The Equilibrium Law

States *"If the concentrations of all the substances present at equilibrium are raised to the power of the number of moles they appear in the equation, the product of the concentrations of the products divided by the product of the concentrations of the reactants is a constant, provided the temperature remains constant" ...* ***WOW!***

Calculating Equilibrium Constants

Types **K_c** equilibrium values are **concentrations in mol dm^{-3}**

K_p equilibrium values are **partial pressures** - system at constant temperature

The partial pressure expression can be used for reactions involving gases

Calculating K_c for a reaction of the form **$a\,A + b\,B \rightleftharpoons c\,C + d\,D$**

then (at constant temperature)

$$\boxed{\frac{[C]^c\,.\,[D]^d}{[A]^a\,.\,[B]^b} = \text{a constant, } (K_c)}$$

[ ] denotes the equilibrium concentration in mol dm^{-3}

K_c is known as the Equilibrium Constant

Value of K_c

- **AFFECTED** by a change of **temperature**
- **NOT AFFECTED** by a change in **concentrations**
  a change of **pressure**
  adding a **catalyst**

Q.1 *What happens to the theoretical yield of a reaction if...*

- *K_c increases*
- *K_c decreases ?*

Q.2 *What happens to the value of K_c if ...*

- *the **temperature is increased** in an **exothermic** reaction*
- *the **temperature is decreased** in an **exothermic** reaction*
- *the **temperature is increased** in an **endothermic** reaction*
- *the **temperature is decreased** in an **endothermic** reaction*

Q.3 *Write expressions for the equilibrium constant, K_c of the following reactions. Remember, equilibrium constants can have units.*

$Fe^{3+}(aq) + NCS^{-}(aq) \rightleftharpoons FeNCS^{2+}(aq)$ **K_c =**

$NH_4OH(aq) \rightleftharpoons NH_4^{+}(aq) + OH^{-}(aq)$ **K_c =**

$2Fe^{3+}(aq) + 2I^{-}(aq) \rightleftharpoons 2Fe^{2+}(aq) + I_2(aq)$ **K_c =**

Calculating value of K_c

- construct the balanced equation, including state symbols (aq), (g) etc.
- determine the number of moles of each species at equilibrium
- divide moles by volume (dm^3) to get the equilibrium concentrations in mol dm^{-3} (If no volume is quoted, use a V; it will probably cancel out)
- from the equation constructed in the first step, write out an expression for K_c.
- substitute values from third step and calculate the value of K_c with any units

Example 1 *Ethanoic acid (1 mol) reacts with ethanol (1 mol) at 298K. When equilibrium is reached, two thirds of the acid has reacted. Calculate the value of K_c.*

	$CH_3COOH_{(l)}$ +	$C_2H_5OH_{(l)}$ $\rightleftharpoons$	$CH_3COOC_2H_{5(l)}$ +	$H_2O_{(l)}$
initial moles	**1**	**1**	**0**	**0**
equilibrium moles	**$1 - ^2/_3$**	**$1 - ^2/_3$**	**$^2/_3$**	**$^2/_3$**
	If ⅔ mol of the acid has reacted then take the value away from the initial number of moles of acid	If ⅔ mol of the acid has reacted, then ⅔ mol of ethanol will also have reacted. Take ⅔ mol away from the original.	According to the equation, for every mol of acid that reacts you make 1 mol of ester and 1 mol of water. Therefore, if ⅔ mol of acid has reacted, ⅔ mol of ester and ⅔ mol of water are produced.	
equilibrium concs.	**$^1/_3$ / V**	**$^1/_3$ / V**	**$^2/_3$ / V**	**$^2/_3$ / V**

V *= volume (dm^3) of the equilibrium mixture*

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{^2/_3 / V \;.\; ^2/_3 / V}{^1/_3 / V \;.\; ^1/_3 / V} = \mathbf{4}$$

Example 2 *Consider the reaction* $P + 2Q \rightleftharpoons R + S$ *(all are aqueous)*

1 mol of P and 1 mol of Q are mixed. Once equilibrium has been achieved, 0.6 mol of P are present. How many moles of Q, R and S are present at equilibrium ?

	P	+	**2Q**	$\rightleftharpoons$	**R**	+	**S**
Initial moles	**1**		**1**		**0**		**0**
At equilibrium	**0·6**		**0·2**		**0·4**		**0·4**
	(0·4 reacted)		(2 x 0·4 reacted)		(get 1 R and 1 S for every P that reacts)		
	1- 0·6 remain		1- 0·8 remain				

Explanation
- *if 0.6 moles of P remain of the original 1 mole, 0.4 moles have reacted*
- *the equation states that 2 moles of Q react with every 1 mole of P*
- *this means that 0.8 (2 x 0.4) moles of Q have reacted, leaving 0.2 moles*
- *one mole of R and S are produced from every mole of P that reacts*
- *this means 0.4 moles of R and 0.4 moles of S are present at equilibrium*

Q.4 *The questions refer to the equilibrium* $A + B \rightleftharpoons C + D$ *(all aqueous)*

(a) *If the original number of moles of A and B are both 1 and 0.4 moles of A are present at equilibrium, how many moles of B, C and D are present?*

What will be the value of K_c *?*

(b) *At a higher temperature, the original moles of A and B were 2 and 3 respectively. If 1 mole of A is present at equilibrium, how many moles of B, C and D are present? What else does this tell you about the reaction?*

Calculations involving Gases

Method

- carried out in a similar way to those involving concentrations
- one has the **choice of using K_c or K_p** for the equilibrium constant
- **when using K_p only take into account gaseous species** for the expression
- quotes the partial pressure of the gas in the equilibrium mixture
- pressure is usually quoted in Nm^{-2} or Pa - (atmospheres are sometimes used)
- the **units of the constant K_p depend on the stoichiometry** of the reaction

total pressure = sum of the partial pressures

partial pressure = total pressure x mole fraction

$$\textbf{mole fraction} = \frac{\textbf{number of moles of a substance}}{\textbf{number of moles of all substances present}}$$

Calculating K_p for a reaction of the form $a\,A(g) + b\,B(g) \rightleftharpoons c\,C(g)$

then (at constant temperature)

$$\boxed{\frac{P_C^{\,c}}{P_A^{\,a} \times P_B^{\,b}} = \text{a constant, } (K_p)}$$

P denotes the partial pressure of a gaseous component at equilibrium

K_p is the Equilibrium Constant in terms of partial pressures

Example $N_2O_4(g) \rightleftharpoons 2\,NO_2(g)$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} \quad \text{(units of pressure)}$$

Q.5 *Write expressions for the equilibrium constant, K_p of the following reactions. Remember, equilibrium constants can have units. (assume the pressure is in MPa)*

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ K_p =

$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$ K_p =

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ K_p =

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ K_p =

Example 1 *A mixture of 16g of O_2 and 42g of N_2, exerts a total pressure of 20000 Nm^{-2}. What is the partial pressure of each gas ?*

moles of O_2 = mass / molar mass = 16g / 32g = 0.5 mol
moles of N_2 = mass / molar mass = 42g / 28g = 1.5 mol   Total = 2 mol

mole fraction of O_2 = 0.5 / 2 = 0.25
mole fraction of N_2 = 1.5 / 2 = 0.75   sum of mole fractions = 1

partial pressure of O_2 = mole fraction x total pressure
= 0.25 x 20000 Nm^{-2} = **5000 Nm^{-2}**

partial pressure of N_2 = mole fraction x total pressure
= 0.75 x 20000 Nm^{-2} = **15000 Nm^{-2}**

Example 2 *Nitrogen (1 mol) and hydrogen (3 mol) react at constant temperature at a pressure of 1MPa. At equilibrium, half the nitrogen has reacted. Calculate K_p .*

	$N_{2(g)}$	+ $3H_{2(g)}$ $\rightleftharpoons$	$2NH_{3(g)}$
initial moles	1	3	0
at equilibrium	1 - 0.5 = 0.5 mol	3 - 1.5 = 1.5 mol	2 x 0.5 = 1 mol
mole fractions	0.5 / 3	1.5 / 3	1 / 3
partial pressures	(0.5 / 3) x 1MPa.	1.5 / 3 x 1MPa.	1 / 3 x 1MPa.

applying the equilibrium law $K_p = \dfrac{(PNH_3)^2}{(PN_2) . (PH_2)^3} = \dfrac{⅓ \text{ x } ⅓}{⅙ \text{ x } ½ \text{ x } ½ \text{ x } ½}$ MPa^{-2}

therefore **K_p = 5.33 MPa^{-2}**

Example 3 *0.102g of solid ammonium sulphide is heated in a closed container at 100°C until equilibrium is reached at a pressure of 0.1MPa. It is found that 75% of the ammonium sulphide has dissociated. Calculate the equilibrium constant K_p for the reaction at 100°C.*

	$NH_4HS_{(s)}$ $\rightleftharpoons$	$NH_{3(g)}$ +	$H_2S_{(g)}$
initial mass (g)	0.102	0	0
initial moles	0.102 / 51 = 2 x 10^{-3}	0	0
moles at equilibrium	0.5 x 10^{-3}	1.5 x 10^{-3}	1.5 x 10^{-3}
	75% has dissociated 1.5 moles have reacted	***1 mole of NH_3 formed***	***1 mole of H_2S formed***
		for every 1 mole of NH_4HS reacted	
mole fractions	(moles / total moles)	1.5 / 3	1.5 / 3
partial pressures		(1.5 / 3) x 0.1MPa = 0.05 MPa	(1.5 / 3) x 0.1MPa = 0.05 MPa

applying the equilibrium law $K_p = PNH_3 \text{ x } PH_2S$ = 0.05MPa x 0.05MPa
(the partial pressure of a solid is more or less constant so is ignored)
K_p = 2.5 x 10^{-3} MPa^2