Edexcel International A Level (IAL) Chemistry

Your notes

Chemical Equilibria

Contents

- Equilibrium Constant, Kc
- Equilibrium Constant, Kp
- Equilibrium Constant & Conditions
- Equilibrium Constant & Temperature
- Equilibrium Constant & Entropy

Your notes

Kc Expressions – Deduction

Equilibrium expression & constant

- The **equilibrium constant expression** is an expression that links the **equilibrium constant**, ***K***, to the **concentrations of reactants and products** at equilibrium taking the **stoichiometry** of the equation into account
- So, for a given reaction:

$$\mathbf{aA + bB \rightleftharpoons cC + dD}$$

- The corresponding **equilibrium constant expression** is written as:

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

- Where:
  - [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 corresponding reactants and products
- **Solids** are ignored in equilibrium constant expressions
- The K_c of a reaction is specific to a given reaction and only changes if the **temperature** of the reaction changes

Worked Example

Deducing equilibrium expressions

Deduce the equilibrium constant expression for the following reactions

1. $Ag^+(aq) + Fe^{2+}(aq) \rightleftharpoons Ag(s) + Fe^{3+}(aq)$
2. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
3. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Answer 1:

$$K = \frac{[Fe^{3+}(aq)]}{[Fe^{2+}(aq)][Ag^+(aq)]}$$

- [Ag (s)] is not included in the equilibrium constant expression as it is a solid

Answer 2:

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

Answer 3:

$$K = \frac{[SO_3\,(g)]^2}{[SO_2\,(g)]^2\,[O_2\,(g)]}$$

Your notes

Kc Expressions – Calculations

Calculations involving K_c

- In the equilibrium expression each figure within a square bracket represents the concentration in **mol dm^{-3}**
- The **units** of K_c therefore depend on the form of 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

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

Equation to calculate concentration from number of moles and volume

Worked Example

Calculating K_c of ethanoic acid

In the reaction:

$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$

ethanoic acid ethanol ethyl ethanoate water

500 cm^3 of the reaction mixture at equilibrium 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

- $[CH_3COOH\,(l)] = \frac{0.235}{0.500} = 0.470 \text{ mol dm}^{-3}$
- $[C_2H_5OH\,(l)] = \frac{0.035}{0.500} = 0.070 \text{ mol dm}^{-3}$
- $[CH_3COOC_2H_5\,(l)] = \frac{0.182}{0.500} = 0.364 \text{ mol dm}^{-3}$

- $[H_2O\ (l)] = \frac{0.182}{0.500} = 0.364\ mol\ dm^{-3}$

Step 2: Write the equilibrium constant for this reaction in terms of concentration

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

Step 3: Substitute the equilibrium concentrations into the expression

- $K_c = \frac{[0.364] \times [0.364]}{[0.070] \times [0.470]} = 4.03$

Step 4: Deduce the correct units for K_c

- $K_c = \frac{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}$
  - All units cancel out

Therefore, K_c = **4.03**

Examiner Tips and Tricks

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 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:

$CH_3COOC_2H_5\ (l) + H_2O\ (l) \rightleftharpoons CH_3COOH\ (l) + C_2H_5OH\ (l)$

ethyl ethanoate water ethanoic acid ethanol

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 1.00 dm^3. At equilibrium, 0.0654 mol of water are present.

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

Answer

Your notes

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

Your notes

$CH_3COOC_2H_5(l) + H_2O(l) \rightleftharpoons CH_3COOH(l) + C_2H_5OH(l)$				
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

Step 2: Calculate the concentrations of the reactants and products

- $[CH_3COOC_2H_5(l)] = \frac{0.0654}{1.00} = 0.0654 \text{ mol dm}^{-3}$
  - $[H_2O(l)] = \frac{0.0654}{1.00} = 0.0654 \text{ mol dm}^{-3}$
  - $[CH_3COOH(l)] = \frac{0.0346}{1.00} = 0.0346 \text{ mol dm}^{-3}$
  - $[C_2H_5OH(l)] = \frac{0.0346}{1.00} = 0.0346 \text{ mol dm}^{-3}$

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

- $K_c = \frac{[0.346] \times [0.346]}{[0.654] \times [0.654]} = 0.28$

Step 4: Deduce the correct units for K_c

- $K_c = \frac{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}{[mol\ dm^{-3}] \times [mol\ dm^{-3}]}$
  - All units cancel out

Therefore, K_c = **0.28**

Your notes

Kp Expressions – Deduction

We have seen previously that equilibrium reactions can be quantified by reference to an equilibrium expression and equilibrium constant The **equilibrium expression** links the **equilibrium constant**, K_c, to the **concentrations of reactants and products** at equilibrium taking the **stoichiometry** of the equation into account So, for a given reaction:

$$\mathbf{aA + bB \rightleftharpoons cC + dD}$$

K_c is defined as follows:

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

[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

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

- **Solids** are ignored in equilibrium expressions
- The K_c of a reaction is constant and only changes if the **temperature** of the reaction changes

Homogeneous reactions

- In the generic example above, if all the substances are gases, we can show the equation with that state symbol

$$\mathbf{aA\,(g) + bB\,(g) \rightleftharpoons cC\,(g) + dD\,(g)}$$

- We can write a different equilibrium expression in terms of the **partial pressure** of the gases
- This equilibrium constant is called K_p and is defined as follows

$$K_p = \frac{p^c C(g)\,eqm\ p^d D(g)\,eqm}{p^a A(g)\,eqm\ p^b B(g)\,eqm}$$

p^aA AND p^bB = EQUILIBRIUM REACTANT PARTIAL PRESSURES (kPa)

p^cC AND p^dD = EQUILIBRIUM PRODUCT PARTIAL PRESSURES (kPa)

a, b, c AND d = COEFFICIENTS IN THE BALANCED EQUATION

Equilibrium expression linking the partial pressures of reactants and products at equilibrium

Your notes

Heterogeneous reactions

- For heterogenous reactions, **solids** and **liquids** are ignored in K_p equilibrium expressions
- The K_p of a reaction is constant and only changes if the **temperature** of the reaction changes

Worked Example

Write a K_p expression for the following equilibria and deduce the units of K_p :

1. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
2. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Answer 1

$$K_p = \frac{p^2NH_3(g)\,eqm}{pN_2(g)eqm\ p^3H_2(g)\,eqm} = \frac{kPa^2}{kPa \times kPa^3} = kPa^{-2}$$

Answer 2

$$K_p = pCO_2(g)$$

Kp Expressions – Calculations

Calculations involving K_p

- In the equilibrium expression, the *p* represents the partial pressure of the reactants and products in **Pa**
- The **units** of K_p therefore depend on the form of the equilibrium expression

Worked Example

Calculating K_p of a gaseous reaction

Sulfur dioxide and oxygen react according to the following equation:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

The equilibrium partial pressures at constant temperature are:

- $SO_2 = 1.0 \times 10^6$ Pa
- $O_2 = 7.0 \times 10^6$ Pa
- $SO_3 = 8.0 \times 10^6$ Pa

Calculate the value of K_p for this reaction.

Answer

- **Step 1:** Write the equilibrium constant for the reaction in terms of partial pressures

$$K_p = \frac{p^2\ SO_3}{p^2\ SO_2 \times pO_2}$$

- **Step 2:** Substitute the equilibrium concentrations into the expression

$$K_p = \frac{(8.0 \times 10^6)^2}{(1.0 \times 10^6)^2 \times (7.0 \times 10^6)}$$

$K_p = 9.1 \times 10^{-6}$

- **Step 3:** Deduce the correct units of K_p

$$K_p = \frac{Pa^2}{Pa^2 \times Pa}$$

The units of K_p are Pa^{-1}

Therefore, $K_p = 9.1 \times 10^{-6}\ Pa^{-1}$

- Some questions only give the **number of moles** of gases present and the total pressure
- The number of moles of each gas should be used to first calculate the **mole fractions**
- The mole fractions are then used to calculate the **partial pressures**
- The values of the partial pressures are then substituted in the **equilibrium expression**

Worked Example

Calculating K_p of hydrogen iodide equilibrium reaction

The equilibrium between hydrogen, iodine and hydrogen iodide, at 600 K, is as follows:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

At equilibrium, the number of moles present are:

- $H_2 = 1.71 \times 10^{-3}$
- $I_2 = 2.91 \times 10^{-3}$
- $HI = 1.65 \times 10^{-2}$

The total pressure is 100 kPa. Calculate the value of K_p for this reaction.

Answer

- **Step 1:** Calculate the total number of moles

Total number of moles = $1.71 \times 10^{-3} + 2.91 \times 10^{-3} + 1.65 \times 10^{-2}$

Total number of moles = 2.112×10^{-2}

- **Step 2:** Calculate the mole fraction of each gas

Your notes

Your notes

$$H_2 = \frac{1.71 \times 10^{-3}}{2.112 \times 10^{-2}} = 0.0810$$

$$I_2 = \frac{2.91 \times 10^{-3}}{2.112 \times 10^{-2}} = 0.1378$$

$$HI = \frac{1.65 \times 10^{-2}}{2.112 \times 10^{-2}} = 0.7813$$

- **Step 3:** Calculate the partial pressure of each gas

H_2 = 0.0810 x 100 = 8.10 kPa

I_2 = 0.1378 x 100 = 13.78 kPa

HI = 0.7813 x 100 = 78.13 kPa

- **Step 4:** Write the equilibrium constant in terms of partial pressure

$$K_p = \frac{p^2HI}{pH_2 \times pI_2}$$

- **Step 5:** Substitute the values into the equilibrium expression

$$K_p = \frac{78.13^2}{8.10 \times 13.78}$$

K_p = 54.7

- **Step 6:** Deduce the correct units for K_p

$$K_p = \frac{Pa^2}{Pa \times Pa}$$

All units cancel out

Therefore, K_p = 54.7

- Other questions related to equilibrium expressions may involve calculating quantities present at equilibrium given appropriate data

Your notes

Changing Conditions – General

Effects of temperature

- How the equilibrium shifts with temperature changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE
DECREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE

Effect on the value of K_c

- For a reaction that is exothermic in the forward direction, increasing the temperature pushes the equilibrium from right to left
- Therefore, the value of K_c will decrease as the ratio of [products] to [reactants] decreases
- Conversely, if the temperature is raised in an endothermic reaction, the value of K_c will increase

Effect on the value of K_p

- For a reaction that is exothermic in the forward direction, increasing the temperature pushes the equilibrium from right to left
- Therefore, the value of K_p will decrease as the ratio of [products] to [reactants] decreases
- Conversely, if the temperature is raised in an endothermic reaction, the value of K_p will increase

Effects of pressure

- Changes in pressure only affect reactions where the reactants or products are gases
- How the equilibrium shifts with pressure changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **SMALLER** NUMBER OF MOLECULES OF GAS TO DECREASE THE PRESSURE AGAIN
DECREASE IN PRESSURE	EQUILIBRIUM SHIFTS IN THE DIRECTION THAT PRODUCES THE **LARGER** NUMBER OF MOLECULES OF GAS TO INCREASE THE PRESSURE AGAIN


Your notes

Effect on the value of Kc

- The value of K_c is not affected by any changes in pressure as this does not involve gases.

Effect on the value of K_p

- The value of K_p is not affected by any changes in pressure.
- Changes in pressure cause a shift in the position of equilibrium to a new position which restores the value of K_p
- This is analogous to what happens to K_c when you change concentration in an aqueous equilibrium; a shift restores equilibrium to a new position maintaining K_c

Presence of a catalyst

- If all other conditions stay the same, the equilibrium constant K_p is **not affected** by the presence of a catalyst
- A catalyst speeds up both the forward and reverse reactions at the same rate so the ratio of [products] to [reactants] remains unchanged
- Catalysts only cause a reaction to reach equilibrium **faster**
- Catalysts therefore have **no effect** on the **position of the equilibrium** once this is reached

Worked Example

Factors affecting K_c

An equilibrium is established in the reaction

$$AB\,(aq) + CD\,(aq) \rightleftharpoons AC\,(aq) + BD\,(aq) \quad \Delta H = +180\ kJ\ mol^{-1}$$

Which factors would affect the value of K_c in this equilibrium?

Answer

- Only a change in temperature will affect the value of K_c and any other changes in conditions would result in the position of the equilibrium moving in such way to

oppose this change.

- Adding a catalyst will increase the rate of reaction meaning the state of equilibrium will be reached faster but will have no effect on the position of the equilibrium and therefore K_c is unchanged.

Your notes

Your notes

Changing Conditions – Temperature

- Changes in temperature **change** the equilibrium constants K_c and K_p
- For an endothermic reaction such as:

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$$

$$K_c = \frac{[H_2]\,[I_2]}{[HI]^2}$$

- With an increase in temperature:
  - $[H_2]$ and $[I_2]$ **increases**
  - $[HI]$ **decreases**
  - Because $[H_2]$ and $[I_2]$ are **increasing** and $[HI]$ is **decreasing**, the equilibrium constant **increases**
- For an exothermic reaction such as:

$$2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

- With an increase in temperature:
  - $[SO_3]$ **decreases**
  - $[SO_2]$ and $[O_2]$ **increases**
  - Because $[SO_3]$ **decreases** and $[SO_2]$ and $[O_2]$ **increases** the equilibrium constant decreases

Worked Example

Increasing K_p

What will increase the value of K_p for the following equilibrium?

$$2A\,(g) + B\,(g) \rightleftharpoons 2C\,(g)$$

$$\Delta H = +6.5\ kJ\ mol^{-1}$$

Answer

Only temperature changes permanently affect the value of K_p

An increase in temperature shifts the reaction in favour of the products.

The [products] increases and [reactants] decreases, therefore, the K_p value increases.

Your notes

How the equilibrium shifts with temperature changes:

CHANGE	HOW THE EQUILIBRIUM SHIFTS
INCREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **ENDOTHERMIC** DIRECTION TO REVERSE THE CHANGE
DECREASE IN TEMPERATURE	EQUILIBRIUM MOVES IN THE **EXOTHERMIC** DIRECTION TO REVERSE THE CHANGE

Effect on the value of the equilibrium constant

- For a reaction that is exothermic in the forward direction, increasing the temperature pushes the equilibrium from right to left
- Therefore, the value of the equilibrium constant will decrease as the ratio of [products] to [reactants] decreases
- Conversely, if the temperature is raised in an endothermic reaction, the value of the equilibrium constant will increase

Your notes

Equilibrium Constant & Entropy

- The equation for calculating the total entropy change is:

$$\Delta S^{\ominus}_{total} = \Delta S^{\ominus}_{sys} + \Delta S^{\ominus}_{surr}$$

(sys = system and surr = surroundings)

- Remember that $\Delta S^{\ominus}_{total}$ is positive for all spontaneous changes
- There is very little change in $\Delta S^{\ominus}_{sys}$ with a change in temperature unless there is a change in the state of one of the reactants or products
- There will be a significant change in $\Delta S^{\ominus}_{surr}$ however
- The entropy change of the surroundings during a chemical reaction is

$$\Delta S^{\theta}_{Sur} = -\frac{\Delta H}{T}$$

- Where ΔH is the enthalpy change and T is the absolute temperature (measured in kelvin)
- We can use this information to determine whether a reaction is spontaneous at a given temperature

Worked Example

Is the decomposition of calcium carbonate into calcium oxide and carbon dioxide spontaneous at the given temperatures?

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ $\Delta H = +177.9\ kJ\ mol^{-1}$ $\Delta S_{sys} = +160.4\ J\ K^{-1}\ mol^{-1}$

1. 293K (20 °C)
2. 1173K (900 °C)

Answer 1: at 293 K (20°C)

- $\Delta S_{surroundings} = -\frac{+177900\ J\ mol^{-1}}{293\ K} = -607.2\ J\ K^{-1}\ mol^{-1}$
- $\Delta S_{total}(293K) = (+160.4 - 607.2) = -446.8\ J\ K^{-1}\ mol^{-1}$
- The decomposition of calcium carbonate is not spontaneous at 293K

Answer 2: at 1173K (900°C)

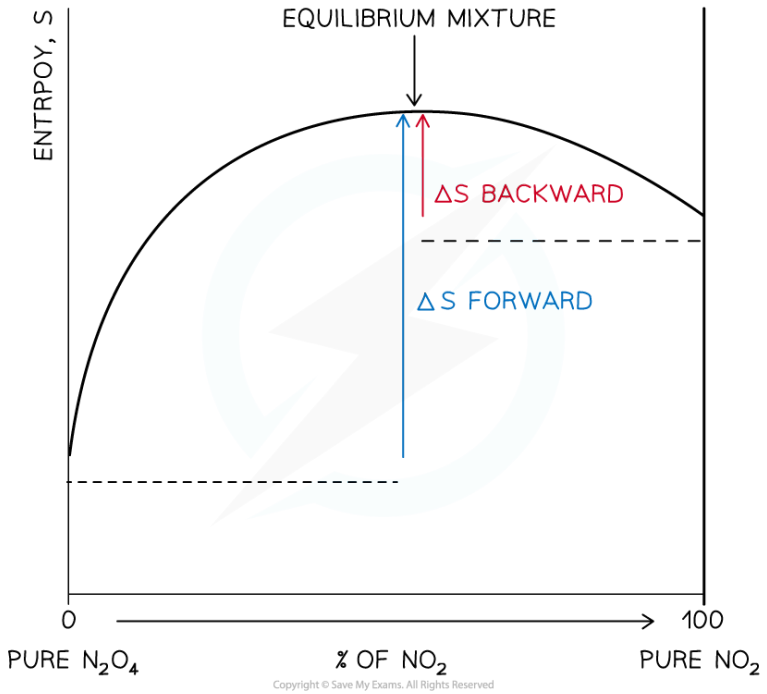
- $\Delta S_{surroundings} = -\frac{+177900\ J\ mol^{-1}}{1173} = -151.7\ J\ K^{-1}\ mol^{-1}$
- $\Delta S_{total}(1173) = (+160.4 - 151.7) = +8.7\ J\ K\text{-}1\ mol\text{-}1$
- The decomposition of calcium carbonate is spontaneous when heated to 1173K

Relationship between entropy change and equilibrium constant

Your notes

- For a reversible reaction that can reach equilibrium, the equilibrium position can be reached from either side of the reaction
- This means that both the forward and backward reactions are spontaneous
  - ΔS must be positive in both directions
- For example, consider the following reaction:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$



A graph of entropy against the percentage of NO_2 in a mixture of N_2O_4 and NO_2

- The entropy of N_2O_4 is less than the entropy of the equilibrium mixture
- The change in entropy from pure N_2O_4 to the equilibrium mixture is positive
  - The change is spontaneous
- The entropy change for NO_2 to the equilibrium mixture is also positive
  - This change is also spontaneous
- The entropy change for a mixture of the gases in any proportions moving towards the equilibrium position is also positive
- Neither the forward nor backward reaction can go to completion as the entropy change from the equilibrium mixture to either the reactants or products is negative
- At equilibrium, the total entropy change is zero

$$\Delta S_{total}\text{ [forward reaction]} = \Delta S_{total}\text{ [backward reaction]}$$

- The relationship between the total entropy of the reaction and the equilibrium constant (K_c or K_p) is

$$\Delta S_{total} = R \ln K$$

Using total entropy change to calculate an equilibrium constant

- Rearranging the equation mentioned above we get:

$$\ln K = \frac{\Delta S_{total}}{R}$$

- Hence:

$$K = e^{\frac{\Delta S_{total}}{R}}$$

Relationship between equilibrium constant and equilibrium position

- There is no hard rule for the relationship between equilibrium constant and the position of equilibrium
- As a general rule, we can say a very large value of K suggests the equilibrium position is pushed towards the products (right-hand side)
- Similarly, a very small value of K suggests the equilibrium position is pushed towards the reactants (left-hand side)

Your notes