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Topic 8.7: pH and pKa

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: the four p-scales and their definitions, the direction of the strength ranking, the two sums that come from Kw, the pH against pKa comparison, and the significant figure rule for logarithms. Section B practises the skills: conversions in both directions with round-trip checks, Ka ratios from pKa gaps, conjugate pKb and Kb values, percent ionized targets, and pKa or pH estimated from a single measurement. Section C is exam style: a diprotic acid to map, a flawed student answer to take apart, and a four-acid data table to mine.

Conventions: 25 °C throughout, $K_w = 1.0 \times 10^{-14}$, so pH + pOH = 14.00 and pKa + pKb = 14.00 for a conjugate pair. The data set for this sheet, taken from the quiz for this topic: HF has pKa = 3.17 ($K_a = 6.8 \times 10^{-4}$); CH_3COOH has pKa = 4.74 ($K_a = 1.8 \times 10^{-5}$); HCN has $K_a = 4.9 \times 10^{-10}$ (pKa = 9.31); NH_3 has $K_b = 1.8 \times 10^{-5}$ (pKb = 4.74); H_2CO_3 has pKa1 = 6.37 and pKa2 = 10.33; HCl is strong, with $K_a \approx 10^{7}$ and pKa ≈ −7.

Two habits tie the sheet together. First, round-trip every conversion: turn Ka into pKa, then turn the pKa back, and only move on when the starting value returns. A conversion that does not round-trip is wrong, however confident it looks. Second, read every pKa gap as an exponent: a gap of n units is always a factor of 10^n in Ka, never a factor of n.

Two checks run through the sheet. The direction check: the acid with the lower pKa must have the larger Ka, in every pair, every time. The sum check: for any conjugate pair you quote, pKa + pKb must come to 14.00; if it does not, the pair is not conjugate or a conversion has slipped.

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The answer key gives the full working for every question. Do not look at it until you have attempted every question.

Section A: Recall and Concepts

A1. (a) Write the definitions of pKa and pKb as equations. (b) An acid has pKa = 5.00. State its Ka. (c) Explain in one or two sentences why a log scale is used at all, when Ka values such as 4.9×10^{-10} are available directly.

A2. (a) Rank acids with pKa values 10.0, 7.0, 2.0 and 4.0, strongest first. (b) Of pKa values 4.8, 9.3, 7.2 and 3.5, which belongs to the weakest acid? (c) State the rule that connects the pKa order to the strength order.

A3. (a) Write the relationship between pH and pOH at 25 °C, and name the constant it comes from. (b) Write the corresponding relationship for the pKa of an acid and the pKb of its conjugate base. (c) State the two conditions the second relationship needs before it can be used.

A4. A weak acid HA sits in a solution whose pH is held fixed. (a) At pH = pKa, how do [HA] and $[A^-]$ compare, and what percent of the acid is ionized? (b) At a pH one unit below pKa, which form dominates, and roughly what percent is ionized? (c) At a pH two units above pKa, what is $[A^-] \div [HA]$, and what percent is ionized?

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A5. (a) A strong acid has Ka greater than 1. What does that force the sign of its pKa to be, and what is the approximate pKa of HCl? (b) A measurement gives $[H_3O^+] = 5.62 \times 10^{-5}$ M. Calculate the pH, state how many decimal places it should carry, and say why. (c) A student reports pH = 4.2505 for a solution made from a 0.020 M concentration. What is wrong with the report?

Section B: Core Practice

B1. (a) Calculate the pKa of an acid with $Ka = 4.9 \times 10^{-10}$. (b) Calculate the Ka of an acid with pKa = 3.17. (c) Calculate the pKa of an acid with $Ka = 2.5 \times 10^{-4}$. (d) Round-trip check: take your answer to (b) and convert it back to a pKa.

B2. CH_3COOH has pKa = 4.74 and HCN has pKa = 9.31. (a) Which acid is stronger, and by how many pKa units? (b) Use the pKa gap to calculate the ratio of the two Ka values. (c) Confirm the ratio directly from $Ka = 1.8 \times 10^{-5}$ and $Ka = 4.9 \times 10^{-10}$.

B3. (a) Calculate the pKb of CN^- from the pKa of HCN, 9.31. (b) Calculate Kb of CN^- in two independent ways and show that they agree. (c) NH_3 has pKb = 4.74. Calculate the pKa of NH_4^+ and the Ka of NH_4^+.

B4. An acid has pKa = 4.74. (a) At what pH is it exactly 90% ionized? Give the ratio $[A^-] \div [HA]$ first, then the pH. (b) At what pH is it 99% ionized? (c) At what pH is it only 1% ionized?

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B5. A 0.10 M solution of a weak acid HA has pH 3.00. (a) Calculate $[H_3O^+]$. (b) Write the Ka expression for $HA + H_2O \rightleftharpoons H_3O^+ + A^-$, calculate Ka, and state the approximation you use for [HA]. (c) Calculate the pKa. (d) Check the approximation: what percent of the acid is ionized?

B6. An acid has pKa = 6.00, and a 0.050 M solution is prepared. (a) Convert the pKa to Ka. (b) Estimate $[H_3O^+]$ and the pH. (c) Justify the shortcut in (b) with a percent check, and state how many decimal places the pH should carry.

Section C: Exam Style

C1. Carbonic acid, H_2CO_3, has pKa1 = 6.37 and pKa2 = 10.33. (a) Write the two ionization equations, one for each proton. (b) Which form, H_2CO_3, HCO_3^- or CO_3^{2-}, dominates at pH 8.0, and why? (c) Which form dominates at pH 5.0, and which at pH 11.5? (d) A different diprotic acid H_2A has pKa1 = 2.0 and pKa2 = 7.0. Estimate the pH at its first equivalence point, and name the species that dominates there.

C2. A student writes: "HCN (pKa 9.31) is a stronger acid than CH_3COOH (pKa 4.74), because 9.31 is the bigger number. Its Ka is about twice as large, since 9.31 is roughly double 4.74. And because pKa + pKb = 14, the pKb of CH_3COO^- must be 14.00 − 9.31 = 4.69." (a) Correct the strength claim. (b) Correct the Ka comparison, giving the real ratio of the two Ka values. (c) Find the error in the pKb calculation, give the correct pKb of CH_3COO^-, and state which species the value 4.69 actually belongs to.

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C3. Four acids have pKa values: HF 3.17, CH_3COOH 4.74, H_2CO_3 (first proton) 6.37, HCN 9.31. (a) Rank the four acids, strongest first. (b) Rank the four conjugate bases, strongest base first. (c) Calculate Kb for the strongest base in your (b) ranking. (d) A CH_3COOH and CH_3COO^- mixture sits at pH 4.74. What is $[CH_3COO^-] \div [CH_3COOH]$ there, and at what pH would the ratio reach 100? (e) Using only the pKa table, identify the acid that is about 37 times stronger than CH_3COOH, showing the gap arithmetic that proves it.

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Answer Key

A1. (a) pKa = −log Ka and pKb = −log Kb, the negative base-10 logarithms of the two equilibrium constants, exactly as pH = −log [H_3O^+]. (b) Ka = $10^{-5.00}$ = 1.0×10^{-5}. (c) Ka values span many powers of ten, from about 10^7 down past 10^{-10}. The logarithm compresses that range into a short scale of ordinary numbers, so strengths can be ranked and gaps read off without juggling exponents.

A2. (a) pKa 2.0 > pKa 4.0 > pKa 7.0 > pKa 10.0 in strength: strongest is the acid with pKa 2.0, weakest the one with pKa 10.0. (b) 9.3, the largest pKa of the four. (c) Lower pKa means larger Ka and a stronger acid, so the strength order is always the exact reverse of the pKa order.

A3. (a) pH + pOH = 14.00 at 25 °C. It comes from Kw: [H_3O^+] × [OH^-] = Kw = 1.0×10^{-14}, and taking −log turns the product into the sum. (b) pKa + pKb = 14.00, from Ka × Kb = Kw for the pair. (c) The two species must be a genuine conjugate pair, differing by exactly one proton, and the temperature must be 25 °C, since Kw, and therefore the 14.00, changes with temperature.

A4. (a) [HA] = [A^-]; the ratio is 1, so exactly 50% of the acid is in the ionized form. (b) HA dominates. The ratio [A^-] ÷ [HA] = 10^{-1} = 0.1, so the percent ionized is 0.1 ÷ 1.1, about 9%. (c) [A^-] ÷ [HA] = 10^2 = 100, and the percent ionized is 100 ÷ 101, about 99%.

A5. (a) Negative: −log of a number greater than 1 is negative. HCl has Ka ≈ 10^7, so pKa ≈ −7. (b) pH = −log(5.62×10^{-5}) = 4.250. It carries three decimal places, because the concentration has three significant figures, and for a logarithm the significant figures of the concentration set the decimal places of the p-value. (c) The concentration 0.020 M has two significant figures, so its pH can carry only two decimal places: 4.25. Reporting 4.2505 claims four decimal places of precision that the data cannot support; the extra digits are noise, not measurement. Parts (b) and (c) are the same rule at different precisions.

B1. (a) pKa = −log(4.9×10^{-10}) = 9.31. (b) Ka = $10^{-3.17}$ = 6.8×10^{-4}. (c) pKa = −log(2.5×10^{-4}) = 3.60. (d) −log(6.8×10^{-4}) = 3.17, the starting pKa, so the conversion in (b) round-trips and is confirmed.

B2. (a) CH_3COOH is stronger; its pKa is lower. The gap is 9.31 − 4.74 = 4.57 units. (b) Ratio = $10^{4.57}$ ≈ 3.7×10^4: the Ka of CH_3COOH is about 37,000 times the Ka of HCN. (c) Directly: $1.8 \times 10^{-5} \div 4.9 \times 10^{-10} = 3.7 \times 10^4$. The two routes agree, as the gap method requires.

B3. (a) pKb of CN^- = 14.00 − 9.31 = 4.69, since CN^- is the conjugate base of HCN. (b) First way: Kb = $10^{-4.69} = 2.0 \times 10^{-5}$. Second way: Kb = Kw ÷ Ka = $1.0 \times 10^{-14} \div 4.9 \times 10^{-10} = 2.0 \times 10^{-5}$. They agree. (c) pKa of NH_4^+ = 14.00 − 4.74 = 9.26. Ka of NH_4^+ = $10^{-9.26} = 5.5 \times 10^{-10}$; Kw ÷ Kb = $1.0 \times 10^{-14} \div 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$, agreeing within the rounding of the quoted Kb.

B4. (a) 90% ionized means 90 parts A^- to 10 parts HA, so [A^-] ÷ [HA] = 9. Then pH = pKa + log 9 = 4.74 + 0.95 = 5.69. (b) 99% ionized means a ratio of 99, so pH = 4.74 + log 99 = 4.74 + 2.00 = 6.74. (c) 1% ionized means a ratio of 1/99, so pH = 4.74 − 2.00 = 2.74. Parts (b) and (c) sit symmetrically two units either side of the pKa, as the benchmarks promise.

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B5. (a) $[H_3O^+] = 10^{-3.00} = 1.0 \times 10^{-3}$ M. (b) Ionization gives $[H_3O^+] = [A^-] = 1.0 \times 10^{-3}$ M, and Ka = $[H_3O^+][A^-] \div [HA]$. The approximation is [HA] ≈ 0.10 M, the starting concentration, because the amount ionized is small beside it. Ka = $(1.0 \times 10^{-3})^2 \div 0.10 = 1.0 \times 10^{-6} \div 0.10 = 1.0 \times 10^{-5}$. (c) pKa = −log($1.0 \times 10^{-5}$) = 5.00. (d) Percent ionized = $(1.0 \times 10^{-3} \div 0.10) \times 100 = 1.0\%$. Only one part in a hundred of the acid has ionized, so using 0.10 M for [HA] cost very little; the exact denominator, 0.099 M, returns pKa = 5.00 as well.

B6. (a) Ka = $10^{-6.00} = 1.0 \times 10^{-6}$. (b) For HA + H_2O ⇌ $H_3O^+ + A^-$ with $[H_3O^+] = [A^-] = x$ and [HA] ≈ 0.050, Ka = $x^2 \div 0.050$, so $x = \sqrt{(1.0 \times 10^{-6} \times 0.050)} = \sqrt{(5.0 \times 10^{-8})} = 2.24 \times 10^{-4}$ M. pH = −log(2.24×10^{-4}) = 3.65. (c) Percent ionized = $(2.24 \times 10^{-4} \div 0.050) \times 100 = 0.45\%$, far below the level at which the approximation distorts the answer, and the exact quadratic also gives pH 3.65. The pH carries two decimal places because 0.050 M has two significant figures.

C1. (a) $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$, then $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$. Both are balanced for atoms and charge: the first moves one proton from a neutral acid to water, the second from a 1- anion. (b) HCO_3^- dominates. pH 8.0 lies between pKa1 (6.37) and pKa2 (10.33): the first proton has mostly been surrendered, because the pH is above pKa1, and the second mostly kept, because the pH is below pKa2. (c) At pH 5.0, below pKa1, H_2CO_3 dominates. At pH 11.5, above pKa2, CO_3^{2-} dominates. (d) The middle form HA^- dominates at the first equivalence point, and pH ≈ (pKa1 + pKa2) ÷ 2 = (2.0 + 7.0) ÷ 2 = 4.5.

C2. (a) The claim is backwards. Lower pKa means stronger acid, so CH_3COOH (4.74) is far stronger than HCN (9.31). (b) A pKa gap is an exponent, not a multiplier. The gap is 9.31 − 4.74 = 4.57, so the Ka ratio is $10^{4.57} \approx 3.7 \times 10^4$, confirmed directly by $1.8 \times 10^{-5} \div 4.9 \times 10^{-10} = 3.7 \times 10^4$. Acetic acid's Ka is about 37,000 times larger, not about twice. (c) The student paired the pKa of HCN with CH_3COO^-, which is not its conjugate base. The sum rule applies to conjugate pairs only, so the pKa that pairs with CH_3COO^- is that of its own acid: pKb = 14.00 − 4.74 = 9.26. The value 4.69 is real but belongs to CN^-, the conjugate base of HCN: 14.00 − 9.31 = 4.69.

C3. (a) By pKa, lowest first: HF (3.17) > CH_3COOH (4.74) > H_2CO_3 (6.37) > HCN (9.31). (b) Reverse the acid order exactly: $CN^- > HCO_3^- > CH_3COO^- > F^-$. The weakest acid, HCN, gives the strongest base, and the strongest acid, HF, gives the weakest. (c) The strongest base is CN^-. Its Kb = Kw ÷ Ka of HCN = $1.0 \times 10^{-14} \div 4.9 \times 10^{-10} = 2.0 \times 10^{-5}$, equivalently $10^{-4.69}$ from pKb = 14.00 − 9.31 = 4.69. (d) At pH = pKa the ratio is 1: $[CH_3COO^-] = [CH_3COOH]$. A ratio of 100 needs pH = pKa + log 100 = 4.74 + 2.00 = 6.74. (e) HF. The gap is 4.74 − 3.17 = 1.57 units, and $10^{1.57} \approx 37$, so Ka of HF is about 37 times Ka of CH_3COOH, matching the direct ratio $6.8 \times 10^{-4} \div 1.8 \times 10^{-5} \approx 37.8$ within the rounding of the quoted pKa values.

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