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Topic 8.9: Henderson-Hasselbalch Equation

Worksheet · AP Chemistry

UNIT 8 · ACIDS AND BASES

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How to Use This Worksheet

Work in order. Section A checks fluency with the equation itself: its parts and where it comes from, reading the log term in both directions, the base form, percent in each form, and judging where the equation can be trusted. Section B practises the working skills: a direct pH, a ratio designed backwards from a target pH, an addition handled by recount, the base form by both routes, a missing concentration found from a pH, and a mixture where the equation must not be trusted. Section C is exam style: a buffer designed to a specification with mixing volumes, a cyanide buffer under acid attack, and a diprotic pair read at three pH values.

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 $NH_3 = 1.8 \times 10^{-5}$ (pKb 4.74, so pKa of $NH_4^+ = 9.26$), pKa of HCN = 9.31.

One working habit ties the sheet together: the equation reads a ratio, and a ratio is only as good as the recount behind it. After any addition of strong acid or base, convert one member into the other mole for mole, confirm both still stand, and only then substitute. Inside one solution the ratio of concentrations equals the ratio of moles, because both members share the same volume; when separate solutions are mixed, work in moles and let the common final volume cancel at the end.

One check runs through the whole sheet, the trust check: the equation treats the amounts mixed as the amounts at equilibrium. Before trusting a result, compare the ionization shift, roughly the size of $[H_3O^+]$ or $[OH^-]$, with the smaller stock. If the shift is a tiny fraction of that

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stock, the equation and an exact equilibrium solve agree; if it is a sizable fraction, the exact solve is the value to report, and Section B ends with a case where they part company.

The answer key shows every recount, ratio and logarithm step in full, with exact-solve comparisons wherever the sheet asks for one. Do not look at it until you have attempted every question in Sections A, B and C.

Section A: Recall and Concepts

A1. (a) Write the Henderson-Hasselbalch equation, stating what $[A^-]$, [HA] and pKa each refer to. (b) Starting from Ka = $[H_3O^+][A^-] \div [HA]$, show the rearrangement that gives $[H_3O^+]$ directly, and state in one sentence how the log form follows. (c) State the pH when $[A^-] = [HA]$, and the feature of the log term that makes it so.

A2. An acid member has pKa = 6.00. For each value of the ratio $[A^-] \div [HA]$, state the pH and whether the mixture sits above, at, or below pKa: (a) 10; (b) 1.0; (c) 0.10; (d) 100; (e) 0.010. (f) State the ratio that would put the pH exactly 0.50 above pKa.

A3. (a) Write the base form of the equation for a weak base B with its conjugate acid BH^+, and state which species stands on top of the ratio. (b) For NH_3 / NH_4^+, with Kb of $NH_3 = 1.8 \times 10^{-5}$, calculate pKb of NH_3 and pKa of NH_4^+. (c) A student writes pOH = pKb + log($[NH_3] \div [NH_4^+]$). State the error, and what it does to a calculated pOH when $[NH_4^+]$ exceeds $[NH_3]$.

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A4. (a) At pH = pKa + 1, what percent of the pair is in base form? Show the step that produces the percent from the ratio. (b) At pH = pKa − 2, what percent is in acid form? (c) For an acid of pKa 5.00, at what pH is it 99.9% in acid form? (d) State the pattern connecting the minority form's percent to the distance from pKa.

A5. Judge each case: the equation is trustworthy as it stands, or an exact equilibrium solve is needed, or the equation does not apply at all. Justify each verdict by the sizes involved. Ka of CH_3COOH = 1.8×10^{-5} throughout. (a) 0.20 mol L^{-1} CH_3COOH with 0.10 mol L^{-1} CH_3COO^-; (b) 1.0×10^{-4} mol L^{-1} of each member; (c) 0.10 mol L^{-1} CH_3COOH with 0.0010 mol L^{-1} CH_3COO^-; (d) 0.10 mol L^{-1} CH_3COOH alone; (e) 0.10 mol L^{-1} HCl with 0.10 mol L^{-1} NaCl.

Section B: Core Practice

B1. Calculate the pH of a buffer holding 0.050 mol L^{-1} HCN and 0.20 mol L^{-1} NaCN, pKa of HCN = 9.31. State the value an exact equilibrium solve returns, and whether the trust check passes.

B2. An NH_4^+ / NH_3 buffer must read pH 9.00; pKa of NH_4^+ = 9.26. (a) Calculate the ratio $[NH_3] \div [NH_4^+]$ required. (b) If $[NH_4^+]$ = 0.20 mol L^{-1}, calculate $[NH_3]$. (c) Verify the design by calculating the pH of your mixture. (d) State the scarcer member's percent of the pair, and whether the ratio lies inside the effective buffer range of 0.10 to 10.

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B3. A 1.0 L buffer holds 0.20 mol of CH_3COOH and 0.20 mol of CH_3COO^-, Ka = 1.8×10^{-5}. Then 0.040 mol of NaOH is added, volume change negligible. (a) Recount the moles of each member, stating which member the OH^- attacks and writing the equation. (b) Calculate the new pH and its change from the starting pH.

B4. A buffer holds 0.10 mol L^{-1} NH_3 and 0.20 mol L^{-1} NH_4Cl, Kb of NH_3 = 1.8×10^{-5}. (a) Calculate the pH using the base form of the equation. (b) Calculate it again through the pKa of NH_4^+. (c) State why the two routes must agree, and the exact-solve value.

B5. A buffer reads pH 4.60. Its acid member has pKa 4.00 and [HA] = 0.050 mol L^{-1}. (a) Calculate the ratio $[A^-] \div [HA]$. (b) Calculate $[A^-]$. (c) A second buffer of the same pair reads pH 3.40 at the same [HA]. Calculate its $[A^-]$, and state each buffer's percent in base form.

B6. A mixture holds 0.10 mol L^{-1} CH_3COOH and 0.0010 mol L^{-1} CH_3COO^-, Ka = 1.8×10^{-5}. (a) Calculate the pH the equation gives. (b) An exact equilibrium solve gives pH 3.03, with equilibrium $[CH_3COO^-]$ = 0.0019 mol L^{-1}. Explain the disagreement, identifying the assumption that fails and the size of the ionization that breaks it. (c) State which value a careful student reports, and the condition that would have made the equation reliable for this pair.

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Section C: Exam Style

C1. Design 1.0 L of an HF / F^- buffer of pH 3.50 whose two members total 0.40 mol L^{-1}, mixed from stock solutions of 0.40 mol L^{-1} HF and 0.40 mol L^{-1} NaF. Ka of HF = 6.8×10^{-4} (pKa 3.17). (a) Calculate the ratio $[F^-] \div [HF]$ required. (b) Calculate each member's concentration in the final buffer. (c) Calculate the volume of each stock solution to mix. (d) Verify the design: calculate the pH from your concentrations, state the exact-solve value, and confirm the scarcer member clears the 9% edge of the effective range.

C2. A 1.0 L buffer holds 0.10 mol of HCN and 0.20 mol of NaCN, pKa of HCN = 9.31. (a) Calculate its pH. (b) Then 0.010 mol of HCl is added, volume change negligible. Write the equation for what the added H_3O^+ does, and recount the moles of each member. (c) Calculate the new pH and the size of the change. (d) State the pH if the same 0.010 mol of HCl were added to 1.0 L of pure water, and what the comparison shows.

C3. A diprotic acid H_2A has pKa1 = 3.00 and pKa2 = 8.00. (a) A solution holds $[H_2A] = [HA^-]$. State its pH, naming the pKa used, and calculate the ratio $[A^{2-}] \div [HA^-]$ at that pH to show the other step barely stirs. (b) At pH 5.50, calculate the ratios $[HA^-] \div [H_2A]$ and $[A^{2-}] \div [HA^-]$, and hence the percent of the total present as HA^-. (c) State the pH at which $[HA^-] = [A^{2-}]$, and which form dominates just below it.

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Answer Key

A1. (a) pH = pKa + log([A^-] ÷ [HA]). [HA] is the weak acid member of the pair, [A^-] its conjugate base, and pKa = −log Ka of that acid member; both concentrations are the equilibrium values in the mixture. (b) From Ka = [H_3O^+][A^-] ÷ [HA], multiply both sides by [HA] ÷ [A^-]: [H_3O^+] = Ka × [HA] ÷ [A^-]. Taking the negative logarithm of the Ka expression separates it into −log Ka = −log[H_3O^+] − log([A^-] ÷ [HA]), which rearranges to the log form. (c) pH = pKa: the ratio is 1 and log(1) = 0, so the log term vanishes.

A2. pH = 6.00 + log(ratio). (a) Ratio 10: pH 7.00, one unit above pKa. (b) Ratio 1.0: pH 6.00, at pKa. (c) Ratio 0.10: pH 5.00, one unit below. (d) Ratio 100: pH 8.00, two units above. (e) Ratio 0.010: pH 4.00, two units below. (f) The ratio is $10^{0.50}$ = 3.16: a half-unit of pH is a factor of about 3.2 in the ratio, not a factor of 5 or a half.

A3. (a) pOH = pKb + log([BH^+] ÷ [B]): the conjugate acid, the protonated member, stands on top. It comes from Kb = [BH^+][OH^-] ÷ [B] the same way the acid form comes from Ka. (b) pKb = −log(1.8×10^{-5}) = 4.74. pKa of NH_4^+ = 14.00 − 4.74 = 9.26. (c) The ratio is inverted: NH_3, the base member, has been put on top in place of NH_4^+. When [NH_4^+] exceeds [NH_3] the true log term is positive, but the inverted form makes it negative, so the calculated pOH comes out low by twice the term, and the pH derived from it comes out high by the same amount.

A4. (a) pH = pKa + 1 means the ratio is 10, so the base form's share is 10 ÷ (10 + 1) = 10/11 = 91%. (b) pH = pKa − 2 means the ratio is 0.01, so the acid form's share is 1 ÷ 1.01 = 99%. (c) 99.9% acid form means the base form is 0.1% of the pair: ratio = 0.001, log(ratio) = −3.00, so pH = 5.00 − 3.00 = 2.00. (d) Each unit of distance from pKa divides the minority form's share by about ten: about 9% at one unit (the dominant form holds 91%), about 1% at two units, about 0.1% at three.

A5. (a) Trustworthy. [H_3O^+] = Ka × [HA] ÷ [A^-] = $1.8 \times 10^{-5} \times 0.20 \div 0.10 = 3.6 \times 10^{-5}$ mol L^{-1}, a tiny fraction of the smaller stock, 0.10 mol L^{-1}; the equation gives pH 4.44 and the exact solve returns 4.44. (b) Exact solve needed. The equation reads ratio 1 and reports 4.74, but [H_3O^+] in the exact solve reaches 1.4×10^{-5} mol L^{-1}, a sizable fraction of a 1.0×10^{-4} stock, and water's ions are no longer negligible; the exact pH is 4.86. (c) Exact solve needed. The scarce member's stock, 0.0010 mol L^{-1}, is the same size as the ionization the acid itself produces, so the stock cannot stand in for the equilibrium concentration; B6 works this case in full. (d) Does not apply. A lone weak acid has no standing pair and no ratio to read; its pH belongs to an ICE table on Ka (Topic 8.3). (e) Does not apply. HCl is fully ionized and Cl^- never accepts a proton in water, so there is no weak pair; the strong acid's concentration sets the pH directly.

B1. pH = 9.31 + log(0.20 ÷ 0.050) = 9.31 + log(4.0) = 9.31 + 0.60 = 9.91. The exact equilibrium solve returns 9.91. The trust check passes: the shift is of the order of [H_3O^+] = Ka × [HA] ÷ [A^-] = $4.9 \times 10^{-10} \times 0.050 \div 0.20 = 1.2 \times 10^{-10}$ mol L^{-1}, utterly negligible beside the smaller stock of 0.050 mol L^{-1}.

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B2. (a) The ratio is $10^{(pH-pKa)} = 10^{(9.00-9.26)} = 10^{-0.26} = 0.55$. (b) $[NH_3] = 0.55 \times 0.20 = 0.11$ mol L^{-1}. (c) pH = 9.26 + log(0.11 ÷ 0.20) = 9.26 + log(0.55) = 9.26 − 0.26 = 9.00, as designed; the exact solve returns 9.00. (d) The scarcer member is NH_3 at 0.11 ÷ 0.31 = 35% of the pair, and the ratio 0.55 sits comfortably inside 0.10 to 10.

B3. (a) OH^- attacks the acid member: $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$. CH_3COOH falls to 0.20 − 0.040 = 0.16 mol and CH_3COO^- rises to 0.20 + 0.040 = 0.24 mol. (b) Equal members at the start, so the buffer starts at pH = pKa = 4.74. The new pH = 4.74 + log(0.24 ÷ 0.16) = 4.74 + log(1.5) = 4.74 + 0.18 = 4.92, a rise of 0.18; the exact solve also returns 4.92.

B4. (a) Base form: pOH = pKb + log($[NH_4^+]$ ÷ $[NH_3]$) = 4.74 + log(0.20 ÷ 0.10) = 4.74 + 0.30 = 5.04, so pH = 14.00 − 5.04 = 8.96. (b) Acid form: pKa of NH_4^+ = 14.00 − 4.74 = 9.26, and pH = 9.26 + log($[NH_3]$ ÷ $[NH_4^+]$) = 9.26 + log(0.10 ÷ 0.20) = 9.26 − 0.30 = 8.96. (c) The two routes describe one equilibrium and are linked by pKa + pKb = 14.00, so they cannot disagree; the exact solve returns 8.96.

B5. (a) The ratio is $10^{(4.60-4.00)} = 10^{0.60} = 3.98$. (b) $[A^-] = 3.98 \times 0.050 = 0.20$ mol L^{-1}. (c) The second buffer's ratio is $10^{(3.40-4.00)} = 10^{-0.60} = 0.25$, so $[A^-] = 0.25 \times 0.050 = 0.013$ mol L^{-1}. Percent in base form: the first buffer holds 3.98 ÷ 4.98 = 80% of its pair as A^-; the second holds 0.25 ÷ 1.25 = 20%. The two pH values sit symmetrically about pKa, and so do the two compositions.

B6. (a) pH = 4.74 + log(0.0010 ÷ 0.10) = 4.74 + log(0.010) = 4.74 − 2.00 = 2.74. (b) The equation assumes the concentrations mixed are the concentrations at equilibrium. Here the acid's own ionization produces about 9×10^{-4} mol L^{-1} of CH_3COO^-, which is the same size as the entire 0.0010 mol L^{-1} stock of that member: at equilibrium $[CH_3COO^-]$ is 0.0019 mol L^{-1}, nearly double the stock the equation read. The acid member, at 0.10 mol L^{-1}, is barely dented by the same ionization, so the failure is concentrated in the scarce member, exactly where the ratio is most sensitive. (c) Report 3.03, the exact value. The equation would have been reliable if both stocks had been large compared with the shift of about 10^{-3} mol L^{-1}, so that ionization could not move either member's concentration by more than a small fraction; at these stock levels that test fails, which is what the trust check of A5 is for.

C1. (a) The ratio is $10^{(3.50-3.17)} = 10^{0.33} = 2.14$. (b) With $[F^-] = 2.14 \times [HF]$ and the two totalling 0.40 mol L^{-1}: $3.14 \times [HF] = 0.40$, giving $[HF] = 0.127$ mol L^{-1} and $[F^-] = 0.273$ mol L^{-1}. (c) Moles needed in 1.0 L: 0.127 mol of HF and 0.273 mol of F^-. From 0.40 mol L^{-1} stocks: HF stock = 0.127 ÷ 0.40 = 0.319 L = 319 mL; NaF stock = 0.273 ÷ 0.40 = 0.681 L = 681 mL; the volumes total 1000 mL, as they must. (d) Check: pH = 3.17 + log(0.273 ÷ 0.127) = 3.17 + log(2.14) = 3.17 + 0.33 = 3.50, as designed; the exact solve returns 3.50. The scarcer member, HF, is 0.127 ÷ 0.40 = 32% of the pair, well clear of the 9% edge.

C2. (a) pH = 9.31 + log(0.20 ÷ 0.10) = 9.31 + log(2.0) = 9.31 + 0.30 = 9.61; the exact solve returns 9.61. (b) The added H_3O^+ converts CN^- into HCN: $CN^- + H_3O^+ \rightarrow HCN + H_2O$. CN^- falls to 0.20 − 0.010 = 0.19 mol and HCN rises to 0.10 + 0.010 = 0.11 mol. (c) The new pH = 9.31 + log(0.19 ÷ 0.11) = 9.31 + 0.24 = 9.55, a fall of 0.06; the exact solve returns 9.55. (d) In pure water the 0.010 mol of HCl stands

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as 0.010 mol L^{-1} H_3O^+, pH = 2.00. The same addition moves the buffer by 0.06 units and unbuffered water from 7.00 to 2.00: the pair absorbed the attack by conversion, and only the small ratio change reached the pH.

C3. (a) The pair H_2A / HA^- belongs to the first step, so the pKa is pKa1: equal members give pH = pKa1 = 3.00. The second step's ratio at that pH is $[A^{2-}] \div [HA^-] = 10^{(3.00-8.00)} = 10^{-5}$, so only one HA^- in a hundred thousand has lost its second proton; the step barely stirs. (b) $[HA^-] \div [H_2A] = 10^{(5.50-3.00)} = 10^{2.50} = 316$. $[A^{2-}] \div [HA^-] = 10^{(5.50-8.00)} = 10^{-2.50} = 0.0032$. Taking $[H_2A]$ as 1 unit: HA^- = 316 units and A^{2-} = 316 × 0.0032 = 1 unit, a total of 318 units, so HA^- is 316 ÷ 318 = 99% of the total. (c) $[HA^-] = [A^{2-}]$ when pH = pKa2 = 8.00. Just below it, HA^- dominates A^{2-}, as it has dominated everything since well below pH 5.50.

Continue Revising

Topic 8.9 Revision Notes

Topic 8.9 Quiz: Henderson-Hasselbalch Equation

Previous Worksheet: Topic 8.8 Properties of Buffers

Next Worksheet: Topic 8.10 Buffer Capacity

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