Ionic equilibrium   الاتزان الأيوني

It is the dynamic equilibrium established between the unionized molecules and the ions released by weak electrolytes in their solutions.

هو التوازن الديناميكي القائم بين الجزيئات الغير متأينة والايونات التي تطلقها الالكتروليتات الضعيفة في محاليلها.

Materials in their aqueous solution classified into two types: electrolytes and non-electrolytes.
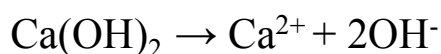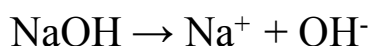
المواد في محاليلها المائية تقسم الى نوعين: الكتروليتية ولاالكتروليتية.

Electrolytes divided into

A. Strong electrolytes:

Solutes that are completely ionized in their aqueous solutions. These electrolytes are conduct electricity well, high solubility, such as strong acids, strong bases and many salts.

الالكتروليتات القوية هي المواد التي تتأين تماما في محاليلها المائية. هذه الالكتروليتات هي موصلات جيدة للتيار الكهربائي، ذوبانيتها عالية، مثل هذه المواد الأحماض القوية ،القواعد القوية والعديد من الاملاح.

$$H_2O$$

$$HCl \rightarrow H^+ + Cl^-$$
$$NaOH \rightarrow Na^+ + OH^-$$
$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$
$$NaCl \rightarrow Na^+ + Cl^-$$

B. Weak electrolytes:

Solutes that are partially ionized in their aqueous solutions. They exist as a mixture of ions and un-ionized molecules in solution and there is a balance between the forward and reverse reactions (reaching ionic equilibrium). These electrolytes conduct electricity weakly, such as weak acids and bases.

الالكتروليتات الضعيفة هي المواد التي تتأين جزئيا في محاليلها المائية. هذه الالكتروليتات ضعيفة التوصيل للتيار الكهربائي مثل هذه المواد الأحماض الضعيفة ،القواعد الضعيفة.

$$H_2O$$

$$HCN \rightleftharpoons H^+ + CN^-$$
$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
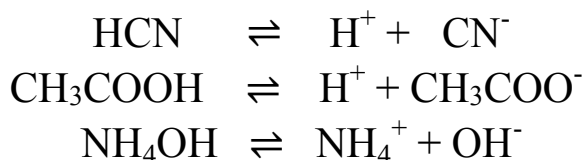
Non-electrolytes materials:

These are the materials that do not release any ions in their aqueous solutions such as ethanol or glucose.

المواد اللاالكتروليتية هي المواد التي لا تحرراي ايون في محاليلها المائية مثل هذه المواد الايثانول او سكر الكلوكوز.

$$H_2O$$

$$C_2H_5OH \rightleftharpoons C_2H_5OH$$
$$Glucose \rightleftharpoons Glucose$$
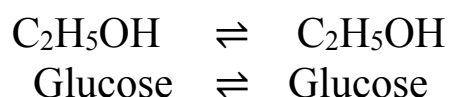
## *Acids and bases*   الحوامض والقواعد

There are different definitions (concepts) of acids and bases, each useful in their particular situations.

هناك تعاريف (مفاهيم) مختلفة للأحماض والقواعد، كل منها مفيدة في السياقات الخاصة بهم.

1. Arrhenius concept

Acid is a substance that ionized in water to give hydrogen ions (or hydronium ions), while base is a substance that ionized in water to give hydroxide ions.

وفقا لمبدأ أرهينيوس فان الحامض هو المادة التي تتأين في الماء لتعطي أيونات الهيدروجين (أو أيونات الهيدرونيوم)، بينما القاعدة فهي المادة التي تتأين في الماء لتعطي أيونات الهيدروكسيد.

$$HCl \rightarrow H^+ + Cl^-$$
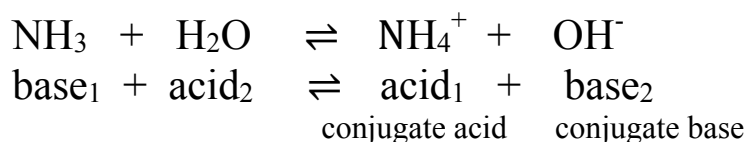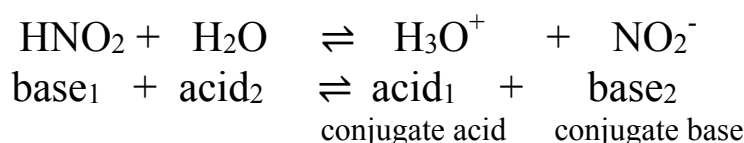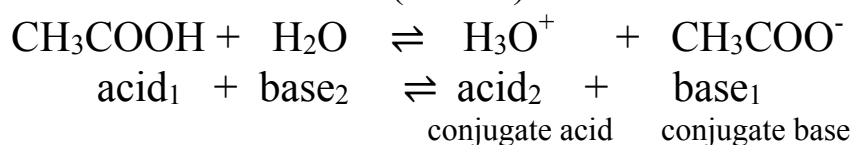
$$NaOH \rightarrow Na^+ + OH^-$$
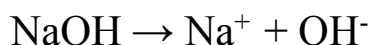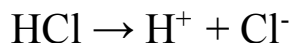
2. Brønsted and Lowry concept

Acid is any substance that is capable of donating proton, while base is any substance can accept a proton.

حسب مبدأ برونشتيد-لوري فان الحامض هو اي مادة لها القدرة على منح البروتون، بينما القاعدة فهي المادة التي لها القدرة على اكتساب البروتون.

An acid donates protons only in the presence of a proton acceptor (a base). Likewise, a base accepts protons only in the presence of a proton donor (an acid). An important feature of the Brønsted-Lowry concept is the conjugate acids and bases. A conjugate base (base$_1$) is formed when an acid (acid$_1$) loses a proton. A conjugate acid (acid$_2$) is formed when a base (base$_2$) accepts a proton.

الحامض يهب البروتونات فقط بوجود متقبل البروتون (القاعدة). وبالمثل، القاعدة لاتتقبل البروتونات إلا بوجود مانح البروتون (الحامض). سمة هامة لمفهوم برونشتد-لوري هي متقارنة الأحماض والقواعد. تتكون القاعدة القرينة عندما يفقد الحامض (حامض1) بروتونا. ويتكون الحامض القرين عندما تتقبل القاعدة (القاعدة2) بروتونا.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
$$acid_1 + base_2 \rightleftharpoons acid_2 + base_1$$
$$\text{conjugate acid} \quad \text{conjugate base}$$

$$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$$
$$base_1 + acid_2 \rightleftharpoons acid_1 + base_2$$
$$\text{conjugate acid} \quad \text{conjugate base}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
$$base_1 + acid_2 \rightleftharpoons acid_1 + base_2$$
$$\text{conjugate acid} \quad \text{conjugate base}$$

Note: The conjugate acid of water is the hydrated proton written as H_3O^+. This species is called hydronium ion, and it consists of a proton covalently bonded to a single water molecule.

From the last two equations, we consider water as amphiprotic solvent because it exhibits both acidic and basic properties.

يعتبر الماء مذيب امفوتيري لكونه يمتلك الخواص الحامضية والقاعدية.

After an acid has donate a proton the species that remains is capable of accepting proton to reform the original acid then every acid is paired with its corresponding base which is called as conjugate base.

بعد ان يفقد الحامض البروتون فانه يتحول الى صنف قادر على اكتساب بروتون ليعيد تكوين الحامض الاصلي، وكل حامض يقترن مع القاعدة المعنية والتي تدعى بالقاعدة القرينة.

3. Lewis concept

Acid is any material capable of accepting pair of electrons such as $AlCl_3$, BF_3 and base is any substance can donate pair of electrons such as F^-, NH_3.

حسب مفهوم لويس فان الحامض هو اي مادة لها القابلية على تقبل زوج الكتروني والقاعدة هي اية مادة لها القابلية على منح زوج الكتروني.

$$BF_3 + :NH_3 \rightarrow F_3B:NH_3$$
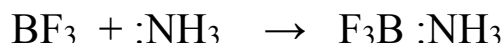
Ion product constant of water   ثابت الحاصل الايوني للماء

Aqueous solutions contain small concentrations of hydronium and hydroxide ions (which are strongly contacted to water molecules) as a result of the dissociation reaction:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
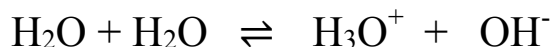
المحاليل المائية تحتوي على تراكيز صغيرة من ايوني الهيدرونيوم والهيدروكسيد (اللذان يرتبطان بقوة مع جزيئات الماء) كنتيجة لتفاعل التفكك المذكور.

Applying mass action law, an equilibrium constant (K) for this reaction can be written as shown in the following equation:

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

The concentration of water in dilute aqueous solutions is enormous (molar concentration of water equal to 55.5 M), however, when compared with the concentration of hydronium and hydroxide ions. As a result, $[H_2O]^2$ in the equation can be taken as constant, and we write:

تركيز الماء في المحاليل المائية المخففة كبير جدا مقارنة بتراكيز ايونات الهيدرونيوم والهيدروكسيد، نتيجة لذلك يمكن اعتبار تركيز الماء في المعادلة اعلاه قيمة ثابتة فيكون:

$$K \, [H_2O]^2 = K_w = [H_3O^+][OH^-]$$

or $K_w = [H^+][OH^-]$

Where the constant Kw is the **ion-product constant** for water, and by using water concentration:

$$K \, (55.5)^2 = K_w = 1.008 \times 10^{-14} \quad \text{at } 25°C.$$

The approximation at room temperature is $K_w \approx 1.00 \times 10^{-14}$.

K_w depending on temperature (i.e. increasing with the increase in temperature), for example at (50°C) $K_w = 5.47 \times 10^{-14}$ and at (100°C) $K_w = 49.0 \times 10^{-14}$.

The ion-product constant for water permits us to easily find the hydronium and hydroxide ion concentrations of aqueous solutions.

ثابت الحاصل الأيوني للماء يتيح لنا سهولة حساب تركيز ايونات الهيدرونيوم والهيدروكسيد في المحاليل المائية.

For pure water:

$$K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$$

$$[H^+] = [OH^-] = \sqrt{K_w} \Rightarrow\Rightarrow\Rightarrow [H^+] = [OH^-] = 1.00 \times 10^{-7} \text{ M}$$

By taking the logarithm of the ion product equation:

$$-\log K_w = -\log [H^+][OH^-]$$

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

By the definition of p-function (pX= -log [X]):

$$\mathbf{pK_w = pH + pOH = 14}$$

if pH < 7 then the solution is acidic.

if pH > 7 then the solution is basic.

If pH = 7 then the solution is neutral.

Ex. 1 Calculate the hydronium and hydroxide ion concentrations of pure water at 25°C and 100°C (at (25°C) $K_w = 1.00 \times 10^{-14}$ and at (100°C) $K_w = 49.0 \times 10^{-14}$).

Because OH^- and H_3O^+ are formed only from the dissociation of water, their concentrations must be equal:

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

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

$[H_3O^+] = [OH^-] = \sqrt{K_w}$

at 25°C: $[H_3O^+] = [OH^-] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7}$

at 100°C: $[H_3O^+] = [OH^-] = \sqrt{49.0 \times 10^{-14}} = 7.00 \times 10^{-7}$

Ex. 2 Calculate the pH and pOH values of a solution in which $[H_3O^+]$ is 0.002 M.

$[H_3O^+] = [H^+]$

pH = -log $[H^+]$ = -log (2×10^{-3}) = 2.699

pH + pOH = 14 $\Rightarrow\Rightarrow\Rightarrow$ pOH = 14 - pH

$\qquad\qquad\qquad\qquad$ = 14 - 2.699 = 11.301

Applying acid-base dissociation constants:

تطبيق ثوابت تفكك حامض-قاعدة

Calculation of hydronium and hydroxide ions concentrations for strong acids and bases and weak acids and bases are illustrated as follow:

1- Strong acids and strong bases

The strong acids will completely ionized in their aqueous solution as shown in the general equation:

$$HA \rightarrow H^+ + A^-$$

Therefore $[H^+] = [A^-]$

Ex. 1 Calculate $[H^+]$ and pH of 0.01 M HCl solution.

$$HCl \rightarrow H^+ + Cl^-$$

	HCl	H⁺	Cl⁻
before ionization	0.01	0.0	0.0
after ionization	0.0	0.01	0.01

$[H^+] = 0.01 M$

$pH = -\log [H^+] = -\log 0.01 = 2.0$

Ex. 2 Calculate pH and pOH of 0.15 M H_2SO_4 solution.

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

	H_2SO_4	$2H^+$	SO_4^{2-}
before ionization	0.15	0.0	0.0
after ionization	0.0	2x0.15	0.15

$[H^+] = 2 \times 0.15 M = 0.3 M$

$pH = -\log [H^+] = -\log 0.3 = 0.523$

$pK_w = pH + pOH = 14 \Rightarrow\Rightarrow pOH = 14 - 0.523 = 13.477$

The strong bases will completely ionized in their aqueous solution and represented by one arrow in the reaction equation. For example:

$$NaOH \rightarrow Na^+ + OH^-$$
$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Ex. Calculate $[H^+]$ and $[OH^-]$ in 0.2 M aqueous NaOH solution.

	NaOH	→	Na^+	+	OH^-
before ionization	0.2		0.0		0.0
after ionization	0.0		0.2		0.2

$[OH^-] = 0.2$ M

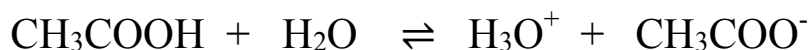$[H^+] = K_w / [OH^-]$

$= 1.00 \times 10^{-14} / 0.2 = 5.00 \times 10^{-14}$ mole/L

Exercise. Calculate pH and pOH of 0.15 M $Ca(OH)_2$ solution.

2- Weak acids and weak bases

The weak acids (as well as weak bases) will partially ionized in their aqueous solution and represented by an equilibrium arrow ($\rightleftharpoons$) in their reaction equation, so ionic equilibrium is occurring.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$

$$K_a = \frac{a\ H_3O^+ .\ a\ CH_3COO^-}{a\ CH_3COOH\ .\ a\ H_2O}$$

$a = c\ .\ f$ for dilute solutions $f = 1$, then

$$K_a = \frac{[H_3O^+]\ [CH_3COO^-]}{[CH_3COOH]\ [H_2O]}$$

$$K_a = \frac{[H_3O^+]\ [CH_3COO^-]}{[CH_3COOH]}\ ,\ \text{since } [H_2O] = \text{constant}$$

K_a is a ratio between the ionized and unionized parts of the weak acid, and called acid ionization constant or acid dissociation constant. K_a is a constant only if temperature and pressure are constant.

In an analogous way, the base dissociation constant for ammonia is:

K_a يمثل النسبة بين الجزء الذائب الى الجزء غير الذائب من الحامض الضعيف ويدعى ثابت تأين او تفكك الحامض وهو ثابت بثبوت درجة الحرارة والضغط .

بطريقة مماثلة فان ثابت تفكك القاعدة للأمونيا هو:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$
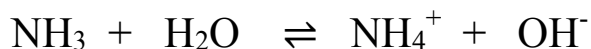
$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]}\ ,\quad \text{since } [H_2O] = \text{constant}$$

Ex. 1 Calculate $[H^+]$, pH and pOH of 0.01 M CH_3COOH at 25 °C ($K_a = 1.8 \times 10^{-5}$)

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

before ionization   0.01   0.0   0.0

after ionization   0.01- X   X   X

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} = \frac{(X)(X)}{(0.01 - X)}$$

X in the denominator (المقام) is small value and hence it neglected

$1.8 \times 10^{-5} = X^2 / 0.01 \Rightarrow\Rightarrow\Rightarrow X^2 = \sqrt{1.8 \times 10^{-7}}$

$X = [H^+] = 4.242 \times 10^{-4}$ mole/L

$pH = -\log[H^+] = -\log 4.242 \times 10^{-4} = 3.372$

$pOH = 14 - pH = 14 - 3.372 = 10.628$

Ex. 2 Calculate $[OH^-]$, pH and pOH of 0.1 M ammonia solution at 25 °C ($K_b = 1.8 \times 10^{-5}$)

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

before ionization   0.1   0.0   0.0

after ionization   0.1- X   X   X

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5} = \frac{(X)(X)}{(0.1 - X)}$$

X in the denominator (المقام) is small value and hence it neglected
$1.8 \times 10^{-5} = X^2 / 0.1 \Rightarrow\Rightarrow\Rightarrow X^2 = \sqrt{1.8 \times 10^{-6}}$

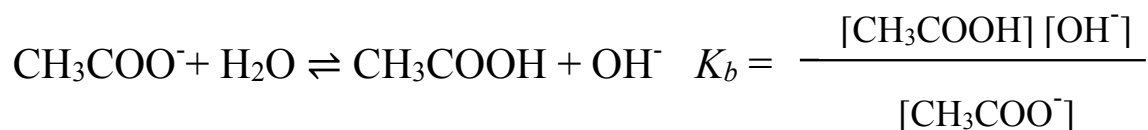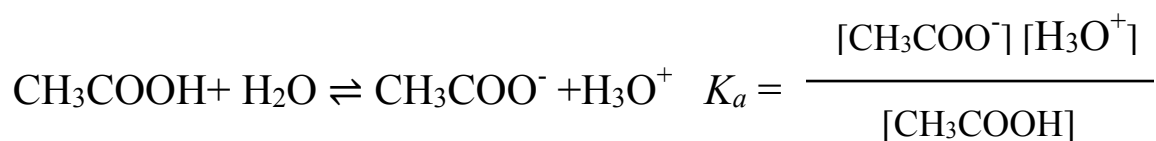$X = [OH^-] = 1.342 \times 10^{-3}$ mole/L

$pOH = -\log[OH^-] = -\log 1.342 \times 10^{-3} = 2.872$

$pH = 14 - pOH = 14 - 2.872 = 11.128$

Equilibrium constant for conjugate acid-base pairs:

<div dir="rtl">

ثابت الأتزان لمزدوج حامض ـ قاعدة

</div>

The general relationship for all conjugate acid/base pairs is obtained by multiplying one equilibrium-constant expression by the other for the pairs.

Consider the acid dissociation-constant expression for acetic acid and the base dissociation constant expression for its conjugate base, acetate ion:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+ \qquad K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^- \qquad K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

$$K_a\,K_b = \frac{[\cancel{CH_3COO^-}][H_3O^+]}{[\cancel{CH_3COOH}]} \quad \times \quad \frac{[\cancel{CH_3COOH}][OH^-]}{[\cancel{CH_3COO^-}]}$$
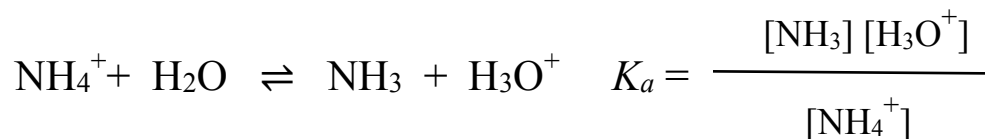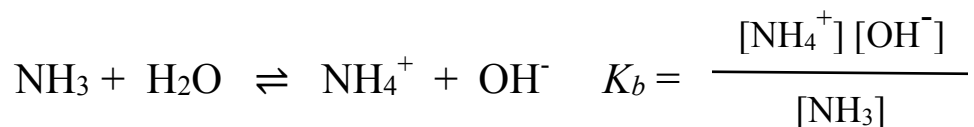
but

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

Therefore

$$\boldsymbol{K_w = K_a\,K_b}$$

In an analogous way, the base equilibrium constant for conjugate acid-base pairs of the ammonia is:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+ \quad K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$K_a\,K_b = \frac{[\cancel{NH_3}][H_3O^+]}{[\cancel{NH_4^+}]} \quad \times \quad \frac{[\cancel{NH_4^+}][OH^-]}{[\cancel{NH_3}]}$$

but

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

Therefore

$$\boldsymbol{K_w = K_a\,K_b}$$

This relationship is general for all conjugate acid/base pairs.