Exam 1 Corrections due 1 week from Wednesday

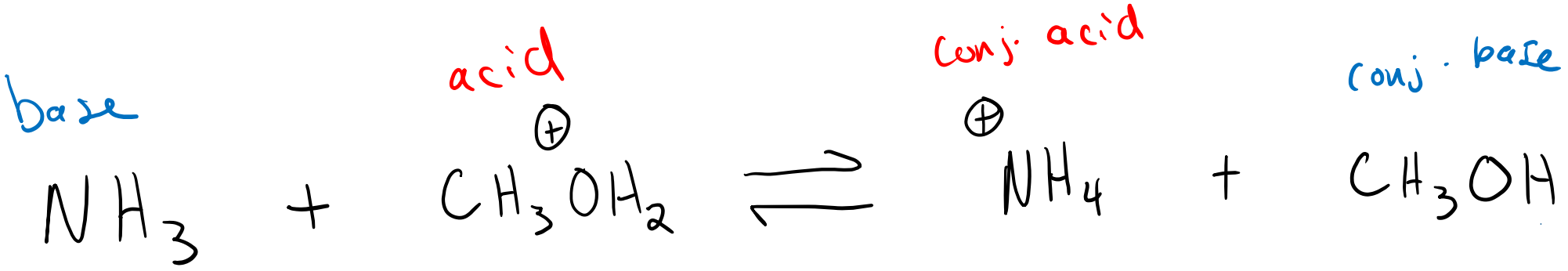
Acid/Base Review

Exam 2 2 weeks from Friday

Acidity of C-H Bonds

3/13/2023

Acid-Base Reactions (Ch. 3)



Which side is favored at equilibrium? "more stable" side

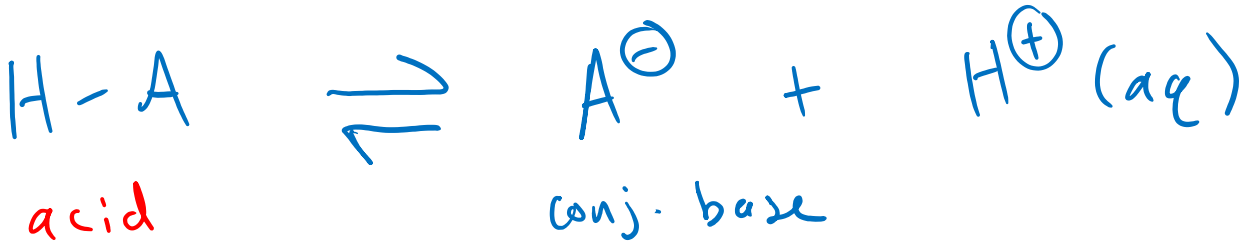
- weaker acid / weaker base
  - ↳ comparing acid vs. conj. acid

Two ways to approach…

Qualitative: if two molecules are structurally similar to each other
"apples to apples" comparison

☆ Quantitative: use experimentally determined pKa values

Quantifying Acid Strength



$$K_a = \frac{[A^-][H^+]}{[H-A]}$$

$$pK_a = -\log K_a$$

$$K_a = 10^{-pK_a}$$

pka tells us about the exponent (magnitude) of Ka

large Ka : lots of H^+
= strong acid

small Ka : lots of H-A "intact"
= weak acid

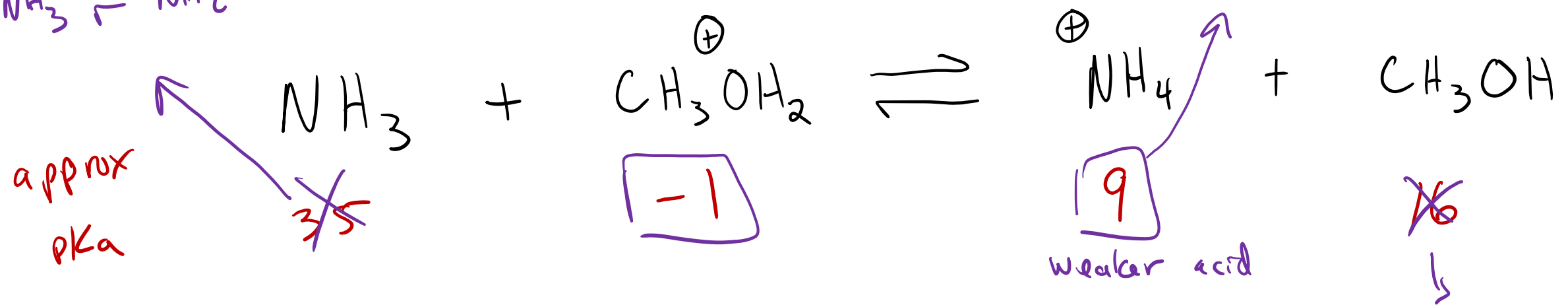
small pKa (or negative)
= large Ka = strong acid

high pKa = weak acid

How to use pKa values (to predict an acid-base reaction)

$NH_4^+ \rightleftharpoons NH_3 + H^+$

$NH_3 \rightleftharpoons NH_2^- + H^+$



$CH_3OH \rightleftharpoons CH_3O^- + H^+$

Eq. lies on side w/ weaker acid. (higher pKa)

Which pKa's do I compare - acid vs conj acid

Right side favored - by how much?

using Hess's law: $Ka_{CH_3OH_2^+} \cdot Ka^{-1}_{NH_4^+} = 10^{1} \cdot \frac{1}{10^{-9}} = 10^{10} = K_{eq}$

simplified = $10^{\Delta pKa}$ make exponent (+) or (-) depending on favored side

CAN Comparing Acidity: Qualitatively

also works for base strength, just opposite trends

1. Charge of molecule

(+) more acidic than neutral, Neutral is more acidic than (−)

$H_2\overset{\oplus}{O}-H$ pKa ~ -2

$HO-H$ pKa 14

$\overset{\ominus}{O}-H$ ↑ not acidic at all!

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2. Atom bound to H

H bound to more EN atom = stronger acid (unless comparing two atoms in same column)

↓

larger atom = stronger acid

$HO-H$ pKa 14

$H-NH_2$ 35

$H-OH$ pKa 14

$H-SH$ 10

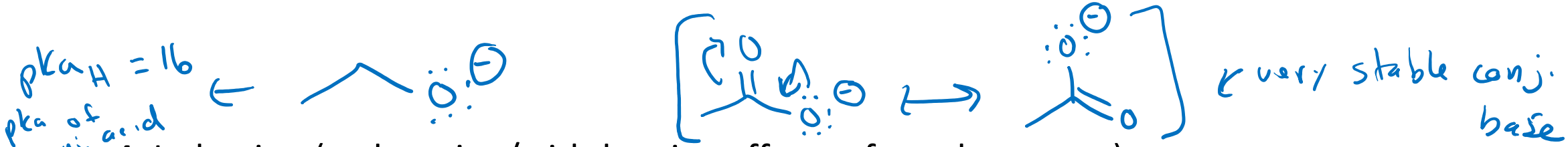
Comparing Acidity: Qualitatively (CARI)

3. Resonance

look @ conj. base stability

more stable conj. base = stronger acid

pka ~ 16 ~ 4

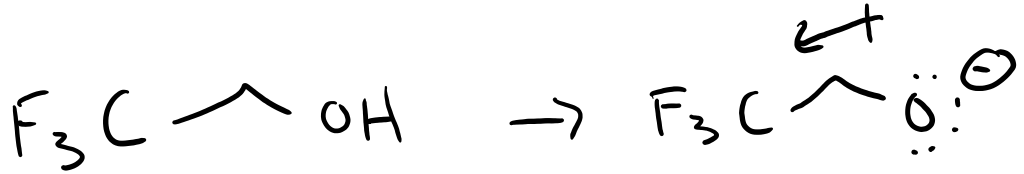


very stable conj. base

4. Induction (e^- donating/withdrawing effects of nearby groups)

EDG makes ⊖ less stable

pka 16



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EWG stabilizes ⊖ charge

What a pKa can tell you

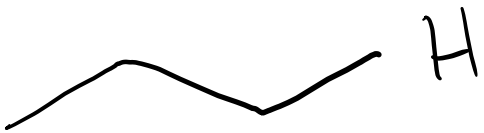
pka of HA tells us about.....

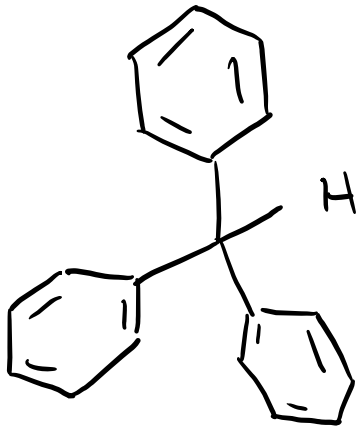
- acidity of HA
- stability of HA
  strength of H-A bond

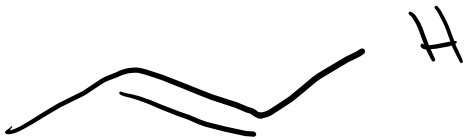
- basicity of $A^{\ominus}$
- ★ stability of $A^{\ominus}$
  ~ nucleophilicity of $A^{\ominus}$ (w/o sterics)
- LG ability of $A^{\ominus}$

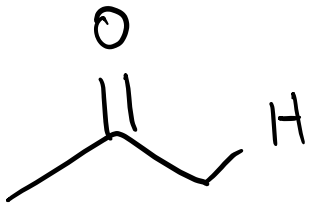
can use to predict relative stability / likelihood of intermediates in mechanism

Acidity of C-H bonds









Ch 21: “Alpha Carbon” Chemistry