Reactions at equilibrium – part I

Law of the mass action

◆ The law of mass action is a mathematical model that explains and predicts behaviours of solutions in dynamic equilibrium

◆ When in a closed system, with P and T constant, a reaction occurs → the rates at which products are formed and reagents consumed are equal

◆ This is a chemical dynamic equilibrium → the reactions are reversible and the concentrations of the reactants and products do not change with time
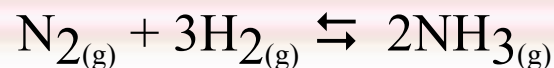
$$aA + bB \leftrightarrows cC + dD$$

aA+bB ⇄ cC+dD

◆ For each dynamic equilibrium reaction we can calculate an equilibrium constant from the ratio between the single reactions rate constants

◆ This ratio can also be expressed in terms of concentration

$$K_e = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

◆ Reagents and products can be in the same physical state → *homogeneous reaction* $N_{2(g)} + 3H_{2(g)} ⇄ 2NH_{3(g)}$

◆ or in different states → *heterogeneous reaction*

$$CaCO_{3(s)} ⇄ CaO_{(s)} + CO_{2(g)}$$

$$K_e = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

◆ **What does K measure?** The direction of the equilibrium
 ◆ $K > 1 \rightarrow$ the reaction is in favour of the products
 ◆ $K = 1 \rightarrow$ the reagents and products concentrations are the same
 ◆ $K < 1 \rightarrow$ the reaction is in favour of the reagents

◆ The constant of a reaction written in one way, is the mathematical reciprocal of the same reaction written in the opposite way

$H_2 + I_2 \leftrightarrows 2HI$ $2HI \leftrightarrows H_2 + I_2$
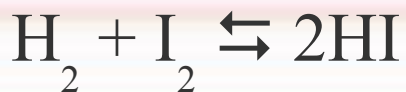
$$K_e = \frac{[HI]^2}{[H_2][I_2]}$$ $$K_e' = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_e = \frac{1}{K_e'}$$

What does it happen if we change the concentrations of reagents and/or products?

- Given a chemical reaction at equilibrium with **T constant**, every external intervention, which perturbs the equilibrium, will be counteracted by the system (*Le Chatelier principle*)

- If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to reverse the change.
  - Case A: increase of **products** concentration → the reaction moves towards the reagents (leftwards)
  - Case B: increase of **reagents** concentration → the reaction moves towards the products (rightwards)

$$CO_2 + H_2 \rightleftharpoons H_2O + CO$$

$$K_c = \frac{[H_2O][CO]}{[CO_2][H_2]}$$

Equilibrium reactions in the gas phase

◆ In case of a reaction in the gas phase, the partial pressures of reagents and products can be used instead of their molar concentrations

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

◆ It is easy to convert Kp into Kc and viceversa, using the ideal gas law: $P_j V = n_j RT \quad \rightarrow P_j = [J]RT$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}} = K_c (RT)^{(c+d-a-b)}$$

◆ In case (c+d-a-b)=0, then $K_p = K_c$

How do we calculate the concentrations at equilibrium?

◆ The following homogeneous reaction in the gas phase: $N_2 + 3H_2 \leftrightarrows 2NH_3$ is started by inserting 0.01 mol of N_2 and 0.01 mol of H_2 in an insulated box of 1L. At equilibrium 10^{-3} mol of NH_3 are formed. Which is the value of K_c?

no. moles	N_2	H_2	NH_3
At start	0.01	0.01	0
Consumed/ produced	-x	-3x	+2x
At equilibrium			10^{-3}

• The stoichiometric coefficient (aka stoichiometric number) of any given component gives the number of molecules which participate in the reaction as written

• In this case **-x** moles of N_2 are consumed, **-3x** moles of H_2 are consumed and **+2x** moles of NH_3 are produced

How do we calculate the concentrations at equilibrium?

◆ How do we fill in the table?
   We calculate the algebraic sum of each column
◆ How do we calculate *x*?
   We choose the appropriate column

no. moles	N_2	H_2	NH_3
At start	0.01	0.01	0
Consumed/ produced	-x	-3x	+2x
At equilibrium	0.01-x	0.01-3x	$0+2x=10^{-3}$

● In this case **x** can be calculated from the column of NH_3:

$2x=10^{-3} \rightarrow x=5 \cdot 10^{-4}$ mol

● Hence we can calculate all the remaining terms

$N_2 = 0.01-5 \cdot 10^{-4} = 9.5 \cdot 10^{-3}$ mol

$H_2 = 0.01-(3 \cdot 5 \cdot 10^{-4}) = 8.5 \cdot 10^{-3}$ mol

How do we calculate the concentrations at equilibrium?

no. moles	N_2	H_2	NH_3
At start	0.01	0.01	0
Consumed/ produced	-x	-3x	+2x
At equilibrium	$9.5 \cdot 10^{-3}$	$8.5 \cdot 10^{-3}$	10^{-3}

Now that the table is complete, we can calculate the concentrations of re-agents and products at equilibrium and also the equilibrium constant

$[N_2]= n/V = 0.0095/1 = 9.5 \cdot 10^{-3} M$

$[H_2]= n/V = 0.0085/1 = 8.5 \cdot 10^{-3} M$

$[NH_3]= n/V = 0.001/1 = 1.0 \cdot 10^{-3} M$

$$K_e = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(10^{-3})^2 M^2}{(9.5 \times 10^{-3})M \times (8.5 \times 10^{-3})^3 M^3} = \frac{10^{-6}}{9.5 \times 10^{-3} \times 6.14 \times 10^{-7}} = \frac{1}{5.83 \times 10^{-3}} = 171.53 M^{-2}$$

Exercise 1

Calculate the equilibrium constant of the reaction $N_2 + 3H_2 \leftrightharpoons 2NH_3$. This has been started by inserting 9 mol of H_2 and 6 mol of N_2 in a cylinder of 3L. At equilibrium there were 4 mol of NH_3.

No. moles	H_2	N_2	NH_3
At start	9	6	0
consumed/produced	-3x	-x	+2x
At equilibrium			4

$0 + 2x = 4 \rightarrow x = 2$

Exercise 1

Calculate the equilibrium constant of the reaction $N_2 + 3H_2 \leftrightarrows 2NH_3$. This has been started by inserting 9 mol of H_2 and 6 mol of N_2 in a cylinder of 3L. At equilibrium there were 4 mol of NH_3.

No. moles	H_2	N_2	NH_3
At start	9	6	0
consumed/produced	-3x	-x	+2x
At equilibrium	3	4	4

Now we can calculate the concentrations of the components at equilibrium
$[H_2] = n/V = 3/3 = 1M$
$[N_2] = n/V = 4/3 = 1.33M$
$[NH_3] = n/V = 4/3 = 1.33M$

$$K_e = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.33)^2 M^2}{(1.33)M \times (1)^3 M^3} = 1.33 M^{-2}$$

Exercise 2

◆ At room temperature, the equilbrium constant of the reaction:
α-glucose ⇄ β-glucose in water is 1.8. How many grams of β-glucose are in equilibrium with 100g of α-glucose in 1L?   [FW$_{glucose}$=180]

K_c= [β]/[α]   →   [β]=K_c·[α]= 1.8·(100/180)= 1M

M=g/FW·V   →   g= M·FW·V= 1 ·180 ·1 = 180g

Exercise 3

◆ 2 mol of CH_4 and 1 mol of H_2S in the gas phase are filling in a box at 727°C. At equilibrium there are 0.4 mol of H_2 and the total pressure is 0.2 atm. Calculate the volume of the box.

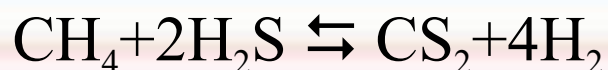$$CH_4 + 2H_2S \leftrightarrows CS_2 + 4H_2$$
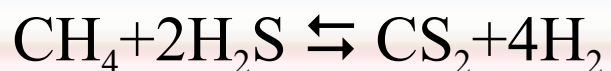
moles	CH_4	H_2S	CS_2	H_2
At start	2	1	0	0
consumed/produced	-x	-2x	+x	+4x
At equilibrium				0.4

$0 + 4x = 0.4 \quad \rightarrow x = 0.1$

Exercise 3

◆ 2 mol of CH_4 and 1 mol of H_2S in the gas phase are filling in a box at 727°C. At equilibrium there are 0.4 mol of H_2 and the total pressure is 0.2 atm. Calculate the volume of the box.

$$CH_4 + 2H_2S \leftrightarrows CS_2 + 4H_2$$

moles	CH_4	H_2S	CS_2	H_2
At start	2	1	0	0
consumed/produced	-x	-2x	+x	+4x
At equilibrium	1.9	0.8	0.1	0.4

In order to calculate the volume, we need to calculate the total no. mol at equilibrium:

$N_{tot} = 1.9 + 0.8 + 0.1 + 0.4 = 3.2$ mol

$V = n_{tot} RT / V = (3.2 \cdot 0.082 \cdot 1000)/0.2 = 1312$ L

Exercise 4

◆ The equilibrium constant at 793K of the reaction: $2HF \leftrightarrows H_2 + F_2$ is $1.56 \cdot 10^{-2}$. The reaction is started by adding 0.5mol F_2 and 1mol of H_2 to an isothermal box of 10 L. Calculate the molar concentration of the three species at equilibrium.

mol	HF	H_2	F_2
At start	0	1	0.5
consumed/produced	2x	-x	-x
At equilibrium	2x	1-x	0.5-x

$$K_c = \frac{(1-x)(0.5-x)}{(2x)^2} = 1.56 \times 10^{-2}$$

$$0.5 - x - 0.5x + x^2 = 6.24 \times 10^{-2} x^2$$

$$0.938 x^2 - 1.5x + 0.5 = 0$$

It is worth recalling that the solution of a generic second grade equation:

$$ax^2 + bx + c = 0$$

is: $x = \dfrac{-b \pm \sqrt{b^2 - 4ac}}{2a}$

$$x = \frac{1.5 \pm \sqrt{2.25 - 1.876}}{1.876}$$

$x_1 = 0.474$ $\quad$ $x_2 = 1.12$

Why do we choose x_1 and not x_2?

Both values are mathematical correct, BUT in our case x represents the no of moles → it must be both a positive number and it must give a positive number after all the calculations

HF = 2·0.474=0.948 mol $\qquad$ → [HF] = 0.948/10 = 9.48·10⁻²M

H_2 = 1-x = 0.52 mol $\qquad$ → [H_2] = 0.526/10 = 5.26·10⁻²M

F_2 = 0.5-x = 0.026 mol $\qquad$ → [F_2] = 0.026/10 = 2.6·10⁻³M

Exercise 5

◆ In a box of 0.5L, 8g of PCl_5 are introduced at 250°C. The constant of the reaction in the gaseous phase: $PCl_5 \leftrightarrows PCl_3 + Cl_2$ is 0.041 M. Calculate the concentration of the three species at equilibrium.   [FW_{PCl5}=208]

PCl_5 at the beginning = g/FW = 8/208 = 0.038 mol

moli	PCl_5	PCl_3	Cl_2
start	0.038	0	0
consumed/produced	-x	+x	+x
equilibrium	0.038-x	x	x

$$K_c = \frac{\dfrac{x}{V} \times \dfrac{x}{V}}{\dfrac{0.038 - x}{V}} = \frac{x^2}{V(0.038 - x)} = 0.041M$$

$x^2 = 0.041 \cdot 0.5(0.038-x) = 0.0205(0.038-x)$

$x^2 = 7.79 \cdot 10^{-4} - 0.0205x$

$x^2 + 0.0205x - 7.79 \cdot 10^{-4} = 0$

$$x = \frac{0.0205 \pm \sqrt{4.2 \times 10^{-4} + 31.16 \times 10^{-4}}}{2} = \frac{-0.205 \pm 0.0595}{2}$$

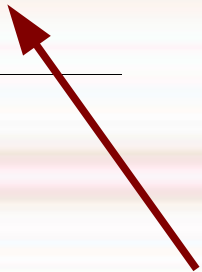$$x_1 = 0.0195 \qquad x_2 = -0.04$$

[PCl$_3$]=[Cl$_2$]=x/V = 0.0195/0.5 = 0.039M

[PCl$_5$]= (0.038-x)/V = (0.038-0.0195)/0.5= 0.038M

Exercise 6

◆ 4 mol of A and 8 mol of B are introduced in a box of 1L. The equilibrium is attained when there are 4 mol of C in the box. Calculate Kc for the equilibrium: A + 3B ⇄ 2C

no. mol	A	B	C
start	4	8	0
Consumed/produced	-x	-3x	+2x
equilibrium			4

C: 0+2x=4 → x=2mol

A: 4-x → 4-2=2mol

B: 8-3x → 8-6=2mol

$$K_c = \frac{[C]^2}{[A][B]^3} = \frac{4^2}{2 \times 2^3} = 1M^{-2}$$

Exercise 7

◆ In a box of 2L at high T, there are 4g of PCl_5. At equilibrium there are 0.8g of PCl_3. Calculate how many grams of Cl_2 are needed to obtain 0.5g of PCl_3.

$$PCl_5 \leftrightarrows PCl_3 + Cl_2$$

Starting quantity of $PCl_5 = 4/208 = 1.92 \cdot 10^{-2}$ mol
equilibrium quantity of $PCl_3 = 0.8/138 = 5.8 \cdot 10^{-3}$ mol

mol	PCl_5	PCl_3	Cl_2
start	$1.92 \cdot 10^{-2}$	0	0
consumed/produced	-x	+x	+x
equilibrium			$5.8 \cdot 10^{-3}$

$[PCl_5]_{eq} = 1.92 \cdot 10^{-2} - x = 1.34 \cdot 10^{-2}/2 = 6.7 \cdot 10^{-3}$ M
$[PCl_3]_{eq} = + x = 5.8 \cdot 10^{-3}/2 = 2.9 \cdot 10^{-3}$ M
$[Cl_2]_{eq} = + x = 5.8 \cdot 10^{-3}/2 = 2.9 \cdot 10^{-3}$ M

$$K_c = \frac{(2.9\,10^{-3})^2}{6.7\,10^{-3}} = 1.25\,10^{-3}\,M$$

After adding Cl_2, the quantity of PCl_3 becomes: $0.5/138 = 3.64 \cdot 10^{-3}$ mol

The new starting condition is the previous equilibrium point:

mol	PCl_5	PCl_3	Cl_2
start	$1.34 \cdot 10^{-2}$	$5.8 \cdot 10^{-3}$	$5.8 \cdot 10^{-3}+y$
consumed/produced	$+x$	$-x$	$-x$
equilibrium		$3.64 \cdot 10^{-3}$	

This time we can calculate the new x from the second column
$\rightarrow$ $5.8 \cdot 10^{-3} -x = 3.64 \cdot 10^{-3}$ $\rightarrow$ $x = 2.16 \cdot 10^{-3}$ mol

$[PCl_3] = 3.64 \cdot 10^{-3} /2 = 1.82 \cdot 10^{-3}$ M
$[PCl_5] = (1.34 \cdot 10^{-2} +x)/2 = 7.78 \cdot 10^{-3}$ M
$[Cl_2] = (5.8 \cdot 10^{-3}+y-x)/2 = (5.8 \cdot 10^{-3} - 2.16 \cdot 10^{-3} +y)/2 =$
     $= (3.64 \cdot 10^{-3} +y)/2 = (1.82 \cdot 10^{-3} +y/2)$ M

$$K_c = 1.25\,10^{-3} = \frac{1.82 \cdot 10^{-3} \cdot (1.82 \cdot 10^{-3} + y/2)}{7.78\,10^{-3}}$$

$$9.72 \cdot 10^{-6} = 3.18 \cdot 10^{-6} + 8.75 \cdot 10^{-4} y$$

$$6.54 \cdot 10^{-6} = 8.75 \cdot 10^{-4} y$$

$y = 7.47 \cdot 10^{-3}$ mol of Cl_2 need to be added,
which correspond to a mass of:

$g = n \cdot PM = 7.47 \cdot 10^{-3} \cdot 70.8 = 0.53 g$

Exercise 8

◆ 1 mol of H_2 and 1 mol of I_2 are inserted in a box of 1L. In these con-ditions Kc=50. Calculate the concentration of the three species for the equilibrium reaction $H_2 + I_2 \leftrightarrows 2HI$

Mol	H_2	I_2	HI
start	1	1	0
consumed/produced	-x	-x	+2x
equilibrium	1-x	1-x	2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x)^2}{(1-x)(1-x)} = 50$$

$$4x^2 = 50(1 - 2x + x^2)$$

$$46x^2 - 100x + 50 = 0$$

$$x = \frac{100 \pm \sqrt{10000 - 9200}}{92}$$

$x_1 = 1.39$

$x_2 = 0.77$

$[H_2] = 1\text{-}0.77 = 0.23M$

$[I_2] = 1\text{-}0.77 = 0.23M$

$[HI] = 2\cdot 0.77 = 1.54M$