

## Chapter 2: Acids and Bases

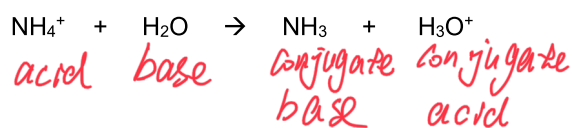
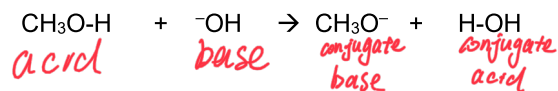
### 2.1 Brønsted-Lowry Definition of Acids and Bases

*Acid* – donates a hydrogen ion ( $H^+$  or proton)

*Base* – accepts the hydrogen ion

*Conjugate Base* – what the acid becomes after losing a proton

*Conjugate Acid* – what the base becomes after gaining a proton

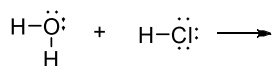
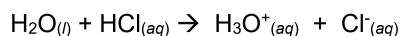


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### 2.2 Properties of Acids and Bases

Strong acids or bases completely ionize in  $H_2O$

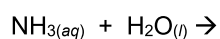
Dissolving HCl (g) in water leads to complete ionization:



Examples of strong acids: HCl, HBr, HI,  $HNO_3$ ,  $H_2SO_4$



Examples of strong bases: LiOH, NaOH, KOH, NaOEt,  $KO^tBu$

Weak acids or bases partially ionize in  $H_2O$



2.2

**TABLE 2.1** Some Acids and Their Conjugate Bases

	Acid	Name	Conjugate Base	Name	
 Strong Acids	HI	hydroiodic acid	$I^-$	iodide ion	 Weak Bases
	HCl	hydrochloric acid	$Cl^-$	chloride ion	
	$H_2SO_4$	sulfuric acid	$HSO_4^-$	hydrogen sulfate ion	
	$HNO_3$	nitric acid	$NO_3^-$	nitrate ion	
	$H_3O^+$	hydronium ion	$H_2O$	water	
	$HSO_4^-$	hydrogen sulfate ion	$SO_4^{2-}$	sulfate ion	
	$H_3PO_4$	phosphoric acid	$H_2PO_4^-$	dihydrogen phosphate ion	
	$CH_3COOH$	acetic acid	$CH_3COO^-$	acetate ion	
	$H_2CO_3$	carbonic acid	$HCO_3^-$	bicarbonate ion	
	$H_2S$	hydrogen sulfide	$HS^-$	hydrogen sulfide ion	
	$H_2PO_4^-$	dihydrogen phosphate ion	$HPO_4^{2-}$	hydrogen phosphate ion	
	$NH_4^+$	ammonium ion	$NH_3$	ammonia	
	HCN	hydrocyanic acid	$CN^-$	cyanide ion	
	$C_6H_5OH$	phenol	$C_6H_5O^-$	phenoxide ion	
	$HCO_3^-$	bicarbonate ion	$CO_3^{2-}$	carbonate ion	
	$HPO_4^{2-}$	hydrogen phosphate ion	$PO_4^{3-}$	phosphate ion	
Weak Acids	$H_2O$	water	$OH^-$	hydroxide ion	Strong Bases
	$C_2H_5OH$	ethanol	$C_2H_5O^-$	ethoxide ion	

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Acids can be (+), neutral or (-)Examples:  $H_3O^+$ ,  $H_2CO_3$ ,  $H_2PO_4^-$ 

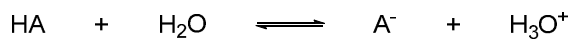
Depending on the number of acidic protons, acids can be classified as *monoprotic*, *diprotic*, or *triprotic* ( $HNO_3$ ,  $H_2SO_4$ ,  $H_3PO_4$ )

Bases can be (-) or neutralExamples:  $HO^-$ ,  $RO^-$ ,  $H_2O$ ,  $NH_3$ Amphoteric compounds can act as either acid or base**Water** acts as either an acid or a base

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**2.3 The Strength of Brønsted-Lowry Acids and Bases:  $K_a$  and  $pK_a$** 

**Acidity equilibrium constant** –  $K_a$  or proton-donating ability



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$pK_a = -\log K_a$$

- The lower the  $pK_a$  value, the stronger the acid (and the weaker its conjugate base)
- The higher the  $pK_a$  value, the weaker the acid (and the stronger its conjugate base)
- A strong acid will have a weak conjugate base (acid and base strength are inversely proportional)

- Equilibrium favors the formation of weak acids & bases (neutralization)

$pK_a$  values are tabulated and can be used to determine the position of the equilibrium in acid base reactions.

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 **$pK_a$  Values for Some Organic and Inorganic Acids**

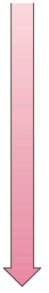
	Acid	Formula	$pK_a$	Conjugate Base	
↑ Weaker acid	ethane	$\text{CH}_3\text{CH}_3$	51	$\text{CH}_3\text{CH}_2^-$	Stronger base
	ammonia	$\text{NH}_3$	38	$\text{NH}_2^-$	
	ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	15.9	$\text{CH}_3\text{CH}_2\text{O}^-$	
	water	$\text{H}_2\text{O}$	15.7	$\text{HO}^-$	
	methylammonium ion	$\text{CH}_3\text{NH}_3^+$	10.64	$\text{CH}_3\text{NH}_2$	
	bicarbonate ion	$\text{HCO}_3^-$	10.33	$\text{CO}_3^{2-}$	
	phenol	$\text{C}_6\text{H}_5\text{OH}$	9.95	$\text{C}_6\text{H}_5\text{O}^-$	
	ammonium ion	$\text{NH}_4^+$	9.24	$\text{NH}_3$	
	carbonic acid	$\text{H}_2\text{CO}_3$	6.36	$\text{HCO}_3^-$	
	acetic acid	$\text{CH}_3\text{COOH}$	4.76	$\text{CH}_3\text{COO}^-$	
	benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	4.19	$\text{C}_6\text{H}_5\text{COO}^-$	
	phosphoric acid	$\text{H}_3\text{PO}_4$	2.1	$\text{H}_2\text{PO}_4^-$	
	hydronium ion	$\text{H}_3\text{O}^+$	-1.74	$\text{H}_2\text{O}$	
	sulfuric acid	$\text{H}_2\text{SO}_4$	-5.2	$\text{HSO}_4^-$	
	hydrogen chloride	$\text{HCl}$	-7	$\text{Cl}^-$	
	hydrogen bromide	$\text{HBr}$	-8	$\text{Br}^-$	
	hydrogen iodide	$\text{HI}$	-9	$\text{I}^-$	
↓ Stronger acid					Weaker base

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**2.4 Determination of the Position of Equilibrium in an Acid-Base Reaction**How to Determine the Position of Equilibrium for Acid-Base Reaction


1. Identify the two acids.
2. Determine the stronger and weaker acid using  $\text{pK}_a$  values.
3. Identify the stronger and weaker base. Remember the stronger acid yields the weak conjugate base and vice versa
4. The position of the equilibrium lies towards the weaker acid and weaker base.

Examples: Complete the following acid-base reactions with the appropriate arrows.

	Acid	Formula	$\text{pK}_a$	
Weaker acid  Stronger acid	ethane	$\text{CH}_3\text{CH}_3$	51	$\text{CH}_3\text{CO}_2\text{H} + \text{NaHCO}_3 \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}_2\text{CO}_3$
	ammonia	$\text{NH}_3$	38	
	ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	15.9	
	water	$\text{H}_2\text{O}$	15.7	
	methylammonium ion	$\text{CH}_3\text{NH}_3^+$	10.64	
	bicarbonate ion	$\text{HCO}_3^-$	10.33	$\text{CH}_3\text{CO}_2\text{H} + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{NH}_4^+$
	phenol	$\text{C}_6\text{H}_5\text{OH}$	9.95	
	ammonium ion	$\text{NH}_4^+$	9.24	
	hydrogen cyanide	$\text{HCN}$	9.21	
	carbonic acid	$\text{H}_2\text{CO}_3$	6.36	
	acetic acid	$\text{CH}_3\text{COOH}$	4.76	$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{H}_3\text{O}^+$
	benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	4.19	
	phosphoric acid	$\text{H}_3\text{PO}_4$	2.1	
	hydronium ion	$\text{H}_3\text{O}^+$	-1.74	
	sulfuric acid	$\text{H}_2\text{SO}_4$	-5.2	$\text{CH}_3\text{CO}_2\text{H} + \text{NaOH} \rightleftharpoons \text{CH}_3\text{CO}_2^-\text{Na}^+ + \text{H}_2\text{O}$
	hydrogen chloride	$\text{HCl}$	-7	
	hydrogen bromide	$\text{HBr}$	-8	
	hydrogen iodide	$\text{HI}$	-9	

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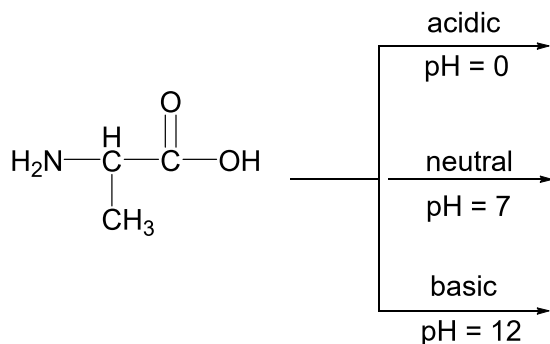
If you only have half of the equation, you will have to decide which molecule is the stronger acid.

	Acid	Formula	$\text{pK}_a$	
Weaker acid  Stronger acid	ethane	$\text{CH}_3\text{CH}_3$	51	$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O}$
	ammonia	$\text{NH}_3$	38	
	ethanol	$\text{CH}_3\text{CH}_2\text{OH}$	15.9	
	water	$\text{H}_2\text{O}$	15.7	
	methylammonium ion	$\text{CH}_3\text{NH}_3^+$	10.64	
	bicarbonate ion	$\text{HCO}_3^-$	10.33	$\text{HCO}_3^- + \text{OH}^-$
	phenol	$\text{C}_6\text{H}_5\text{OH}$	9.95	
	ammonium ion	$\text{NH}_4^+$	9.24	
	hydrogen cyanide	$\text{HCN}$	9.21	
	carbonic acid	$\text{H}_2\text{CO}_3$	6.36	
	acetic acid	$\text{CH}_3\text{COOH}$	4.76	
	benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	4.19	
	phosphoric acid	$\text{H}_3\text{PO}_4$	2.1	
	hydronium ion	$\text{H}_3\text{O}^+$	-1.74	
	sulfuric acid	$\text{H}_2\text{SO}_4$	-5.2	
	hydrogen chloride	$\text{HCl}$	-7	$\text{NaHCO}_3 + \text{HCl}$
	hydrogen bromide	$\text{HBr}$	-8	
	hydrogen iodide	$\text{HI}$	-9	

2.8

**2.5 Acids with Multiple Acidic Hydrogen Atoms: Amino Acids**Alanine, an amino acid

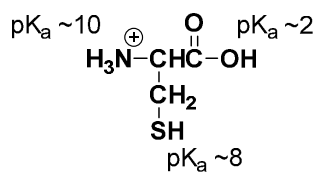
Changing the pH of a system, changes also the extent of protonation. When pH of the solution  $> pK_a$  of the dissolved acid, a proton is lost.



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**b) Cysteine**

What is the predominant structure of cysteine at  $\text{pH} = 1, 4, 7, 9,$  and  $12$ ?



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## 2.6 Structural Factors that Influence Acidity

### a) Periodic trends

1A	2A																	3A	4A	5A	6A	7A
Li 1.0	Be 1.5																	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2																	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0	3B	4B	5B	6B	7B	8B				1B	2B	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8					
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5						
Cs 0.7	Ba 0.9	Hf 1.1	Ta 1.3	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.5							

- Electronegativity of **A-H**:  
Acidity of H-A in a row is determined by the stability of  $A^-$   
(Greater electronegativity of A = greater stability of  $A^-$  = stronger HA)

H <sub>3</sub> C-H	H <sub>2</sub> N-H	HO-H	F-H
pK <sub>a</sub> = 48	pK <sub>a</sub> = 38	pK <sub>a</sub> = 15.7	pK <sub>a</sub> = 3.2

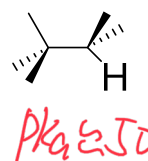
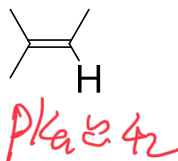
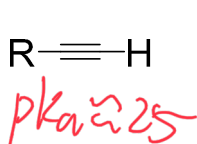
- Bond strength of X-H: Within a column, acidity increases due to weaker bonds

F-H	$pK_a = 3.2$
Cl-H	$pK_a = 7$
Br-H	$pK_a = 9$
I-H	$pK_a = 10$

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### b) Hybridization

- The more s-character the C-H orbital has, the more acidic is the C-H bond.



### c) Inductive Effects

- Works through  $\sigma$ -bonds (polarity of bonds)
- Removal of electron density from H-A bond by withdrawing groups

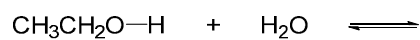
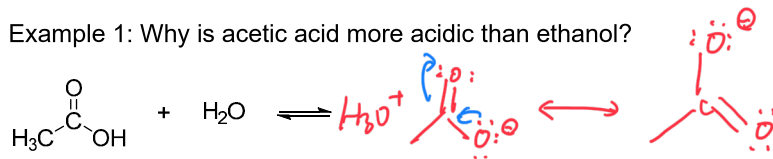
Example 1: Why is  $\text{CCl}_3\text{CO}_2\text{H}$  less acidic than  $\text{CF}_3\text{CO}_2\text{H}$ ?

Example 2: Why is  $\text{CH}_3\text{CHClCO}_2\text{H}$  more acidic than  $\text{CH}_2\text{ClCH}_2\text{CO}_2\text{H}$ ?

**d) Resonance Effect / Delocalization of Charge****d) Resonance Effect / Delocalization of Charge**

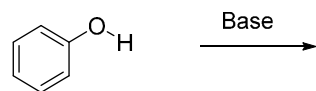
- Distributing the resulting charge over several atoms (by resonance) stabilizes the conjugate base and makes the acid stronger
- Works through  $\pi$ -bonds (and lone-pairs)

Example 1: Why is acetic acid more acidic than ethanol?

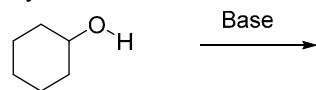


Example 2: Why is phenol more acidic than cyclohexanol?

*Phenol*

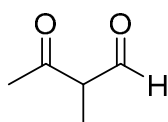
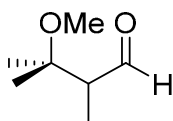


*Cyclohexanol*



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Example 3: Which is the most acidic hydrogen and why?



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**2.7. Lewis Acids and Lewis Bases (Definition)***Lewis Acid* – accepts a lone pair of electrons into a vacant valence orbital*Lewis Base* – has an atom with a lone pair of electrons that is donated to the acid