Al-Mustaqbal-College University<br>Chemical Engineering and Petroleum<br>Industry Department<br>Analytical chemistry<br>First class / first term<br>Lecture Four<br>Acid-Base Equilibria By

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## 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- $\mathrm{H}^{+}$And $\mathrm{OH}^{-}$

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, $\mathrm{H}_{3} \mathrm{O}^{+}$):

$$
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-}
$$

A base ionizes in water to give hydroxide ions. Weak (partially ionized) bases generally ionize as follows: $\quad \mathrm{B}+\mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{BH}^{+}+\mathrm{OH}^{-}$ while strong bases such as metal hydroxides (e.g., NaOH ) dissociate as $\mathrm{M}(\mathrm{OH})_{\mathrm{n}} \rightarrow \mathrm{Mn}^{+}+\mathrm{nOH}^{-}$

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 $\mathrm{NH}_{3}$ 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:
$2 \mathrm{H}_{2} \mathrm{O} \leftrightarrow \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{OH}^{-} \quad$ or $\quad 2 \mathrm{NH}_{3} \leftrightarrow \mathrm{NH}_{4}^{+}+\mathrm{NH}_{2}^{-}$

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.

### 4.1.3 Bronsted—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 $=\mathbf{H}^{+}+$base

## Table 1 : Example :

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

| Solvent | Acid $_{1}$ | + | Basc $_{2}$ | $\rightarrow$ | Acid $_{2}$ | + | Basc $_{1}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathrm{NH}_{3}$ (liq.) | HOAc |  | $\mathrm{NH}_{3}$ |  | $\mathrm{NH}_{4}{ }^{+}$ |  | $\mathrm{OAc}^{-}$ |
| $\mathrm{H}_{2} \mathrm{O}$ | HCl |  | $\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{H}_{3} \mathrm{O}^{+}$ |  | $\mathrm{Cl}^{-}$ |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{NH}_{4}{ }^{+}$ |  | $\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{H}_{3} \mathrm{O}^{+}$ |  | $\mathrm{NH}_{3}$ |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{OAc}^{-}$ |  | HOAc |  | $\mathrm{OH}^{-}$ |
| $\mathrm{H}_{2} \mathrm{O}$ | $\mathrm{HCO}_{3}{ }^{-}$ |  | $\mathrm{OH}^{-}$ |  | $\mathrm{H}_{2} \mathrm{O}$ |  | $\mathrm{CO}_{3}{ }^{2-}$ |
| $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ | $\mathrm{NH}_{4}{ }^{+}$ |  | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{O}^{-}$ |  | $\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}$ |  | $\mathrm{NH}_{3}$ |
| $\mathrm{C}_{6} \mathrm{H}_{6}$ | H picrate |  | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}$ |  | $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{3}{ }^{+}$ |  | picrate ${ }^{-}$ |

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### 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 contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogencontaining substances are included as acids. Examples of acid-base reactions in the Lewis theory are as follows:

$$
\begin{gathered}
\mathrm{H}^{+}(\text {solvated })+: \mathrm{NH}_{3} \rightarrow \mathrm{H}: \mathrm{NH}_{3}^{+} \\
\mathrm{AlCl}_{3}+: \mathrm{O}_{\mathrm{R}}^{\mathrm{R}} \rightarrow \mathrm{Cl}_{3}{\mathrm{Al}: \mathrm{OR}_{2}}_{\mathrm{O}}^{\mathrm{O}}+\mathrm{H}^{+} \rightarrow \mathrm{H}_{2} \mathrm{O}: \mathrm{H}^{+} \\
\mathrm{H}^{+}+: \mathrm{OH}^{-} \rightarrow \mathrm{H}: \mathrm{OH}
\end{gathered}
$$

(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 2 lists some common electrolytes, some strong and some weak.

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

## $\Rightarrow$ Relation between $\mathrm{p}\left[\mathrm{H}^{+}\right]$and $\mathrm{p}\left[\mathrm{OH}^{-}\right]$:

pH vs. pOH scale:

|  | pH |  | pOH |
| :---: | :---: | :---: | :---: |
| 1 M sodium hydroxide ( NaOH ) | 14 |  | 0 |
|  | 13 | $\uparrow$ | 1 |
| household ammonia | 12 | $\stackrel{\square}{n}$ | 2 |
|  | 11 | 今0 | 3 |
| toothpaste | 10 | 흘 | 4 |
| baking soda solution | 9 |  | 5 |
|  | 8 |  | 6 |
| pure water | 7 |  | 7 |
| urine | 6 |  | 8 |
| black coffee | 5 |  | 9 |
|  | 4 | 는 | 10 |
| cola or vinegar | 3 | ¢ | 11 |
|  | 2 | ¢ | 12 |
| gastric juices | 1 | $\downarrow$ | 13 |
| 1 M hydrochloric acid (HCl) | 0 |  | 14 |

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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.
$\mathbf{p H}=-\log \left[\mathbf{H}^{+}\right]$
$\mathrm{p}(\mathrm{OH})$ is the negative logarithm to the base ten of hydroxide ion concentration in moles per liter.
$\mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]$
In aqueous solutions, $\mathbf{p H}+\mathbf{p}(\mathbf{O H})=14$.
pH scale is based on neutral water, where $[\mathrm{H}+]=[\mathbf{O H}-]=\mathbf{1 0 - 7}$
For a neutral solution $\mathbf{p H}=-\log [\mathrm{H}+]=-\log [10-7]=+7$
Finding $\mathbf{p}[\mathrm{OH}]=-\log \left[\mathrm{OH}^{-}\right] \quad, \quad \mathbf{p H}=14-\mathbf{p O H}$
Finding $[\mathrm{OH}]$ in bases :
$\mathbf{p H}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$
$1 \times 10^{-14}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]$

Example $1 \backslash$ A solution of acetic acid $\left(\mathrm{CH}_{3} \mathrm{O}_{2} \mathrm{H}\right)$ has an $\mathrm{H}^{+}$concentration of $5 \times 10^{-5} \mathrm{M}$. what is the pH of the solution?
Sol. :
$\mathbf{p H}=-\log \left[\mathbf{H}^{+}\right]$
$\mathrm{pH}=-\log \left[5 \times 10^{-5}\right]$
$=4.3$, it is relatively weak acid .

