

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 (mol dm^{-3})

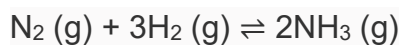
[C] AND [D] = EQUILIBRIUM PRODUCT CONCENTRATIONS (mol dm^{-3})

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

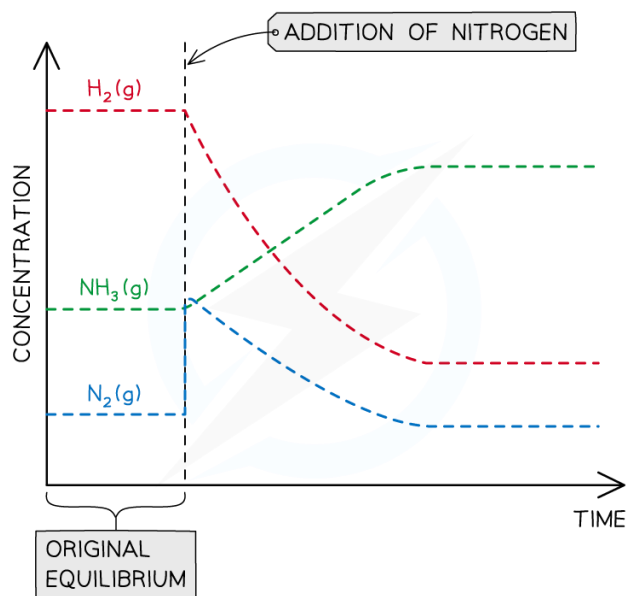
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Equilibrium expression linking the equilibrium concentration of reactants and products at equilibrium

- 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:



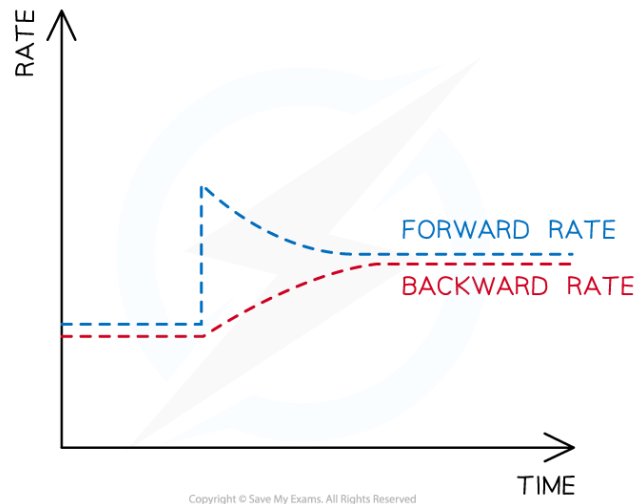
- An increase in the amount of nitrogen will cause the following:
 - The equilibrium to shift to the right
 - An increase in the amount of ammonia
 - A decrease in the amount of hydrogen
 - K_c will remain unchanged



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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 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

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

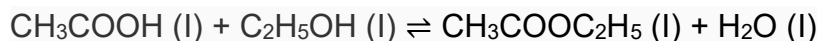
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Equation to calculate concentration from number of moles and volume

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 cm³ of the reaction mixture contained 0.235 mol of ethanoic acid and 0.035 mol of ethanol together with 0.182 mol of ethyl ethanoate and 0.182 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:

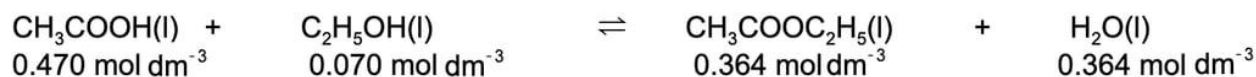
$$[\text{CH}_3\text{COOH(l)}] = \frac{0.235}{0.500} = 0.470 \text{ mol dm}^{-3}$$

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

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

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

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:

$$K_c = \frac{(0.364) \times (0.364)}{(0.070) \times (0.470)}$$
$$= 4.03$$

Step 5: Deduce the correct units for K_c :

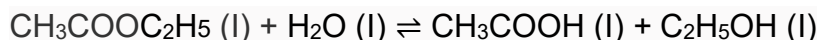
$$K_c = \frac{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}{(\text{mol dm}^{-3}) \times (\text{mol dm}^{-3})}$$

- 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

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 dm³. 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:

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

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

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

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

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

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

Step 4: Substitute the equilibrium concentrations into the expression:

$$K_c = \frac{(0.0346) \times (0.0346)}{(0.0654) \times (0.0654)} = 0.28$$

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, $K_c = 0.28$

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, ΔG^\ominus , according to the following (van't Hoff's) equation:

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

- ΔG^\ominus = Gibbs free energy change (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

Exam Tip

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

- ΔG^\ominus is measure in 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, ΔG^\ominus , can be used to determine whether the forward or backward reaction is favoured

Equilibrium constant, K	Description	Gibbs free energy change, ΔG
$K > 1$	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, ΔG^\ominus

- At a given temperature, a negative ΔG 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 ΔG becomes more negative:
 - The forward reaction is favoured more
 - The value of the equilibrium constant increases

Free Energy & Equilibrium Calculations

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

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

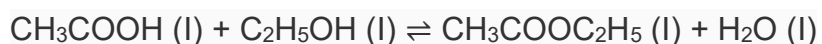
- The rearrangement of this equation makes it possible to:
 - Calculate the equilibrium constant
 - Deduce the position of equilibrium for the reaction

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

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, ΔG^\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

Answers

Answer 1:

Step 1: Convert any necessary values

- ΔG^\ominus into 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 positive