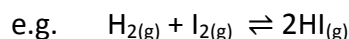


## Chemical Equilibria

Chemical equilibrium is a **dynamic equilibrium**.

Features of a dynamic equilibrium, which can only be established in a closed system (nothing added or removed):

- rates of forward and reverse reactions are the same (and non-zero!)
- equilibrium can be achieved from either direction
- concentrations of reactants and products remain constant at equilibrium



This does not mean that the reaction mixture contains 50%  $\text{H}_2$  and  $\text{I}_2$  and 50%  $\text{HI}$ . The **position of equilibrium** describes qualitatively whether the equilibrium lies towards the reactants or towards the products. We know that the position of equilibrium changes in response to changes in temperature, concentrations etc. What we need is a quantitative approach so we know HOW MUCH of the reactants and products there are at equilibrium.

### Equilibrium in terms of concentration

$K_c$  is the **equilibrium constant**, and tells us the relative concentrations of reactants and products at equilibrium.

- If  $K_c > 10^{10}$  we say the reaction has gone to completion (and we would show this with a single arrow, not reversible).
- If  $K_c < 10^{-10}$  we say that the reaction doesn't happen.

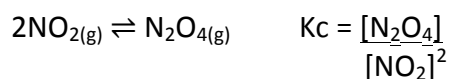
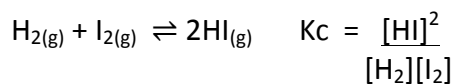
The **equilibrium law** tells us how to write the **equilibrium expression**, from which  $K_c$  is calculated:



$$\text{then } K_c = \frac{[\text{C}]^c[\text{D}]^d}{[\text{A}]^a[\text{B}]^b} \quad \text{where } [\text{C}] = \text{equilibrium conc. of C etc.}$$

Examples:

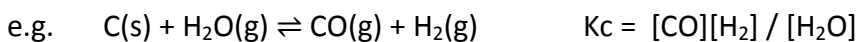
We may be asked to write expressions for  $K_c$  given a balanced equation to work from:



Note that equilibria are either **homogeneous** (all species at equilibrium in the same state) or **heterogeneous** (species in different states).

- For homogeneous equilibria, all the species are taken into account in the equilibrium expression.

- For heterogeneous equilibria, the concentration of solids and pure liquids in great excess (e.g. also as a solvent) do not change significantly so are taken as constant and become part of  $K_c$ .



Using the equilibrium expression, the value of  $K_c$  can be worked out

- so long as we work with concentrations AT EQUILIBRIUM
- so long as the temperature doesn't change (because  $K_c$  changes with temp)

$K_c$  has units which depend on the equilibrium law expression. We can find the units of  $K_c$  by substituting the units of concentration ( $\text{mol dm}^{-3}$ ) and cancelling top and bottom.

e.g.  $K_c = \frac{[N_2O_4]}{[NO_2]^2}$       Units:  $\frac{\text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \text{dm}^3 \text{ mol}^{-1}$

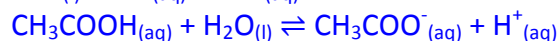
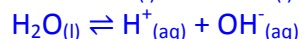
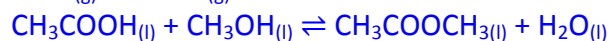
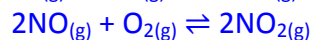
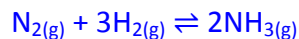
[Note: the convention is to put positive indices first]

$K_c = \frac{[HI]^{2-}}{[H_2][I_2]}$       Units:  $\frac{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3}}$

In some cases all the units cancel – in this case  $K_c$  has no units, it is just a number.

### Practice:

Write the  $K_c$  expressions and give the units for the following reactions:

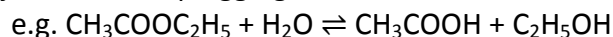


### Working with $K_c$ - examples

General hint: Use the same number of sig figs in your answer as are given in the question!

#### 1) Working out $K_c$ when given concentrations at equilibrium

This is just a case of plugging the values into the  $K_c$  expression.

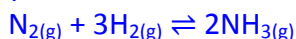


Equilibrium conc. / $\text{mol dm}^{-3}$	ethyl ethanoate	15.4
	water	5.27 (not a big excess)
	ethanoic acid	4.33
	ethanol	4.33

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5][H_2O]} = \frac{4.33 \times 4.33}{15.4 \times 5.27} = 0.231 \text{ no units}$$

Practice:

A) In a closed system,  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{NH}_3$  exist in an equilibrium:



The equilibrium concentrations are  $\text{N}_2$   $1.20 \text{ mol dm}^{-3}$ ,  $\text{H}_2$   $2.00 \text{ mol dm}^{-3}$ , and  $\text{NH}_3$   $0.876 \text{ mol dm}^{-3}$ . Calculate the value of  $K_c$  under these conditions.

2) Working out  $K_c$  when given amounts rather than concentrations

Same as above, but we have to work out the concentrations before plugging into the  $K_c$  expression.

e.g. "At equilibrium 0.40 moles of  $\text{N}_2\text{O}_4$  and 3.2 moles of  $\text{NO}_2$  were present in a reaction volume of  $2 \text{ dm}^3$ .  $\text{N}_2\text{O}_{4(\text{g})} \rightleftharpoons 2 \text{ NO}_{2(\text{g})}$  Calculate  $K_c$  under these conditions:"

Convert moles to  $[\ ]$  first:

$$[\text{N}_2\text{O}_4] = 0.40/2 = 0.2 \text{ mol dm}^{-3}$$

$$[\text{NO}_2] = 3.2/2 = 1.6 \text{ mol dm}^{-3}$$

$$K_c = (1.6)^2 / 0.2 = 12.8 = 13.0 \text{ (to 2 sf) mol dm}^{-3}$$

**BEWARE:** in situations where  $K_c$  would have no units, the volumes will cancel top and bottom just like the units did. In such situations the volume may not be specified in the question even though amounts rather than concentrations are given. Use 'V' for the volume and see that it cancels in the  $K_c$  expression:

e.g. "The equilibrium mixture contained 0.25 moles of ethanol and 0.25 moles of ethanoic acid. 0.61 moles of ethyl ethanoate and 0.44 moles of water remained unreacted."

Convert moles to  $[\ ]$  first,

$$[\text{CH}_3\text{COOH}] = 0.25/V \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{OH}] = 0.25/V \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5] = 0.61/V \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}] = 0.44/V \text{ mol dm}^{-3}$$

$$K_c = \frac{\frac{0.125}{V} \times \frac{0.125}{V}}{\frac{0.305}{V} \times \frac{0.220}{V}} = 0.233$$

Practice:

B) In an experiment,  $\text{N}_2\text{O}$  was heated in a  $0.5 \text{ dm}^3$  container until equilibrium was reached.  $2\text{N}_2\text{O} \rightleftharpoons 2\text{N}_2 + \text{O}_2$  At equilibrium there was found to be 0.1 moles of  $\text{N}_2\text{O}$ , 0.9 moles of  $\text{N}_2$  and 0.45 moles of  $\text{O}_2$ . Calculate  $K_c$ .

3) Similarly, we may be given the value of  $K_c$  and be expected to work out the concentration of a component at equilibrium:

e.g. "At equilibrium the concentrations of SO<sub>2</sub> and O<sub>2</sub> in the mixture:

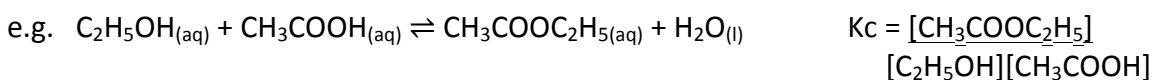
$2\text{SO}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{SO}_{3(g)}$  were  $0.020 \text{ mol dm}^{-3}$  and  $0.010 \text{ mol dm}^{-3}$   
 If the value of K<sub>c</sub> is  $1.28 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ , what is the equilibrium concentration of SO<sub>3</sub> ?"

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} \text{ so } [\text{SO}_3] = \sqrt{K_c [\text{SO}_2]^2[\text{O}_2]}$$

$$= \sqrt{0.0512}$$

$$= \mathbf{0.23 \text{ mol dm}^{-3}}$$

4) You may be given initial concentrations and enough information to work out the concentrations remaining at equilibrium. The key is to remember that the mole ratios from the balanced equation tell you how many moles of each product are made for every mole of reactant used. A table format helps:



"2.0 mol of ethanol is mixed with 0.50 mol of ethanoic acid in an aqueous solution with volume  $1 \text{ dm}^3$ . At equilibrium it is found by titration that 0.17 moles of ethanoic acid remained. Calculate K<sub>c</sub> under these reaction conditions."

If 0.50 mol of ethanoic acid was used initially, and 0.17 mol remains at equilibrium then  $0.50 - 0.17 = 0.33 \text{ mol}$  of ethanoic acid has reacted.

The stoichiometry of the reaction tells us that 0.33 mol of ethanol must have reacted, and 0.33 mol each of ethyl ethanoate (and water, but we can ignore this) have been produced.

	ethanol	ethanoic acid	ethyl ethanoate
Initial moles	2.0	0.50	0
Change moles	-0.33	-0.33	+0.33
Moles at eqm.	=1.67	=0.17	=0.33

We convert the equilibrium moles to concentrations:

Conc at eqm. ( $\text{mol dm}^{-3}$ )	1.67	0.17	0.33
---------------------------------------	------	------	------

Now we can use the K<sub>c</sub> expression:

$$K_c = 0.33 / 1.67 \times 0.17 = 1.16 \text{ dm}^3 \text{ mol}^{-1}$$

### Practice:

C) "1.00 moles of HI is allowed to dissociate in a  $0.5 \text{ dm}^3$  vessel at  $440^\circ\text{C}$ . At equilibrium only 0.78 moles of HI remained. Calculate K<sub>c</sub>."

And finally, we may get all sorts of attempts to complicate matters – this is a kind of synoptic question (drawing together various different parts of your knowledge).

**Practice**

D) e.g. Consider the reaction  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$   $K_c = 1.9 \text{ mol dm}^{-3}$   
 A sample of  $\text{PCl}_5$  is heated in a  $2.0 \text{ dm}^3$  container until equilibrium is established. The mixture is found to contain  $4.170 \text{ g}$  of  $\text{PCl}_5$ .

- Calculate the concentration in  $\text{g dm}^{-3}$  of  $\text{Cl}_2$  present in the equilibrium mixture.
- Calculate the mass of the original sample of  $\text{PCl}_5$

**Equilibrium in terms of pressure**

We more commonly work with pressures rather than concentrations for gases. We know, from the ideal gas equation that  $pV=nRT$ ; rearranging  $p = n/V \times RT$ .  $n/V$  is moles/volume and is therefore a measure of concentration. Therefore pressure is equivalent to concentration so long as the temperature remains constant. We can therefore write the equilibrium expression in terms of pressures.

**Partial pressures and mole fractions**

The total pressure of a mixture of gases is made up from contributions to the pressure from each gas present. The size of the contribution from each gas is independent of the actual gas, and proportional to how many moles of the gas are present.

The **mole fraction**  $x(A)$  of a gas A =  $\frac{\text{number of moles of gas A}}{\text{total moles of gas in the mixture}}$

*\* this means the sum of the mole fractions for each gas must add up to 1*

The pressure each gas contributes is called its **partial pressure**, which is defined as

Partial pressure of gas A,  $p(A) = \text{mole fraction of that gas} \times \text{total pressure, } P$

*\* this means that the sum of the partial pressures of all the gases = total pressure*

We also know that the same number of moles of any gas occupies the same volume (i.e. 1 mole of any gas occupies  $24.0 \text{ dm}^3$  at room temperature and pressure), so the % by volume gas A is its mole fraction  $\times 100$ .

e.g. in air we have 78% nitrogen, so  $x(\text{N}_2) = 0.78$ . A typical air pressure would be  $100 \text{ kPa}$ , so the partial pressure of nitrogen  $p(A) = 0.78 \times 100 = 78 \text{ kPa}$ .

**Equilibrium expression and  $K_p$** 

Equilibrium expressions in terms of  $K_p$  are written in the same way as for  $K_c$ , but with the partial pressure of each gas replacing the concentration term:



For a **homogeneous equilibrium**, the partial pressure of each gas forms part of the equilibrium expression.

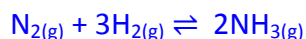
For a **heterogeneous equilibrium**, only the gaseous species contribute to the equilibrium expression.

### Units

Suitable units for partial pressures are kPa, Pa or atm. The same units have to be used for every partial pressure. The units are cancelled top and bottom as previously to determine the units of  $K_p$ .

### Practice

E i) An equilibrium mixture at 400°C contains 18 mol  $N_2$ , 54 mol  $H_2$ , and 48 mol  $NH_3$ .



The total pressure is 200atm. Show that  $K_p = 2.9 \times 10^{-4} \text{ atm}^{-2}$ .

E ii) When calcium carbonate is heated in a closed system an equilibrium is set up:



At 600°C the total pressure was  $2.5 \times 10^{-2} \text{ atm}$ . Write the  $K_p$  expression, and use it to determine the value of  $K_p$ .

### What affects the value of $K_c$ or $K_p$ ?

- $K_c$  and  $K_p$  ARE affected by changes in temperature
- $K_c$  and  $K_p$  are NOT affected by changes in pressure, concentration, or presence of a catalyst

*... but that doesn't mean the position of equilibrium can't shift !!*

### Effect of temperature changes on $K_c$ and $K_p$

We know the effect a change in temperature has on the position of equilibrium (Le Chatelier's principle), and we can use the sign of  $\Delta H$  to predict the change in position of equilibrium. We can therefore say how  $K_c$  or  $K_p$  will change, since they simply measure quantity of products over quantity of reactants.

For a reaction which is exothermic (in the forward direction) i.e.  $\Delta H$  is -ve.

- **increasing temperature** moves the PoE in the endothermic (backward) direction
- which means the [reactants] increases and the [products] decrease
- so  $K_c$  or  $K_p$  decreases

For a reaction which is endothermic i.e.  $\Delta H$  is +ve

- **increasing temperature** moves the PoE in the forward direction
- which means the [reactants] decreases and [products] increases #
- so  $K_c$  or  $K_p$  increases

e.g. 
$$K_p = \frac{p(SO_3)^2}{p(O_2) \times p(SO_2)^2} \quad \Delta H = -197 \text{ kJmol}^{-1}$$

The value of  $\Delta H$  shows us that the reaction is exothermic in the forward direction, so an increase in temperature will cause the position of equilibrium to move in the backward direction, so  $p(\text{SO}_3)$  will decrease and  $p(\text{O}_2)$  and  $p(\text{SO}_2)$  will increase. Looking at the equilibrium expression we can see how  $K_p$  must decrease.

Conversely we should be able to look at a change in  $K_c$  or  $K_p$  with temperature and decide if the forward reaction is endothermic or exothermic:

e.g. "When the temperature was increased from 500K to 800K the value of  $K_c$  decreased from 5000 to 0.3 – give the sign of  $\Delta H$  for the forward reaction."

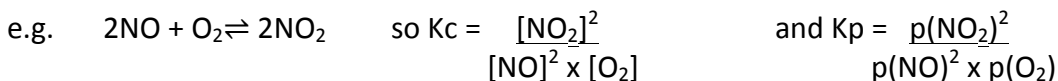
Answer: Decreasing  $K_c$  with increasing temperature shows the PoE is shifting towards the reactants/left. This must therefore be the endothermic direction. The forward reaction is exothermic, so  $\Delta H$  is –ve.

### Practice:

When the temperature was increased from 500K to 800K the value of  $K_c$  changed from  $4.5 \times 10^{-2}$  to  $2.8 \times 10^3$ . Explain how you can tell that the reaction is endothermic.

### Effect of concentration or pressure changes on $K_c$ and $K_p$

We have already stated that changing the concentration or pressure of a reactant or product has **no effect on the value of  $K_c$  or  $K_p$** . In fact, the position of equilibrium shifts when concentrations and pressures change because the equilibrium constant remains constant.



What happens if we double the concentration or pressure of NO?

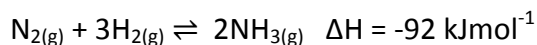
- i) we no longer have an equilibrium – the closed system has been disturbed
- ii) because  $K_p$  and  $K_c$  cannot change, the concentrations or pressures of the other reactants and products have to change to keep  $K_p$  or  $K_c$  the same.
- iii) in this case, because the concentration or pressure of NO has increased, the concentration or pressure of  $\text{NO}_2$  must increase, and of  $\text{O}_2$  decrease. In other words, when we add NO,  $\text{O}_2$  will be used up reacting with the added NO to make  $\text{NO}_2$ : the position of equilibrium has shifted in the forward direction as Le Chatelier states, but  $K_c$  and  $K_p$  remain unchanged.

### Effect of presence of a catalyst on $K_c$ and $K_p$

A catalyst has no effect on the value of  $K_c$  or  $K_p$ . Catalysts speed up the forward and backward reactions equally, so the position of equilibrium remains unchanged – we just reach equilibrium more quickly. There is no change in position of equilibrium, or concentrations or partial pressures of reactants or products.

**Haber process revisited**

This is an example of industrial compromise – a high temperature is undesirable because it produces a low yield of ammonia, but a low temperature is also undesirable because the rate of reaction is too slow. A compromise temperature is used.



We can describe the reaction in terms of equilibrium constant ( $K_c$  or  $K_p$ ) and rate constant ( $k$ ).

At low temperatures,  $k$  is low (rate increases with temperature) but  $K_c$  and  $K_p$  are high (forward direction is exothermic). We get a high yield of ammonia but only very slowly.

At high temperatures,  $k$  is high but  $K_c$  and  $K_p$  are low (because the position of equilibrium has shifted in the endothermic direction). Equilibrium is reached quickly, but there's little ammonia present in the equilibrium mixture.

The industrial compromise is getting the right balance between  $K_c$  or  $K_p$  and  $k$ . The compromise temperature increases  $k$  without decreasing  $K_c$  or  $K_p$  too much. A catalyst allows  $k$  to be increased without affecting  $K_c$  or  $K_p$ . Removing the ammonia as it is formed decreases the concentration of ammonia. This shifts the position of equilibrium to the left (making more ammonia) because the system has to restore the value of  $K_c$  to its constant value.



**Answers to Practice Questions**

$$\begin{aligned} \text{A) } K_c &= [\text{NH}_3]^2 / [\text{N}_2][\text{H}_2]^3 = (0.876)^2 / (1.20 \times 2.00^3) \\ &= 0.767 / 9.6 = 7.99 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2} \end{aligned}$$

$$\begin{aligned} \text{B) } [\text{N}_2\text{O}] &= 0.1/0.5 = 0.20 \text{ mol dm}^{-3} \\ [\text{N}_2] &= 0.9/0.5 = 1.8 \text{ mol dm}^{-3} \\ [\text{O}_2] &= 0.45/0.5 = 0.90 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} K_c &= [\text{N}_2]^2[\text{O}_2] / [\text{N}_2\text{O}]^2 = (1.8)^2 \times 0.90 / (0.20)^2 = 3.24 \times 0.90 / 0.04 \\ &= 72.9 \text{ mol dm}^{-3} \end{aligned}$$

C)	HI	H <sub>2</sub>	I <sub>2</sub>
Initial moles	1.00	0	0
Eqm moles	0.78	0.11*	0.11*
Used/made	0.22	0.11	0.11

\*0.22 moles of HI have been used. The equation shows us that 0.22 moles of HI make 0.11 moles of H<sub>2</sub> and 0.11 moles of I<sub>2</sub>.

We'd now convert moles to concentration, but the volumes cancel in this example (K<sub>c</sub> has no units).  $K_c = (0.11 \times 0.11) / 0.78^2 = 0.020$

$$\text{D) } K_c = [\text{PCl}_3][\text{Cl}_2] / [\text{PCl}_5]$$

i) Mass of PCl<sub>5</sub> = 4.170 and M<sub>r</sub> of PCl<sub>5</sub> = 208.5 → moles PCl<sub>5</sub> = 0.02  
Concentration of PCl<sub>5</sub> = 0.02 moles in 2dm<sup>3</sup> = 0.01 mol dm<sup>-3</sup>

Since every mole of PCl<sub>5</sub> which decomposes produces 1 mole of PCl<sub>3</sub> and 1 mole of Cl<sub>2</sub>, and since there is no Cl<sub>2</sub> or PCl<sub>3</sub> present initially, [Cl<sub>2</sub>] = [PCl<sub>3</sub>]

Therefore  $K_c \times [\text{PCl}_5] = [\text{Cl}_2]^2 \rightarrow [\text{Cl}_2] = \sqrt{(1.9 \times 0.01)} = 0.1378 \text{ mol dm}^{-3}$   
Therefore concentration in g dm<sup>-3</sup> = 0.1378 x 71 = 9.78 g dm<sup>-3</sup>

ii) Since [Cl<sub>2</sub>] = [PCl<sub>3</sub>] we can state that 0.1378 x 2 mol of each is present in the vessel.  
Converting each to mass:

$$\text{Mass of Cl}_2 = 0.2756 \times 71 = 19.57\text{g}$$

$$\text{Mass of PCl}_3 = 0.2756 \times 137.5 = 37.89\text{g}$$

By law of mass conservation, mass of PCl<sub>5</sub> which has reacted = 19.57g + 37.89g  
Hence original mass of PCl<sub>5</sub> = 19.57 + 37.89 + 4.17 = 61.63g (to 4sf.)

$$\begin{aligned} \text{E i) Total moles of gas} &= 18+54+48 = 120 \\ x(\text{N}_2) &= 18/120 \quad \Rightarrow p(\text{N}_2) = 200 \times (18/120) = 30 \text{ atm} \\ x(\text{H}_2) &= 54/120 \quad \Rightarrow p(\text{H}_2) = 200 \times (54/120) = 90 \text{ atm} \\ x(\text{NH}_3) &= 48/120 \quad \Rightarrow p(\text{NH}_3) = 200 \times (48/120) = 80 \text{ atm} \end{aligned}$$

$$K_p = \frac{p(\text{NH}_3)^2}{p(\text{N}_2) \times p(\text{H}_2)^3} = 80^2 / (30 \times 80^3) = 2.9 \times 10^{-4} \text{ atm}^{-2}$$

E ii) When calcium carbonate is heated in a closed system an equilibrium is set up:



At 600°C the total pressure was  $2.5 \times 10^{-2}$  atm. Write the  $K_p$  expression, and use it to determine the value of  $K_p$ .

$K_p = p(\text{CO}_2)$   $x(\text{CO}_2) = 1$  since it is the only gas present, so  $p(\text{CO}_2) = 2.5 \times 10^{-2}$  atm.  
Hence  $K_p = 2.5 \times 10^{-2}$  atm.