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Topic 8.6: Molecular Structure of Acids and Bases

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 two structural levers behind acid strength, the group and period trends for binary acids, the two oxyacid rules, the inductive effect, and the mirror rule for bases. Section B practises the skills: rankings with a named rule for every step, and Ka and pKa arithmetic on the data set below. Section C is exam style: a flawed student answer to take apart, a five-acid data table to mine, and two explanation questions.

Conventions: 25 °C throughout, Kw = 1.0×10^{-14}. The data set for this sheet, taken from the quiz for this topic: Ka of HClO = 3.0×10^{-8}, Ka of HBrO = 2.0×10^{-9}, Ka of HIO = 2.3×10^{-11}, Ka of CH_3COOH = 1.8×10^{-5}, Ka of $ClCH_2COOH$ = 1.4×10^{-3}. $HClO_4$ and HI are strong acids, fully ionized; no Ka value is needed for them.

One working habit ties the sheet together: name the comparison before you rank. Ask whether the pair is binary or oxyacid, whether it runs down a group or across a period, and whether the central atom or the oxygen count is what changes. The named comparison picks the rule, and the rule produces the ranking; a ranking without its rule is a guess.

Two checks run through the sheet. The reversal check: any base ranking must be the exact reverse of its conjugate acid ranking; if it is not, one of them is wrong. The data check: wherever Ka values are given, the ranking they imply must match the structural ranking; a disagreement means the wrong rule was used.

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

Section A: Recall and Concepts

A1. (a) State the two structural questions that decide how strong an acid HA is. (b) For binary acids, which of them dominates the comparison down a group, and what changes down the group to make it dominate? (c) Which dominates across a period, and why can it dominate there?

A2. (a) Rank HF, HCl, HBr and HI in increasing acid strength. (b) Explain why HF does not follow the prediction that electronegativity alone would make. (c) State what happens to the length and strength of the H-X bond as X goes from F to I.

A3. (a) Rank HClO, $HClO_2$, $HClO_3$ and $HClO_4$ in increasing acid strength. (b) Give the two distinct reasons why adding oxygens to the same central atom strengthens an oxyacid. (c) Rank HClO, HBrO and HIO, and state the rule you used.

A4. (a) Define the inductive effect. (b) Use it to explain why $ClCH_2COOH$ is a stronger acid than CH_3COOH. (c) A student writes: "$ClCH_2COOH$ is stronger because its anion has more resonance." Correct the claim in one or two sentences.

A5. (a) Rank F^-, Cl^-, Br^- and I^- as bases, strongest first. (b) Rank ClO^-, ClO_2^-, ClO_3^- and ClO_4^- as bases, strongest first. (c) State the general rule that produces both rankings.

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Section B: Core Practice

B1. Rank H_2SO_4, H_2SeO_4 and H_2SO_3, strongest acid first. Justify each adjacent pair in the order with the specific rule that decides it.

B2. Use Ka of HClO = 3.0×10^{-8}, Ka of HBrO = 2.0×10^{-9} and Ka of HIO = 2.3×10^{-11}. (a) Rank the three acids by Ka, weakest first. (b) Calculate the pKa of each. (c) Calculate how many times larger Ka of HClO is than Ka of HIO, and how many times larger than Ka of HBrO.

B3. Use Ka of CH_3COOH = 1.8×10^{-5} and Ka of $ClCH_2COOH$ = 1.4×10^{-3}. (a) Calculate the pKa of each acid. (b) Calculate the ratio of the two Ka values. (c) Explain the ratio in terms of the stability of the two conjugate bases, naming the effect responsible.

B4. (a) Rank CH_4, NH_3, H_2O and HF in increasing acid strength. (b) Name the factor that dominates this comparison. (c) Explain why the rule that orders HF, HCl, HBr and HI would give the wrong answer if it were applied here.

B5. (a) Write the three successive ionization equations of H_3PO_4 in water, one for each proton. (b) Rank H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} in decreasing acid strength. (c) Justify the ranking using the charges of the species involved.

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B6. Use the parent acid data: HClO, Ka = 3.0×10^{-8}; CH_3COOH, Ka = 1.8×10^{-5}; $ClCH_2COOH$, Ka = 1.4×10^{-3}; $HClO_4$, strong. (a) Rank ClO^-, CH_3COO^-, $ClCH_2COO^-$ and ClO_4^- as bases, strongest first. (b) Calculate Kb of ClO^- and Kb of CH_3COO^-. (c) Calculate how many times larger the larger Kb is than the smaller, and state which base it belongs to.

Section C: Exam Style

C1. A student answers a ranking question as follows: "Fluorine is the most electronegative element, so HF is the strongest of HF, HCl, HBr and HI. For the same reason, HClO is a weaker acid than HBrO, because chlorine is smaller than bromine and holds its proton more tightly." (a) Give the correct ranking for the hydrohalic acids, and name the factor that actually decides it. (b) Give the correct ranking for HClO against HBrO, quoting the Ka evidence. (c) Explain why electronegativity settles the HClO and HBrO comparison but gives the wrong answer for HF against HCl.

C2. Five acids have Ka values: HClO 3.0×10^{-8}, HBrO 2.0×10^{-9}, HIO 2.3×10^{-11}, CH_3COOH 1.8×10^{-5}, $ClCH_2COOH$ 1.4×10^{-3}. (a) Calculate the pKa of all five acids. (b) Rank the five acids, strongest first. (c) Rank the five conjugate bases, strongest base first. (d) Calculate Kb for the strongest base in your part (c) ranking. (e) Identify the one pair in the table whose comparison isolates the inductive effect, and the one trio whose comparison isolates the central atom effect, stating in each case what is held constant.

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C3. (a) Describe, in words, how the negative charge is distributed in CH_3COO^- and in $CH_3CH_2O^-$, and use the difference to explain why CH_3COOH is a much stronger acid than CH_3CH_2OH. (b) ClO^- is a far stronger base than ClO_4^-. Explain this twice over: once using the strengths of their conjugate acids, and once using the distribution of charge in the two anions. (c) Predict whether H_2SO_3 or H_2SeO_3 is the stronger acid, and justify the prediction with the rule it rests on.

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Answer Key

A1. (a) First, how easily the H-A bond breaks: a weaker bond, and a bond polarized away from the hydrogen, releases H^+ more readily. Second, how stable the conjugate base A^- is: charge spread over more atoms, or held on electronegative atoms, makes A^- more stable and pulls $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ to the right. (b) Bond strength dominates down a group. The atom bonded to hydrogen grows much larger, so the H-X bond becomes much longer and weaker, and that change outweighs everything else. (c) Electronegativity dominates across a period. The atoms are all a similar size there, so bond strengths stay comparable, and the growing polarity of the H-X bond is the difference that remains.

A2. (a) HF < HCl < HBr < HI. (b) Electronegativity alone predicts HF strongest, because fluorine pulls electron density hardest. In fact the H-F bond is exceptionally short and strong, because fluorine is so small, and it resists breaking, so HF ionizes only slightly and is a weak acid. Down this group the deciding factor is bond strength, not polarity. (c) The bond gets longer and weaker: H-F is the shortest and strongest of the four, H-I the longest and weakest, which is why the ranking in (a) rises down the group.

A3. (a) $HClO < HClO_2 < HClO_3 < HClO_4$. (b) First, each extra electronegative oxygen withdraws electron density from the O-H bond, weakening it so the proton is held less tightly. Second, the conjugate base is stabilized by resonance: more oxygens give more atoms over which to delocalize the negative charge, from ClO^- with the charge confined to one oxygen to ClO_4^- with it spread over four. (c) HClO > HBrO > HIO. The rule: at a fixed oxygen count, the smaller and more electronegative central atom gives the stronger acid, because it holds the oxygens closer and their withdrawal polarizes the O-H bond more.

A4. (a) The inductive effect is the withdrawal (or donation) of electron density through the sigma bonds of a molecule by an electronegative (or electron-donating) substituent. (b) Chlorine withdraws electron density through the sigma framework towards itself. That stabilizes the conjugate base $ClCH_2COO^-$ by drawing charge away from the negatively charged carboxylate group, so the ionization equilibrium of $ClCH_2COOH$ lies further right than that of CH_3COOH and its Ka is larger. (c) Both anions delocalize the charge over two oxygens in exactly the same way, so resonance cannot separate them; the difference is chlorine's inductive withdrawal, which CH_3COO^- has no equivalent of.

A5. (a) $F^- > Cl^- > Br^- > I^-$. (b) $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$. (c) Conjugate base strength runs opposite to acid strength: rank the conjugate acids, then reverse. HF is the weakest hydrohalic acid, so F^- is the strongest halide base, and I^-, from the strongest acid HI, is the weakest. HClO is the weakest chlorine oxyacid, so ClO^- is the strongest base of its series, and ClO_4^-, from strong $HClO_4$, is the weakest.

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B1. H_2SO_4 > H_2SeO_4 > H_2SO_3. H_2SO_4 against H_2SeO_4: both carry four oxygens, so the central atom decides; sulfur is smaller than selenium, its oxygens are held closer and withdraw more strongly, so H_2SO_4 is stronger. H_2SeO_4 against H_2SO_3: compare the oxygen counts; four oxygens against three means more electron withdrawal and more resonance spread in the conjugate base, so H_2SeO_4 is the stronger acid despite its larger central atom.

B2. (a) By Ka, weakest first: HIO (2.3×10^{-11}) < HBrO (2.0×10^{-9}) < HClO (3.0×10^{-8}). (b) pKa of HClO = $-\log(3.0 \times 10^{-8}) = 7.52$. pKa of HBrO = $-\log(2.0 \times 10^{-9}) = 8.70$. pKa of HIO = $-\log(2.3 \times 10^{-11}) = 10.64$. The pKa order is the reverse of the strength order, as it must be: the weakest acid has the largest pKa. (c) Ka of HClO over Ka of HIO = $3.0 \times 10^{-8} / 2.3 \times 10^{-11} = 1.3 \times 10^{3}$, about 1,300 times larger. Ka of HClO over Ka of HBrO = $3.0 \times 10^{-8} / 2.0 \times 10^{-9} = 15$ times larger. Both gaps match the structural rule: at one oxygen each, the smaller central atom wins, and the win grows as the size gap grows.

B3. (a) pKa of CH_3COOH = $-\log(1.8 \times 10^{-5}) = 4.74$. pKa of $ClCH_2COOH$ = $-\log(1.4 \times 10^{-3}) = 2.85$. (b) The ratio is $1.4 \times 10^{-3} / 1.8 \times 10^{-5} = 78$: chloroacetic acid's Ka is about 78 times larger. (c) The two conjugate bases have identical resonance, a charge shared over two oxygens. What $ClCH_2COO^-$ has extra is chlorine pulling electron density away through the sigma bonds, the inductive effect, which stabilizes the anion. A more stable conjugate base means the ionization equilibrium lies further right, hence the 78-fold larger Ka and the pKa lower by 1.89 units.

B4. (a) CH_4 < NH_3 < H_2O < HF. (b) Electronegativity of the atom bonded to hydrogen, acting through bond polarity: C < N < O < F in electronegativity, the H-X bond becomes more polar at each step, and H^+ is lost more easily. (c) In the hydrohalic series the order is set by bond strength falling down a group, because the atoms change size dramatically. Across this period the atoms C, N, O and F are close in size, their bonds to hydrogen are comparable in strength, and there is no large bond-strength trend to override polarity. Applying the group rule here would mean ranking by a factor that barely changes, and missing the one that does.

B5. (a) $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$; then $H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$; then $HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$. (b) H_3PO_4 > $H_2PO_4^-$ > HPO_4^{2-}. (c) The first proton leaves a neutral molecule. The second must be pulled away from a 1^- anion, whose negative charge attracts and holds the positive H^+. The third must leave a 2^- anion, where the attraction is stronger still. Each step's reactant is more negative than the last, so each step is harder, and the acid strength falls every time: Ka1 > Ka2 > Ka3.

B6. (a) Reverse the parent acid order. By Ka the acids run HClO (3.0×10^{-8}) < CH_3COOH (1.8×10^{-5}) < $ClCH_2COOH$ (1.4×10^{-3}) < $HClO_4$ (strong), so the bases run ClO^- > CH_3COO^- > $ClCH_2COO^-$ > ClO_4^-. (b) Kb of ClO^- = Kw / Ka of HClO = $1.0 \times 10^{-14} / 3.0 \times 10^{-8} = 3.3 \times 10^{-7}$. Kb of CH_3COO^- = $1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$. (c) The ratio is $3.3 \times 10^{-7} / 5.6 \times 10^{-10} = 600$: Kb of ClO^- is about 600 times larger, belonging to ClO^-, the strongest base of the four as part (a) required. The two methods agree, which is the reversal check passing.

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C1. (a) The correct order is HF < HCl < HBr < HI. The deciding factor is H-X bond strength, which falls down the group as the halogen grows and the bond lengthens; HF, with the shortest and strongest bond, is the weak acid of the family. (b) HClO is the stronger acid: its Ka is 3.0×10^{-8} against 2.0×10^{-9} for HBrO, 15 times larger, so the student's second claim is also backwards. (c) In HClO and HBrO the proton sits on oxygen in both molecules; the H is never bonded to the halogen at all. What changes is the central atom behind the oxygen, and the smaller, more electronegative chlorine withdraws electron density more strongly through that oxygen, weakening the O-H bond. Size and bond length of an H-X bond are irrelevant because there is no H-X bond. In HF against HCl, the proton is bonded directly to the halogen, the H-F bond is far shorter and stronger than H-Cl, and that bond strength difference is large enough to defeat fluorine's electronegativity advantage.

C2. (a) pKa of HClO = 7.52, of HBrO = 8.70, of HIO = 10.64, of CH_3COOH = 4.74, of $ClCH_2COOH$ = 2.85. (b) By Ka, strongest first: $ClCH_2COOH$ (1.4×10^{-3}) > CH_3COOH (1.8×10^{-5}) > HClO (3.0×10^{-8}) > HBrO (2.0×10^{-9}) > HIO (2.3×10^{-11}). (c) Reverse (b): IO^- > BrO^- > ClO^- > CH_3COO^- > $ClCH_2COO^-$. (d) The strongest base is IO^-, conjugate base of the weakest acid, HIO. Its Kb = Kw / Ka of HIO = 1.0×10^{-14} / 2.3×10^{-11} = 4.3×10^{-4}. (e) The inductive effect is isolated by CH_3COOH against $ClCH_2COOH$: same carboxylic acid framework, same conjugate base resonance, only the substituent changes from H to Cl on the neighboring carbon. The central atom effect is isolated by HClO, HBrO and HIO: all three are HOX with exactly one oxygen, so the oxygen count is held constant and only the central halogen changes.

C3. (a) In CH_3COO^- the negative charge is delocalized by resonance over two oxygens: two equivalent structures share it, so each oxygen carries about half. In $CH_3CH_2O^-$ the charge is localized on the single oxygen, with no second atom to share it. A delocalized charge is a lower energy, more stable arrangement, so acetate is the more stable conjugate base, its formation is favored, and CH_3COOH ionizes far more readily than CH_3CH_2OH. (b) By conjugate acids: HClO is a weak acid (Ka = 3.0×10^{-8}) while $HClO_4$ is strong, fully ionized, and a weaker parent acid means a stronger conjugate base, so ClO^- far outranks ClO_4^-. By charge distribution: ClO^- carries its charge on one oxygen, concentrated and eager to reclaim a proton, while ClO_4^- spreads the same charge over four oxygens by resonance, diluting it until the ion has almost no drive to accept H^+ back. (c) H_2SO_3 is stronger. Both acids carry three oxygens, so the oxygen count is tied and the central atom decides: sulfur is smaller than selenium, holds the oxygens closer, and withdraws more strongly, exactly as H_2SO_4 outranks H_2SeO_4 in the four-oxygen pair.

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