

Chapter 16

Acids & Bases



Figure 14.1 Sinkholes such as this are the result of reactions between acidic groundwaters and basic rock formations, like limestone. (credit: modification of work by Emil Kehnel)

Outline

1. Transition from the Arrhenius to the Brønsted-Lowry acid-base model
2. K_w , the ion product of water
3. pH and pOH
4. Weak acids and their equilibrium constants
5. Weak bases and their equilibrium constants
6. Acid-base properties of salt solutions
7. Extending the concept of acids and bases: the Lewis model

Review from Chem 1127

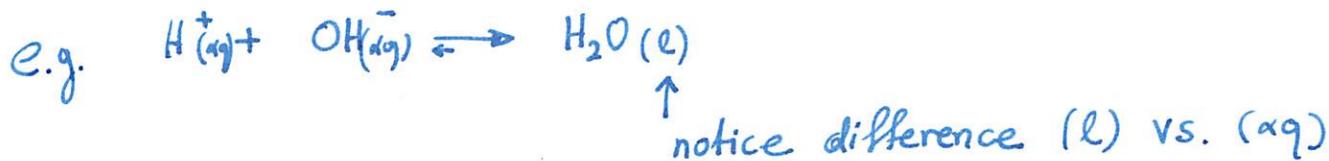
- The Arrhenius definition of acid and base
 - Acids produce H^+ in water



- Bases produce OH^- in water



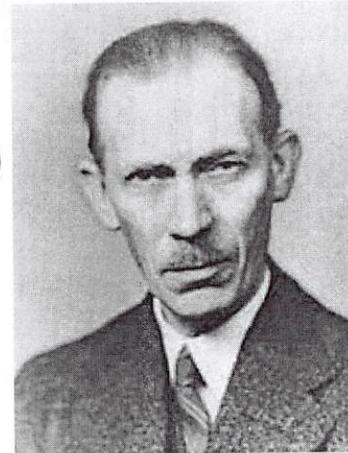
- H^+ from acids combines with OH^- from bases to produce water in a reaction called a neutralization



Brønsted-Lowry Acid-Base Model

- Brønsted-Lowry

- Johannes Brønsted (Danish 1879-1947)
- Thomas Lowry (English 1874-1936)



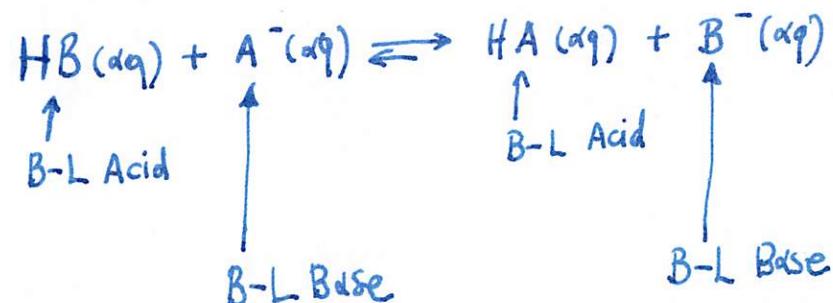
Johannes Brønsted



Thomas Lowry

- Brønsted-Lowry model focuses on the ***reaction that takes place between acid and base***, rather than on the independent nature of the acid or base, as the Arrhenius model does

- Acids donate H⁺ to bases
- Bases accept H⁺ from acids



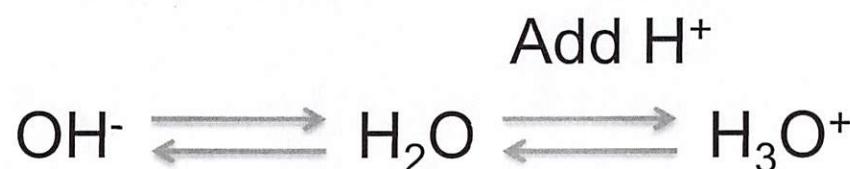
The Nature of H⁺

- The H⁺ ion is the medium of exchange in a Brønsted-Lowry reaction
 - H⁺ can also be called a proton
 - ***Acid-base reactions involve proton exchange***

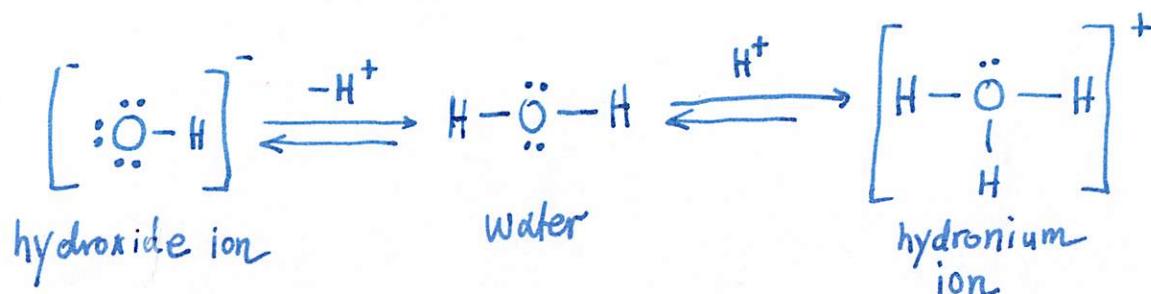


Conjugate Pairs

- The species that forms when a proton is removed from an acid is called the **conjugate base** of the acid
 - If HB is the acid is, B^- is its conjugate base
- A species can then either accept or donate a proton is called **amphiprotic**
 - Consider water:

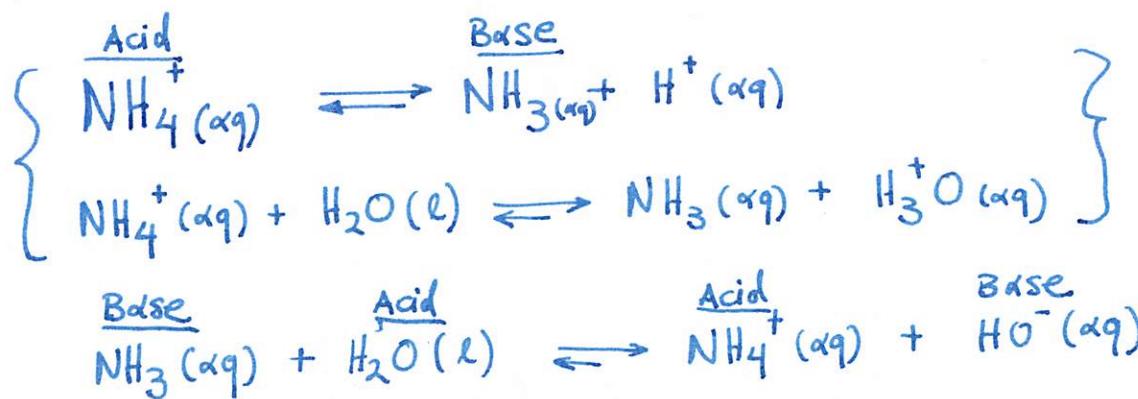


Remove H^+



Examples of Conjugate Acid-Base Pairs

Conjugate Acid	Conjugate Base
HF	F ⁻
HSO ₄ ⁻	SO ₄ ²⁻
NH ₄ ⁺	NH ₃



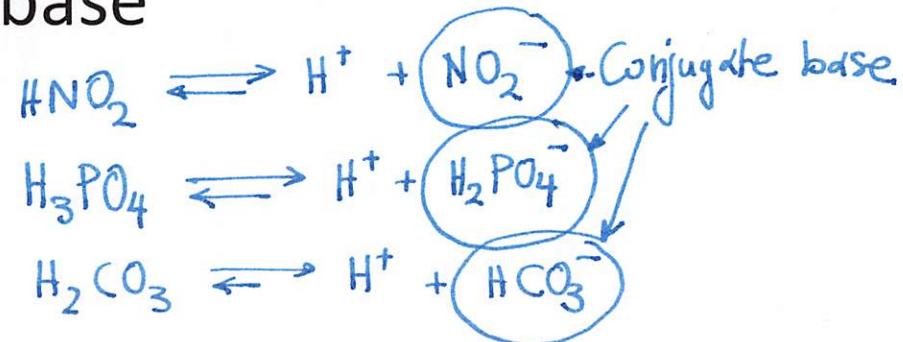
Conjugate Acids and Bases

- Every acid has a conjugate base

What is the conjugate base of HNO_2 ?

>> >> >> >> >> H_3PO_4 ?

>> >> >> >> >> H_2CO_3 ?

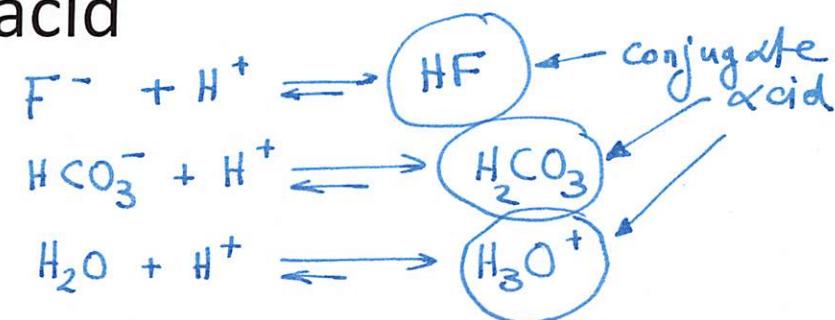


- Every base has a conjugate acid

What is the conjugate acid of F^- ?

>> >> >> >> >> HCO_3^- ?

>> >> >> >> >> H_2O ?



- For weak acids and bases we have to keep this in mind because the acid/base and its conjugate are in equilibrium.

Water Ionization and its Equilibrium

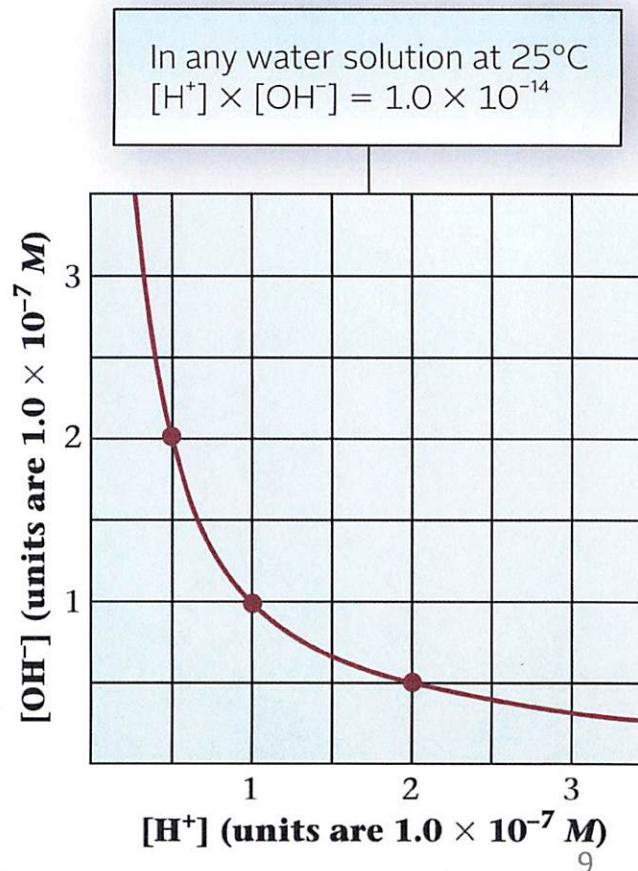


- The equilibrium constant K for this reaction is $K = [\text{H}^+][\text{OH}^-]$
- This K is called the ***ion product constant of water, K_w***
 - $K_w = [\text{H}^+][\text{OH}^-]$
 - At 25 °C, $K_w = 1.0 \times 10^{-14}$

In pure water, the two concentrations are equal: $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$

If $[\text{H}^+] > 1.0 \times 10^{-7} \text{ M}$, then $[\text{OH}^-] < 1.0 \times 10^{-7} \text{ M}$ and the solution is acidic

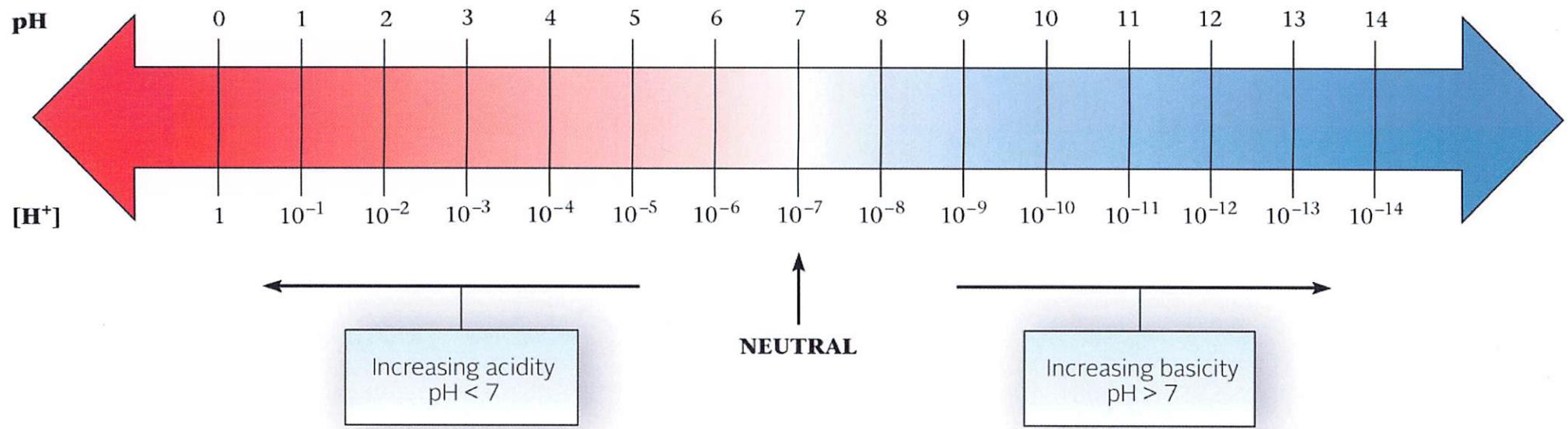
If $[\text{OH}^-] > 1.0 \times 10^{-7} \text{ M}$, then $[\text{H}^+] < 1.0 \times 10^{-7} \text{ M}$ and the solution is basic



Defining pH

$$pH = -\log[H^+]$$

$$[H^+] = \text{antilog}(-pH) = 10^{-pH}$$



- The higher the pH, the less acidic (more basic) is the solution
- The lower the pH, the more acidic (less basic) is the solution

Defining pOH

$$pOH = -\log[OH^-]$$

$$[OH^-] = \text{antilog}[-pOH] = 10^{-pOH}$$

- The lower the pOH, the more basic (less acidic) is the solution
- The higher the pOH, the more acidic (less basic) is the solution
- Relationship between pH and pOH

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$pH + pOH = 14.00$$

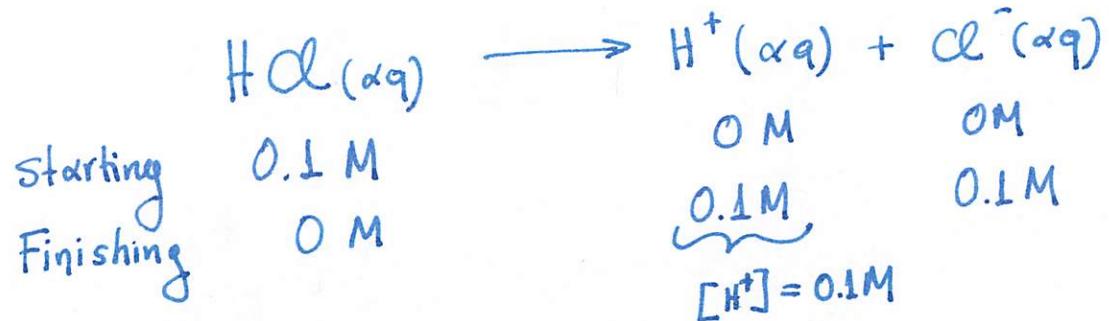
pH of Some Common Materials

TABLE 13.1 pH of Some Common Materials

Lemon juice	2.2–2.4	Urine, human	4.8–8.4
Wine	2.8–3.8	Cow's milk	6.3–6.6
Vinegar	3.0	Saliva, human	6.5–7.5
Tomato juice	4.0	Drinking water	5.5–8.0
Beer	4–5	Blood, human	7.3–7.5
Cheese	4.8–6.4	Seawater	8.3

You have 0.1 M HCl in aqueous solution. What is the pH and POH of the solution?

HCl ionizes completely (strong acid)



$$\text{pH} = -\log 0.1 = 1$$

$$\text{POH} = 14 - \text{pH} = 13$$

$$[\text{OH}^-] = \text{antilog } [-13] = 10^{-13} = \underline{\underline{1 \times 10^{-13} \text{M}}}$$

What is the pOH of an aqueous solution in which $[H^+] = 5.0[OH^-]$?

You know that $K_w = 10^{-14} = [H^+][OH^-]$

Now substitute the $[H^+]$ with that of $5.0[OH^-]$

$$K_w = 10^{-14} = 5.0[OH^-][OH^-] = 5.0 * [OH^-]^2$$

$$\Rightarrow [OH^-] = \sqrt{\frac{10^{-14}}{5.0}} = 4.5 \times 10^{-8} M$$

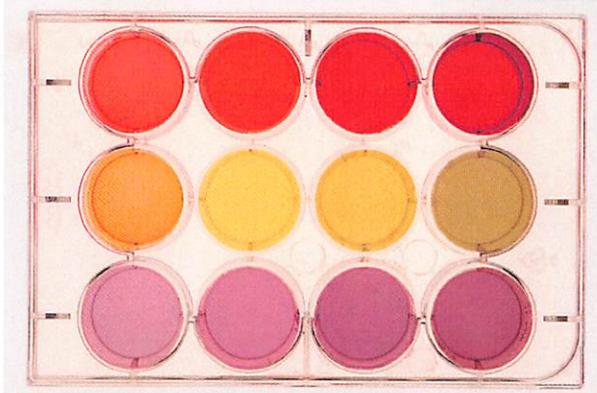
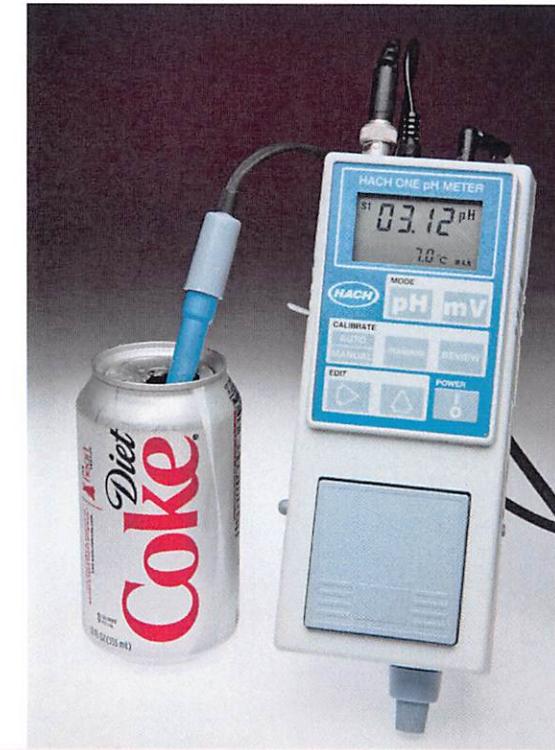
$$\Rightarrow p[OH] = -\log(4.5 \times 10^{-8} M) = 7.3$$

pH of Strong Acids and Strong Bases

- Recall from Chapter 4 that some acids are strong
 - HCl, HBr, HI, HClO_4 , HNO_3 , H_2SO_4
 - These completely ionize in water
 - $[\text{H}^+]$ is equal to the concentration of the strong acid
- Similar there are bases that are strong:
 - LiOH, NaOH, KOH, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$
 - These bases ionize completely to OH^-
 - pOH is equal to the concentration of the strong base
 - For an 0.10 M solution of NaOH,
 - $[\text{Na}^+] = [\text{OH}^-] = 0.10 \text{ M}$
 - $\text{pOH} = 1.00$
 - $\text{pH} = 13.00$

Measuring pH

- pH can be measured with a pH meter
 - Translates $[H^+]$ into an electrical signal
 - Signal is shown on an analog or digital meter calibrated in pH units
- By universal indicator
 - Mixture of substances that change color depending on the concentration of H^+
 - Less accurate than pH meter
 - Depending on the indicator used, can display pH over a narrow or wide range of $[H^+]$
- Some plants can act as pH indicators
 - Color of some flowers in plants is dependent on the pH of the soil in which the plant is grown

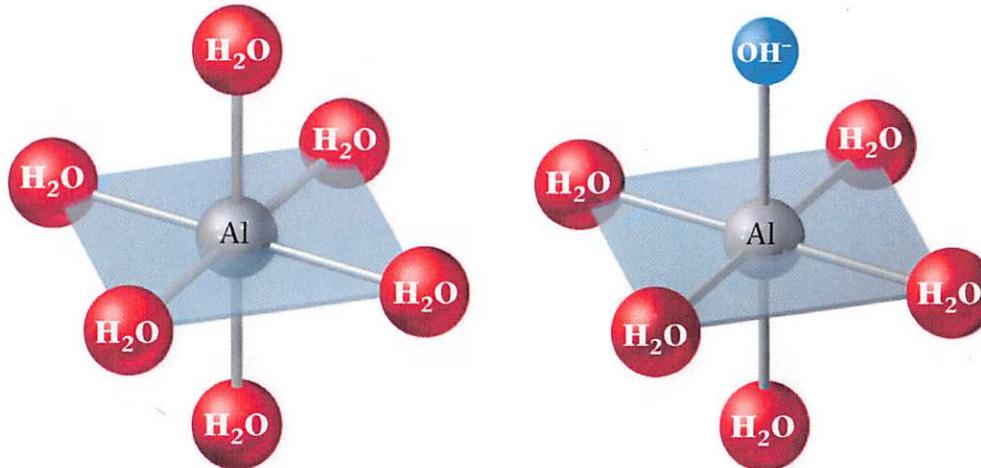
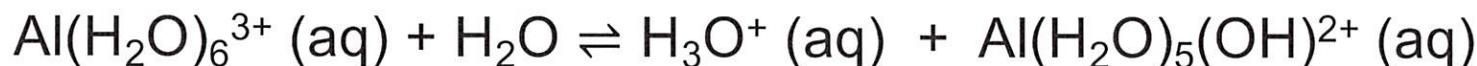


Weak Acids and their Equilibrium Constants

- Weak acids ionize only partially
- Prototype reaction
 - $\text{HB} \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{B}^- \text{ (aq)}$
- Two types of species that behave as weak acids
 1. Molecules with an ionizable hydrogen atom
 - $\text{HNO}_2 \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{NO}_2^- \text{ (aq)}$
 2. Cations
 - $\text{NH}_4^+ \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ \text{ (aq)} + \text{NH}_3 \text{ (aq)}$

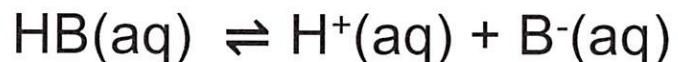
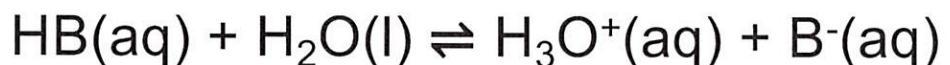
Metal Cations as Acids

- Many metal cations act as weak acids in water solutions



- The bond that forms between the oxygen and the metal ion weakens the O-H bond
- H⁺ is more easily ionized as a result of the weakened bond

Equilibrium Constants for Weak Acids



- K_a is the acid equilibrium constant

$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$$

- K_a values are related to acid strength
 - The smaller K_a is, the weaker the acid is
- $\text{p}K_a = -\log K_a$
- The smaller $\text{p}K_a$ is, the stronger the acid
- $\text{p}K_a$ follows the trend for pH

TABLE 13.2 Equilibrium Constants for Weak Acids and Their Conjugate Bases

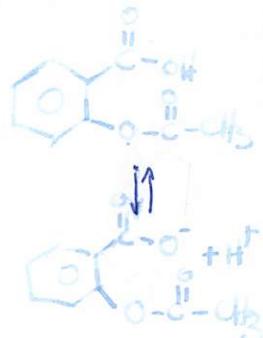
	Acid	K_a	Base	K_b
Sulfurous acid	H_2SO_3	1.7×10^{-2}	HSO_3^-	5.9×10^{-13}
Hydrogen sulfate ion	HSO_4^-	1.0×10^{-2}	SO_4^{2-}	1.0×10^{-12}
Phosphoric acid	H_3PO_4	7.1×10^{-3}	H_2PO_4^-	1.4×10^{-12}
Hexaaquairon(III) ion	$\text{Fe}(\text{H}_2\text{O})_6^{3+}$	6.7×10^{-3}	$\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$	1.5×10^{-12}
Hydrofluoric acid	HF	6.9×10^{-4}	F^-	1.4×10^{-11}
Nitrous acid	HNO_2	6.0×10^{-4}	NO_2^-	1.7×10^{-11}
Formic acid	HCHO_2	1.9×10^{-4}	CHO_2^-	5.3×10^{-11}
Lactic acid	$\text{HC}_3\text{H}_5\text{O}_3$	1.4×10^{-4}	$\text{C}_3\text{H}_5\text{O}_3^-$	7.1×10^{-11}
Benzoic acid	$\text{HC}_7\text{H}_5\text{O}_2$	6.6×10^{-5}	$\text{C}_7\text{H}_5\text{O}_2^-$	1.5×10^{-10}
Acetic acid	$\text{HC}_2\text{H}_3\text{O}_2$	1.8×10^{-5}	$\text{C}_2\text{H}_3\text{O}_2^-$	5.6×10^{-10}
Hexaaquaaluminum(III) ion	$\text{Al}(\text{H}_2\text{O})_6^{3+}$	1.2×10^{-5}	$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{2+}$	8.3×10^{-10}
Carbonic acid	H_2CO_3	4.4×10^{-7}	HCO_3^-	2.3×10^{-8}
Dihydrogen phosphate ion	H_2PO_4^-	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
Hydrogen sulfite ion	HSO_3^-	6.0×10^{-8}	SO_3^{2-}	1.7×10^{-7}
Hypochlorous acid	HClO	2.8×10^{-8}	ClO^-	3.6×10^{-7}
Hydrocyanic acid	HCN	5.8×10^{-10}	CN^-	1.7×10^{-5}
Ammonium ion	NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
Tetraaquazinc(II) ion	$\text{Zn}(\text{H}_2\text{O})_4^{2+}$	3.3×10^{-10}	$\text{Zn}(\text{H}_2\text{O})_3\text{OH}^+$	3.0×10^{-5}
Hydrogen carbonate ion	HCO_3^-	4.7×10^{-11}	CO_3^{2-}	2.1×10^{-4}
Hydrogen phosphate ion	HPO_4^{2-}	4.5×10^{-13}	PO_4^{3-}	2.2×10^{-2}

$$\text{HB(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{B}^-(\text{aq}) \quad K_a = \frac{[\text{H}^+] \times [\text{B}^-]}{[\text{HB}]}$$

$$\text{B}^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HB(aq)} + \text{OH}^-(\text{aq}) \quad K_b = \frac{[\text{HB}] \times [\text{OH}^-]}{[\text{B}^-]}$$

1.26 g of aspirin ($\text{HC}_9\text{H}_7\text{O}_4$), a weak organic acid, is dissolved in 350.0 ml of aqueous solution. The pH of this solution is found to be 2.60. Calculate its K_a .

$$\text{MW}_{\text{HC}_9\text{H}_7\text{O}_4} = 180.15 \text{ g/mol}$$



Calculate the initial molarity of the solution of aspirin

$$\frac{1.26 \text{ g}}{180.15 \text{ g/mol}} = 0.0200 \text{ M}$$

$$\frac{}{0.3500 \text{ L}}$$

We then write the equilibrium

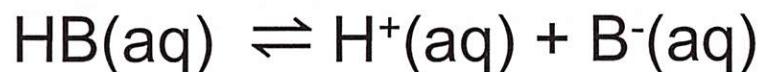
	$\text{HC}_9\text{H}_7\text{O}_4$	\rightleftharpoons	$\text{C}_9\text{H}_7\text{O}_4^-$	$+ \text{H}^+$
Starting	0.0200 M		0 M	x M
at equilibrium	0.0200 - x		x M	x M

Since we know that the pH of the solution is 2.60, then $[\text{H}^+] = x = 10^{-2.60} = 2.51 \times 10^{-3} \text{ M}$

$$\text{Then } K_a = \frac{[\text{C}_9\text{H}_7\text{O}_4^-] \cdot [\text{H}^+]}{[\text{HC}_9\text{H}_7\text{O}_4]} = \frac{x^2}{0.0200 - x} = \frac{(2.51 \times 10^{-3})^2}{(0.0200 - 2.51 \times 10^{-3})} = 3.60 \times 10^{-4}$$

Percent Ionization

The percent ionization of a weak acid is defined as:



$$\% \text{ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HB}]_{\text{initial}}} \times 100\%$$

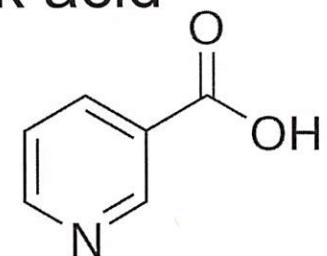
What is the percent ionization of the previous exercise involving aspirin?

$$\left. \begin{array}{l} [\text{HC}_9\text{H}_7\text{O}_4]_{\text{initial or } o} = 0.0200 \text{ M} \\ [\text{H}^+]_{\text{eq}} = [\text{C}_9\text{H}_7\text{O}_4^-]_{\text{eq}} = 2.51 \times 10^{-3} \text{ M} \end{array} \right\} \quad \% \text{ionization} = \frac{2.51 \times 10^{-3} \text{ M}}{0.0200 \text{ M}} \times 100\% = 12.6\%$$

Note that the percent ionization depends on the ^{starting}~~150~~ molarity of the weak acid

Calculating $[H^+]$ in an aqueous solution of a weak acid

This calculation is similar to the equilibrium pressure for the gaseous reactions we examined in Chapter 12



Determine the pH of 3.0 g of nicotinic acid ($HC_6H_4O_2N$, HNic, MW=123.11 g/mol) dissolved in 245 mL of solution. ($K_a = 1.4 \times 10^{-5}$)

Calculate the starting molarity of HNic: $\frac{3.0 \text{ g} / 123.11 \text{ g/mol}}{0.245 \text{ L}} = 0.10 \text{ M} = [HNic]_0$

Write the ionization reaction



Write the ionization table

Starting [] ₀	0.10	O	O
$\Delta []$	-X	X	X
equilib. [] _{eq}	0.10-X	X	X

$$K_a = 1.4 \times 10^{-5} = \frac{[H^+]_{eq} [Nic^-]_{eq}}{[HNic]_{eq}} = \frac{X^2}{0.10-X} = 1.4 \times 10^{-5}$$

This is a polynomial equation that can be solved in two fashions

Approximate solution: Assume $X \ll 0.10$ and simplify $\frac{X^2}{0.1} = 1.4 \times 10^{-5} \Rightarrow X = \sqrt{1.4 \times 10^{-6}} = 1.2 \times 10^{-3}$

Exact solution: $X^2 = (0.10-X) \cdot 1.4 \times 10^{-5} \Rightarrow X^2 + 1.4 \times 10^{-5}X - 1.4 \times 10^{-6} = 0$ $X = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$X_1 = \frac{-1.4 \times 10^{-5} + \sqrt{(1.4 \times 10^{-5})^2 + 4 \cdot 1.4 \times 10^{-6}}}{2} = 0.001176 = 1.2 \times 10^{-3}$$

$$X_2 = \frac{-1.4 \times 10^{-5} - \sqrt{(1.4 \times 10^{-5})^2 + 4 \cdot 1.4 \times 10^{-6}}}{2} = -0.00119 \text{ (invalid)}$$

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The pH of the solution is $-\log(1.2 \times 10^{-3}) = 2.9$

Approximations Used in Calculations (I)

- The value of K_a is usually known no more accurately than about $\pm 5\%$.

$$K_a = \frac{x^2}{a - x}$$

$$\frac{x}{a} \leq 0.05 \times 100 = 5\%$$

$$a - x \approx a$$

- If the percent ionization is less than 5% then this assumption is valid since it does not introduce error greater than 5%.

- In the previous exercise, for $K_a = 1.4 \times 10^{-5}$ and $[HB]_0 = 0.10 \text{ M}$, the percent ionization was:

From the previous exercise we know that $[H^+] = 1.2 \times 10^{-3} \text{ M}$

$$\% \text{ ionization} = \frac{[H^+]}{[HB]_0} \times 100 = \frac{1.2 \times 10^{-3}}{0.10} \times 100 = 1.2\% < 5\%$$

So the % ionization = 1.2% is lesser than 5%

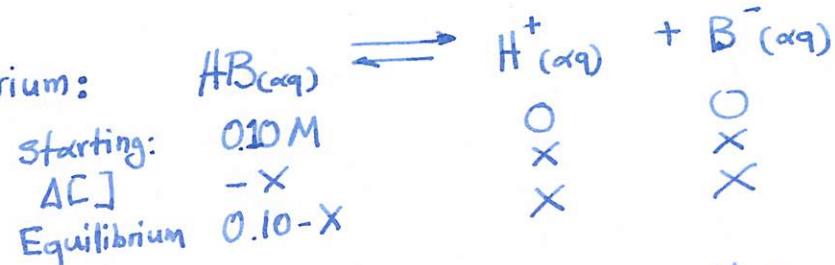
which makes the $0.1 - x = 0.1 - [H^+] \approx 0.1$ assumption

VALID

Approximations Used in Calculations (II)

If however, in the previous exercise, for K_a was not 1.4×10^{-5} but rather $K_a = 6.0 \times 10^{-4}$ and $[HB]_0 = 0.10\text{M}$, would that $(0.10-x) = (0.10-[H^+]) \approx 0.10$ assumption valid?

Lets write again the equilibrium:



$$K_a = 6.0 \times 10^{-4} = \frac{x^2}{0.10-x}$$

If you assume $0.10-x \approx 0.10$ then

$$x = [H^+] = \sqrt{6.0 \times 10^{-4} \times 0.10} = 7.7 \times 10^{-3}$$

Let's check if this assumption is correct: % ionization = $\frac{[H^+]_{\text{approx}}}{[HB]_0} \times 100 = \frac{7.7 \times 10^{-3}}{0.10} \times 100 = 7.7\% > 5\%$
This is not a valid assumption!!!

This means that we have to solve this equation exact:

$$K_a = 6.0 \times 10^{-4} = \frac{x^2}{0.10-x} \Rightarrow x^2 + 6.0 \times 10^{-4} \cdot x - 0.10 \cdot 6.0 \times 10^{-4} = 0$$

$$\Rightarrow \frac{ax^2 + bx + c}{c} = 0 \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

solutions: $x_1 = 0.0074\text{M}$ (accepted)
 $x_2 = -0.0080\text{M}$ (Not valid)

The right solution $7.4 \times 10^{-3}\text{M}$
 is substantially different than the
 approximated $7.7 \times 10^{-3}\text{M}$ solution!

Polyprotic Weak Acids (I)

- Acids containing more than one ionizable hydrogen are called **polyprotic**



- The anion formed in one step produces another H^+ in a successive ionization step
- The equilibrium constant becomes smaller with each successive step ($K_{a1} > K_{a2} > K_{a3}$)
- With each successive step, ***the acid becomes progressively weaker***

Polyprotic Weak Acids (II)

TABLE 13.3 Equilibrium Constants for Some Weak Polyprotic Acids at 25°C

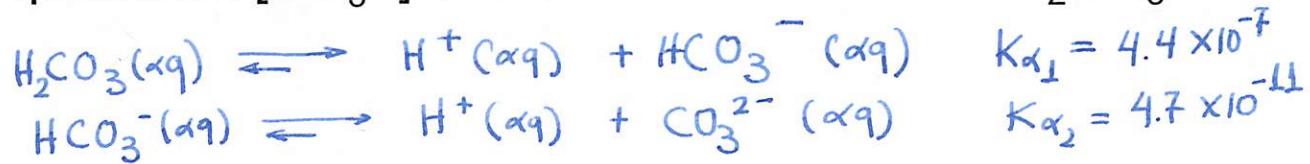
Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid*	H_2CO_3	4.4×10^{-7}	4.7×10^{-11}	
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	5.9×10^{-2}	5.2×10^{-5}	
Phosphoric acid	H_3PO_4	7.1×10^{-3}	6.2×10^{-8}	4.5×10^{-13}
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.0×10^{-8}	

*Carbonic acid is a water solution of carbon dioxide:

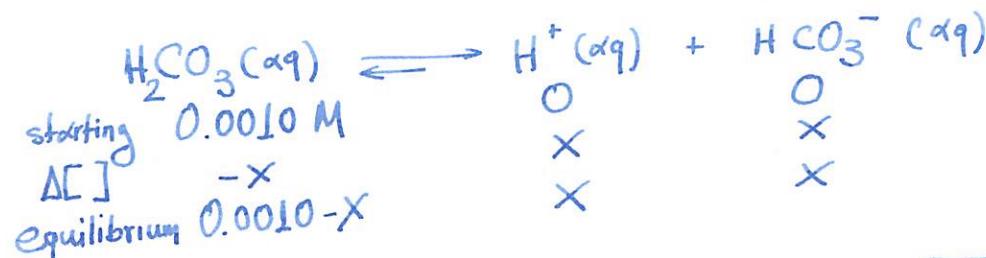


Calculate the pH and equilibrium $[CO_3^{2-}]$ of a 0.0010M solution of H_2CO_3

Lets write the two equilibria:



Clearly the first equilibrium will dominate the pH. Since it is 10^4 times larger!!!

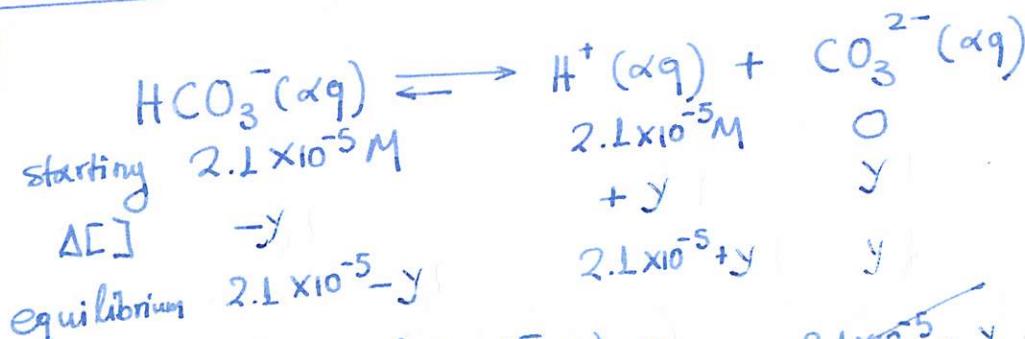


$$K_{\alpha_1} = 4.4 \times 10^{-7} = \frac{x^2}{0.0010 - x} \approx \frac{x^2}{0.0010} \rightarrow x = [H^+] = \sqrt{4.4 \times 10^{-7} \times 0.0010} = 2.1 \times 10^{-5}\text{ M}$$

Always check if assumption is correct: % ionization = $\frac{[H^+]}{[H_2CO_3]_0} \times 100\% = \frac{2.1 \times 10^{-5}}{0.0010} \times 100\% = 2.1\%$ VALID ASSUMPTION less than 5%

$$\boxed{pH = -\log(2.1 \times 10^{-5}\text{ M}) = 4.7}$$

The $[CO_3^{2-}]$ will be controlled by the second equilibrium



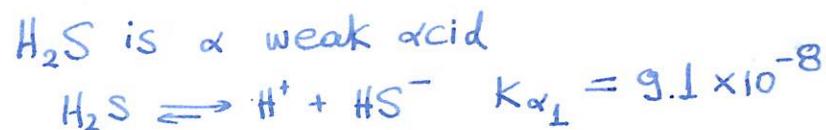
$$K_{\alpha_2} = 4.7 \times 10^{-11} = \frac{[H^+] \cdot [CO_3^{2-}]}{[HCO_3^-]} = \frac{(2.1 \times 10^{-5} + y) \cdot y}{(2.1 \times 10^{-5} - y)} \approx \frac{2.1 \times 10^{-5} \cdot y}{2.1 \times 10^{-5}} \Rightarrow y = 4.7 \times 10^{-11} = [CO_3^{2-}]$$

Check assumption: $\frac{y}{2.1 \times 10^{-5}} \times 100\% = 0.00022\% \quad \underline{\text{Assumption is valid!!!}}$

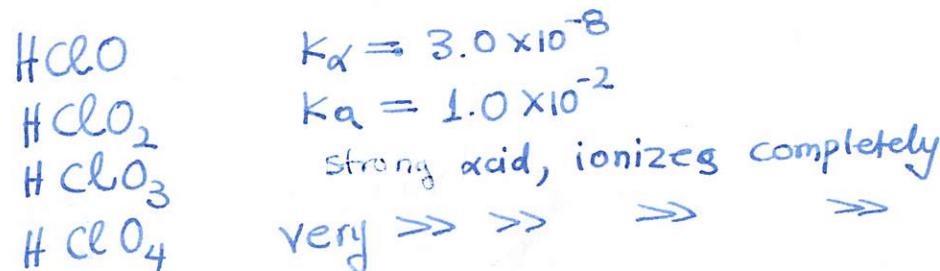
Estimating Acid strength

- If the H⁺ is with a single atom then it depends on the electronegativity (except HF)

HCl, HBr, HJ
are strong acids
ionize completely



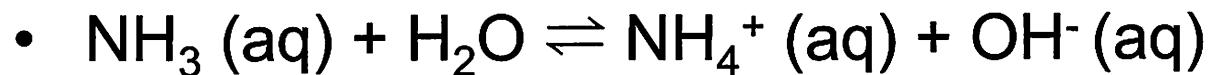
- If it's an oxy-anion, the more oxygen atoms attached the stronger the acid.



Weak Bases and their Equilibrium Expressions

- Types of weak bases
 - Molecules
 - Ammonia, NH_3 , and amines
 - $\text{NH}_3 \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ \text{ (aq)} + \text{OH}^- \text{ (aq)}$
 - Anions
 - Anions derived from weak acids are weak bases
 - $\text{I}^- \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{HI} \text{ (aq)} + \text{OH}^- \text{ (aq)}$
 - $\text{CH}_3\text{COO}^- \text{ (aq)} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} \text{ (aq)} + \text{OH}^- \text{ (aq)}$

Weak Base Equilibrium Constant



The **base equilibrium constant**, K_b is

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- For a generic weak base where

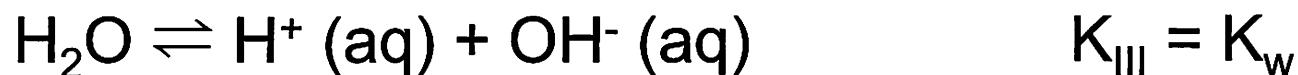
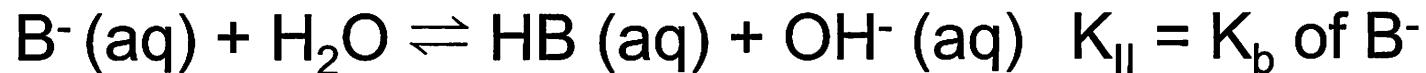


$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$$

- As K_b becomes larger, base strength increases
- Similar with acids and K_a , we can define a $\text{p}K_b = -\log K_b$
- As $\text{p}K_b$ becomes smaller, base strength increases

Relation between K_a and K_b

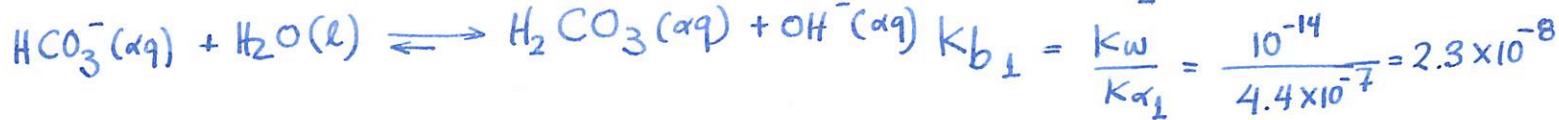
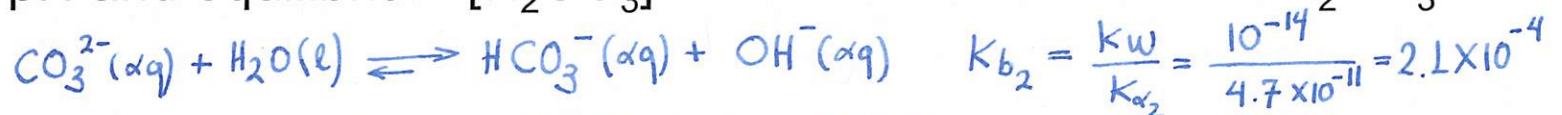
- Consider the relation between a conjugate acid-base pair



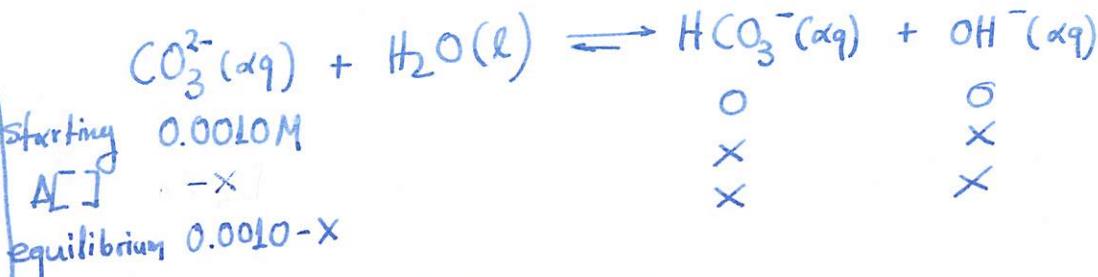
- Since $K_I \cdot K_{II} = K_{III}$, $K_a \cdot K_b = K_w = 1.0 \times 10^{-14}$
 - This is true only for a conjugate acid base pair
 - In log form, $pK_a + pK_b = pK_w = 14.00$

Calculate the pH and equilibrium $[H_2CO_3]$ of a 0.0010M solution of Na_2CO_3

Lets write the
two equations:



Clearly the first
equilibrium will
dominate the pH
Since it is 10^4 times
larger!!!



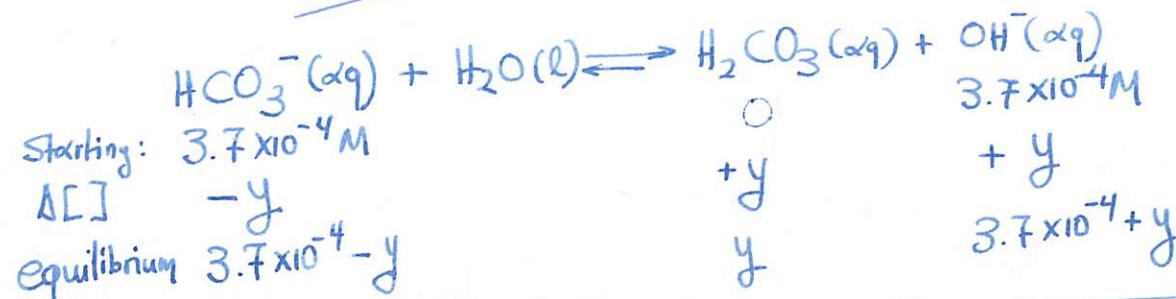
$$K_{b2} = 2.1 \times 10^{-4} = \frac{[HCO_3^-] \cdot [OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.0010-x} \approx \frac{x^2}{0.0010} \Rightarrow x = [OH^-] = \sqrt{2.1 \times 10^{-4} \times 0.0010} = 4.6 \times 10^{-4} M$$

$$\text{Check validity of assumption: \% ionization} = \frac{[OH^-]}{[CO_3^{2-}]_0} \times 100\% = \frac{x}{0.0010} \times 100\% = \frac{4.6 \times 10^{-4}}{0.0010} = 46\% \gg 5\%$$

Solve this analytically $x_1 = 3.7 \times 10^{-4} M = [OH^-] \Rightarrow pOH = 3.4 \Rightarrow pH = 14 - 3.4 = 10.6$

$$x_2 = -5.8 \times 10^{-4} M$$

The $[H_2CO_3]$ is
controlled by
the second equi-
librium:



$$K_{b1} = 2.3 \times 10^{-8} = \frac{[H_2CO_3] \cdot [OH^-]}{[HCO_3^-]} = \frac{y \cdot (3.7 \times 10^{-4} + y)}{(3.7 \times 10^{-4} - y)} \approx \frac{y \cdot (3.7 \times 10^{-4})}{3.7 \times 10^{-4}} = y = [H_2CO_3] = 2.3 \times 10^{-8}$$

$$\text{Check validity \% ioniz} = \frac{y \times 100}{3.7 \times 10^{-4}} = \frac{2.3 \times 10^{-8}}{3.7 \times 10^{-4}} = 0.0062\% \underline{\text{VALID}}$$

Extra space if needed for the previous exercise

TABLE 13.4 Relative Strengths of Brønsted-Lowry Acids and Bases

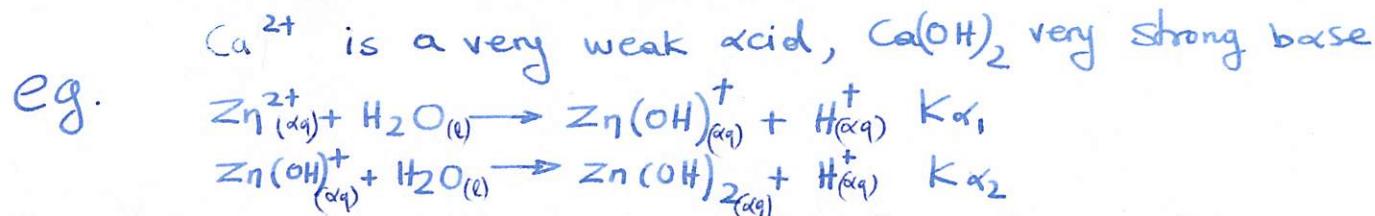
K_a	Conjugate Acid	Conjugate Base	K_b
Very large	HClO_4	ClO_4^-	Very small
Very large	HCl	Cl^-	Very small
Very large	HNO_3	NO_3^-	Very small
H_3O^+		H_2O	
6.9×10^{-4}	HF	F^-	1.4×10^{-11}
1.8×10^{-5}	$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$	5.6×10^{-10}
1.2×10^{-5}	$\text{Al}(\text{H}_2\text{O})_6^{3+}$	$\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{2+}$	8.3×10^{-10}
4.4×10^{-7}	H_2CO_3	HCO_3^-	2.3×10^{-8}
2.8×10^{-8}	HClO	ClO^-	3.6×10^{-7}
5.6×10^{-10}	NH_4^+	NH_3	1.8×10^{-5}
4.7×10^{-11}	HCO_3^-	CO_3^{2-}	2.1×10^{-4}
H_2O		OH^-	
Very small	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{O}^-$	Very large
Very small	OH^-	O^{2-}	Very large
Very small	H_2	H^-	Very large

Acid-Base Properties of Solutions of Salts (I)

We can predict whether a salt will be acidic, basic or neutral by

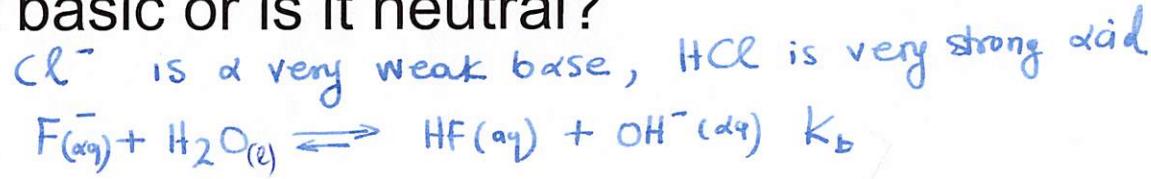
1. Deciding what effect the cation has on water

- Is it acidic or is it neutral?



2. Deciding what effect the anion has on water

- Is it basic or is it neutral?



3. Combining the two effects to decide the behavior of the salt in water

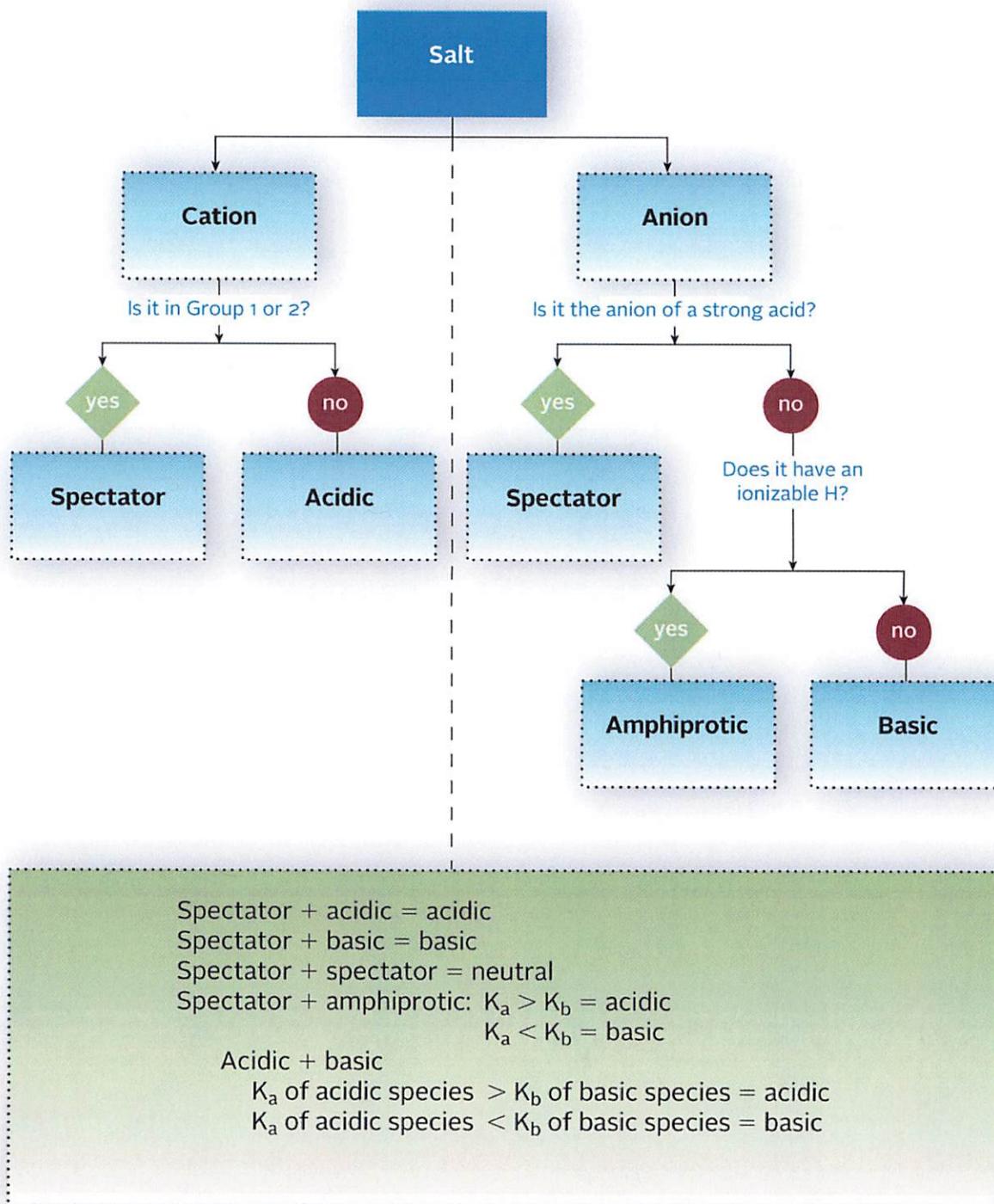
Compare the K_a and K_b

Acid-Base Properties of Solutions of Salts (II)

TABLE 13.5 Acid-Base Properties of Ions* in Water Solution

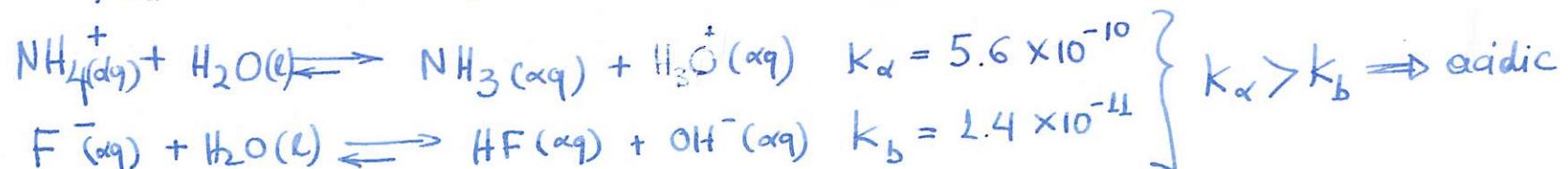
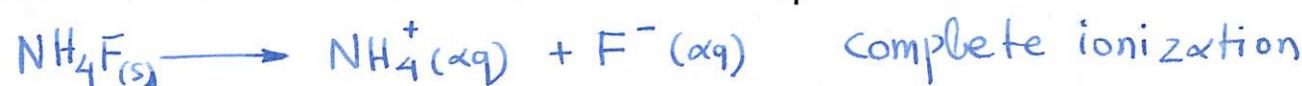
	Spectator		Basic		Acidic
Anion	Cl ⁻	NO ₃ ⁻	C ₂ H ₃ O ₂ ⁻	CO ₃ ²⁻	
Cation	Br ⁻	ClO ₄ ⁻	F ⁻	PO ₄ ³⁻	
	I ⁻		Many others		
	Li ⁺	Ca ²⁺			NH ₄ ⁺
	Na ⁺	Sr ²⁺			Mg ²⁺
	K ⁺	Ba ²⁺			Transition metal ions

*For the acid-base properties of amphiprotic anions such as HCO₃⁻ or H₂PO₄⁻, see the discussion at the end of this section.

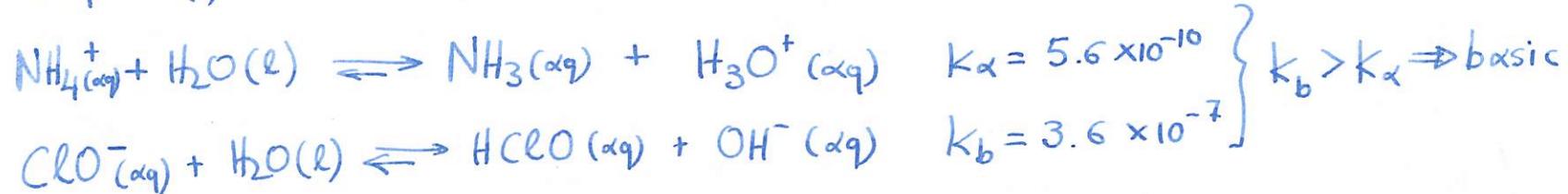


Salts: Acidic, Basic or Neutral

- By comparing the K_a of an acidic cation with the K_b of a basic anion, the salt of both can be classified as acidic, basic or neutral
- Lets examine the case of NH_4F



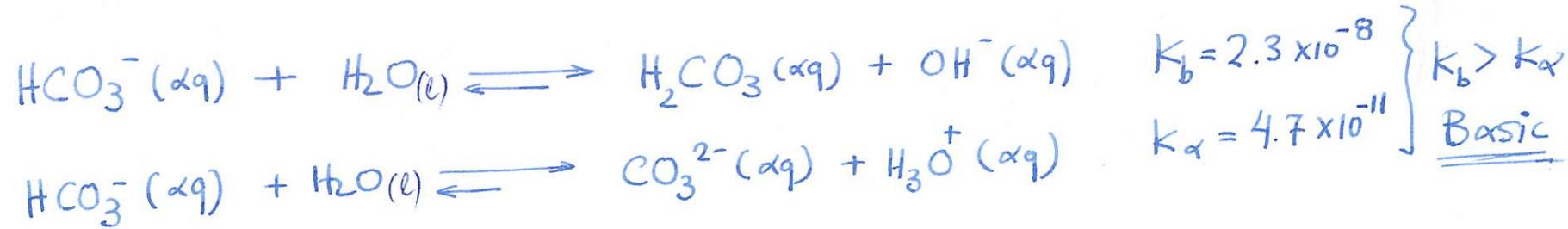
- Lets examine the case of NH_4ClO



Salts with Amphiprotic Anions

Lets examine the case of NaHCO_3

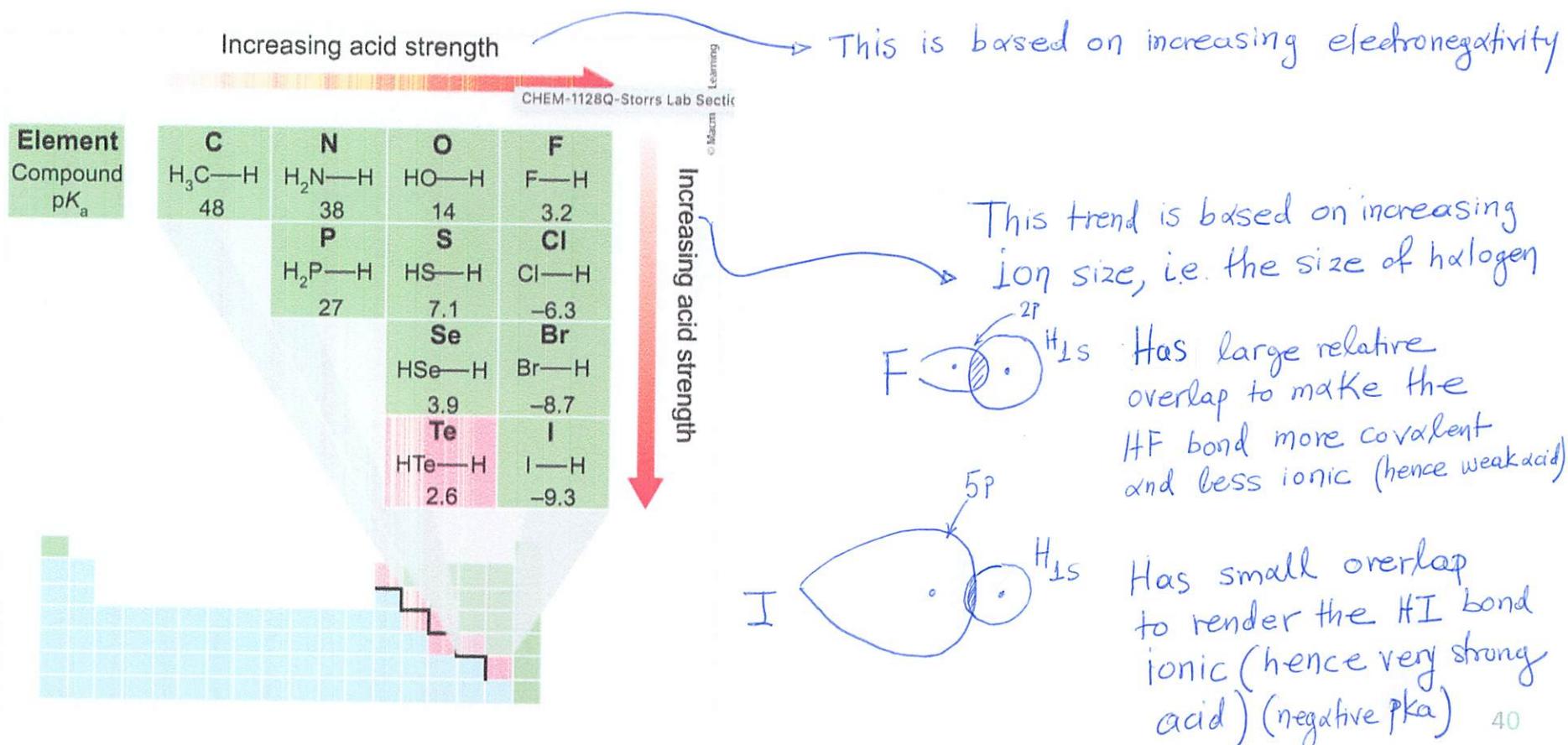
(spectator ion)



Relating Acid Strength to Structure



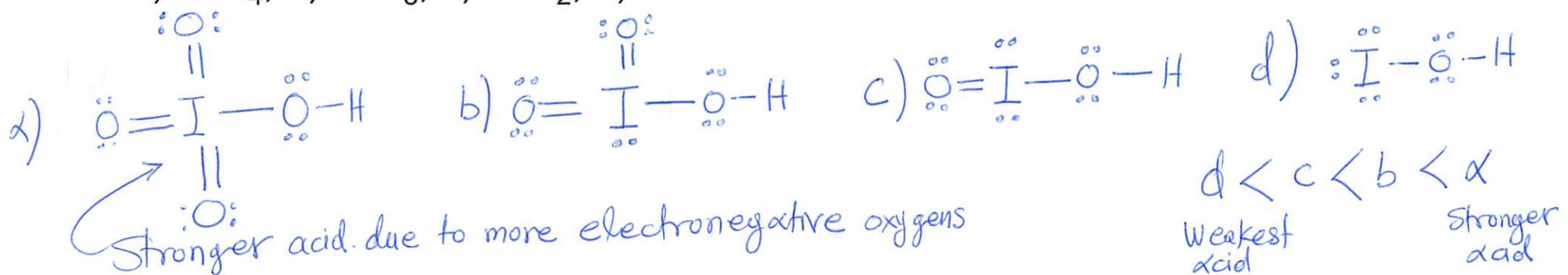
- The strength of the H-B bond, is inversely proportional on the acidity (or acid strength) of the given acid
- For similar structure acids the: **anion size & electronegativity** matters



Typical Problems with ranking acid strength

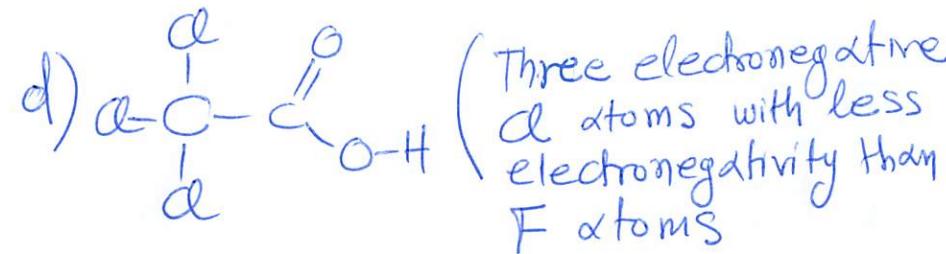
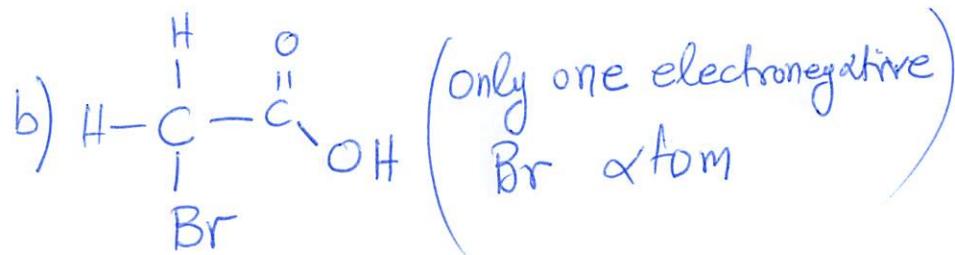
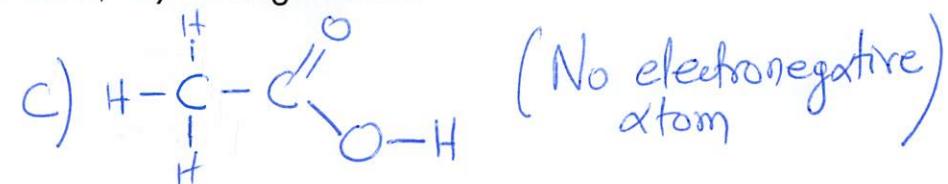
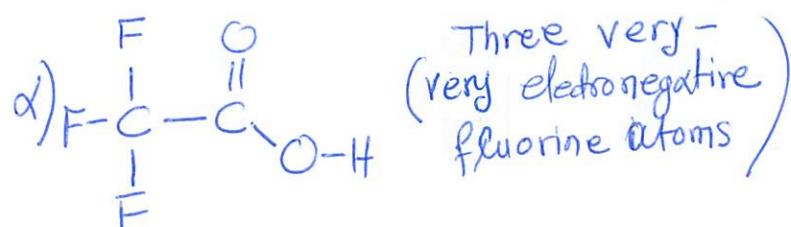
1. Rank the following acids from weakest to strongest:

- a) HIO₄, b) HIO₃, c) HIO₂, d) HIO



2. Rank the following acetic-based acids from weakest to strongest:

- a) CF₃COOH, b) CH₂BrCOOH, c) CH₃COOH, d) CCl₃COOH



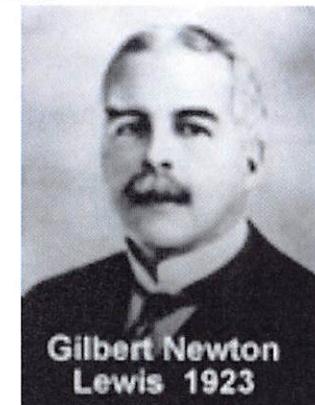
Ranking: $c < b < d < a$

Annotations:
Weakest
Strongest

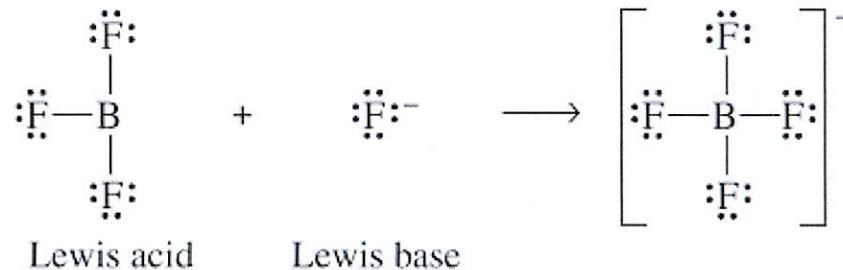
Extending the Concept of Acids and Bases

The Lewis Model

- A Lewis base donates a pair of electrons



Gilbert Newton
Lewis 1923



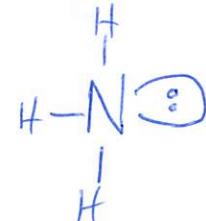
- A Lewis acid accepts a pair of electrons

TABLE 13.6 Alternative Definitions of Acids and Bases

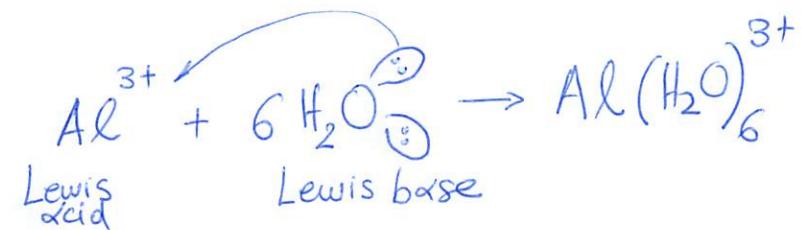
Model	Acid	Base
Arrhenius	Supplies H ⁺ to water	Supplies OH ⁻ to water
Brønsted-Lowry	H ⁺ donor	H ⁺ acceptor
Lewis	Electron pair acceptor	Electron pair donor

Typical Lewis Acids & Bases

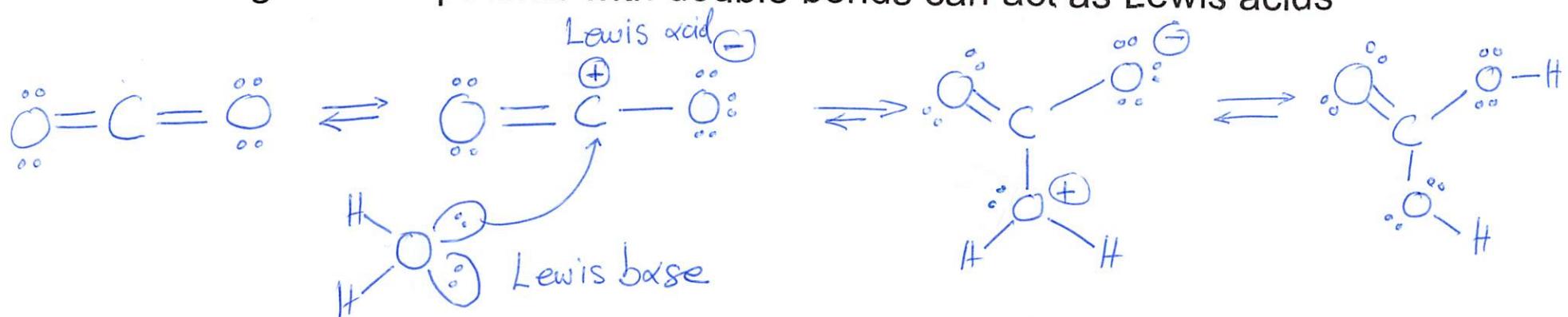
- Ammonia is a classical Lewis base



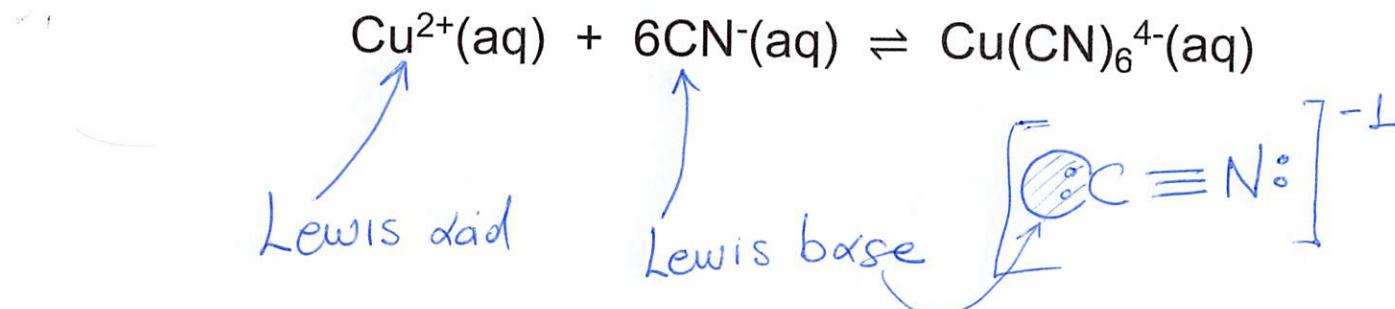
- Metal cations, like Al^{3+} , act Lewis acids



- Organic compounds with double bonds can act as Lewis acids



Problem: Identify the Lewis acid and Lewis base in the following reaction:



Chapter 16 in review

1. Classify a substance as a Brønsted-Lowry acid or base
2. Given $[H^+]$, $[OH^-]$, pH and pOH can be calculated based on $K_w = 10^{-14}$
3. Given the pH and the original concentration of a weak acid or a weak base, K_a or K_b can be calculated, respectively
4. Given K_a for a weak acid, the K_b of its conjugate base (or vice-versa) can be calculated based on $K_w = 10^{-14} = K_a \cdot K_b$
5. The pH of an aqueous solution of a dissolved salt can be predicted if it will be acidic, basic or neutral
6. Discussed the similarities and differences between Lewis and Brønsted-Lowry acids and bases