Topic 8.6: Molecular Structure of Acids and Bases

Revision Notes · AP Chemistry

UNIT 8 · ACIDS AND BASES

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Strength Means the Equilibrium Leans Right

An acid in water sits in the equilibrium:

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

The stronger the acid, the further right that equilibrium lies and the larger its Ka. Structure decides the position, and every comparison here reduces to two questions about the molecule.

How easily does the H-A bond break? A weaker bond, and a bond polarized away from the hydrogen, gives up the proton more readily.

How stable is A^- once it forms? A conjugate base that spreads its charge out, or holds it on electronegative atoms, is stable, and pulls the equilibrium right.

Binary Acids Down a Group: Bond Strength Decides

For the hydrohalic acids the order is HF < HCl < HBr < HI. Down the group the halogen grows, the H-X bond gets longer and weaker, so acid strength rises.

The HF exception. Fluorine is the most electronegative element, and electronegativity alone would make HF the strongest of the four. It is the weakest: fluorine is so small that the H-F bond is very short and very strong, and resists ionization. HCl, HBr and HI are all strong acids; HF is weak.

Electronegativity falls down the group, F > Cl > Br > I, which predicts the opposite order. When size changes a lot, bond strength beats polarity.

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Binary Acids Across a Period: Electronegativity Decides

Across the second period the hydrides run CH_4 < NH_3 < H_2O < HF in acid strength. Carbon is barely acidic, and each step right gives a stronger acid.

Here the atoms bonded to hydrogen are all a similar size, so bond strengths are comparable. The more electronegative the atom, the more polar the H-X bond becomes, and the more easily H^+ leaves.

Oxyacids with the Same Central Atom: Count the Oxygens

For the chlorine oxyacids the order is HClO < $HClO_2$ < $HClO_3$ < $HClO_4$. $HClO_4$ is a strong acid; HClO is weak, with Ka = 3.0×10^{-8}. The only change along the series is the oxygen count.

Each extra oxygen strengthens the acid twice over. First, oxygen is highly electronegative and withdraws electron density from the O-H bond, loosening the proton. Second, resonance stabilizes the conjugate base: ClO_4^- delocalizes its negative charge over four oxygens, ClO_2^- over two, and ClO^- has a single oxygen and nowhere to spread the charge.

Oxyacids with Different Central Atoms: Smaller and More Electronegative Wins

Hold the oxygen count fixed and compare down a group: HClO > HBrO > HIO, with Ka values 3.0×10^{-8}, 2.0×10^{-9} and 2.3×10^{-11}.

The smaller central atom holds its oxygens closer, so their electron withdrawal polarizes the O-H bond more. Smaller also means more electronegative: the acid with the smaller, more electronegative central atom is stronger.

Substituents: The Inductive Effect

Chloroacetic acid, $ClCH_2COOH$, has Ka = 1.4×10^{-3} against 1.8×10^{-5} for acetic acid, CH_3COOH: roughly 78 times stronger.

The chlorine pulls electron density towards itself through the sigma bonds. That is the inductive effect. It stabilizes the conjugate base, $ClCH_2COO^-$, by drawing charge away from the carboxylate group, so the equilibrium leans further right and Ka grows.

Resonance is not the difference here: CH_3COO^- and $ClCH_2COO^-$ delocalize their charge over two oxygens. Where resonance does decide a comparison is acetate against ethoxide, $CH_3CH_2O^-$,

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whose charge is trapped on one oxygen, which is why carboxylic acids are far stronger acids than alcohols.

Polyprotic Acids: Each Proton Is Harder to Remove

In the series H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, acid strength falls at every step: Ka1 > Ka2 > Ka3. The three ionizations are:

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$

$HPO_4^{2-} + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$

The reason is electrostatic. Taking H^+ from a 1^- anion means pulling a positive charge away from a negative one, and from a 2^- anion the attraction is stronger still. Each deprotonation leaves a more negative species holding its remaining protons tighter.

Bases: The Same Rankings Read Backwards

Conjugate base strength runs opposite to acid strength: the stronger the acid, the weaker its conjugate base. To rank bases, rank their conjugate acids first, then reverse the order.

For the halides, HI is the strongest acid, so I^- is the weakest base: $I^- < Br^- < Cl^- < F^-$. For the chlorine oxyanions, HClO is the weakest acid of its series, so ClO^- is the strongest base: $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$. ClO_4^-, conjugate base of a strong acid, is a negligible base.

Worked Examples

Example 1: Two rules in one ranking. Rank H_2SO_4, H_2SeO_4 and H_2SO_3, strongest first. Oxygen count comes first: H_2SO_4 and H_2SeO_4 carry four oxygens each against three in H_2SO_3, so both outrank H_2SO_3. Between the two four-oxygen acids, sulfur is smaller than selenium. Final order: $H_2SO_4 > H_2SeO_4 > H_2SO_3$.

Example 2: Finding the strongest base from Ka values. Rank ClO^-, CH_3COO^-, $ClCH_2COO^-$ and ClO_4^- as bases. Read the parent acids by Ka: HClO 3.0×10^{-8} (pKa 7.52), CH_3COOH 1.8×10^{-5} (pKa 4.74), $ClCH_2COOH$ 1.4×10^{-3} (pKa 2.85), $HClO_4$ strong. The weakest acid is HClO, so ClO^- is the strongest base: $ClO^- > CH_3COO^- > ClCH_2COO^- > ClO_4^-$. Kb confirms it: Kb of ClO^- = Kw / Ka = 3.3×10^{-7}, against 5.6×10^{-10} for CH_3COO^-, about 600 times larger.

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Example 3: PKa values confirm the central-atom rule. For HClO, HBrO and HIO, the Ka values are 3.0×10^{-8}, 2.0×10^{-9} and 2.3×10^{-11}, giving pKa values 7.52, 8.70 and 10.64. The weakest acid has the largest pKa. HClO beats HIO by $3.0 \times 10^{-8} / 2.3 \times 10^{-11}$, about 1,300 times, and beats HBrO by 15 times.

Example 4: The strongest base among four. Rank ClO^-, F^-, ClO_4^- and CH_3COO^- as bases. Read their parent acids by Ka: HClO 3.0×10^{-8}, HF 6.8×10^{-4}, $HClO_4$ strong, CH_3COOH 1.8×10^{-5}. The weakest acid is HClO, so ClO^- is the strongest base: $ClO^- > CH_3COO^- > F^- > ClO_4^-$. Kb confirms it: Kb of ClO^- is 3.3×10^{-7}, against 5.6×10^{-10} for CH_3COO^- and 1.5×10^{-11} for F^-.

Traps That Cost Marks in Topic 8.6

"Fluorine is the most electronegative element, so HF is the strongest hydrohalic acid." Backwards. The very strong H-F bond makes HF the weakest of the four; down a group, bond strength decides.

Using the period rule down a group, or the group rule across a period. Electronegativity decides across a period, where sizes are similar. Bond strength decides down a group, where sizes change sharply. Name the comparison correctly.

"More hydrogens means a stronger acid." Hydrogen count decides nothing: HClO and $HClO_4$ each have one acidic hydrogen, yet $HClO_4$ is millions of times stronger.

"$ClCH_2COOH$ beats CH_3COOH because of resonance." Both conjugate bases have identical resonance. The difference is chlorine's inductive withdrawal stabilizing $ClCH_2COO^-$.

"The conjugate base of a strong acid is a strong base." Exactly reversed. I^- and ClO_4^- sit at the bottom of their basicity rankings because HI and $HClO_4$ sit at the top of the acidity rankings.

"Each proton of a polyprotic acid leaves equally easily." Strength falls at every deprotonation, because each H^+ is pulled from a more negative species than the last.

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Key Relationships to Remember

- Stronger acid means larger Ka and an equilibrium lying further right; structure decides through bond breaking and base stability
- Binary acids down a group: HF < HCl < HBr < HI; bond strength decides because the H-X bond weakens as X grows
- Binary acids across a period: CH_4 < NH_3 < H_2O < HF; electronegativity decides because the atoms are similar in size
- Oxyacids, same central atom: more oxygens means stronger acid, HClO < $HClO_2$ < $HClO_3$ < $HClO_4$, through O-H weakening and resonance spread
- Oxyacids, same oxygen count: smaller, more electronegative central atom wins, HClO > HBrO > HIO and H_2SO_4 > H_2SeO_4
- Inductive effect: an electronegative substituent withdraws electron density through sigma bonds and stabilizes the conjugate base
- Polyprotic acids: strength falls at each deprotonation, Ka1 > Ka2 > Ka3, because H^+ leaves an increasingly negative species
- Bases invert acids: rank the conjugate acids, then reverse

Continue Revising

Topic 8.6 Quiz: Molecular Structure of Acids and Bases

Topic 8.6 Worksheet

Unit 8: All Topics

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