

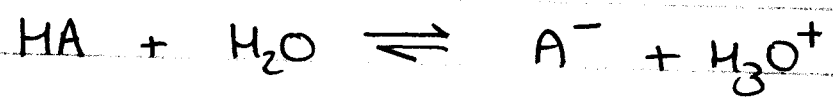
- ① ACID/BASE EQUILIBRIA
- ② STRUCTURE AND ACIDITY
- ③ PROTONATING ORGANIC STRUCTURES
- ④ LEWIS ACIDS/BASES

READING: CH 4

HMK: DO THE MIDTERM AGAIN!
: 4.1 → 4.45

MIDTERM: HIGH 98, LOW 13, MEAN 52
"HOW-TO" GUIDE

① ACID/BASE EQUILIBRIA



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

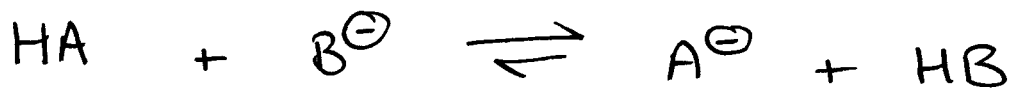
$$pK_a = -\log_{10} K_a$$

LARGER pK_a → WEAKER ACID
 AND STRONG ACID ≡ WEAK CONJUGATE BASE
 WEAK ACID ≡ STRONG CONJUGATE BASE

(2)

Scan through pKa table Page 141

Acid/Base Equilibrium



Competition between B^{\ominus} and A^{\ominus} for the H^+

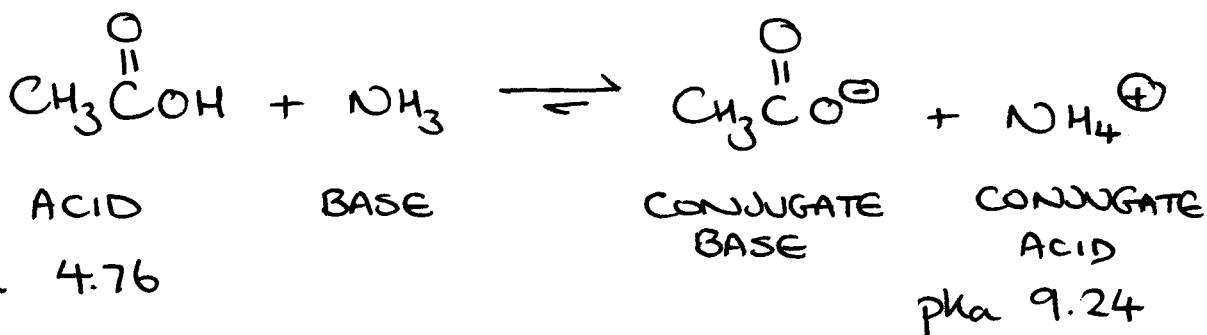
$$K_{\text{eq}} = \frac{[\text{A}^{\ominus}][\text{HB}]}{[\text{HA}][\text{B}^{\ominus}]}$$

multiply by $\frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]}$

$$K_{\text{eq}} = \frac{[\text{A}^{\ominus}][\text{H}_3\text{O}^+]}{[\text{HA}]} \times \frac{[\text{HB}]}{[\text{B}^{\ominus}][\text{H}_3\text{O}^+]}$$

$$K_{\text{eq}} = \frac{K_{\text{HA}} \quad (\text{ACID})}{K_{\text{HB}} \quad (\text{CONJUGATE ACID})}$$

$$pK_{\text{eq}} = pK_{\text{HA}} - pK_{\text{HB}}$$



3

So,

$$pK_{eq} = 4.76 - 9.24 = -4.48$$

$$K_{eq} = 10^{-pK_{eq}}$$

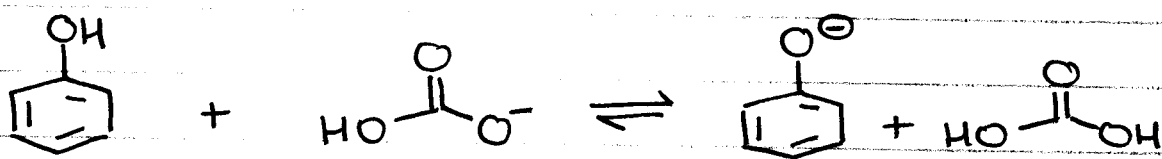
$$= 3 \times 10^4$$

STRONGER ACID AND STRONGER BASE
REACT TO GIVE WEAKER ACID + WEAKER BASE

If stronger acid is on left side of equation, K_{eq} will be > 1

If stronger acid is on the right side of equation, K_{eq} will be < 1

For example:



$pK_a \sim 10$

STRONGER ACID $\Rightarrow pK_a \sim 6.4$

So equilibrium lies to the left, and

$$K_{eq} = 10^{-3.6}$$

② STRUCTURE AND ACIDITY

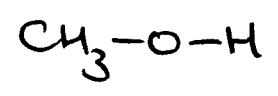
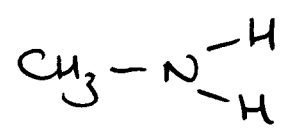
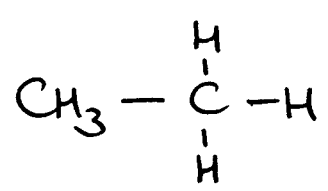


all about A^-

The more stable A^- , the more acidic HA is.

a) Electronegativity

consider



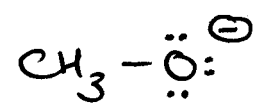
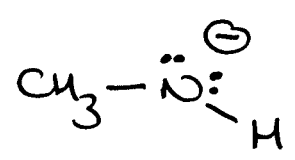
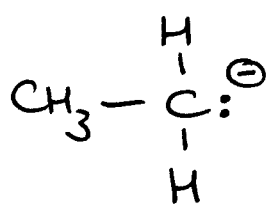
pKa

51

38

16

→ INCREASING ACIDITY



conjugate bases

← INCREASING BASICITY

C
2.5

N
3.0

O
3.5

Bigger EN, electrons held more strongly, ^⑤
 A^- is more stable \rightarrow

THIS TREND holds within any given row
of the periodic table.

b) ATOM SIZE

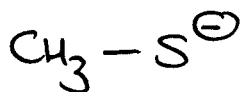
consider



pha

7

16



\uparrow

more stable

NEGATIVE CHARGE IS SPREAD OVER A
LARGER VOLUME (lower charge density)

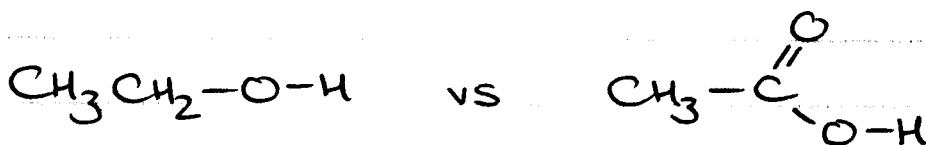
So for HALOGEN ACIDS



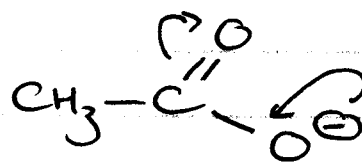
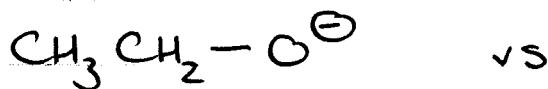
6

c) RESONANCE

consider:



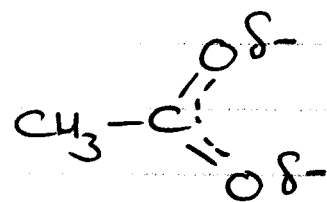
pKa 16



charge localized
on ONE atom

charge
delocalized

→

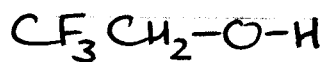
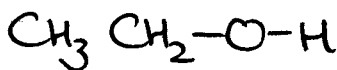


DELOCALIZATION \equiv STABILITY

(HOT POTATO ANALOGY)

d) INDUCTIVE EFFECT

consider:



pKa

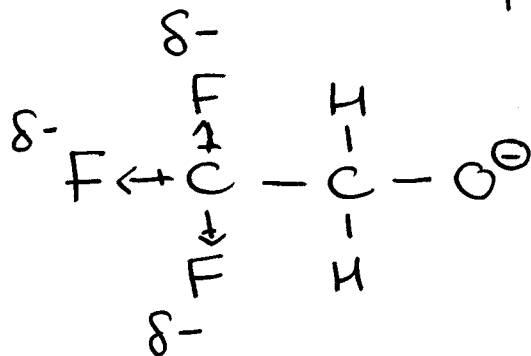
15.9

12.4

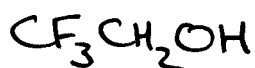
(7)

So,

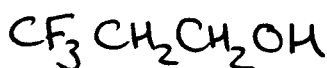
$\text{CF}_3\text{CH}_2\text{O}^\ominus$ is more stable than $\text{CH}_3\text{CH}_2\text{O}^\ominus$



THROUGH BOND - FALLS OFF RAPIDLY WITH DISTANCE



12.4

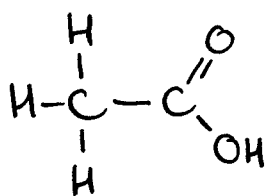


14.6

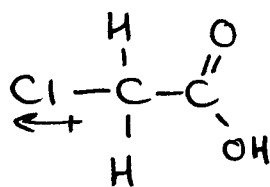


15.4

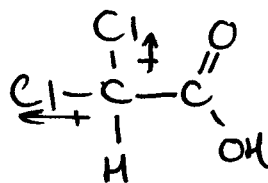
Same effect on carboxylic acids



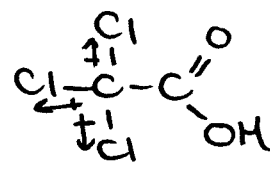
4.75



2.85



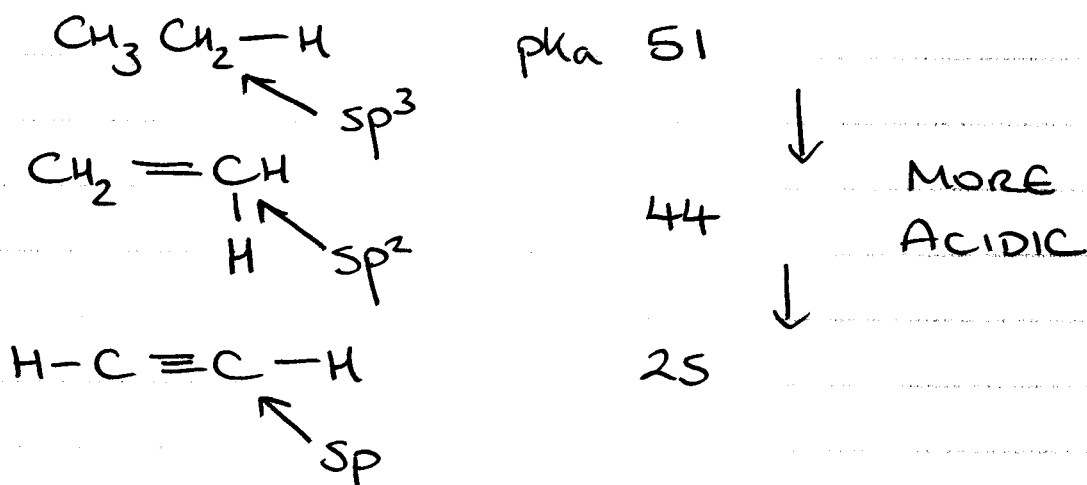
1.48



0.64

8

e) HYBRIDIZATION



S character of orbital

25% → 33% → 50%

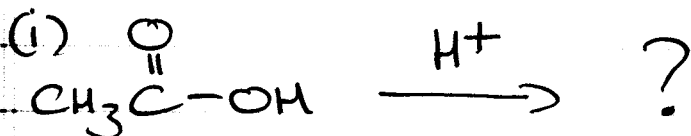


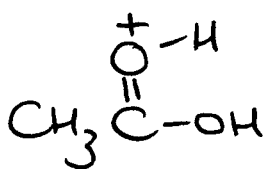
- electrons held closer to the nucleus
- more stable anion
- more acidic

IMPORTANCE OF EFFECT → in order presented

Atom / (Size) / Resonance / Induction / Orbital

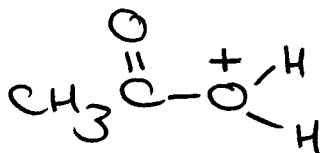
③ ORGANIC STRUCTURES





(A)

or

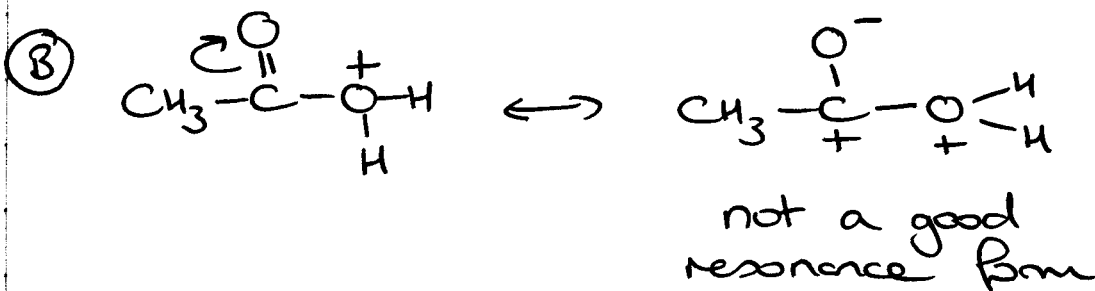
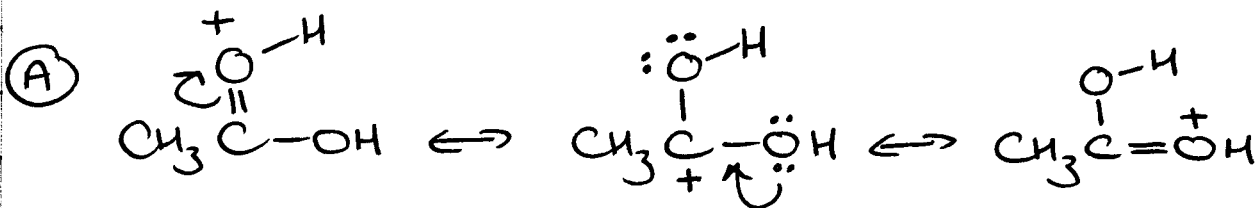


(B)

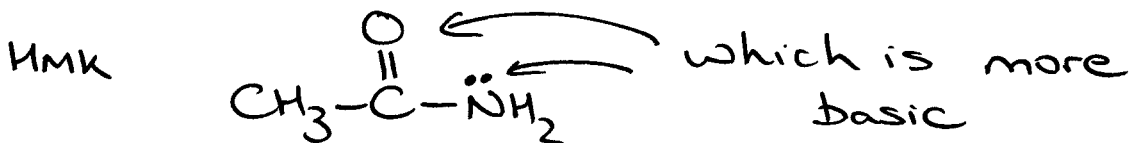
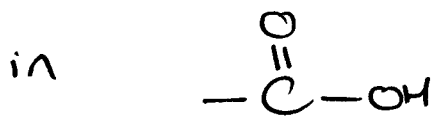
?

(9)

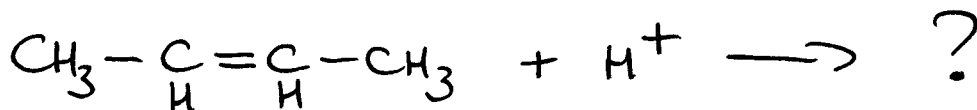
Consider resonance

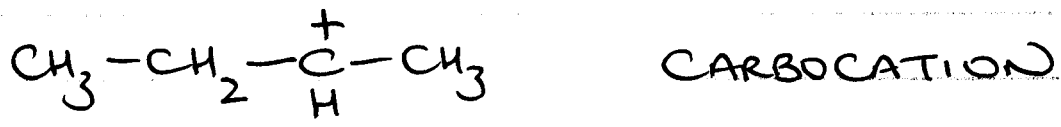
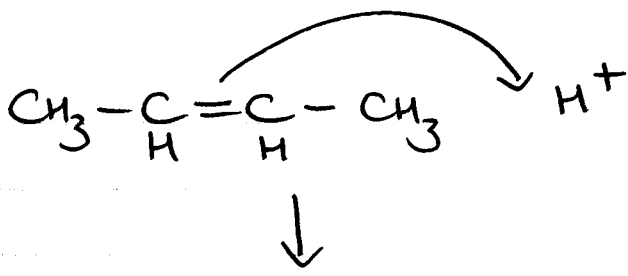


So, $\overset{\text{O}}{\parallel}\text{C}$ more basic than $\text{C}-\overset{\text{O}}{\text{H}}$



(ii)





(See these a lot more — soon)

4. LEWIS ACIDS/BASES

About e^- pairs, not H^+

LEWIS ACID accepts an e^- pair
 LEWIS BASE donates an e^- pair

