Acid-Base Reactions: Proton Transfers - Chapter 3 (Klein)

1) Definitions (3.1, 3.2, 3.10)
2) Factors affecting acidity (3.4, 3.5, "***ARIO***")
   a) Periodic Trends (***A****tom*)
   b) Inductive Effects (***I****nduction*)
   c) Resonance Effects (***R****esonance*)
3) Comparing strengths of bases (3.6, 3.7, 3.8)
4) Common Acids and Bases, K_a and pK_a (3.3)

Note: curved arrows show the flow of electrons to form and break bonds - this is described as the "mechanism" of the reaction (3.2)

1) Definitions: acids and bases can be defined by Lewis (3.9) or Bronsted-Lowry (3.1) theories

Lewis Acid: electron-pair acceptor (also called an **Electrophile, E^+**)

* has a vacancy
* common Lewis acids: $AlCl_3$ BF_3

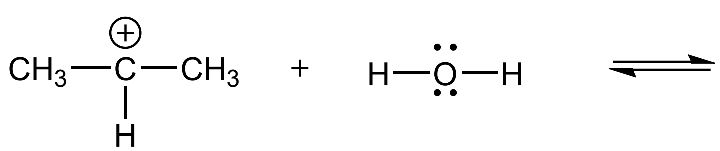
Lewis Base: electron-pair donor (also called an **Nucleophile, Nu:**)

* has a lone pair or a pi bond

examples:

$:NH_3$ + $AlCl_3$ $\rightleftharpoons$

base "acid"



see SkillBuilder 3.12

"Acid-Base" reaction usually means Bronsted-Lowry type

Acid: $H^{\oplus}$ (proton) donor **Base:** $H^{\oplus}$ (proton) acceptor *(Bronsted-Lowry definitions)*

A general "proton-transfer" reaction

B: + H—A $\rightleftharpoons$

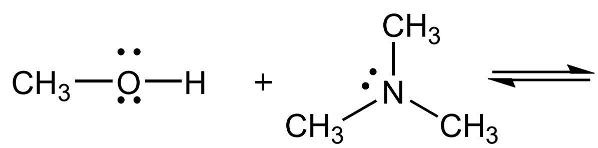
base acid

Two acids are in competition - forward and reverse reactions are in **equilibrium**.

****Equilibrium lies in the direction of the ______________ acid/base pair ****

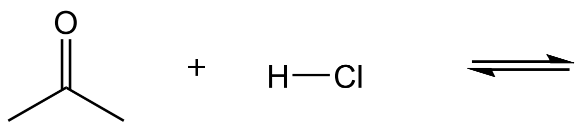
Which is the stronger acid? Use pK_a table or predict... ***see SkillBuilders 3.1, 3.2, 3.4***

Predict the products, label them (conj. acid, conj. base) and predict direction of equilibrium:



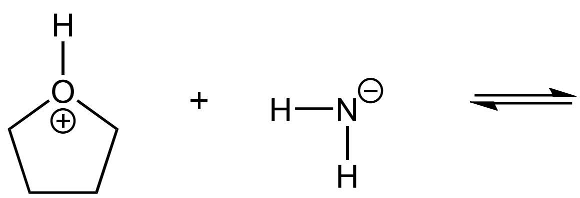
acid base

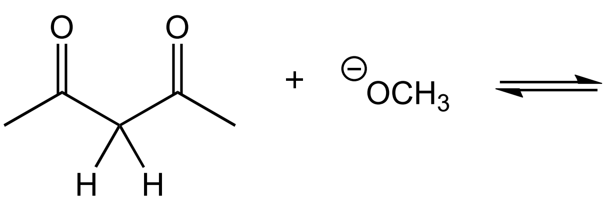
Group work: *protonate* each compound with the given acid (add missing lone pairs, draw curved arrows to show mechanism, draw the products and label them C.A. and C.B.).



$HC\equiv C^{\ominus}$ + $CH_3O—H$ $\rightleftharpoons$

Group work: *deprotonate* each compound with the given base (add missing lone pairs, draw curved arrows to show mechanism, draw the products and label them C.A. and C.B.).





Clicker question: Using a pK_a table to predict direction of equilibrium

	$NH_4^{\oplus}$	+	H_2O	$\rightleftharpoons$	NH_3	+	$H_3O^{\oplus}$
pK_a	9		16		36		-2

see SkillBuilder 3.4

Clicker question:

Draw the conjugate acid or conjugate base, as directed, for each.

conjugate base of	conjugate acid of	conjugate acid of
NH_3	H_2O	$H:^{\ominus}$

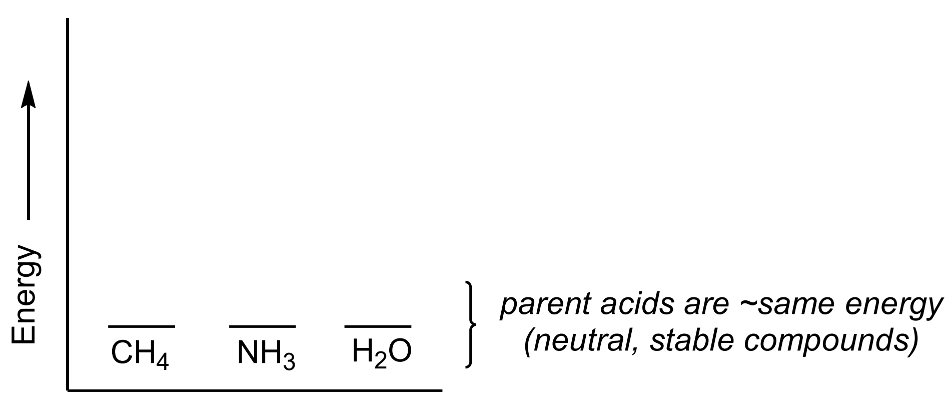
2a) Periodic Trends "Atom" (across row)

compare these acids:	CH_4	NH_3	H_2O
pK_a	50	38	16

why such a large difference in pK_a? Look at conjugate bases!

draw the conj. bases:

Conclusion: the stronger acid is the one with the most stable (less reactive, weaker) conjugate base!



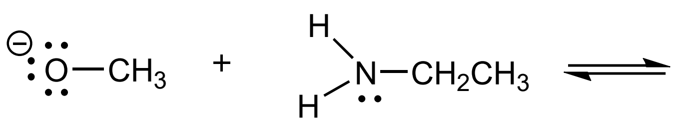
2a) Periodic Trends "Atom" (down column/family)

compare these acids:	HF	HCl	HBr	HI
pK_a	3	-7	-9	-10

draw the conj. bases:

why such a large difference in pK_a? Look at conjugate bases!

Group work: Predict the products, use curved arrows to show the mechanism for the proton transfer reaction, determine the favored direction of equilibrium, and explain your choice.



base acid

Clicker question: Which is the stronger acid? Explain briefly.

H_2O H_2S

A) H_2O is the stronger acid because HO^- is **more** stable than HS^-.

B) H_2O is the stronger acid because HO^- is **less** stable than HS^-.

C) H_2S is the stronger acid because HS^- is **more** stable than HO^-.

D) H_2S is the stronger acid because HS^- is **less** stable than HO^-.

E) It's impossible to predict acid strength without pK_a data.

see SkillBuilder 3.5

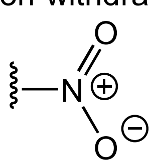
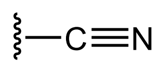
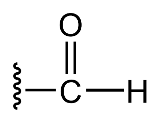
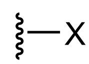
2b) Inductive Effects "Induction"

Which is the stronger acid (i.e., which is the more acidic proton, H_A or H_B)?

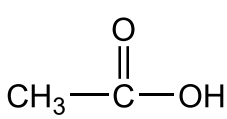
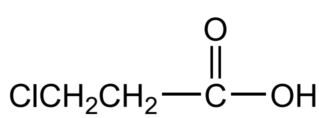
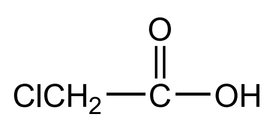
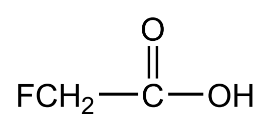
CH_3OH_A vs. CF_3OH_B

draw the
conj. bases:

F is an electron-withdrawing group (EWG) Other EWG:

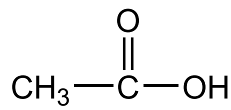
Inductive effects decrease with distance (more bonds to travel through)

pK_a 4.76 3.98 2.86 2.66

see SkillBuilder 3.7

2c) Resonance Effects

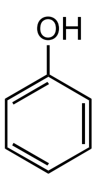
$CH_3CH_2—OH$ vs. 

I, pK_a 16 **II**, pK_a 5

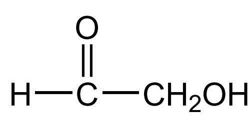
II is 100,000,000,000 (100 **BILLION**) times more acidic than **I** !! Why?! Compare conj. bases!

CB-I CB-II

Example: Which is most acidic? Least acidic?



I



II

CH_3CH_2OH

III

see SkillBuilder 3.6

3) Comparing strengths of bases (3.6, 3.7)

Example: Which is more basic (stronger base)?

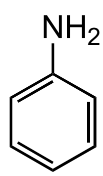
CH_3OH I

CF_3OH II

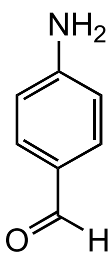
Example: Which is most basic (strongest base)?

CH_3CH_2NH
2

I



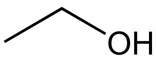
II



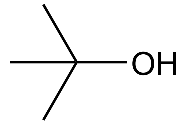
III

see SkillBuilders 3.3, 3.10

FYI: bulky bases aren't well-stabilized by solvent molecules, so they are stronger than smaller bases (therefore, bulky acids like t-butanol are harder to deprotonate/less acidic) (Klein 3.7)

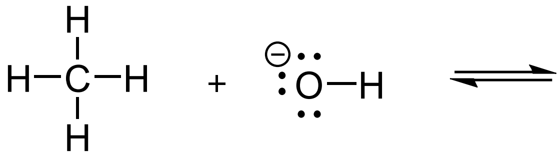


ethanol
pK_a 16

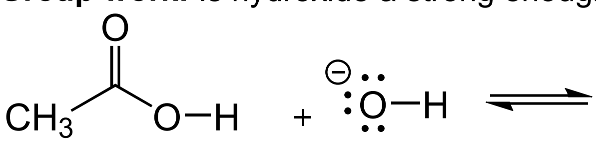


t-butanol
pK_a 18

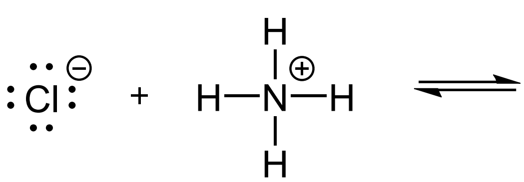
Group work: Is hydroxide a strong enough base to deprotonate methane (CH_4)? Explain.



Group work: Is hydroxide a strong enough base to deprotonate acetic acid (CH_3CO_2H)? Explain.



Group work: Is chloride a strong enough base to deprotonate ammonium (NH_4^+)? Explain.



see SkillBuilders 3.9, 3.11

4) Common Acids and Bases

see pK_a Table 3.1

strong acids	**weak acids**	**very weak acids**	**extremely weak acids (not acids!)**
$pK_a < 0$	$0 < pK_a < 16$	$pK_a > 16$	$pK_a > 40$

Acid Dissociation Constant, K_a, and pK_a : a measure of acid strength (3.3)

$$HA + H_2O \rightleftharpoons A^{\ominus} + H_3O^{\oplus}$$

if HA is a STRONG acid

if HA is a WEAK acid

K_{eq} is the equilibrium constant

$$K_{eq} = \frac{[\text{products}]}{[\text{reactants}]}$$

K_a is the acid dissociation constant

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

since K_a is often VERY large or VERY small, it's easier to work with pK_a

$$pK_a = -\log(K_a)$$

if K_a is a LARGE number (>1), then the acid is stronger weaker

if an acid is stronger, then the pK_a is higher lower

for example, sulfuric acid (H_2SO_4) has a K_a of ~1.6×10^5 and a pK_a of -5.2

acetic acid (CH_3CO_2H) has a K_a of 1.8×10^{-5} and a pK_a of 4.75

Chapter 3 Summary: Acid/Base, Proton-Transfer Reactions (Klein)

I. Definitions (3.1, 3.2) ***SkillBuilders 3.1***
  a. Lewis acid/base (3.10, e- pair acceptor/donor, Electrophile/Nucleophile) ***SkillBuilders 3.13***
  b. Bronsted-Lowry acid/base (proton, H+, donor/acceptor)
  c. curved arrows to show reaction mechanisms

How can we predict relative strenths or acids and bases? (3.4, 3.5)

II. Periodic trends in acid strength (*ARIO: Atom*) ***SkillBuilders 3.5***
  a. ROH > R_3CH and HI > HCl. Why? Compare conjugate bases...
  b. The stronger acid has the more stable (weaker) conjugate base!

III. Inductive effects on acid strength (*ARIO: Induction*) ***SkillBuilders 3.7***
  a. electron-withdrawing groups (EWG) stabilize negative charges
  b. inductive effects decrease with distance

IV. Effect of resonance (*ARIO: Resonance*) ***SkillBuilders 3.6***
  a. acid strength: resonance can stabilize a conjugate base
  b. base strength: resonance can tie up and stabilize a lone pair

V. Common acids (see pK_a Table 3.1) ***SkillBuilders 3.2, 3.3, 3.4***
  a. use pK_a table to identify strong/weak/very weak acids (3.3)
  b. determine direction of equilibrium (3.6), with or without pK_a table

skip: ARIO: Orbital (skip SkillBuilder 3.8), 3.7 Leveling effect, 3.8 Solvating effect .