

## Mark schemes

1

(a) Bonds broken =  $2(\text{C}=\text{O}) + 3(\text{H}-\text{H}) = 2 \times 743 + 3 \times \text{H}-\text{H}$

Bonds formed =  $3(\text{C}-\text{H}) + (\text{C}-\text{O}) + 3(\text{O}-\text{H}) = 3 \times 412 + 360 + 3 \times 463$

*Both required*

1

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

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

*Both required*

1

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

*Allow 483.3(3)*

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- (b) Mean bond enthalpies are not the same as the actual bond enthalpies in  $\text{CO}_2$  (and / or methanol and / or water)

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

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- (d) 4 mol of gas form 2 mol

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

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This increases the yield of methanol

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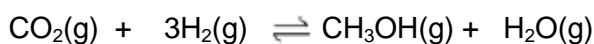
- (e) Impurities (or sulfur compounds) block the active sites

*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	$(3-3 \times 0.86)$ = 0.42	0.86	0.86

1

Stage 2: Partial pressure calculations

Total moles of gas = 2.28

Partial pressures = mol fraction  $\times$   $p_{\text{total}}$

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

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

*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 =*

$$pp_{\text{CH}_3\text{OH}} = 0.3772 \times 500$$

$$pp_{\text{H}_2\text{O}} = 0.3772 \times 500$$

1

Stage 3: Equilibrium constant calculation

$$K_p = p_{\text{CH}_3\text{OH}} \times p_{\text{H}_2\text{O}} / p_{\text{CO}_2} \times (p_{\text{H}_2})^3$$

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

*Answer must be to 2 significant figures*

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Units = kPa<sup>-2</sup>

1

[16]

**2** D

[1]

**3** (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<sub>3</sub> 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<sub>c</sub>)

*Allow the system will no longer be at equilibrium*

*Do not allow references to equilibrium position shifting alone*

1

**[6]**

**4**

- (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<sub>p</sub> wrong in (a)(i) CE)

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MPa<sup>-2</sup>

*(allow any unit of P<sup>-2</sup> provided ties to P used for K<sub>p</sub> value)*

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

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(Rate is) slow (at lower temperatures)

1

[8]

5

(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<sub>2</sub> = 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 
$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \times P_{\text{H}_2}^2}$$
 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)	$2.2(l)\times 10^{-8}$	$2.2(l)\times 10^{-14}$	1
M8	$\text{MPa}^{-2}$	$\text{kPa}^{-2}$	$\text{Pa}^{-2}$	1

*If no subtraction lose M1, M2 and M3*  
*(If x2 missed in M2, lose both M2 and M3)*  
*(If M1 gained but moles of  $\text{H}_2 = 73.2$  (i.e. double CO), M2 and M3 lost)*  
*(If M1 gained but mol  $\text{H}_2 = 2(146 - 26.2)$ , 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  $\text{kPa}^{-2}$ )*

[14]

**6**

[1]

**7**

(a) 12 (kPa)

1

$pp = \text{mole fraction} \times \text{total pressure}$  or  $\text{mole fraction} = 12/104$

1

= 0.115

*(allow 0.12)*

1

(b) 68 (kPa)

1

(c) 
$$K_p = \frac{(p\text{SO}_3)^2}{(p\text{SO}_2)^2 \times (p\text{O}_2)}$$

*(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<sup>-1</sup>

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]**

8

- (a) M1  $K_p = (p_Y)^3 \cdot (p_Z)^2 / (p_W)^2 \cdot (p_X)$  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<sub>3</sub>COCl 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

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

*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  $\Delta G$  consequentially to incorrect  $\Delta S$ )*

*(e.g.  $\Delta S = -84$  gives  $\Delta G = +3.4 \text{ kJ mol}^{-1}$ )*

 1

**[15]**