

Lecture four

4. Acid–Base Equilibria

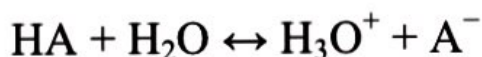
4.1 Acid–Base Theories

Several acid–base theories have been proposed to explain or classify acidic and basic which is applicable only to water. Other theories are more general and are applicable to other solvents or even the gas phase.

We describe the common acid–base theories below :

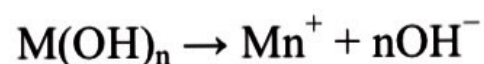
4.1.1 Arrhenius Theory-H⁺ And OH⁻

Arrhenius, as a graduate student, introduced a dramatically new theory that an acid is any substance that ionizes (partially or completely) in water to give hydrogen ions (which associate with the solvent to give hydronium ions, H₃O⁺):



A base ionizes in water to give hydroxide ions. Weak (partially ionized) bases generally ionize as follows: $\text{B} + \text{H}_2\text{O} \leftrightarrow \text{BH}^+ + \text{OH}^-$

while strong bases such as metal hydroxides (e.g., NaOH) dissociate as



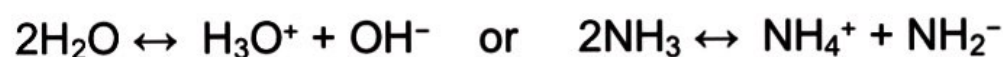
This theory is obviously restricted to water as the solvent.

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4.1.2 Theory of Solvent Systems- Solvent Cations and Anions

Franklin and German's theory is similar to the Arrhenius theory but is applicable also to other ionizable solvents.

In 1905, Franklin was working in liquid NH_3 as solvent and noticed the similarity with acid-base behavior in water. In 1925, Germann, working with liquid COCl_2 as solvent acids and bases. This theory recognizes the ionization of a solvent to give a cation and an anion; for example:



An acid is defined as a solute that yields the characteristic cation of the solvent while a base is a solute that yields the characteristic anion of the solvent.

Cations are ions that are positively charged. Anions are ions that are negatively charged.

4.1.3 Brønsted—Lowry Theory—Taking And Giving Protons

The theory of solvent systems is suitable for ionizable solvents, but it is not applicable to acid–base reactions in nonionizable solvents such as benzene or dioxane. This theory states that an acid is any substance that can donate a proton, and a base is any substance that can accept a proton. Thus, we can write a “half-reaction” a **acid = H^+ + base**

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Table 1 : Example :

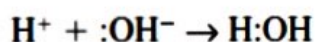
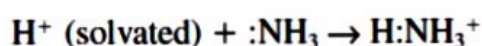
Bronsted Acid–Base Reactions: Conjugate acid base pairs are denoted in the same color

Solvent	Acid ₁	+	Base ₂	→	Acid ₂	+	Base ₁
NH ₃ (liq.)	HOAc		NH ₃		NH ₄ ⁺		OAc ⁻
H ₂ O	HCl		H ₂ O		H ₃ O ⁺		Cl ⁻
H ₂ O	NH ₄ ⁺		H ₂ O		H ₃ O ⁺		NH ₃
H ₂ O	H ₂ O		OAc ⁻		HOAc		OH ⁻
H ₂ O	HCO ₃ ⁻		OH ⁻		H ₂ O		CO ₃ ²⁻
C ₂ H ₅ OH	NH ₄ ⁺		C ₂ H ₅ O ⁻		C ₂ H ₅ OH		NH ₃
C ₆ H ₆	H picrate		C ₆ H ₅ NH ₂		C ₆ H ₅ NH ₃ ⁺		picrate ⁻

4.1.4 Lewis Theory–Taking And Giving Electrons

In the Lewis theory, an acid is a substance that can accept an electron pair and a base is a substance that can donate an electron pair. The latter frequently (base) contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogen-containing substances are included as acids.

Examples of acid–base reactions in the Lewis theory are as follows:



(The Lewis theory assumes a donation (sharing) of electrons from a base to an acid)

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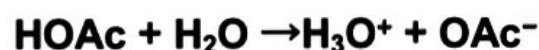
4.2 Acid–Base Equilibria In Water

We see from the above that when an acid or base is dissolved in water, it will dissociate, or ionize, the amount of ionization being dependent on the strength of the acid or the base. A “strong” electrolyte is completely dissociated, while a “weak” electrolyte is partially dissociated. Table 1: lists some common electrolytes, some strong and some weak.

Hydrochloric acid is a strong acid, and in water, its ionization is complete:



Acetic acid¹ is a weak acid, which ionizes only partially in water (a few percent):



¹We shall use the symbol OAc^- to represent the acetate ion $\text{CH}_3\text{—}\overset{\text{O}}{\parallel}\text{C—O}^-$.

Table 1 :

Some Strong Electrolytes and Some Weak Electrolytes

Strong	Weak
HCl	CH_3COOH (acetic acid)
HClO_4	NH_3
H_2SO_4^a	$\text{C}_6\text{H}_5\text{OH}$ (phenol)
HNO_3	HCHO_2 (formic acid)
NaOH	$\text{C}_6\text{H}_5\text{NH}_2$ (aniline)
	CH_3COONa

4.3 Relation between $p[H^+]$ and $p[OH^-]$:

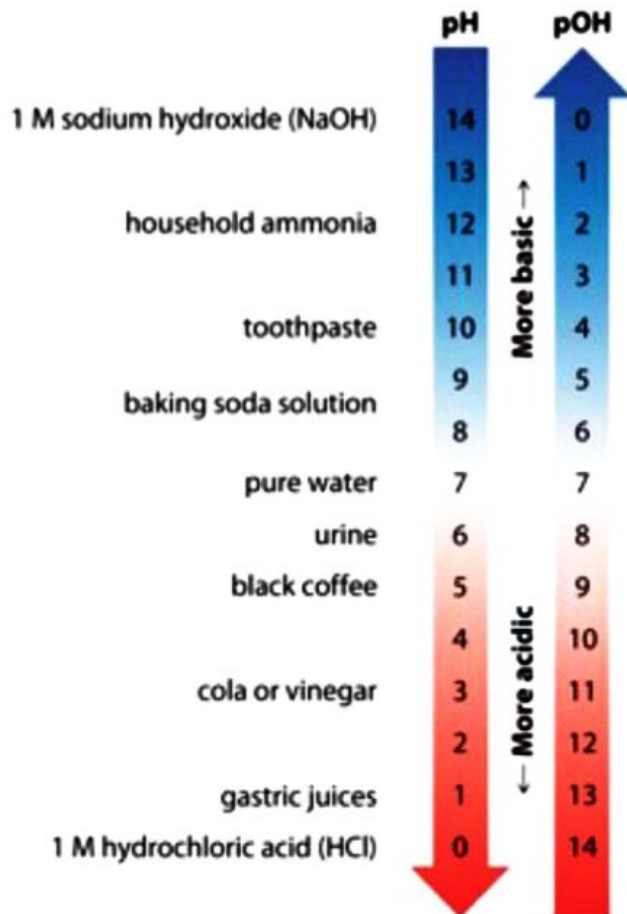
pH vs. pOH scale:

Both acids and bases can be measured using the pH or pOH scale. Both scales provide a measure of either the H^+ concentration or the OH^- concentration.

Notice that each scale shows where acids and bases both are located.

- When acids are measured, the pH is less than 7, but the pOH is greater than 7.
- When bases are measured, the pH is greater than 7, but the pOH is less than 7.

Both scales are dependent on what ion you are measuring.



Acid solutions usually have protons and basic solutions have hydroxide ions. Concentrations of the ions are low (negative power of ten). pH scale is a convenient way of expressing these low concentrations in simple numbers between 1 and 14.

pH is the negative logarithm to the base ten of hydrogen ion concentration in moles per liter. $pH = -\log[H^+]$

p(OH) is the negative logarithm to the base ten of hydroxide ion concentration in moles per liter. $pOH = -\log[OH^-]$

In aqueous solutions, $pH + p(OH) = PK_w = 14$

pH scale is based on neutral water, where $[H^+] = [OH^-] = 10^{-7}$

For a neutral solution $pH = -\log [H^+] = -\log [10^{-7}] = +7$

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Pure water ionizes slightly, or undergoes autoprotolysis :



$$K_w = \frac{[\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{O}]^2} \quad \text{----- (1)}$$

$$[\text{H}_2\text{O}] = 1, [\text{H}_3\text{O}^+] = [\text{H}^+]$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] \quad \text{----- (2)}$$

$$\text{PH} = -\log[\text{H}^+], \text{PH of water} = 7 \quad \text{----- (3)}$$

$$7 = -\log[\text{H}^+]$$

$$[\text{H}^+] = 10^{-\text{PH}} \quad \text{-----(4)}$$

$$[\text{H}^+] = 10^{-7}$$

$$\text{POH} = -\log[\text{OH}^-], \text{POH of water} = 7 \quad \text{-----(5)}$$

$$7 = -\log[\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{POH}} \quad \text{-----(6)}$$

$$[\text{OH}^-] = 10^{-7}$$

$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+]$$

$$K_w = 10^{-7} * 10^{-7}$$

$$K_w = 10^{-14}$$

$$p^{K_w} = -\log [10^{-14}] = 14$$

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Example 1 \ A solution of acetic acid ($\text{CH}_3\text{O}_2\text{H}$) has an H^+ concentration of 5×10^{-5} M. what is the pH of the solution?

Sol. :

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pH} = -\log[5 \times 10^{-5}]$$

= 4.3 , it is relatively weak acid .

Example 2 \ find the pH of a 0.012 M sodium hydroxide (NaOH) solution.

Sol. :

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

$$= -\log [0.012] = 1.92$$

$$\text{pH} + \text{p(OH)} = 14$$

$\text{pH} = 14 - 1.92 = 12.08$, the solution has **pH of 12.08** and is a **strong base**.

Ex/ What is the pH of a 0.0005 M solution of NaOH at 25 °C ?

Solution /



$$[\text{OH}^-] = 0.0005 \text{ M} = 5 \times 10^{-4} \text{ M}$$

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

$$= -\log 5 \times 10^{-4}$$

$$= -\log 5 + 4 \log 10$$

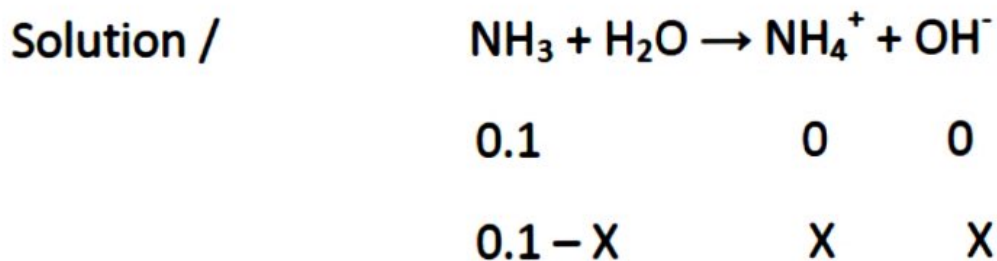
$$= -0.699 + 4$$

$$= 3.301$$

$$\text{pH} = 14 - 3.401 = 10.7$$

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Ex/ What is the pH of a 0.1 M NH_3 solution ? K_b 1.8×10^{-5}



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

$$1.8 \times 10^{-5} = (X)(X) / 0.1 - X$$

$$1.8 \times 10^{-5} = X^2 / 0.1$$

$$X^2 = 1.8 \times 10^{-6}$$

$$X = 1.34 \times 10^{-3} = [\text{OH}^-]$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 1.34 \times 10^{-3} = 2.87$$

$$\text{pOH} + \text{pH} = 14$$

$$\text{pH} = 14 - 2.87 = 11.12$$