Q19.

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

$2W(g) + X(g) \rightleftharpoons 3Y(g) + 2Z(g)$ $\quad \Delta H = -200 \text{ kJ mol}^{-1}$

Write an expression for the equilibrium constant, K_p, for this reaction.
State one change in the conditions which would both increase the rate of reaction and decrease the value of K_p. Explain your answers.

(7)

(b) Ethyl ethanoate can be prepared by the reactions shown below.

Reaction 1

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ $\Delta H^{\ominus} = -2.0$ kJ mol^{-1}

Reaction 2

$CH_3COCl(l) + C_2H_5OH(l) \rightarrow CH_3COOC_2H_5(l) + HCl(g)$ $\Delta H^{\ominus} = -21.6$ kJ mol^{-1}

(i) Give one advantage and one disadvantage of preparing ethyl ethanoate by **Reaction 1** rather than by **Reaction 2**.

(2)

(ii) Use the information given above and the data below to calculate values for the standard entropy change, $\Delta S^{\ominus}$, and the standard free-energy change, $\Delta G^{\ominus}$, for **Reaction 2** at 298 K.

	$CH_3COCl(l)$	$C_2H_5OH(l)$	$CH_3COOC_2H_5(l)$	$HCl(g)$
$S^{\ominus}$/JK^{1}mol^1	201	161	259	187

(6)

(Total 15 marks)

Q20.

The equation for the combustion of butane in oxygen is

$$C_4H_{10} + 6\tfrac{1}{2}O_2 \rightarrow 4CO_2 + 5H_2O$$

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

D 0.200

(Total 1 mark)

Q21.

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

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g) \qquad \Delta H^{\ominus} = +93 \text{ kJ mol}^{-1}$$

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.

_____

(1)

(Total 14 marks)

Q22.

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.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \qquad \Delta H^{\ominus} = -93 \text{ kJ mol}^{-1}$$

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)

Q23.

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

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

Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} 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 dm^3. At equilibrium, the vessel contains 0.0500 mol of $SO_2(g)$, 0.0800 mol of $O_2(g)$ and 0.0700 mol of $SO_3(g)$.

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)

Q24.

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

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

Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} 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 dm^3. At equilibrium, the vessel contains 0.0500 mol of $SO_2(g)$, 0.0800 mol of $O_2(g)$ and 0.0700 mol of $SO_3(g)$.

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)

Q25.

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

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

Thermodynamic data for the components of this equilibrium are:

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} 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 dm^3. At equilibrium, the vessel contains 0.0500 mol of $SO_2(g)$, 0.0800 mol of $O_2(g)$ and 0.0700 mol of $SO_3(g)$.

Possible units for the equilibrium constant K_p include

A no units

B kPa

C Mpa^{-1}

D kPa^{-2}

(Total 1 mark)

Q26.

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

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

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.
The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	−110	198
H_2(g)	0	131
CH_3OH(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)

Q27.

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

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

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.
The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	−110	198
H_2(g)	0	131
CH_3OH(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)

Q28.

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

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

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.
The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	−110	198
H_2(g)	0	131
CH_3OH(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)

Q29.

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

$CO(g) + 2H_2(g) \rightleftharpoons CH3OH(g)$

At equilibrium, when the temperature is 68 °C, the total pressure is 1.70 MPa.
The number of moles of CO, H_2 and CH_3OH present are 0.160, 0.320 and 0.180, respectively.

Thermodynamic data are given below.

Substance	$\Delta H_f^{\ominus}$ / kJ mol^{-1}	$S^{\ominus}$ / J K^{-1} mol^{-1}
CO(g)	−110	198
H_2(g)	0	131
CH_3OH(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)

Q30.

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.

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

(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 $C_6H_{12}O_2$

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)

Q31.

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 reversere 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 Scheme

Q19.

(a) *M1* $K_p = (_PY)^3 . (_PZ)^2 / (_PW)^2 . (_PX)$ *NB [ ] wrong* **1**

M2 temperature **1**

M3 increase **1**

M4 particles have more energy or greater velocity/speed **1**

M5 more collisions with $E > E_a$ or more successful collisions **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 CH_3COCl expensive

NB Allow converse answers
Do not allow reactions with other reagents e.g. water or ease of separation **1**

(ii) $\Delta S = \Sigma S$ products $- \Sigma S$ reactants **1**

$\Delta S = (259 + 187) - (201 + 161)$ **1**

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

Allow – 84 to score ***(1)*** *mark* **1**

$\Delta G = \Delta H - T\Delta S$ **1**

= – 21.6 – 298 × 84/1000
= – 46.6 kJ mol^{-1} or – 46 600 J mol^{-1}

1

*Allow **(2)** for – 46.6 without units*
(Mark ΔG consequentially to incorrect ΔS)
(e.g. ΔS = –84 gives ΔG = +3.4 kJ mol^{-1})

1

[15]

Q20.

A

[1]

Q21.

(a) $K_p = \frac{P_{SO_2} \times P_{Cl_2}}{P_{SO_2Cl_2}}$ **(1)**

1

(b) 0.25 + 0.75 + 0.75 = 1.75 **(1)** **(1)**

2

(c) (i) *p* = Total pressure × mol fraction **(1)**

(ii) *Partial of SO_2Cl_2*: $125 \times \frac{0.25}{1.75}$ = 17.9 kPa **(1)**

Partial pressure of Cl_2: $125 \times \frac{0.75}{1.75}$ = 53.6 kPa **(1)** **(1)**

5

(d) $K_p = \frac{53.6 \times 53.6}{17.9}$ **(1)** = 161 **(1)** kPa **(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 SO_2Cl_2 can be scored in part (c) (ii) if not gained in (b)

1.75 get **(2)**

If moles of SO_2Cl_2 = 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 SO_2Cl_2 = 1 in (c)(ii), lose both marks in (c)(ii) for pp of SO_2Cl_2 = (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 SO_2Cl_2 = 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 $p_A = x_A \times p_{tot}$

(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 pCl_2 is not equal to pSO_2 or any number used in K_p is not conseq 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 "equm shifts to right", mark on.
In the explanation, the word "endothermic" (or its equivalent) is essential.

[14]

Q22.

(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
conseq on (i)

3

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

Partial pressure of PCl_3: pp = mol fⁿ × total P **(1)**
= 0.400 × 225 = 90 **(1)** kPa **(1)**

3

(c) (i) $K_p = \dfrac{P_{PCl_5}}{P_{PCl_3} \times P_{Cl_2}}$ **(1)**
ignore brackets except [ ]
must show P

(ii) $K_p = \frac{83.6}{90.1 \times 51.3}$ **(1)** = 1.8**(1)** × 10^{-2} **(1)** Kpa^{-1} **(1)** (or 1.81 × 10^{-5} Pa^{-1})

If 83.6 and 51.3 wrong way round, AE – 1, answer = 6.81 × 10^{-3}

If K_p × in (i) allow max 2 for substitution of numbers and conseq units

4

(d) (i) increased **(1)**

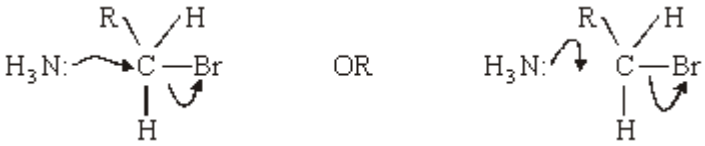
(ii) increased **(1)**

2

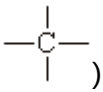
[12]

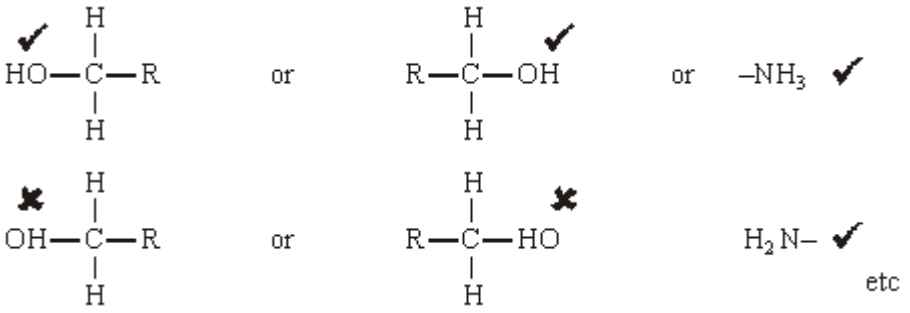
Organic points

(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. ) once per paper



Penalise once per paper

allow CH_3– or $–CH_3$ or  or CH_3 or H_3C–

Q23.

B

[1]

Q24.

C

[1]

Q25.

C

[1]

Q26.

D

[1]

Q27.

B

[1]

Q28.

B

[1]

Q29.

D

[1]

Q30.

(a) (i) 0.86 **(1)**

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

$\therefore$ **mole fraction of H_2** = $\frac{0.86}{1.375}$ = 0.625 **(1)**

(0.62 - 0.63)

Conseq on (i)

(iii) pp = mole fract^n × total P **(1)**
= 0.625 × 1.75 × 10^4
= 1.09 × 10^4 (kPa) **(1)**
or 1.1(0)
Ignore units
Conseq on (ii)

(b) (i) $K_p = \frac{P_{CH3OH}}{P^2_{H_2} \times P_{CO}}$ **(1)**

Penalise [ ]

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

OR 2.37×10^{-15}

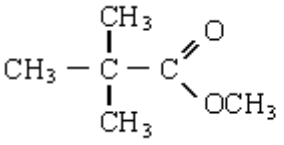
Units: kPa^{-2} **(1)**

or Pa^{-2}

not conseq to wrong K_p expression

3

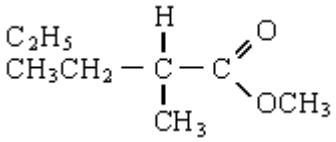
(c) *Isomer **E**:*



(1)

allow $(CH_3)_3CCOOCH_3$ or $(CH_3)_3CCO_2CH_3$

*Isomer **F**:*



(1)

2

[10]

Q31.

D

[1]