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Ionic equilibria

By
Dr. Mohammed Sattar
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Outlines

- Objectives
- Theories
- Acid-base equilibria
- Calculation of pH, acidity constants
- The effect of ionic strength.

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Objectives

- Define of acids and bases
- Concept of Sörensen's pH scale.
- Understanding different terminology such as Ampholytes, Aprotic , etc
- Ionization of Polyprotic electrolytes.
- pKa and pH calculation of aqueous solutions with different composition

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Theories

Arrhenius Theory

- Arrhenius defined an acid as a substance that liberates **hydrogen ions** and a base as a substance that supplies **hydroxyl ions** on dissociation in aqueous media.

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Brönsted–Lowry theory

- According to the Brönsted–Lowry theory, an acid is a substance, charged or uncharged, that is capable of donating a proton, and a base is a substance, charged or uncharged, that is capable of accepting a proton from an acid.

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Solvent classification

- ***Protophilic***.
- ***Protogenic***.
- ***Amphiprotic***
- ***Aprotic***

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Protolytic reactions or *protolysis.*

$$\underset{\text{Acid}_1}{HCl} + \underset{\text{Base}_2}{H_2O} \rightarrow \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Cl^-}$$

TABLE 7–1. *Examples of Acid–Base Reactions*

	$Acid_1$		$Base_2$		$Acid_2$		$Base_1$
Neutralization	NH_4^+	+	OH^-	=	H_2O	+	NH_3
Neutralization	H_3O^+	+	OH^-	=	H_2O	+	H_2O
Neutralization	HCl	+	NH_3	=	NH_4^+	+	Cl^-
Hydrolysis	H_2O	+	CH_3COO^-	=	CH_3COOH	+	OH^-
Hydrolysis	NH_4^+	+	H_2O	=	H_3O^+	+	NH_3
Displacement	HCl	+	CH_3COO^-	=	CH_3COOH	+	Cl^-

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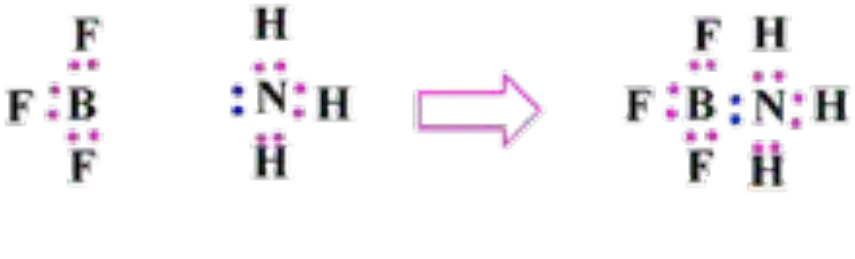
Lewis Electronic Theory.

BF_3 can act as a Lewis acid:



Acid Base

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Sörensen's pH

- The hydrogen ion concentration of a solution varies from approximately 1 in a 1 M solution of a strong acid to about 1×10^{-14} in a 1 M solution of a strong base
- The pH of a solution can be considered in terms of a numeric scale having values from 0 to 14, which expresses in a quantitative way the degree of acidity (7 to 0) and alkalinity (7-14).

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Ionic Equilibria

$$\underset{\text{Acid}_1}{HAc} + \underset{\text{Base}_2}{H_2O} \rightleftharpoons \underset{\text{Acid}_2}{H_3O^+} + \underset{\text{Base}_1}{Ac^-}$$

Rate of forward $= k_1 \times [HAc]^1 \times [H_2O]^1$

Rate of backward $= k_2 \times [H_3O^+]^1 \times [Ac^-]^1$

At equilibrium

$$k_1 \times [HAc] \times [H_2O] = k_2 \times [H_3O^+] \times [Ac^-]$$

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Relationship Between K_a and K_b

$$K_a K_b = \frac{[H_3O^+][B^-]}{[HB]} \cdot \frac{[OH^-][HB]}{[B^-]} = [H_3O^+][OH^-] = K_w$$

$K_a = K_w/K_b$ $K_b = K_w/K_a$

K_w. known as the *autoprotolysis constant,* or the *ion product* of water

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EXAMPLE 7–1

In a liter of a 0.1 M solution, acetic acid was found by conductivity analysis to dissociate into 1.32×10^{-3} g ions ("moles") each of hydrogen and acetate ion at 25°C. What is the acidity or dissociation constant K_a for acetic acid?

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Ionization of Polyprotic Electrolytes.

$$H_3PO_4 + H_2O = H_3O^+ + H_2PO_4^-$$

$$\frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]} = K_1 = 7.5 \times 10^{-3}$$

$$H_2PO_4^- + H_2O = H_3O^+ + HPO_4^{2-}$$

$$\frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} = K_2 = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} + H_2O = H_3O^+ + PO_4^{3-}$$

$$\frac{[H_3O^+][PO_4^{3-}]}{[HPO_4^{2-}]} = K_3 = 2.1 \times 10^{-13}$$

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^-$$

$$K_{b1} = \frac{[HPO_4^{2-}][OH^-]}{[PO_4^{3-}]} = 4.8 \times 10^{-2}$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^-$$

$$K_{b2} = \frac{[H_2PO_4^-][OH^-]}{[HPO_4^{2-}]} = 1.6 \times 10^{-7}$$

$$H_2PO_4^- + H_2O \rightleftharpoons H_3PO_4 + OH^-$$

$$K_{b3} = \frac{[H_3PO_4][OH^-]}{[H_2PO_4^-]} = 1.3 \times 10^{-12}$$

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Ampholytes

$$^+NH_3CH_2COOH + H_2O \rightleftharpoons {}^+NH_3CH_2COO^- + H_3O^+$$

$$^+NH_3CH_2COO^- + H_2O \rightleftharpoons {}^+NH_2CH_2COO^- + H_3O^+$$

Amphoteric compound

$$^+NH_3CH_2COO^- + H_2O \rightleftharpoons {}^+NH_3CH_2COOH + OH^-$$

Zwitterion

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