

Acid-Base Equilibria

- Acids - sharp, sour taste; Bases - soapy, bitter taste
- Neutralization (proton transfer) reactions
 - acid + base \rightarrow salt + water (or other products)
- Proton (H^+) – strongly hydrated in water $H(H_2O)_n^+$
- Hydronium ion – H_3O^+

18.1 Acid-Base Definitions

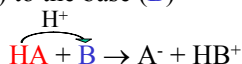
- **Arrhenius definition** – defines acids and bases in terms of their behavior in water
 - **Acids** – contain H and **release H^+** in water
 - **Bases** – contain OH and **release OH^-** in water

- Arrhenius acid-base reaction – a combination of the H^+ from the acid with the OH^- from the base

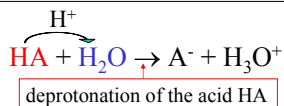


- The Arrhenius definition has severe limitations
 - Limited to water solutions
 - Some bases do not contain OH (NH_3 , amines, Na_2S , Na_2CO_3 , ...)
- **Brønsted-Lowry definition** – defines acids and bases in relation to the H^+ ion (**proton**)
 - **Acids** – **proton donors** (must contain H)
 - **Bases** – **proton acceptors** (must contain a lone pair to bind the H^+)
 - All Arrhenius bases are also B-L bases, but not all B-L bases are Arrhenius bases

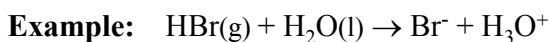
- **B-L acid-base reaction** – a proton transfer from the acid (**HA**) to the base (**B**)



- The dissolution of acids and bases in water is also a **B-L acid-base reaction**



- **Strong acids** – completely deprotonated (dissociated, ionized) in H_2O
 - $\rightarrow HCl, HBr, HI, HNO_3, HClO_3, HClO_4, H_2SO_4$

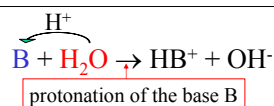


➤ **Weak acids** – partially deprotonated in H_2O

- $\rightarrow HF, HCN, H_2S, HCOOH, CH_3COOH, \dots$

Example: $HF(aq) + H_2O(l) \leftrightarrow F^- + H_3O^+$

- \rightarrow Only a small fraction (~2.5%) of the HF molecules are dissociated to ions



➤ **Strong bases** – completely protonated (dissociated, ionized) in H_2O

- \rightarrow Group I and II oxides and hydroxides



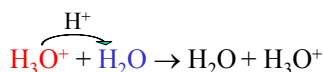
➤ **Weak Bases** – partially protonated in H_2O

- $\rightarrow NH_3$, amines (RNH_2, R_2NH, R_3N), ...

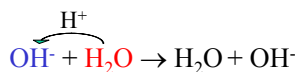
Example: $NH_3(aq) + H_2O(l) \leftrightarrow NH_4^+ + OH^-$

- \rightarrow Only a small fraction (~0.5%) of the NH_3 molecules are dissociated to ions

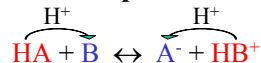
➤ H_3O^+ is a strong acid in water



➤ OH^- is a strong base in water



➤ **Conjugate acid-base pairs**



\rightarrow The reverse reaction is viewed as a B-L acid-base reaction too

$\rightarrow HA/A^-$ and HB^+/B are called conjugate acid-base pairs (**acid/base** – acid component is written first)

- \rightarrow Differ from each other by a proton (H^+) – the acid component of the pair has one more H^+

Examples: $HF/F^-, H_3O^+/H_2O, NH_4^+/NH_3, H_2O/OH^-$

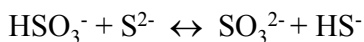
- B-L acid-base reactions occur when an acid and a base react to form their conjugate base and acid

$$Acid_1 + Base_2 \leftrightarrow Base_1 + Acid_2$$

Table 18.4 The Conjugate Pairs in Some Acid-Base Reactions

Acid	+	Base	\rightleftharpoons	Base	+	Acid
HF	+	H ₂ O	\rightleftharpoons	F ⁻	+	H ₃ O ⁺
HCOOH	+	CN ⁻	\rightleftharpoons	HCOO ⁻	+	HCN
NH ₄ ⁺	+	CO ₃ ²⁻	\rightleftharpoons	NH ₃	+	HCO ₃ ⁻
H ₂ PO ₄ ⁻	+	OH ⁻	\rightleftharpoons	HPO ₄ ²⁻	+	H ₂ O

Example: Identify the conjugate acid-base pairs in the reaction



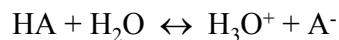
→ HSO₃⁻/SO₃²⁻

→ HS⁻/S²⁻

Quantifying Acid/Base Strengths

• Acid ionization constant (K_a)

– For a general weak acid, HA, in water



$$K_c = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]} \rightarrow [\text{H}_2\text{O}] \text{ can be assumed constant and combined with } K_c$$

$$\Rightarrow K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \rightarrow K_a = K_c[\text{H}_2\text{O}]$$

$\uparrow K_a \Leftrightarrow \uparrow [\text{H}_3\text{O}^+]$ and $\uparrow [\text{A}^-] \Leftrightarrow \uparrow \%$ dissociation

Higher $K_a \Leftrightarrow$ Stronger acid

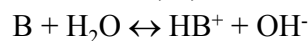
Table 18.2 K_a Values for Some Monoprotic Acids at 25°C

Name (Formula)	Lewis Structure*	K_a
Chlorous acid (HClO ₂)		1.12×10^{-2}
Nitrous acid (HNO ₂)		7.1×10^{-4}
Hydrofluoric acid (HF)		6.8×10^{-4}
Formic acid (HCOOH)		1.8×10^{-4}
Acetic acid (CH ₃ COOH)		1.8×10^{-5}
Hypochlorous acid (HClO)		2.9×10^{-8}
Hypobromous acid (HBrO)		2.3×10^{-9}
Hydrocyanic acid (HCN)		6.2×10^{-10}
Hypoiodous acid (HIO)		2.3×10^{-11}



• Base ionization constant (K_b)

– For a general weak base, B, in water



$$K_c = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]} \rightarrow [\text{H}_2\text{O}] \text{ can be assumed constant and combined with } K_c$$

$$\Rightarrow K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} \rightarrow K_b = K_c[\text{H}_2\text{O}]$$

$\uparrow K_b \Leftrightarrow \uparrow [\text{HB}^+]$ and $\uparrow [\text{OH}^-] \Leftrightarrow \uparrow \%$ dissociation

Higher $K_b \Leftrightarrow$ Stronger base

→ A key structural feature of all B-L bases is a lone pair of e^s needed to bind the proton

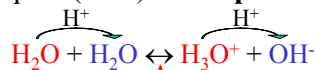
Table 18.6 K_b Values for Some Molecular (Amine) Bases at 25°C

Name (Formula)	Lewis Structure*	K_b
Diethylamine [(CH ₃ CH ₂) ₂ NH]		8.6×10^{-4}
Dimethylamine [(CH ₃) ₂ NH]		5.9×10^{-4}
Methylamine (CH ₃ NH ₂)		4.4×10^{-4}
Ammonia (NH ₃)		1.76×10^{-5}
Pyridine (C ₅ H ₅ N)		1.7×10^{-9}
Aniline (C ₆ H ₅ NH ₂)		4.0×10^{-10}



18.2 Autoionization of Water and pH

• Water can act as both proton donor (acid) and proton acceptor (base) → **amphoteric**



Autoionization (autoprotolysis)

• Ion-product constant of water (K_w)

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2} \rightarrow [\text{H}_2\text{O}] \text{ can be assumed constant and combined with } K_c$$

$$\Rightarrow K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \rightarrow K_w = K_c[\text{H}_2\text{O}]^2$$

K_w → ion-product (autoprotolysis) constant of water

➤ At 25°C, $K_w = 1.0 \times 10^{-14}$

➤ In pure water $\rightarrow [H_3O^+] = [OH^-] = x$

$$\rightarrow K_w = x^2 \rightarrow x = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$$

$$\Rightarrow [H_3O^+] = [OH^-] = 1.0 \times 10^{-7} \text{ M}$$

➤ In water solutions $\rightarrow [H_3O^+]$ and $[OH^-]$ are inversely proportional to each other

$$\rightarrow K_w = [H_3O^+][OH^-] \Rightarrow \uparrow[H_3O^+] \Leftrightarrow \downarrow[OH^-]$$

$\Rightarrow H_3O^+$ and OH^- are present in different proportions in both acid and base solutions

Neutral solutions $\rightarrow [H_3O^+] = [OH^-]$

Acidic solution $\rightarrow [H_3O^+] > [OH^-]$

Basic solutions $\rightarrow [H_3O^+] < [OH^-]$

Example: Calculate the concentrations of H_3O^+ and OH^- in 0.10 M HCl and 0.10 M $Ba(OH)_2$ solutions.

\rightarrow HCl is a strong acid \rightarrow completely dissociated in water solutions; $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

$$\Rightarrow 0.10 \text{ M HCl} \rightarrow [H_3O^+] = 0.10 \text{ M}$$

$$\Rightarrow [OH^-] = K_w / [H_3O^+] = 1.0 \times 10^{-14} / 0.10$$

$$\Rightarrow [OH^-] = 1.0 \times 10^{-13} \text{ M} \Rightarrow [H_3O^+] \gg [OH^-]$$

$\rightarrow Ba(OH)_2$ is a strong base \rightarrow completely dissociated in water solutions; $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

$$\Rightarrow 0.10 \text{ M } Ba(OH)_2 \rightarrow [OH^-] = 0.20 \text{ M}$$

$$\Rightarrow [H_3O^+] = K_w / [OH^-] = 1.0 \times 10^{-14} / 0.20$$

$$\Rightarrow [H_3O^+] = 5.0 \times 10^{-14} \text{ M} \Rightarrow [H_3O^+] \ll [OH^-]$$

The pH Scale

• The pH scale is a logarithmic scale

$$pH = -\log[H_3O^+]$$

$$\rightarrow \log[H_3O^+] = -pH \Rightarrow [H_3O^+] = 10^{-pH}$$

$$\uparrow[H_3O^+] \Leftrightarrow \downarrow pH$$

\rightarrow If $[H_3O^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$ (neutral solution)

$$\rightarrow pH = -\log(1 \times 10^{-7}) \rightarrow \text{neutral solution} \rightarrow pH = 7$$

\rightarrow If $[H_3O^+] > 1 \times 10^{-7} \text{ M} \rightarrow$ acidic solution $\rightarrow pH < 7$

\rightarrow If $[H_3O^+] < 1 \times 10^{-7} \text{ M} \rightarrow$ basic solution $\rightarrow pH > 7$

Examples: $[H_3O^+] = 1 \rightarrow pH = -\log 1 = 0$

$$[H_3O^+] = 10^{-14} \rightarrow pH = -\log 10^{-14} = 14$$

• The p-notation $\rightarrow pX = -\log X$

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

$$\rightarrow \log[OH^-] = -pOH \Rightarrow [OH^-] = 10^{-pOH}$$

$$pK_w = -\log K_w$$

$$\rightarrow [H_3O^+][OH^-] = K_w \leftarrow (\text{take a } -\log)$$

$$\rightarrow -\log[H_3O^+] + (-\log[OH^-]) = -\log K_w$$

$$\Rightarrow pH + pOH = pK_w$$

$$\rightarrow \text{At } 25^\circ\text{C, } K_w = 1.0 \times 10^{-14} \rightarrow pK_w = 14.00$$

$$\Rightarrow pH + pOH = 14.00$$

$$\rightarrow \text{If } pH = 7 \rightarrow pOH = 7 \rightarrow \text{neutral solution}$$

$$\rightarrow \text{Acidic } (\downarrow pH, \uparrow pOH); \text{ Basic } (\uparrow pH, \downarrow pOH)$$

	$[H_3O^+]$	pH	$[OH^-]$	pOH
BASIC	1.0×10^{-15}	15.00	1.0×10^1	-1.00
	1.0×10^{-14}	14.00	1.0×10^0	0.00
	1.0×10^{-13}	13.00	1.0×10^{-1}	1.00
	1.0×10^{-12}	12.00	1.0×10^{-2}	2.00
	1.0×10^{-11}	11.00	1.0×10^{-3}	3.00
	1.0×10^{-10}	10.00	1.0×10^{-4}	4.00
	1.0×10^{-9}	9.00	1.0×10^{-5}	5.00
	1.0×10^{-8}	8.00	1.0×10^{-6}	6.00
NEUTRAL	1.0×10^{-7}	7.00	1.0×10^{-7}	7.00
ACIDIC	1.0×10^{-6}	6.00	1.0×10^{-8}	8.00
	1.0×10^{-5}	5.00	1.0×10^{-9}	9.00
	1.0×10^{-4}	4.00	1.0×10^{-10}	10.00
	1.0×10^{-3}	3.00	1.0×10^{-11}	11.00
	1.0×10^{-2}	2.00	1.0×10^{-12}	12.00
	1.0×10^{-1}	1.00	1.0×10^{-13}	13.00
	1.0×10^0	0.00	1.0×10^{-14}	14.00
	1.0×10^1	-1.00	1.0×10^{-15}	15.00

Example: A household ammonia solution has a pH of 11.92. What is the pOH and the concentration of OH^- in it?

$$\rightarrow pOH = 14.00 - pH = 14.00 - 11.92 = 2.08$$

$$\rightarrow [OH^-] = 10^{-pOH} = 10^{-2.08} = 8.3 \times 10^{-3}$$

Note: The # of sig. figs in $[OH^-]$ (or $[H_3O^+]$) equals the number of decimal places in pOH (or pH)

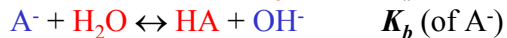
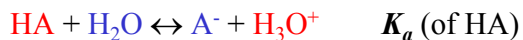
• Measuring pH in the laboratory

– Indicators – have different colors at different pH (pH paper, indicator solutions)

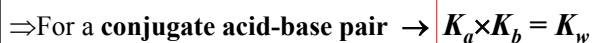
– pH meters – measure the pH by measuring the potential of a pH sensitive electrode immersed in the solution (more accurate)

K_a and K_b of a Conjugate Acid-Base Pair

- In a solution of the weak acid HA, both HA and its conjugate base, A^- , react with water



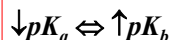
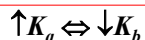
$$K_a \times K_b = \frac{[H_3O^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$



$$-\log K_a + (-\log K_b) = -\log K_w$$



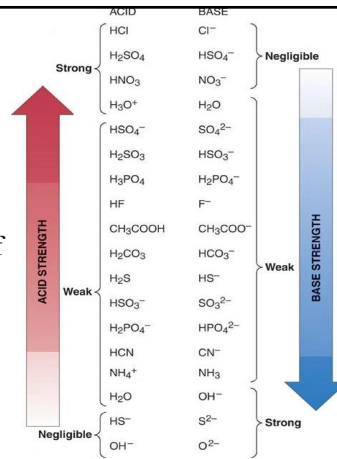
➤ The stronger the acid, the weaker its conjugate base and vice versa



Example: The K_a of HF is 6.8×10^{-4} . What is the K_b of F^- ?

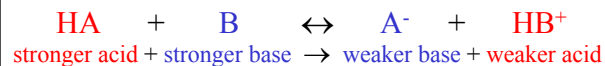
$$K_b = K_w / K_a = 1.0 \times 10^{-14} / 6.8 \times 10^{-4}$$

$$K_b = 1.5 \times 10^{-11}$$



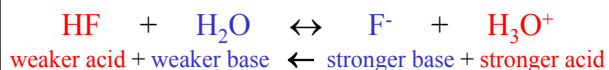
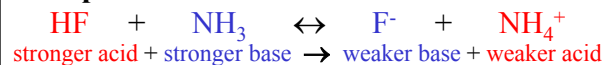
18.3 Relative Acid-Base Strength and the Net Direction of Reaction

- An acid-base reaction proceeds to a greater extent from the stronger acid and stronger base towards the weaker acid and weaker base



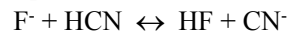
\rightarrow The reaction is shifted towards A^- and HB^+ ($K_c > 1$)

Examples:



Example:

Given $K_a(\text{HF}) = 6.8 \times 10^{-4}$ and $K_a(\text{HCN}) = 6.2 \times 10^{-10}$, determine the preferred direction of the reaction



\rightarrow Compare the strengths of the acids on both sides

\rightarrow HF is stronger than HCN (HF has higher K_a value)

\rightarrow Compare the strengths of the bases on both sides

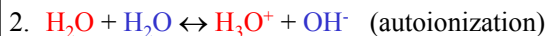
\rightarrow Since HF is a stronger acid than HCN, the conjugate base of HF, F^- , is a weaker base than the conjugate base of HCN, CN^-

\rightarrow CN^- is stronger than F^- (CN^- has higher K_b value)

$\Rightarrow F^- + \text{HCN} \leftrightarrow \text{HF} + \text{CN}^-$ is shifted to the left ($K_c < 1$)

18.4 Solving Problems Involving Weak Acid Equilibria

- In a water solution of the weak acid, HA, there are two sources of H_3O^+ :



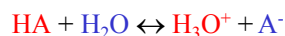
$$\rightarrow [H_3O^+]_1 = [A^-] \quad \text{and} \quad [H_3O^+]_2 = [OH^-]$$

$$\rightarrow [H_3O^+] = [H_3O^+]_1 + [H_3O^+]_2 = [A^-] + [OH^-]$$

\rightarrow If HA is not very dilute or very weak, the autoionization can be neglected and $[OH^-] \ll [A^-]$

$$\Rightarrow [H_3O^+] \approx [A^-] = x$$

- In water solution, the weak acid HA exists in two forms \rightarrow undissociated (HA) and dissociated (A^-)



$\rightarrow C_{HA}$ – total concentration of HA

$$\rightarrow C_{HA} = [HA] + [A^-]$$

$$\Rightarrow [HA] = C_{HA} - [A^-] = C_{HA} - x$$

\rightarrow So $[H_3O^+] = x$, $[A^-] = x$, $[HA] = C_{HA} - x$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{x^2}{C_{HA} - x}$$

➤ Using equilibrium tables

→ If the autoionization of water is neglected

	[]	HA + H ₂ O ↔ H ₃ O ⁺ + A ⁻			$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$
i + c = e	i	C _{HA}	0	0	$K_a = \frac{x^2}{C_{HA} - x}$
	c	-x	+x	+x	
	e	C _{HA} - x	x	x	

→ The quadratic equation can be solved for x in order to determine [H₃O⁺] and pH

→ If x is less than 5% of C_{HA}, x can be neglected in the denominator (5% rule) → works if C_{HA} is relatively large and K_a is small (C_{HA}/K_a > 400)

$$K_a = x^2/C_{HA} \quad x = (K_a C_{HA})^{1/2} = [\text{H}_3\text{O}^+]$$

Finding K_a Given Concentrations or pH

Example: If the pH of a 0.20 M HCN solution is 4.95, calculate the K_a of HCN.

$$\rightarrow [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.95} = 1.1 \times 10^{-5} = x$$

$$\rightarrow C_{\text{HCN}} = 0.20 \quad \rightarrow x \ll 5\% \text{ of } C_{\text{HCN}}$$

	[]	HCN + H ₂ O ↔ H ₃ O ⁺ + CN ⁻			$K_a = \frac{[\text{H}_3\text{O}^+][\text{CN}^-]}{[\text{HCN}]}$
i + c = e	i	0.20	0	0	$K_a = \frac{x^2}{C_{\text{HCN}} - x} \approx \frac{x^2}{C_{\text{HCN}}}$
	c	-x	+x	+x	
	e	0.20 - x	x	x	

$$\Rightarrow K_a = x^2/C_{\text{HCN}} = (1.1 \times 10^{-5})^2/0.20 = \boxed{6.3 \times 10^{-10}}$$

[Note: C_{HA}/K_a = 0.20/6.3 × 10⁻¹⁰ = 3.2 × 10⁸ >> 400]

Finding Concentrations and pH Given K_a

Example: What is the pH of a 0.30 M HF solution? (K_a = 6.8 × 10⁻⁴ for HF)

	[]	HF + H ₂ O ↔ H ₃ O ⁺ + F ⁻			$K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}$
i + c = e	i	0.30	0	0	$K_a = \frac{x^2}{C_{\text{HF}} - x} \approx \frac{x^2}{C_{\text{HF}}}$
	c	-x	+x	+x	
	e	0.30 - x	x	x	

→ C_{HF} = 0.30 → assume x < 5% of 0.30

$$\Rightarrow x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 0.30)^{1/2} = 1.4 \times 10^{-2} = [\text{H}_3\text{O}^+]$$

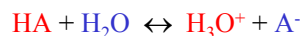
$$\Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.4 \times 10^{-2}) = \boxed{1.85}$$

[Check assumption: (1.4 × 10⁻²/0.30) × 100 = 4.8% < 5%]

[Note: C_{HF}/K_a = 0.30/6.8 × 10⁻⁴ = 441 > 400]

Extent of Acid Dissociation

• Percent dissociation



$$\rightarrow C_{\text{HA}} = [\text{HA}] + [\text{A}^-] \quad \rightarrow [\text{A}^-] \approx [\text{H}_3\text{O}^+]$$

$$\rightarrow [\text{A}^-] = x \text{ (dissociated form of the acid)}$$

$$\% \text{ dissociated} = \frac{[\text{A}^-]}{C_{\text{HA}}} \times 100 = \frac{[\text{H}_3\text{O}^+]}{C_{\text{HA}}} \times 100 = \frac{x}{C_{\text{HA}}} \times 100$$

➤ For a given acid, % dissociated decreases with increasing the total concentration of the acid, C_{HA}

$$\uparrow C_{\text{HA}} \Leftrightarrow \downarrow \% \text{ dissociation}$$

Example: Calculate the % dissociation for two HF solutions with concentrations 0.30 and 3.0 M. (K_a = 6.8 × 10⁻⁴ for HF)

→ For the 0.30 M HF from the previous example:

$$x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 0.30)^{1/2} = 1.4 \times 10^{-2} = [\text{H}_3\text{O}^+]$$

$$\% \text{ dissociated} = (1.4 \times 10^{-2}/0.30) \times 100 = 4.8\%$$

→ For the 3.0 M HF similarly:

$$x = (K_a C_{\text{HF}})^{1/2} = (6.8 \times 10^{-4} \times 3.0)^{1/2} = 4.5 \times 10^{-2} = [\text{H}_3\text{O}^+]$$

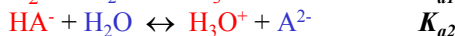
$$\% \text{ dissociated} = (4.5 \times 10^{-2}/3.0) \times 100 = 1.5\%$$

⇒ Increasing the concentration from 0.30 to 3.0 M decreases the % dissociated from 4.8 to 1.5%

The Behavior of Polyprotic Acids

• **Polyprotic Acids** – can donate more than one proton (H₂SO₄, H₃PO₄, ...)

– For a general diprotic acid, H₂A



$$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{HA}^-]}{[\text{H}_2\text{A}]} \quad K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{A}^{2-}]}{[\text{HA}^-]}$$

➤ Almost all polyprotic acids (except H₂SO₄) are weak in all stages of dissociation and become weaker with each successive dissociation

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

Table 18.5 Successive K_a Values for Some Polyprotic Acids at 25°C

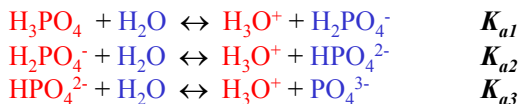
Name (Formula)	Lewis Structure*	K_{a1}	K_{a2}	K_{a3}
Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$)		5.6×10^{-2}	5.4×10^{-5}	
Phosphorous acid (H_3PO_3)		3×10^{-2}	1.7×10^{-7}	
Sulfurous acid (H_2SO_3)		1.4×10^{-2}	6.5×10^{-8}	
Phosphoric acid (H_3PO_4)		7.2×10^{-3}	6.3×10^{-8}	4.2×10^{-13}
Arsenic acid (H_3AsO_4)		6×10^{-3}	1.1×10^{-7}	3×10^{-12}
Carbonic acid (H_2CO_3)		4.5×10^{-7}	4.7×10^{-11}	
Hydrosulfuric acid (H_2S)		9×10^{-8}	1×10^{-17}	

↑ ACID STRENGTH

➤ The second and third dissociations are less pronounced because it's harder to remove an H^+ from negatively charged ions

➤ Equilibrium calculations are greatly simplified by **neglecting subsequent dissociations** since they contribute negligible amounts of H_3O^+

Example: Calculate the pH and the concentrations of all ionized forms for a **0.10 M** H_3PO_4 solution.
($K_{a1} = 7.2 \times 10^{-3}$, $K_{a2} = 6.3 \times 10^{-8}$, $K_{a3} = 4.2 \times 10^{-13}$)



→ Consider only the first dissociation to get the pH

	H_3PO_4	H_2O	\leftrightarrow	H_3O^+	$+$	H_2PO_4^-	$K_{a1} = \frac{[\text{H}_3\text{O}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$
i	0.10			0		0	
c	$-x$			$+x$		$+x$	
e	$0.10 - x$			x		x	

$$K_{a1} = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

→ Assume $x < 5\%$ of **0.10**

$$\Rightarrow x = (K_{a1} \times 0.10)^{1/2} = (7.2 \times 10^{-3} \times 0.10)^{1/2} = 2.7 \times 10^{-2}$$

→ Check assumption: $(2.7 \times 10^{-2} / 0.10) \times 100 = 27\% > 5\%$

⇒ The assumption is not justified – must solve the quadratic equation

$$\begin{aligned} x^2 &= K_{a1}(0.10 - x) & x^2 + K_{a1}x - 0.10K_{a1} &= 0 \\ x^2 + 7.2 \times 10^{-3}x - 7.2 \times 10^{-4} &= 0 \end{aligned}$$

$$x = \frac{-7.2 \times 10^{-3} + \sqrt{(7.2 \times 10^{-3})^2 + 4 \times 7.2 \times 10^{-4}}}{2} = 2.3 \times 10^{-2}$$

$$\Rightarrow x = [\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] = \boxed{2.3 \times 10^{-2} \text{ M}}$$

$$\Rightarrow pH = -\log[\text{H}_3\text{O}^+] = -\log(2.3 \times 10^{-2}) = \boxed{1.63}$$

→ To calculate the concentrations of the other species, use the $[\text{H}_3\text{O}^+]$ and $[\text{H}_2\text{PO}_4^-]$ from the 1st ionization

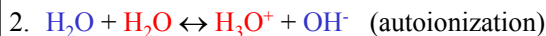
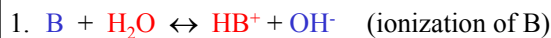
$$K_{a2} = \frac{[\text{H}_3\text{O}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \quad K_{a3} = \frac{[\text{H}_3\text{O}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

$$[\text{HPO}_4^{2-}] = \frac{K_{a2}[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{O}^+]} = \frac{6.3 \times 10^{-8} \times 2.3 \times 10^{-2}}{2.3 \times 10^{-2}} = \boxed{6.3 \times 10^{-8}}$$

$$[\text{PO}_4^{3-}] = \frac{K_{a3}[\text{HPO}_4^{2-}]}{[\text{H}_3\text{O}^+]} = \frac{4.2 \times 10^{-13} \times 6.3 \times 10^{-8}}{2.3 \times 10^{-2}} = \boxed{1.1 \times 10^{-18}}$$

18.5 Solving Problems Involving Weak Base Equilibria

• In a water solution of the weak base, B, there are two sources of OH^- :



$$\rightarrow [\text{OH}^-]_1 = [\text{HB}^+] \quad \text{and} \quad [\text{OH}^-]_2 = [\text{H}_3\text{O}^+]$$

$$\rightarrow [\text{OH}^-] = [\text{OH}^-]_1 + [\text{OH}^-]_2 = [\text{HB}^+] + [\text{H}_3\text{O}^+]$$

→ If B is not very dilute or very weak, the autoionization can be neglected and $[\text{H}_3\text{O}^+] \ll [\text{HB}^+]$

$$\Rightarrow [\text{OH}^-] \approx [\text{HB}^+] = x$$

• In water solution, the weak base B exists in two forms → unionized (B) and ionized (HB^+)



→ C_B – total concentration of B

$$\rightarrow C_B = [\text{B}] + [\text{HB}^+]$$

$$\Rightarrow [\text{B}] = C_B - [\text{HB}^+] = C_B - x$$

→ So $[\text{OH}^-] = x$, $[\text{HB}^+] = x$, $[\text{B}] = C_B - x$

$$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]} = \frac{x^2}{C_B - x}$$

→ The equation is equivalent to that for weak acids

➤ Using equilibrium tables

→ If the autoionization of water is neglected

	[]	B + H ₂ O ↔ HB ⁺ + OH ⁻		$K_b = \frac{[\text{HB}^+][\text{OH}^-]}{[\text{B}]}$
i + c = e	i	C _B	0	0
	c	-x	+x	+x
	e	C _B - x	x	x

$$K_b = \frac{x^2}{C_B - x}$$

→ The quadratic equation can be solved for x in order to determine [OH⁻], pOH and pH

→ If x is less than 5% of C_B, x can be neglected in the denominator (5% rule) → works if C_B is relatively large and K_b is small (C_B/K_b > 400)

$$K_b = x^2/C_B \quad x = (K_b C_B)^{1/2} = [\text{OH}^-]$$

Finding pH Given K_b

Example: What is the pH of a 0.10 M NH₃ solution? (K_b = 1.8 × 10⁻⁵ for NH₃)

	[]	NH ₃ + H ₂ O ↔ NH ₄ ⁺ + OH ⁻		$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$
i + c = e	i	0.10	0	0
	c	-x	+x	+x
	e	0.10 - x	x	x

$$K_b = \frac{x^2}{C_{\text{NH}_3} - x} \approx \frac{x^2}{C_{\text{NH}_3}}$$

→ C_{NH3} = 0.10 → assume x < 5% of 0.10

$$\Rightarrow x = (K_b C_{\text{NH}_3})^{1/2} = (1.8 \times 10^{-5} \times 0.10)^{1/2} = 1.3 \times 10^{-3} = [\text{OH}^-]$$

$$\Rightarrow \text{pOH} = -\log[\text{OH}^-] = -\log(1.3 \times 10^{-3}) = 2.87$$

$$\Rightarrow \text{pH} = 14.00 - \text{pOH} = 14.00 - 2.87 = \boxed{11.13}$$

[Check assumption: (1.3 × 10⁻³/0.10) × 100 = 1.3% < 5%]

Extent of Base Ionization

• Percent ionization



$$\rightarrow C_B = [\text{B}] + [\text{HB}^+] \rightarrow [\text{HB}^+] \approx [\text{OH}^-]$$

$$\rightarrow [\text{HB}^+] = x \text{ (ionized form of the base)}$$

$$\% \text{ ionized} = \frac{[\text{HB}^+]}{C_B} \times 100 = \frac{[\text{OH}^-]}{C_B} \times 100 = \frac{x}{C_B} \times 100$$

➤ For a given base, % ionized decreases with increasing the total concentration of the base, C_B

$$\uparrow C_B \Leftrightarrow \downarrow \% \text{ dissociation}$$

Example: Calculate the % ionization for two NH₃ solutions with concentrations 0.10 and 1.0 M. (K_b = 1.8 × 10⁻⁵ for NH₃)

→ For the 0.10 M NH₃ from the previous example:

$$x = (K_b C_{\text{NH}_3})^{1/2} = (1.8 \times 10^{-5} \times 0.10)^{1/2} = 1.3 \times 10^{-3} = [\text{OH}^-]$$

$$\% \text{ ionized} = (1.3 \times 10^{-3} / 0.10) \times 100 = \mathbf{1.3\%}$$

→ For the 1.0 M NH₃ similarly:

$$x = (K_b C_{\text{NH}_3})^{1/2} = (1.8 \times 10^{-5} \times 1.0)^{1/2} = 4.2 \times 10^{-3} = [\text{OH}^-]$$

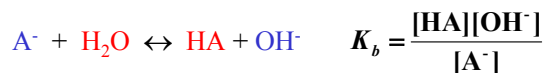
$$\% \text{ ionized} = (4.2 \times 10^{-3} / 1.0) \times 100 = \mathbf{0.42\%}$$

⇒ Increasing the concentration from 0.10 to 1.0 M decreases the % ionized from 1.3 to 0.42%

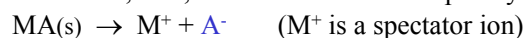
Anions of Weak Acids as Weak Bases

• The anion of the weak acid (HA) is its conjugate base (A⁻)

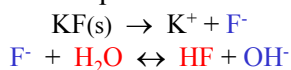
– A⁻ reacts as a weak base in water:



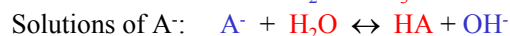
– A⁻ can be produced in solution by means of the soluble salt, MA, which dissociates completely:



Example: For an aqueous solution of KF



➤ HA and A⁻ are present in both, solutions of the weak acid HA, and solutions of its anion A⁻



➤ Both equilibria are shifted to the left so

➤ Solutions of HA are acidic (H₃O⁺) and [HA] >> [A⁻]

➤ Solutions of A⁻ are basic (OH⁻) and [A⁻] >> [HA]

➤ HA and A⁻ are a conjugate acid base pair so

$$K_a(\text{HA}) \times K_b(\text{A}^-) = K_w \rightarrow K_b(\text{A}^-) = K_w / K_a(\text{HA})$$

➤ Equilibrium calculations for A⁻ are carried out using the same method as for the neutral base B

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{x^2}{C_{\text{A}^-} - x}$$

Example: What is the pH of a **0.10 M** KF solution? ($K_a = 6.8 \times 10^{-4}$ for HF)



[]	$\text{F}^- + \text{H}_2\text{O} \leftrightarrow \text{HF} + \text{OH}^-$	$K_b = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]}$	
<i>i</i>	0.10	0	0
<i>c</i>	-x	+x	+x
<i>e</i>	0.10 - x	x	x

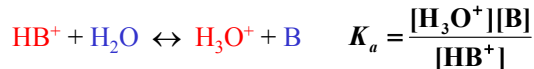
$$K_b = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$\rightarrow K_b(\text{F}^-) = K_w/K_a(\text{HF}) = 1.0 \times 10^{-14}/6.8 \times 10^{-4} = 1.5 \times 10^{-11}$
 $\Rightarrow x = (K_b \times 0.10)^{1/2} = (1.5 \times 10^{-11} \times 0.10)^{1/2} = 1.2 \times 10^{-6} = [\text{OH}^-]$
 $\Rightarrow pOH = -\log[\text{OH}^-] = -\log(1.2 \times 10^{-6}) = 5.92$
 $\Rightarrow pH = 14.00 - pOH = 14.00 - 5.92 = \boxed{8.08}$ (basic)
 [Check assumption: $(1.2 \times 10^{-6}/0.10) \times 100 = 0.0012\% < 5\%$]

Cations of Weak Bases as Weak Acids

- The cation of the weak base (B) is its conjugate acid (HB^+)

– HB^+ reacts as a weak acid in water:



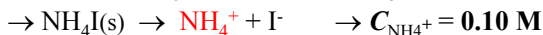
➤ HB^+ and B are a conjugate acid-base pair so

$$K_a(\text{HB}^+) \times K_b(\text{B}) = K_w \rightarrow K_a(\text{HB}^+) = K_w/K_b(\text{B})$$

➤ Equilibrium calculations for HB^+ are carried out using the same method as for the neutral acid HA

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{B}]}{[\text{HB}^+]} = \frac{x^2}{C_{\text{HB}^+} - x}$$

Example: What is the pH of a **0.10 M** NH_4I solution? ($K_b = 1.8 \times 10^{-5}$ for NH_3)



[]	$\text{NH}_4^+ + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{NH}_3$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]}$	
<i>i</i>	0.10	0	0
<i>c</i>	-x	+x	+x
<i>e</i>	0.10 - x	x	x

$$K_a = \frac{x^2}{0.10 - x} \approx \frac{x^2}{0.10}$$

$K_a(\text{NH}_4^+) = K_w/K_b(\text{NH}_3) = 1.0 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$
 $\Rightarrow x = (K_a \times 0.10)^{1/2} = (5.6 \times 10^{-10} \times 0.10)^{1/2} = 7.5 \times 10^{-6}$
 $\Rightarrow [\text{H}_3\text{O}^+] = 7.5 \times 10^{-6} \text{ M}$
 $\Rightarrow pH = -\log[\text{H}_3\text{O}^+] = -\log(7.5 \times 10^{-6}) = \boxed{5.13}$ (acidic)
 [Check assumption: $(7.5 \times 10^{-6}/0.10) \times 100 = 0.0075\% < 5\%$]

18.6 Molecular Properties and Acid Strength

- Binary acids** (H_nX) – consist of H and a second element, X (HF, HCl, H_2O , H_2S , ...)

➤ **Acid strength increases across a period** (the *EN* of X increases → the H–X bond becomes more polar → greater δ^+ charge on the H → greater attraction of the H to the O atom of H_2O)
 $\delta^+ \text{X-H}^{\delta^+} \text{-----} \text{:OH}_2 \leftrightarrow \text{H}_3\text{O}^+ + \text{X}^-$

Example: $\text{NH}_3 \ll \text{H}_2\text{O} < \text{HF}$

➤ **Acid strength increases down a group** (X becomes larger → the H–X bond becomes longer and weaker → the H^+ comes off more easily)

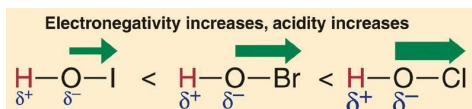
Example: $\text{HF} \ll \text{HCl} < \text{HBr} < \text{HI}$

- Oxoacids** (H_nXO_m) – consist of H, O and a third element, X (HClO_2 , H_2SO_4 , H_3PO_4 , ...)

– The acidic H atoms are attached to O atoms

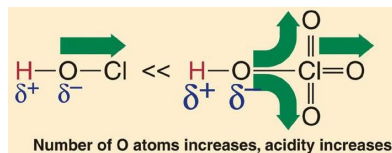
➤ For oxoacids with the same # of O atoms, **acid strength increases with increasing the *EN* of X** (X withdraws electron density from the O–H bond and makes it more polar → greater δ^+ charge on the H → the H^+ comes off more easily)

Example: $\text{HOI} < \text{HOBr} < \text{HOCl}$



➤ For oxoacids having the same X, **acid strength increases with increasing the # of O atoms** (the high *EN* of O draws electron density from the O–H bond and makes it more polar → greater δ^+ charge on the H → the H^+ comes off more easily)

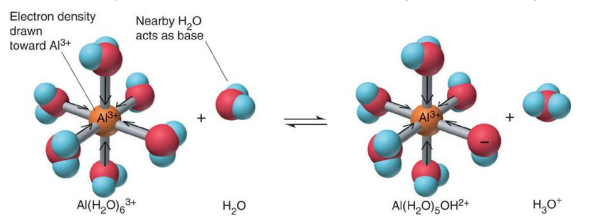
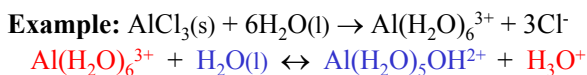
Example: $\text{HClO} < \text{HClO}_2 \ll \text{HClO}_3 < \text{HClO}_4$



➤ Adding more *EN* atoms to the molecule increases the acidity further (**Ex:** $\text{CH}_3\text{COOH} < \text{CF}_3\text{COOH}$)

Acidity of Hydrated Metal Ions

- Metal ions are hydrated in water solutions
 - If the ion is **small and highly charged** (M^{2+} or M^{3+}), it draws electron density from the bound water molecules $\rightarrow H^+$ can be released \rightarrow **acidic**

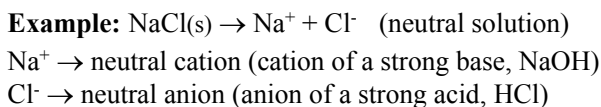


18.7 Acid-Base Properties of Salt Solutions

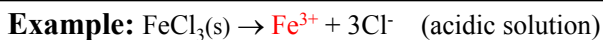
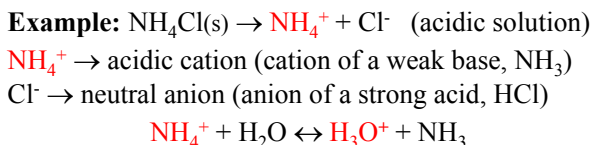
- The acidity (basicity) of salt solutions depends on the acid-base properties of their ions
- **Acidic cations** – act as weak acids in water
 - The cations (conjugate acids) of weak bases (NH_4^+ , $CH_3NH_2^+$, ...) \rightarrow act as weak acids
 - Small, highly charged metal cations (Al^{3+} , Fe^{3+} , Cr^{3+} , Cu^{2+} , ...) \rightarrow 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) \rightarrow 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-} ...) \rightarrow 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) \rightarrow 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^-) \rightarrow 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**



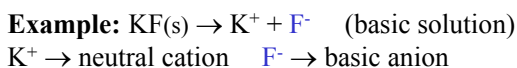
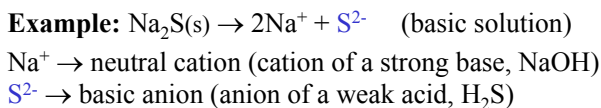
➤ Salts of **acidic cations** and **neutral anions** yield **acidic solutions**



$Fe^{3+} \rightarrow$ acidic cation (highly charged, small cation)
 $Cl^- \rightarrow$ neutral anion (anion of a strong acid, HCl)

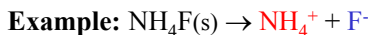


➤ Salts of **neutral cations** and **basic anions** yield **basic solutions**



➤ 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)



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

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



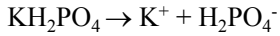
$K_a(NH_4^+) > K_b(F^-) \Rightarrow NH_4^+$ is a stronger acid than F^- is a base \Rightarrow the solution is **slightly acidic**

➤ 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)

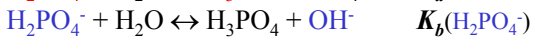
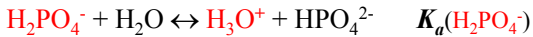
➤ If K_a of the anion is smaller than its K_b , the solution is basic (the anion is a stronger base)

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



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

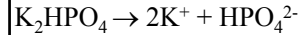
$\text{H}_2\text{PO}_4^- \rightarrow$ amphoteric anion ???



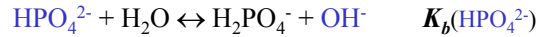
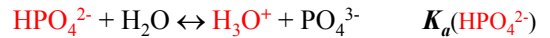
$$K_a(\text{H}_2\text{PO}_4^-) = K_{a2}(\text{H}_3\text{PO}_4) = 6.3 \times 10^{-8}$$

$$K_b(\text{H}_2\text{PO}_4^-) = K_w / K_{a1}(\text{H}_3\text{PO}_4) = 10^{-14} / 7.2 \times 10^{-3} = 1.4 \times 10^{-12}$$

$K_a(\text{H}_2\text{PO}_4^-) \gg K_b(\text{H}_2\text{PO}_4^-) \Rightarrow \text{H}_2\text{PO}_4^-$ is a stronger acid than it is a base \Rightarrow the solution is **acidic**



$\text{HPO}_4^{2-} \rightarrow$ amphoteric anion ???



$$K_a(\text{HPO}_4^{2-}) = K_{a3}(\text{H}_3\text{PO}_4) = 4.2 \times 10^{-13}$$

$$K_b(\text{HPO}_4^{2-}) = K_w / K_{a2}(\text{H}_3\text{PO}_4) = 10^{-14} / 6.3 \times 10^{-8} = 1.6 \times 10^{-7}$$

$K_a(\text{HPO}_4^{2-}) \ll K_b(\text{HPO}_4^{2-}) \Rightarrow \text{HPO}_4^{2-}$ 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 ($\text{H}^+ \leftarrow \text{:B} \leftrightarrow \text{H-B}^+$)

\Rightarrow All B-L acids donate a Lewis acid (H^+)

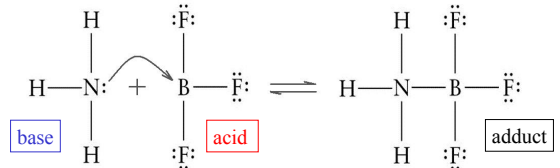
- Lewis bases must contain an e^- pair to donate
- Lewis acids must have a vacant orbital in order to accept the e^- pair from the base

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

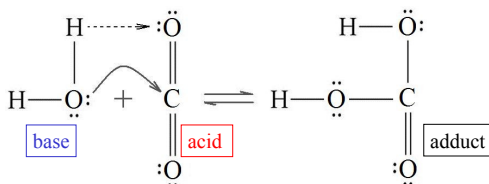


\rightarrow A-B is called an **adduct** or a **Lewis acid-base complex**

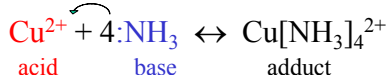
- Lewis acids with **electron deficient atoms** – have incomplete octets (B, Be, ...)



- 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^+ , ...)



– 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:

$\rightarrow \text{BF}_3$ is a Lewis acid but not a B-L or Arrhenius acid

$\rightarrow \text{F}^-$ is a Lewis and B-L base but not an Arrhenius base

