

## 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*

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

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

*Both required*

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

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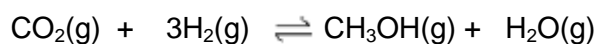
- (e) Impurities (or sulfur compounds) block the active sites

*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

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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 =*

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

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

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

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

*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>

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[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.*

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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

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(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;

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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]**