Ch(4) : chemical equilibrium

I- Introduction

A reversible reaction is a chemical reaction where the reactants form the products that react together at the same time to give the reactants back. Reversible reactions will reach an equilibrium state when the concentrations of reactants remained and of products formed will no longer change.

In reality, a great many reactions do not proceed entirely to completion.

II- Reversible reactions

Reversible reactions are represented as the following general form :

$$a\,A + b\,B \underset{2}{\overset{1}{\rightleftarrows}} c\,C + d\,D$$

$$a\,A + b\,B \underset{2}{\overset{1}{\rightleftharpoons}} c\,C + d\,D$$

The direction (1) is called forward direction.

The direction (2) is called reverse direction (or backward direction).

Examples of reversible reactions

Reaction of formation of (NO) :

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2\,NO_{(g)}$$

Esterification reaction :

Carboxylic acid + alcohol $\rightleftharpoons$ Ester + water.

Reaction of carboxylic acids with water :

$$R\text{-}COOH + H_2O \rightleftharpoons R\text{-}COO^- + H_3O^+$$

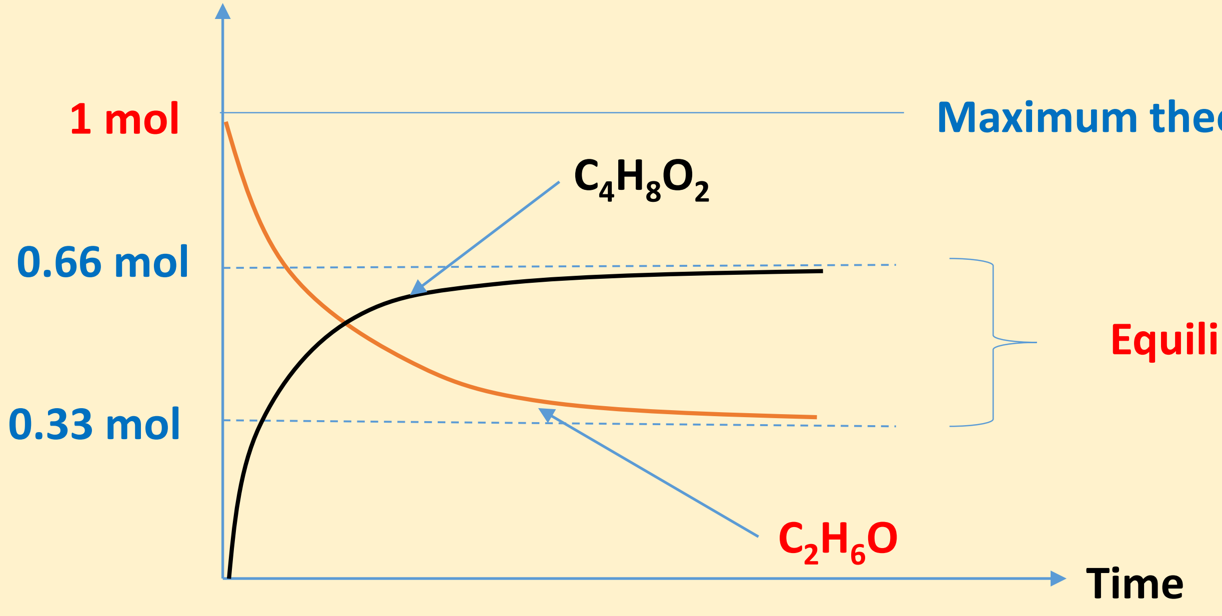
Consider the esterification reaction of 1 mol of ethanol (C_2H_6O) with 1 mol of ethanoic acid ($C_2H_4O_2$) :

$$C_2H_6O + C_2H_4O_2 \rightleftharpoons C_4H_8O_2 + H_2O$$

The following table is obtained experimentally.

Initial number of moles	1 mol	1 mol	0	0
Number of moles at equilibrium	0.33 mol	0.33 mol	0.66 mol	0.66 mol

The kinetic curves of C_2H_6O and of $C_4H_8O_2$ are the following :



III- Equilibrium constant K_c

Consider the general equation : $a\,A \;+\; b\,B \;\underset{2}{\overset{1}{\rightleftarrows}}\; c\,C \;+\; d\,D$

Each reversible reaction has a specific equilibrium state and it is characterized by a specific constant called equilibrium constant relative to concentrations, this constant is designated by K_c :

$$K_c = \frac{[C]^c_{\text{formed}} \times [D]^d_{\text{formed}}}{[A]^a_{\text{remaining}} \times [B]^b_{\text{remaining}}}$$

Where [A], [B], [C] and [D] are respectively the concentrations of reactants remained and the concentrations of products formed when the equilibrium is established.

IV- Degree of conversion of a reactant and yield of reaction

The degree of conversion of reactant (A for example) is designated by alfa (α) :

$$\alpha(A) = \frac{n\,(A)\ \text{reacted at equilibrium}}{n_0\,(A)}$$

The percentage of conversion is equal to $\alpha \times 100$

The yield of the reaction is calculated with respect to a product (C for example) :

$$\text{Yield} = \frac{n\,(C)\ \text{formed at equilibrium}}{n(C)\ \text{theoretical}}$$

The percentage yield is : yield $\times$ 100

Application 1

Consider the reaction of formation of ammonia (NH_3) :

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

At a temperature T = 472℃, 0.0415 mol of N_2 is mixed initially with 0.131 mol of H_2 in a container of volume V = 1 L, when the equilibrium is established, the number of moles of NH_3 obtained is n = 0.00272 mol

1. **Determine the number of moles of N_2 and of H_2 remained at equilibrium.**
2. **Calculate the equilibrium constant K_c of this reaction.**
3. **Deduce the degree of conversion α of N_2**

Answer

1. At equilibrium, acc. to. SR :

$$n(N_2)_{reacted}/1 = n(H_2)_{reacted}/3 = n(NH_3)_{formed}/2 = 0.00272/2 = 0.00136$$

$$n(N_2)_{reacted} = 0.00136 \text{ mol}$$

$$n(H_2)_{reacted} = 3\times(0.00136) = 0.00408 \text{ mol}$$

$$n(N_2)_{remained} = n(N_2)_0 - n(N_2)_{reacted} = 0.0415 - 0.00136 = 0.0401 \text{ mol}$$

$$n(H_2)_{remained} = n(H_2)_0 - n(H_2)_{reacted} = 0.131 - 0.00408 = 0.126 \text{ mol.}$$

2. $K_c = [NH_3]^2_{formed} / [N_2]_{rem} \times [H_2]^3_{rem}$

$$= (0.00272/1)^2/(0.0401/1)\times(0.126/1)^3 = 0.0922$$

3. The degree of conversion : $\alpha\ (N_2) = n(N_2)_{reacted\ at\ eq}/n(N_2)_0$

$$= 0.00136/0.0415 = 0.0327\ (3.27\ \%)$$

Application 2

Consider the following esterification reaction :

$$C_2H_4O_{2(l)} + C_2H_6O_{(l)} \leftrightarrow C_4H_8O_{2(l)} + H_2O_{(l)}$$

The equilibrium constant of this reaction is : $K_c = 4$

The reaction is started by mixing certain number of moles of reactants in a container of volume V=2 L.

After certain time t, the number of moles of reactants remained and of products formed are measured, we found :

$n(C_2H_4O_2)_t = 1$ mol $\quad$ $n(C_2H_6O)_t = 3$ mol

$n(C_4H_8O_2)_t = 0.5$ mol $\quad$ $n(H_2O)_t = 2$ mol

Specify whether the system reached its equilibrium state or not at this time.

Answer

We calculate the quotient Q :

$$Q = [C_4H_8O_2]\times[H_2O]/\ [C_2H_4O_2]\times[C_2H_6O]$$

$$= (0.5/2)\times(2/2)/(1/2)\times(3/2) = 1/3 = 0.333 < 4$$

$Q < K_c$, thus the system did not reach its equilibrium state yet.

Application 3

Consider the following reaction :

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

4 mol of $COCl_2$ is introduced initially in a container of volume V= 1L.

The equilibrium constant of this reaction at 25℃ is $K_c = 2.19\times10^{-10}$

1. **Determine the molar concentrations of the reactant and of the products when the reaction reaches its equilibrium state.**
2. **Calculate the percentage of conversion of $COCl_2$.**

Answer

1. Let x be the number of moles of $COCl_2$ reacted at equilibrium.

Acc.to.SR at equilibrium :

$$n(COCl_2)_{reacted}/1 = n(CO)_{formed}/1 = n(Cl_2)_{formed}/1$$

$$x = n(CO)_{formed} = n(Cl_2)_{formed}$$

Thus : $n(CO)_{formed} = x$, $n(Cl_2)_{formed} = x$ and $n(COCl_2)_{reacted} = x$

$n(COCl_2)_{remaining} = n_0 - n_{reacted} = 4\text{-}x$ mol

	$COCl_2$	CO	Cl_2
Initial state (mol)	4	0	0
Final state (equilibrium state) (mol)	4-x	x	x

$$K_c = [CO]_{formed} \times [Cl_2]_{formed} / [COCl_2]_{remaining}$$

$$= x^2/4\text{-}x = 2.19\times10^{-10}$$

$$x^2 = 4\times2.19\times10^{-10} - 2.19\times10^{-10}\,x$$

$$x^2 + 2.19\times10^{-10}x - 8.76\times10^{-10} = 0$$

We find $x_1 = 2.95\times10^{-5}$ mol : accepted

$x_2 = -2.95\times10^{-5}$ mol : rejected

$[COCl_2]_{remaining} = 4 - 2.95\times10^{-5} = 3.99$ mol/L

$[CO]_{formed} = [Cl_2]_{formed} = 2.95\times10^{-5}$ mol/L

2. % of conversion of $COCl_2 = n(COCl_2)_{reacted\ at\ eq} \times 100/n_0(COCl_2)$

$= x \times 100/4 = 2.95\times10^{-5} \times 100/4$

$= 7.37\times10^{-4}\%$

Generalization about the determination of the composition of the system at equilibrium

Consider the general equation : $a\ A + b\ B \leftrightarrow c\ C + d\ D$

For example we give : $n_0(A) = 2$ mol and $n_0(B) = 3$ mol

The equilibrium constant of this reaction is given, for example:

$K_c = 5$ and $V(\text{container}) = 1L$

How to determine the number of moles of each reactant and of each product at equilibrium?

Let x be the number of moles of (A) reacted at equilibrium.

Acc.to.SR. at equilibrium:

$$n(A)_{reacted}/a = n(B)_{reacted}/b = n(C)_{formed}/c = n(D)_{formed}/d$$

Thus : $x/a = n(B)_{reacted}/b = n(C)_{formed}/c = n(D)_{formed}/d$

Therefore : $n(B)_{reacted} = bx/a$ $n(C)_{formed} = cx/a$ $n(D)_{formed} = dx/a$

$n(A)_{rem} = n_0(A) - n(A)_{reacted} = 2\text{-}x$

$n(B)_{rem} = n_0(B) - n(B)_{reacted} = 3 - bx/a$

$K_c = [C]^c{}_{formed} \times [D]^d{}_{formed} / [A]^a{}_{rem} \times [B]^b{}_{rem}$

$= (cx/a)^c \times (dx/a)^d / (2-x)^a \times (3-bx/a)^b = 5$

After multiplication, we obtain a quadratic equation.

By solving the equation we obtain two roots x_1 and x_2

The accepted value of x is the positive one.

If the two values of x are positive, thus :

$x_1 < n_0(A)$ **is accepted**

$x_2 > n_0(A)$ **is rejected**

Application 4

6.55 g of $NOCl_{(g)}$ was introduced in a container of volume V = 2 L at T= 25 ℃

25% of NOCl are decomposed to give an equilibrium state according to the following reaction :

$$2\ NOCl_{(g)} \leftrightarrow 2NO_{(g)} + Cl_{2(g)}$$

Given

M(N) = 14   M(O) = 16   M(Cl) = 35.5 $g.mol^{-1}$

1. Show that $[NOCl]_{remaining}$ at equilibrium is equal to 0.0375 $mol.L^{-1}$.
2. Calculate the concentrations of the products formed at equilibrium.
3. Show that the equilibrium constant of this reaction is $K_c = 6.94\times 10^{-4}$

Answer

1. $M(NOCl) = 14 + 16 + 35.5 = 65.5$ g/mol

$n_0(NOCl) = m/M = 6.55/65.5 = 0.1$ mol

$\alpha(NOCl) = n(NOCl)_{reacted}/n_0(NOCl) = 25\% = 0.25$

$n(NOCl)_{reacted} = 0.25\ n_0(NOCl) = 0.25 \times 0.1 = 0.025$ mol

$n(NOCl)_{remaining} = n_0(NOCl) – n(NOCl)_{reacted} = 0.1-0.025 = 0.075\ mol.L^{-1}$

$[NOCl]_{remaining} = n/V = 0.075/2 = 0.0375\ mol.L^{-1}$

2. Acc. to SR. at equilibrium :

$n(NOCl)_{reacted}/2 = n(NO)_{formed}/2 = n(Cl_2)_{formed}/1$

$0.0125/2 = n(NO)_{formed}/2 = n(Cl_2)_{formed}/1$

$n(NO)_{formed} = 0.025$ mol $\qquad n(Cl_2)_{formed} = 0.0125$ mol

$[NO]_{formed} = 0.025/2 = 0.0125$ mol/L $\qquad [Cl_2]_{formed} = 0.0125/2 = 6.25\times 10^{-3}$ mol/L

3. $K_c = [NO]^2_{formed} \times [Cl_2]_{formed} / [NOCl]^2_{rem}$

$$= (0.0125)^2 \times (6.25 \times 10^{-3})/(0.0375)^2$$

$$= 6.94 \times 10^{-4}$$

Application 5

2 mol of Ethanoic acid ($C_2H_4O_2$) is mixed initially with 3 mol of ethanol (C_2H_6O) in a container of volume V = 3L, the mixture is heated to reach the equilibrium state producing the ester ($C_4H_8O_2$) and water as the following equation:

$$C_2H_4O_{2(l)} \; + \; C_2H_6O_{(l)} \; \leftrightarrow \; C_4H_8O_{2)l)} \; + \; H_2O_{(l)}$$

The equilibrium constant of this reaction is $K_c = 4$

1. Determine the composition of the system at equilibrium in mol.
2. Determine the % yield of this reaction.

Answer

1. Let x be the number of moles of $C_2H_4O_2$ reacted at equilibrium.

Acc. to. SR at equilibrium :

$$n(C_2H_4O_2)_{reacted} = n(C_2H_6O)_{reacted} = n(C_4H_8O_2)_{formed} = n(H_2O)_{formed}$$

$$x = n(C_2H_6O)_{reacted} = n(C_4H_8O_2)_{formed} = n(H_2O)_{formed}$$

$$n(C_2H_4O_2)_{rem} = n_0(C_2H_4O_2) - n(C_2H_4O_2)_{reacted}$$

$$= 2 - x$$

$$n(C_2H_6O)_{rem} = n_0(C_2H_6O) - n(C_2H_6O)_{reacted}$$

$$= 3 - x$$

$$K_c = [C_4H_8O_2]_{formed} \times [H_2O]_{formed} / [C_2H_4O_2]_{rem} \times [C_2H_6O]_{rem}$$

$$= (x/2) \times (x/2) \;/\; ((2-x)/2) \times ((3-x)/2) = 4$$

$$= x^2/(2-x)(3-x) = 4$$

$$x^2/(6-5x + x^2) = 4$$

$$x^2 = 24 - 20x + 4x^2 \qquad\qquad 3x^2 - 20x + 24 = 0$$

We find $x_1 = 1.56 < 2$ accepted and $x_2 = 5.097 > 2$ rejected

The composition of the system at equilibrium is :

$n(C_2H_4O_2)_{rem} = 2\text{-}x = 2\text{-} 1.56 = 0.44$ mol

$n(C_2H_6O)_{rem} = 3\text{-}x = 3 – 1.56 = 1.44$ mol

$n(C_4H_8O_2)_{formed} = n(H_2O)_{formed} = x = 1.56$ mol

2. $R(C_2H_4O_2) = 2/1 < R(C_2H_6O) = 3/1$, thus $C_2H_4O_2$ is the limiting reactant.

Acc. to.SR: $n(C_4H_8O_2)_{max\ theoretical} = n_0(C_2H_4O_2)_0 = 2$ mol

$\%\ yield = n(C_4H_8O_2)_{formed\ at\ equilibrium} \times 100/n(C_4H_8O_2)_{max\ theoretical}$

$= 1.56 \times 100/2 = 78\ \%$