## Equilibria, Energetics and Elements How Far?

1. (a) rate of forward reaction = rate of reverse reaction (1) concentrations of reactants and products are constant but they are constantly interchanging (1)
(b) (i) $K_{\mathrm{c}}=\left[\mathrm{CH}_{3} \mathrm{OH}\right] /[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}$ (1)
(ii) use of $K_{\mathrm{c}}=\left[\mathrm{CH}_{3} \mathrm{OH}\right] /[\mathrm{CO}]\left[\mathrm{H}_{2}\right]^{2}$ and moles to obtain a calculated value (1)
convert moles to concentration by $+2:[\mathrm{CO}]=3.10 \times 10^{-3} \mathrm{~mol} \mathrm{dm}^{-3}$; $\left[\mathrm{H}_{2}\right]=2.60 \times 10^{-5} \mathrm{~mol} \mathrm{dm}{ }^{-3} ;\left[\mathrm{CH}_{3} \mathrm{OH}\right]=2.40 \times 10^{-2} \mathrm{~mol} \mathrm{dm}^{-3} \mathbf{( 1 )}$
$K_{\mathrm{c}}=\left[2.60 \times 10^{-5}\right] /\left[3.10 \times 10^{-3}\right]\left[2.40 \times 10^{-2}\right]^{2}=14.6 / 14.56(\mathbf{1})$
If moles not converted to concentration, calculated $K_{c}$ value $=3.64$ (scores 1st and 3rd marks)
units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2}$ (1)
(c) (i) fewer moles of gas on right hand side (1)
(ii) None (1) 1
(d) (i) moved to left hand side/reactants increase/less products (1)
(ii) $\Delta H$ negative because high temperature favours the endothermic direction (1)
(e) (i) $\mathrm{CH}_{3} \mathrm{OH}+1 \frac{1}{2} \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}(1) \quad 1$
(ii) adds oxygen/oxygenated (1) 1
2. (a) $K_{\mathrm{c}}=\frac{\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{PCl}_{5}\right]}$ (1) 1
(b) (i) $\mathrm{PCl}_{5}>0.3 \mathrm{~mol} \mathrm{dm}{ }^{-3} ; \mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}<0.3 \mathrm{~mol} \mathrm{dm}^{-3}$ (1)
(ii) At start, system is out of equilibrium with too much $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$ and not enough $\mathrm{PCL}_{5}$ /

$$
\frac{0.3 \times 0.3}{0.3}=0.3 \text { is greater than } K_{\mathrm{c}}=0.245 \mathrm{~mol} \mathrm{dm}^{-3}(\mathbf{1})
$$

(c) (i) $\quad K_{\mathrm{c}}$ does not change as temperature is the same (1) 1
(ii) Fewer moles on left hand side (1)
system moves to the left to compensate for increase in pressure by producing less molecules (1)
(d) (i) $K_{\mathrm{c}}$ decreases (as more reactants than products)(1)
(ii) Forward reaction is exothermic/ reverse reaction is endothermic (1) equilibrium $\rightarrow$ left to oppose increase in energy/ because $K_{\mathrm{c}}$ decreases (1)
3. (a) $\mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O} \rightarrow 3 \mathrm{H}_{2}+\mathrm{CO}$
$\mathrm{CH}_{4}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 4 \mathrm{H}_{2}+\mathrm{CO}_{2}$
$\mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{H}_{2}+\mathrm{CH}_{2} \mathrm{O} / \mathrm{HCHO}$
$\mathrm{CH}_{4}+2 \mathrm{H}_{2} \mathrm{O} \rightarrow 2 \mathrm{H}_{2}+\mathrm{CH}_{2} \mathrm{O}_{2} / \mathrm{HCOOH}$
or $\mathrm{CH}_{4}+\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2}+\mathrm{CH}_{3} \mathrm{OH} \checkmark$
(b) (i) $\quad k_{c}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}} \checkmark$
$\left[\mathrm{NH}_{3}\right]^{2}=\left(\mathrm{K}_{\mathrm{c}} \times\left[\mathrm{N}_{2}\right] \times\left[\mathrm{H}_{2}\right]^{3}\right)$

$$
=0.768
$$

(ii) $\left[\mathrm{NH}_{3}\right]=\sqrt{ } 0.78=0.876 / 0.88\left(\mathrm{~mol} \mathrm{dm}^{-3}\right)$ If no powers, then rearrangement mark only.
(c) High pressure:
adv: Fewer moles on r.h.s. $\rightarrow$ equilibrium moves to right
Greater pressure $\rightarrow$ faster rate/more frequent collisions
dis: Safety issues from (high) pressure
Expense of (high) pressure

## High temperature:

adv: more collisions exceed activation energy/
more successful collisions/more energetic
collisions/molecules have more energy
dis: Equilibrium moves to left/reverse direction because (forward) reaction is exothermic

## Catalyst:

lowers activation energy/
allows reaction to take place at a lower temperature
QWC: Uses 2 words following list in the correct context:
exothermic/endothermic, activation energy, collisions, equilibrium/Le Chatelier
4. (a) $K_{\mathrm{c}}=\frac{[\mathrm{HI}]^{2}}{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}$ (1)
(b)

| (i) | $\mathrm{H}_{2}$ | $\mathrm{I}_{2}$ | HI |
| :--- | :--- | :--- | :--- |
|  | 0.30 |  | 0.20 |
|  | 0.14 |  | 0.04 |
|  |  | (1) |  |
|  |  |  | 0.32 |
|  |  |  | (1) |

(1)
(1)
(ii) $K_{\mathrm{c}}=\frac{0.32^{2}}{0.14 \times 0.04}=18.28571429$ (1)
$=18$ (to 2 sig figs) (1)
no units (1)
(or ecf based on answers to (i) and/or (a))
(c) $K_{\mathrm{c}}$ is constant (1)

Composition of mixture is the same (1)
5. (a) (change in) concentration/mass/volume with time 1
(b) (i) $\quad \mathrm{O}_{2}$ :

Exp 2 has $4 \times\left[\mathrm{O}_{2}\right]$ as Exp. 1: rate increases by 4 (1), so order $=1$ with respect to $\mathrm{O}_{2}(\mathbf{1})$

NO:
Exp 3 has $3 \times[\mathrm{NO}]$ as Exp. 3: rate has increases by 9 (1), so order $=2$ with respect to NO (1)
(ii) $\quad$ rate $=k\left[\mathrm{O}_{2}\right][\mathrm{NO}]^{2}(\mathbf{1}) \quad 1$
(iii) $k=\frac{\text { rate }}{\left[\mathrm{O}_{2}\right][\mathrm{NO}]^{2}}=\frac{7.10}{0.0010 \times 0.0010^{2}}=7.10 \times 10^{9}(\mathbf{1})$
units: $\mathrm{dm}^{6} \mathrm{~mol}^{-2} \mathrm{~s}^{-1}(\mathbf{1})$
6. (a) $K_{\mathrm{p}}=\frac{\mathrm{p}\left(\mathrm{SO}_{3}\right)^{2}}{\mathrm{p}\left(\mathrm{SO}_{2}\right)^{2} \times \mathrm{p}\left(\mathrm{O}_{2}\right)}$ (1)(1)

1 mark for correct powers but wrong way up.
1 mark for square brackets
(b) An increase in pressure moves equilibrium to the right because there are less gaseous moles on the right hand side (1)
Increased pressures are expensive to generate/safety problems with walls of containers/enables gases to flow (1)
$K_{\mathrm{p}}$ gets less with increasing temperature (1)
$\mathrm{SO}_{2}$ and $\mathrm{O}_{2}$ increase/ $\mathrm{SO}_{3}$ decreases (1)
Equilibrium $\rightarrow$ left to oppose increase in temperature (1)
Forward reaction is exothermic or $\Delta \mathrm{H}$ is -ve /reverse reaction is endothermic or $\Delta \mathrm{H}$ is +ve because $K_{\mathrm{p}}$ gets less with increasing temperature (1)
QoWC: organises relevant information clearly and coherently, using specialist vocabulary where appropriate (1)
(c) $3.0 \times 10^{2}=\frac{\mathrm{p}\left(\mathrm{SO}_{3}\right)^{2}}{10^{2} \times 50}(\mathbf{1})$
$\mathrm{p}\left(\mathrm{SO}_{3}\right)=\sqrt{ }\left(3.0 \times 10^{2} \times 10^{2} \times 50\right)=1225 \mathrm{kPa}(\mathbf{1})$
$\%\left(\mathrm{SO}_{3}\right)=100 \times 1225 /(1225+10+50)=95 \%(\mathbf{1})$
(d) (i) $2 \mathrm{ZnS}+3 \mathrm{O}_{2} \rightarrow 2 \mathrm{ZnO}+2 \mathrm{SO}_{2}$ (1)(1) $\mathrm{ZnS}, \mathrm{O}_{2}$ as reactants and $\mathrm{SO}_{2}$ as a product: 1st mark. ZnO and balance: $2^{\text {nd }}$ mark 2
(ii) ZnS is more available than S . (1) 1
7. (a) (i) $\mathrm{O}_{3}: 1$ and $\mathrm{C}_{2} \mathrm{H}_{4}(\mathbf{1})$
(ii) 2 (1) 1
(iii) rate $=\mathrm{k}\left[\mathrm{O}_{3}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right](\mathbf{1}) \quad 1$
(b) (i) measure gradient/tangent (1)

$$
\text { at } t=0 / \text { start of reaction }(\mathbf{1})
$$

(ii) $\mathrm{k}=\frac{\text { rate }}{\left[\mathrm{O}_{2}\right]\left[\mathrm{C}_{2} \mathrm{H}_{4}\right]}$
$\mathrm{k}=\frac{1.0 \times 10^{-12}}{0.5 \times 10^{-7} \times 1.0 \times 10^{-8}}=2 \times 10^{3}(\mathbf{1}) \mathrm{dm}^{3} \operatorname{mol}^{-1} \mathrm{~s}^{-1}(\mathbf{1})$
(iii) 2 mol CH 2 O forms for every $0.5 \mathrm{~mol} \mathrm{O}_{2} /$
stoichiometry of $\mathrm{CH}_{2} \mathrm{O}: \mathrm{O}_{2}$ is not $1: 1(\mathbf{1})$
(iv) rate increases (1) k increases (1)
8. (i) each atom has two unpaired electrons (1)
(ii) 2 oxygen atoms bonded by double bond (1)
third oxygen bonded by a covalent bond and outer shells correct (1) For $2^{\text {nd }}$ mark, all O atoms must have an octet.
A triangular molecule would have 3 single covalent bonds for $1^{\text {st }}$ mark but the origin of each electron must be clear for $2^{\text {nd }}$ mark
(iii) amount of $\mathrm{O}_{3}$ in $150 \mathrm{~kg}=150 \times 10^{3} / 48=3.13 \times 10^{3} \mathrm{~mol}$ (1)
amount of Cl radicals in $1 \mathrm{~g}=1 / 35.5=2.82 \times 10^{-2} \mathrm{~mol}(\mathbf{1})$
1 mol Cl destroys $3.13 \times 10^{3} / 2.82 \times 10^{-2}=1.11 \times 10^{5} \mathrm{~mol} \mathrm{O}_{3}$
1 Cl radical destroys $1.11 \times 10^{5} \mathrm{O}_{3}$ molecules (1)
(calculator: 110937)
9. (a) High Pressure

Equilibrium $\rightarrow$ right as fewer moles on right hand side and the shift reduces number of molecules/compensates for increasing pressure (1)
Rate increases/ more collisions (1)

## High temperature

Equilibrium $\rightarrow$ left as equilibrium goes to the left to compensate for increased temperature/absorbs the energy/in endothermic direction (ora) (1)
Rate increases/ more successful collisions (1)

## Other effect

High pressures expensive/ high temperatures expensive
/high pressures cause safety problems (1)
QWC: One correct statement followed by correct explanation (1)
(b)
$\begin{array}{lll}\text { (i) } & \mathrm{CO} & \mathrm{H}_{2} \\ & 1.0 & 2.0 \\ & 0.9 & 1.8(\mathbf{1}) \\ & 0.9 / 2.8 \text { or } 0.321 & \text { or } 0.32 / 0.3 \\ 0.64 / 0.6 & 0.1 / 2.8 \text { or } 0 \\ 3.21(\mathrm{MPa}) & 6.43(\mathrm{MPa}) \\ & \text { In } 3^{\text {rd }} \text { and } 4^{\text {th }} \text { rows, ecf from pr } \\ & & \\ \text { (ii) } & \mathrm{K}_{\mathrm{p}}=\frac{\mathrm{p}\left(\mathrm{CH}_{3} \mathrm{OH}\right)}{\mathrm{p}(\mathrm{CO}) \times \mathrm{p}\left(\mathrm{H}_{2}\right)^{2}} & \end{array}$
1 mark for $K_{\mathrm{c}}$ / use of any [ ]/inverted/power missing.
(iii) $\quad K_{\mathrm{p}}$ stays the same (1)
Equilibrium position moves to the right/yield increases (1) in response to increase in reactants (1)
$K_{\mathrm{p}}=\frac{0.261}{3.70 \times 5.10^{2}}=2.71 \times 10^{-3}(\mathbf{1}) \mathrm{MPa}^{-2}(\mathbf{1})$
(iv) calc value $2.7120546 \times 10^{-3}$; answer and/or units ecf from (ii)
(c) $\mathrm{CH}_{3} \mathrm{OH}+1.5 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}(\mathbf{1}) \quad 1$

