

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)

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

[] 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**

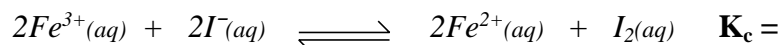
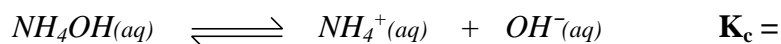
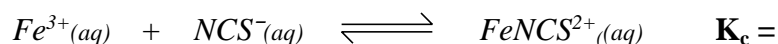
Q.1 What happens to the theoretical yield of a reaction if...

- 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.



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	$1 - \frac{2}{3}$	$1 - \frac{2}{3}$	$\frac{2}{3}$	$\frac{2}{3}$
	If $\frac{2}{3}$ mol of the acid has reacted then take the value away from the initial number of moles of acid	If $\frac{2}{3}$ mol of the acid has reacted, then $\frac{2}{3}$ mol of ethanol will also have reacted. Take $\frac{2}{3}$ 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 $\frac{2}{3}$ mol of acid has reacted, $\frac{2}{3}$ mol of ester and $\frac{2}{3}$ mol of water are produced.	
equilibrium concs.	$\frac{1}{3} / V$	$\frac{1}{3} / V$	$\frac{2}{3} / V$	$\frac{2}{3} / V$

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

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{\frac{2}{3} / V \cdot \frac{2}{3} / V}{\frac{1}{3} / V \cdot \frac{1}{3} / V} = 4$$

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) 1 - 0.6 remain		(2 x 0.4 reacted) 1 - 0.8 remain		(get 1 R and 1 S for every P that reacts)		

- 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

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

Calculating K_p

for a reaction of the form $a \text{A(g)} + b \text{B(g)} \rightleftharpoons c \text{C(g)}$

then (at constant temperature)

$$\frac{P_{\text{C}}^c}{P_{\text{A}}^a \times P_{\text{B}}^b} = \text{a constant, } (K_p)$$

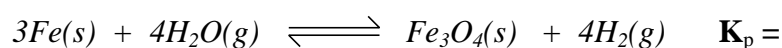
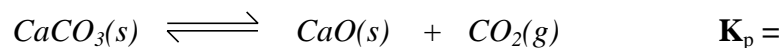
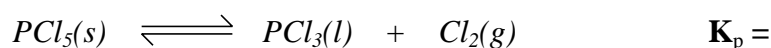
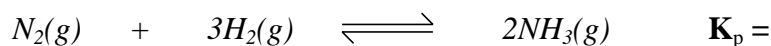
P denotes the partial pressure of a gaseous component at equilibrium

K_p is the Equilibrium Constant in terms of partial pressures

Example $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$ $K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})}$ (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)



Example 1 A mixture of 16g of O₂ and 42g of N₂, exerts a total pressure of 20000 Nm⁻². What is the partial pressure of each gas ?

$$\begin{aligned} \text{moles of O}_2 &= \text{mass} / \text{molar mass} = 16\text{g} / 32\text{g} = 0.5 \text{ mol} \\ \text{moles of N}_2 &= \text{mass} / \text{molar mass} = 42\text{g} / 28\text{g} = 1.5 \text{ mol} \quad \text{Total} = 2 \text{ mol} \end{aligned}$$

$$\begin{aligned} \text{mole fraction of O}_2 &= 0.5 / 2 = 0.25 \\ \text{mole fraction of N}_2 &= 1.5 / 2 = 0.75 \quad \text{sum of mole fractions} = 1 \end{aligned}$$

$$\begin{aligned} \text{partial pressure of O}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.25 \times 20000 \text{ Nm}^{-2} = \mathbf{5000 \text{ Nm}^{-2}} \end{aligned}$$

$$\begin{aligned} \text{partial pressure of N}_2 &= \text{mole fraction} \times \text{total pressure} \\ &= 0.75 \times 20000 \text{ Nm}^{-2} = \mathbf{15000 \text{ Nm}^{-2}} \end{aligned}$$

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)}	⇌	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.

$$\text{applying the equilibrium law} \quad K_p = \frac{(PNH_3)^2}{(PN_2) \cdot (PH_2)^3} = \frac{\frac{1}{3} \times \frac{1}{3}}{\frac{1}{6} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}} \text{ MPa}^{-2}$$

$$\text{therefore} \quad \mathbf{K_p = 5.33 \text{ MPa}^{-2}}$$

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 ₄ HS(s)	⇌	NH _{3(g)}	+	H ₂ S(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
	<i>75% has dissociated 1.5 moles have reacted</i>		<i>1 mole of NH₃ formed for every 1 mole of NH₄HS reacted</i>		<i>1 mole of H₂S formed for every 1 mole of NH₄HS reacted</i>
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

$$\begin{aligned} \text{applying the equilibrium law} \quad K_p &= P_{NH_3} \times P_{H_2S} = 0.05\text{MPa} \times 0.05\text{MPa} \\ \text{(the partial pressure of a solid is} & \\ \text{more or less constant so is ignored)} & \quad \mathbf{K_p = 2.5 \times 10^{-3} \text{ MPa}^2} \end{aligned}$$