40 mol L^{-1} in 1.0 L holds 0.40 mol and absorbs 0.40 mol, ten times as much, at the same pH. Dilution preserves the pH and destroys the capacity.

B6. (a) The added H_3O^+ converts F^- into HF mole for mole. F^- runs out after 0.10 mol of the HCl has been absorbed: at that moment F^- = 0, HF = 0.10 + 0.10 = 0.20 mol, and 0.050 mol of H_3O^+ is still to arrive. (b) With no F^- member standing, there is no pair and no ratio for a buffer equation to read; the remaining strong acid accumulates as free H_3O^+ and dominates the pH. (c) Leftover H_3O^+ = 0.050 mol in 1.0 L = 0.050 mol L^{-1}, so pH = $-\log(0.050)$ = 1.30. The full charge balance solve gives $[H_3O^+]$ = 0.053 mol L^{-1} and pH 1.28: the strong acid dominates, as the survival check predicted.

C1. (a) P: pH = 4.74 + log(0.10 ÷ 0.90) = 3.79. Q: pH = 4.74 + log(0.90 ÷ 0.10) = 5.70. R: equal members, pH = pKa = 4.74. (b) Against HCl the attack spends CH_3COO^-: Q, with 0.90 mol of it, resists acid best. Against NaOH the attack spends CH_3COOH: P, with 0.90 mol, resists base best. R holds 0.50 mol each way. (c) The HCl converts CH_3COO^- into CH_3COOH mole for mole. Q: CH_3COO^- falls to 0.85 mol and CH_3COOH rises to 0.15 mol, so pH = 4.74 + log(0.85 ÷ 0.15) = 5.50, a fall of 0.20. R: CH_3COO^- falls to 0.45 mol and CH_3COOH rises to 0.55 mol, so pH = 4.74 + log(0.45 ÷ 0.55) = 4.66, a fall of 0.09. (d) pH responds to the percentage change in the ratio, not to absolute moles. In

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Q the addition removes only 5.6% of the large CH_3COO^- stock but inflates the small CH_3COOH stock by 50%, 0.10 to 0.15 mol, so the ratio collapses from 9.0 to 5.67. In R the same moles move each stock by 10% in opposite directions: ratio 1.0 to 0.82. A buffer's weakness is set by its smaller member, whichever direction the attack comes from.

C2. (a) $[HCO_3^-] \div [H_2CO_3] = 10^{(pH-pKa)} = 10^{(7.40-6.37)} = 10^{1.03} = 10.7$. (b) $[H_2CO_3] = 0.024 \div 10.7 = 0.0022$ mol L^{-1}. (c) The consumed HCO_3^- becomes H_2CO_3: $[HCO_3^-]$ falls to 0.022 mol L^{-1} and $[H_2CO_3]$ rises to 0.0042 mol L^{-1}. The new ratio is $0.022 \div 0.0042 = 5.19$, so pH = 6.37 + log(5.19) = 7.09, a fall of 0.31. (d) H_2CO_3 is the scarce member, about a tenth of its partner, so the system is least stocked against added base, whose defence spends H_2CO_3; in the body the open system keeps resupplying it.

C3. (a) The ratio required is $10^{(5.00-4.74)} = 10^{0.26} = 1.8$. (b) With $[CH_3COO^-] = 1.8 \times [CH_3COOH]$ and the two totalling 0.20 mol L^{-1}: $2.8 \times [CH_3COOH] = 0.20$, giving $[CH_3COOH] = 0.071$ mol L^{-1} and $[CH_3COO^-] = 0.129$ mol L^{-1}. (c) Start with 0.20 mol of CH_3COOH in the litre and add 0.129 mol of NaOH: the OH^- converts 0.129 mol of the acid into CH_3COO^-, leaving the design composition standing. (d) Check: pH = 4.74 + log(0.129 ÷ 0.071) = 4.74 + 0.26 = 5.00, as designed. The scarcer member is 0.071 ÷ 0.20 = 36% of the pair, well above the 9% edge of the range (pKa ± 1, 3.74 to 5.74, which also contains 5.00).

Continue Revising

Topic 8.8 Revision Notes

Topic 8.8 Quiz: Properties of Buffers

Previous Worksheet: Topic 8.7 pH and pKa

Next Worksheet: Topic 8.9 Henderson-Hasselbalch Equation

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