

5.1.2 How Far? Equilibrium

Equilibrium constant K_c

For a generalised reaction



m, n, p, q are the stoichiometric balancing numbers

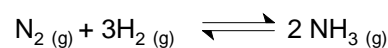
A, B, C, D stand for the chemical formula

[] means the equilibrium concentration

K_c = equilibrium constant

$$K_c = \frac{[C]^p [D]^q}{[A]^m [B]^n}$$

Example 1



$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3}$$

The unit of K_c changes and depends on the equation.

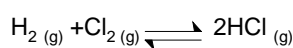
Working out the unit of K_c

Put the unit of concentration (mol dm^{-3}) into the K_c equation

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} \rightarrow \text{Unit} = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]^3} \xrightarrow{\text{Cancel out units}} \text{Unit} = \frac{1}{[\text{mol dm}^{-3}]^2} \rightarrow \text{Unit} = [\text{mol dm}^{-3}]^{-2} \downarrow$$

$$\text{Unit} = \text{mol}^{-2} \text{dm}^6$$

Example 2: writing K_c expression



$$K_c = \frac{[HCl(g)]^2}{[H_2(g)][Cl_2(g)]}$$

Working out the unit

$$\text{Unit } K_c = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]} = \text{no unit}$$

Calculating K_c

Most questions first involve having to work out the equilibrium moles and then concentrations of the reactants and products.

Usually the question will give the initial amounts (moles) of the reactants, and some data that will help you work out the equilibrium amounts.

Calculating the moles at equilibrium

moles of reactant at equilibrium = initial moles – moles reacted

moles of product at equilibrium = initial moles + moles formed

Example 1

For the following equilibrium $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

In a container of volume 600cm^3 there were initially 0.5mol of H_2 and 0.6mol of Cl_2 . At equilibrium there were 0.2moles of HCl . Calculate K_c

	H_2	Cl_2	HCl
Initial moles	0.5	0.6	0
Equilibrium moles			0.2

It is often useful to put the mole data in a table.

Using the balanced equation if 0.2moles of HCl has been formed it must have used up 0.1 of Cl_2 and 0.1moles of H_2 (as $1:2$ ratio)

Work out the moles at equilibrium for the reactants

moles of hydrogen at equilibrium = $0.5 - 0.1 = 0.4$

moles of reactant at equilibrium = initial moles – moles reacted

moles of chlorine at equilibrium = $0.6 - 0.1 = 0.5$

	H_2	Cl_2	HCl
Initial moles	0.5	0.6	0
Equilibrium moles	0.4	0.5	0.2
Equilibrium concentration (M)	$0.4/0.6 = 0.67$	$0.5/0.6 = 0.83$	$0.2/0.6 = 0.33$

If the K_c has no unit then there are equal numbers of reactants and products. In this case you do not have to divide by volume to work out concentration and equilibrium moles could be put straight into the k_c expression

$$K_c = \frac{[HCl(g)]^2}{[H_2(g)][Cl_2(g)]}$$

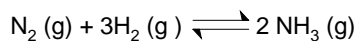
$$K_c = \frac{0.33^2}{0.67 \times 0.83} = 0.196 \text{ no unit}$$

Work out the equilibrium concentrations

conc = moles/vol (in dm^3)

Finally put concentrations into K_c expression

Example 2



For the following equilibrium

Initially there were 1.5 moles of N_2 and 4 mole of H_2 in a 1.5 dm^3 container. At equilibrium 30% of the Nitrogen had reacted. Calculate K_c

	N_2	H_2	NH_3
Initial moles	1.5	4.0	0
Equilibrium moles			

30% of the nitrogen had reacted = $0.3 \times 1.5 = 0.45$ moles reacted.
Using the balanced equation 3×0.45 moles of H_2 must have reacted and 2×0.45 moles of NH_3 must have formed

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = $1.5 - 0.45 = 1.05$ moles of hydrogen at equilibrium = $4.0 - 0.45 \times 3 = 2.65$

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = $0 + (0.45 \times 2) = 0.9$

	N_2	H_2	NH_3
Initial moles	1.5	4.0	0
Equilibrium moles	1.05	2.65	0.9
Equilibrium concentration (M)	$1.05/1.5 = 0.7$	$2.65/1.5 = 1.77$	$0.9/1.5 = 0.6$

Finally put concentrations into K_c expression

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

$$K_c = \frac{0.6^2}{0.7 \times 1.77^3} = 0.0927 \text{ mol}^{-2} \text{ dm}^6$$

Work out the equilibrium concentrations

conc = moles/ vol (in dm^3)

Partial Pressures and Kp

If a reaction contains gases an alternative equilibrium expression can be set up using the partial pressures of the gases instead of concentrations

Partial Pressure

The partial pressure of a gas in a mixture is the pressure that the gas would have if it alone occupied the volume occupied by the whole mixture.

If a mixture of gases contains 3 different gases then the total pressure will equal the 3 partial pressure added together

$$P = p_1 + p_2 + p_3$$

partial pressure of gas 1 = mole fraction of gas 1 x total pressure of gas 1

$$p_1 = x_1 P$$

mole fraction

mole fraction = $\frac{\text{number of moles of a gas}}{\text{total number of moles of all gases}}$

For a 3 part mixture

$$x_1 = \frac{y_1}{y_1 + y_2 + y_3}$$

Example 3 : A mixture contains 0.2 moles N₂, 0.5 moles O₂ and 1.2 moles of CO₂. If the total pressure is 3atm. What are the partial pressures of the 3 gases?

$$\begin{aligned} \text{Total moles of gas} &= 0.5 + 1.2 + 0.2 \\ &= 1.9 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of N}_2 &= 0.2/1.9 \\ &= 0.105 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of O}_2 &= 0.5/1.9 \\ &= 0.263 \end{aligned}$$

$$\begin{aligned} \text{mole fraction of CO}_2 &= 1.2/1.9 \\ &= 0.632 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of N}_2 &= 0.105 \times 3 \\ &= 0.315 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of O}_2 &= 0.263 \times 3 \\ &= 0.789 \end{aligned}$$

$$\begin{aligned} \text{Partial pressure of CO}_2 &= 0.632 \times 3 \\ &= 1.896 \end{aligned}$$

Writing an expression for K_p



$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

p means the partial pressure of that gas

K_p = equilibrium constant

Only include gases in the K_p expression. Ignore solids, liquids, and aqueous substances.

Working out the unit of K_p

Put the unit of pressure(atm) into the K_p equation

$$K_p = \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})}$$

Cancel out units

$$\text{Unit} = \frac{\text{atm}^2}{\text{atm} \text{atm}^3}$$

$$\text{Unit} = \frac{1}{\text{atm}^2}$$

$$\text{Unit} = \text{atm}^{-2}$$

However, if the equation is written the other way round, the value of K_p will be the inverse of above and the units will be atm^2 . It is important therefore to write an equation when quoting values of K_p .

Example 4

For the following equilibrium
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$

1 mole of N_2 and 3 moles of H_2 are added together and the mixture is allowed to reach equilibrium. At equilibrium 20% of the N_2 has reacted. If the total pressure is 2atm what is the value of K_p ?

	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles			

20% of the nitrogen had reacted = $0.2 \times 1.0 = 0.2$ moles reacted.
Using the balanced equation 3×0.2 moles of H_2 must have reacted and 2×0.2 moles of NH_3 must have formed

Work out the moles at equilibrium for the reactants and products

moles of reactant at equilibrium = initial moles – moles reacted

moles of nitrogen at equilibrium = $1.0 - 0.2 = 0.8$ moles of hydrogen at equilibrium = $3.0 - 0.20 \times 3 = 2.40$

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = $0 + (0.2 \times 2) = 0.4$

	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles	0.80	2.40	0.40
Mole fractions	$0.8/3.6$ =0.222	$2.40/3.6$ =0.667	$0.40/3.6$ =0.111
Partial pressure	0.222×2 = 0.444	0.667×2 =1.33	0.111×2 = 0.222

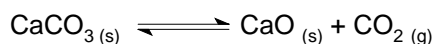
Finally put concentrations into K_p expression

$$K_p = \frac{p^2 \text{NH}_3(\text{g})}{p \text{N}_2(\text{g}) p^3 \text{H}_2(\text{g})}$$

$$K_c = \frac{0.222^2}{0.444 \times 1.33^3} = 0.0469 \text{ atm}^{-2}$$

Heterogeneous equilibria for K_p

K_p expressions only contain gaseous substances. Any substance with another state is left out



$$K_p = p \text{CO}_2$$

Unit atm

Effect of changing conditions on value of Kc or Kp

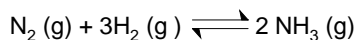
The larger the Kc the greater the amount of products.
If Kc is small we say the equilibrium favours the reactants

Kc and Kp only change with temperature.
It does not change if pressure or concentration is altered.
A catalyst also has no effect on Kc or Kp

Effect of Temperature on position of equilibrium and Kc

Both the **position of equilibrium** and the value of **Kc or Kp will change** if temperature is altered

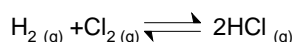
In this equilibrium which is exothermic in the forward direction



If temperature is increased the reaction will shift to oppose the change and move in the backwards endothermic direction. The position of equilibrium shifts left. The value of Kc gets smaller as there are fewer products.

Effect of Concentration on position of equilibrium and Kc

Changing concentration would shift the **position of equilibrium** but the value of **Kc would not change.**



Increasing concentration of H₂ would move equilibrium to the right lowering concentration of H₂ and Cl₂ and increasing concentration of HCl. The new concentrations would restore the equilibrium to the same value of Kc

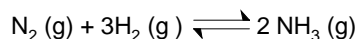
Effect of catalysts on position of equilibrium and Kc and Kp

Catalysts have **no effect** on the value of Kc or Kp or the position of equilibrium as they speed up both forward and backward rates by the same amount.

Effect of Pressure on position of equilibrium and Kc

The position of equilibrium will change if pressure is altered but the value of **Kc stays constant** as Kc only varies with temperature

In this equilibrium which has fewer moles of gas on the product side



If pressure is increased the reaction will shift to oppose the change and move in the forward direction to the side with fewer moles of gas. The position of equilibrium shifts right. The value of Kc stays the same though as only temperature changes the value of Kc.

Increasing pressure does not change Kc.

The increased pressure increases concentration terms on bottom of Kc expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right increasing concentrations of products and decreases the concentrations of reactants. The top of Kc expression therefore increases and the bottom decreases until the original value of Kc is restored

$$K_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3}$$

Effect of Pressure on position of equilibrium and Kp

The position of equilibrium will change if pressure is altered but the value of **Kp stays constant** as Kp only varies with temperature

Increasing pressure does not change Kp.

The increased pressure increases the pressure terms on bottom of Kp expression more than the top. The system is now no longer in equilibrium so the equilibrium shifts to the right increasing mole fractions of products and decreases the mole fractions of reactants. The top of Kp expression therefore increases and the bottom decreases until the original value of Kp is restored

$$K_p = \frac{p^2 \text{NH}_3}{p \text{N}_2 p^3 \text{H}_2}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot P \cdot x^3 \text{H}_2 \cdot P^3}$$

$$K_p = \frac{x^2 \text{NH}_3 \cdot P^2}{x \text{N}_2 \cdot x^3 \text{H}_2 \cdot P^4}$$

Where P is total pressure and x mole fraction