M1.D

[1]

M2.B

[1]

M3.A

[1]

M4.B

[1]

M5.C

[1]

M6.C

[1]

M7.D

[1]

M8.D

[1]

M9. B

[1]

M10. B

[1]

M11. D

[1]

M1.(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]

M2.(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)	0.86	0.86

= 0.42

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 × 188.6 / 30.7 × $(92.1)^3$ = 1.483×10^{-3} = 1.5×10^{-3}

Answer must be to 2 significant figures

1

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

1

[16]

M3.A

[1]

M4.B

[1]

M5.D

[1]

M6. (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)×10^{-8} 2.2(l)×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 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]

M7. (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]

M1. (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) $K_p = \dfrac{(pSO_3)^2}{(pSO_2)^2 \times (pO_2)}$

(If K_p wrong, allow consequential units only)

(penalise square brackets in expression but then mark on)

1

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

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

<u>Exothermic</u>

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]

M2.B

[1]

M3.D

[1]

M4.C

[1]

M5.D

[1]

M6.B

[1]

M7.C

[1]

M8. (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

$= -21.6 - 298 \times 84/1000$
$= -46.6$ 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]

M9. (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 f^{n} × 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) $K_p = \dfrac{83.6}{90.1 \times 51.3}$ **(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)**

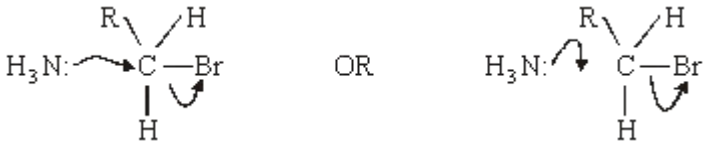
(ii) increased **(1)**

2

[12]

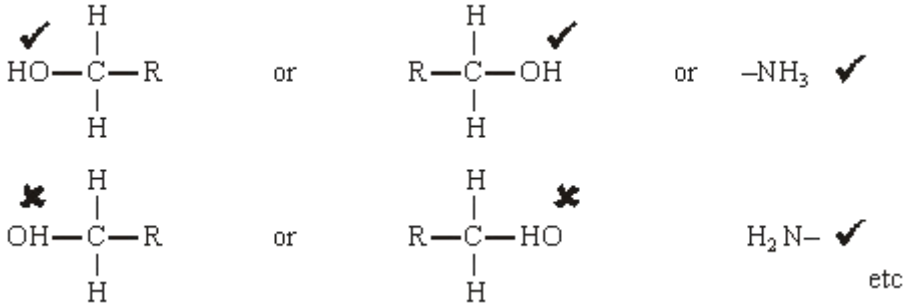
Organic points

(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–

M10. (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 <u>endothermic</u> 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]

M1.B

[1]

M2.D

[1]

M3. (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)

5

(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) × 10^{-9} **(1)**

OR 2.37 × 10^{-15}

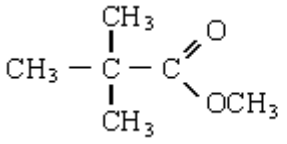
Units: kPa^{-2} **(1)**

or Pa^{-2}

not conseq to wrong K_p *expression*

3

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



(1)

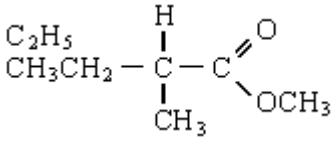
allow

$(CH_3)_3CCOOCH_3$

or

$(CH_3)_3CCO_2CH_3$

*Isomer **F**:*



(1)

2

[10]

M4.D

[1]