# 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 <u>new theory that an</u> **acid** is any substance that ionizes (partially or completely) in water to give hydrogen ions (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$
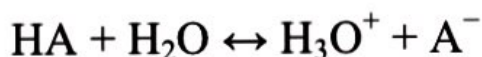
A **base** ionizes in water to give hydroxide ions. Weak (partially ionized) bases generally ionize as follows: $\quad B + H_2O \leftrightarrow BH^+ + OH^-$

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

$$M(OH)_n \rightarrow Mn^+ + nOH^-$$
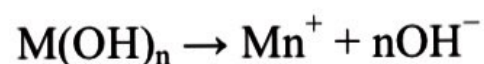
This theory is obviously restricted to water as the solvent.

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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:

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \text{or} \quad 2NH_3 \leftrightarrow NH_4^+ + NH_2^-$$
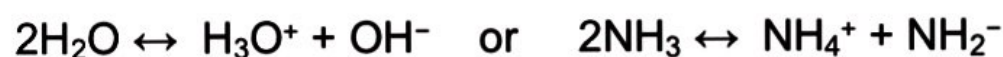
An acid is defined as a solute that yields the characteristic cation of the solvent while a base is a solute that yields the characteristic anion of the solvent.

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 :

Brønsted 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_2O	HCl		H_2O		H_3O^+		Cl^-
H_2O	NH_4^+		H_2O		H_3O^+		NH_3
H_2O	H_2O		OAc^-		HOAc		OH^-
H_2O	HCO_3^-		OH^-		H_2O		CO_3^{2-}
C_2H_5OH	NH_4^+		$C_2H_5O^-$		C_2H_5OH		NH_3
C_6H_6	H picrate		$C_6H_5NH_2$		$C_6H_5NH_3^+$		picrate$^-$

4.1.4 Lewis Theory–Taking And Giving Electrons

In the Lewis theory, <u>an acid is a substance that can accept an electron pair and a base is a substance that can donate an electron pair</u>. 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:

$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H:NH_3^+$$

$$H^+ + :OH^- \rightarrow H:OH$$
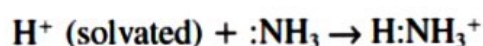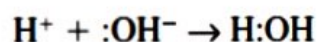
(The Lewis theory assumes a donation (sharing) of electrons from a base to an acid)

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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:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
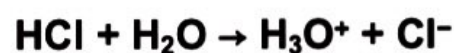
Acetic acid[1] is a weak acid, which ionizes only partially in water (a few percent):

$$HOAc + H_2O \rightarrow H_3O^+ + OAc^-$$

$$\begin{array}{c} O \\ \parallel \end{array}$$
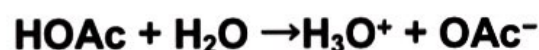
[1] We shall use the symbol OAc^- to represent the acetate ion $CH_3-\overset{\overset{\displaystyle O}{\parallel}}{C}-O^-$.

Table 1 :

Some Strong Electrolytes and Some Weak Electrolytes

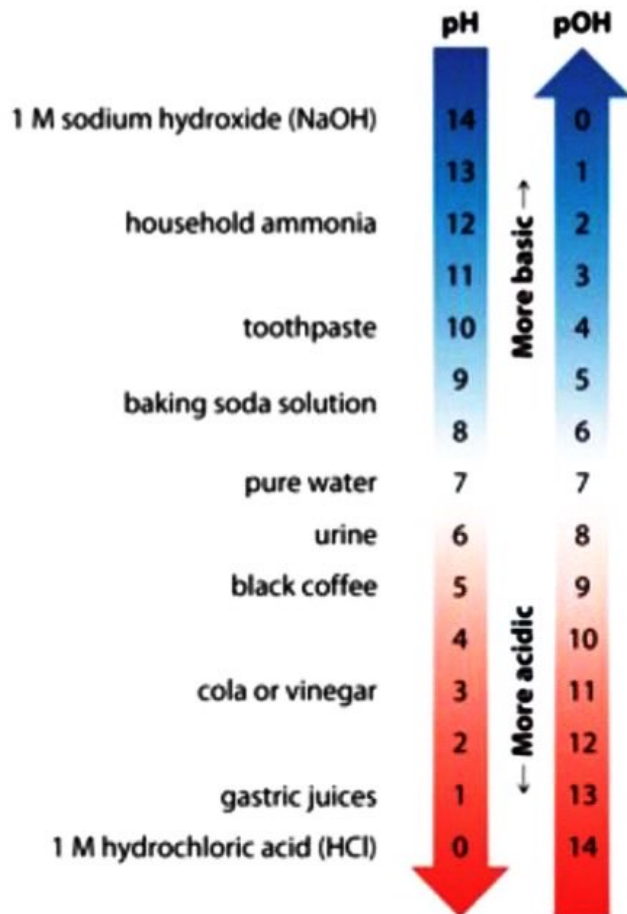| Strong	Weak
HCl	CH_3COOH (acetic acid)
$HClO_4$	NH_3
$H_2SO_4{}^a$	C_6H_5OH (phenol)
HNO_3	$HCHO_2$ (formic acid)
NaOH	$C_6H_5NH_2$ (aniline)
	CH_3COONa

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

pH vs. pOH scale:

Both acids and bases can 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 were 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.

	pH	pOH
1 M sodium hydroxide (NaOH)	14	0
	13	1
household ammonia	12	2
	11	3
toothpaste	10	4
	9	5
baking soda solution	8	6
pure water	7	7
urine	6	8
black coffee	5	9
	4	10
cola or vinegar	3	11
	2	12
gastric juices	1	13
1 M hydrochloric acid (HCl)	0	14

More basic →

← More acidic

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) = PKw= 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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<u>Pure water ionizes slightly, or undergoes autoprotolysis :</u>

$2H_2O \leftrightarrow H_3O^+ + OH^-$

$$K_w = \frac{[OH]^- [H3O]^+}{[H2O]^2} \quad \text{------------ (1)}$$

$[H_2O] = 1$, $[H_3O^+] = [H^+]$

$$K_w = [OH^-][H_3O^+] \quad \text{------------------ (2)}$$

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

$7 = -\log[H^+]$

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

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

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

$7 = -\log[OH^-]$

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

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

$K_w = [OH^-][H_3O^+]$

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

$K_w = 10^{-14}$

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

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Example 1 \\ A solution of acetic acid (CH_3O_2H) has an H^+ concentration of $5x10^{-5}$ M. what is the pH of the solution?

Sol. :

$pH = -log[H^+]$

$pH = -log[5x10^{-5}]$

$= 4.3$, it is relatively weak acid .

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

Sol. :

$pOH = -log[OH^-]$

$= -log [0.012] = 1.92$

$pH + p(OH) = 14$

$pH = 14 - 1.92 = 12.08$, 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 / $NaOH \rightarrow Na^+ + OH^-$

$[OH^=] = 0.0005 M = 5 X 10^{-4} M$

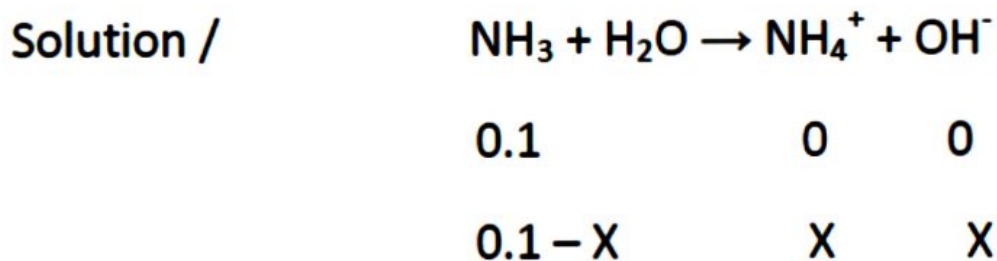$pOH = - log [OH^-]$

$= - log 5 x 10^{-4}$

$= - log 5 + 4 log 10$

$= -0.699 + 4$

$= 3.301$

$pH = 14 - 3.401 = 10.7$

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

Solution / $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

                                      0.1   0   0

                                  0.1 – X   X   X

$$K_b = [NH_4^+] [OH^-] / [NH_3]$$

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

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

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

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

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

$$pOH + pH = 14$$

$$pH \; 14 - 2.87 = 11.12$$

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5.1 Weak Acids and Bases

We have limited our calculations so far to strong acids and bases in which ionization is assumed to be complete. Since the concentration of H+ or OH− is determined readily from the concentration of the acid or base, the calculations are straight forward.

As seen in Equation ($HOAc + H_2O \rightarrow H_3O^+ + OAc^-$), weak acids (or bases) are only partially ionized. While mineral (inorganic) acids and bases such as HCl, $HClO_4$, HNO_3, and NaOH are strong electrolytes that are totally ionized in water.

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Example 1 Calculate the pH and pOH of a 1×10^{-3} M solution of acetic acid $Ka = 1.75 \times 10^{-5}$, as seen in eq. $HOAc + H_2O \leftrightarrow H_3O^+ + OAc^-$.

Solve :

$$K = \frac{[H3O+][OAc-]}{[HOAc]}$$

1)

	HOAc	$\leftrightarrow$	H3O+	+	OAc⁻
initial	$1 * 10^{-3}$		0		0
change	-x		+x		+x
equilibrium	$1 * 10^{-3}$ -x		x		x

$$1.75 \times 10^{-5} = \frac{(x)(x)}{0.001-x}$$

$$1.75 \times 10^{-5} = \frac{x^2}{0.001} \rightarrow x = 1.32 \times 10^{-4} \text{ M} = [H_3O^+]$$

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

$pH = -\log (1.32 \times 10^{-4}) = 4 - \log 1.32 = 4 - 0.12 = 3.88$

$pOH = 14 - pH = 14 - 3.88 = 10.12$

5.2 Salts of Weak Acids and Bases

The salt of a weak acid, for example, NaOAc, is a strong electrolyte, like (almost) all salts, and completely ionizes. In addition the anion of the salt of a weak acid is a **Bronsted base**, which will accept protons.

⇒ **It partially hydrolyzes in water (a Bronsted acid) to form hydroxide ion and the corresponding undissociated acid. For example,**

$$OAc^- + H_2O \leftrightarrow HOAc + OH^- \qquad (1)$$

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The **HOAc** here is undissociated and therefore does not contribute to the pH. This ionization is also known as **Hydrolysis** of the salt ion.
Because it hydrolyzes, sodium acetate is a weak base (the conjugate base of acetic acid). The ionization constant for Equation **(1)** is equal to the basicity constant of the salt anion.

We can write an equilibrium constant:

$$K_H = K_b = \frac{[OH-][HOAc]}{[OAc-]} \qquad (2)$$

K_H : is called the **hydrolysis constant** of the salt and is the same as the basicity constant.
K_b : use to emphasize that these salts are treated the same as for **any other weak base.**

The value of Kb can be calculated from Ka of acetic acid and Kw if we multiply both the numerator and denominator by [H+]:

$$K_b = \frac{[HOAc][OH-]}{[OAc-]} * \frac{[H+]}{[H+]} \qquad (3)$$

Rearrange the equation number (3) to become :

$$K_b = \frac{[HOAc]}{[OAc-][H+]} * [OH^-][H^+]$$

$$[H^+][OH^-] = K_w \qquad (4)$$

$$\frac{[HOAc]}{[OAc-][H+]} = \frac{1}{K_a} \qquad (5)$$

K_a : constant of any weak acid

Substitute Equation No. 4 & 5 into Equation No. 3

$$K_b = \frac{1}{K_a} * K_w$$

$$K_b = \frac{K_w}{K_a} \qquad (6)$$

$$K_w = K_a * K_b \qquad (7)$$

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⇒ **Similar equations can be derived for the <u>cations of salts of weak bases</u>** (the salts are completely dissociated). These are Bronsted acids and ionize (hydrolyze) in water:

$$BH^+ + H_2O \leftrightarrow B + H_3O^+ \qquad (1)$$

BH^+ : **cations of salts of weak bases**.

The B is undissociated and does not contribute to the pH. The acidity constant is :

$$K_H = K_a = \frac{[H3O][B]}{[BH+]} \qquad (2)$$

K_H : is called the **hydrolysis constant** of the salt and is the same as the acidity constant.
K_a : use to emphasize that these salts are treated the same as for **any other weak acid** .

The acidity constant (hydrolysis constant) can be derived by multiplying the numerator and denominator by [OH−]:

$$K_a = \frac{[H3O][B]}{[BH+]} * \frac{[OH-]}{[OH-]} \qquad (3)$$

Rearrange the equation number (3) to become :

$$K_a = \frac{[B]}{[BH+][OH-]} * [H_3O^+][OH^-]$$

$$[H_3O^+][OH^-] = K_w \qquad (4)$$

$$\frac{[B]}{[BH+][OH-]} = \frac{1}{K_b} \qquad (5)$$

K_b : constant of any weak base.

Substitute Equation No. 4 & 5 into Equation No. 3
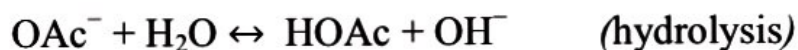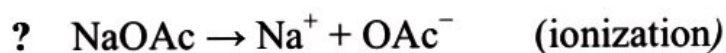
$$K_a = \frac{1}{K_b} * K_w$$

$$K_a = \frac{K_w}{K_b} \qquad (6)$$

$$K_w = K_a * K_b \qquad (7)$$

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Example 2 / Calculate the pH of a 0.10 M solution of sodium acetate. $K_a = 1.75 * 10^{-5}$

? $\quad NaOAc \rightarrow Na^+ + OAc^-$ $\qquad$ (ionization)

$OAc^- + H_2O \leftrightarrow HOAc + OH^-$ $\qquad$ (hydrolysis)

Solution :

$$K_b = \frac{[HOAc][OH-]}{[OAc-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1*10^{-14}}{1.75*10^{-5}} = 5.7 * 10^{-10}$$

	OAc^-	$\leftrightarrow$	$HOAc$	+	OH^-
initial	0.1		0		0
change	-x		+x		+x
equilibrium	0.1 -x		x		x

0.1-x $\cong$ 0.1

$$5.7 \times 10^{-10} = \frac{[HOAc][OH-]}{[OAc-]}$$

$$5.7 \times 10^{-10} = \frac{x * x}{0.1}$$

$x^2 = 0.1 * 5.7 * 10^{-10}$

$x = \sqrt{(0.1 * 5.7 * 10^{-10})} = 7.6 * 10^{-6} M = [OH^-]$

$[H^+][OH^-] = 1 * 10^{-14}$

$[H^+] = (1 * 10^{-14}) / (7.6 * 10^{-6}) = 1.3 * 10^{-9} M$

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

$\quad = -\log 1.3 * 10^{-9} = 9 - 0.11 = 8.89$

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Example 3 / Calculate the pH of a 0.25 M solution of ammonium chloride, $K_b = 1.75 * 10^{-5}$?

$NH_4Cl \rightarrow NH_4^+ + Cl^-$ (ionization)

$NH_4^+ + H_2O \leftrightarrow NH_4OH + H^+$ (hydrolysis)
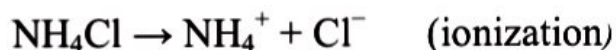
Solution :

$$\frac{[NH4OH][H+]}{[NH4+]} = K_a = \frac{K_w}{K_b}$$

$$K_a = \frac{1*10^{-14}}{1.75*10^{-5}} = 5.7 * 10^{-10}$$

	NH_4^+	$\leftrightarrow$	NH_4OH	+	H^+
initial	0.25		0		0
change	-x		+x		+x
equilibrium	0.25 -x		x		x

0.25-x $\cong$ 0.25

$$K_a = \frac{[NH4OH][H+]}{[NH4+]} \rightarrow 5.7 * 10^{-10} = \frac{x^2}{0.25}$$

$X^2 = 0.25 * 5.7 * 10^{-10}$

$X = \sqrt{(0.25 * 5.7 * 10^{-10})} = 1.2 \times 10^{-5} M = [H^+]$

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

$pH = -\log 1.2 \times 10^{-5}$

$pH = 5-0.08 = 4.92$