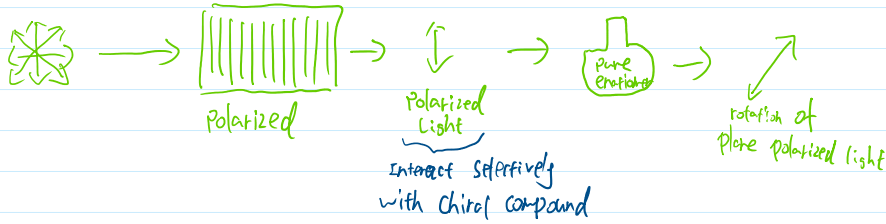- "optical active"
- Acid and Base

If a molecule is chiral, it rotates the plane of plane polarized light in a concentration dependent manner.

Polarized

Polarized Light
Interact selectively with Chiral compound

rotation of plane polarized light

Two enantiomers will rotate polarized light in the opposite direction, but to the equal extents

    If   R-enantiomer   rotate   41.7° to clockwise ("+")
         S-enantiomer   rotate   41.7° to counterclockwise ("−")

Can't always get

- R ≠ "+", R ≠ "−" → "▼/≦"

A racemic mixture won't rotate rotate the plane of polarized light
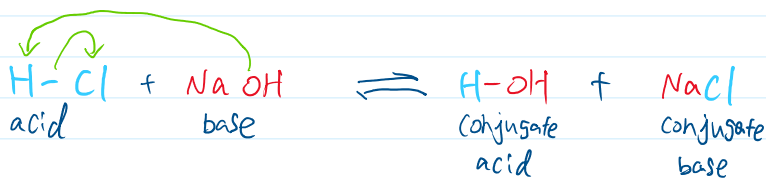
    ↳ 1:1 mixture of 2 enantiomers

A compound is "optical active" if it rotates the plane of polarized light.
      - racemic mixtures and meso compounds are not optical active.

Acid and Base

$H^{\oplus}$

  Acid = Proton Donor   } Brønsted theory
  Base = proton Acceptor

H−Cl + Na OH ⇌ H−OH + NaCl
acid   base   Conjugate   Conjugate
                 acid   base

we can describe mathematically "how far" a reaction proceed by defining an equilibrium constant.
       A ⇌ B   A and B can interconvert.
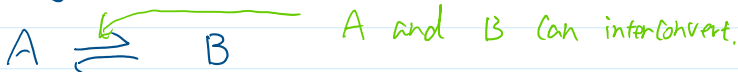
$$K_{eq} = \frac{[B]}{[A]} = \frac{products}{reactants}$$ (with known pka, $K_{eq} = 10^{pKa_{product} - pKa_{reactant}}$)

Keq tells us which side (starting materials / left side / reactants)

vs

(products / right side)
is favored at e.q.

If $K_{eq} = 1 \rightarrow$ each side same amount of A and B

$K_{eq} \rightarrow \infty \rightarrow$ NO A present, all B

$K_{eq} = 0.00000\underset{0000000000001}{00000} \rightarrow$ lots of A , little B

For acids and bases : $H-A + \overset{\curvearrowright}{:}B \rightleftharpoons H-B + A^{\ominus}$
$\quad\quad\quad\quad\quad\quad\quad$ acid $\quad$ base $\quad\quad$ conjugate $\quad$ conjugate
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ acid $\quad\quad\quad$ base

$$K_A = \frac{[H\text{-}B][A^{\ominus}]}{[H\text{-}A][:B^{\ominus}]}$$

since K_A ranges from $\underset{pKa=20}{10^{-20}}$ to $\underset{pKa=-55}{10^{55}}$
$\rightarrow$ we took the log scale , so the # is smaller.

$pKa = -\log K_A$

K_A and pKa tell us how much an acid will be
deprotonated vs. protonated at a specific pH
$\quad\rightarrow$
$\quad\quad$ pKa and K_A reflect a given acid's <u>intrinsic</u> ability
$\quad\quad$ to protonate the <u>base</u>
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\rightarrow$ usually H_2O for pKa/K_A

Smaller pKa values $\longrightarrow$ Stronger acid $\Rightarrow$ more stable anion
(lower)
(more negative) $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ more stable (weak)
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ conjugate base

$H-\overset{..}{\underset{..}{C}}l: \rightleftharpoons H^{\oplus} + :\overset{..}{\underset{..}{C}}l^{\ominus}$
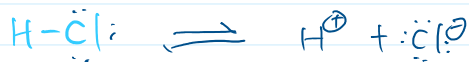
$pKa = -7$

☆ e.q. favors formation of the WEAKER ACID
$\quad\rightarrow$ for a given pair of "acids" the smaller/lower the pKa
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\underset{!!}{}$
$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ the stronger the acid

the stronger the acid

$\hookrightarrow$ A stronger acid will react to form a more **stable** anion

⊗ A given acid will be **protonated** (deprotonated) if the <u>pH</u> of the solution is <u>less (large)</u> than the <u>pKa</u> of the acid
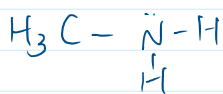
$$H-A \ + \ H-\overset{..}{\underset{..}{O}}-H \ \rightleftharpoons \ A:^{\ominus} \ + \ H-\overset{\oplus}{\underset{\overset{|}{H}}{\overset{..}{O}}}-H$$
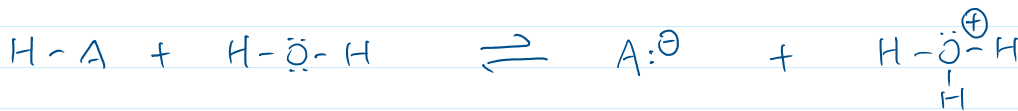
If pH = pKa, $[H-A] = [A:^{\ominus}]$

50:50 protonated vs. deprotonated

pH > pKa, $[H-A] < [A:^{\ominus}]$

the acid $[H-A]$ is mostly deprotonated

pH < pKa, $[H-A] > [A:^{\ominus}]$

the acid $[H-A]$ is mostly protonated

$H_3C-\overset{..}{\underset{\overset{|}{H}}{N}}-H$

Acid ?
or
Base ?
$\downarrow$
It depends

The molecular environment (pH) determines whether a molecular functions as an acid or base

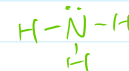The number of H-atoms on sp^3 N-atom is <u>changing w/ pH</u>

$\hookrightarrow$ recall lower pH = more acidic environment = a lot of $H^{\oplus}$ around

If there are a lot of protons in solution (acidic)

N will be bonded to more protons $\longrightarrow$ $H-\overset{\overset{|}{H}}{\underset{\overset{|}{H}}{N}}{}^{\oplus}H$

than it would be if there are less $H^{\oplus}$ $\longrightarrow$ $H-\overset{..}{\underset{\overset{|}{H}}{N}}-H$

or $H-\overset{..}{\underset{..}{N}}{}^{\ominus}H$

let's follow 100 amine $(R-\overset{..}{N}H_2)$ molecules in a solution as we raise pH from 0 (very acidic) to pH 50 (super basic)

let's follow 100 amine (R- $\ddot{N}H_2$) molecules in a solution
as we raise pH from 0 (very acidic) to pH 50 (super basic)

consider two relevant pkas: R- $\overset{\oplus}{N}H_3$ pKa ~ 10 ←

R- NH_2 pka ~ 40 ←

pH 0	pH 10	pH 15	pH 40	pH 50
100 R- $\overset{\oplus}{N}H_3$	50 R- $\overset{\oplus}{N}H_3$ 50 R- $\ddot{N}H_2$	100 R- $\ddot{N}H_2$	50 R- $\ddot{N}H_2$ 50 R- $\ddot{\overset{\ominus}{N}}H$	100 R- $\ddot{\overset{\ominus}{N}}H$

pKa table

compound	pKa	(conjugate base)	
$H_3O^{\oplus}$	-1.7	H_2O	pH > -1.7, mostly H_2O pH < -1.7, mostly $H_3O^{\oplus}$
$H_4N^{\oplus}$	9.2	$H_3\ddot{N}$	pH > 9.2, mostly $H_3\ddot{N}$ pH < 9.2, mostly $H_4N^{\oplus}$

In Human body : pH ~7

Generic Amino Acid :
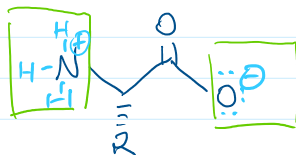
	pKa
R- $\overset{\oplus}{N}H_3$	~ 9.2
R- COOH	3-5

Amine is _Protonated_ @ PH 7
   PH < pKa

acid
Carboxylic is _deprotonated_ @ pH 7
   pH > pKa

More Stable Anion has $\ominus$ ∝ "full negative charge"

① on a more E.N. atom (across ^a row in periodic table)

② On an atom w/ more S-character (sp > sp2 > sp3) (mostly for comparing
                                                    negative charge on c)

③ on a _____ atom

② On an atom w/ more s-character (sp > sp² > sp³) (mostly for comparing negative charge on C)

③ On a larger atom   (down a column)

④ stablized by resonance delocalization
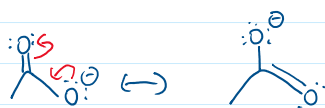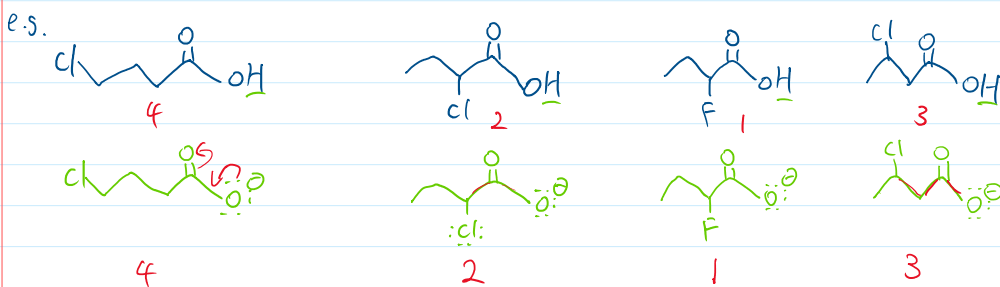
⑤ stablized by inductive effect from nearby E.N. atoms

e.g: 1 = most acidic   4 = least acidic

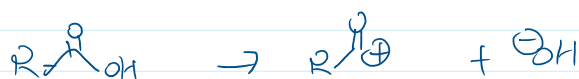Acid: H_2O CH_4 NH_3 H_2S
        2   4   3   1

① Draw $\ominus$:ÖH $\ominus$:CH₃ $\ominus$:ṄH₂ $\ominus$:ṠH
the anion: 2   4   3   1
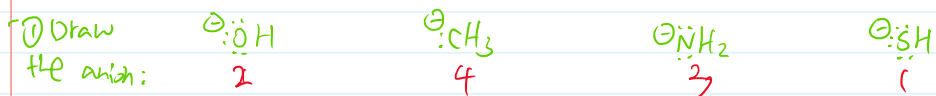
② Alternatively, look them up in pka table:

	H_2O	CH_4	NH_3	H_2S
pka	15.7	51	40	8-9
	2	4	3	1

e.s.

4   2   1   3
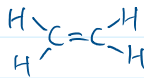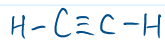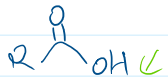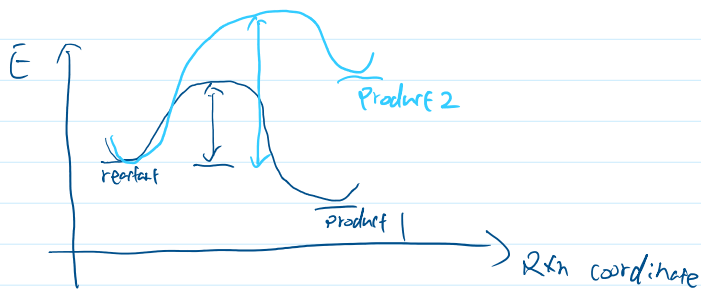

4   2   1   3

• Resonance is in play in all of them!
• negative charge is not directly on a halogen atom, so rule #3 does not apply.

Inductive effect: "pulling" of e$\ominus$ density through σ-bonds by E.N. atoms / groups.

Q.5

E ↑

Product 2

reactant

Product 1

→ Rxn coordinate

$R \overset{O}{\underset{}{\diagup}} OH$ ⟵

$H-C\equiv C-H$

$H \diagdown \overset{H}{\underset{H}{C=C}} \diagup$

$\overset{H \quad H}{H-\underset{H \quad H}{C-C}-H}$

$R \overset{O}{\underset{:\ddot{O}:^{\ominus}}{\diagup}}$ ⟵

$H-C\equiv C:^{\ominus}$

$H \diagdown \overset{H}{\underset{H}{C=C}}:^{\ominus}$

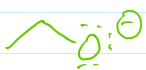$\overset{H \quad H}{H-\underset{H \quad :\ddot{O}}{C-C}-H}$

↑(red)
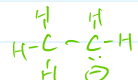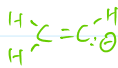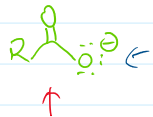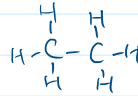
sp

sp²

sp³

1
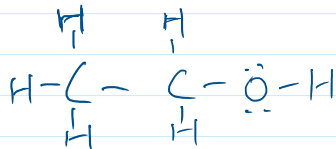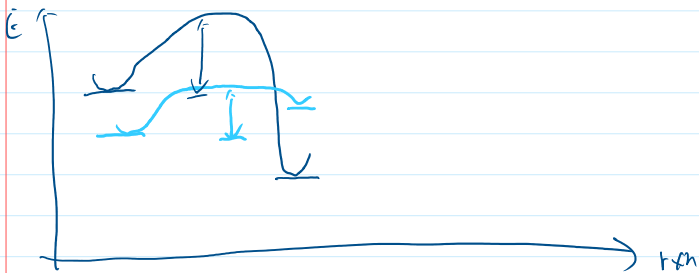
2

3
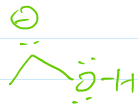
3f

why 1 is more stable then 2:

① the carboxylate has ⊖ on more E.N. atom (rule #1)

② the carboxylate has resonance stabilization (rule # 4)

③ al though alkyne has sp hybridication, but because it's a negative charge on carbon,

---

E ↑

→ rxn

$\overset{H \quad H}{H-\underset{H \quad H}{C}-\underset{}{C}-\ddot{O}-H}$

$\diagdown\diagup\ddot{O}:^{\ominus}$ vs $\overset{\ominus}{\diagup\diagdown}\underset{}{\ddot{O}-H}$ vs $\overset{\ddot{O}}{\diagup}\diagdown\ddot{O}H$

1   2   3

$H \diagdown \overset{O}{\underset{H \quad H}{C}} \ddot{O}-H$ ~~$H-\overset{O}{\underset{H}{C}} \diagup\diagdown \ddot{O}-H$~~