Q10.

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.

Figure 1

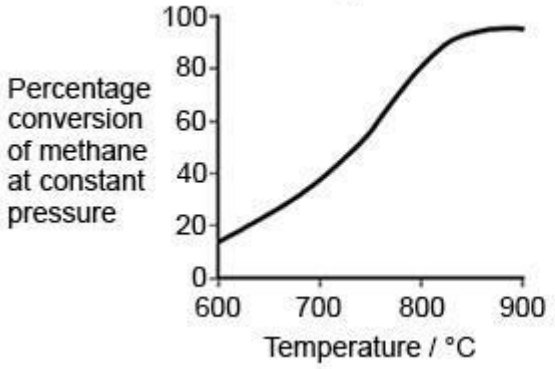
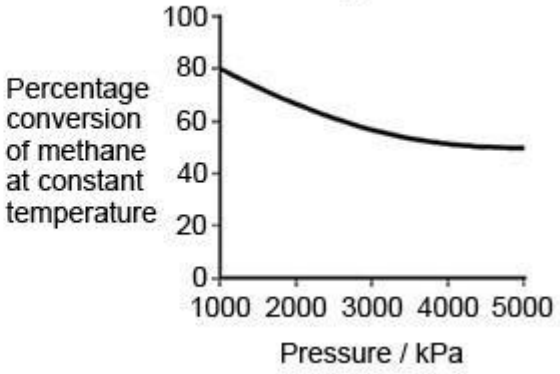


Figure 2



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.

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

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)

Q11.

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

$$W + X + Y_2 \rightleftharpoons WXY + Y \qquad \Delta H = -46 \text{ kJ mol}^{-1}$$

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)

Q12.

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.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \qquad \Delta H = -49 \text{ kJ mol}^{-1}$$

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.

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

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)

Q13.

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

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

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)

Q14.

An experiment was carried out to determine the equilibrium constant, K_c, for the following reaction.

$CH_3CH_2COOH + CH_3CH_2CH_2OH \rightleftharpoons CH_3CH_2COOCH_2CH_2CH_3 + H_2O$

A student added measured volumes of propan-1-ol and propanoic acid to a conical flask. A measured volume of concentrated hydrochloric acid was added to the flask, which was then sealed.

After 1 week, the contents of the flask were poured into water and the solution was made up to a known volume.
This solution was titrated with standard sodium hydroxide solution.

(a) Explain how the student could determine the amount, in moles, of propan-1-ol added to the flask.

_____

_____

_____

_____

(2)

(b) The titration described above gives the total amount of acid in the equilibrium mixture. Explain how, by carrying out a further experiment, the student could determine the amount of propanoic acid in the equilibrium mixture.

_____

_____

_____

_____

(2)

(c) In a repeat experiment, the student failed to seal the flask that contained the equilibrium mixture.

Explain why this error would lead to the student obtaining an incorrect value for the equilibrium constant K_c

_____

_____

_____

_____

(2)

(Total 6 marks)

Q15.

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.

$$X(g) + 3Y(g) \rightleftharpoons 2Z(g)$$

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)

Q16.

The manufacture of methanol can be achieved in two stages.

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

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

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)

(b) In the second stage, carbon monoxide and hydrogen react according to the following equation.

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

A 62.8 mol sample of carbon monoxide was added to 146 mol of hydrogen. When equilibrium was reached at a given temperature, the mixture contained 26.2 mol of methanol at a total pressure of 9.50 MPa.

Write an expression for the equilibrium constant, K_p, for this reaction. Calculate a value for K_p at this temperature and give its units.

(8)

(Total 14 marks)

Q17.

This question is about the reaction given below.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

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

Substance	CO(g)	$H_2O(g)$	$CO_2(g)$	$H_2(g)$
$\Delta H_f^{\ominus}$ / 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)

Q18.

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

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H^{\ominus} = -196 \text{ kJ mol}^{-1}$$

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)

Mark Scheme

Q10.

(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) $K_p = \dfrac{pp(CH_3OH)}{pp(CO) \times pp(H_2)2}$

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

$pp(CO) = \dfrac{2.76}{7.63} \times 630$ (kPa) (= 228 (kPa))

$pp(H_2) = \dfrac{4.51}{7.63} \times 630$ (kPa) (= 372 (kPa))

$pp(CH_3OH) = \dfrac{0.36}{7.63} \times 630$ (kPa) (= 29.7 (kPa))

All 3 pp of CO, H_2 and CH_3OH = 2 marks

2 pp correct = 1 mark

2

$Kp = \dfrac{29.7}{228 \times (372)2} = 9.4(1) \times 10^{-7}$ or $9.4(1) \times 10^{-13}$ 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]

Q11.

A

[1]

Q12.

(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 × 743 + 3 × (H–H)] – [3 × 412 + 360 + 3 × 463]

3(H–H) = –49 – 2 × 743 + [3 × 412 + 360 + 3 × 463] = 1450

Both required

1

H–H = 483 (kJ mol^{-1})

Allow 483.3(3)

1

(b) Mean bond enthalpies are not the same as the actual bond enthalpies in CO_2 (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

$$CO_2(g) + 3H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g)$$

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_{CO2} = mol fraction × p_{total} = 0.14 × 500 / 2.28 = 30.7 kPa

p_{H2} = mol fraction × p_{total} = 0.42 × 500 / 2.28 = 92.1 kPa

M3 is for partial pressures of both reactants

Alternative M3 =

pp_{CO2} = 0.0614 × 500

pp_{H2} = 0.1842 × 500

1

p_{CH3OH} = mol fraction × p_{total} = 0.86 × 500 / 2.28 = 188.6 kPa

p_{H2O} = mol fraction × p_{total} = 0.86 × 500 / 2.28 = 188.6 kPa

M4 is for partial pressures of both products

Alternative M4 =

pp_{CH3OH} = 0.3772 × 500
pp_{H2O} = 0.3772 × 500

1

Stage 3: Equilibrium constant calculation
$K_p = p_{CH3OH} \times p_{H2O} / p_{CO2} \times (p_{H2})^3$

1

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

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

1

[16]

Q13.

D

[1]

Q14.

(a) Multiply volume of propan−1−ol by density

Allow measure the mass of the volume added

Any reference to concentration of propan−1−ol CE = 0

1

Divide the mass by the M_r of propan−1−ol

1

(b) Titrate a measured volume of the concentrated HCl added initially to determine moles of HCl used in the experiment

Allow addition of $AgNO_3$ to form AgCl precipitate. Use mass of precipitate to calculate initial moles of HCl added.

1

Subtract this number of moles of HCl from the total moles of acid at equilibrium

1

(c) M1 ester will evaporate / escape

Allow reactants / products will evaporate

1

M2 incorrect values used (to determine K_c)

Allow the system will no longer be at equilibrium

Do not allow references to equilibrium position shifting alone

1

[6]

Q15.

(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 × 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

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]

Q16.

(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 $$K_p = \frac{PCH_3OH}{PCO \times P^2H_2}$$ **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) $2.2(l)\times10^{-8}$ $2.2(l)\times10^{-14}$ **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 H_2 = 73.2 (i.e. double CO), M2 and M3 lost)
(If M1 gained but mol H_2 = 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]

Q17.

B

[1]

Q18.

(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) $K_p = \frac{(pSO_3)^2}{(pSO_2)^2 \times (pO_2)}$

(If K_p wrong, allow consequential units only)
(penalise square brackets in expression but then mark on)

1

$= \frac{68^2}{24^2 \times 12}$

1

= 0.669

(Allow 0.67)
(Allow full marks in calculation consequential on their values in (a) and (b))

1

kPa^{-1}

1

(d) T_2

(Must be correct to score any marks in this section)

1

Exothermic

1

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

1

None

1

[13]