$$[NH_4^+] + [H_3O^+] = [Cl^-] + [OH^-]$$

$$[NH_4^+] = [Cl^-] = \frac{V\ {}_aV_a}{{}_aC + V_b}$$

$$[NH_4OH]_{rem} = [NH_4OH]\ - [NH_4^+]$$

$$[NH_4O\underset{H}{\ \ }]_{rem} = \frac{C_bV_b}{V_a + V_b} - \frac{C_aV_a}{V_a + V_b}$$

$$[NH_4OH]\ = \frac{C_bV_b - C_aV_a}{V_a + V_b}$$

$$pH = pKa + \ \log\frac{C_bV_b - C_aV_a}{C_aV_a}$$

At half-neutralisation:

$$[NH_4OH]_{\ rem} = [NH_4^+]_{formed}$$

⇨ $pH = pKa$

c- At neutralisation :**$V_a = V_N$**

$C_aV_a = C_bV_b$

$$(H_3O^+, Cl^-) + (NH_4^+, OH^-) \xrightarrow{\qquad\qquad} (NH_4^+, Cl^-) + 2H_2O$$

The salt (NH_4^+, OH^-) originates from a strong acid and a weak base=> weakly acidic salt

=> Hydrolyzable salt.

The hydrolysis reaction $NH_4^+ + H_2O \ \ === \ \ NH_3 + H_3O^+$

Acidity increases, pH decreases.

$$pH = \frac{1}{2}pKa - \ \frac{1}{2}\log C_{salt}$$

d- After neutralisation : **$V_a > V_N$** the acid is in excess

$C_aV_a > C_bV_b$

$$n_{H_3O^+ex} = C_aV_a - C_bV_b \Rightarrow [H_3O^+] = \frac{C_aV_a - C_bV_b}{V_a + V_b}$$

$$pH = -log\frac{C_aV_a - C_bV_b}{V_a + V_b}$$

IX- Buffer solutions:

A buffer solution is an ionic solution whose pH varies upon the addition of an acid or a base, or by dilution ($+H_2O$). The medium is also said to be buffered.

In both cases, the areas corresponding to an excess of acid or an excess of base, the pH curve is almost horizontal. The pH value is almost constant in (only) one such mixture the pH is always that of the acid and its conjugate base

$pH = pk + log\frac{[Base]}{[Acid]}$

A (solution) dilution ($+H_3O^+$) decreases the concentration of the acid; its conjugate base will decrease in the same proportions. Therefore, the ratio $\frac{[Base]}{[Acid]}$ remains constant. As a result, the pH does not vary due to dilution.

Let d $[A^-]$ and d [HA] of the base and the acid: - d $[A^-]$ = d [HA].

$d\,(pH) = \frac{d[A^-]}{[A^-]} - \frac{d[HA]}{[HA]} = d(\frac{1}{[A^-]} + \frac{1}{[HA]})$

The buffer capacity, denoted as $\beta = \frac{dn}{dpH}$

dpH :change in pH of the solution caused by the addition of dn millimoles of strong acid or strong base. It is generally accepted that a solution is considered buffered if T (β)> 10.

Importance

Acids and bases play an important role in many chemical, biological, and industrial processes. They are essential in :

- **Digestion**: Hydrochloric acid in the stomach helps digest food.
- **Batteries**: Acids like sulfuric acid are used in car batteries.
- **Manufacturing**: Bases like sodium hydroxide are used in the production of soaps and paper.

Examples:

- **Sodium hydroxide (NaOH)**: Used in the production of soaps and detergents.
- **Ammonia (NH_3)**: Used in household cleaners and as a fertilizer.
- **Calcium hydroxide ($Ca(OH)_2$)**: Used in water treatment and as a liming agent.

X- Application Exercise

Exercise N° 01:

a) The pH of human blood is 7.3, and that of a dog is 6.9. What are the respective concentrations of H_3O^+ and OH^- ions?

b) Consider a barium hydroxide $Ba(OH)_2$ solution with a pH of 12.7. What is the molarity of this strong base?

c) Consider a commercial vinegar containing 30g of acetic acid CH_3COOH per liter of solution.

1- Calculate the pH of this vinegar knowing that the pKa of acetic acid is 4.75.

2- What volume of a 1.8 M sulfuric acid solution would be needed to prepare one liter of an aqueous solution of this acid with the same pH as the vinegar?

Exercise N°02:

a) Determine the pH of the following solutions: 0.1M NaOH, 0.1M HCl, 0.01M H_2SO_4, and 0.1M $Ca(OH)_2$.

b) Calculate the pH of a 0.01 mole/L HF solution. Deduce the value of the dissociation coefficient given that pKa = 3.2.

Exercise N° 03:

a) Determine the molarity of an acetic acid solution ionized at 2% (Ka = 1.8 x 10^-5) at 25°C. What are the concentrations of the different species present in the solution? b) Calculate the pH using two methods.

Exercise N° 04:

a) Calculate the dissociation coefficient and the pH of a 0.1M ammonia solution with a pKb of 4.75.

b) To one liter of the previous solution, an equal volume of water is added. Calculate the new ionization coefficient and the pH.

Exercise N° 05:

Calculate the pH of the following 0.01M salt solutions: NaCl, Na_2SO_4, CH_3COONa, NH_4Cl, NH_4CN. The respective pKa values for acetic acid, ammonium ion, and hydrocyanic acid are given: 4.75, 9.25, and 9.4.

Solution

Solution 01:

a) $PH = 7,3 = -\log [H_3O^+] \Rightarrow \log [H_3O^+] = -7,3 = -8 + 0,7$

$[H_3O^+] = 10^{-8} \times 10^{0,7} = 5\ 10^{-8}$ mole/l.

$[H_3O^+]\ [OH^-] = 10^{-14} \Rightarrow [OH^-] = \frac{10^{-14}}{5\ 10^{-8}} = 2\ 10^{-7}$ mole/l.

PH = 6,9 => $[H_3O^+]$ = 1,26 10^{-7} mole/l ; $[OH^-]$ =7,93 10^{-8} mole/l.

b) $Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$ Soit C= $[OH^-]$

$[H_3O^+]\,[OH^-] = 10^{-14}$ => log $([H_3O^+]\,[OH^-])$ = 14 $\boxed{PH = 14 + \log C}$

log C = 14 + 12,7 = -1,3 = -2 + 0,7 => C = $[OH^-]$ = 5 10^{-2} N.

Since 1 mole of $Ba(OH)_2$ releases 2 gram equivalents of OH^- ions, the molarity of the solution is: $M = \frac{C}{\text{nbre eq.g}} = [Ba(OH)_2] = \frac{5\,10^{-2}}{2} = 2{,}5\ 10^{-2}$ M.

c)

- CH_3COOH: M = 60g/mole => $C = \frac{30}{60}$ = 0,5 mole/l = 0,5 M.

pH = ½ (pka – log C) ; for vinegar pH = ½ (4,75 – log 0,5) = 2,52

- H_2SO_4 strong acid: pH = - log C => C = 310^{-3} M

H_2SO_4 initial for normality 1,8 x 2 = 3,6 N.

So, it all comes down to a dilution problem.

$C_{initial}$ x $V_{initial}$ = C_{final} x V_{final}

3,6 x V = 3 10^{-3} x1000 => $V = \frac{3}{3{,}6}$ = 0,83 ml.

Solution 02:

- $NaOH_{(S)} \longrightarrow NaOH_{(L)} \longrightarrow Na^+ + OH^-$ (strong base), $C_O = 10^{-1}M = 10^{-1}N$

pOH = -log $[OH^-]$ = -log C_0 = -log 10^{-1} = 1

pH + pOH = 14 => pH = 14 – pOH => pH = 14 – 1 = 13

- $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$ (strong Acide), $C_0 = 10^{-1}M = 10^{-1}N$

pH = -log $[H_3O^+]$ = -log C_0 = -log 10^{-1} = 1

- $H_2SO_4 + H_2O \underset{2}{\overset{1}{\rightleftarrows}} SO_4^{2+} + 2H_3O^+$ (Acide forte), $C_0 = 10^{-2}M$

pH = -log $[H_3O^+]$ = -log 2 C_0 = -log 2 10^{-2} = 1,70

- $Ca(OH)_4 \rightleftarrows Ca^{2+} + 2OH^-$, $C_O = 10^{-1}M$

$pOH = -\log [OH^-] = -\log 2\ C_0 = -\log 2\ 10^{-1} = 0{,}70 \Rightarrow PH = 13{,}3.$

a) Hydrofluoric Acid HF:

$$\begin{cases} HF + H_2O \rightleftarrows H_3O^+ + F^- \\ 2H_2O \rightleftarrows H_3O^+ + OH^- \end{cases}$$

$K_a = \frac{[H_3O^+][F^-]}{[HF]}$

$pH = \frac{1}{2}\ pK_a - \frac{1}{2} \log C_0$ (Weak acid).

$pH = \frac{1}{2}\ 3{,}2 - \frac{1}{2} \log 10^{-2} = 2{,}60.$

$pH = -\log [H_3O^+] = -\log C_0\ \alpha = 10^{-pH} \Rightarrow \alpha = \frac{10^{-pH}}{C_0} = \frac{10^{-2{,}60}}{10^{-2}} = 10^{-0{,}60} \Rightarrow \alpha = 0{,}251$

(we can not neglect α).

$K_a = \frac{C_0\alpha^2}{1-\alpha}$ if $\alpha \ll 1 \Rightarrow K_a\ (1-\alpha) = C_0\ \alpha^2 \Rightarrow \alpha^2 = (\frac{K_a}{C_0})^{1/2} = (\frac{10^{-3{,}2}}{10^{-2}})^{1/2}$

$\alpha = (10^{-1{,}2})^{1/2} = 10^{-0{,}60} = 0{,}251$ (Result found by a 2nd method).

$Ka = \frac{C_0\alpha^2}{1-\alpha} \Rightarrow C_0\ \alpha^2 = (1-\alpha)\ K_a \Rightarrow C_0\ \alpha^2 = K_a - \alpha K_a \Rightarrow C_0\ \alpha^2 + \alpha K_a - K_a = 0$

$\Delta = (K_a)^2 - 4\ K_a\ C_0$

$\Delta = 10^{-6{,}4} + 4\ 10^{-3{,}2}\ 10^{-2}$

$\Delta = 10^{-6{,}4} + 4\ 10^{-5{,}2}$

$\Delta = 41\ 10^{-6{,}2}$

$\sqrt{\Delta} = 6{,}403\ 10^{-3{,}2}$

$\alpha_1 = \frac{10^{-3{,}2} + 6{,}403\ 10^{-3{,}2}}{2\ 10^{-2}} = \frac{5{,}403\ 10^{-3{,}2}}{2\ 10^{-2}} = \frac{5{,}403\ 10^{-1{,}2}}{2} = 2{,}701\ 10^{-1{,}2}$

$\alpha_1 = 2{,}701\ 10^{-1{,}2} = 0{,}170$

$\alpha = 0{,}170 < 0{,}251$

Solution 03:

a) $\alpha = 2\% = 0{,}02$, $C_0 = ?$

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

T=0 C_0 0 0

Teq $C_0\,(1-\alpha)$ $C_0\alpha$ $C_0\alpha$ $K_a = \frac{C_0\alpha^2}{1-\alpha}$

$\alpha = 0{,}02 \ll 1 \Rightarrow K_a = C_0\alpha^2 \Rightarrow C_0 = \frac{K_a}{\alpha^2} = \frac{1{,}8\ 10^{-5}}{4\ 10^{-4}} = 0{,}045$ M/l

$[CH_3COO^-] = [H_3O^+] = C_0\alpha = 0{,}045\ 0{,}02 = 9\ 10^{-4}$ mole/litre.

$[CH_3COOH] = C_0\,(1-\alpha) = 0{,}045\,(1-0{,}02) = 441\ 10^{-4}$ mole/litre.

pH = ? $C_0 = 0{,}045$ M/l, $K_a = 1{,}8\ 10^{-5} \Rightarrow Pk_a = -\log 1{,}8\ 10^{-5} = 4{,}75$

$pH = \frac{1}{2} Pk_a - \frac{1}{2}\log C_0$

$pH = \frac{1}{2} 4{,}75 - \frac{1}{2}\log 0{,}045$

pH = 3,048 (first méthod).

Calculation of pH by a second method:

$pH = -\log C_0\alpha$

$pH = -\log 9\ 10^{-4}$

pH = 3,046

We notice that the results are the same.

Solution 04:

a) $C_0 = 10^{-1}$M

$$NH_3\,(G\,) + H_2O \longrightarrow NH_4OH \rightleftarrows NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$T = 0$	C'_0	C'	0	0
T_{eq}	$C_0\ (1-\alpha)$		$C_0\alpha$	$C_0\alpha$

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{C_0\alpha^2}{1-\alpha}$

Si $\alpha<<1 \Rightarrow K_b \# C_0\alpha^2$ from where $\alpha = \sqrt{\frac{K_b}{C_0}} = \sqrt{\frac{10^{-4,71}}{10^{-1}}} = 10^{-3,7}$

$\alpha = 10^{-1,85} = 0,0133$ ($\alpha<<1$).

$[OH^-] = C_0\alpha = 10^{-1}\ 0,0133 = 0,00133 \Rightarrow pOH = -\log(0,00133) = 2,876$

$pH + pOH = 14 \Rightarrow pH = 14 - pOH \Rightarrow pH = 14 - 2,876 \Rightarrow PH = 11,12$

again: $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C_0$ avec $pk_a = pK_{NH4}{}^+ = 9,25$

$pH = 7 + \frac{1}{2}9,25 + \frac{1}{2}\log 10^{-1} \# 12,12$

b) If we add 1 liter of water to the previous solution, the concentration would be halved, but Kb remains constant:

$K_b = \frac{C_0\alpha^2}{1-\alpha} = \frac{C'_0\alpha'^2}{1-\alpha}$ with $C'_0 = \frac{C_0}{2}$

$\cancel{C_0}\alpha^2 = C'_0\alpha'^2 = \frac{\cancel{C_0}}{2}\alpha'^2 \Rightarrow \alpha^2 = \frac{\alpha'^2}{2} \Rightarrow \alpha' = \alpha\sqrt{2}$

$\alpha' = 0,0133\sqrt{2} = 0,0188 \# 0,019$

$[OH^-] = C'_0\alpha' = \frac{C_0}{2}0,019 = \frac{0,1}{2}0,019 = 9,5\ 10^{-4}$

$pOH = -\log[OH-] = -\log 9,5\ 10^{-4} = 3,022.$

$pH = 14 - POH = 14 - 3,022 \Rightarrow pH = 10,977 \# 10,98$

Solution 05:

- NaCl: Na^+, Cl^-: there is no hydrolysis.

$HCl + NaOH \longrightarrow Na^+, Cl^- + H_2O$ the equation is neutral pH = 7.

- Na_2SO_4: 2Na+, SO_4^{2-}: there is no hydrolysis, pH =7

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

- CH3COONa:

$CH_3COO- + H_2O \longrightarrow CH_3COOH + OH^-$ $K_b = K_h$

$K_b = \frac{[OH^-][CH_3COOH]}{[CH3COO^-]} = K_h$

There is a release of OH^- from a weak acid, so the pH is slightly basic.

$=> pH = 7 + \frac{1}{2}\,pK_a - \frac{1}{2}\log C_{sel}.$

- NH_4^+, Cl^-:

$NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$ $K_h = K_a$

There is a release of H_3O^+ ions from a weak base, hence the pH is slightly acidic.

$=> pH = \frac{1}{2}\,pK_a - \frac{1}{2}\log C_{sel}.$

- NH_4^+, CN^-: generally the same concentration, to reveal the equivalence point:

$NH_4OH + HCN \rightleftarrows NH_4CN + H_2O$

Weak weak salt

(1) $NH_4^+ + H_2O \rightleftarrows NH_4OH + H^+$ $K_a = K_h$; $[NH_4^+] = [NH_4OH] = C_0$

(2) $CN^- + H_2O \rightleftarrows HCN + OH^-$ $K_b' = K_h'$; $[CN^-] = [HCN] = C_0'$

(3) $HCN + H_2O \rightleftarrows H_3O^+ + CN^-$

(1) $=> K_a = K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]}$

(3) $=> K_a' = \frac{[H_3O^+][CN^-]}{[HCN]}$

$K_a\, K_a' = \frac{[H^+][NH_4\cancel{O}H]}{[\cancel{NH_4^+}]}\,\frac{[H_3O^+][C\cancel{N^-}]}{[H\cancel{CN}]}$

$K_a\, K_a' = [H^+] = [H_3O^+] = [H_3O^+]^2$

$[H_3O^+] = (K_a\, K_a')^{1/2}$

$pH = -\log[H_3O^+] = -\log(K_a\, K_a')^{1/2} = \frac{1}{2}\,pK_a - \frac{1}{2}\log pK_a'.$

$pH = \frac{1}{2}\, pK_a - \frac{1}{2} \log pK_a'.$

$pH = \frac{1}{2}\,(9{,}25 + 9{,}4) = 9{,}325$

Therefore, the pH depends neither on CN^- nor on NH_4^+, as both are weak.

I- Definition:

Chemical equilibrium refers to any reaction that proceeds in both directions:

(Direction 1 => forward direction, and Direction2 => reverse direction). In such reactions, the consumption of reactants is not complete, indicating limited reactions.

$$\alpha A + \beta B \underset{2}{\overset{1}{\rightleftarrows}} \gamma C + \delta D$$

Where α, β, $\gamma$and δ are stoichiometric coefficients.

II- Law of mass action

Chemical equilibrium is characterized by an, k, related to the concentration **K_c** or the equilibrium constant pressure **K_p.** This equilibrium constant represents the ratio between the products of the concentrations of the products and the products of the concentrations of the reactants.

K_c is the equilibrium constant related to concentration.

K_p is the equilibrium constant related to pressure.

$$K_c = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}}$$

If the components are gases, the equilibrium constant K_p can be used. According to the ideal gas law:

$$PV = nRT \quad \text{therefore} \quad P = \frac{n}{V}RT$$

For each component i, we can write : $P_i = [i]RT \Rightarrow [i] = \frac{P_i}{RT}$

$$K_p = \frac{P_C^{\gamma}\ P_D^{\delta}}{P_A^{\alpha}\ P_B^{\beta}}$$

Where P_A, P_B, P_C, and PD are partial pressures of the constituents A, B, C, and D

Finally, we can write:

Partial pressure of A $\mathbf{P_A = [A]RT.}$

Partial pressure of B $\mathbf{P_B = [B]RT.}$

Partial pressure of C $\mathbf{P_C = [\mathit{C}]RT.}$

Partial pressure of D $\mathbf{P_D = [D]RT.}$

- In the K_c relation, both liquids and gases are considered.
- In the K_p relation, only gases are considered.

  By convention: $\mathbf{[Solid] = 1}$

  $\mathbf{P_{solid} = P_{liquid} = 1}$

Consider the following reactions:

► $N_{2(g)} + 3H_{2(g)} \rightleftarrows 2NH_{3(g)}$

$$K_c = \frac{[NH_3]^2}{[H_2]^3[N_2]} \quad \text{and} \quad K_p = \frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3}$$

► $C_{(s)} + O_{2(g)} \rightleftarrows CO_{2(g)}$

$$K_c = \frac{[CO_2]}{[O_2]} \quad \text{and} \quad K_p = \frac{P_{CO_2}}{P_{O_2}}$$

► $CO_{2(g)} + H_{2\,(g)} \rightleftarrows CO_{(g)} + H_2O_{(l)}$

$$Kc = \frac{[CO][H_2O]}{[CO_2]\,[H_2]} \quad \text{and} \quad K_p = \frac{P_{CO}P_{H_2O}}{P_{CO_2}P_{H_2}}$$

► $H_{2\,(g)} + S_{(s)} + 2O_{2(g)} \rightleftarrows H_2SO_{4(l)}$

$$Kc = \frac{[H_2SO_4]}{[H_2]\,[O_2]^2} \quad \text{and} \quad K_p = \frac{1}{P_{H_2}P_{O_2}^2}$$

K_p and K_c are constants independent of concentration; they only depend on the temperature T.

II-1-The relationship between k_p and k_c :

Consider the following gaseous mixture:

$$\alpha\, A_{(g)} + \beta\, B_{(g)} \rightleftarrows \gamma\, C_{(g)} + \delta\, D_{(g)}$$

$$K_c = \frac{[C]^\gamma [D]^\delta}{[A]^\alpha [B]^\beta}$$

$$K_p = \frac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta}$$

According to the ideal gas law, for each constituent i, pressure can be related to concentration:

$$P_i V = n_i RT$$

$$P_i = \frac{n_i}{V} RT$$

$$P_i = [i]RT \Rightarrow [i] = \frac{P_i}{RT}$$

We can express either concentration in terms of pressure or vice versa. Starting from the expression for K_p

$$K_p = \frac{P_C^\gamma P_D^\delta}{P_A^\alpha P_B^\beta}$$

We replace the partial pressures in the expression for K_p:

$$P_A = [A]RT, \quad P_B = [B]RT, \quad P_C = [C]RTP_D = [D]RT.$$

$$K_p = \frac{([C]RT)^\gamma ([D]RT)^\delta}{([A]RT)^\alpha ([B]RT)^\beta}$$

$$K_p = \frac{[C]^\gamma [D]^\delta (RT)^{\gamma+\delta}}{[A]^\alpha [B]^\beta (RT)^{\alpha+\beta}}$$

$$K_p = K_c \frac{(RT)^{\gamma+\delta}}{(RT)^{\alpha+\beta}}$$

$$K_p = K_c (RT)^{(\gamma+\delta)-(\alpha+\beta)}$$

Given :

$$\Delta n = (\gamma+\delta) - (\alpha+\beta)$$

Δn: Represents the difference between the sum of stoichiometric coefficients of the products and the sum of stoichiometric coefficients of the reactants for the gases.

$$\Delta n = \sum \text{coefficient}_{\text{product}} - \sum \text{coefficient}_{\text{reactant}}$$

Starting from Kc, we find :

$$K_c = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \Rightarrow K_c = \frac{\left(\frac{P_C}{RT}\right)^{\gamma}\left(\frac{P_D}{RT}\right)^{\delta}}{\left(\frac{P_A}{RT}\right)^{\alpha}\left(\frac{P_B}{RT}\right)^{\beta}} = \frac{P_C^{\gamma}P_D^{\delta}}{P_A^{\alpha}P_B^{\beta}}(RT)^{(\alpha+\beta)-(\gamma+\delta)}$$

The relationship between K_p and K_c :

$$\mathbf{K_p = K_c(RT)^{\Delta n}} \qquad \textbf{\textit{or}} \qquad \mathbf{K_c = K_p(RT)^{-\Delta n}}$$

Example :

$$\mathbf{\frac{3}{2}H_{2(g)} + \frac{1}{2}N_{2(g)} \rightleftharpoons NH_{3(g)}}$$

$$K_c = \frac{[NH_3]}{[N_2]^{\frac{1}{2}}[H_2]^{\frac{3}{2}}}$$

$$\Delta n = \sum \text{coefficient}_{\text{product}} - \sum \text{coefficient}_{\text{reactant}}$$

$$\Delta n = 1 - \left(\frac{3}{2} + \frac{1}{2}\right) \qquad \Delta n = -1$$

$$K_p = K_c(RT)^{\Delta n} \qquad K_p = K_c(RT)^{-1} \quad or \quad K_p = \frac{K_c}{RT}$$

$$\mathbf{Cl_{2_{(g)}} + H_{2_{(g)}} \rightleftarrows 2HCl_{(g)}}$$

$$K_p = \frac{P^2_{HCl}}{P_{Cl_2}P_{H_2}} \qquad K_p = \frac{[\cancel{H}Cl]^2(RT)^2}{[Cl_2]\ [\cancel{H}_2]\ (RT)^2}$$

$$K_p = \frac{[HCl]^2}{[Cl_2]\,[H_2]} \quad \text{because}$$

$$\Delta n = (\gamma + \delta) - (\alpha + \beta)$$

$$\Delta n = 2 - (1 + 1) = 0$$

$$\Delta n = 0 \qquad \text{so } K_p = K_c$$

The value of $R = 0{,}082$ L. atm. mol^{-1}. K^{-1}

Example :

$\frac{1}{2}N_{2_{(g)}} + \frac{3}{2}H_{2_{(g)}} \rightleftarrows NH_{3_{(g)}}$ at temperature $T = 298$ K

$$K_p = \frac{P_{NH_3}}{P^{\frac{3}{2}}_{H_2}P^{\frac{1}{2}}_{N_2}} = 0{,}153\ atm^{-1}$$

$$K_c = K_p(RT)^{-\Delta n}$$

$$K_c = 0{,}153(0{,}082\,.298)^1$$

$$K_c = 3.738$$

III- Equilibrium factors:

These are factors that influence the direction of a reaction's movement. The equilibrium of a chemical reaction can be shifted by one of the following factors:

1- Temperature.

2- Concentration of a component.

3- Partial pressure of a component.

4- La pression totale.

III-1- Influence of temperature:

In thermodynamics, in terms of heat, three types of reactions are distinguished:

- Endothermic reactions **$\Delta H > 0$,** which absorb heat.
- Exothermic reactions **$\Delta H < 0$,**which release heat.
- Athermal reactions **$\Delta H = 0$,** which do not depend on heat.

▶If the temperature is increased, the equilibrium will shift towards the endothermic direction.

▶If the temperature is decreased, the equilibrium will shift towards the exothermic direction.

$C_{(s)} + O_{2\,(g)} \quad ==== \quad CO_{2\,(g)} \; \Delta H = 80 \text{ Kcal/mol}$

If the temperature increases, the equilibrium will shift in the endothermic direction (forward direction 1, the direction of reactant consumption).

If the temperature decreases, the equilibrium shifts in the exothermic direction (indirect direction 2, the direction of product consumption).

$\mathbf{N_2 + 3H_2 \quad === \quad 2NH_3 \quad \Delta H = -25 \text{ Kcal/mol}}$

If the temperature increases, the equilibrium shifts in the endothermic direction (direction 2, the direction of product consumption).

If the temperature decreases, the equilibrium shifts in the exothermic direction (direction 1, the direction of reactant consumption).

$\mathbf{H_2 + CO_2 \quad === \quad H_2O + CO \quad \Delta H = 0 \text{Kcal/mol}}$

If the temperature increases or decreases, there is no influence.

Since K_p and K_c are functions of temperature, an increase or decrease in temperature leads to a change in the equilibrium constant.

Consider the following equilibrium:

$\boldsymbol{\alpha \, A + \beta \, B \quad === \quad \gamma \, C + \delta \, D \quad \Delta H > 0}$

If the temperature increases, the equilibrium shifts towards the endothermic direction (direction 1, the direction where the concentration of products increases and that of reactants decreases).

$K_c = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \Rightarrow \searrow$ K_c increases

If the temperature decreases, the equilibrium shifts towards the exothermic direction (direction 2, the direction where the concentration of products decreases and that of reactants increases).

$K_c = \frac{[C]^{\gamma}[D]^{\delta}}{[A]^{\alpha}[B]^{\beta}} \Rightarrow \begin{smallmatrix}\searrow \\ \nearrow\end{smallmatrix}$ K_c decreases

In general:

For an endothermic reaction:

If the temperature increases, the equilibrium constant increases.

If the temperature decreases, the equilibrium constant decreases.

For an exothermic reaction :

If the temperature increases, the equilibrium constant decreases.

If the temperature decreases, the equilibrium constant increases.

The variation of the equilibrium constant with temperature is given by the Van't Hoff equation.

$$\log\frac{K_2}{K_1} = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

III-2- Influence of concentration:

▶ If the concentration of a component is increased, the equilibrium shifts in the direction of the disappearance of that component.

▶ If the concentration of a component is decreased, the equilibrium shifts in the direction of the appearance of that component.

Or alternatively :

▶ If the concentration of a reactant is increased, the equilibrium shifts towards the products.

▶ If the concentration of a product is increased, the equilibrium shifts towards the reactants.

Example :

$$\mathbf{H_2 + CO_2 \quad === \quad H_2O + CO}$$

▶ If

$[H_2]$ increases, the equilibrium shifts towards the disappearance of H_2 ,the forward(direct) direction, direction 1.

▶ If

$[H_2O]$ increases, the equilibrium shifts towards the disappearance of H_2O , the reverse (indirect) direction, direction 2.

▶ If

$[H_2O]$ decreases, the equilibrium shifts towards the appearance of H_2O , the forward direction, direction 1.

III-3- Influence of partial pressure:

▶ If the partial pressure of a component is increased, the equilibrium shifts in the direction of the disappearance of that component.

▶ If the partial pressure of a component is decreased, the equilibrium shifts in the direction of the appearance of that component.

Or alternatively:

Example:

$\mathbf{N_2 + 3H_2 \quad === \quad 2NH_3}$

▶ If P_{H2} increases, the equilibrium shifts towards the disappearance of H_2 , the forward direction, direction 1.

▶ If P_{NH3} increases, the equilibrium shifts towards the disappearance of NH_3, the indirect direction, direction 2.

▶If P_{N2} decreases, the equilibrium shifts towards the appearance of N_2, the forward direction, direction 1.

III-4- Influence of total pressure:

▶If the total pressure in the mixture increases, the equilibrium shifts in the direction that reduces the number of gas moles.

▶If the total pressure in the mixture decreases, the equilibrium shifts in the direction that increases the number of gas moles.

Example:

$$H_{2(g)} + S_{(s)} + 2O_{2(g)} === H_2SO_{4(l)}$$

▶If the total pressure increases, the equilibrium shifts in the direction that reduces the number of gas moles. Direction 1 (forward direction).

▶If the total pressure decreases, the equilibrium shifts in the direction that increases the number of gas moles. Direction 2 (reverse direction).

$$C_{(s)} + O_{2\,(g)} ==== CO_{2\,(g)}$$

▶If the total pressure increases or decreases, the equilibrium does not shift as the number of gas moles is the same in both reactants and products.

IV- Application exercise

Exercise N° 01:

For the reaction: $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)$, at 1000 K the equilibrium constant K_P=1.39 Assuming the gases are ideal, calculate:

a) The composition of the equilibrium mixture (in % by volume), and then when water has been completely removed.

b) Determine the partial pressures if the total pressure is 1 atm.

c) Determine the variance.

Exercise N° 02:

a) What is the effect of an increase in pressure and a decrease in temperature on the following equilibria:

- $N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2NH_3\ (g)\ \Delta H < 0$
- $CO\ (g) + H_2O\ (g) \rightleftharpoons CO_2\ (g) + H_2\ (g)\ \Delta H < 0$
- $CH_4\ (g) + H_2O\ (g) \rightleftharpoons CO\ (g) + 3H_2\ (g)\ \Delta H > 0$

b) Variance?

c) At 900 K, $K_P = 0.153$ for the reaction:

$SO_3\ (g) \rightleftharpoons SO_2\ (g) + \frac{1}{2} O_2\ (g)$.

Calculate K_P for the reaction: $2SO_2\ (g) + O_2\ (g) \rightleftharpoons SO_3\ (g)$. $\Delta H < 0$.

What is the effect of temperature and pressure?

Exercise N°03:

For the following equilibrium, what is the influence of:

1. An increase in pressure.
2. A decrease in temperature.

3. $N_2\ _{(}G_{\ )} + 3H_2 \longleftrightarrow 2NH_3\ _{(G)}$ $\Delta H°_1 = -22$ kcal.
$_{(}G_{\ )}$ 4. $CO\ _{(}G_{\ )} + \longleftrightarrow 2CO_2\ _{(G)} + H_2$ $\Delta H°_2 = -10,2$ kcal.
$H_2O\ _{(}G_{\ )}$ $(\ _{G)}$
$\longleftrightarrow$
$CH_4\ _{(}G_{\ )} + H_2O$ $CO\ _{(G)} + 3H_3\ _{(G)}$ $\Delta H°_3 = -49,3$ kcal

$_{(}G_{\ )}$ For the reaction:

$CO_2\ _{(}G_{\ )} + H_2\ _{(}G_{\ )} \longleftrightarrow CO\ _{(G)} + H_2O\ _{(G)}$

What is the influence of an increase in the pressure of H2 and a decrease in the pressure of H_2O on the equilibrium?

Exercise N° 04:

At a temperature of 900°K, the equilibrium constant Kp for the reaction:

$SO_3\ _{(G)} \longleftrightarrow SO_2\ _{(G)} + \frac{1}{2} O_2\ _{(G)}$ is 0,153

Calculate the equilibrium constant for the reaction:

$2\ SO_2\ _{(}G_{\ )} + O_2\ _{(}G_{\ )} \longleftrightarrow 2\ SO_3\ _{(G)}$ $\Delta H_1 = -68$ kcal.

1. What is the influence of temperature, pressure, and the partial pressure of SO2 on the first equilibrium? Deduce its ΔG°**.**

ExerciseN°05:

The equilibrium constant for the endothermic reaction:

$CO_2\,_{(G)} \longleftrightarrow CO\,_{(G)} + ½\, O_2$ is 1.10^{-6} atm at 1400 K.

Calculate the value of the constant at 2000 K, knowing that the enthalpy of the reaction in this temperature range is 68 kcal.

Exercise N° 06:

The synthesis of ammonia is represented by:

$N_2\,_{(G)} + 3H_2\,_{(G)} \longleftrightarrow 2\,NH_3\,_{(G)}$ ΔH = 22,1 kcal/mole.

1. Express Kp and Kc and the relation between them.
2. In which direction does the reaction shift if the temperature increases, if the pressure decreases, and if H_2 is added?
3. Denote by $X = \frac{P_{NH3}}{P_T}$. Starting from the initial mixture of 1 mole of N_2 and 3 moles of H_2, what is the number of moles of each constituent formed at equilibrium in terms of α (degree of dissociation)? Deduce the relation between X and α, as well as the relation between X, P_T, and K_P.

Solution :

Solution N°01:

$CO\,_{(g)} + H_2O\,_{(g)} \longleftrightarrow CO_2\,_{(g)} + H_2\,_{(g)}$, T = 1000 K; $K_P = 1{,}39$.

a) α?

$$K_P = \frac{P_{H2}P_{CO2}}{P_{CO}P_{H2O}} = K_n\left(\frac{P}{\sum n}\right)^{\Delta n}$$

The number of moles remains constant during the reaction. ($\Delta n = 0$), on a: $K_P = K_n$

$$CO_{(g)} + H_2O_{(g)} \longleftrightarrow CO_{2\,(g)} + H_{2\,(g)}$$

A t = 0 1 1 0 0

A t = eq 1-α 1-α α α

Total number: (1-α) + (1-α) + α + α = 2

$K_P = \frac{\alpha^2}{(1-\alpha)^2} = 1{,}39 \Rightarrow \alpha^2 = (1-\alpha)^2\ 1{,}39 \Rightarrow \alpha = 0{,}542$

Before the elimination of water, we have:

CO 1-α = 1-0,542 => α = 0,458

H_2O 1-α = 1-0,542 => α = 0,458

CO_2 α = 0,542

H_2 α = 0,542

Total number: (1-α) + (1-α) + α + α = 2

Comparison of the mixture in % by volume:

$CO = H_2O = \frac{100\ 0{,}458}{2} = 22{,}9\%$

$CO_2 = H_2 = \frac{100\ 0{,}542}{2} = 27{,}1\%$

- After the élimination of water:

CO_2 α ……………. = 0,542

H_2 α ……………. = 0,542

CO 1- α ……………. = 0,458

Total number: (1+α) = 1,542

Composition of the mixture in % by volume:

$CO_2 = H_2 = \frac{100\ 0{,}542}{1{,}542} = 35{,}14\%$

$\text{CO} = \frac{100\ 0{,}458}{1{,}542} = 29{,}70\%$

Partial pressure:

$$CO_{(G)} + H_2O_{(G)} \longleftrightarrow CO_{2\ (G)} + H_{2\ (G)}$$

$1 \qquad 1 \qquad\qquad 0 \qquad 0$

$1\text{-}\alpha \qquad 1\text{-}\alpha \qquad\qquad \alpha \qquad \alpha$

Total number: $(1\text{-}\alpha) + (1\text{-}\alpha) + \alpha + \alpha = 2$

Mole fraction:

$X_{CO} = \frac{1-\alpha}{2} = X_{H2O}$ $\qquad\qquad$ $X_{CO2} = X_{H2} = \frac{\alpha}{2}$

$X_{CO} = X_{H2O} = \frac{1-\alpha}{2} = \frac{1-0{,}542}{2} = 0{,}229$

$X_{CO2} = X_{H2} = \frac{\alpha}{2} = \frac{0{,}542}{2} = 0{,}271$

$P_i = X_i\ P$ avec $P_{total} = 1$ atm.

$P_{iCO} = P_{iH2O} = \frac{1-\alpha}{2}\ P_{total} = \frac{1-0{,}542}{2}\ 1 = 0{,}229$ atm.

$P_{iCO2} = P_{iH2} = \frac{\alpha}{2}\ P_{total} = \frac{0{,}542}{2}\ 1 = 0{,}271$ atm.

b) Variance:

$(n = 4, r = 1)$

n: the number of constituant.

r: the number of relationships.

℮: the number of Phases.

$\upsilon = C + 2 -$ ℮

$C = n - r \Rightarrow C = 4 - 1 \Rightarrow C = 3$

D'où $\upsilon = 3 + 2 -$ ℮ $\Rightarrow \upsilon = 4$

Solution N°02:

a)

$N_{2\,(G)} + 3H_{2\,(G)} \underset{2}{\overset{1}{\rightleftarrows}} 2NH_{3\,(G)}$ $\Delta H<0$

P ↗ $\Delta n = 2 - 4 = -2$ ↘ sense (1).

T ↘ $\Delta H<0$, exothermic, direction (1)

$CO_{(G)} + H_2O_{(G)} \underset{2}{\overset{1}{\rightleftarrows}} CO_{2\,(G)} + H_{2\,(G)}$ $\Delta H<0$

P ↗ $\Delta n = 2 - 2 = 0$ therefore no difference in pressure

T ↘ $\Delta H<0$, exothermic, sense (1).

$CH_{4\,(G)} + H_2O_{(G)} \underset{2}{\overset{1}{\rightleftarrows}} CO_{(G)} + 3H_{2\,(G)}$ $\Delta H>0$

P ↗ $\Delta n = 4 - 2 = 2$ ↗ sense (2).

T ↘ $\Delta H>0$, endothermic, sense (2).

b) Variance:

1st réaction: $\upsilon = C + 2 - \varphi$ and $C = n - r \Rightarrow C = 3 - 1 = 2 \Rightarrow \upsilon = 2 + 2 - 1 \Rightarrow \upsilon = 3$

2nd réaction: $\upsilon = C + 2 - \varphi$ and $C = n - r \Rightarrow C = 4 - 1 = 3 \Rightarrow \upsilon = 3 + 2 - 1 \Rightarrow \upsilon = 4$

3rd réaction: $\upsilon = C + 2 - \varphi$ and $C = n - r \Rightarrow C = 4 - 1 = 3 \Rightarrow \upsilon = 3 + 2 - 1 \Rightarrow \upsilon = 4$

c) $T = 900$ K, $K_{P1} = 0{,}153$.

$SO_{3\,(g)} \underset{2}{\overset{1}{\rightleftarrows}} SO_{2\,(g)} + \frac{1}{2} O_{2\,(g)}$ $\Delta H<0$

$2SO_{2\,(g)} + O_{2\,(g)} \underset{2}{\overset{1}{\rightleftarrows}} SO_{3\,(g)}$ $K_{P1} = ?$

$$K_{P1} = \frac{P_{SO_2} P_{O_2}^{1/2}}{P_{SO_3}}$$

$$K_{P2} = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \frac{1}{\frac{P^2_{SO_2}P_{O_2}}{P^2_{SO_3}}} = \frac{1}{K^2_{P_1}} = \frac{1}{(0{,}153)^2} \Rightarrow K_{P2} = 42{,}71.$$

- Influence of Temperature and pressure:

P ↗ $\Delta n = 1 - 3 = -2$ ↘ sense (1), P ↘ sense (2).

T ↗ $\Delta H<0$, exothermic, sense (2), T ↘ sense (1).

Solution No. 03

1) $N_{2\,(G)} + 3H_{2\,(G)} \longleftrightarrow 2NH_{3\,(G)}$ $\Delta H°_1 = -22$ kcal.

- If pressure (P_T) increases: The equilibrium shifts towards the side with fewer moles of gas, so towards the production of NH3 (to the right, direction 1).
- If temperature (T) decreases: The equilibrium shifts towards the exothermic side, so towards the production of NH3 (to the right, direction 1).

2) $CO_{(g)} + H_2O_{(g)} \longleftrightarrow 2CO_{2\,(g)} + H_{2\,(g)}$ $\Delta H°_2 = -10{,}2$ kcal.

- If pressure (P_T) increases: No change in equilibrium since the number of moles of gas is the same on both sides.
- If temperature (T) decreases: The equilibrium shifts towards the exothermic side, so towards the production of CO_2 and H_2 (to the right, direction 1).

3) $CH_4(g)+H_2O(g) \rightleftharpoons CO(g)+3H_2(g)$ $\Delta H°3=-49.3$kcal

- If pressure (P_T) increases: The equilibrium shifts towards the side with fewer moles of gas, so towards the reactants (to the left, direction 2).
- If temperature (T) decreases: The equilibrium shifts towards the exothermic side, so towards the production of CO and H_2 (to the right, direction 1).

I- For the reaction:

$$CO_{2\,(g)} + H_{2\,(g)} \longleftrightarrow CO_{(g)} + H_2O_{(g)}$$

If the partial pressure of a constituent increases, the equilibrium shifts towards the side where that constituent is consumed.

- If the partial pressure of a constituent decreases, the equilibrium shifts towards the side where that constituent is produced.

Therefore, if PH $_2$ increases, the equilibrium shifts towards the consumption of H_2 (to the right, direction 1).

If P_{H2O} decreases, the equilibrium shifts towards the production of H_2O (to the right, direction 1).

Solution N°04

a) SO_3 (G $\rightleftarrows$ SO_2 (G) + ½ O_2 (G) at 900 K => K_{P1} = 0,153.

$$K_{P1} = \frac{P_{SO_2}P_{O_2}^{1/2}}{P_{SO_3}}$$

$2SO_2$ (G) + O_2 (G) $\underset{2}{\overset{1}{\rightleftarrows}}$ $2SO_3$ (G) ΔH = -68 kcal.

$$K_{P2} = \frac{P^2_{SO_3}}{P^2_{SO_2}P_{O_2}} = \left(\frac{P_{SO_3}}{P_{SO_2}P_{O_2}^{1/2}}\right)^2 = \left(\frac{1}{K_{P_1}}\right)^2 \Rightarrow K_{P2} = \left(\frac{1}{0,153}\right)^2 = 42,71$$

- If temperature (T) increases: The equilibrium shifts towards the endothermic side (to the left, direction 2).
- If temperature (T) decreases: The equilibrium shifts towards the exothermic side (to the right, direction 1).
- If pressure (P) increases: The equilibrium shifts towards the side with fewer moles of gas (to the right, direction 1).
- If pressure (P) decreases: The equilibrium shifts towards the side with more moles of gas (to the left, direction 2).
- If P_{SO2} increases: The equilibrium shifts towards the consumption of SO_2 (to the right, direction 1).

- If P_{SO_2} decreases: The equilibrium shifts towards the production of SO_2 (to the left, direction 2).
- $\Delta G° = \Delta H° - T\Delta S°$
- $\Delta G° = - RT \ln K \Rightarrow \Delta G° = - 8{,}31\ (900) \ln 42{,}71$
- $\Delta G° = - 28079{,}4\ J \Rightarrow \Delta G° = - 28{,}079\ KJ.$

Solution N°05

$$CO_{2\,(g)} \rightleftarrows CO_{(g)} + \tfrac{1}{2} O_2$$

$K_{P1} = 10^{-6}$ atm at 1400 K, $\Delta H = 68$ kcal

K_{P2} at 2000K ?

$\frac{d\ln K_P}{dT} = \frac{\Delta H}{RT^2}$ according to the law of Vant Hoff

$$\ln\frac{K_{P_2}}{K_{P_1}} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\frac{K_{P_2}}{K_{P_1}} = \frac{6{,}8\ 10^3}{8{,}31}\left(\frac{1}{1400} - \frac{1}{2000}\right) = \frac{6{,}8\ 10^3}{8{,}31}\left(\frac{2000-1400}{28\ 10^5}\right)$$

$$\ln\frac{K_{P_2}}{K_{P_1}} = \frac{6{,}8}{8{,}31}\left(\frac{600}{28\ 10^2}\right) \qquad \ln\frac{K_{P_2}}{K_{P_1}} = \frac{6{,}8}{8{,}31}\left(\frac{6}{28}\right)$$

$$\ln\frac{K_{P_2}}{K_{P_1}} = 232{,}68 \Rightarrow \ln K_{P2} = 232{,}68 - \ln K_{P1}$$

$\Rightarrow \ln K_{P2} = 226{,}68$

$\Rightarrow K_{P2} = 2{,}79$

Solution N°05

$N_{2\,(G)} + 3H_{2\,(G)} \longleftrightarrow 2\ NH_{3\,(G)}$ $\qquad \Delta H = 22{,}1$ kcal/mole.

1-

$$K_P = \frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}$$

$P_{NH3} = [NH_3]\ RT$, $P_{N2} = [N_2]\ RT$, $P_{H2} = [H_2]\ RT$

$$K_P = \frac{[NH_3]^2(RT)^2}{[N_2]RT[H_2]^3(RT)^3} = \frac{[NH_3]^2}{[N_2][H_2]^3(RT)^2} = \frac{[NH_3]^2}{[N_2][H_2]^3}(RT)^{-2}$$

$K_P = K_C\ (RT)^{-2}$ with $K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Of shape $K_P = K_C\ (RT)^{\Delta n}$, $\Delta n = -2$

I-1- Introduction

Kinetics is a fundamental branch of chemistry that studies the rates of reactions as well as the mechanisms that govern them. In other words, it focuses on understanding the speed at which reactants are transformed into products and the factors that influence this rate. To contextualize this discipline, it is essential to distinguish it from thermodynamics, another important field of chemistry. The main difference between chemical kinetics and thermodynamics lies in their respective objectives. While chemical kinetics examines the temporal and dynamic aspects of reactions, studying how and at what rate reactants transform into products, thermodynamics focuses more on the energetic and equilibrium aspects of reactions. In other words, chemical kinetics is concerned with the rate at which reactions occur, whereas thermodynamics analyzes the energies associated with these reactions and the conditions under which they occur spontaneously. These two fields are complementary and essential for a comprehensive understanding of chemical processes.

I-2- Formal Kinetics

Formal kinetics offers a practical mathematical representation of the changes in concentrations over time, but it may not account for all the details of the actual reaction mechanism. It is often used in contexts where the precision of molecular details of the mechanism is not the priority, but where a general understanding of the reaction rate and kinetics is necessary. Thus, formal kinetics simplifies the analysis of chemical reactions, but it is important to recognize its limitations compared to real kinetics.

I-2-1- Rate Equation

The rate equation in chemical kinetics expresses the relationship between the change in the concentration of a reactant or product and the time elapsed during a chemical reaction. This equation is fundamental for understanding how the concentration of the chemical species involved in the reaction evolves over time. In other words, it allows for quantifying the speed at which reactants are transformed into products or the decrease in reactants during the reaction.

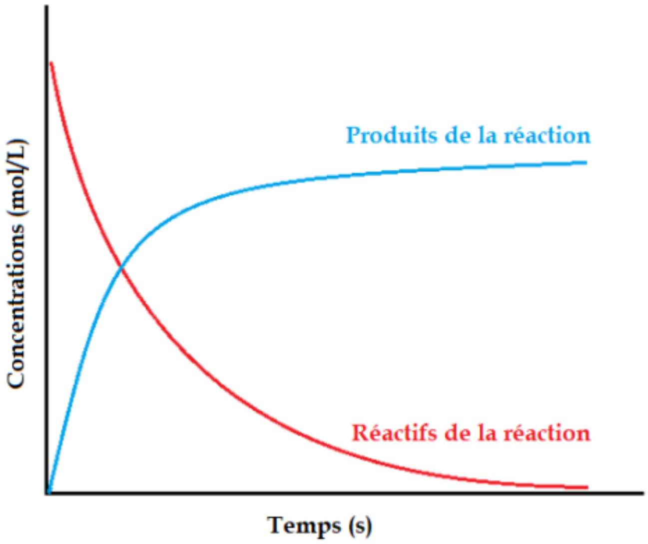
Let the following chemical reaction be:

$$a\,A + b\,B \rightarrow \qquad c\,C + d\,D$$

The expression for the rate of this reaction can be written as follows:

$$V = \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} = \frac{\Delta[A]}{\Delta t}$$

Where $[A]t_1$ and $[A]t_2$ represent the concentrations of reactant A at times t_1 and t_2, respectively.



Evolution of reactant and product concentrations over time.

The blue curve illustrates the evolution of the concentration of the products. It shows a gradual increase over time, which results in a positive change. In parallel, the red curve represents the change in the concentration of the reactants. Observing this curve reveals a decrease over time due to the reduction in reactant concentrations, indicating a negative change. The rate of the reaction is then expressed as:

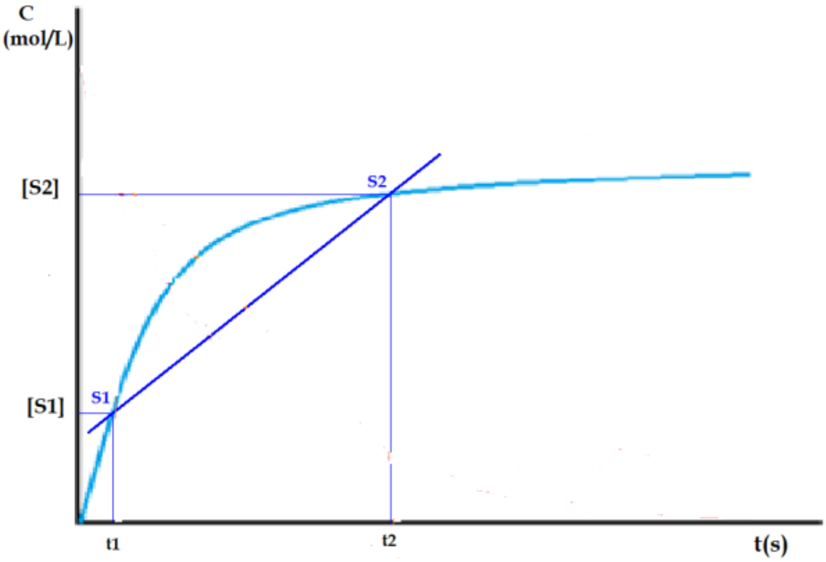
V= V (formation of products) = +d [product]/dt (the products appear)

Or V= V (disappearance of reactants) = -d [reactant]/dt (the reactants disappear)

In general, when monitoring the kinetics of a chemical reaction, one can define an average rate, an instantaneous rate, and an overall rate.

I-2-1-1- The Average Rate

Chemical reactions can involve various mechanisms and steps, and the rate at which these steps occur can vary significantly. Some stages of the reaction may exhibit increased speed, while others may proceed more slowly, creating a complex temporal dynamic. The average rate in chemical kinetics represents an overall average of the reaction speed over a defined period of time. This average rate is generally not constant due to various factors such as changes in reactant concentrations over time, temperature fluctuations, or variations in the reaction steps. By understanding the average rate of a chemical reaction over a given interval, one gains a comprehensive view of the reaction's dynamics during that specific period, thereby allowing for a better understanding of the variations and influencing factors in the chemical process.



Curve of the evolution of product concentration as a function of time. The slope of the line S_1S_2 indicates the value of the average rate over the time interval t_1 to t_2.

Based on the data presented in Figure 4.2.1.1 and using the concentrations of the product [S1] and [S2] over the time interval t_1 to t_2, it is possible to determine the average rate of appearance of the product using the following relationship:

$$\overline{V_m} = \frac{[S_2]-[S_1]}{t_2-t_1} \qquad \text{eq.4.2.1.3.}$$

It is worth noting that this rate can also be calculated in a similar manner by evaluating the concentrations of the reactants over a specific time interval.

I-2-1-2- The Instantaneous Rate

This rate represents the speed at which a reaction occurs at a specific moment during its progression. It is specific to a particular point in the reaction and is influenced by various factors such as the concentration of reactants, temperature, and pressure. The instantaneous rate can vary throughout the reaction due to changes in the system's conditions. It is important to note that this rate is a measurement at a specific point in time, providing a precise picture of the state of the reaction at that moment. Unlike the average rate, which considers a broader time period, the instantaneous rate allows for a detailed understanding of the evolution of the reaction. This kinetic quantity is expressed by the following relationship:

$$V_i = \frac{d[S]}{dt} = \lim \left(\frac{[S_2]-[S_1]}{t_2-t_1}\right)_{(t_2-t_1)\to 0} \qquad \text{eq.4.2.1.4.}$$

The determination of this rate is performed graphically; it corresponds to the slope of the tangent to the curve at the point corresponding to a given moment t.

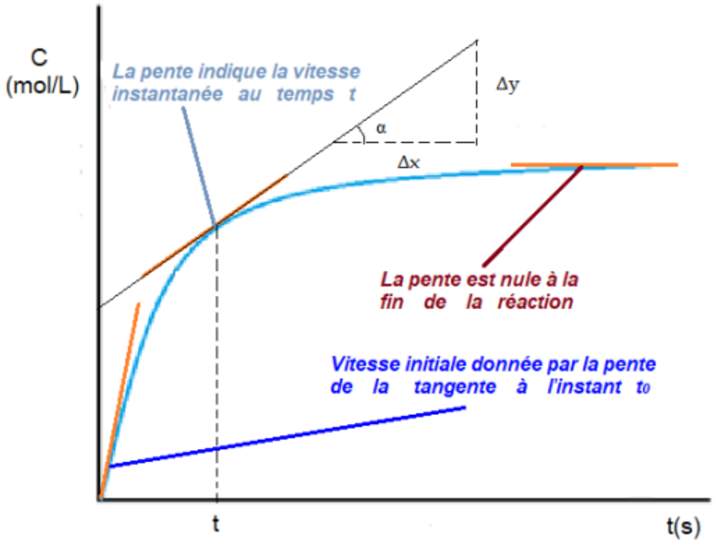


Fig. 4.2.1.2. Curve of the evolution of product concentration as a function of time. The slope of the tangent indicates the value of the instantaneous rate at time t.

I-3- The overall rate.

The overall (or general) rate of a chemical reaction relates to the change in concentration of a specific substance divided by its stoichiometric coefficient in the balanced chemical equation of the reaction. This expression reflects the speed at which the reaction occurs as a whole. More specifically, it measures the rate of decrease in the concentration of the reactants or the increase in the concentration of the products per unit of time.

If we consider the following generic chemical reaction:

$$aA + bB \rightarrow cC + dD$$

where a, b, c, and d are the corresponding stoichiometric coefficients, the expression for the overall rate would be expressed in terms of the change in concentration of one of the substances (for example, A, B, C, or D) divided by its stoichiometric coefficient. This provides a quantitative measure of the speed at which the reaction occurs as a whole, taking into account the contribution of each reactant or product based on its stoichiometric significance. The expression defining the overall rate of reaction is as follows:

$$V(t) = -\frac{d[A]}{a.dt} = -\frac{d[B]}{b.dt} = +\frac{d[C]}{c.dt} = +\frac{d[D]}{d.dt} \qquad \text{eq.4.2.1.5.}$$

Example: Consider the decomposition reaction of dinitrogen pentoxide:

$$N_2O_{5(g)}N_2O_{5(g)} \rightarrow 2NO_{2(g)} + \frac{1}{2}O_{2(g)}$$

The disappearance of N_2O_5 occurs at a rate twice that of the production of O_2, as two molecules of N_2O_5 are consumed for each molecule of O_2 produced. We have:

$$V(t) = -\frac{d[N_2O_5]}{dt} = 2\frac{d[O_2]}{dt} \qquad \text{eq.4.2.1.6.}$$

On the other hand, the rate at which N_2O_5 disappears is half the rate of NO_2 production because two molecules of NO_2 are formed for each molecule of N_2O_5 that decomposes.

Thus: $V(t) = -\frac{d[N_2O_5]}{dt} = \frac{d[NO_2]}{2dt}$ eq.4.2.1.7.

The curve showing the evolution of the concentrations of the reactant and the products of the reaction has the following shape:

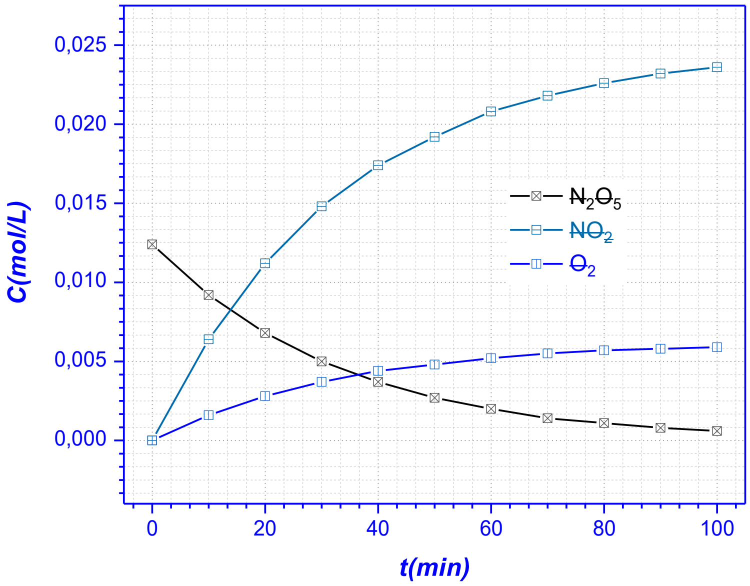


Fig. 4.2.1.3. Courbe de l'évolution des concentrations relatives à la réaction de décomposition du pentoxyde de diazote.

Based on this curve, we observe that, at a specific time during the reaction, the production of NO_2 is twice as significant as the consumption of N_2O_5.

1-4- Rate Law (or Kinetic Law): Rate Constant

When studying reaction kinetics, experimental trials have revealed the existence of a proportional relationship between the rate of a reaction and the concentrations of the reactants involved. This relationship indicates that as the concentrations of the reactants increase, the reaction rate also increases. Moreover, it has been observed that the rate of a reaction is often raised to a certain power, meaning that the reaction rate can depend non-linearly on the concentrations of the reactants. This dependence of the reaction rate on reactant concentrations is formalized in rate laws. These laws allow us to quantify the relationship between the reaction rate and the concentrations of the reactants, which is essential for understanding and predicting the behavior of chemical reactions. Experimentally, the rate of reaction in equation 4.2.1.1 can be

expressed as follows:

$V = K.[A]^{\alpha}.[B]_{\beta}$ eq.4.3.1.1.

The rate constant, denoted as K, is defined as the proportionality constant in the reaction rate equation. The partial order with respect to reactant A is represented by α, while the partial order with respect to reactant B is represented by β. The sum of the partial orders, α+β, gives the overall order of the reaction. The partial reaction orders do not necessarily correspond to the stoichiometric coefficients. The order of a chemical reaction can generally be an integer (0, 1, 2, 3…), a fractional value (1/2, 1/3, 3/4, ...), or can be quite complex, sometimes even lacking a specific order.

Examples.4.2.2.

Réactions	**Rate laws**	**Order of the réaction**
$2HI + H_2O_2$ ❼ $I_2 + 2H_2O$	$v = k.[HI].[H_2O_2]$	2
$3NO$ ❼ $NO_2 + N_2O$	$v = k.[NO]^2$	

1.4.1. Zero-Order Kinetics

Some reactions exhibit unique characteristics where the rate does not depend on the concentrations of the reactants. This may seem unusual, but it can be explained by other factors influencing the reaction kinetics.

For example, consider a reaction that requires light absorption. The rate of this reaction depends on the intensity of the light. The higher the light intensity, the faster the reaction occurs. This is because light acts as an energy source that activates reactive molecules, promoting the necessary collisions for the reaction. On the other hand, in the case of a surface-catalyzed reaction, the rate depends on the available surface area of the catalyst. The catalyst provides a reaction site where molecules can attach and react more easily. Imagine two conditions, C1 and C2, with different reactant concentrations. Despite these concentration variations, the reaction rate remains the same if the catalyst surface is saturated, meaning all reaction sites are occupied. Thus, the reaction kinetics are mainly influenced by the availability of the catalytic surface rather than the reactant concentrations.

Examples

i. i. The biological oxidation of ethanol to acetaldehyde by the liver enzyme alcohol dehydrogenase is zero-order with respect to ethanol.

ii. The catalytic decomposition of phosphine (PH_3) on tungsten follows zero-order kinetics at high pressure. At low pressure, the kinetics is first-order.

For a zero-order kinetics, it generally involves a reaction of the following type :

A → Product

In this case, the form of the rate law is as follows:

$$v = -\frac{d[A]}{dt}$$

On the other hand, $v = k[A]^0 = k$, since the reaction is zero-order and is independent of concentration. The kinetic equation is written as:

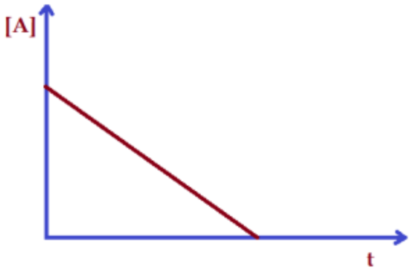
$$-\frac{d[A]}{dt} = k$$

Subsequently,the integrated rate law can be expressed as:

$$\int_{[A]_0}^{[A]} d[A] = -\int_0^t k.dt \Rightarrow [A] = -k.t + [A]_0$$

Moreover, the half-life of the reaction ($t=t_{1/2}$ et $[A]=[A]_0/2$) is given by:

$$\frac{[A]_0}{2} = -k.t_{\frac{1}{2}} + [A]_0 \Rightarrow t_{\frac{1}{2}} = \frac{[A]_0}{2k}$$



Graphical representation of zero-order kinetics.

The unit of the rate constant in this case is $mol \cdot L^{-1} \cdot s^{-1}$."

I-4-2- First-Order Kinetics.

A first-order reaction is a reaction whose rate has a linear dependence on the concentration of the reactant. For a first-order reaction of the type:

A ➐ produits

The rate law is of the type: $v = -\frac{d[A]}{dt} = k[A]^1$

$$\Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt \Rightarrow ln\frac{[A]}{[A]_0} = -kt \Rightarrow [A] = [A]_0 e^{-kt}$$

On the other hand, the half-life is given by:

$$t_{\frac{1}{2}} = \frac{ln2}{k} = \frac{0.693}{k}$$

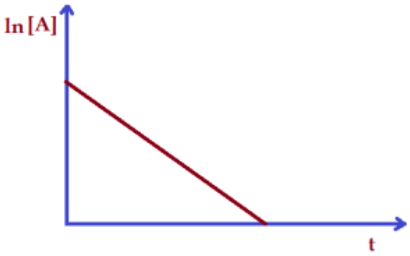


Fig.4.2.2.2. Graphical representation of first-order kinetics.

The unit of kkk in this case is s^{-1}.

I-4-3- Second-Order Kinetics.

A second-order reaction is characterized by a rate that depends either on the concentrations of two distinct reactants, each raised to the first power, or on the concentration of a single reactant raised to the second power. Considering the following reaction:

A+B ❼ produits

The rate law is expressed as follows:

$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A]^1[B]^1$$

With $[A]=[A]_0-x$ et $[B]\ ]=[B]_0-x$. The integration of the differential equation leads to the following equation:

$$\frac{1}{[B]_0 - [A]_0} \ln\left[\frac{[\mathrm{A}]_0([\mathrm{B}]_0 - \mathrm{x})}{[\mathrm{B}]_0([\mathrm{A}]_0 - \mathrm{x})}\right] = kt$$

Considering that the first term of this equation is equal to a function GGG and by plotting this function against ttt, we obtain a line that passes through the origin witha slope of k

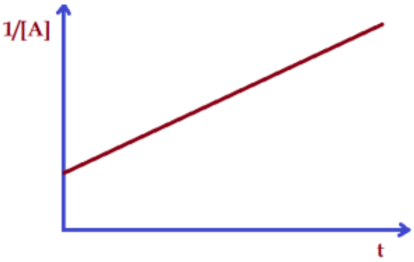


Fig.4.2.2.2. Graphical representation of second-order kinetics.

Note : when $[A]_0=[B]_0$, The corresponding rate law is as follows.:

$v = -\frac{d[A]}{dt} = k[A]^2$ From where: $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$ et $t_{\frac{1}{2}} = \frac{1}{k[A]_0}$

Note : when$[A]_0 << [B]_0$, The reactant A is said to be the limiting reactant because the reaction finishes when the reactant A is completely consumed. Furthermore, $[B]=[B]_0=$cte. So :

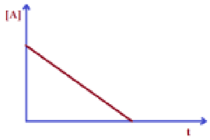
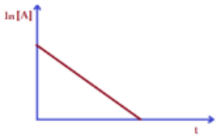
$$v = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k[A].[B]_0 = k'[A]$$

In this case, we refer to pseudo-first-order kinetics:

$\ln\frac{[A]}{[A]_0} = -k't$ or even $[A] = [A]_0.e^{-k't}$ with $t_{\frac{1}{2}} = \frac{ln2}{k'}$

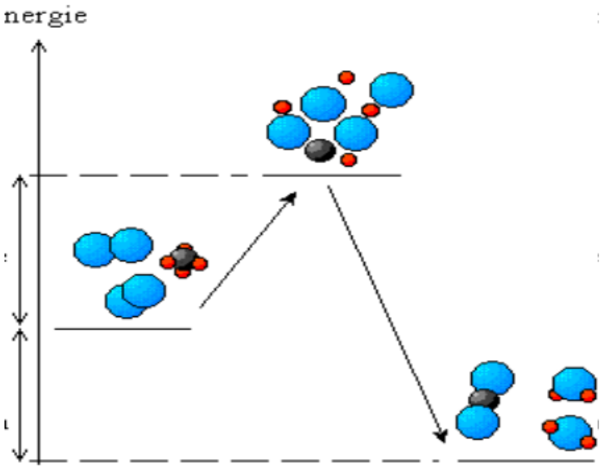
Note : For reactions occurring in the gaseous phase, and assuming that the gases are ideal, all the previous equations can be expressed in terms of partial pressures.

Summary of zero, first, and second-order kinetics.

	Ordre		
	0	**1**	**2**
Loi de vitesse différentielle	$-\frac{d[A]}{dt} = k$	$-\frac{d[A]}{dt} = k[A]$	$-\frac{d[A]}{dt} = k[A]^2$
Séparation des variables	$-d[A] = k.dt$	$-\frac{d[A]}{[A]} = k.dt$	$-\frac{d[A]}{[A]^2} = k.dt$
Intégration	$-\int_{[A]_0}^{[A]} d[A] = k.\int_0^t dt$	$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k.\int_0^t dt$	$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k.\int_0^t dt$
Loi de vitesse intégrée sous forme linéaire	$[A] = -k.t + [A]_0$	$\ln[A] = -k.t + ln[A]_0$	$\frac{1}{[A]} = k.t + \frac{1}{[A]_0}$
	$[A] \propto t$	$ln[A] \propto t$	$\frac{1}{[A]} \propto t$
Représentation graphique			
Constante de vitesse	k=-(Pente)	k=-(Pente)	k=(Pente)
Temps de demi réaction, $t_{1/2}$	$\frac{[A]_0}{2k}$	$\frac{0.693}{k}$	$\frac{1}{k[A]_0}$
Unité de la constante de vitesse.	$mol.L^{-1}.s^{-1}$	s^{-1}	$L.mol^{-1}.s^{-1}$

I-5- Activation energy

A chemical reaction releases energy when it has a negative ΔG, but it still requires energy to start. This is explained by the fact that, during the reaction, the chemical bonds of the reactants must be broken to allow the formation of new bonds and the creation of products. The molecules of the reactants must pass through an unstable state called the transition state, which involves the distortion of the molecules. This Transition state has a relatively high energy.



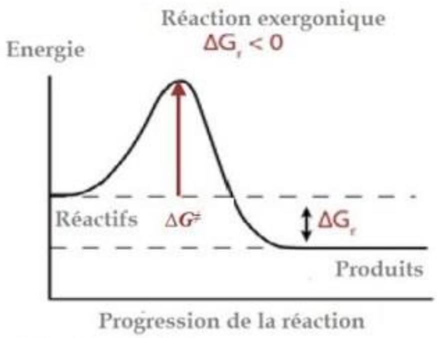


Fig.4.2.3.1. Réaction exergonique.

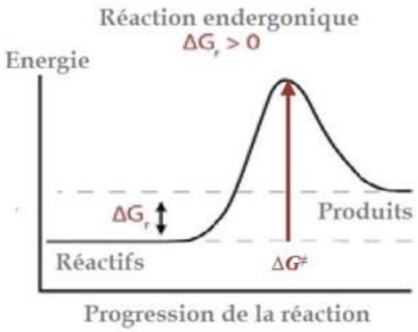


Fig.4.2.3.2. Réaction endergonique.

Using a graphical representation to illustrate this, an exergonic reaction shows that the activation energy is necessary to reach the transition state. In the case of an endergonic reaction, the transition state remains the same, but the activation energy is greater.

The rate of a chemical reaction is directly related to its activation energy. A higher activation energy value leads to a slower reaction because the molecules can only proceed with the reaction after overcoming the peak of the activation energy barrier.

1-5-1- Arrhenius law.

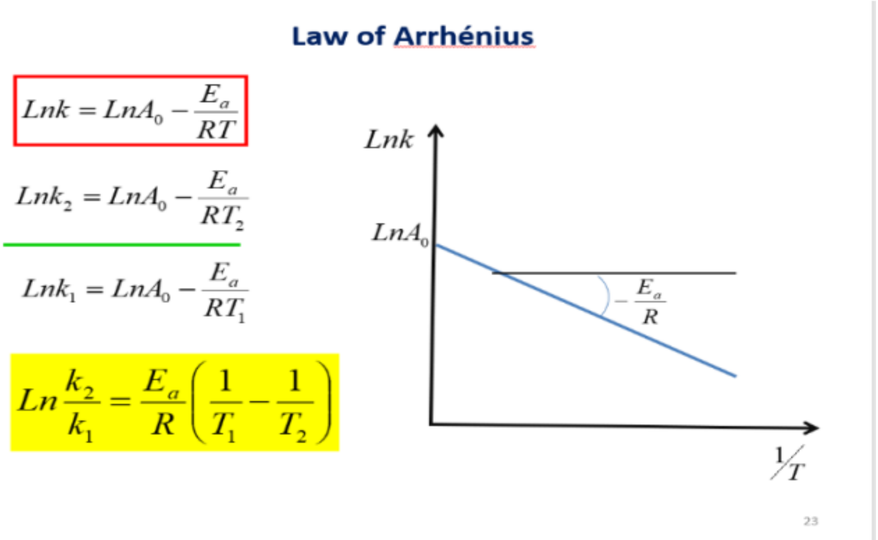
In chemical kinetics, the Arrhenius equation establishes the dependence of the rate of a chemical reaction on temperature. The Arrhenius equation is expressed as follows:

$$k = A.e^{-\frac{Ea}{R.T}}$$

In this equation k represents the rate constant.A is the pre-exponential factor, also known as the frequency factor, which accounts for the frequency of collisions and steric effects. The terms Ea, R, and T represent the activation energy, the ideal gas constant, and the absolute temperature, respectively.Introducing the natural logarithm to this equation leads to another expression of the Arrhenius law:

$$lnk = lnA - \frac{Ea}{R}.\frac{1}{T}$$

The value of the activation energy can be determined by plotting lnk as a function of 1/T. This results in a straight line with a slope of −Ea/R.



Law of Arrhénius

$$\boxed{Lnk = LnA_0 - \frac{E_a}{RT}}$$

$$Lnk_2 = LnA_0 - \frac{E_a}{RT_2}$$

$$Lnk_1 = LnA_0 - \frac{E_a}{RT_1}$$

$$Ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Examples:

Consider the following reactions:

1- Synthesis of hydroiodic acid:

$$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$$

The rate expression for this reaction is given by:

$$v = k.[H_2].[I_2]$$

This reaction follows Van't Hoff's law due to the equality between the partial reaction orders and the stoichiometric coefficients.

2- Synthesis of phosgene:

$$Cl_{2(g)} + CO_{(g)} \rightarrow COCl_{2(g)}$$

Experimentally, the rate of this reaction is given by the following formula:

$$v = k.[Cl_2]^{\frac{3}{2}}.[CO]$$

This reaction does not follow Van't Hoff's law because the partial reaction orders differ from the stoichiometric coefficients.

3- Oxidation of iodide ions by hydrogen peroxide:

$$2HI + H_2O_2 \rightarrow 2H_2O + I_2$$

This reaction would be elementary if its molecularity were 3 and if its reaction order were equal to the molecularity, that is 3. However, the rate law indicates an order of 2, which means that this reaction is not elementary. In fact, this reaction occurs in two distinct steps:

First step : $HI + H_2O_2 \rightarrow HOI + H_2O$ (slowly)

Second step : $HOI + HI \rightarrow I_2 + H_2O$ (fast)

The rate-determining or limiting step is the slow step, which dictates the overall reaction rate. This is why the rate expression is given by: $v = k\,[HI].[H_2O_2]$ And the overall order of the reaction is equal to 2.

I-6- Complex réactions

In a chemical reaction, one can consider composed reactions, also called complex reactions, which consist of a set of elementary steps combined either in series, opposing, or parallel. Chain mechanisms represent a more complicated category of complex reactions.

The majority of chemical reactions are of a complex nature, meaning that the overall equation does not provide detailed information about the mechanism involved. A complex reaction proceeds through a series of elementary reactions, each with its own rate. The overall rate of the complex reaction, often called the mechanism rate, is determined by the slowest step among them.

I-6-1- Consecutive (in series) Reactions:

The products of a reaction can, in turn, serve as reactants for another reaction. This forms a system of consecutive reactions, step-by-step, in an open sequence. These reactions proceed in a fixed order, always from the side of the reactants to that of the products:

$$A + B \rightarrow C + D \rightarrow E + F \rightarrow \ldots \rightarrow H + K$$

In the case of a reaction involving multiple steps, the overall rate of formation of the final product is dictated by the rate of the slowest phase, called the rate-determining step.

I-6-2- Parallel Reactions (Competitive and coupled):

Parallel reactions refer to distinct sets of reactions that share the same reactants but lead to different products. The first type of these reactions is called competitive parallel reactions:

$$A + B \rightarrow C$$

$$A + E \rightarrow D$$

The second type is called coupled reactions; these are reactions that have the same reactants but yield different products.

$$\begin{tikzcd} & C + D \\ A + B \arrow[ur] \arrow[dr] & \\ & E + F \end{tikzcd}$$

For example, during the nitration of phenol, the three isomers ortho, meta, and para of mono-nitrophenol are formed simultaneously.

The rate of conversion of the reactants is thus the sum of the rates of the individual reactions.

I-6-3- Reversible Reactions (Equilibrium or opposite).

Some reactions can proceed in both directions, and they are referred to as opposing reactions. In such cases, the system reaches a state of dynamic equilibrium. Macroscopically, the reaction appears complete because the composition of the system no longer changes.

$$A + B \rightleftharpoons C + D$$

The progress rate, denoted as α, varies between 0 and 1, indicating that it is an incomplete reaction. However, microscopically, the forward and reverse reactions persist at equal rates