


# DP IB Chemistry: HL

  
Your notes

## 17.1 The Equilibrium Law

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## 17.1.1 Applying the Equilibrium Law

### Explaining Le Châtelier's Principle

#### Le Châtelier's principle

- Le Châtelier's principle says that if a change is made to a system at dynamic equilibrium, the position of the equilibrium moves to minimise this change
- The principle can be used to predict changes to the position of equilibrium when there are changes in temperature, pressure or concentration

#### Explaining Le Châtelier's Principle

- The equilibrium law can explain and quantify the effect of changes in concentration at a particular temperature
- These explanations are based on the idea that  $K_c$  is not affected by a change in concentration
  - Remember that the position of equilibrium is affected by a change in concentration:

Effects of Concentration Table

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE RIGHT TO REDUCE THE EFFECT OF INCREASE IN THE CONCENTRATION OF A REACTANT
DECREASE IN CONCENTRATION	EQUILIBRIUM SHIFTS TO THE LEFT TO REDUCE THE EFFECT OF A DECREASE IN REACTANT (OR AN INCREASE IN THE CONCENTRATION OF PRODUCT)

- $K_c$  for a general reaction such  $aA + bB \rightleftharpoons cC + dD$  is:

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

[A] AND [B] = EQUILIBRIUM REACTANT CONCENTRATIONS ( $\text{mol dm}^{-3}$ )

[C] AND [D] = EQUILIBRIUM PRODUCT CONCENTRATIONS ( $\text{mol dm}^{-3}$ )

a, b, c AND d = NUMBER OF MOLES OF REACTANTS AND PRODUCTS

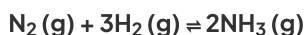
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*Equilibrium expression linking the equilibrium concentration of reactants and products at equilibrium*

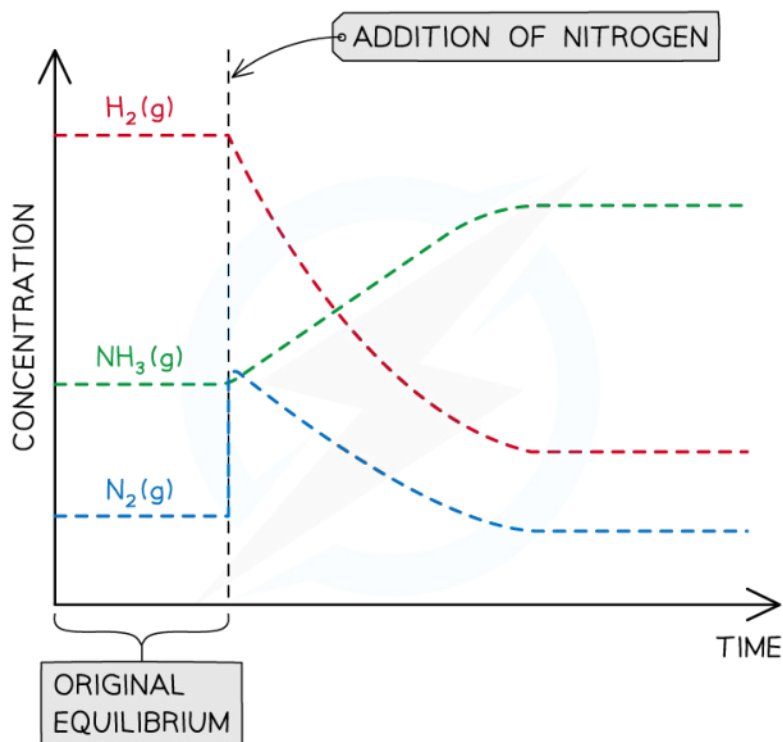


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- If the concentration of A increases
  - The position of equilibrium shifts to the right as the forward reaction works to remove excess A
  - The concentrations of C and D increase to minimise this change
  - The concentration of B decreases because it is being used up to minimise the change
  - Therefore, the value of  $K_c$  remains unchanged
- If the concentration of A decreases
  - The position of equilibrium shifts to the left as the backward reaction works to replace A
  - The concentrations of C and D decrease to minimise this change
  - The concentration of B increases because it is also being produced when C and D react
  - Therefore, the value of  $K_c$  remains unchanged
- The Haber Process is represented by the following chemical equation:



- An increase in the amount of nitrogen will cause the following:
  - The equilibrium to shift to the right
  - An increase in the amount of ammonia
  - A decrease in the amount of hydrogen
  - $K_c$  will remain unchanged



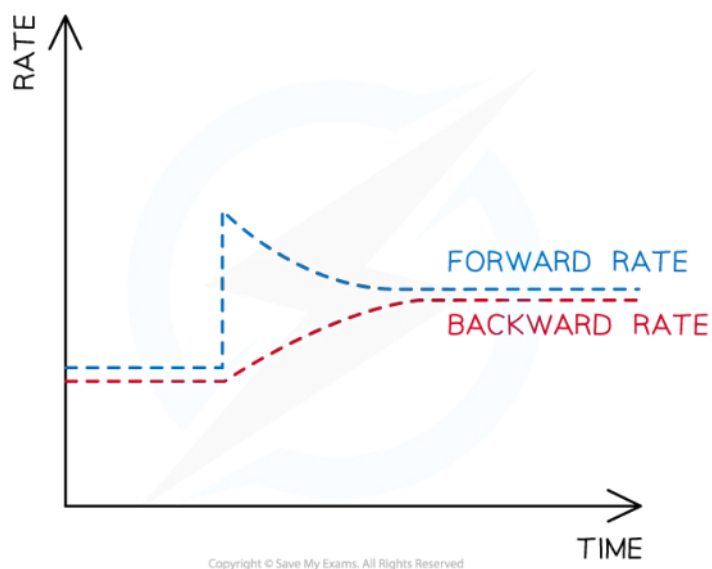
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**Graph showing the effects of adding nitrogen on the concentration of reactants and products in the Haber Process**

- An increase in the amount of nitrogen causes the rate of the forward reaction to increase
- This means that more ammonia is produced, causing the rate of the backward reaction to increase
- This process of increasing forward and backward reactions continues until a new equilibrium is established
- The rate at this newly established equilibrium will be higher than the original rate



**Graph showing the effects of adding nitrogen on the rate of reaction in the Haber Process**

- Similar points about concentrations and rates can be made for the addition of hydrogen or the removal of ammonia
  - Regardless, the value of  $K_c$  remains unchanged
  - Only changes in temperature affect  $K_c$

## Equilibrium Problems

### Calculations involving $K_c$

- In the equilibrium expression, each term inside a square bracket represents the concentration of that chemical in  $\text{mol dm}^{-3}$
- Therefore, the units of  $K_c$  depend on the equilibrium expression
- Some questions give the number of moles of each of the reactants and products at equilibrium together with the volume of the reaction mixture
- The concentrations of the reactants and products can then be calculated from the number of moles and total volume

$$\text{CONCENTRATION (mol dm}^{-3}\text{)} = \frac{\text{NUMBER OF MOLES}}{\text{VOLUME (dm}^3\text{)}}$$

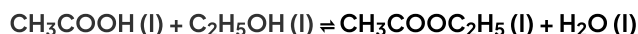
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*Equation to calculate concentration from number of moles and volume*

#### Worked example

##### Calculating $K_c$ of ethanoic acid

Ethanoic acid and ethanol react to form the ester ethyl ethanoate and water as follows:



At equilibrium,  $500 \text{ cm}^3$  of the reaction mixture contained  $0.235 \text{ mol}$  of ethanoic acid and  $0.035 \text{ mol}$  of ethanol together with  $0.182 \text{ mol}$  of ethyl ethanoate and  $0.182 \text{ mol}$  of water.

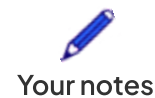
Use this data to calculate a value of  $K_c$  for this reaction.

**Answer:**

**Step 1:** Calculate the concentrations of the reactants and products:



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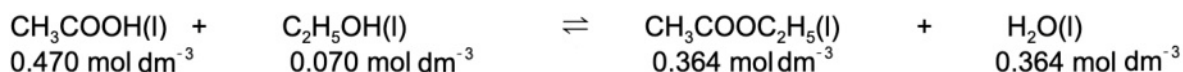
$$[\text{CH}_3\text{COOH}(\text{l})] = \frac{0.235}{0.500} = 0.470 \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{OH}(\text{l})] = \frac{0.035}{0.500} = 0.070 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})] = \frac{0.182}{0.500} = 0.364 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}(\text{l})] = \frac{0.182}{0.500} = 0.364 \text{ mol dm}^{-3}$$

**Step 2:** Write out the balanced symbol equation with the concentrations of each chemical underneath:



**Step 3:** Write out the equilibrium constant for the reaction:

$$K_c = \frac{[\text{H}_2\text{O}] [\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{C}_2\text{H}_5\text{OH}] [\text{CH}_3\text{COOH}]}$$

**Step 4:** Substitute the equilibrium concentrations into the expression and calculate the answer:

$$\begin{aligned} K_c &= \frac{(0.364) \times (0.364)}{(0.070) \times (0.470)} \\ &= 4.03 \end{aligned}$$

**Step 5:** Deduce the correct units for  $K_c$ :

$$K_c = \frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

- All units cancel out
  - Therefore,  $K_c = 4.03$
  - Note that the smallest number of significant figures used in the question is 3, so the final answer should also be given to 3 significant figures
- 
- Some questions give the initial and equilibrium concentrations of the reactants but not the products

- An initial, change and equilibrium (ICE) table should be used to determine the equilibrium concentration of the products using the molar ratio of reactants and products in the stoichiometric equation

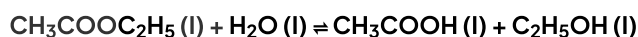


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### Worked example

#### Calculating $K_c$ of ethyl ethanoate

Ethyl ethanoate is hydrolysed by water:



0.1000 mol of ethyl ethanoate are added to 0.1000 mol of water. A little acid catalyst is added and the mixture made up to 1 dm<sup>3</sup>. At equilibrium 0.0654 mol of water are present. Use this data to calculate a value of  $K_c$  for this reaction.

**Answer:**

**Step 1:** Write out the balanced chemical equation with the concentrations of beneath each substance using an initial, change and equilibrium table:

$\text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l})$				
Initial moles	0.1000	0.1000	0	0
Change	-0.0346	-0.0346	+0.0346	+0.0346
Equilibrium moles	0.0654	0.0654	0.0346	0.0346

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**Step 2:** Calculate the concentrations of the reactants and products:

$$[\text{CH}_3\text{COOC}_2\text{H}_5(\text{l})] = \frac{0.0654}{1.000} = 0.0654 \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{O}(\text{l})] = \frac{0.0654}{1.000} = 0.0654 \text{ mol dm}^{-3}$$

$$[\text{CH}_3\text{COOH}(\text{l})] = \frac{0.0346}{1.000} = 0.0346 \text{ mol dm}^{-3}$$

$$[\text{C}_2\text{H}_5\text{OH}(\text{l})] = \frac{0.0346}{1.000} = 0.0346 \text{ mol dm}^{-3}$$



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**Step 3:** Write the equilibrium constant for this reaction in terms of concentration:

$$K_c = \frac{[C_2H_5OH][CH_3COOH]}{[H_2O][CH_3COOC_2H_5]}$$

**Step 4:** Substitute the equilibrium concentrations into the expression:

$$\begin{aligned} K_c &= \frac{(0.0346) \times (0.0346)}{(0.0654) \times (0.0654)} \\ &= 0.28 \end{aligned}$$

**Step 5:** Deduce the correct units for  $K_c$ :

$$K_c = \frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

- All units cancel out
- Therefore,  $K_c = 0.28$





Your notes

## 17.1.2 Gibbs Free Energy & the Equilibrium Constant

### Gibbs Free Energy & the Equilibrium Constant

#### Gibbs Free Energy & the Equilibrium Constant

- The equilibrium constant,  $K_c$ , gives no information about the individual rates of reaction
  - It is independent of the kinetics of the reaction
- The equilibrium constant,  $K_c$ , is directly related to the Gibbs free energy change,  $\Delta G^\ominus$ , according to the following (van't Hoff's) equation:

$$\Delta G^\ominus = -RT \ln K$$

- $\Delta G^\ominus$  = Gibbs free energy change ( $\text{kJ mol}^{-1}$ )
- $R$  = gas constant ( $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )
- $T$  = temperature (Kelvin, K)
- $K$  = equilibrium constant
- This equation is provided in section 1 of the data booklet

#### Examiner Tip

When completing calculations using the  $\Delta G^\ominus = -RT \ln K$  equation, you have to be aware that:

- $\Delta G^\ominus$  is measure in  $\text{kJ mol}^{-1}$
- $R$  is measured in  $\text{J K}^{-1} \text{ mol}^{-1}$

This means that one of these values will need adjusting by a factor of 1000

- This relationship between the equilibrium constant,  $K_c$ , and Gibbs free energy change,  $\Delta G^\ominus$ , can be used to determine whether the forward or backward reaction is favoured

Equilibrium constant, $K$	Description	Gibbs free energy change, $\Delta G$
$K > 1$	Products favoured	$\Delta G < 0$ (negative)
$K = 1$	Reaction at equilibrium Neither reactants nor products are favoured	$\Delta G = 0$
$K < 1$	Reactants favoured	$\Delta G > 0$ (positive)

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**The relationship between the equilibrium constant,  $K_c$ , and Gibbs free energy change,  $\Delta G^\ominus$** 

- At a given temperature, a negative  $\Delta G$  value for a reaction indicates that:
  - The reaction is feasible / spontaneous
  - The equilibrium concentration of the products is greater than the equilibrium concentration of the reactants
  - The value of the equilibrium constant is greater than 1
- As  $\Delta G$  becomes more negative:
  - The forward reaction is favoured more
  - The value of the equilibrium constant increases



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## Free Energy & Equilibrium Calculations

- The relationship between Gibbs free energy change,  $\Delta G^\ominus$ , temperature and the equilibrium constant,  $K_c$ , is described by the equation:

$$\Delta G^\ominus = -RT \ln K$$

- The rearrangement of this equation makes it possible to:
  - Calculate the equilibrium constant
  - Deduce the position of equilibrium for the reaction

$$\ln K = -\frac{\Delta G}{RT}$$



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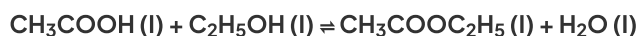


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## Worked example

### Calculating $K_c$

Ethanoic acid and ethanol react to form the ester ethyl ethanoate and water as follows:



At 25 °C, the free energy change,  $\Delta G^\ominus$ , for the reaction is  $-4.38 \text{ kJ mol}^{-1}$ . ( $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ )

1. Calculate the value of  $K_c$  for this reaction
2. Using your answer to part (1), predict and explain the position of the equilibrium

#### Answer 1:

- **Step 1:** Convert any necessary values
  - $\Delta G^\ominus$  into  $\text{J mol}^{-1}$ :
    - $-4.38 \times 1000 = -4380 \text{ J mol}^{-1}$
  - $T$  into Kelvin
    - $25 + 273 = 298 \text{ K}$
- **Step 2:** Write the equation:
  - $\Delta G^\ominus = -RT \ln K_c$
- **Step 3:** Substitute the values:
  - $-4380 = -8.31 \times 298 \times \ln K_c$
- **Step 4:** Rearrange and solve the equation for  $K_c$ :
  - $\ln K_c = -4380 \div (-8.31 \times 298)$
  - $\ln K_c = 1.77$
  - $K_c = e^{1.77}$
  - $K_c = 5.87$

#### Answer 2:

- From part (1), the value of  $K_c$  is 5.87
- Therefore, the equilibrium lies to the right / products side because the value of  $K_c$  is greater than 1