OCR A Chemistry A-Level

Module 5 - Physical Chemistry & Transition Elements

Equilibria

Notes and Example Calculations

Answers given at the end of the booklet

The Equilibrium Constant, Kc

Le Chatelier Principle

If a closed system under equilibrium is subjected to a change, the system will move to minimise the effect of the change. These changes can be either temperature, pressure or concentration.

The equilibrium constant shows where the equilibrium lies for a general reaction:

$$aA + bB \rightleftharpoons pP + qQ$$

The equilibrium constant expression is:

$$Kc = \frac{[P]^p\,[Q]^q}{[A]^a\,[B]^b}$$

Example 1:

Write the equilibrium constant expression for this reaction and include the units:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Step 1: Write an expression for Kc.
[Remember it is always products over reactants.]

⇒ **Kc =** $\mathbf{\dfrac{[NH3]^2}{[N2]\,[H2]^3}}$

Step 2: Find the units for Kc.

$$\frac{\cancel{Mol}\ dm^{-3} \times \cancel{Mol}\ dm^{-3}}{\cancel{Mol}\ dm^{-3} \times \cancel{Mol}\ dm^{-3} \times Mol\ dm^{-3} \times Mol\ dm^{-3}}$$

⇒ Units: **<u>mol^{-2}dm^{6}</u>**

Example 2:

For the equilibrium:

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 are 1.0, 0.205 and 0.205 mol dm^{-3} respectively. Calculate the value of K_c.

Step 1: Write an equilibrium constant expression for this reaction.

$$\Rightarrow Kc = \frac{[Cl2]\,[PCl3]}{[PCl_5]}$$

Step 2: Input the values with the corresponding molecules into the expression.

$$\Rightarrow Kc = \frac{(0.205) \times (0.205)}{1}$$

$= \underline{\mathbf{0.042}}$ **moldm^{-3}**

Worked Exam Style Questions

Question 1

Syngas is a mixture of carbon monoxide and hydrogen gases, used as a feedstock for the manufacture of methanol.

A dynamic equilibrium was set up between carbon monoxide, CO, hydrogen, H_2, and methanol, CH_3OH, in a 2.0 dm^3 sealed vessel.

The equilibrium is shown below.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

The number of moles of each component at equilibrium is shown below

component	$CO(g)$	$H_2(g)$	$CH_3OH(g)$
number of moles at equilibrium	6.20×10^{-3}	4.80×10^{-2}	5.20×10^{-5}

(i) Write an expression for K_c for this equilibrium system.

(ii) Calculate K_c for this equilibrium. State the units.

K_c = ……………………… units:………………

[4]

Step 1: Write the Kc expression.

$\Rightarrow Kc = \dfrac{[CH3OH]}{[CO]\,[H2]^2}$

Step 2: Convert moles to concentration. Use the formula: Concentration = Moles / Volume.

$6.2 \times 10^{-3} / 2 = 3.1 \times 10^{-3}$
$4.8 \times 10^{-2} / 2 = 2.4 \times 10^{-2}$
$5.2 \times 10^{-5} / 2 = 2.6 \times 10^{-5}$

Step 3: Input the values into the expression.

$Kc = \dfrac{2.6 \times 10^{-5}}{(2.4 \times 10^{-2})^2 \times 3.1 \times 10^{-3}}$

= **<u>14.56</u>**

Step 4: Work out the units

$$\frac{\cancel{\text{Mol}\,\text{dm}^{-3}}}{\cancel{\text{Mol}\,\text{dm}^{-3}} \times \text{Mol dm}^{-3} \times \text{Mol dm}^{-3}}$$

$\Rightarrow$ **<u>$mol^{-2}dm^{6}$</u>**

Question 2

Nitrogen gas and hydrogen gas produce ammonia gas as shown below.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H = -92 \text{ kJ mol}^{-1}$

(i) Write the expression for K_c for this equilibrium.

At 500 °C, $K_c = 8.00 \times 10^{-2} \text{ dm}^6 \text{ mol}^{-2}$.

At equilibrium, the concentration of N_2 is 1.20moldm^{-3} and the concentration of H_2 is 2.00moldm^{-3}.

Calculate the equilibrium concentration of ammonia under these conditions.

equilibrium concentration of NH_3 = ... moldm^{-3}

[3]

Step 1: Write the Kc expression.

$$\Rightarrow Kc = \frac{[NH3]^2}{[N2]\,[H2]^3}$$

Step 2: Rearrange the expression so that ammonia is the subject.

$\Rightarrow [NH3]^2 = Kc \times [N2] \times [H2]^3$

Step 3: Input values into the expression.

$\Rightarrow [NH3]^2 = 8 \times 10^{-2} \times 1.2 \times 2^3$
$= 0.768$
$[NH3] = \sqrt{0.78}$
$= \underline{\mathbf{0.88\ moldm^{-3}}}$

Question 3

The preparation of hydrogen iodide, HI(g), from hydrogen and iodine gases is a reversible reaction which reaches equilibrium at constant temperature.

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

(a) Write the expression for K_c for this equilibrium.

(b) A student mixed together 0.30 mol $H_2(g)$ with 0.20 mol $I_2(g)$ and the mixture was allowed to reach equilibrium. At equilibrium, 0.14 mol $H_2(g)$ was present.

(i) Complete the table below to show the amount of each component in the equilibrium mixture.

component	$H_2(g)$	$I_2(g)$	$HI(g)$
initial amount / mol	0.30	0.20	0
equilibrium amount / mol			

[2]

Step 1: Write the Kc expression.

$$\Rightarrow Kc = \frac{[HI]^2}{[H2]\,[I2]}$$

Step 2: Work out the change between initial and equilibrium moles present of H_2.

⇒ 0.3 - 0.14 = 0.16 mol

Step 3: Calculate the equilibrium moles for the other reactants by subtracting the difference in moles that was calculated in step 1 from the initial moles of each reactant.

⇒ I_2 : 0.2 - 0.16 = 0.04 mol

Step 4: Calculate the equilibrium moles of the product by adding the difference in moles that was calculated in step 1 to the initial amount.

⇒ 0 + 0.16 + 0.16 = 0.32 mol

[Two lots of 0.16 is added because from the balanced equation the ratio between the reactants and products is 1:2.]

Try these questions …

1. The preparation of hydrogen iodide, HI(g), from hydrogen and iodine gases is a reversible reaction which reaches equilibrium at constant temperature.

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

[1 mark]

(a) Write the expression for K_c for this equilibrium.

(b) A student mixed together 0.30 mol H_2(g) with 0.20 mol I_2(g) and the mixture was allowed to reach equilibrium. At equilibrium, 0.14 mol H_2(g) was present.

(i) Complete the table below to show the amount of each component in the equilibrium mixture.

component	H_2(g)	I_2(g)	HI(g)
initial amount / mol	0.30	0.20	0
equilibrium amount / mol			

[2]

(ii) Calculate K_c to an appropriate number of significant figures. State the units, if any.

[3 marks]

2.

A chemist investigates the equilibrium reaction between sulfur dioxide, oxygen, and sulfur trioxide, shown below.

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

- The chemist mixes together SO_2 and O_2 with a catalyst.
- The chemist compresses the gas mixture to a volume of 400 cm^3.
- The mixture is heated to a constant temperature and is allowed to reach equilibrium without changing the total gas volume.

The equilibrium mixture contains 0.0540 mol SO_2 and 0.0270 mol O_2.

At the temperature used, the numerical value for K_c is $3.045 \times 10^4\,dm^3\,mol^{-1}$.

(i) Write the expression for K_c and the units of K_c for this equilibrium.

[2 marks]

(ii) Determine the amount, in mol, of SO_3 in the equilibrium mixture at this temperature.

Give your final answer to an **appropriate** number of significant figures.

Show all your working.

[4 marks]

Partial Pressure and Kp

The partial pressure of a gas is the contribution that each gas in a mixture makes towards the total pressure P_{tot}.

Consider mixtures of gas made up of gas A, gas B, gas C.

$$\text{Mole fraction of A} = \frac{\text{number of moles of sample A}}{\text{total number of moles in gas mixture}}$$

$$P_{tot} = pA + pB + pC$$

To work out the partial pressure of a gas in a gas mixture you multiply the mole fraction of the gas by the total pressure.

Kp can only used for mixtures of gases.

Example 1:

Write an expression for the equilibrium constant, Kp, for this reaction:

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

Step 1: Form the expression with partial pressures of the products over the reactants.

$$\Rightarrow \mathbf{Kp = \frac{p(NH_3)^2}{{}_P(N_2){}_P(H_2)^3}}$$

Example 2:

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

A mixture at equilibrium contains 0.320 mol N2, 0.960 mol H2 and 0.120 mol NH3. What is the mole fraction of H2 in the equilibrium mixture?

Step 1: Sub in the values to find the molar fraction of A.

⇒ mole fraction of A = number of moles of sample A / total number of moles in mixture

$$\Rightarrow \frac{0.96}{0.96 + 0.120 + 0.32}$$

= **0.686**

Worked Exam Style Questions

Question 1

Methanol, $CH_3OH(g)$, is manufactured from carbon monoxide and hydrogen in an equilibrium reaction.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -91\ \text{kJ mol}^{-1}$$

This equilibrium reaction is normally carried out at 10MPa pressure and 550 K, and starting with a 1 : 2 CO : H_2 mixture. At equilibrium, only 10% of the CO has reacted.

(i) Deduce the equilibrium amounts, mole fractions and partial pressures of CO, H_2 and CH_3OH present at equilibrium. Write your answers in the table below.

Assume that you have started with a mixture of 1.0 mol CO and 2.0 mol H_2.

	CO	H_2	CH_3OH
initial amount /mol	1.0	2.0	0.0
equilibrium amount /mol	0.9		
mole fraction at equilibrium			
partial pressure at equilibrium /MPa			

[4]

Step 1: Work out the change between initial and equilibrium moles present of CO.

[this is because you have both data for this substance.]

$\Rightarrow$ 1 - 0.9 = 0.1

Step 2: Work out the equilibrium amount of H_2 and CH_3OH.

[To work out the equilibrium amount for a reactant subtract the change in moles from the initial amount.]

⇒ 2.0 - 0.1 - 0.1 = **1.8** mol of H_2

[To work out the equilibrium amount of a product add the change in moles to the initial amount of that substance.]

0 + 0.1 = **0.1** mol of CH_3OH

Step 3: Work out mole fraction of each gas

⇒ Total number of moles in gas mixture = 2.8 moles

CO = 0.9 / 2.8 = **0.321**
H2 = 1.8 / 2.8 = **0.643**
CH3OH = 0.1 / 2.8 = **0.036**

Step 4: To work out partial pressure of each gas multiply mole fraction by the total pressure given in the question

CO - 0.321 X 10 = **3.21 MPa**
H2 - 0.643 X 10 = **6.43 MPa**
CH3OH - 0.036 X 10 = **0.36 MPa**

(ii) Write the expression for K_p for this equilibrium.

⇒ **Kp =** $\mathbf{\dfrac{p(CH3OH)}{p(H2)^2 p(CO)}}$

(iv) In another experiment, the equilibrium partial pressures were:

CO, 3.70 MPa; H_2, 5.10 MPa; CH_3OH, 0.261 MPa.

Calculate the value of K_p for this equilibrium. Express your answer to an appropriate number of significant figures. State the units of K_p.

Step 1: Input the values into the Kp expression.

$$Kp = \frac{0.261}{(5.10)^2 \times (3.70)}$$

= **2.71×10^{-3}**

Question 2

I When heated, chlorine gas, Cl_2 dissociates into gaseous chlorine atoms.

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

A chemist placed some chlorine gas in a container which was heated to 1400 K. The container was left until equilibrium had been reached.

Under these conditions, the equilibrium partial pressure of $Cl_2(g)$ is 85.0 kPa and that of $Cl(g)$ is 3.0 kPa.

(b) Determine the mole fraction of Cl in the equilibrium mixture.

Step 1: Find the total pressure in this gas mixture.

⇒ 85 + 3 = 88 kPa

Step 2: Work out the mole fraction of Cl.

⇒ 3 / 88 = **0.034**

(c) (i) Write an expression for K_p for this equilibrium.

$$\Rightarrow \mathbf{Kp = \frac{p(Cl)^2}{p(Cl2)}}$$

(ii) Calculate K_p for this equilibrium. State the units.

⇒ Kp = $\frac{3^2}{\;}$ = **0.106**

85

$$\frac{\text{kPa} \times \cancel{\text{kPa}}}{\cancel{\text{kPa}}} \Rightarrow \frac{\text{kPa} \times \text{kPa}}{\text{kPa}}$$

⇒ Units = **kPa**

Try these questions…

3.

Ethanoic acid can be manufactured by the following reaction, which is carried out between 150 °C and 200 °C.

$$CH_3OH(g) + CO(g) \rightleftharpoons CH_3COOH(g)$$

(a) A mixture of 50.0 mol of methanol and 50.0 mol of carbon monoxide reaches equilibrium at a pressure of 32.0 atm. At 175 °C, the equilibrium partial pressure of ethanoic acid is 22.2 atm.

(i) Write the expression for the equilibrium constant in terms of pressure, K_p, for this reaction.

(1)

(ii) Calculate the partial pressures of methanol and carbon monoxide at equilibrium.

(2)

(iii) Calculate the value of K_p for this reaction at 175 °C. Include a unit in your answer and give your answer to **three** significant figures.

(2)

(b) Another sample of 50.0 mol of methanol and 50.0 mol of carbon monoxide was allowed to reach equilibrium at the same pressure of 32.0 atm, but at a lower temperature. 93.6 % of the methanol was converted at equilibrium.

(i) Complete the table below to show the number of moles of each species in the equilibrium mixture.

(2)

	CH_3OH	CO	CH_3COOH
Number of moles at start	50.0	50.0	0
Number of moles at equilibrium			

(ii) Calculate the partial pressure of ethanoic acid in the equilibrium mixture.

(1)

Answers

Q1.

(a) $K_c = \dfrac{[HI]^2}{[H_2][I_2]}$ **(1)** 1

(b) (i)

H_2	I_2	HI
0.30	0.20	0
0.14	0.04	0.32
	(1)	**(1)**

2

(ii) $K_c = \dfrac{0.32^2}{0.14 \times 0.04} = 18.28571429$ **(1)**

= 18 (to 2 sig figs) **(1)**

no units **(1)**

(or ecf based on answers to (i) and/or (a)) 3

Q2

(i)	$(K_c =)\ \dfrac{[SO_3]^2}{[SO_2]^2\,[O_2]}$ ✓ Units: $dm^3\ mol^{-1}$ ✓

(ii)	**FIRST, CHECK THE ANSWER ON ANSWER LINE** **IF** answer = 2.45, Award **4 marks.** -- **Equilibrium concentrations (moles × 2.5) 1 MARK** SO_2 = 0.135 (mol dm^{-3}) **AND** O_2 = 0.0675 (mol dm^{-3}) ✓ **Calculation of [SO_3(g)] 2 MARKS** $[SO_3] = \sqrt{(K_c \times [SO_2]^2 \times O_2)}$ **OR** $\sqrt{((3.045 \times 10^4) \times 0.135^2 \times 0.0675)}$ ✓ = 6.12039291 (mol dm^{-3}) ✓ *Answer scores both [SO_3] marks automatically* **Calculation of *n*(SO_3) in 400 cm^3 1 MARK** *n*(SO_3) = 6.12039291/2.5 = 2.45 (mol) ✓ ***3SF required (Appropriate number)***	4	**FULL ANNOTATIONS NEEDED** **IF** there is an alternative answer, check to see if there is any **ECF** credit possible using working below -- **ALLOW ECF** from incorrect concentrations of SO_2 and/or O_2 **ALLOW ECF** from incorrect [SO_3] **ALLOW 3 SF**, 6.12, up to calculator value of 6.12039291 correctly rounded. **Common errors** **37.5 1 mark** *No √for [SO_3]^2 and no scaling by 1/2.5* **15.0 2 marks** *No √for [SO_3]^2* **0.619 3 marks** *Use of mol of SO_2 and O_2* **1.55 2 marks** *No conc used and Use of mol of SO_2 and O_2*

Q3.

(a)(i)	(K_p =) $\frac{pCH_3CO_2H}{pCH_3OH\ (x)\ pCO}$ Partial pressure symbol can be shown in various ways, eg pp, p_{CO}, (CO)p, etc *ALLOW* p in upper or lower case, round brackets *IGNORE* units	[ ] State symbols given as (l) + in bottom line	**1**
(a)(ii)	P CH_3OH = 4.9 (atm) **(1)** P CO = 4.9 (atm) **(1)** 1 mark for recognition that pressures are equal *IGNORE* units		**2**

(a)(iii)	$K_p = ((22.2)/(4.9)^2)$ $= 0.925$ **(1)** atm^{-1} **(1) stand alone mark but must match expression used in (a)(iii)** **OR** $9.25 \times 10^4\ Pa^{-1}$ / $92.5\ kPa^{-1}$ **(2)** *ALLOW* TE from (a)(i) if inverted and/or (a)(ii)	Answers to other than 3 significant figures	**2**
(b)(i)	CH_3OH: 3.2 CO : 3.2 **(1)** for both values CH_3CO_2H: 46.8 **(1)** *ALLOW* TE for moles of ethanoic acid based on numbers of methanol and carbon monoxide used, as long as moles of methanol and carbon monoxide are equal and moles ethanoic acid + moles methanol = 50		**2**
(b)(ii)	$\left(\frac{46.8 \times 32}{53.2}\right) = 28.2$ / 28.1504 (atm) *IGNORE* sf except 1 Value = 28.16 if mol fraction rounded *ALLOW* TE from (b)(i)	28.1 $\frac{46.8 \times 32}{50} =$ 29.95 (atm)	**1**