

AQA A-LEVEL CHEMISTRY • 7405

CHEMISTRY



EXAM QUESTION PACK

3.1.10 EQUILIBRIUM CONSTANT K_p

SCORE

/139

PERCENTAGE

%

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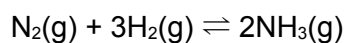
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Q1.

Nitrogen and hydrogen were mixed in a 1:3 mole ratio and left to reach equilibrium in a flask at a temperature of 550 K. The equation for the reaction between nitrogen and hydrogen is shown.



- (a) When equilibrium was reached, the total pressure in the flask was 150 kPa and the mole fraction of $\text{NH}_3(\text{g})$ in the mixture was 0.80

Calculate the partial pressure of each gas in this equilibrium mixture.

Partial pressure of nitrogen _____ kPa

Partial pressure of hydrogen _____ kPa

Partial pressure of ammonia _____ kPa

(3)

- (b) Give an expression for the equilibrium constant (K_p) for this reaction.

K_p

(1)

- (c) In a different equilibrium mixture, under different conditions, the partial pressures of the gases are shown in the table.

Gas	Partial pressure / kPa
N_2	1.20×10^2
H_2	1.50×10^2
NH_3	1.10×10^3

Calculate the value of the equilibrium constant (K_p) for this reaction and give its units.

K_p _____ Units _____

(2)

- (d) The enthalpy change for the reaction is -92 kJ mol^{-1}

State the effect, if any, of an increase in temperature on the value of K_p for this reaction.

Justify your answer.

Effect on K_p _____

Justification _____

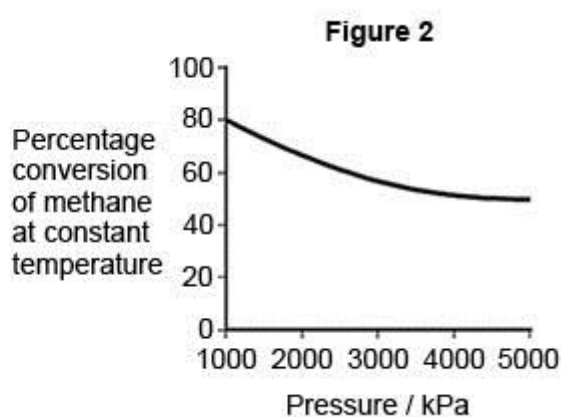
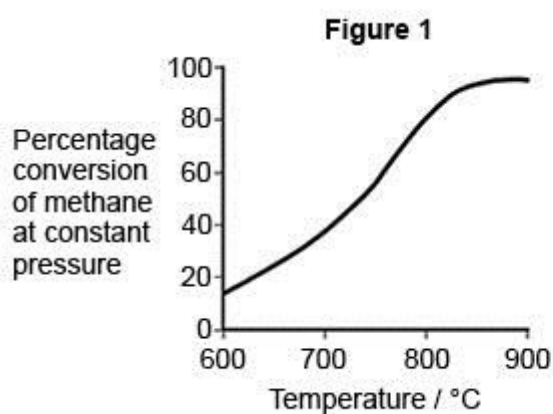
(3)

(Total 9 marks)

Q2.

There are several stages in the industrial production of methanol from methane.

- (a) The first stage involves a gaseous equilibrium between the reactants (methane and steam), and some gaseous products. **Figures 1** and **2** show the percentage conversion of methane into the gaseous products under different conditions at equilibrium.

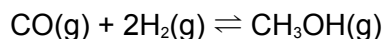


Deduce the optimum conditions for the industrial conversion of methane and steam into the gaseous products.

Explain your deductions.

(6)

- (b) The equation shows the final stage in the production of methanol.



20.1 mol of carbon monoxide and 24.2 mol of hydrogen were placed in a sealed container. An equilibrium was established at 600 K. The equilibrium mixture contained 2.16 mol of methanol.

Calculate the amount, in moles, of carbon monoxide and of hydrogen in the equilibrium mixture.

Amount of carbon monoxide = _____ mol

Amount of hydrogen = _____ mol

(2)

- (c) A different mixture of carbon monoxide and hydrogen was allowed to reach equilibrium at 600 K

At equilibrium, the mixture contained 2.76 mol of carbon monoxide, 4.51 mol of hydrogen and 0.360 mol of methanol. The total pressure was 630 kPa

Calculate a value for the equilibrium constant, K_p , for this reaction at 600 K and state its units.

Value of K_p _____ Units _____

(6)

(Total 14 marks)

Q3.

An equilibrium mixture is prepared in a container of fixed volume.



The temperature of this mixture is decreased and the mixture is allowed to reach a new equilibrium.

Which is greater for the new equilibrium than for the original equilibrium?

- A** The mole fraction of carbon monoxide ☐
- B** The partial pressure of chlorine ☐
- C** The total pressure of the mixture ☐
- D** The value of the equilibrium constant, K_p ☐

(Total 1 mark)

Q4.

Which statement about K_p is correct for this reaction in the gas phase?



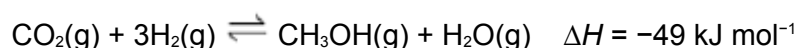
- A** The value of K_p is independent of pressure. ☐
- B** The value of K_p increases as pressure increases. ☐
- C** The value of K_p increases as temperature increases. ☐
- D** The value of K_p is independent of temperature. ☐

(Total 1 mark)

Q5.

Many chemical processes release waste products into the atmosphere. Scientists are developing new solid catalysts to convert more efficiently these emissions into useful products, such as fuels. One example is a catalyst to convert these emissions into methanol. The catalyst is thought to work by breaking a H–H bond.

An equation for this formation of methanol is given below.



Some mean bond enthalpies are shown in the following table.

Bond	C=O	C–H	C–O	O–H
Mean bond enthalpy / kJ mol^{-1}	743	412	360	463

- (a) Use the enthalpy change for the reaction and data from the table to calculate a value for the H–H bond enthalpy.

H–H bond enthalpy = _____ kJ mol⁻¹

(3)

- (b) A data book value for the H–H bond enthalpy is 436 kJ mol⁻¹.

Suggest **one** reason why this value is different from your answer to part (a).

(1)

- (c) Suggest **one** environmental advantage of manufacturing methanol fuel by this reaction.

(1)

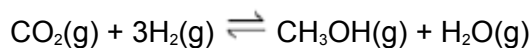
- (d) Use Le Chatelier's principle to justify why the reaction is carried out at a high pressure rather than at atmospheric pressure.

(3)

- (e) Suggest why the catalyst used in this process may become less efficient if the carbon dioxide and hydrogen contain impurities.

(1)

- (f) In a laboratory experiment to investigate the reaction shown in the equation below, 1.0 mol of carbon dioxide and 3.0 mol of hydrogen were sealed into a container. After the mixture had reached equilibrium, at a pressure of 500 kPa, the yield of methanol was 0.86 mol.



Calculate a value for K_p

Give your answer to the appropriate number of significant figures.

Give units with your answer.

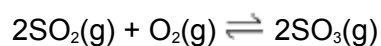
$K_p =$ _____ Units = _____

(7)

(Total 16 marks)

Q6.

Which change would alter the value of the equilibrium constant (K_p) for this reaction?

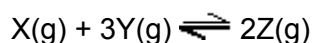


- | | | |
|----------|--|--------------------------|
| A | Increasing the total pressure of the system. | ☐ |
| B | Increasing the concentration of sulfur trioxide. | ☐ |
| C | Increasing the concentration of sulfur dioxide. | ☐ |
| D | Increasing the temperature. | ☐ |

(Total 1 mark)

Q7.

A sealed flask containing gases **X** and **Y** in the mole ratio 1:3 was maintained at 600 K until the following equilibrium was established.



The partial pressure of **Z** in the equilibrium mixture was 6.0 MPa when the total pressure was 22.0 MPa.

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

- (ii) Calculate the partial pressure of **X** and the partial pressure of **Y** in the equilibrium mixture.

Partial pressure of **X** _____

Partial pressure of **Y** _____

- (iii) Calculate the value of K_p for this reaction under these conditions and state its units.

Value of K_p _____

Units of K_p _____

(6)

- (b) When this reaction is carried out at 300 K and a high pressure of 100 MPa, rather than at 600 K and 22.0 MPa, a higher equilibrium yield of gas **Z** is obtained.

Give two reasons why an industrialist is unlikely to choose these reaction conditions.

Reason 1 _____

Reason 2 _____

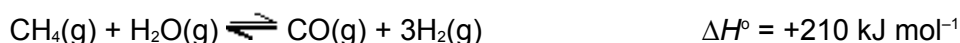
(2)

(Total 8 marks)

Q8.

The manufacture of methanol can be achieved in two stages.

- (a) In the first stage, methane and steam react according to the following equation.



Discuss, with reasons, the effects of increasing separately the temperature and the pressure on the yield of the products and on the rate of this reaction.

(6)

(8)
(Total 14 marks)

Q9.

This question is about the reaction given below.



Enthalpy data for the reacting species are given in the table below.

Substance	CO(g)	H ₂ O(g)	CO ₂ (g)	H ₂ (g)
$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	-110	-242	-394	0

Which one of the following statements is **not** correct?

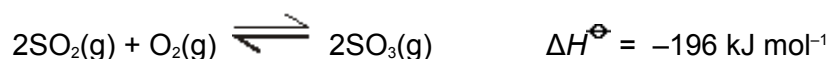
- A** The value of K_p changes when the temperature changes.
- B** The activation energy decreases when the temperature is increased.
- C** The entropy change is more positive when the water is liquid rather than gaseous.
- D** The enthalpy change is more positive when the water is liquid rather than gaseous.

(Total 1 mark)

Q10.

Sulphur dioxide and oxygen were mixed in a 2:1 mol ratio and sealed in a flask with a catalyst.

The following equilibrium was established at temperature T_1



The partial pressure of sulphur dioxide in the equilibrium mixture was 24 kPa and the total pressure in the flask was 104 kPa.

- (a) Deduce the partial pressure of oxygen and hence calculate the mole fraction of oxygen in the equilibrium mixture.

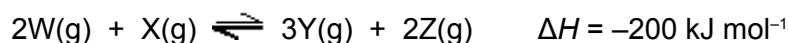
Partial pressure of oxygen _____

Mole fraction of oxygen _____

- _____ (3)
- (b) Calculate the partial pressure of sulphur trioxide in the equilibrium mixture.
- _____ (1)
- (c) Write an expression for the equilibrium constant, K_p , for this reaction. Use this expression to calculate the value of K_p at temperature T_1 and state its units.
- Expression for K_p* _____
- _____
- Calculation* _____
- _____
- _____
- Units* _____ (4)
- (d) When equilibrium was established at a different temperature, T_2 , the value of K_p was found to have increased. State which of T_1 and T_2 is the lower temperature and explain your answer.
- Lower temperature* _____
- Explanation* _____
- _____ (3)
- (e) In a further experiment, the amounts of sulphur dioxide and oxygen used, the catalyst and the temperature, T_1 , were all unchanged, but a flask of smaller volume was used.
- Deduce the effect of this change on the yield of sulphur trioxide and on the value of K_p .
- Effect on yield of SO_3* _____
- Effect on K_p* _____
- _____ (2)
- (Total 13 marks)

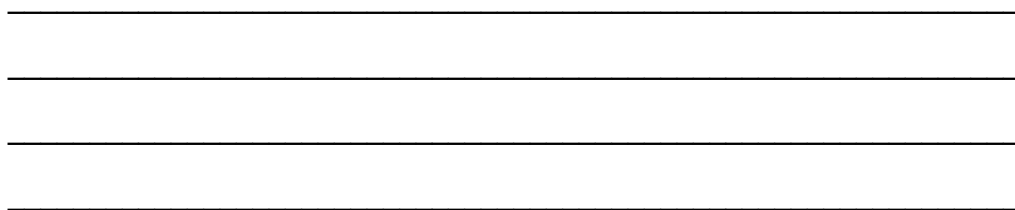
Q11.

- (a) The gaseous reactants **W** and **X** were sealed in a flask and the mixture left until the following equilibrium had been established.



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Reaction 1



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	CH ₃ COCl(l)	C ₂ H ₅ OH(l)	CH ₃ COOC ₂ H ₅ (l)	HCl(g)
S [⊖] /JK ¹ mol ¹	201	161	259	187

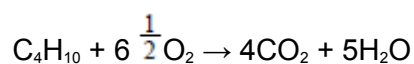
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(6)

(Total 15 marks)

Q12.

The equation for the combustion of butane in oxygen is



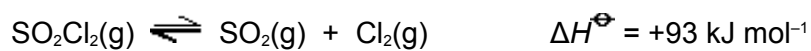
The mole fraction of butane in a mixture of butane and oxygen with the minimum amount of oxygen required for complete combustion is

- | | |
|----------|-------|
| A | 0.133 |
| B | 0.153 |
| C | 0.167 |
| C | 0.200 |

(Total 1 mark)

Q13.

At high temperatures, SO_2Cl_2 dissociates according to the following equation.



When 1.00 mol of SO_2Cl_2 dissociates, the equilibrium mixture contains 0.75 mol of Cl_2 at 673 K and a total pressure of 125 kPa.

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

(1)

- (b) Calculate the total number of moles of gas present in the equilibrium mixture.

(2)

- (c) (i) Write a general expression for the partial pressure of a gas in a mixture of gases in terms of the total pressure.

- (ii) Calculate the partial pressure of SO_2Cl_2 and the partial pressure of Cl_2 in the equilibrium mixture.

Partial pressure of SO_2Cl_2 _____

Partial pressure of Cl_2 _____

(5)

- (d) Calculate a value for the equilibrium constant, K_p , for this reaction and give its units.

(3)

- (e) State the effect, if any, of an increase in temperature on the value of K_p for this reaction.
Explain your answer.

Effect on K_p _____

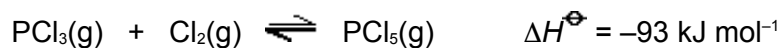
Explanation _____

(2)

- (f) State the effect, if any, of an increase in the total pressure on the value of K_p for this reaction.

Q14.

When a mixture of 0.345 mol of PCl_3 and 0.268 mol of Cl_2 was heated in a vessel of fixed volume to a constant temperature, the following reaction reached equilibrium.



At equilibrium, 0.166 mol of PCl_5 had been formed and the total pressure was 225 kPa.

- (a) (i) Calculate the number of moles of PCl_3 and of Cl_2 in the equilibrium mixture.

Moles of PCl_3 _____

Moles of Cl_2 _____

- (ii) Calculate the total number of moles of gas in the equilibrium mixture.

(3)

- (b) Calculate the mole fraction and the partial pressure of PCl_3 in the equilibrium mixture.

Mole fraction of PCl_3 _____

Partial pressure of PCl_3 _____

(3)

- (c) (i) Write an expression for the equilibrium constant, K_p , for this equilibrium.

- (ii) The partial pressures of Cl_2 and PCl_5 in the equilibrium mixture were 51.3 kPa and 83.6 kPa, respectively, and the total pressure remained at 225 kPa. Calculate the value of K_p at this temperature and state its units.

(4)

- (d) State the effect on the mole fraction of PCl_3 in the equilibrium mixture if

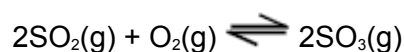
- (i) the volume of the vessel were to be increased at a constant temperature,

-
- (ii) the temperature were to be increased at constant volume.
-

(2)
(Total 12 marks)

Q15.

This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:



Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
$\text{SO}_3(\text{g})$	-396	+257
$\text{SO}_2(\text{g})$	-297	+248
$\text{O}_2(\text{g})$	0	+204

This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm³. At equilibrium, the vessel contains 0.0500 mol of $\text{SO}_2(\text{g})$, 0.0800 mol of $\text{O}_2(\text{g})$ and 0.0700 mol of $\text{SO}_3(\text{g})$.

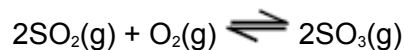
The mole fraction of SO_3 in the equilibrium mixture is

- A 0.250
B 0.350
C 0.440
D 0.700

(Total 1 mark)

Q16.

This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:



Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
$\text{SO}_3(\text{g})$	-396	+257
$\text{SO}_2(\text{g})$	-297	+248
$\text{O}_2(\text{g})$	0	+204

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This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm³. At equilibrium, the vessel contains 0.0500 mol of SO₂(g), 0.0800 mol of O₂(g) and 0.0700 mol of SO₃(g).

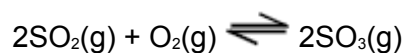
Possible units for the equilibrium constant K_p include

- A no units
- B kPa
- C Mpa⁻¹
- D kPa⁻²

(Total 1 mark)

Q17.

This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:



Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
SO ₃ (g)	-396	+257
SO ₂ (g)	-297	+248
O ₂ (g)	0	+204

This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm³. At equilibrium, the vessel contains 0.0500 mol of SO₂(g), 0.0800 mol of O₂(g) and 0.0700 mol of SO₃(g).

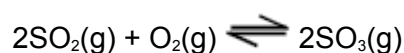
With pressures expressed in MPa units, the value of the equilibrium constant, K_p , is

- A 4.90
- B 6.48
- C 9.07
- D 16.8

(Total 1 mark)

Q18.

This question relates to the equilibrium gas-phase synthesis of sulphur trioxide:



Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
$\text{SO}_3(\text{g})$	-396	+257
$\text{SO}_2(\text{g})$	-297	+248
$\text{O}_2(\text{g})$	0	+204

This equilibrium, at a temperature of 585 K and a total pressure of 540 kPa, occurs in a vessel of volume 1.80 dm³. At equilibrium, the vessel contains 0.0500 mol of $\text{SO}_2(\text{g})$, 0.0800 mol of $\text{O}_2(\text{g})$ and 0.0700 mol of $\text{SO}_3(\text{g})$.

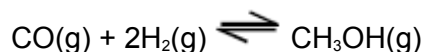
At equilibrium in the same vessel of volume 1.80 dm³ under altered conditions, the reaction mixture contains 0.0700 mol of $\text{SO}_3(\text{g})$, 0.0500 mol of $\text{SO}_2(\text{g})$ and 0.0900 mol of $\text{O}_2(\text{g})$ at a total pressure of 623 kPa. The temperature in the equilibrium vessel is

- A 307 °C
- B 596 K
- C 337 °C
- D 642 K

(Total 1 mark)

Q19.

The following information concerns the equilibrium gas-phase synthesis of methanol.



At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa. The number of moles of CO, H₂ and CH₃OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
$\text{CO}(\text{g})$	-110	198
$\text{H}_2(\text{g})$	0	131
$\text{CH}_3\text{OH}(\text{g})$	-201	240

Possible units for the equilibrium constant, K_p , for this reaction are

- A no units
- B kPa

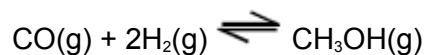
C MPa⁻¹

D kPa⁻²

(Total 1 mark)

Q20.

The following information concerns the equilibrium gas-phase synthesis of methanol.



At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa. The number of moles of CO, H₂ and CH₃OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
CO(g)	-110	198
H ₂ (g)	0	131
CH ₃ OH(g)	-201	240

The mole fraction of hydrogen in the equilibrium mixture is

A 0.242

B 0.485

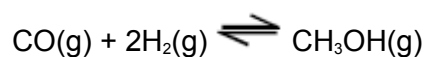
C 0.653

D 0.970

(Total 1 mark)

Q21.

The following information concerns the equilibrium gas-phase synthesis of methanol.



At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa. The number of moles of CO, H₂ and CH₃OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
CO(g)	-110	198
H ₂ (g)	0	131

CH ₃ OH(g)	-201	240

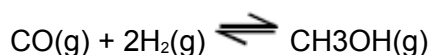
With pressures expressed in MPa units, the value of the equilibrium constant, K_p , under these conditions is

- A 1.37
- B 1.66
- C 2.82
- D 4.80

(Total 1 mark)

Q22.

The following information concerns the equilibrium gas-phase synthesis of methanol.



At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa. The number of moles of CO, H₂ and CH₃OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
CO(g)	-110	198
H ₂ (g)	0	131
CH ₃ OH(g)	-201	240

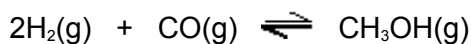
Which one of the following statements applies to this equilibrium?

- A The value of K_p increases if the temperature is raised.
- B The value of K_p increases if the pressure is raised.
- C The yield of methanol decreases if the temperature is lowered.
- D The yield of methanol decreases if the pressure is lowered.

(Total 1 mark)

Q23.

Hydrogen and carbon monoxide were mixed in a 2:1 mole ratio. The mixture was allowed to reach equilibrium according to the following equation at a fixed temperature and a total pressure of 1.75×10^4 kPa.



- (a) The equilibrium mixture contained 0.430 mol of carbon monoxide and 0.0850 mol of methanol.

- (i) Calculate the number of moles of hydrogen present in the equilibrium mixture.

- (ii) Hence calculate the mole fraction of hydrogen in the equilibrium mixture.

- (iii) Calculate the partial pressure of hydrogen in the equilibrium mixture.

(5)

- (b) In a different mixture of the three gases at equilibrium, the partial pressure of carbon monoxide was 7550 kPa, the partial pressure of hydrogen was 12300 kPa and the partial pressure of methanol was 2710 kPa.

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

- (ii) Calculate the value of the equilibrium constant, K_p , for the reaction under these conditions and state its units.

K_p _____

Units _____

(3)

- (c) Two isomeric esters **E** and **F** formed from methanol have the molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$

Isomer **E** has only 2 singlet peaks in its proton n.m.r. spectrum.

Isomer **F** is optically active.

Draw the structures of these two isomers.

Isomer **E**

Isomer **F**

(2)
(Total 10 marks)

Q24.

Summarised directions for recording responses to multiple completion questions			
A (i), (ii) and (iii) only	B (i) and (iii) only	C (ii) and (iv) only	D (iv) alone

Which of the following statements about a catalyst is / are true?

- (i) It speeds up the forward reaction and slows down the reverse action.
- (iii) It increases the proportion of molecules with higher energies.
- (iii) A homogeneous catalyst usually acts in the solid state.
- (iv) It does not alter the value of the equilibrium constant.

(Total 1 mark)

Mark schemes

Q1.

(a) $pp \text{ nitrogen} = 0.25 \times 30 = \underline{7.5} \text{ kPa}$

1

$pp \text{ hydrogen} = 0.75 \times 30 = \underline{22.5 \text{ or } 23} \text{ kPa}$

1

$pp \text{ of ammonia} = 0.8 \times 150 = \underline{120} \text{ kPa}$

1

(pp hydrogen + nitrogen = 150 - 120 = 30 kPa)

Alternative method

pp hydrogen = 0.15 × 150 = 22.5 or 23 kPa

pp nitrogen = 0.05 × 150 = 7.5 kPa

(b) $K_p = \frac{(ppNH_3)^2}{(ppN_2) \times (ppH_2)^3}$

Penalise []

1

(c) $K_p = \frac{(1.10 \times 10^3)^2}{(1.50 \times 10^2)^3 \times 1.20 \times 10^2}$

No mark for this expression

1

$= 0.0029 \text{ to } 0.003(0) \text{ or } 2.9 \times 10^{-3} \text{ to } 3(.0) \times 10^{-3}$

kPa^{-2}

If expression inverted in 02.2 allow 1 mark for kPa^2

Allow $2.9 \text{ to } 3(.0) \times 10^{-9} \text{ Pa}^{-2}$

1

(d) decrease/smaller/lower

If increase or no change, 0 marks

If blank, mark on

1

(Reaction/equilibrium) shifts/moves/goes in the endothermic direction (which is to the left)

Allow reaction is exothermic so equilibrium moves to the left side

1

to reduce the temperature OR oppose the increase in temperature

1

[9]

Q2.

(a) This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

Level 3 (5 – 6 marks)

All stages are covered and the explanation of each stage is generally correct and virtually complete. To access Level 3, statement 3a must be considered.

Answer is communicated coherently and shows a logical progression from stage 1 (including 1b) to stage 2 and stage 3

Level 2 (3 – 4 marks)

All stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies OR two stages are covered and the explanations are generally correct and virtually complete.

Answer is mainly coherent and shows progression from stage 1 to stage 2 and/or stage 3.

Level 1 (1 – 2 marks)

Two stages are covered but the explanation of each stage may be incomplete or may contain inaccuracies, OR only one stage is covered but the explanation is generally correct and virtually complete.

Answer includes isolated statements but these are presented in a logical order, with sensible reasoning.

Level 0 (0 marks)

Insufficient correct chemistry to gain a mark.

Indicative chemistry content**Stage 1 – Deductions from graph**

1a Yield increases as temperature increases (or converse)

1b After a certain temperature yield no longer increases

1c Yield decreases as pressure increases (or converse)

Stage 2 – Optimum temperature and explanation

2a High temperature results in high energy costs/expensive

2b (After a certain temperature) yield no longer increases therefore there is no gain in using a higher temperature

2c Optimum temperature is between 780-880oC

Stage 3 – Optimum pressure and explanation

3a Low pressure may be too slow

3b So compromise pressure required

3c Optimum pressure is 1000-2000kPa or moderate pressure used

6

(b) Moles of carbon monoxide 17.9

Allow 17.94

1

Moles of hydrogen 19.9

Allow 19.88

1

(c)
$$K_p = \frac{pp(\text{CH}_3\text{OH})}{pp(\text{CO}) \times pp(\text{H}_2)^2}$$

ignore brackets

If K_p expression incorrect can only score M2 & M3 & M4

1

Total moles of gas = (2.76 + 4.51 + 0.36) = 7.63

If CE in M2 allow ecf for M3, M4 and M6

If no total moles calculated then can only score M1 and M6

1

$$pp(\text{CO}) = \frac{2.76}{7.63} \times 630 \text{ (kPa)} \quad (= 228 \text{ (kPa)})$$

$$pp(\text{H}_2) = \frac{4.51}{7.63} \times 630 \text{ (kPa)} \quad (= 372 \text{ (kPa)})$$

$$pp(\text{CH}_3\text{OH}) = \frac{0.36}{7.63} \times 630 \text{ (kPa)} \quad (= 29.7 \text{ (kPa)})$$

All 3 pp of CO, H₂ and CH₃OH = 2 marks

2 pp correct = 1 mark

2

$$K_p = \frac{29.7}{228 \times (372)^2} = 9.4(1) \times 10^{-7} \quad \text{or } 9.4(1) \times 10^{-13} \text{ if pp in Pa}$$

can also score M1 from this expression

Allow 9.39 to 9.50 × 10⁻⁷ (kPa⁻²)

1

kPa⁻² or **Pa⁻²** (if converted to 630 000)

*If no marks awarded allow M6 only for **kPa⁻²** or **Pa⁻²***

1

[14]

Q3.

D

[1]

Q4.

A

[1]

Q5.

(a) Bonds broken = 2(C=O) + 3(H-H) = 2 × 743 + 3 × H-H

Bonds formed = 3(C-H) + (C-O) + 3(O-H) = 3 × 412 + 360 + 3 × 463

Both required

1

$$-49 = [2 \times 743 + 3 \times (\text{H-H})] - [3 \times 412 + 360 + 3 \times 463]$$

$$3(\text{H-H}) = -49 - 2 \times 743 + [3 \times 412 + 360 + 3 \times 463] = 1450$$

Both required

1

$$\text{H-H} = 483 \text{ (kJ mol}^{-1}\text{)}$$

Allow 483.3(3)

1

- (b) Mean bond enthalpies are not the same as the actual bond enthalpies in CO₂ (and / or methanol and / or water)

1

- (c) The carbon dioxide (produced on burning methanol) is used up in this reaction

1

- (d) 4 mol of gas form 2 mol

1

At high pressure the position of equilibrium moves to the right to lower the pressure / oppose the high pressure

1

This increases the yield of methanol

1

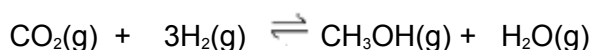
- (e) Impurities (or sulfur compounds) block the active sites

Allow catalyst poisoned

1

- (f) Stage 1: moles of components in the equilibrium mixture

Extended response question



Initial moles	1.0	3.0	0	0
Eqm moles	(1-0.86) = 0.14	(3-3×0.86) = 0.42	0.86	0.86

1

Stage 2: Partial pressure calculations

Total moles of gas = 2.28

Partial pressures = mol fraction × p_{total}

1

$$p_{\text{CO}_2} = \text{mol fraction} \times p_{\text{total}} = 0.14 \times 500 / 2.28 = 30.7 \text{ kPa}$$

$$p_{\text{H}_2} = \text{mol fraction} \times p_{\text{total}} = 0.42 \times 500 / 2.28 = 92.1 \text{ kPa}$$

M3 is for partial pressures of both reactants

Alternative M3 =

$$pp_{\text{CO}_2} = 0.0614 \times 500$$

$$pp_{\text{H}_2} = 0.1842 \times 500$$

1

$$p_{\text{CH}_3\text{OH}} = \text{mol fraction} \times p_{\text{total}} = 0.86 \times 500 / 2.28 = 188.6 \text{ kPa}$$

$$p_{\text{H}_2\text{O}} = \text{mol fraction} \times p_{\text{total}} = 0.86 \times 500 / 2.28 = 188.6 \text{ kPa}$$

M4 is for partial pressures of both products

Alternative M4 =

$$pp_{CH_3OH} = 0.3772 \times 500$$

$$pp_{H_2O} = 0.3772 \times 500$$

1

Stage 3: Equilibrium constant calculation

$$K_p = p_{CH_3OH} \times p_{H_2O} / p_{CO_2} \times (p_{H_2})^3$$

1

$$\text{Hence } K_p = 188.6 \times 188.6 / 30.7 \times (92.1)^3 = 1.483 \times 10^{-3} = 1.5 \times 10^{-3}$$

Answer must be to 2 significant figures

1

$$\text{Units} = \text{kPa}^{-2}$$

1

[16]

Q6.

D

[1]

Q7.

(a) (i) $(K_p) = (p_z)^2 / (p_x)(p_y)^3$
(penalise use of square brackets, allow ())

1

(ii) **X** $(22-6)/4 = 4$ (MPa)
(mark is for value 4 only, ignore units)

1

Y obtained by multiplying value for **X** by 3
(allow conseq on wrong value for **X**)

1

Y $4.0 \times 3 = 12$ (MPa)
(mark is for value 12 only)

1

(iii) $K_p = 6.0^2 / 4.0 \times 12.0^3 = 5.21 \times 10^{-3}$

(allow conseq on wrong values for **X** and **Y** e.g. $6^2/3 \times 9^3 = 0.165$)

(if K_p wrong in (a)(i) CE)

1

$$\text{MPa}^{-2}$$

(allow any unit of P^{-2} provided ties to P used for K_p value)

1

(b) high pressure expensive (due to energy or plant costs)

1

(Rate is) slow (at lower temperatures)

1

[8]

Q8.

(a) *(must state correct effect on yield or rate to score the reason mark)*

T effect: higher temp: yield greater or shifts equilibrium to right;

1

effect: higher temp: rate increased;

1

reason: endothermic

OR

more particles have $E > E_a$

1

OR

more successful/productive collisions;

1

P effect: higher pressure: yield less or shifts equilibrium to left;

1

effect: higher pressure: rate increased;

reason: increase in gas moles L to R

OR

greater collision frequency;

(Q of L mark)

1

(b) M1 equilibrium moles of CO = $62.8 - 26.2 = 36.6$

1

M2 equilibrium moles of $H_2 = 146 - 2(26.2) = 93.6$

1

M3 total no moles = $36.6 + 93.3 + 26.2 = 156.4$

1

M4 partial pressure = mole fraction x total pressure

1

M5
$$K_p = \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

1

$$M6 = \frac{\left(\frac{26.2}{156.4} \times 9.50\right)}{\left(\frac{36.6}{156.4} \times 9.50\right) \times \left(\frac{93.6}{156.4} \times 9.50\right)^2}$$

$$\frac{(0.168 \times 9.5)}{(0.234 \times 9.50) \times (0.598 \times 9.5)^2}$$

$$\frac{(1.59)}{(2.22) \times (5.69)^2}$$

1

M7 0.022(1) $2.2(1) \times 10^{-8}$ $2.2(1) \times 10^{-14}$

1

M8 MPa⁻² kPa⁻² Pa⁻²

1

*If no subtraction lose M1, M2 and M3)
 (If ×2 missed in M2, lose both M2 and M3)
 (If M1 gained but moles of H₂ = 73.2 (i.e. double CO), M2 and M3 lost)
 (If M1 gained but mol H₂ = 2(146 – 26.2), M2 and M3 lost)
 (If M1 and M2 correct but M3 lost for CE, penalise M6 also)
 (M4 can be gained from the numbers in the expression for M6 even if these numbers are wrong)
 (If K_p contains [] lose M5 but then mark on)
 (If chemically wrong expression for K_p, lose M5, M6 and M7 (allow M8 conseq on their K_p))
 (If divided by 9.5, or not used 9.5 at all, lose M6 and M7 (and M4))
 (If tried to convert to kPa and is factor(s) of 10 out, penalise in M6 and allow M8 for kPa⁻²)*

[14]

Q9.

B

[1]

Q10.

(a) 12 (kPa)

1

pp = mole fraction × total pressure **or** mole fraction = 12/104

1

= 0.115

(allow 0.12)

1

(b) 68 (kPa)

		1
(c)	$K_p = \frac{(p\text{SO}_3)^2}{(p\text{SO}_2)^2 \times (p\text{O}_2)}$ <i>(If K_p wrong, allow consequential units only)</i> <i>(penalise square brackets in expression but then mark on)</i> $= \frac{68^2}{24^2 \times 12}$ $= 0.669$ <i>(Allow 0.67)</i> <i>(Allow full marks in calculation consequential on their values in (a) and (b))</i> kPa⁻¹	1
(d)	T_2 <i>(Must be correct to score any marks in this section)</i> <u>Exothermic</u> Reduce T to shift equilibrium to the right or forward reaction favoured by low T or K_p increases for low T or low T favours exothermic reaction	1
(e)	Increase None	1
		1
		[13]

Q11.

(a)	M1 $K_p = (pY)^3 \cdot (pZ)^2 / (pW)^2 \cdot (pX)$ NB [] wrong M2 temperature M3 increase M4 particles have more energy or greater velocity/speed M5 more collisions with $E > E_a$ or more successful collisions	1
		1
		1
		1
		1

1

M6 Reaction exothermic or converse

1

M7 Equilibrium moves in the left

1

Marks for other answers

Increase in pressure or concentration allow M1, M5, M6 Max 3

Addition of a catalyst; allow M1, M5, M6 Max 3

Decrease in temperature; allow M1, M2, M6 Max 3

Two or more changes made; allow M1, M6 Max 2

- (b) (i) Advantage; reaction goes to completion, not reversible or faster

1

Disadvantage; reaction vigorous/dangerous
(exothermic must be qualified)

or HCl(g) evolved/toxic
or CH₃COCl expensive

NB Allow converse answers

Do not allow reactions with other reagents e.g. water
or ease of separation

1

- (ii) $\Delta S = \Sigma S \text{ products} - \Sigma S \text{ reactants}$

1

$$\Delta S = (259 + 187) - (201 + 161)$$

1

$$\Delta S = 84 \text{ (JK}^{-1} \text{ mol}^{-1}) \text{ (Ignore units)}$$

Allow – 84 to score (1) mark

1

$$\Delta G = \Delta H - T\Delta S$$

1

$$= -21.6 - 298 \times 84/1000$$

$$= -46.6 \text{ kJ mol}^{-1} \text{ or } -46\,600 \text{ J mol}^{-1}$$

1

Allow (2) for – 46.6 without units

(Mark ΔG consequentially to incorrect ΔS)(e.g. $\Delta S = -84$ gives $\Delta G = +3.4 \text{ kJ mol}^{-1}$)

1

[15]

Q12.

A

[1]

Q13.

- (a) $K_p = \frac{P_{\text{SO}_2} \times P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}} \quad (1)$ 1
- (b) $0.25 + 0.75 + 0.75 = 1.75 \quad (1) \quad (1)$ 2
- (c) (i) $p = \text{Total pressure} \times \text{mol fraction} \quad (1)$
- (ii) *Partial of SO₂Cl₂*: $125 \times \frac{0.25}{1.75} = 17.9 \text{ kPa} \quad (1)$
- Partial pressure of Cl₂*: $125 \times \frac{0.75}{1.75} = 53.6 \text{ kPa} \quad (1) \quad (1)$ 5
- (d) $K_p = \frac{53.6 \times 53.6}{17.9} \quad (1) = 161 \quad (1) \text{ kPa} \quad (1)$ 3
- (e) *Effect on K_p*: increase **(1)**
Explanation: increase T sends equilibrium in endothermic direction **(1)** 2
- (f) no effect **(1)** 1

Notes

- (a) If K_p has [] lose mark in (a) but allow full marks in (d)
 If K_p wrong/upside down etc, allow max 2 in (d) for substitution of numbers **(1)** and consequential units **(1)**
- (b) Mark for moles of SO₂Cl₂ can be scored in part (c) (ii) if not gained in (b)
 1.75 get **(2)**
 If moles of SO₂Cl₂ = 1, this is a Chemical Error, hence a 2 mark penalty
- If total moles given in (b) = 1.75, this scores [2] in (b); but if the no moles of SO₂Cl₂ = 1 in (c)(ii), lose both marks in (c)(ii) for pp of SO₂Cl₂ = (1/1.75) × 125, i.e. the 2 mark penalty is in (c)(ii).
 - If total moles given in (b) = 2.5, score zero in (b), but can gain full marks in (c)(ii) consequentially, i.e. the 2 mark penalty is in (b).
 - If moles of SO₂Cl₂ = 1 and total in (b) does not equal 2.5, still lose both in (b) but can get all 4 conseq in (c)(ii) for 1/x etc and 0.75/x etc
- (c) (i) Allow "Total pressure = sum of partial pressures" for **(1)** or $p_A = x_A \times p_{\text{tot}}$
- (ii) First mark is for mole fraction.
 If either number in either mole fraction is not consequential on (b), then lose both marks for that partial p.

- (d) If p_{Cl_2} is not equal to p_{SO_2} or any number used in K_p is not consequent on (c)(ii), allow units only

SIG FIGS; must be 3 sig figs in (b) but then allow 2 sig figs in (c) and (d); (ignore extra figs) but penalise incorrect rounding

- (e) If effect wrong, no marks for explanation.
If effect missing, e.g. answer states "equilibrium shifts to right", mark on.
In the explanation, the word "endothermic" (or its equivalent) is essential.

[14]

Q14.

- (a) (i) Moles of PCl_3 : $0.345 - 0.166 = 0.179$ (1)

Moles of Cl_2 : $0.268 - 0.166 = 0.102$ (1)

3 sig figs

- (ii) 0.447 (1)

allow 2 sig figs
consequent on (i)

3

- (b) Mole fraction of PCl_3 : $0.179/0.447$ (1) = 0.4(00)

Partial pressure of PCl_3 : $pp = \text{mol f}^n \times \text{total P}$ (1)
= $0.400 \times 225 = 90$ (1) kPa (1)

3

- (c) (i) $K_p = \frac{P_{\text{PCl}_3}}{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}$ (1)
ignore brackets except []
must show P

- (ii) $K_p = \frac{83.6}{90.1 \times 51.3}$ (1) = $1.8(1) \times 10^{-2}$ (1) kPa^{-1} (1) (or $1.81 \times 10^{-5} \text{ Pa}^{-1}$)
If 83.6 and 51.3 wrong way round, AE – 1,
answer = 6.81×10^{-3}
If $K_p \times$ in (i) allow max 2 for substitution of numbers and
consequent units

4

- (d) (i) increased (1)

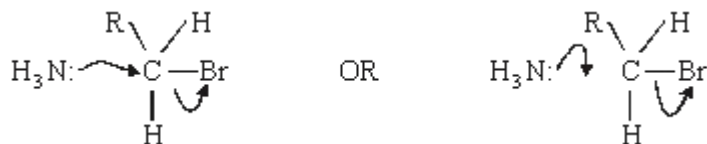
- (ii) increased (1)

2

[12]

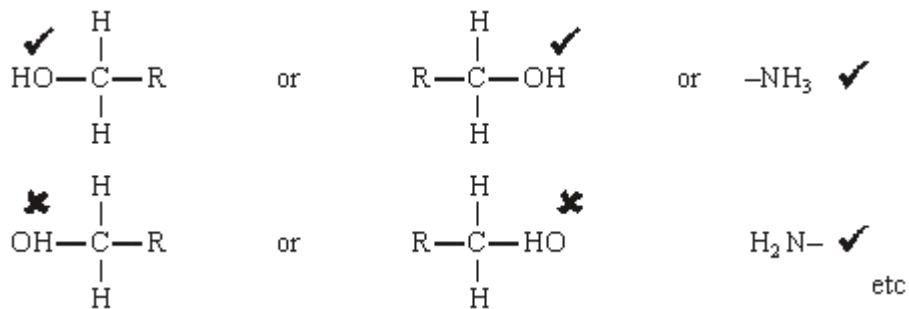
Organic points

- (1) Curly arrows: must show movement of a pair of electrons,
i.e. from bond to atom or from lp to atom / space
e.g.



(2) Structures

penalise sticks (i.e. $\begin{array}{c} | \\ -\text{C}- \\ | \end{array}$) once per paper



Penalise once per paper

allow
 CH_3- or $-\text{CH}_3$ or $\begin{array}{c} \text{CH}_3 \\ | \end{array}$ or CH_3
 or $\text{H}_3\text{C}-$

Q15.

B

[1]

Q16.

C

[1]

Q17.

C

[1]

Q18.

D

[1]

Q19.

D

[1]

Q20.

B

[1]

Q21.

B

[1]

Q22.

D

[1]

Q23.

(a) (i) 0.86 (1)

(ii) total moles = 0.86 + 0.43 + 0.085 = 1.375 (1)

$$\therefore \text{mole fraction of H}_2 = \frac{0.86}{1.375} = 0.625 \text{ (1)}$$

(0.62 - 0.63)

Conseq on (i)

(iii) pp = mole fractⁿ × total P (1)

$$= 0.625 \times 1.75 \times 10^4$$

$$= 1.09 \times 10^4 \text{ (kPa) (1)}$$

or 1.1(0)

Ignore units

Conseq on (ii)

5

(b) (i) $K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 \times P_{\text{CO}}} \text{ (1)}$
Penalise []

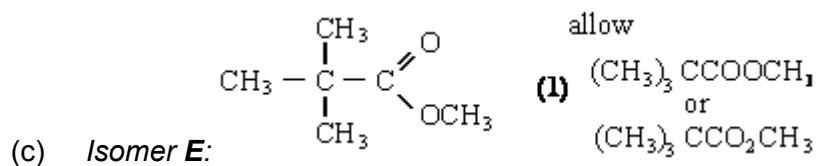
(ii) $K_p = \frac{2710}{(12300)^2 \times (7550)} = 2.37 \text{ (2.4)} \times 10^{-9} \text{ (1)}$
OR 2.37×10^{-15}

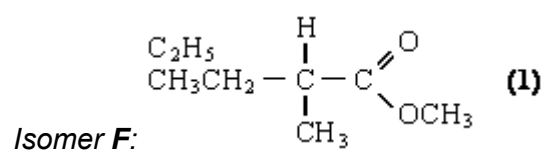
Units: kPa⁻² (1)

or Pa⁻²

not conseq to wrong K_p expression

3





2

[10]

Q24.

D

[1]

Examiner reports

Q1.

- (a) Most students calculated the partial pressure of ammonia correctly but could not calculate the partial pressures of the other two gases; the idea that the total pressure is the sum of the partial pressures was missed by many students.
- (b) Students answered this part well and most (70.8%) gave the correct expression; common errors included using square brackets, that denote concentration, or inverting the expression.
- (c) Most students were able to calculate the equilibrium constant, but often the units were given as $\text{mol}^2 \text{dm}^{-6}$.
- (d) Most students could state that the value of K_p would decrease because the reaction was exothermic but failed to link this to Le Chatelier's principle and did not state that the equilibrium shifts/moves to oppose the increase in temperature.

Q2.

- (a) Students answered this question quite well, with a good awareness of the range of temperatures and pressures needed. Most students failed to describe the information given in the graph; only the best students noted that the yield plateaued over about 850°C . The relationship between pressure and rate was often missed and this also limited students' marks. Many students discussed conclusions that could be drawn from using *Le Chatelier's Principle*; this was not what the question was asking.
- (b) Only a few students did not understand what was being asked for; most errors were either arithmetic errors or rounding errors.
- (c) Many completely correct answers were seen (48.9% of students). Some students, however, could not calculate the total number of moles or could not calculate the partial pressures of the gases. Most students could write the expression for K_p but some forgot to square the partial pressure of hydrogen. Units were sometimes incorrectly given in moles.

Q7.

Good candidates were able to score high marks for this question. In part (a)(i) some weaker candidates gave an expression for K_c rather than for K_p . In part (a)(ii) a very common error was to give the partial pressure of X as 3.0 MPa, half of Z. The partial pressure of Y was then given as 9 MPa. Such answers were awarded only one out of three marks for recognising that the pressure of Y should be three times that of X. Consequential marking was adopted for part (a)(iii) and answers usually gained both marks though it was surprising to find that a candidate sometimes only squared the partial pressure of Y even though the same candidate had shown the pressure of Y cubed in part (a)(i). In part (b) the extra cost of using a high pressure was more often given than the disadvantage of a lower reaction rate.

Q8.

Part (a) was answered well as expected as the topic overlaps with qualitative equilibria in CHM2. Some candidates lost marks by discussing only the effect of increased temperature on the yield and not on the rate also. Several also suggested that the rate

was unaffected or decreased by an increase of pressure. Part (b) was answered impressively by the better candidates, who were able to set out the answer clearly. Most were able to score marks for the expression for K_p or the definition of partial pressure (stated or inferred from a calculation). Too many, however, failed to realise that the amounts of the reagents at equilibrium were less than the initial amounts given. Even those who realised that the equilibrium amount of carbon monoxide was $62.8 - 26.2$ mol did not always realise that, because of the 1:2 ratio in the equation, the equilibrium amount of hydrogen was $62.8 - (2 \times 26.2)$ mol. However if this was their only error, six marks were still available. The pressure was given in MPa and the answer for K_p was expected with units MPa^{-2} . Many attempted unnecessarily to convert the pressure into kPa or even into Pa and got into difficulties with the powers often.

Q10.

This question was answered well by most candidates, particularly part (a). The 2:1 ratio or moles of sulphur dioxide to moles of oxygen was sometimes reversed, but marks were allowed in this part and in part (b) for correct use of their incorrect number of moles of oxygen. Most were able to write the expression for K_p correctly in part (c), although some were penalised for the use of square brackets. Full marks were available for correct substitution of wrong partial pressure values from parts (a) and (b). No marks were allowed for the calculation if the expression for K_p was wrong, but a mark was allowed for units correctly consequential on their expression. In part (d), better candidates were able both to predict and explain that T_2 was the lower temperature using the information given that the reaction was exothermic.

In part (e) most correctly stated that the yield of SO_3 would increase, but only the better candidates remembered that K_p is independent of pressure changes.

Q11.

Many candidates gave a correct expression for the equilibrium constant, K_p , for the reaction given in part (a). Some, who gave correct indices, lost a mark as they included square brackets, which are specific used to indicate concentration, in their expression. Identifying the one change which would increase the rate of reaction and decrease the value of K_p proved challenging but part marks were awarded for answers which addressed either of the two required changes. Candidates who gave more than one change of condition were able to score one mark for a correct K_p expression. There were many vague answers to part (b)(i), some of which assumed there were other reactants present with the most common example being water in Reaction 2. By contrast, (b)(ii) was very well answered with many candidates scoring full marks. Most candidates now remember to use either kJ mol^{-1} or J mol^{-1} throughout these calculations but a small number still failed to do this. Consequential marks were awarded in each part of the calculation.

Q13.

This question was well answered by many candidates and full marks were common for the most able. In part (a) a few candidates were penalised for using square brackets, e.g. $[\text{SO}_2]$ meaning concentration of SO_2 instead of using p for partial pressure, and a very few wrote the expression for K_p upside down. Part (b) caused the most problems. Many candidates forgot that, in order to produce 0.75 mol of Cl_2 (and 0.75 mol of SO_2), 0.75 mol of SO_2Cl_2 would be used up leaving only 0.25 mol in the equilibrium mixture. Both of the marks in part (b) were lost for this error, but full marks could be gained subsequently in parts (c)(ii) and (d) for correct working in the calculations. In part (e) most were able to deduce and explain that an increase in temperature would cause K_p to increase. However there were many who thought, incorrectly, that pressure had a similar effect.

Q14.

The first three parts of this question were answered well even by some of the weaker candidates. Credit was given throughout for correct working consequential to errors in a previous part. Many candidates gained full marks in parts (a) and (b). In part (c)(i), most answers were correct except where square brackets were used. These are essential in K_c expressions but should not be used in expressions for K_p . Wrong substitution of the partial pressures values were sadly common but the correct units kPa^{-1} were usually given. After well-answered numerical sections, it was less common for the answers to both parts of (d) to be correct. Part (d)(i), which involved an increase in the volume of the vessel thereby causing a reduction in the total pressure, discriminated particularly well.

Q23.

The equilibrium parts of this question were generally answered well. In part (a)(i), the correct value of 0.86 was the most common answer but this was the least well-answered section of part (a). Full marks were awarded in parts (ii) and (iii) if the number of moles of hydrogen given in part (i) was used correctly. Even if the numbers were not used correctly, a mark was given in part (iii) for the correct statement that partial pressure equals mole fraction multiplied by the total pressure. In part (b) common errors were to include square brackets in the expression for K_p or to forget that the partial pressure of hydrogen should be squared. The units of K_p expected were kPa^{-2} but Pa^{-2} were accepted as long as the value given for K_p was 2.37×10^{-15} . Part (c) was poorly answered. Many structures were not esters at all and of those which were, few were methyl esters of C_5 acids. F was answered better than E but only the better candidates scored any marks here.