18.7 Acid-Base Properties of Salt Solutions

- The acidity (basicity) of salt solutions depends on the acid-base properties of their ions

- **Acidic cations** – act as weak acids in water
  - The cations (conjugate acids) of weak bases (NH_4^+, $CH_3NH_2^+$, …) → act as weak acids
  - Small, highly charged metal cations (Al^{3+}, Fe^{3+}, Cr^{3+}, Cu^{2+}, …) → act as weak acids
- **Neutral cations** – do not influence the ***pH***
  - The cations of strong bases (Group I, Ca^{2+}, Sr^{2+}, Ba^{2+}) and metal cations with +1 charge (Ag^+, Cu^+, …) are extremely weak acids (weaker than H_2O) → do not influence the ***pH***

- **Basic anions** – act as weak bases in water
  - The anions (conjugate bases) of weak acids (F^-, CN^-, S^{2-}, PO_4^{3-} …) → act as weak bases
- **Neutral anions** – do not influence the ***pH***
  - The anions (conjugate bases) of strong acids (Cl^-, Br^-, I^-, NO_3^-, ClO_4^- …) are extremely weak bases (weaker than H_2O) → do not influence the ***pH***
- **Amphoteric anions of polyprotic acids** – can act as weak acids or bases in water
  - Anions with ionizable protons ($H_2PO_4^-$, HPO_4^{2-}, HS^-, HSO_3^-, HSO_4^-) → act as either weak acids or weak bases depending on the relative values of their K_a and K_b constants)

➢ Salts of **neutral cations** and **neutral anions** yield **neutral solutions**

Example: $NaCl(s) \rightarrow Na^+ + Cl^-$ (neutral solution)

Na^+ → neutral cation (cation of a strong base, NaOH)

Cl^- → neutral anion (anion of a strong acid, HCl)

➢ Salts of **acidic cations** and **neutral anions** yield **acidic solutions**

Example: $NH_4Cl(s) \rightarrow NH_4^+ + Cl^-$ (acidic solution)

NH_4^+ → acidic cation (cation of a weak base, NH_3)

Cl^- → neutral anion (anion of a strong acid, HCl)

$$NH_4^+ + H_2O \leftrightarrow H_3O^+ + NH_3$$

Example: $FeCl_3(s) \rightarrow Fe^{3+} + 3Cl^-$ (acidic solution)

Fe^{3+} → acidic cation (highly charged, small cation)

Cl^- → neutral anion (anion of a strong acid, HCl)

$$Fe(H_2O)_6^{3+} + H_2O \leftrightarrow H_3O^+ + Fe(H_2O)_5OH^{2+}$$

➢ Salts of **neutral cations** and **basic anions** yield **basic solutions**

Example: $Na_2S(s) \rightarrow 2Na^+ + S^{2-}$ (basic solution)

Na^+ → neutral cation (cation of a strong base, NaOH)

S^{2-} → basic anion (anion of a weak acid, H_2S)

$$S^{2-} + H_2O \leftrightarrow HS^- + OH^-$$

Example: $KF(s) \rightarrow K^+ + F^-$ (basic solution)

K^+ → neutral cation F^- → basic anion

- Salts of **acidic cations** and **basic anions** yield either **acidic or basic solutions**
  - If K_a of the cation is larger than K_b of the anion, the solution is acidic (cation is a stronger acid)
  - If K_a of the cation is smaller than K_b of the anion, the solution is basic (anion is a stronger base)

Example: $NH_4F(s) \rightarrow NH_4^+ + F^-$

$NH_4^+ \rightarrow$ acidic cation (cation of a weak base, NH_3)

$F^- \rightarrow$ basic anion (anion of a weak acid, HF)

$NH_4^+ + H_2O \leftrightarrow H_3O^+ + NH_3$ $\quad K_a(NH_4^+) = 5.7\times10^{-10}$

$F^- + H_2O \leftrightarrow HF + OH^-$ $\quad K_b(F^-) = 1.5\times10^{-11}$

$K_a(NH_4^+) > K_b(F^-) \Rightarrow NH_4^+$ is a stronger acid than F^- is a base $\Rightarrow$ the solution is **slightly acidic**

- Salts of **neutral cations** and **amphoteric anions** yield either **acidic or basic solutions**
  - If K_a of the anion is larger than its K_b, the solution is acidic (the anion is a stronger acid)
  - If K_a of the anion is smaller than its K_b, the solution is basic (the anion is a stronger base)

Example: Predict whether solutions of KH_2PO_4 and K_2HPO_4 are acidic, basic or neutral.

$KH_2PO_4 \rightarrow K^+ + H_2PO_4^-$

$K^+ \rightarrow$ neutral cation (cation of a strong base, KOH)

$H_2PO_4^- \rightarrow$ amphoteric anion ???

$H_2PO_4^- + H_2O \leftrightarrow H_3O^+ + HPO_4^{2-}$ $\quad K_a(H_2PO_4^-)$

$H_2PO_4^- + H_2O \leftrightarrow H_3PO_4 + OH^-$ $\quad K_b(H_2PO_4^-)$

$K_a(H_2PO_4^-) = K_{a2}(H_3PO_4) = 6.3\times10^{-8}$

$K_b(H_2PO_4^-) = K_w/K_{a1}(H_3PO_4) = 10^{-14}/7.2\times10^{-3} = 1.4\times10^{-12}$

$K_a(H_2PO_4^-) >> K_b(H_2PO_4^-) \Rightarrow H_2PO_4^-$ is a stronger acid than it is a base $\Rightarrow$ the solution is **acidic**

$K_2HPO_4 \rightarrow 2K^+ + HPO_4^{2-}$

$HPO_4^{2-} \rightarrow$ amphoteric anion ???

$HPO_4^{2-} + H_2O \leftrightarrow H_3O^+ + PO_4^{3-}$ $\quad K_a(HPO_4^{2-})$

$HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^-$ $\quad K_b(HPO_4^{2-})$

$K_a(HPO_4^{2-}) = K_{a3}(H_3PO_4) = 4.2\times10^{-13}$

$K_b(HPO_4^{2-}) = K_w/K_{a2}(H_3PO_4) = 10^{-14}/6.3\times10^{-8} = 1.6\times10^{-7}$

$K_a(HPO_4^{2-}) << K_b(HPO_4^{2-}) \Rightarrow HPO_4^{2-}$ is a stronger base than it is an acid $\Rightarrow$ the solution is **basic**

18.8 The Lewis Acid-Base Definition

- **Acids** – electron pair acceptors
- **Bases** – electron pair donors

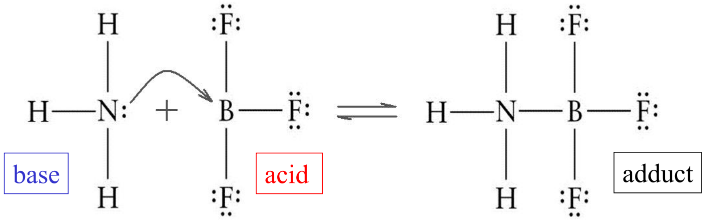
- The Lewis acid-base definition does not require the exchange of a proton (Lewis acids don't have to have H in their formulas)
  - Expands the scope of possible acids
  - H^+ itself is a Lewis acid since it accepts an e^- pair from a base ($H^+ + :B \leftrightarrow H\text{–}B^+$)
    $\Rightarrow$ All B-L acids donate a Lewis acid (H^+)
- Lewis bases must contain an e^- pair to donate
- Lewis acids must have a vacant orbital in order to accept the e^- pair from the base

- A Lewis acid-base reaction results in the formation of a **coordinate covalent bond** between the acid and the base

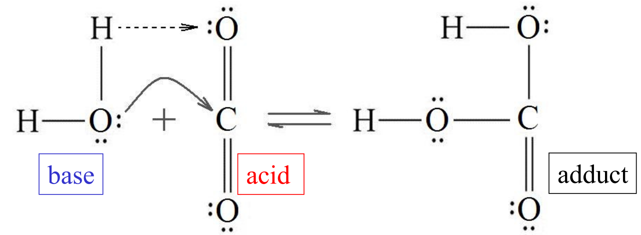
$$A + :B \leftrightarrow A\text{–}B$$

→ A–B is called an **adduct** or a **Lewis acid-base complex**

➢ Lewis acids with **electron deficient atoms** – have incomplete octets (B, Be, …)



➢ Lewis acids with **polar multiple bonds** (CO_2, SO_2, …)



➢ **Metal cations** as Lewis acids – metal cations have vacant orbitals in their valence shells (Al^{3+}, Fe^{3+}, Ni^{2+}, Cu^{2+}, Ag^{+}, …)

$$\underset{\text{acid}}{Cu^{2+}} + \underset{\text{base}}{4{:}NH_3} \leftrightarrow \underset{\text{adduct}}{Cu[NH_3]_4^{2+}}$$

– Many metals act as Lewis acids in biomolecules (Fe in hemoglobin, Mg in chlorophyll, …)

- The Lewis definition has the widest scope of the three acid-base definitions, while the Arrhenius definition has the narrowest scope

Examples:

→BF_3 is a Lewis acid but not a B-L or Arrhenius acid

→F^- is a Lewis and B-L base but not an Arrhenius base

Lewis → $\underset{\text{acid}}{BF_3} + \underset{\text{base}}{:F^-} \leftrightarrow \underset{\text{adduct}}{BF_4^-}$

B-L → $\underset{\text{base}}{:F^-} + \underset{\text{acid}}{H_2O} \xrightarrow{H^+} \underset{\text{acid}}{HF} + \underset{\text{base}}{OH^-}$