

## A-Level Chemistry

## Equilibria and Le Chatelier's

 PrincipleMark Scheme

Time available: 62 minutes Marks available: 54 marks

This question is marked using levels of response. Refer to the Mark Scheme Instructions for Examiners for guidance on how to mark this question.

| Level 3 | All stages are covered and the explanation of each stage is <br> generally correct and virtually complete. <br> 5-6 <br> Marks |
| :--- | :--- |
| Answer is well structured with no repetition or irrelevant points. <br> Accurate and clear expression of ideas with no errors in use of <br> technical terms. |  |
| 3-4 <br> Marks | All stages are covered but the explanation of each stage may be <br> incomplete or may contain inaccuracies OR two stages are covered <br> and the explanations are generally correct and virtually complete. <br> Answer shows some attempt at structure. Ideas are expressed with <br> reasonable clarity with, perhaps, some repetition or some irrelevant <br> points. <br> Some minor errors in use of technical terms. |
| Level 1 | Two stages are covered but the explanation of each stage may be <br> incomplete or may contain inaccuracies, OR only one stage is <br> covered but the explanation is generally correct and virtually <br> complete. <br> Answer includes isolated statements but these are not presented in <br> a logical order or show some confusion. <br> Answer may contain valid points which are not clearly linked to an <br> argument structure. Errors in the use of technical terms. |
| Marks |  |

## Indicative chemistry content

## Stage 1: Temperature

1a. The reaction is endothermic (so equilibrium shifts to RHS to reduce the temperature)
1b. So, higher temperature increases the yield 1c. High temperatures are costly (so compromise temperature used)

## Stage 2: Pressure

2a. More moles of gas on the right hand side, (so equilibrium shifts to RHS to increase the yield)
2b. So, lower pressure increases the yield
2c. A low pressure means a low cost

## Stage 3: Catalyst

3a. Catalyst has no effect on yield
3b. Adding a catalyst allows a lower temperature to be used
3c. So, this lowers the cost
2. (a) M1 $\frac{\left.\left[\mathrm{CO}^{2}\right]_{2}\right]^{4}}{\left[\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]}$

M2 $\mathrm{mol}^{4} \mathrm{dm}^{-12}$
M2 allow for units that are consequential on M1
(b) M1 clear attempt made to divide moles by volume to find concentrations
$7.66 \times 10^{-3}$ scores M1,2,3
$7.66 \times 10^{-15}$ scores M1,3
M1 can use 0.750 or 750 (or $75,7.5,0.075,0.0075$, etc)

M2 $\frac{\left[\frac{0.110}{0.750}\right]^{2}\left[\frac{0.220}{0.750}\right]^{4}}{\left[\frac{0.075}{0.750}\right]\left[\frac{0.156}{0.750}\right]}$
M2 $\frac{(0.147)^{2}(0.293)^{4}}{(0.100)(0.208)}$ or $\frac{(0.0215)(0.00740)}{(0.100)(0.208)}$
for M2 volume used must be 0.750 or 750 (if use $V$ at this stage, then must be one of these values of $V$ used later on)

M3 $\quad 7.66 \times 10^{-3}$
M3 ignore units
If moles are used in place of concentration
penalise M1, but M2 and M3 could score for ECF
M2 $\frac{(0.110)^{2}(0.220)^{4}}{(0.075)(0.156)} M 32.42 \times 10^{-3}$
Allow ECF if incorrect expression for $K_{c}$ is used
(c) M1 yield would decrease
mark each point independently

M2 equilibrium (position) moves left / shifts left / in direction of reverse reaction to oppose increase in pressure / to reduce pressure

M2 need both parts; ignore favours reverse reaction for the first part

M3 fewer moles/molecules of gas on left hand side / fewer moles/molecules of gaseous reactants

M3 2 moles/molecules (of gas) on left hand side v 6
moles/molecules (of gas) on right hand side

M4 no effect on $K_{\text {c }}$
3. (a) 3 minutes

M2 dependent on M1 or near miss
(At equilibrium, rate ${ }_{f \text { fwd }}=$ rate $_{\text {back }} \mathrm{So}$ ) concentrations (of $\mathrm{O}_{2}$ and $\mathrm{SO}_{3}$ ) remain constant
Not concentrations are the same/equal
Allow (after this point) gradient is zero / curve flattens out
(b) Sketch begins at origin and goes up until 3 mins

Levels off at $0.3 \mathrm{~mol} \mathrm{dm}^{-3}$
Mark Independently
(c) $\quad \mathrm{T}_{2}$ (Not worth a mark alone)

$$
T_{1}, C E=0
$$

Equilibrium has moved / shifted to RHS/forward in endothermic direction
Both RHS / forward and endothermic needed

Equilibrium has opposed the increase in T / Equilibrium moves to decrease the T
Not just to oppose the change
4. (a) M1 no effect (on yield)

$$
C E=0 \text { if yield changes }
$$

M2 increases rate / speed of both / forward and reverse reactions equally / by the same amount

If no reference to effect on yield, could still score M2
Ignore reference to no change in position of equilibrium, and reference to lowering activation energies
M2 allow changes rate of both / forward and reverse reactions equally / by the same amount
(b) $\quad\left(K_{c}=\right) \frac{\left[\mathrm{CH}_{3} \mathrm{OH}\right]}{[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}}$

Must be square brackets
Ignore state symbols
Ignore units
(c) M1 divides moles by volume ( 0.250 or $\frac{250}{1000}$ )

M2 $\quad K_{c}=\frac{\frac{0.0610}{0.250}}{\left[\frac{0.340}{0.250}\right]\left[\frac{0.190}{0.250}\right]^{2}}\left(=\frac{0.244}{1.36 \times 0.76^{2}}\right)$

M3 $\quad 0.311$
Correct answer scores 3; M3 to at least 2sf (0.3106159 ...); ignore units
Allow ECF from M1 to M2 if an attempt to calculate concentration has been made by dividing by some factor of $250 \mathrm{~cm}^{3}$
Allow ECF from M2 to M3 for use of an expression containing each reagent in a correctly substituted $K_{c}$ expression
If volume not used, then allow M3 only for 4.97 (4.96985 ... to at least 2sf)
(d) M1 $\frac{1}{\text { Answer to (c) }}=3.22$

M1 to at least 2sf (0.31 gives 3.2(258))
M1 = 1.21 if alternative answer to 8.3 used
If an error was made in 8.3, but the candidate produced an answer in 8.4 that did fit the inverted calculation from 8.3, then candidate could score M1

M2 $\mathrm{mol}^{2} \mathrm{dm}^{-6}$
(if volumes are not used, then candidate would get 0.20(12.)
5. (a) Initial amount of $A=6.4 \times 10^{-3}$ If M1 wrong can score max 3

Equ $\mathrm{A}=6.4 \times 10^{-3}-2 \mathrm{x} \therefore \mathrm{x}=1.25 \times 10^{-3}$
If incorrect $x$ can score max 3
$B=9.5 \times 10^{-3}-x=8.25 \times 10^{-3}$
Allow 2 or more sig figs

$$
C=2.8 \times 10^{-2}+3 x=0.0318
$$

$D=x=1.25 \times 10^{-3}$
(b) $\quad K_{\mathrm{c}}=\frac{[C]^{3}[D]}{[A]^{2}[B]}$

Penalise ( ) but mark on in (b) \& (c)

Units $=\mathrm{mol} \mathrm{dm}^{-3}$
If $K_{c}$ wrong no mark for units
(c) M 1 for correct rearrangement $[A]^{2}=\frac{[C]^{3}[D]}{K_{c}[B]}$ or $[A]=\sqrt{\frac{[C]^{3}[D]}{K_{c}[B]}}$

If $K_{c}$ wrong in (b) can score 1 for dividing by correct volume

M2 for division of mol of B, C and D by correct volume
If $K_{c}$ correct but incorrect rearrangement can score
1 for dividing by correct volume
M2
$[A]^{2}=\frac{\left.\left.\left[^{1.05}\right] / 0.5^{3}\right]^{0.076} / 0.5\right]}{116 \times\left[\left[^{0.21 / 0.5}\right]\right.}$
M3 for final answer: $[\mathrm{A}]=\underline{0.17}$ (must be 2 sfs)
(d) (All) conc fall: (ignore dilution)
$O R K_{c}=$ mole ratio $\times 1 / \mathrm{V}$

Equm moves to side with more moles
If vol increases, mole ratio must increase

To oppose the decrease in conc
To keep $K_{c}$ constant
If only conc of $A$ falls $C E=0$
If pressure falls $C E=0$
6. (a) Decrease

Increasing pressure moves equilibrium to the side of least moles i.e. backward reaction

To oppose the increase in pressure or to decrease the pressure
(b) A catalyst speeds up the rate of the forward and backward reaction

By the same amount
1
(c) $\Delta H=-111-(-75-242)$ $206\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$
(d) $\Delta \mathrm{S}=3 \times 131+198-(186+189)=216 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}$
$\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$
$0=206-T \frac{216}{1000}$
$\mathrm{T}=953.7$ or 954 K
$\mathrm{T}=681\left({ }^{\circ} \mathrm{C}\right)$
If the value given in the question is used then the answer is 283 $\left({ }^{\circ} \mathrm{C}\right)$

