5.1.2 How Far? Equilibrium

Equilibrium constant K_c

For a generalised reaction

$mA + nB \rightleftharpoons pC + qD$

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

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

K_c = equilibrium constant

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

[ ] means the equilibrium concentration

Example 1

$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2\,NH_{3\,(g)}$
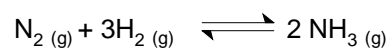
$$K_c = \frac{[NH_{3\,(g)}]^2}{[N_{2\,(g)}][H_{2\,(g)}]^3}$$
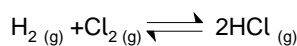
The unit of K_c changes and depends on the equation.

Working out the unit of K_c

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

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

$\downarrow$

Unit = mol^{-2} dm^{+6}

Example 2: writing K_c expression

$H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$

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

Working out the unit

$\rightarrow$ Unit $K_c = \dfrac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}$ **= 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.
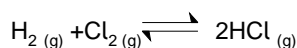
Calculating the moles at equilibrium

moles of reactant at equilibrium = initial moles – moles reacted

moles of product at equilibrium = initial moles + moles formed

Example 3

For the following equilibrium $\quad H_{2\,(g)} + Cl_{2\,(g)} \rightleftharpoons 2HCl_{(g)}$

In a container of volume 600cm^3 there were initially 0.500mol of H_2 and 0.600 mol of Cl_2.
At equilibrium there were 0.200 mol 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 0.2 moles of HCl has been formed it must have used up 0.1 of Cl_2 and 0.1 moles of H_2 (as 1:2 ratio)

Work out the moles at equilibrium for the reactants

moles of reactant at equilibrium = initial moles – moles reacted

moles of hydrogen at equilibrium = 0.5 – 0.1 = 0.4

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. Equilibrium moles can be put straight into the K_c expression.

Work out the equilibrium concentrations

conc = moles/ vol (in dm^3)

Finally put concentrations into K_c expression

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

$K_c = \dfrac{0.33^2}{0.67 \times 0.83}$ **= 0.196 no unit**

Example 4

For the following equilibrium $N_2 (g) + 3H_2 (g) \rightleftharpoons 2 NH_3 (g)$
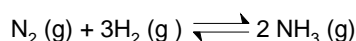
Initially there were 1.5 moles of N_2 and 4 mole of H_2 in a 1.5 dm³ container. At equilibrium 30% of the Nitrogen had reacted. Calculate K_c

	N_2	H_2	NH_3
Initial moles	1.5	4.0	0
Equilibrium moles			

30% of the nitrogen had reacted = 0.3 x1.5 = 0.45 moles reacted. Using the balanced equation 3 x 0.45 moles of H_2 must have reacted and 2x 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 x3 = **2.65**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.45 x 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

Work out the equilibrium concentrations

conc = moles/ vol (in dm³)

Finally put concentrations into K_c expression

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

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

Practical: Working out equilibrium constant K_c

A common experiment is working out the equilibrium constant for an esterification reaction. Ethanol and ethanoic acid are mixed together with a sulfuric acid catalyst.

$CH_3CO_2H + CH_3CH_2OH \rightleftharpoons CH_3CO_2CH_2CH_3 + H_2O$

Ethanoic acid   Ethanol   Ethyl Ethanoate
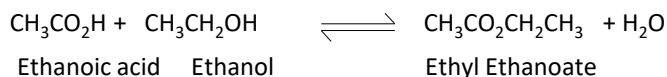
Method
Part 1 Preparing the equilibrium mixture
1 Use burettes to prepare a mixture in boiling tube of carboxylic acid, alcohol, and dilute sulfuric acid.
2 Swirl and bung tube. Leave the mixture to reach equilibrium for one week

Part 2 Titrating the equilibrium mixture
1 Rinse a 250 cm³ volumetric flask with distilled water.
Use a funnel to transfer the contents of the boiling tube into the flask. Rinse the boiling tube with water and add the washings to the volumetric flask.
2 Use distilled water to make up the solution in the volumetric flask to exactly 250 cm³.
Stopper the flask, then invert and shake the contents thoroughly.
3 Use the pipette to transfer 25.0 cm³ of the diluted equilibrium mixture to a 250 cm³ conical flask.
4 Add 3 or 4 drops of phenolphthalein indicator to the conical flask.
5 Set up the burette with sodium hydroxide solution..
6 Add the sodium hydroxide solution from the burette until the mixture in the conical flask just turns pink. Record this burette reading in your table.
7 Repeat the titration until you obtain a minimum of two concordant titres.

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The sodium hydroxide will react with the sulfuric acid catalyst and any unreacted carboxylic acid in the equilibrium mixture.

There are many different calculations that can be based on this experiment. Let's look at general stages. Not all calculations will use all the stages.

Working out initial amount of moles of reactants
The amount of moles of alcohol and carboxylic acid can be calculated from the densities and volumes of liquids added
Mass = density x volume
then
Moles = mass / Mr
The initial amount of moles of acid catalyst used is usually determined by titrating a separate sample of catalyst with sodium hydroxide

Working out equilibrium amount of moles of acid present from the titre results
39.0 cm^3 of 0.400 mol dm^{-3} sodium hydroxide was used in the above titration. The initial moles of sulfuric acid was $5x10^{-4}$ mol. Calculate the moles of ethanoic acid present at equilibrium

Amount of NaOH = vol x conc
$\quad\quad\quad\quad$ = 0.039 x 0.400
$\quad\quad\quad\quad$ = 0.0156 mol
So total amount of H^+ present in $25cm^3$ = 0.0156 mol
So total amount of H^+ present in $250cm^3$ = 0.156 mol

Total mol acid present = moles of carboxylic acid + moles of acid catalyst
So
Amount of carboxylic acid at equilibrium = 0.156 – ($5x10^{-4}$ x 2)
$\quad\quad\quad\quad\quad\quad\quad$ = 0.155 mol

$\longleftarrow$ X 2 because H_2SO_4 has 2 H^+

The pink colour of the phenolphthalein in the titration can fade after the end-point of the titration has been reached because the addition of sodium hydroxide may make the equilibrium shift towards the reactants

Working out equilibrium amount of moles of other substances
Calculate the equilibrium amount of ethanol, ethyl ethanoate and water if there were initially 0.400 mol of ethanol and 0.500 mol of ethanoic acid and at equilibrium there were 0.155 mol of ethanoic acid.

Amount of ethanoic acid that reacted = initial amount – equilibrium amount
$\quad\quad\quad\quad\quad\quad$ = 0.5 – 0.155
$\quad\quad\quad\quad\quad\quad$ = 0.344mol
Amount of ethanol at equilibrium = initial amount - amount that reacted
$\quad\quad\quad\quad\quad\quad$ = 0.400 – 0.344
$\quad\quad\quad\quad\quad\quad$ = 0.056 mol
Amount of ethyl ethanoate at equilibrium = initial amount + amount that formed
$\quad\quad\quad\quad\quad\quad$ = 0 + 0.344
$\quad\quad\quad\quad\quad\quad$ = 0.344 mol
Amount of water at equilibrium = initial amount + amount that formed
$\quad\quad\quad\quad\quad\quad$ = 0 + 0.344
$\quad\quad\quad\quad\quad\quad$ = 0.344 mol

The amount of water at equilibrium would not really be 0 as there would be water present in the acid catalyst

Calculating the equilibrium constant
Finally calculate the equilibrium constant.
To work out equilibrium concentrations divide the equilibrium amounts by the total volume. Then put in K_c expression

$K_c = \dfrac{[CH_3CO_2CH_2CH_3] \ [H_2O]}{[CH_3CO_2H] \ [CH_3CH_2OH]}$

In order to confirm that one week was sufficient time for equilibrium to be established in the mixture from Part 1, several mixtures could be made and left for different amount of time. If the resulting K_c is the same value then it can be concluded the time is sufficient

Partial Pressures and K_p

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

$$p_1 = x_1 \, P$$

mole fraction

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

For a 3 part mixture
$$x_1 = \frac{y1}{y_1 + y_2 + y_3}$$

Example 5 : A mixture contains 0.2 moles N_2, 0.5 moles O_2 and 1.2 moles of CO_2. If the total pressure is 3atm. Calculate the partial pressures of the 3 gases.

Total moles of gas = 0.5 + 1.2+ 0.2
= 1.9

| mole fraction of N_2 | = 0.2/1.9 = 0.105 | mole fraction of O_2 | = 0.5/1.9 = 0.263 | mole fraction of CO_2 | = 1.2/1.9 = 0.632 |

| Partial pressure of N_2 | = 0.105x 3 = 0.315 | Partial pressure of O_2 | = 0.263 x 3 = 0.789 | Partial pressure of CO_2 | = 0.632 x 3 = 1.896 |

Writing an expression for K_p

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

$$K_p = \frac{p\,(NH_3)^{\,2}}{p(N_2)\; p(H_2)^{\,3}}$$

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 Kp

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

$$K_p = \frac{p^{\,2}\,NH_{3\,(g)}}{p N_{2\,(g)}\; p^{\,3}H_{2\,(g)}}$$

Unit = $\dfrac{atm^2}{atm \;\; atm^3}$

Cancel out units   Unit = $\dfrac{1}{atm^2}$

Unit = 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 6

For the following equilibrium

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

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 Kp?

	N_2	H_2	NH_3
Initial moles	1.0	3.0	0
Equilibrium moles			

20% of the nitrogen had reacted = 0.2 x1.0 = 0.2 moles reacted. Using the balanced equation 3 x 0.2 moles of H_2 must have reacted and 2x 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 x3 = **2.40**

moles of product at equilibrium = initial moles + moles formed

moles of ammonia at equilibrium = 0 + (0.2 x 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 x2 = 0.444	0.667 x2 =1.33	0.111 x2 = 0.222

Finally put concentrations into K_p expression

$$K_p = \frac{p^2 NH_{3 (g)}}{pN_{2 (g)} \; p^3 H_{2 (g)}}$$

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

Heterogeneous equilibria for K_p

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

$$CaCO_{3 (s)} \rightleftharpoons CaO_{(s)} + CO_{2 (g)}$$
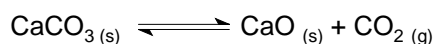
$$K_p = p \, CO_2$$

Unit = atm

Effect of changing conditions on value of K_c or K_p

The larger the Kc the greater the amount of products.
If Kc is small we say the equilibrium favours the reactants
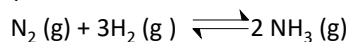
> K_c and K_p only change with temperature.
> It does not change if pressure or
> concentration is altered.
> A catalyst also has no effect on K_c or K_p

Effect of temperature on position of equilibrium and K_c

> Both the **position of equilibrium**
> and the value of K_c **or K_p will
> change** it temperature is altered

> In this equilibrium which is exothermic in the forward direction
> $$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2 NH_3 \text{ (g)}$$
> 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 K_c gets smaller as there are fewer products.

Effect of concentration on position of equilibrium and K_c

> Changing concentration would
> shift the **position of equilibrium
> but** the value of **Kc would not
> change.**
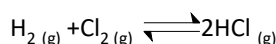
> $$H_2 \text{ (g)} + Cl_2 \text{ (g)} \rightleftharpoons 2HCl \text{ (g)}$$
> Increasing concentration of H_2 would move equilibrium to the right lowering concentration of H_2 and Cl_2 and increasing concentration of HCl. The new concentrations would restore the equilibrium to the same value of K_c.
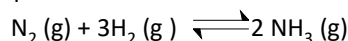
Effect of catalysts on position of equilibrium and K_c and K_p

> Catalysts have **no effect** on the value of Kc or K_p 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 K_c

> The position of equilibrium will
> change it pressure is altered but
> the value of K_c **stays constant** as
> K_c only varies with temperature.

> In this equilibrium which has fewer moles of gas on the product side
> $$N_2 \text{ (g)} + 3H_2 \text{ (g)} \rightleftharpoons 2 NH_3 \text{ (g)}$$
> 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 K_c stays the same though as only temperature changes the value of K_c.

> Increasing pressure does not change K_c.
> The increased pressure increases concentration terms on bottom of K_c 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 the K_c expression therefore increases and the bottom decreases until the original value of K_c is restored.

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

Effect of pressure on position of equilibrium and K_p

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

> Increasing pressure does not change K_p.
> The increased pressure increases the pressure terms on bottom of K_p 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 the K_p expression therefore increases and the bottom decreases until the original value of K_p is restored.

$$K_p = \frac{p^2 NH_3}{p N_2 \, p^3 H_2}$$

$$K_p = \frac{x^2 NH_3 . P^2}{x N_2 . P \; x^3 H_2 . P^3}$$

Where P is total pressure and x mole fraction

$$K_p = \frac{x^2 NH_3 . P^2}{x N_2 \; x^3 H_2 . P^4}$$