## Chapter 8: Equilibrium

## Homework marking scheme

1 a i $\Delta H_{\text {reaction }}=\Delta H_{\mathrm{f}}($ products $)-\Delta H_{\mathrm{f}}($ reactants $)$
$=2(+33.2)-9.2$
$=+57.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$
ii The equilibrium will shift to the right-hand side
because the forward reaction is endothermic.
Heating favours the reaction that cools down (Le Chatelier's principle)
iii Equilibrium shifts to the right-hand side and the pressure of the $\mathrm{NO}_{2}$ will increase.
Therefore, $K_{\mathrm{p}}$ will increase.
b Any two from:
The system is a closed system.
The rate of forward reaction $=$ rate of backward reaction.
The macroscopic properties, pressure, temperature, etc. are constant.
c i $\quad K_{\mathrm{p}}=\frac{P^{2}\left(\mathrm{NO}_{2}\right)}{P\left(\mathrm{~N}_{2} \mathrm{O}_{4}\right)}$
units $=\mathrm{Pa}$, because $K_{\mathrm{p}}=\frac{(\text { pressure })^{2}}{\text { pressure }}$
ii $\quad \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$

|  | $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ | $2 \mathrm{NO}_{2}(\mathrm{~g})$ | Explanation |
| :--- | :--- | :--- | :--- |
| At start | 1 mol | 0 mol |  |
| At equilibrium | $1-0.8 \mathrm{~mol}$ <br> $=0.2 \mathrm{~mol}$ | 1.6 mol | for every mol of $\mathrm{N}_{2} \mathrm{O}_{4}$ converted, 2 mol <br> of $\mathrm{NO}_{2}$ are formed <br> total quantity of gases $=1.8 \mathrm{~mol}$ |

partial pressure of $\mathrm{N}_{2} \mathrm{O}_{4}=1 \times 10^{5} \times \frac{0.2}{1.8}=0.111 \times 10^{5} \mathrm{~Pa}$
partial pressure of $\mathrm{NO}_{2}=(1-0.111) \times 10^{5} \mathrm{~Pa}=0.889 \times 10^{5} \mathrm{~Pa}$
$K_{\mathrm{p}}=\frac{\left(0.889 \times 10^{5}\right)^{2}}{0.111 \times 10^{5}}$
$=7.12 \times 10^{5} \mathrm{~Pa}$
iii In this question $K_{\mathrm{p}}$ remains constant because the temperature remains constant, only $P$
changes

|  | $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ | $2 \mathrm{NO}_{2}(\mathrm{~g})$ | Explanation |
| :--- | :--- | :--- | :--- |
| At start | 1 mol | 0 mol |  |
| At equilibrium | $1-0.2 \mathrm{~mol}$ <br> $=0.8 \mathrm{~mol}$ | 0.4 mol | For every mol of $\mathrm{N}_{2} \mathrm{O}_{4}$ converted, 2 mol <br> of $\mathrm{NO}_{2}$ are formed <br> total quantity of gases $=1.2 \mathrm{~mol}$ |

partial pressure of $\mathrm{N}_{2} \mathrm{O}_{4}=\frac{0.8}{1.2} \times P=0.667 P$
partial pressure of $\mathrm{NO}_{2}=\frac{0.4}{1.2} \times P=0.333 P$
$K_{\mathrm{p}}=\frac{(0.333 P)^{2}}{0.667 P}=7.12 \times 10^{5} \mathrm{~Pa}$
new pressure $=42.6 \times 10^{5} \mathrm{~Pa}$
iv The new pressure is higher than before, which would favour the side of the equilibrium with fewer gas molecules.
Therefore, there is a lower conversion of $\mathrm{N}_{2} \mathrm{O}_{4}$ into $\mathrm{NO}_{2}$.
d $\mathbf{i}$ The oxidation state of nitrogen in $\mathrm{NO}_{2}=+4$
in $\mathrm{NaNO}_{2}$ it is +3 , therefore reduced
in $\mathrm{NaNO}_{3}$ it is +5 , therefore oxidised; hence, a redox reaction.
ii number of mol of $\mathrm{NaOH}=$ number of mol of $\mathrm{NO}_{2}=\frac{480}{24000}=0.02 \mathrm{~mol}$

$$
\begin{equation*}
V=\frac{n}{C}=\frac{0.02}{0.25} \tag{1}
\end{equation*}
$$

$$
\begin{equation*}
=0.0800 \mathrm{dm}^{3} \text { or } 80 \mathrm{~cm}^{3} \tag{1}
\end{equation*}
$$

$2 \quad$ a $\quad K_{\mathrm{p}}=\frac{P^{2}\left(\mathrm{NH}_{3}\right)}{P\left(\mathrm{~N}_{2}\right) \times P^{3}\left(\mathrm{H}_{2}\right)}$
Unit is $\mathrm{Pa}^{-2}$ because $K_{\mathrm{p}}=\frac{(\text { pressure })^{2}}{(\text { pressure })^{4}}$
b

|  | $\mathrm{N}_{2}(\mathrm{~g})$ | $3 \mathrm{H}_{2}(\mathrm{~g})$ | $2 \mathrm{NH}_{3}(\mathrm{~g})$ |  |
| :--- | :--- | :--- | :--- | :--- |
| Number of <br> mol | $1-0.15=0.85$ | $3-0.45=2.55$ | 0.30 | total number <br> of mol $=3.7$ |
| Partial <br> pressures | $\frac{0.85}{3.7} \times 2 \times 10^{7}$ <br> $=4.59 \times 10^{6} \mathrm{~Pa}$ | $\frac{2.55}{3.7} \times 2 \times 10^{7}$ <br> $=1.38 \times 10^{7} \mathrm{~Pa}$ | $\frac{0.30}{3.7} \times 2 \times 10^{7}$ <br> $=1.62 \times 10^{6} \mathrm{~Pa}$ |  |

Therefore, $K_{\mathrm{p}}=\frac{\left(1.62 \times 10^{6}\right)^{2}}{\left(4.59 \times 10^{6}\right) \times\left(1.38 \times 10^{7}\right)^{3}}=2.18 \times 10^{-16} \mathrm{~Pa}^{-2}$
c The extent to which the equilibrium moves to the right-hand side (the products).
d A decrease in $K_{\mathrm{p}}$ means a lower yield of products.
Increasing the temperature favours the backward reaction.
Therefore, the backward reaction is endothermic.
The forward reaction is exothermic.
e i The yield of ammonia would decrease
because the decrease in pressure would favour the side of the reaction with more molecules to counteract the decrease in pressure (Le Chatelier's principle).
ii $\quad K_{\mathrm{p}}$ does not change.
Only temperature affects the value of $K_{\mathrm{p}}$.
f i

three dot-cross bonds
the lone pair on the nitrogen
ii

three dot-cross bonds
dative covalent bond with fourth hydrogen
g The lone pair on the nitrogen in ammonia repels the covalent bonds more than the dative covalent bond in the ammonium ion.
Therefore, the bond angle in ammonia is less than in the ammonium ion.
h

correct dipoles
lone pair electrons on the nitrogen with the hydrogen bond
hydrogen bond as a dashed line.
3 a $+90 \mathrm{~kJ} \mathrm{~mol}^{-1}$
2 mol of NO are formed from its constituent elements in their standard states. Therefore, divide by 2 .
b i $\quad K_{\mathrm{c}}=\frac{[\mathrm{NO}]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{O}_{2}\right]}$
No units
ii $\quad[\mathrm{NO}]^{2}=\left[\mathrm{N}_{2}\right]\left[\mathrm{O}_{2}\right] \times K_{\mathrm{c}}$
$[\mathrm{NO}]=\sqrt{\left(3.59 \times 10^{-2}\right) \times\left(8.42 \times 10^{-3}\right) \times\left(4 \times 10^{-31}\right)}=1 \times 10^{-17} \mathrm{~mol} \mathrm{dm}^{-3}$
rearranging formula to give [ NO ]
correct answer
units.
iii $[\mathrm{NO}]=1 \times 10^{-17} \mathrm{~mol} \mathrm{dm}^{-3}=1 \times 10^{-17} \times 10^{3} \mathrm{~mol} \mathrm{~m}^{-3}$ $=6.023 \times 10^{23} \times 1 \times 1 \times 10^{-17} \times 10^{3}$ particles $=6.023 \times 10^{9}$ particles per $\mathrm{m}^{3}$ converting the number of moles per $\mathrm{dm}^{3}$ to per $\mathrm{m}^{3}$ finding the number of particles using Avogadro's constant.
c i $2 \mathrm{NO}+\mathrm{Br}_{2} \rightarrow 2 \mathrm{NOBr}$
ii nitrogen: its oxidation state increases from +2 to +3 , therefore oxidised
bromine: its oxidation decreases from 0 to -1 , therefore reduced; combination means a redox reaction.
iii
$: \ddot{\mathrm{Br}} \times \times \times \times{ }^{\times} \times$
double bond between N and O (two pairs of electrons)
single $\mathrm{N}-\mathrm{Br}$ bond (one pair of electrons)
all three atoms having outer octet.
iv


The shape is non-linear
around the central nitrogen the electron count is: $\mathrm{N}=5 \mathrm{e} ; \mathrm{O}=2 \mathrm{e} ; \mathrm{Br}=1 \mathrm{e}$
less 2 e for the double bond gives a total of 6 e , in three pairs.
The bond angle is less than $120^{\circ}$ because of the lone pair on the central nitrogen.

