Q1. Methanol can be manufactured by the reaction of carbon monoxide with hydrogen

$$
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})
$$

In an experiment, 0.73 mol of carbon monoxide was heated with 1.25 mol of hydrogen. An equilibrium mixture was formed that contained 0.43 mol of methanol.
(a) Calculate the amount, in moles, of each reactant present at equilibrium.

$$
\begin{aligned}
& \text { Amount of carbon monoxide }=\ldots \\
& \text { Amount of hydrogen }=\ldots
\end{aligned}
$$

(b) Write an expression for the equilibrium constant, $K_{c}$, for this reaction.
(c) In another experiment at a different temperature, the equilibrium mixture contained 0.452 mol of carbon monoxide, 0.106 mol of hydrogen and 0.273 mol of methanol in a flask of volume $9.40 \times 10^{3} \mathrm{~cm}^{3}$.

Calculate the value of the equilibrium constant, $K_{c}$, at this temperature and state the units.
$K_{c}=$ $\qquad$ Units = $\qquad$
(d) The total pressure of this equilibrium mixture in the flask was 482.9 kPa .

Calculate the temperature, in ${ }^{\circ} \mathrm{C}$, of the equilibrium mixture.
(The ideal gas constant $R=8.31 \mathrm{~J} \mathrm{~mol}^{-1} \mathrm{~K}^{-1}$ )

Temperature $=$ $\qquad$ ${ }^{\circ} \mathrm{C}$

Q2. Ethanol and ethanoic acid react reversibly to form ethyl ethanoate and water according to the equation:

$$
\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{3}+\mathrm{H}_{2} \mathrm{O}
$$

A mixture of $8.00 \times 10^{-2} \mathrm{~mol}$ of ethanoic acid and $1.20 \times 10^{-1} \mathrm{~mol}$ of ethanol is allowed to reach equilibrium at $20^{\circ} \mathrm{C}$.

- The equilibrium mixture is placed in a graduated flask and the volume made up to 250 $\mathrm{cm}^{3}$ with distilled water.
- A $10.0 \mathrm{~cm}^{3}$ sample of this equilibrium mixture is titrated with sodium hydroxide added from a burette.
- The ethanoic acid in this sample reacts with $3.20 \mathrm{~cm}^{3}$ of $2.00 \times 10^{-1} \mathrm{~mol} \mathrm{dm}^{-3}$ sodium hydroxide solution.
(a) Calculate the value for $K_{c}$ for the reaction of ethanoic acid and ethanol at $20^{\circ} \mathrm{C}$. Give your answer to the appropriate number of significant figures.

$$
K_{\mathrm{c}} .
$$

$\qquad$
(b) A student obtained the titration results given in Table 1.

Table 1

|  | Rough | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ |
| :--- | :---: | :---: | :---: | :---: |
| Final burette reading $/ \mathbf{c m}^{3}$ | 4.60 | 8.65 | 12.85 | 16.80 |
| Initial burette reading $/ \mathbf{c m}^{3}$ | 0.10 | 4.65 | 8.65 | 12.85 |
| Titre $/ \mathbf{c m}^{\mathbf{3}}$ |  |  |  |  |

Complete Table 1.
(c) Calculate the mean titre and justify your choice of titres.

Calculation

> Mean titre =
$\qquad$ $\mathrm{cm}^{3}$

Justification $\qquad$
$\qquad$
(d) The pH ranges of three indicators are shown in Table 2.

Table 2

| Indicator | pH range |
| :--- | :---: |
| Bromocresol green | $3.8-5.4$ |
| Bromothymol blue | $6.0-7.6$ |
| Thymol blue | $8.0-9.6$ |

Select from Table 2 a suitable indicator for the titration of ethanoic acid with sodium hydroxide.
$\qquad$
(e) The uncertainty in the mean titre for this experiment is $\pm 0.15 \mathrm{~cm}^{3}$.

Calculate the percentage uncertainty in this mean titre.

Percentage uncertainty $=$ $\qquad$ \%
(f) Suggest how, using the same mass of ethanoic acid, the experiment could be improved to reduce the percentage uncertainty.
$\qquad$
$\qquad$
$\qquad$
$\qquad$
$\qquad$

Q3. Ethanoic acid and ethane-1,2-diol react together to form the diester $\left(\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}\right)$ as shown.

$$
2 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{I})+\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}(\mathrm{I}) \rightleftharpoons \mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}(\mathrm{I})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})
$$

(a) Draw a structural formula for the diester $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}$
(b) A small amount of catalyst was added to a mixture of 0.470 mol of ethanoic acid and 0.205 mol of ethane-1,2-diol.

The mixture was left to reach equilibrium at a constant temperature.
Complete Table 1.
Table 1

| Amount in the mixture / mol |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}$ | $\mathrm{H}_{2} \mathrm{O}$ |
| At the start | 0.470 | 0.205 | 0 | 0 |
| At equilibrium | 0.180 |  |  |  |

Space for working
(c) Write an expression for the equilibrium constant, $K_{\mathrm{c}}$, for the reaction.

The total volume of the mixture does not need to be measured to allow a correct value for $K_{c}$ to be calculated.

Justify this statement.
Expression

Justification $\qquad$
$\qquad$
(d) A different mixture of ethanoic acid, ethane-1,2-diol and water was prepared and left to reach equilibrium at a different temperature from the experiment in part (b)

The amounts present in the new equilibrium mixture are shown in Table 2.
Table 2

| Amount in the mixture / mol |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}$ | $\mathrm{C}_{6} \mathrm{H}_{10} \mathrm{O}_{4}$ | $\mathrm{H}_{2} \mathrm{O}$ |  |
| At new <br> equilibrium | To be <br> calculated | 0.264 | 0.802 | 1.15 |  |

The value of $K_{\mathrm{c}}$ was 6.45 at this different temperature.
Use this value and the data in Table 2 to calculate the amount, in mol, of ethanoic acid present in the new equilibrium mixture.

Give your answer to the appropriate number of significant figures.
$\qquad$ mol

Q4. 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 $\mathrm{H}-\mathrm{H}$ bond.

An equation for this formation of methanol is given below.

$$
\mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \quad \Delta H=-49 \mathrm{~kJ} \mathrm{~mol}^{-1}
$$

Some mean bond enthalpies are shown in the following table.

| Bond | $\mathrm{C}=\mathrm{O}$ | $\mathrm{C}-\mathrm{H}$ | $\mathrm{C}-\mathrm{O}$ | $\mathrm{O}-\mathrm{H}$ |
| :--- | :---: | :---: | :---: | :---: |
| Mean bond enthalpy/ $\mathrm{kJ} \mathrm{mol}^{-1}$ | 743 | 412 | 360 | 463 |

(a) Use the enthalpy change for the reaction and data from the table to calculate a value for the $\mathrm{H}-\mathrm{H}$ bond enthalpy.
$\mathrm{H}-\mathrm{H}$ bond enthalpy $=$ $\qquad$ $\mathrm{kJ} \mathrm{mol}^{-1}$
(b) A data book value for the $\mathrm{H}-\mathrm{H}$ bond enthalpy is $436 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

Suggest one reason why this value is different from your answer to part (a).
$\qquad$
$\qquad$
$\qquad$
(c) Suggest one environmental advantage of manufacturing methanol fuel by this reaction.
$\qquad$
$\qquad$
$\qquad$
(d) Use Le Chatelier's principle to justify why the reaction is carried out at a high pressure rather than at atmospheric pressure.
$\qquad$
$\qquad$
$\qquad$
(e) Suggest why the catalyst used in this process may become less efficient if the carbon dioxide and hydrogen contain impurities.
$\qquad$
$\qquad$
$\qquad$
(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.

$$
\mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

Calculate a value for $K_{p}$
Give your answer to the appropriate number of significant figures.
Give units with your answer.
$K_{p}=$ $\qquad$ Units = $\qquad$

Mark schemes

## Q1.

(a) $\mathrm{MolCO}=(0.73-0.43)=0.30(\mathrm{~mol})$

Mol H2 $=(1.25-2(0.43))=0.39(\mathrm{~mol})$
(b) $K^{\mathrm{c}}=\frac{\left[\mathrm{CH}_{3} \mathrm{OH}\right]}{[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}}$
(c) Divides throughout by volume

$$
K_{\mathrm{c}}=\frac{[0.273 / 9.40]}{[0.1 .06 / 9.40]^{2}[0.452 / 9.40]}
$$

$$
K_{\mathrm{c}}=\frac{0.029}{0.0000061146}
$$

$$
K_{\mathrm{C}}=4.75 \times 10^{3}
$$

Unit $=\mathrm{mol}^{-2} \mathrm{dm}^{+6}$
(d) $\mathrm{pV}=\mathrm{nRT}$
$T=\frac{p V}{n R}$
$\mathrm{n}=0.452+0.106+0.273=0.831$ (mol)
Calculation of moles and substitution of all values
$=\frac{482.9 \times 10^{3} \times 9.40 \times 10^{-3}}{0.831 \times 8.31}=657 \mathrm{~K}$
$=384^{\circ} \mathrm{C}$
Conversion to ${ }^{\circ} \mathrm{C}$
(a) Stage 1: Moles of acid at equilibrium

Moles of sodium hydroxide in each titration
$=\left(3.20 \times 2.00 \times 10^{-1}\right) / 1000=6.40 \times 10^{-4}$

Sample $=10 \mathrm{~cm}^{3}$ so moles of acid in $250 \mathrm{~cm}^{3}$ of equilibrium mixture $=25 \times 6.40 \times 10^{-4}=1.60 \times 10^{-2}$

M2 can only be scored if = answer to M1 $\times 25$

Stage 2: Moles of ester and water formed
Moles of acid reacted $=8.00 \times 10^{-2}-1.60 \times 10^{-2}=6.40 \times 10^{-2}$
$=$ moles ester and water formed
M3 is $8.00 \times 10^{-2}-M 2$

Stage 3: Moles of ethanol at equilibrium
Moles of ethanol remaining $=1.20 \times 10^{-1}-6.40 \times 10^{-2}=5.60 \times 10^{-2}$ M4 is $1.20 \times 10^{-1}-\mathrm{M} 3$

Stage 4: Calculation of equilibrium constant

$$
\begin{aligned}
& K_{\mathrm{c}}=\left[\mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{3}\right]\left[\mathrm{H}_{2} \mathrm{O}\right] /\left[\mathrm{CH}_{3} \mathrm{COOH}\right]\left[\mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{OH}\right] \\
& =\left(6.40 \times 10^{-2}\right)^{2} /\left(1.60 \times 10^{-2}\right)\left(5.60 \times 10^{-2}\right) \\
& =4.5714=4.57 \\
& \quad \mathrm{M6} \text { is } \mathrm{M3}^{2} / \mathrm{M} 2 \times \mathrm{M} 4 \\
& \quad \text { Answer must be given to } 3 \text { significant figures }
\end{aligned}
$$

(b)

|  | Rough | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ |
| :--- | :---: | :---: | :---: | :---: |
| Final burette reading / cm |  | 4.60 | 8.65 | 12.85 |
| Initial burette reading / <br> $\mathbf{c m}^{3}$ | 0.10 | 4.65 | 8.65 | 12.85 |
| Titre $/ \mathbf{c m}^{3}$ | 4.50 | 4.00 | 4.20 | 3.95 |

(c) Mean $=4.00+3.95 / 2=3.98\left(\mathrm{~cm}^{3}\right)$

Allow 3.975 (cm ${ }^{3}$ )

Titres 1 and 3 are concordant
Allow titre 2 is not concordant
(d) Thymol blue
(e) Percentage uncertainty: $0.15 / 3.98 \times 100=3.77 \%$

Allow consequential marking on mean titre from 2.3
(f) Use a lower concentration of NaOH

So that a larger titre is required (reduces percentage uncertainty in titre)
1
[13]

Q3.
(a)


Allow $\mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OOCCH}_{3}$ $\mathrm{OR} \mathrm{CH}_{3} \mathrm{COOCH}_{2} \mathrm{CH}_{2} \mathrm{OCOCH}_{3}$ OR

(b) $\mathrm{Mol} \mathrm{HOCH} 2 \mathrm{CH}_{2} \mathrm{OH}=6.00 \times 10^{-2}$ OR 0.06(00)

Mol C6 $\mathrm{H}_{10} \mathrm{O}_{4} \quad=1.45 \times 10^{-1}$ OR 0.145

Mol $\mathrm{H}_{2} \mathrm{O} \quad=2.90 \times 10^{-1} \quad$ OR $0.29(0)$
(c)
$\left(K_{\mathrm{C}}=\right) \frac{[\text { ester }] \times\left[\mathrm{H}_{2} \mathrm{O}\right]^{2}}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]^{2} \times\left[\mathrm{HOCH}_{2} \mathrm{CH}_{2} \mathrm{OH}\right]}$
Allow words for acid and alcohol

The volume cancels out (Penalise a contradictory justification from expression if the volumes do not cancel out)
OR
there are equal no of moles on each side of the equation
OR
there are equal no of molecules on each side of the equation
(d)

$$
(\mathrm{Mol} \mathrm{CH} 33 \mathrm{COOH} / V)^{2}=\frac{\left(8.02 \times 10^{-1} / V\right)(1.15 / V)^{2}}{6.45 \times\left(2.64 \times 10^{-1} / V\right)}
$$

Mol CH $33 \mathrm{COOH}=\sqrt{\frac{\left(8.02 \times 10^{-1}\right) \times(1.15)^{2}}{6.45 \times\left(2.64 \times 10^{-1}\right)}}=\sqrt{0.623}$
$\mathrm{Mol} \mathrm{CH}_{3} \mathrm{COOH}=0.789 \quad$ (must be 3 sfs ) Allow $0.788-0.790$
0.789 scores 3

Allow without $V:\left(n \mathrm{CH}_{3} \mathrm{COOH}\right)^{2}=\frac{\left(8.02 \times 10^{-1}\right)(1.15)^{2}}{6.45 \times\left(2.64 \times 10^{-1}\right)}$
If $\left(n \mathrm{nH}_{3} \mathrm{COOH}\right)^{2}=0.623$ then award M1 and M2
If $K_{c}$ is correct in (c) but incorrect rearrangement, then $C E=0$ except if upside down rearrangement then M3 only awarded for 1.27

If $K_{c}$ is incorrect in (c) then only M1 can be awarded for correct rearrangement.

Q4.
(a) Bonds broken $=2(\mathrm{C}=\mathrm{O})+3(\mathrm{H}-\mathrm{H})=2 \times 743+3 \times \mathrm{H}-\mathrm{H}$

Bonds formed $=3(\mathrm{C}-\mathrm{H})+(\mathrm{C}-\mathrm{O})+3(\mathrm{O}-\mathrm{H})=3 \times 412+360+3 \times 463$
Both required
$-49=[2 \times 743+3 \times(\mathrm{H}-\mathrm{H})]-[3 \times 412+360+3 \times 463]$
$3(\mathrm{H}-\mathrm{H})=-49-2 \times 743+[3 \times 412+360+3 \times 463]=1450$
Both required
$\mathrm{H}-\mathrm{H}=483\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$
Allow 483.3(3)
(b) Mean bond enthalpies are not the same as the actual bond enthalpies in $\mathrm{CO}_{2}$ (and / or methanol and / or water)
(c) The carbon dioxide (produced on burning methanol) is used up in this reaction
(d) 4 mol of gas form 2 mol

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

This increases the yield of methanol
(e) Impurities (or sulfur compounds) block the active sites Allow catalyst poisoned
(f) Stage 1: moles of components in the equilibrium mixture Extended response question

$$
\mathrm{CO}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{~g})
$$

| Initial <br> moles | 1.0 | 3.0 | 0 | 0 |
| :--- | :---: | :---: | :---: | :---: |
| Eqm | $(1-0.86)$ | $(3-3 \times 0.86)$ <br> $=0.14$ | 0.82 | 0.86 |

Stage 2: Partial pressure calculations
Total moles of gas $=2.28$
Partial pressures $=\mathrm{mol}$ fraction $\times \mathrm{p}_{\text {total }}$
$\mathrm{p}_{\mathrm{coz}}=$ mol fraction $\times \mathrm{p}_{\text {total }}=0.14 \times 500 / 2.28=30.7 \mathrm{kPa}$
$p_{\text {H2 }}=$ mol fraction $\times p_{\text {total }}=0.42 \times 500 / 2.28=92.1 \mathrm{kPa}$
M3 is for partial pressures of both reactants
Alternative M3 =
$p p_{\text {Co2 }}=0.0614 \times 500$
$p p_{\text {H } 2}=0.1842 \times 500$

```
рснзон \(=\) mol fraction \(\times p_{\text {total }}=0.86 \times 500 / 2.28=188.6 \mathrm{kPa}\)
\(p_{\text {H2O }}=\) mol fraction \(\times p_{\text {total }}=0.86 \times 500 / 2.28=188.6 \mathrm{kPa}\)
    M4 is for partial pressures of both products
    Alternative M4 =
    рр снзон \(=0.3772 \times 500\)
    \(p p_{\text {но }}=0.3772 \times 500\)
```

Stage 3: Equilibrium constant calculation
$K_{\mathrm{p}}=\mathrm{p}_{\mathrm{CH} 3 \mathrm{OH}} \times \mathrm{p}_{\mathrm{H} 2 \mathrm{O}} / \mathrm{p}_{\mathrm{CO}} \times\left(\mathrm{p}_{\mathrm{H} 2}\right)^{3}$

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

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

