

Chapter 16

ACIDS AND BASES

(Part II)

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Conjugate Acid-Base Pairs

- Dissociation of a **strong** acid.

$$\text{HCl} (aq) \longrightarrow \text{H}^+(aq) + \text{Cl}^-(aq)$$

Strong acid
Conjugate base

Is Cl^- ion a strong or a weak base?

$$\text{Cl}^-(aq) + \text{H}_2\text{O} \not\rightarrow \text{HCl} (aq) + \text{OH}^-(aq)$$

➤ The Cl^- ion is a weak (conjugate) base.
- Dissociation of a **weak** acid.

$$\text{HF} (aq) \rightleftharpoons \text{H}^+(aq) + \text{F}^-(aq)$$

Weak acid
Conjugate base

$$\text{F}^-(aq) + \text{H}_2\text{O} \rightleftharpoons \text{HF} (aq) + \text{OH}^-(aq)$$

➤ The F^- ion is a strong (conjugate) base.

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Conjugate Acid-Base Pairs

- The conjugate base of a **strong acid**, is an example of a **weak conjugate base**. While the conjugate base of a **weak acid**, is an example of a **strong conjugate base**.
- Conversely, a **strong base** has a **weak conjugate acid** and a **weak base** has a **strong conjugate acid**.

| Acid | Example | Conjugate base | Formula | Base | Example | Conjugate acid | Formula |
|--------|------------------|------------------|------------------------------|--------|-----------------|------------------|------------------------------|
| strong | HNO ₃ | weak conjugate | NO ₃ ⁻ | strong | OH ⁻ | weak conjugate | H ₂ O |
| weak | HCN | strong conjugate | CN ⁻ | weak | NH ₃ | strong conjugate | NH ₄ ⁺ |

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Conjugate Acid-Base Pairs

- The conjugate base of a **strong acid**, is an example of a **weak conjugate base**. While the conjugate base of a **weak acid**, is an example of a **strong conjugate base**.
- Conversely, a **strong base** has a **weak conjugate acid** and a **weak base** has a **strong conjugate acid**.

When we say strong conjugate acids / bases, we do not mean the same thing for strong acids / bases. In fact, strong conjugate acids / bases are weak ones! But they are stronger than water when they react with it.

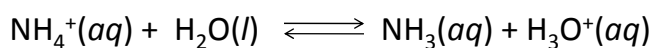
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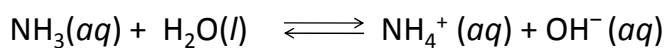
Conjugate Acid-Base Pairs

- A **strong conjugate acid** acts as a weak Brønsted acid, and it *donates* H^+ to water.



$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- A **strong conjugate base** acts as a weak Brønsted base, and it *accepts* H^+ from water.



$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

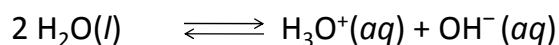
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Conjugate Acid-Base Pairs

- Adding equations 1 and 2 gives:



When two reactions at equilibria are added, the equilibrium constant of the overall reaction is the product of the equilibrium constants of each reaction.

Thus, for any conjugate acid-base pair:

$$K = K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} \quad K = [H_3O^+][OH^-] = K_w$$

$$K_a \times K_b = K_w$$

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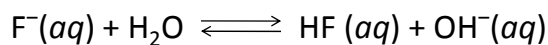
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Conjugate Acid-Base Pairs

TABLE 16.6 Ionization Constants of Some Weak Acids at 25°C

| Name of Acid | Formula | Structure | K_a |
|-------------------|------------------|-----------|----------------------|
| Hydrofluoric acid | HF | H—F | 7.1×10^{-4} |
| Nitrous acid | HNO ₂ | O=N—O—H | 4.5×10^{-4} |



Can you find K_b for fluoride ions at 25°C?

$$K_w = K_a \times K_b$$

$$K_b = K_w / K_a = 1 \times 10^{-14} / 7.1 \times 10^{-4} = 1.4 \times 10^{-11}$$

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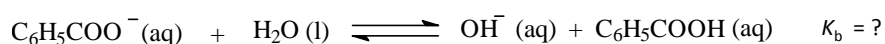
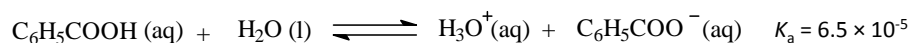
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Conjugate Acid-Base Pairs

▪ **Exercise:**

The benzoate ion is the conjugate base of benzoic acid (C₆H₅COOH). The K_a for benzoic acid is 6.5×10^{-5} at 25°C. Determine K_b of the benzoate ion at 25°C.



$$K_b = \frac{K_w}{K_a}$$

$$K_b = \frac{1.0 \times 10^{-14}}{6.5 \times 10^{-5}} = 1.5 \times 10^{-10}$$

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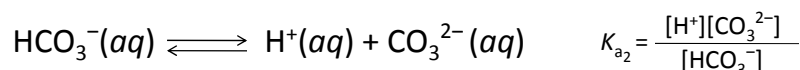
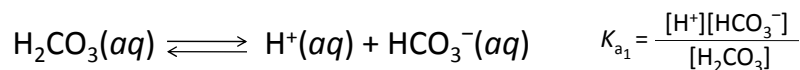
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Diprotic and Polyprotic Acids

- **Diprotic** and **polyprotic** acids undergo successive ionizations, losing one proton at a time.

Each ionization has a K_a associated with it.



- The conjugate base in the first ionization is the acid in the second ionization.
- For a given diprotic or polyprotic acid:

$$K_{a1} > K_{a2} > K_{a3}$$

It is easier to remove a proton from a neutral species than from a negatively charged species.

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Diprotic and Polyprotic Acids

TABLE 16.8 Ionization Constants for Some Diprotic and Polyprotic Acids at 25°C

| Name of Acid | Formula | Structure | K_{a1} | K_{a2} | K_{a3} |
|---------------------------|--|-----------|----------------------|-----------------------|-----------------------|
| Sulfuric acid | H_2SO_4 | | Very large | 1.3×10^{-2} | |
| Oxalic acid | $\text{H}_2\text{C}_2\text{O}_4$ | | 6.5×10^{-2} | 6.1×10^{-5} | |
| Sulfurous acid | H_2SO_3 | | 1.3×10^{-2} | 6.3×10^{-8} | |
| Ascorbic acid (vitamin C) | $\text{H}_2\text{C}_6\text{H}_6\text{O}_6$ | | 8.0×10^{-5} | 1.6×10^{-12} | |
| Carbonic acid | H_2CO_3 | | 4.2×10^{-7} | 4.8×10^{-11} | |
| Hydrosulfuric acid* | H_2S | | 9.5×10^{-8} | 1×10^{-19} | |
| Phosphoric acid | H_3PO_4 | | 7.5×10^{-3} | 6.2×10^{-8} | 4.2×10^{-13} |

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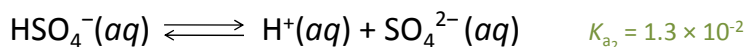
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Calculations Involving K_{a1} and K_{a2}

Strong acids

Exercise:

Calculate the pH for 1.0 M and 0.10 M solutions of sulfuric acid. K_{a2} for sulfuric acid is 1.3×10^{-2} .



For the first dissociation, $[\text{H}^+] = [\text{HSO}_4^-] = 1.0 \text{ M}$

For the second dissociation,

| (M) | HSO_4^- | H^+ | SO_4^{2-} |
|-------------------|------------------|--------------|--------------------|
| Initial conc. | 1.0 | 1.0 | 0 |
| Change in conc. | -x | +x | +x |
| Equilibrium conc. | 1.0 - x | 1.0 + x | x |

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$$K_{a2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = 1.3 \times 10^{-2} = \frac{(1.0 + x)(x)}{1.0 - x} \approx \frac{(1.0)x}{1.0}$$

We applied approximation here

$$x = 1.3 \times 10^{-2} \text{ M} \quad (\text{Is approximation here valid?})$$

$$[\text{H}^+] = 1.0 + 0.013 = 1.013 \text{ M}$$

$$= 1.0 \text{ M} \quad (\text{to the correct no. of sig. fig.})$$

$$\text{pH} = 0.00$$

Notice that the dissociation of HSO_4^- doesn't contribute significantly to the concentration of H^+ ions. The source of protons in the 1.0 M solution of H_2SO_4 is mainly the first dissociation step.

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- What is about the 0.10 M solution of H₂SO₄?

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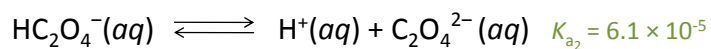
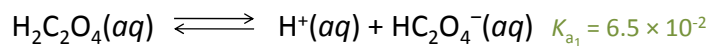
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Calculations Involving K_{a1} and K_{a2}

- Exercise:**

Weak acids

Calculate the concentrations of H₂C₂O₄, HC₂O₄⁻, C₂O₄²⁻, and H⁺ ions in a 0.20 M oxalic acid solution at 25°C.



| | | | | |
|-----------------------------------|-------------------|--|----------------|---|
| 1 st dissociation step | (M) | H ₂ C ₂ O ₄ | H ⁺ | HC ₂ O ₄ ⁻ |
| | Initial conc. | 0.20 | 0 | 0 |
| | Change in conc. | -x | +x | +x |
| | Equilibrium conc. | 0.20 - x | x | x |
| 2 nd dissociation step | (M) | HC ₂ O ₄ ⁻ | H ⁺ | C ₂ O ₄ ²⁻ |
| | Initial conc. | x | x | 0 |
| | Change in conc. | -y | +y | +y |
| | Equilibrium conc. | x - y | x + y | y |

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- 1st dissociation:



$$K_{a_1} = \frac{[\text{HC}_2\text{O}_4^-][\text{H}^+]}{[\text{H}_2\text{C}_2\text{O}_4]} = \frac{x^2}{0.20 \text{ M} - x} = 6.5 \times 10^{-2}$$

Is approximation valid here?

$$x \approx 0.013 \Rightarrow (0.013/0.20) \times 100\% = 6.5\% \text{ (not valid)}$$

$$x^2 + 6.5 \times 10^{-2}x - 1.3 \times 10^{-2} = 0$$

$$x = 0.086 \text{ and } \cancel{-0.151}$$

$$[\text{H}^+] = 0.086 \text{ M}$$

$$[\text{HC}_2\text{O}_4^-] = 0.086 \text{ M}$$

$$[\text{H}_2\text{C}_2\text{O}_4] = 0.20 \text{ M} - 0.086 \text{ M} = 0.11 \text{ M}$$

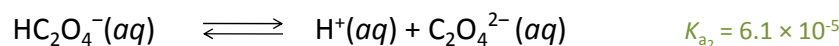
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- 2nd dissociation:



| (M) | HC_2O_4^- | H^+ | $\text{C}_2\text{O}_4^{2-}$ |
|-------------------|---------------------------|--------------|-----------------------------|
| Initial conc. | 0.086 | 0.086 | 0 |
| Change in conc. | -y | +y | +y |
| Equilibrium conc. | 0.086 - y | 0.086 + y | y |

$$K_{a_2} = \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]}{[\text{HC}_2\text{O}_4^-]} = \frac{(0.086 + y)(y)}{0.086 \text{ M} - y} \approx \frac{(0.086 \text{ M})(y)}{0.086 \text{ M}} = 6.1 \times 10^{-5}$$

Is approximation valid here?

yes! So $y = 6.1 \times 10^{-5} \text{ M}$. Then,

$$[\text{H}^+] = 0.086 \text{ M} + 0.000061 = 0.086 \text{ M}$$

$$[\text{HC}_2\text{O}_4^-] = 0.086 \text{ M} - 0.000061 = 0.086 \text{ M}$$

$$[\text{C}_2\text{O}_4^{2-}] = 6.1 \times 10^{-5} \text{ M}$$

The 2nd dissociation step didn't contribute significantly to the proton concentration in the solution. This is in general the case for polyprotic acids, where $[\text{H}^+]$ can be determined just by looking at the 1st dissociation step.

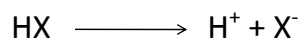
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Molecular Structure and Acid Strength

- The strength of an acid is measured by its tendency to ionize.



- Two factors influence the extent to which the acid undergoes ionization.
 - The *strength* of the bond (Bond enthalpy).
The stronger the bond, the weaker the acid.
 - The *polarity* of the bond.
The more polar the bond is, the weaker it becomes, and the stronger the acid is.

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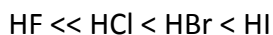
Hydrohalic Acid

- **Hydrohalic Acids** are binary acids formed between a hydrogen and a halogen (HF, HCl, HBr and HI).
 - the more important factor in determining the strength of the hydrohalic acids is bond strength.

TABLE 16.9 Bond Enthalpies for Hydrogen Halides and Acid Strengths for Hydrohalic Acids

| Bond | Bond Enthalpy (kJ/mol) | Acid Strength |
|------|------------------------|---------------|
| H-F | 562.8 | Weak |
| H-Cl | 431.9 | Strong |
| H-Br | 366.1 | Strong |
| H-I | 298.3 | Strong |

The order of acidity strength:



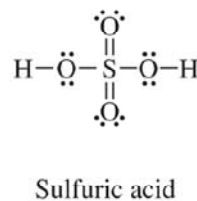
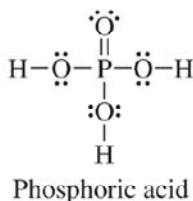
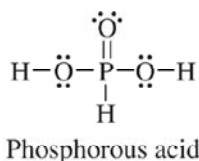
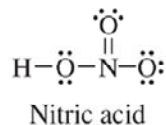
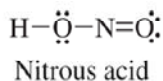
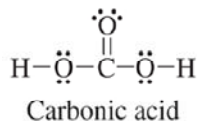
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Oxoacids

- **Oxoacids** are acids that contain hydrogen, oxygen, and a central, nonmetal atom. They contain one or more O—H bonds.



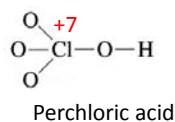
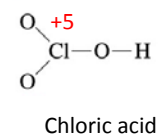
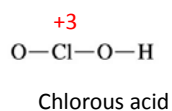
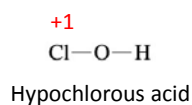
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Oxoacids

- Some oxoacids have the same central atom with different number of oxygen atoms attached to the central atom. the higher the oxidation state of the central atom, the stronger the acid.
- More oxygens attached to the central atom bring the oxidation state of the central atom to be higher. Thus, the central atom withdraws the electron more strongly from the oxygen of OH group, making the O—H bond to be more polar and the acid to be stronger.



Acidity strength

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Oxoacids

- Other oxoacids have different central atoms (from the same group in the periodic table) attached to the same number of oxygen atoms. In this case, acid strength increases with increasing the electronegativity of the central atom.

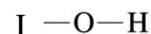
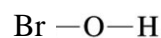


TABLE 14.9 Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids

| Acid | X | Electronegativity of X | K_a for Acid |
|-------------------|-----------------|--------------------------------------|---------------------|
| HOCl | Cl | 3.0 | 4×10^{-8} |
| HOBrl | Br | 2.8 | 2×10^{-9} |
| HOI | I | 2.5 | 2×10^{-11} |
| HOCH ₃ | CH ₃ | 2.3 (for carbon in CH ₃) | $\sim 10^{-15}$ |

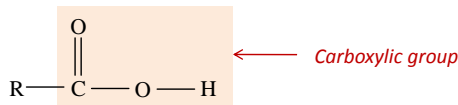
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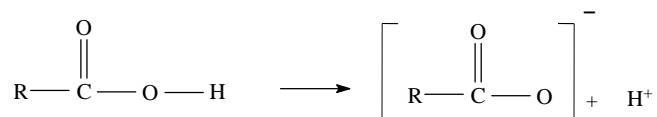
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Carboxylic Acid

- A **Carboxylic acid** is an organic acids with the Lewis structure:



- It ionizes to produce a **carboxylate** anion.



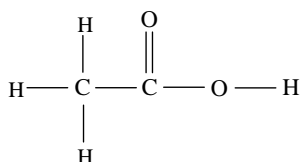
- Increasing the number of electronegative atoms in the *R* group increases the polarity of to O—H bond, and the carboxylic acid becomes stronger.

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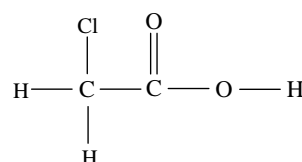
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Carboxylic Acid



Acetic acids
 $K_a = 1.8 \times 10^{-5}$



Chloroacetic acids
 $K_a = 1.4 \times 10^{-3}$

Which carboxylic acid is stronger?

Chloroacetic acid is stronger than acetic acid.

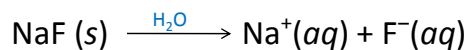
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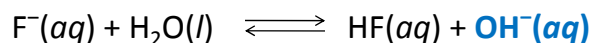
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Acid-Base Properties of Salt Solutions

- When a specific salt (an ionic compound) is dissolved in water, it breaks up into its ions. Under some circumstances, these ions behave like acids or bases.



The F^- ions is the conjugate base of the weak HF acid. The F^- ions react with water (**salt hydrolysis**).



- An anion that is a conjugate base of a weak acid reacts with water to produce OH^- ions, making the solution **basic**.

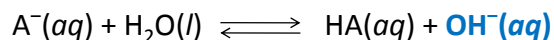
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Basic Salt Solutions

- In general, an anion that is a conjugate base of a weak acid reacts with water to produce OH^- ions, making the solution *basic*.



Examples of A^- are:

- fluoride ions (F^-)
- acetate ions (CH_3COO^-)
- nitrite ions (NO_2^-)
- sulfite ions (SO_3^{2-})
- hydrogen carbonate ions (HCO_3^-)

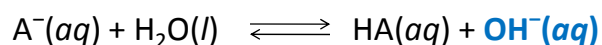
But why not chloride ions (Cl^-), nitrate ions (NO_3^-) or perchlorate ions (ClO_4^-) ?

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Basic Salt Solutions



- The F^- ion is *the conjugate base of the weak HA acid*. The K_b value of the F^- base can be calculated from the K_a value of the HA acid using the fact that: $K_w = K_a \times K_b$.
- The Cl^- ion is *the conjugate base of the strong HCl acid*, so it will not hydrolyze like the F^- ion does. Thus, it doesn't affect the pH of the solution as it doesn't produce OH^- ions.

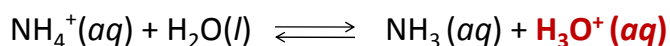
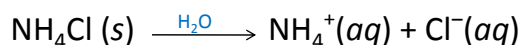
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Acidic Salt Solutions

- A cation that is a conjugate acid of a weak base reacts with water to produce hydronium ions, making the solution *acidic*.



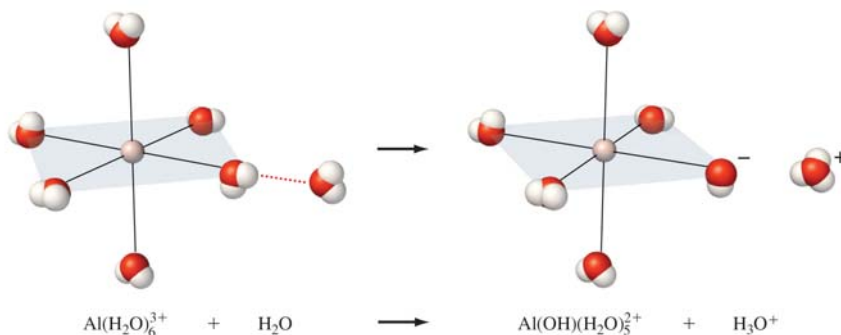
- The NH_4^+ ion is *the conjugate acid of the weak NH_3 base*. You can determine its K_a from the K_b value of NH_3 using the fact that: $K_w = K_a \times K_b$.

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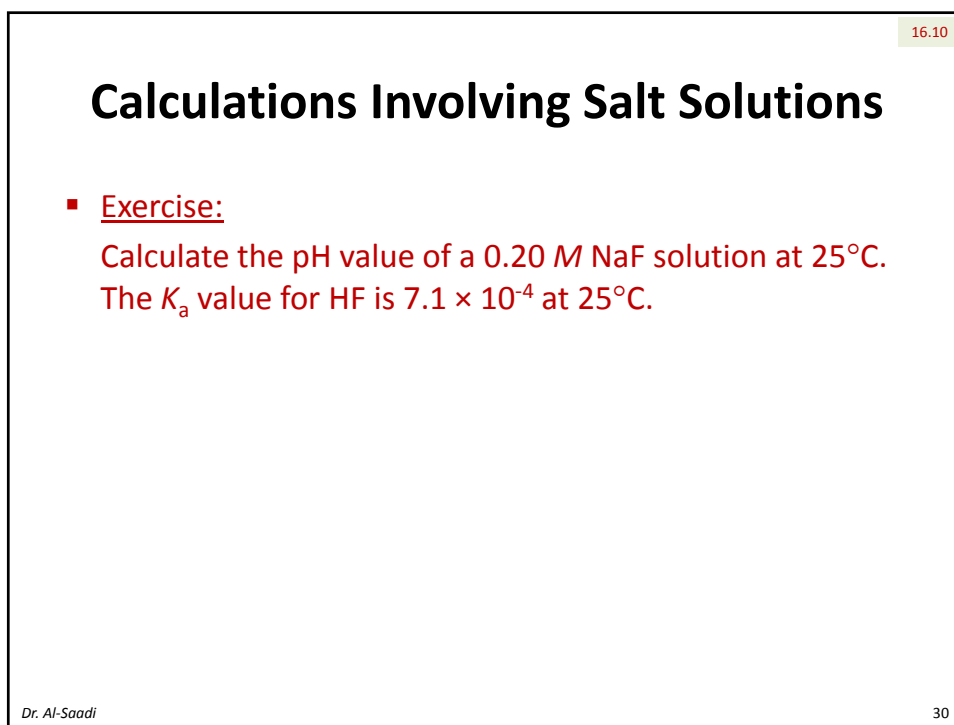
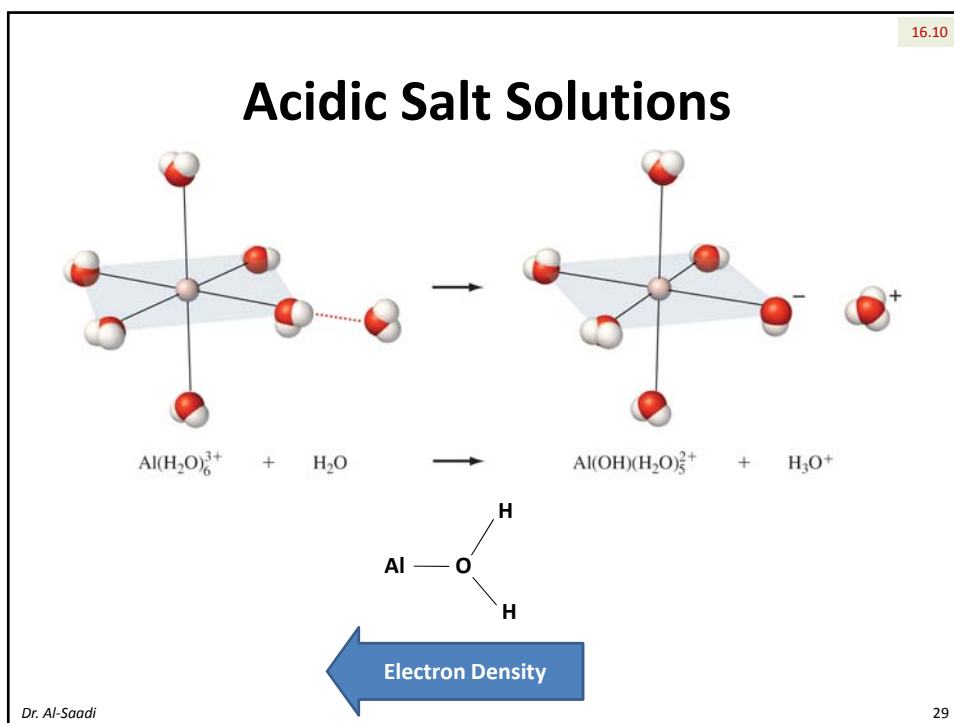
Acidic Salt Solutions



- Small, highly charged metal ions (such as Al^{3+} , Cr^{3+} , Fe^{3+} , Bi^{3+} and Be^{2+}) in dissolved salt can produce acidic solutions. They are hydrated by water molecules. The O—H bonds of the H_2O molecules attached to the metal ion become weaker (more polar) and, thus, can more easily produce hydrogen ions.

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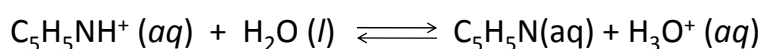


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Calculations Involving Salt Solutions

Exercise:

Determine the pH of a 0.25 M solution of pyridinium nitrate salt ($C_5H_5NHNO_3$) at 25°C. Pyridinium nitrate dissociates in water to give nitrate ions (NO_3^-) and pyridinium ions ($C_5H_5NH^+$) which is the conjugate acid of pyridine (C_5H_5N). K_b for pyridine is 1.7×10^{-9} .



To find K_a for the pyridinium ion:

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.7 \times 10^{-9}} = 5.9 \times 10^{-6}$$

$$K_a = \frac{[C_5H_5N][H_3O^+]}{[C_5H_5NH^+]}$$

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$$K_a = \frac{[C_5H_5N][H_3O^+]}{[C_5H_5NH^+]} = \frac{x^2}{(0.25 M - x)} \cong \frac{x^2}{(0.25 M)} = 5.9 \times 10^{-6}$$

| (M) | $C_5H_5NH^+$ | C_5H_5N | H_3O^+ |
|-------------------|--------------|-----------|----------|
| Initial conc. | 0.25 | 0 | 0 |
| Change in conc. | -x | +x | +x |
| Equilibrium conc. | 0.25 - x | x | x |

$$x = \sqrt{(5.9 \times 10^{-6})(0.25 M)} = 1.2 \times 10^{-3} M$$

The 5% rule

$$\text{Check: } \frac{1.2 \times 10^{-3} M}{0.25 M} \times 100 = 0.49\%$$

$$[H_3O^+] = 1.2 \times 10^{-3} M$$

$$\text{pH} = -\log(1.2 \times 10^{-3} M) = 2.92$$

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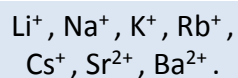
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Neutral Salt Solutions

- Some salts, when dissolved in water, have no impact on the pH of the solutions.

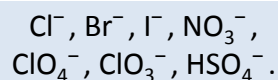
Cation

- Relatively large in size with low positive charge.
- Mostly from Groups 1A and 2A (the cations of the strong bases).
- Exception is Be^{2+} .



Anion

- They are the conjugate bases of the strong acids.



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Types of Ions in Solutions

- The pH of a salt solution can be predicted qualitatively (**acidic**, **basic** or neutral) by identifying the ions present in the solution .

| | Examples |
|--|--|
| A cation that will make a solution acidic is | |
| • The conjugate acid of a weak base | $\text{NH}_4^+, \text{CH}_3\text{NH}_3^+, \text{C}_2\text{H}_5\text{NH}_3^+$ |
| • A small, highly charged metal ion (other than from Group 1A or 2A) | $\text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Bi}^{3+}$ |
| An anion that will make a solution basic is | |
| • The conjugate base of a weak acid | $\text{CN}^-, \text{NO}_2^-, \text{CH}_3\text{COO}^-$ |
| A cation that will not affect the pH of a solution is | |
| • A Group 1A or heavy Group 2A cation (except Be^{2+}) | $\text{Li}^+, \text{Na}^+, \text{Ba}^{2+}$ |
| An anion that will not affect the pH of a solution is | |
| • The conjugate base of a strong acid | $\text{Cl}^-, \text{NO}_3^-, \text{ClO}_4^-$ |

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Other Salt Solutions

- In some other salts, both the cation and the anion hydrolyze.
In this case, pH depends on the relative strengths of the conjugate acid and base.
 - When $K_b > K_a$, the solution is basic.
 - When $K_b < K_a$, the solution is acidic.
 - When $K_b = K_a$, the solution is neutral or nearly neutral.
- Examples are: NH_4NO_2 , AlF_3 and $\text{CH}_3\text{NH}_3\text{CN}$.

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Acid-Base Properties of Salt Solutions

- Exercise:
Predict whether the a 0.10 M solution of each of the following salts will be basic, acidic or neutral.

| | |
|---------------------------------------|----------------|
| (a) KNO_2 | <i>basic</i> |
| (b) CsF | <i>basic</i> |
| (c) NaCl | <i>neutral</i> |
| (d) $\text{CH}_3\text{NH}_3\text{Br}$ | <i>acidic</i> |
| (e) AlCl_3 | <i>acidic</i> |

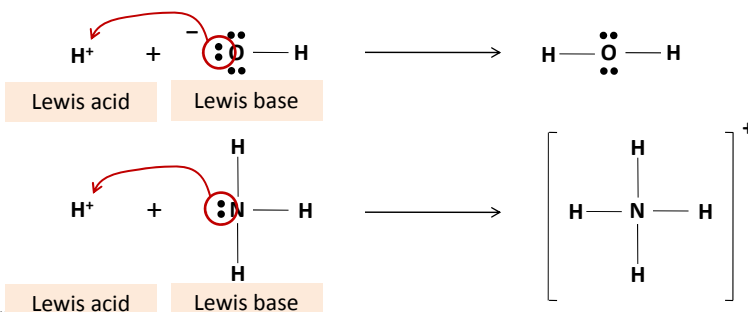
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Lewis Acids and Bases

- The **Brønsted base** is the species that accepts a proton.
 - The **Brønsted acid** is the species that donates a proton.
-
- A **Lewis base** is a species that *donates* a pair of electrons.
 - A **Lewis acid** is a species that *accepts* a pair of electrons.



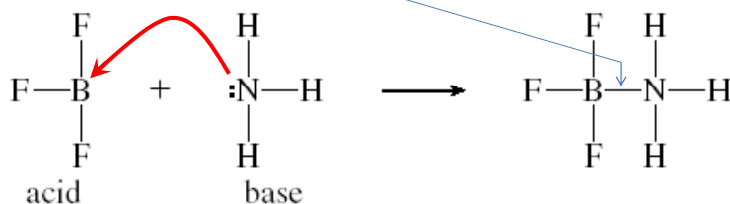
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Lewis Acids and Bases

- **Lewis acid-base reactions** are more general than Brønsted acid-base reactions.
- Lewis acid-base reactions result in the formation of coordinate covalent bonds.



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