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

1) Definitions (Sections 3.1, 3.2, 3.10)

2) Factors affecting acidity (Sections 3.4, 3.5, "***ARI****O*")

   a) Periodic Trends (***A****tom*)

   b) Inductive Effects (***I****nduction*)

   c) Resonance Effects (***R****esonance*)

3) Comparing strengths of bases (Sections 3.6, 3.9)

4) Common Acids and Bases, $K_a$ and p$K_a$ (Section 3.3)

   *Skip Sections 3.7 and 3.8*

   *Skip SkillBuilders 3.8, 3.12, 3.13*

*Note: **curved arrows** show the flow of electrons to **form bonds** and **break bonds** – this is described as the "mechanism" of the reaction (Klein Section 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: $AlCl_3$ $BF_3$

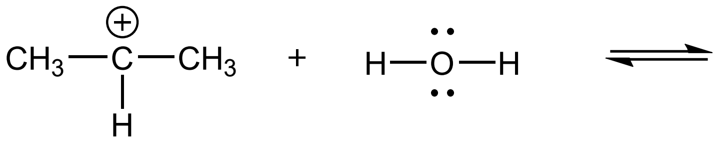
**Lewis Base**: electron-pair donor (also called an **Nucleophile, Nu:**)

* has a lone pair or a pi bond

examples:

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

base "acid"



$$CH_3-\overset{\oplus}{\underset{H}{C}}-CH_3 \quad + \quad H-\ddot{\underset{\cdot\cdot}{O}}-H \quad \rightleftharpoons$$

*FYI: SkillBuilder 3.12 (Lewis acids/bases is not the focus of this chapter!)*
***We will study Nucleophiles and Electrophiles in Chapter 7.***

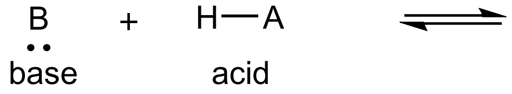
**"Acid-Base" reaction usually means Bronsted-Lowry type**

**Acid:** $H^{\oplus}$ (proton) donor

**Base:** $H^{\oplus}$ (proton) acceptor

*(Bronsted-Lowry definitions)*

A general "proton-transfer" reaction



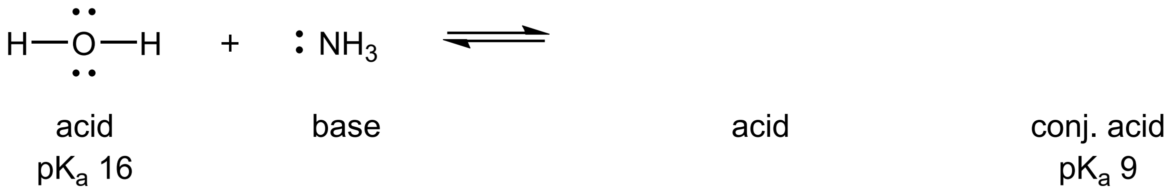
$$\ddot{B} + H{-}A \rightleftharpoons$$

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 p$K_a$ table (see Table 3.1) or predict...

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



$$H{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + :NH_3 \rightleftharpoons$$

***try SkillBuilders 3.1, 3.2, 3.3, 3.4***

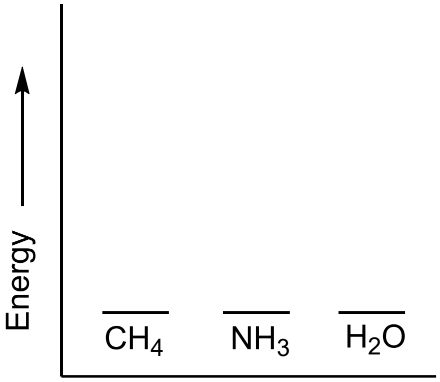
## 2a) Periodic Trends for Acidity: "Atom" (across row)

| | | | |
|---|---|---|---|
| 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!**



*parent acids are ~same energy (neutral, stable compounds)*

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## 2a) Periodic Trends for Acidity: "Atom" (down column/family)

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

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

draw the
conj. bases:

***try SkillBuilder 3.5***

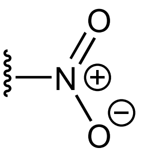
### 2b) Inductive Effects on Acidity: "Induction"

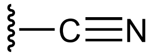
Which is the stronger acid (i.e., which is the more acidic proton, $H_A$ or $H_B$)?

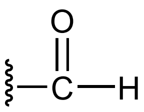
$CH_3OH_A$ vs. $CF_3OH_B$

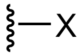
draw the
conj. bases:

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

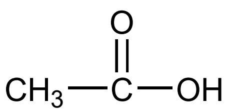




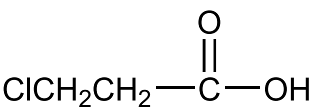




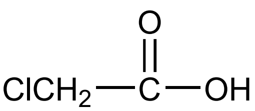
Inductive effects decrease with distance (more bonds to travel through)



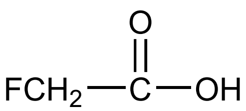
$CH_3-C(=O)-OH$



$ClCH_2CH_2-C(=O)-OH$



$ClCH_2-C(=O)-OH$



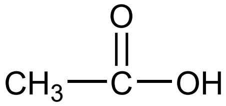
$FCH_2-C(=O)-OH$

$pK_a$ 4.76 3.98 2.86 2.66

***try SkillBuilder 3.7***

## 2c) Resonance Effects on Acidity

$CH_3CH_2-OH$ vs.



$CH_3-C(=O)-OH$

**I**, p$K_a$ 16

**II**, p$K_a$ 5

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

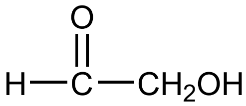
CB-I

CB-II

Example: Which is most acidic? Least acidic?

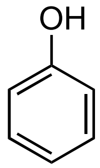
$CH_3CH_2OH$

I



$H-C(=O)-CH_2OH$

II



III

***try SkillBuilder 3.6***

**3) Comparing strengths of bases (3.6, 3.7)**

Example: Which is more basic (stronger base)?

$CH_3OH$

I

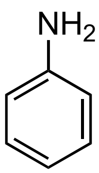
$CF_3OH$

II

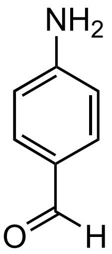
Example: Which is most basic (strongest base)?

$CH_3CH_2NH_2$

I



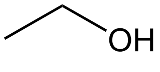
II



III

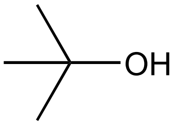
***try SkillBuilders 3.3, 3.9, 3.10, 3.11***

*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

p$K_a$ 16



*t*-butanol

p$K_a$ 18

## 4) Common Acids and Bases see p$K_a$ Table 3.1

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

Using a p$K_a$ table to predict direction of equilibrium

$$\begin{array}{cccccccc} & \overset{\oplus}{NH_4} & + & H_2O & \rightleftharpoons & NH_3 & + & H_3O^{\oplus} \\ pK_a & 9 & & 16 & & 36 & & -2 \end{array}$$

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## Acid Dissociation Constant, $K_a$, and p$K_a$ are measures 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 p$K_a$

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

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

if an acid is stronger, then the p$K_a$ is higher lower

for example, sulfuric acid ($H_2SO_4$) has a $K_a$ of ~$1.6 \times 10^5$ and a p$K_a$ of -5.2
acetic acid ($CH_3CO_2H$) has a $K_a$ of $1.8 \times 10^{-5}$ and a p$K_a$ of 4.75

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

I. Definitions (Sections 3.1, 3.2) ***SkillBuilder 3.1***

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

**How can we predict relative strengths or acids and bases? (Sections 3.4, 3.5)**

II. Periodic trends in acid strength (*ARIO: Atom*) ***SkillBuilder 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*) ***SkillBuilder 3.7***

  a. electron-withdrawing groups (EWG) stabilize negative charges
  b. inductive effects decrease with distance

IV. Effect of resonance (*ARIO: Resonance*) ***SkillBuilder 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 p$K_a$ Table 3.1) ***SkillBuilders 3.2, 3.3, 3.4***

  a. use p$K_a$ table to identify strong/weak/very weak acids (Section 3.3)
  b. determine direction of equilibrium (Section 3.6), with or without p$K_a$ table

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

**Suggested textbook problems (4th edition)**

1-64, but skip 21, 22, 23dg, 24d, 30f, 32-36, 46c, 47d, 49a, 50, 51ac, 64c.