Equilibria, Energetics and Elements
How Far?

100 marks

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}

(a) State **two** features of a system that is in *dynamic equilibrium*.

.....

.....

.....

[2]

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

[1]

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

K_c = ... units:.....

[4]

(c) The pressure was increased whilst keeping the temperature constant. The mixture was left to reach equilibrium.

The equilibrium position above shifted to the right.

(i) Explain why the equilibrium position shifted to the right.

.....

.....

[1]

(ii) What is the effect, if any, on the value of K_c?

.....

[1]

(d) The temperature was increased whilst keeping the pressure constant. The mixture was left to reach equilibrium.

The value of K_c for the equilibrium above decreased.

(i) Explain what happened to the equilibrium position in the equilibrium.

.....

.....

[1]

(ii) Deduce the sign of the enthalpy change for the forward reaction shown in the equilibrium above.

Explain your reasoning.

.....

.....

[1]

(e) Methanol can be used as an additive to petrol.

(i) Write an equation for the complete combustion of methanol, CH_3OH.

.....

[1]

(ii) Suggest why methanol is added to petrol.

.....

.....

[1]

[Total 13 marks]

2. When heated, phosphorus pentachloride, PCl_5, dissociates.

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

A chemist placed a mixture of the three gases into a container. The initial concentration of each gas was the same: 0.30 mol dm^{-3}. The container was left until equilibrium had been reached.

Under these conditions, K_c = 0.245 mol dm^{-3}.

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

[1]

(b) Use the value of K_c for this equilibrium to deduce whether the concentration of each gas increases, decreases or stays the same as the mixture approaches equilibrium.

(i) Show your answer by placing a tick in the appropriate cells in the table below.

	initial concentration / mol dm^{-3}	greater than 0.30 mol dm^{-3}	less than 0.30 mol dm^{-3}	equal to 0.30 mol dm^{-3}
PCl_5	0.30			
PCl_3	0.30			
Cl_2	0.30			

[1]

(ii) Explain your deduction.

.....

.....

.....

.....

[1]

(c) The chemist compressed the equilibrium mixture at constant temperature and allowed it to reach equilibrium under these new conditions.

(i) Explain what happens to the value of K_c.

.....

.....

[1]

(ii) Explain what happened to the composition of the equilibrium mixture.

.....

.....

.....

.....

[2]

(d) The chemist heated the equilibrium mixture and the equilibrium moved to the left.

(i) Explain what happens to the value of K_c.

.....

.....

[1]

(ii) Explain what additional information this observation reveals about the reaction.

.....

.....

.....

.....

[2]

[Total 9 marks]

3. Some ammonia plants are run at 200–300 atm and 500 °C, with an iron catalyst.

(a) The hydrogen for the plants is obtained by reacting methane with steam.

Construct a possible equation for this reaction.

.....

[1]

(b) 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.

[1]

(ii) 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]

(c) In this question one mark is available for the quality of the use and organisation of scientific terms.

Discuss the advantages and disadvantages of running this reaction

- at a pressure of 200–300 atm;
- at a temperature of 500°C;
- with an iron catalyst.

[6]

Quality of Written Communication [1]

[Total 12 marks]

4. 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.

[1]

(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.

K_c = ...

units, if any .....

[3]

(c) The student compressed the equilibrium mixture so that its volume was reduced. The temperature was kept constant.

Comment on the value of K_c **and** the composition of the equilibrium mixture under these new conditions.

.....

.....

.....

.....

[2]

[Total 8 marks]

5. Nitrogen dioxide is one of the major pollutants in air, formed by reaction of nitrogen monoxide with oxygen.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

(a) What is meant by the *rate of reaction*?

.....

.....

[1]

(b) A series of experiments was carried out to investigate the kinetics of this reaction. The results are shown in the table below.

Experiment	$[O_2]$ / mol dm^{-3}	[NO] / mol dm^{-3}	initial rate / mol dm^{-3} s^{-1}
1	0.00100	0.00100	7.10
2	0.00400	0.00100	28.4
3	0.00400	0.00300	256

(i) For each reactant, deduce the order of reaction. Show your reasoning.

$O_2(g)$ .....

.....

.....

.....

NO(g) .....

.....

.....

.....

[4]

(ii) Deduce the rate equation for this reaction.

.....

[1]

(iii) Calculate the rate constant, *k*, for this reaction. State the units for *k*.

k = ... units .....

[2]

[Total 8 marks]

6. In the UK, almost all the sulphuric acid, H_2SO_4, is manufactured by the Contact process.
One stage in the Contact process involves the reaction between sulphur dioxide and oxygen.

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

The table below shows values of the equilibrium constant, K_p, for this equilibrium at different temperatures.

temperature / °C	Kp / kPa^{-1}
25	4.0×10^{22}
200	2.5×10^{8}
800	1.3×10^{-3}

(a) Write an expression for the equilibrium constant, K_p, of this reaction.

[2]

(b) In this question, one mark is available for the quality and use of scientific terms.

- The conversion of sulphur dioxide and oxygen into sulphur trioxide is carried out at slightly above atmospheric pressure. Comment on this statement.
- Explain what happens to the equilibrium amounts of SO_2, O_2 and SO_3 as temperature increases at constant pressure.
- Deduce the sign of ΔH for the forward reaction in the equilibrium. Explain your reasoning carefully.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[6]

Quality of Written Communication [1]

(c) An equilibrium is set up for the SO_2, O_2, SO_3 equilibrium at 400 °C.

At this temperature

- the equilibrium partial pressure of SO_2 is 10 kPa
- the equilibrium partial pressure of O_2 is 50 kPa
- $K_p = 3.0 \times 10^2$ kPa^{-1}.

Calculate the equilibrium partial pressure of SO_3 at 400 °C. Hence determine the percentage of SO_3 in the equilibrium mixture at this temperature.

answer .....%

[3]

(d) In the UK, almost all the sulphuric acid manufactured uses sulphur as a starting material for SO_2 production. In some countries, metal ores such as zinc sulphide, ZnS, are used instead to form SO_2 by heating with air.

(i) Construct a balanced equation to show the reaction that takes place when zinc sulphide is heated in air.

.....

[2]

(ii) Suggest why countries may find it more economic to manufacture sulphuric acid from zinc sulphide.

.....

.....

[1]

[Total 15 marks]

7. One cause of low-level smog is the reaction of ozone, O_3, with ethene. The smog contains methanal, $CH_2O(g)$, and the equation for its production is shown below.

$$O_3(g) + C_2H_4(g) \rightarrow 2CH_2O(g) + \frac{1}{2}O_2(g) \qquad \textbf{equation 1}$$

(a) The rate of the reaction doubles when the initial concentration of either $O_3(g)$ or $C_2H_4(g)$ is doubled.

(i) What is the order of reaction with respect to

O_3 .....

C_2H_4? .....

[1]

(ii) What is the overall order of the reaction?

.....

[1]

(iii) Write the rate equation for this reaction.

.....

[1]

(b) For an initial concentration of ozone of 0.50×10^{-7} mol dm^{-3} and one of ethene of 1.0×10^{-8} mol dm^{-3}, the initial rate of methanal formation was 1.0×10^{-12} mol dm^{-3} s^{-1}.

(i) How could the **initial** rate of methanal formation be measured from a concentration/time graph?

.....

.....

[2]

(ii) Calculate the value of the rate constant and state the units.

rate constant =..... units.....

[3]

(iii) The initial rate of methanal formation is different from that of oxygen formation in **equation 1**.

Explain why.

.....

.....

[1]

(iv) The experiment was repeated but at a higher temperature. What would be the effect of this change on the rate and the rate constant of the reaction?

.....

.....

.....

[2]

[Total 11 marks]

8. In the stratosphere, ozone forms when oxygen free radicals react with oxygen molecules.

$$O_2 + O \rightarrow O_3$$

The oxygen free radicals are initially formed as diradicals when oxygen gas, O_2, is dissociated by strong ultraviolet radiation,

$$O_2(g) \rightarrow 2O(g)$$

(i) Suggest why oxygen free radicals, O, are often called **di**radicals.

.....

.....

[1]

(ii) Draw a '*dot-and-cross*' diagram of an ozone molecule. Show outer electrons only.

[2]

(iii) Chlorine free radicals formed from CFCs deplete the ozone layer in a chain reaction.

Typically, 1 g of chlorine free radicals destroys 150 kg of ozone during the atmospheric lifetime of the chlorine free radical (one to two years).

Calculate how many ozone molecules are destroyed in this chain reaction by a single chlorine free radical before the free radical is destroyed.

answer.....

[3]

[Total 6 marks]

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

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

(a) In this question, one mark is available for the quality of use and organisation of scientific terms.

Explain the advantages and disadvantages of running this reaction

- at a high pressure,
- at a high temperature.

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

[5]

Quality of Written Communication [1]

(b) 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]

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

[2]

(iii) The CO : H_2 ratio in the starting mixture was changed from 1 : 2 to 1 : 3 and the mixture was allowed to reach equilibrium at the same temperature and pressure.

Explain, in terms of K_p, the effect of this change on the equilibrium yield of CH_3OH.

.....

.....

.....

.....

.....

[3]

(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.

K_p = ... units.....

[2]

(c) In the UK, the annual production of methanol is 500 000 tonnes. Methanol has many uses in fuels as a reliable and low pollution form of energy.

Suggest an equation for the combustion of methanol.

.....

[1]

[Total 18 marks]