Equilibria

Past Year Topical Questions

Jan 2010

24 Hydrogen is used in very large quantities as a fuel, as a reducing agent, and in the production of ammonia. Hydrogen is manufactured by steam reforming of methane from natural gas. Two reactions are involved, both being in equilibrium in closed systems.

Reaction I $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$ $\Delta H = +210$ kJ mol^{-1}

Reaction II $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ $\Delta H = -42$ kJ mol^{-1}

(a) Write the expression for the equilibrium constant, K_p, for reaction **I**.

(1)

(b) Reaction **I** occurs at a temperature of 1000 K and a pressure of 30 atm over a nickel catalyst.

(i) State and explain the effect, if any, **on the value of K_p** of increasing the pressure on the reaction.

(1)

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(ii) Explain, in terms of your answers to (a) and (b)(i), why an increase in the pressure leads to a decrease in yield in reaction **I**.

(2)

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(iii) Increasing the pressure on this heterogeneously-catalysed reaction **I** has very little effect on the rate of the reaction. Suggest why this is so.

(2)

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(c) The expression for K_p for reaction **II** is

$$K_p = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}}$$

At a particular temperature and 30 atm pressure, a mixture of equal amounts of carbon monoxide and steam react to give an equilibrium mixture where 75 % of the CO has reacted.

Calculate the value of K_p showing your working.

(3)

June 2010

19 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)

Methanol .....

Carbon monoxide .....

(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)

(iii) Is the reaction exothermic or endothermic? Explain your answer.

(1)

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(c) How, if at all, does the addition of methanol to the equilibrium mixture affect the following? Justify your answers.

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

(i) The equilibrium constant for the formation of ethanoic acid.

(1)

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(ii) The equilibrium yield of ethanoic acid.

(1)

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(d) In industry, catalysts are used even though they are often expensive.

State and explain ONE benefit to the **environment** resulting from the use of catalysts in industrial processes.

(2)

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Jan 2011

(d) The composition of an equilibrium mixture produced at 2.0 atmospheres pressure and at a much higher temperature is shown below.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Amount in equilibrium mixture / mol	0.80	0.80	1.20	3.60

*(i) Write the expression for the equilibrium constant, K_p, of the reaction and calculate its value. Include units in your answer.

(6)

Jan 2012

20 The exothermic reaction between carbon monoxide and hydrogen can be used industrially to make methanol. The process is carried out at 250 °C and between 50 and 100 atm.

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

(a) Explain why increasing the pressure increases the yield of methanol. Give **one** disadvantage of increasing the pressure.

(2)

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June 2012

17 The ester $CH_3CH_2COOCH_3$ can be formed from the reaction between propanoic acid and methanol with an acid catalyst.

$$CH_3CH_2COOH + CH_3OH \rightleftharpoons CH_3CH_2COOCH_3 + H_2O$$

(a) (i) Name the ester.

(1)

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(ii) The same product can be made using propanoyl chloride instead of propanoic acid. Suggest an additional hazard that could occur using this reagent and describe how you would minimise this risk.

(2)

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(b) Complete the table below to show the amounts of each substance present at equilibrium. Use your values to calculate the equilibrium constant, K_c, for the reaction.

(3)

	CH_3CH_2COOH	CH_3OH	$CH_3CH_2COOCH_3$	H_2O
Initial amounts / mol	0.52	0.37	0	1.2
Equilibrium amounts / mol			0.21	

Jan 2013

17 Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l)$$

(a) (i) Give the expression for K_c.

(1)

(ii) An equilibrium was reached when the amounts of substances shown in the table below were used.

Complete the table to show the amounts of each substance present at equilibrium.

(2)

Component	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
Initial amount / mol	0.40	0.30	0.00	0.15
Equilibrium amount / mol	0.20			

(iii) Explain why K_c for this reaction has no units.

(1)

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(iv) Calculate the numerical value of K_c.

(1)

(b) The esterification reaction above was carried out in the presence of hydrochloric acid as the catalyst.

State the effect on the equilibrium position and the rate of attainment of equilibrium if the concentration of the acid catalyst were to be increased.

(2)

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June R 2013

11 This question is about the equilibrium reaction below.

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

The equilibrium is reached slowly.

*(a) Describe the changes you would see if aqueous solutions of iron(II) sulfate and silver nitrate were mixed and allowed to stand for a few hours.

(2)

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(b) The concentration of silver ions in the equilibrium mixture can be found by titration with potassium thiocyanate. Silver thiocyanate precipitates.

$$Ag^{+}(aq) + CNS^{-}(aq) \rightleftharpoons AgCNS(s)$$

When all the silver ions have reacted, a deep red complex ion of iron(III) thiocyanate forms.

In an experiment, 25.0 cm^3 of 0.100 mol dm^{-3} silver nitrate solution was added to 25.0 cm^3 of 0.100 mol dm^{-3} of iron(II) sulfate solution, mixed thoroughly, and allowed to stand overnight in an air-tight container.

10.0 cm^3 samples of the reaction mixture were then titrated with 0.0200 mol dm^{-3} potassium thiocyanate solution. The average titre was 5.60 cm^3.

(i) The initial concentrations of silver ions and iron(II) ions **in the reaction mixture** are the same.

Calculate this initial concentration in mol dm^{-3}.

(1)

(ii) Calculate the number of moles of silver ions in the 10.0 cm^3 sample at equilibrium and hence calculate the equilibrium concentration of silver ions in the mixture.

(2)

(iii) Deduce the equilibrium concentration of iron(II) ions.

(1)

(iv) Hence calculate the equilibrium concentration of iron(III) ions.

(1)

(v) Write the expression for the equilibrium constant, K_c, for the reaction

$$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$$

Calculate its value and give your answer, with appropriate units, to **three** significant figures.

(4)

Jan 2014

(c) The titration above can be used to determine the concentration of ammonia solution when ammonia is distributed between the two immiscible solvents, trichloromethane and water.

An experiment is carried out to find the equilibrium constant for the reaction:

$$NH_3(CHCl_3) \rightleftharpoons NH_3(aq)$$

75 cm^3 of 4.0 mol dm^{-3} aqueous ammonia solution and 75 cm^3 of the trichloromethane are shaken together. The two liquids are allowed to separate and 25.0 cm^3 of the aqueous layer is taken and titrated with 4.0 mol dm^{-3} hydrochloric acid. The whole procedure is repeated.

The average titre is 24.0 cm^3.

(i) Calculate the number of moles of ammonia, and hence the concentration of ammonia, in mol dm^{-3}, in the aqueous layer.

(3)

(ii) The initial volumes of the two solvents are the same.

Hence deduce the concentration of ammonia in the trichloromethane layer in mol dm^{-3}.

(1)

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(iii) Write the expression for the equilibrium constant, K_c, for this reaction and calculate its value.

(1)

(iv) Suggest why ammonia is much more soluble in water than in trichloromethane.

(1)

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June IAL 2014

21 This question concerns the reaction of hydrogen with iodine to form hydrogen iodide at 700 K.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -10 \text{ kJ mol}^{-1}$$

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

(1)

*(ii) 1 mol of hydrogen was mixed with 1 mol of iodine in a sealed container and left to reach equilibrium at 700 K.

The total pressure was 5 atm.

At equilibrium, the amount of iodine remaining was 0.21 mol.

Calculate the partial pressure of each gas at equilibrium.

Use the partial pressures to calculate the value of K_p, stating its units, if any.

(5)

(b) State the effect of increasing the pressure on the equilibrium position. Justify your answer by using the equation:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \quad \Delta H = -10 \text{ kJ mol}^{-1}$$

(1)

(c) (i) Explain how increasing the temperature affects the value of ΔS_{total} of this reaction. Assume that ΔS_{system} does not change when the temperature increases.

(2)

*(ii) Use your answer to (c)(i) to explain the effect of an increase in temperature on the value of K_p and the equilibrium yield of hydrogen iodide.

(2)

Jan 2015

24 (a) Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, $CH_3COOC_2H_5$, and water.

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightleftharpoons CH_3COOCH_2CH_3(l) + H_2O(l) \quad \Delta H = -3.5 \text{ kJ mol}^{-1}$$

(i) Give the expression for the equilibrium constant, K_c, for this reaction.

(1)

(ii) By considering the effect of temperature on the entropy change of the surroundings, suggest why changing the temperature has little effect on this equilibrium.

(3)

*(iii) An experiment was carried out to determine the value of K_c for this reaction.

- 0.120 mol of ethanoic acid was added to 0.220 mol of ethanol.
- 5.00 cm^3 of 1.00 mol dm^{-3} hydrochloric acid was added as a catalyst. This contains 0.278 mol of water.
- The mixture was left to reach equilibrium.
- The mixture was titrated with 1.00 mol dm^{-3} sodium hydroxide, which reacted with **both** of the acids.
- The titre was 45.0 cm^3.

Use these data to determine the value for K_c.

(6)

Jan 2016

18 Methanol is synthesised by the following reaction.

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

A mixture of 39.5 mol of carbon monoxide and 77.5 mol of hydrogen was allowed to reach equilibrium at 500 K and 50 atm pressure. Under these conditions, the equilibrium mixture contained 38.5 mol of methanol.

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

(1)

*(b) Complete the table below.

Hence calculate the value of K_p under these conditions.
Give your answer to **three** significant figures and include the units.

(5)

	CO	H_2	CH_3OH	Total mol
mol at start	39.5	77.5	0	
mol at equilibrium			38.5	

*(c) When the reaction is carried out at 700 K and 50 atm pressure, the value of K_p is smaller.

Use this information to deduce the sign of $\Delta S_{surroundings}$ for the forward reaction.
Justify your answer.

(2)

Jan 2017

24 Nitrosyl chloride, NOCl, is a yellow gas which decomposes on heating.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$$

(a) A sample of 2.00 mol of NOCl was heated in a sealed vessel to a certain temperature, *T*. The volume of the vessel was 5.00 dm^3. When equilibrium was reached, 0.220 mol of NO had been formed.

(i) Write the expression for the equilibrium constant, K_c, for this reaction.

(1)

*(ii) Calculate the value of K_c under these conditions. Include units in your answer.

(4)

*(iii) The volume of the vessel containing the equilibrium mixture in (a) was doubled to 10 dm^3, keeping the temperature constant.

State the effect of this change in volume on the value of K_c and on the number of moles of NO at equilibrium. A calculation is not required but justify your answers.

(2)