Equilibrium Review

Sulfuric acid, H_2SO_4, is made industrially by the Contact process. This reaction is an example of a dynamic equilibrium:

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -98\ KJmol^{-1}$$

(a) State two features of a reaction with a dynamic equilibrium.

- The concentrations of the reactants and the products remain the same.
- The rate of the forward reaction is the same as the rate of the reverse reaction

(b) State and explain what happens to the equilibrium position of this reaction as:

i) the temperature is raised

moves to the left because the forword reaction is exothermic

ii) the pressure is increased

moves to the right because there are fewer molecules of gas on the right

iii) Suggest the optimum conditions for the Contact process

Low temp and high pressure

(c) (i) The conditions used for the Contact process are a temperature of 450°C to 600°C and a pressure of around 10 atmospheres.
Explain why the optimum conditions are not used.

Temp. A compromise is reached between rate and conversion. At low temp the rate is too slow.

Pressure - a compromise is reached between cost and conversion

Catalyst - a catalyst is used to speed up the rate of conversion so that it is cost effective to work at a low pressure.

(ii) Vanadium (v) oxide is used as a catalyst. What effect does this have on the conversion of $SO_2(g)$ into $SO_3(g)$.

The catalyst speeds up the reaction, but it doesn't change the equilibrium position because it speeds up the forward and

(iii) At least three catalyst chambers are used to ensure maximum conversion of $SO_2(g)$. The conversion yield can exceed 98%. State two advantages of this high conversion rate.

More cost efficient and reduces the amount of SO_2 pollution.

reverse reactions equally

Le Chatelier's Principle

Hydrogen and Iodine react according to the equation:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \quad \Delta H = +530\ KJmol^{-1}$$

(a) State Le Chatelier's principle When a system in dynamic equilibrium is subjected to a change, the position of equilibrium will shift to minimise the change

(b) Use Le Chatelier's principle to predict what happens to the position of the equilibrium when:

(i) the temperature is increased
moves to the right - forward reaction is endothermic

(ii) the pressure is increased
No effect - equal number of moles of gas on both sides

(iii) a catalyst is used
Does not alter the position of equilibrium speeds up the rate of the forward and reverse reactions equally

Justify each of your predictions.

(c) Write an expression for K_c for the equilibrium. State the units, if any.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Writing expressions for K_c

For each of the following reactions, write an expression for K_c. Assuming that the units of concentration are mol dm^{-3}, work out the units for K_c in each case. If there are no units, state this.

1. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

2. $2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)$

3. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

4. $4PF_5(g) \rightleftharpoons P_4(g) + 10F_2(g)$

5. $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

6. $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Look at all the examples in which K_c has no units. What do all these reactions have in common?

Writing expressions for K_c

For each of the following reactions, write an expression for K_c. Assuming that the units of concentration are mol dm^{-3}, work out the units for K_c in each case. If there are no units, state this.

1. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

$$K_c = \frac{[H_2(g)][Br_2(g)]}{[HBr(g)]^2}$$

no units

2. $2NH_3(g) \rightleftharpoons 3H_2(g) + N_2(g)$

$$K_c = \frac{[H_2(g)]^3[N_2(g)]}{[NH_3]^2}$$

$mol^2\ dm^{-6}$

3. $NH_3(g) \rightleftharpoons 1\tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,N_2(g)$

$$K_c = \frac{[H_2(g)]^{1.5}[N_2(g)]^{0.5}}{[NH_3]}$$

$mol\ dm^{-3}$

4. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

$$K_c = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]}$$

$mol^{-1}\ dm^{+3}$

5. $4PF_5(g) \rightleftharpoons P_4(g) + 10F_2(g)$

$$K_c = \frac{[P_4(g)][F_2(g)]^{10}}{[PF_5(g)]^4}$$

$mol^7\ dm^{-21}$

6. $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

$$K_c = \frac{[N_2(g)][O_2(g)]}{[NO(g)]^2}$$

no units

7. $C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

$$K_c = \frac{[CH_3COOC_2H_5(l)][H_2O(l)]}{[C_2H_5OH(l)][CH_3COOH(l)]}$$

no units.

Look at all the examples in which K_c has no units. What do all these reactions have in common? Same no. of moles at each side of equation

Looking at K_c Values

1. Consider the equilibrium:

$CH_3COOH(aq) + CH_3CH_2OH(aq) \Leftrightarrow CH_3COOCH_2CH_3(aq) + H_2O(l)$

a) Write an expression for K_c for the esterification process.

$$K_c = \frac{[CH_3COOCH_2CH_3][H_2O]}{[CH_3COOH][CH_3CH_2OH]}$$

b) Write an expression for K_c for the hydrolysis process.

$$K_c' = \frac{[CH_3COOH][CH_3CH_2OH]}{[CH_3COOCH_2CH_3][H_2O]}$$

c) The K_c value for the esterification reaction is 4.0 at 298K. What is the K_c for the hydrolysis reaction at 298K?

$1/4$

d) Why is it important to quote the temperature?

K_c alters with T

2. Use the data below to answer the questions which follow:

example	K_c at 298K
$H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$	794
$H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$	1.00×10^{-5}
$N_2(g) + O_2(g) \Leftrightarrow 2NO(g)$	4×10^{-31}
$N_2O_4(g) \Leftrightarrow 2NO_2(g)$	$0.05\ mol\ dm^{-3}$

a) The equilibrium position depends on the value of K_c

i) For which of these reactions does the equilibrium lie furthest to the left?

$N_2 + O_2 \rightleftharpoons 2NO$

ii) Where does this reaction take place?

Atmosphere

b) What is the K_c value, and units, for the reaction: $2NO_2(g) \Leftrightarrow N_2O_4(g)$ at 298K

$1/0{\cdot}05\ mol^{-1}\ dm^3$

The effect of Temperature on K_c

3. $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

The K_c values for this reaction at four different temperatures are shown below:

temperature/K	K_c
298	794
500	160
700	54
1100	25

$H_2(g) + CO_2(g) \Leftrightarrow H_2O(g) + CO(g)$

The K_c values for this reaction at four different temperatures are shown below:

temperature/K	K_c
298	1.00×10^{-5}
500	7.76×10^{-3}
800	2.88×10^{-1}
900	6.03×10^{-1}

a) For which of these reactions is the forward reaction endothermic?
Explain your answer

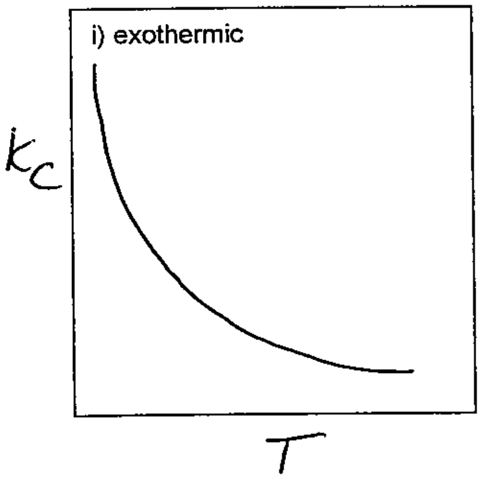
$H_2(g) + CO_2(g) \longrightarrow H_2O(g) + CO(g)$

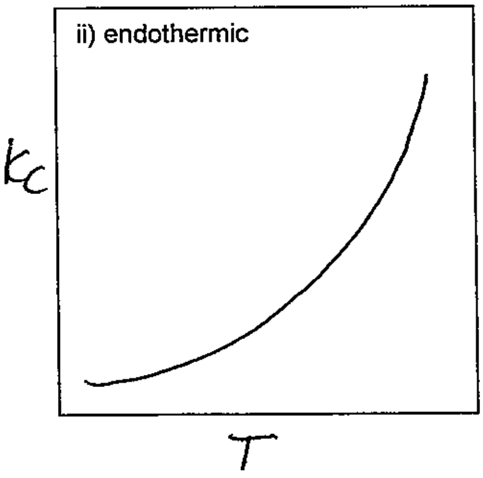
As temp ↑ K_c increases.

b) Sketch graphs in the boxes below to show the change in K_c with temperature for

i) an exothermic
ii) an endothermic reaction.

Label the axes





Kc Calculations

Calculating K_c values from equilibrium concentrations

1. Equilibrium was established at 308K for the system:

$$CO(g) + Br_2(g) \rightleftharpoons COBr_2(g)$$

Analysis of the mixture gave the following concentration values:
$[CO(g)]$ = 8.78×10^{-3} mol dm^{-3}
$[Br_2(g)]$ = 4.90×10^{-3} mol dm^{-3}
$[COBr_2(g)]$ = 3.40×10^{-3} mol dm^{-3}
Calculate the value of the equilibrium constant.

79.0 mol^{-1}dm^{+3}

2. At 250^{0}C, equilibrium for the following system was established:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Analysis of the mixture showed that
$[PCl_3(g)]$ = 1.50×10^{-2} mol dm^{-3}
$[Cl_2(g)]$ = 1.50×10^{-2} mol dm^{-3}
$[PCl_5(g)]$ = 1.18×10^{-3} mol dm^{-3}
Calculate the value of the equilibrium constant.

0.191 mol dm^{-}

Calculating an equilibrium concentration from Kc

3. For the equilibrium:

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

K_c = 0.19 mol dm^{-3} at 250^{0}C.
One equilibrium mixture at this temperature contains PCl_5 at a concentration of 0.20 mol dm^{-3} and PCl_3 at a concentration of 0.010 mol dm^{-3}.
Calculate the concentration of the chlorine in this mixture.

$$Kc = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

$$\therefore [Cl_2(g)] = \frac{Kc \times [PCl_5(g)]}{[PCl_3(g)]}$$

3.8 mol dm^{-3}

4. For the equilibrium:

$$2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$$

K_c = 2.25×10^{-4} mol dm^{-3} at 1400K.
In an equilibrium mixture,
$[H_2S(g)]$ = 4.84×10^{-3} mol dm^{-3} and
$[S_2(g)]$ = 2.33×10^{-3} mol dm^{-3}.
Calculate the equilibrium concentration of hydrogen.

$$[H_2(g)] = \sqrt{\frac{Kc \times [H_2S]^2}{[S_2(g)]}}$$

1.50×10^{-3} mol dm

Calculating K_c values from equilibrium numbers of moles

5. Some phosphorus (V) chloride was heated to 250⁰C in a sealed container until equilibrium was reached according to the following equation.

$Kc = \frac{[\frac{0.040}{2}][\frac{0.040}{2}]}{[\frac{0.0042}{2}]}$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Analysis of the mixture showed that it contained 0.0042 mol of $PCl_5(g)$, 0.040 mol of $PCl_3(g)$ and 0.040 mol of $Cl_2(g)$. The total volume was 2.0 dm^3. Calculate the concentration of each component and hence determine K_c.

$= 0·190$ mol dm^{-3}

6. At 250⁰C, in another equilibrium mixture of the reaction

$Kc = \frac{[\frac{0.15}{2}][\frac{0.090}{2}]}{?}$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

in a 2.0 dm^3 vessel, there is 0.15 mol of $PCl_3(g)$ and 0.090 mol of $Cl_2(g)$.

K_c = 0.19 mol dm^{-3} at 250⁰C.

Calculate the number of moles of $PCl_5(g)$ present at equilibrium.

$? = \frac{[\frac{0.15}{2}][\frac{0.090}{2}]}{0.19}$

$= 0·0178$ ×2 $= 0·0355$

7. The table below shows the composition of two equilibrium mixtures at 485⁰C.

Mixture	No. of moles of $H_2(g)$	No. of moles of $I_2(g)$	No. of moles of $HI(g)$
1	0.02265	0.02840	0.1715
2	0.01699	0.04057	0.1779

a) Write the equation for the formation of hydrogen iodide from hydrogen and iodine. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

b) Write an expression for the equilibrium constant, K_c.

c) For mixture 1, calculate a value for the equilibrium constant, assuming that the total volume is 2.0 dm^3. will cancel 45·72 no units

d) For mixture 2, calculate a value for the equilibrium constant, assuming that the total volume is V dm^3. will cancel 45·91 no units.

8. This question concerns the equilibrium system

$$C_2H_5OH(l) + CH_3COOH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

K_c = 4.0 at 25⁰C

$4.0 = \frac{[0.66][0.66]}{[0.33][alcohol]}$

In a particular experiment, 0.33 mol of $CH_3COOH(l)$, 0.66 mol of $CH_3COOC_2H_5(l)$ and 0.66 mol of $H_2O(l)$ are found to be present. Assuming that the total volume is V dm^3, calculate the number of moles of $C_2H_5OH(l)$ present. 0·33

↑ cancels!

$[alcohol] = \frac{[0.66]^2 \times 0.33}{4.0}$

$= 0·33$

Are there any situations where numbers of moles can be used to calculate K_c without having to be converted to concentrations first?

equal moles on both sides of the balanced equation.

Calculating Kc from Initial amounts

1. 1 mole of ethanoic acid was added to 0.5 moles of ethanol and left in a stoppered flask until equilibrium was reached. At equilibrium 0.58 moles of ethanoic acid were left. Calculate Kc for the reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOCH_2CH_3(l) + H_2O(l)$$

	$CH_3COOH(l)$	$CH_3CH_2OH(l)$	$CH_3COOCH_2CH_3(l)$	$H_2O(l)$
(i)Initial moles	1	0.5	0	0
	−0.42	−0.42	+0.42	+0.42
(ii)Eqm moles	0.58	0.08	0.42	0.42

(iii) Write down the concentrations at equilibrium in moldm^{-3}: assume the total volume is Vdm^3

$CH_3COOH(l)$ $\frac{0.58}{V}$

$CH_3CH_2OH(l)$ $\frac{0.08}{V}$

$CH_3COOCH_2CH_3(l)$ $\frac{0.42}{V}$

$H_2O(l)$ $\frac{0.42}{V}$

(iv) Write the expression for Kc

$$Kc = \frac{[CH_3COOCH_2CH_3]\,[H_2O]}{[CH_3COOH]\,[CH_3CH_2OH]}$$

(v) Use the values in (iii) to calculate Kc and give its units

$$Kc = \frac{\frac{0.42}{\cancel{V}} \times \frac{0.42}{\cancel{V}}}{\frac{0.58}{\cancel{V}} \times \frac{0.08}{\cancel{V}}}$$

$= 3.8$ no units.

2. 24.0g of ethanoic acid was added to 13.8g of ethanol and left in a stoppered flask until equilibrium was reached. At equilibrium 20.0g of ethyl ethanoate were produced Calculate Kc for the reaction:

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOCH_2CH_3(l) + H_2O(l)$$

(i) Calculate the moles of each substance using the mass provided and Mr:

$CH_3COOH(l)$ $\frac{24.0}{60} = 0.4$ $CH_3CH_2OH(l)$ $\frac{13.8}{46} = 0.3$

$CH_3COOCH_2CH_3(l)$ $\frac{20.0}{88} = 0.227$

$$CH_3COOH(l) + CH_3CH_2OH(l) \rightarrow CH_3COOCH_2CH_3(l) + H_2O(l)$$

(i)Initial moles	0.4	0.3	0	0
	−0.227	−0.227	+0.227	+0.227
(ii)Eqm moles	0.173	0.073	0.227	0.227

(iii) Write down the concentrations at equilibrium in moldm^{-3}: assume the total volume is Vdm^3

$CH_3COOH(l)$ $\frac{0.173}{V}$ $CH_3CH_2OH(l)$ $\frac{0.073}{V}$ ∴ V will cancel.

$CH_3COOCH_2CH_3(l)$ $\frac{0.227}{V}$ $H_2O(l)$ $\frac{0.227}{V}$

(iv) Write the expression for Kc

$$Kc = \frac{[CH_3COOCH_2CH_3(l)][H_2O(l)]}{[CH_3COOH(l)][CH_3CH_2OH(l)]}$$

(v) Use the values in (iii) to calculate Kc and give its units

$$= \frac{0.227 \times 0.227}{0.173 \times 0.073}$$

$= 4.08$ no units.

3. 417g of PCl_5 vapour was heated in a vessel of volume $20dm^3$ at 500K. At equilibrium 85.2g of Cl_2 were present. Calculate Kc for the reaction:

$$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$$

(i) Calculate the moles of each substance from the masses provided:

PCl_5 $\frac{417}{208.5} = 2$ Cl_2 $\frac{85.2}{71} = 1.2$

	$PCl_5(g)$	$\rightarrow$ $PCl_3(g)$	+ $Cl_2(g)$
(ii)Initial moles	2	0	0
	− 1.2	+ 1.2	+ 1.2
(iii)Eqm moles	0.8	1.2	1.2
(iv)Eqm concs	$\frac{0.8}{20} = 0.04$	$\frac{1.2}{20} = 0.06$	$\frac{1.2}{20} = 0.06$

(iv) Write the expression for Kc

$$Kc = \frac{[PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$$

(v) Use the values in (iii) to calculate Kc and give its units

$$\frac{mol\,dm^{-3} \times \cancel{mol\,dm}}{\cancel{mol\,dm^{-3}}}$$

$$Kc = \frac{0.06 \times 0.06}{0.04}$$

$$= 0.09 \ mol\,dm^{-3}$$

4. 2g of H_2 and 254g of I_2 vapour were heated in a vessel of volume 5 dm^3 at 600K. At equilibrium 204.8g of HI were present. Calculate Kc for the reaction:

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

(i) Calculate the moles of each substance using the masses provided and the M_r:

$H_2(g)$ $\frac{2}{2} = 1$

$I_2(g)$ $\frac{254}{254} = 1$

$HI(g)$ $\frac{204.8}{128} = 1.6$

	$H_2(g)$ +	$I_2(g)$ →	$2HI(g)$
(ii)Initial moles	1	1	0
	$-\frac{1.6}{2}$	$-\frac{1.6}{2}$	$+1.6$
(iii)Eqm moles	0·2	0·2	1·6
(i[illegible] Eqm [illegible]	$\frac{0.2}{5}$	$\frac{0.2}{5}$	$\frac{1.6}{5}$

but V will cancell out so can compare moles

(iv) Write the expression for Kc

$$Kc = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

(v) Use the values in (iii) to calculate Kc and give its units

$$Kc = \frac{\left[\frac{1.6}{5}\right]^2}{\left[\frac{0.2}{5}\right]\left[\frac{0.2}{5}\right]} = 64 \text{ no units.}$$

Equilibrium Data for Kc

Initial moles of acid **(a)**	Initial moles of alcohol **(b)**	Moles of acid at $\equiv^{m}$ **(a-x)**	Moles of alcohol at $\equiv^{m}$ **(b-x)**	Moles of ester at $\equiv^{m}$ **(x)**	Moles of water at $\equiv^{m}$ **(x)**	Kc
1.00	0.18	0.829	0·009	0·171	0·171	3·92
1.00	0.33	0.707	0·037	0·293	0·293	3·28
1.00	0.50	0.586	0·086	0·414	0·414	3·40
1.00	1.00	0.333	0·333	0·667	0·667	4·01
1.00	2.00	0.142	1·142	0·858	0·858	4·54
1.00	8.00	0.034	7·034	0·966	0·966	3·90

Values vary! experimental error!

NB. As the amount of alcohol added is increased the equilibrium shifts further to the right so the amount of products formed should also increase and the amount of acid left unreacted decreases.

On the addition of 8 moles of alcohol the reaction is virtually complete ie. nearly 1 mole of ester and water are formed.

Equilibria Examination Questions Answers M6 EQ30E

<table>
<tr><th>Question</th><th>Expected Answers</th><th>Marks</th></tr>
<tr><td>1 (a)</td><td>$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]}$ ✓✓
award 1 mark if upside down</td><td>[2]</td></tr>
<tr><td>(b) (i)</td><td><table>
<tr><td>CH_3COOH</td><td>C_2H_5OH</td><td>$CH_3COOC_2H_5$</td><td>H_2O</td></tr>
<tr><td>6.0</td><td>12.5</td><td>0</td><td>0</td></tr>
<tr><td>1</td><td>7.5</td><td>5</td><td>5</td></tr>
<tr><td colspan="2">✓</td><td colspan="2">✓</td></tr>
</table></td><td>[2]</td></tr>
<tr><td>(ii)</td><td>$K_c = \frac{5 \times 5}{1 \times 7.5}$ = 3.3 ✓ no units ✓
(or ecf based on answers to (i) and/or (a))</td><td>[2]</td></tr>
<tr><td>(c)</td><td>leave experiment longer ✓
monitor compositions and repeat until constant value ✓</td><td>[2]</td></tr>
<tr><td>(d) (i)</td><td>more $CH_3COOC_2H_5$ & H_2O / less CH_3COOH & C_2H_5OH ✓
equilibrium ⟶ right ✓ AW</td><td>[2]</td></tr>
<tr><td>(ii)</td><td>K_c stays same ✓</td><td>[1]</td></tr>
<tr><td>(e)</td><td>stays the same/
catalyst does not shift equilibrium position ✓
forward & reverse reactions altered by same amount/
equilibrium achieved in less time ✓</td><td>[2]</td></tr>
<tr><td>(f) (i)</td><td>equilibrium ⟶ left ✓
more reactants / less products ✓</td><td>[2]</td></tr>
<tr><td>(ii)</td><td>forward reaction is exothermic ✓</td><td>[1]</td></tr>
<tr><td></td><td></td><td>Total: 16</td></tr>
</table>

Question	Expected Answers	Marks
2 (a) (i)	$K_c = \frac{[NO]^2}{[N_2]\,[O_2]}$ ✓✓ *award 1 mark if upside down* *K_p expression worth 1 mark*	[2]
(ii)	Equil ⟶ left because K_c is very small	[1]
(iii)	$[O_2(g)] = \frac{[NO]^2}{[N_2] \times K_c} = \frac{(4.0 \times 10^{-16})^2}{1.1 \times 4.8 \times 10^{-31}}$ ✓ = 0.30 mol dm^{-3}✓ (calculator: 0.303030303) answer given to 2 sig figs✓ 3.3 ✓✓ (upside down) calc: 3.3 7.6×10^{14} ✓✓ (missing out ^{2}) calc: 7.5757..... 0.37 ✓✓ (1.1 on top) calc: 0.366666.. 5.2×10^{-48} ✓✓ ('4' values swapped) calc: $5.236363. \times 10^{-48}$	[3]
(b) (i)	ΔH is +ve ✓	
(ii)	equilibrium moves to the right to compensate for increase in temperature/to lower the temperature / to minimise the change ✓ increase in proportion of NO ✓ because K_c increases *Can be linked to either increased proportion of NO or enthalpy change* ✓	[4]
(iii)	$2NO + O_2 \longrightarrow 2NO_2$ ✓✓ *species correct for 1st mark* *'simplest' balanced equation for 2nd mark* $NO + {}^1/_2O_2 \longrightarrow NO_2$ also gets both marks *N_2O_4 is fine* *NO_2 for 1st mark*	[2]

(c)	Optimum Pressure low pressure ✓ fewer gaseous moles on left ✓ Optimum Temperature optimum: low temperature ✓ forward reaction is exothermic ✓ Reason mark can only be awarded if the condition mark is correct. Condition mark is independent 1000°C used to increase rate with more energetic collisions *OR* so that a greater proportion of molecules exceed activation energy ✓ 10 atm used to increase rate by increasing concentration *OR* increasing collisons ✓ Catalyst used to increase rate by lowering the activation energy/providing a lower energy route ✓ *NOT increase equilibrium yield*	[7]
	Quality of written communication: Recognition of a compromise between rate and equilibrium amount ✓	[1]
		Total: 20

3 **(a)** Forward and reverse reactions at same rate ✓

Achievable from either direction ✓, requires closed system ✓

concentrations of reactants and products are constant ✓

max: [2]

(b) **(i)**

$$K_c = \frac{[\,CH_3OH(g)\,]}{[\,CO(g)\,]\,[\,H_2(g)\,]^2}$$ ✓✓ *1 mark for top; 1 mark for bottom*

[2]

(ii)

$$K_c = \frac{(2.6 \times 10^{-5})}{(3.1 \times 10^{-3})\,(2.4 \times 10^{-2})^2}$$ ✓ = 14.6 ✓ ($dm^6\ mol^{-2}$)

[2]

(c) (i) *Why did the equilibrium move to the right*

fewer molecules on right ✓

reaction relieves increase in pressure ✓

[2]

(ii) *What is the effect, if any, on K_c*

K_c stays same ✓

[1]

(iii) *Rate changes*

Rate increases ✓

Increased collisions/more concentrated ✓

Rates initially forward faster than reverse ✓

At equil, rates same ✓

[4]

(d) **(i)** K_c decreases so products decrease/reactants increase ✓

Therefore equilibrium moves to the left/to endothermic side ✓

2nd mark dependent on first.

[2]

(ii) ΔH is negative because of equilibrium change in **(i)** ✓

Mark consequential on (i)

[1]

Abbreviations, annotations and conventions used in the Mark Scheme	/	= alternative and acceptable answers for the same marking point
	;	= separates marking points
	NOT	= answers which are not worthy of credit
	( )	= words which are not essential to gain credit
	___	= (underlining) key words which **<u>must</u>** be used to gain credit
	ecf	= error carried forward
	AW	= alternative wording
	ora	= or reverse argument

4 **(a)** **(i)** $K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$ ✓ [1]

(ii) $K_c = \frac{(0.0150)^2}{(0.0390)} = 5.77 \times 10^{-3}$ ✓ mol dm^{-3} ✓ accept 5.76923 to 5.8×10^{-3}

If (i) is upside down: $\frac{[N_2O_4(g)]}{[NO_2(g)]^2}$, then ans = 173 ✓ $\text{dm}^3\ \text{mol}^{-1}$ ✓ accept 173.33333.....to 170

if no square in (i): $\frac{[NO_2(g)]}{[N_2O_4(g)]}$, then ans = 0.384615..✓ no units ✓ (must be stated)

if no square in (i) and inverse: $\frac{[N_2O_4(g)]}{[NO_2(g)]}$, 2.6 ✓ no units ✓ (must be stated)

[2]

(b) $\Delta H = (2 \times 33) - (9)$ ✓ = (+)57 kJ mol^{-1} ✓

common errors: −57 ✓✗ +24 ✓✗ +75 ✓✗ −24 ✗✗

[2]

(c) *change* more NO_2 / less N_2O_4 ✓

explanation equilibrium position ⟶ right or forwards / K_c increases ✓

reaction is endothermic ✓

THIS ANSWER IS CONSEQUENTIAL ON SIGN OF THE ANSWER TO (i)

BUT, a candidate interpreting a '+' enthalpy change as 'exothermic' (or vice versa) will lose the 3rd mark but the 2 'logic marks' before are still consequentially available.

[3]

(d) 1 mol N_2O_4 reacts with 2 mol NaOH ✓

amount of NaOH required = 0.00930 mol ✓

volume NaOH = 1000 x 0.0093/0.300 = 31.0 cm^3 / 0.0310 dm^3 ✓

Common errors

3.1×10^x (where x is incorrect) ✓✓✗

15.5 cm^3 / 0.0155 dm^3 ✓✓✗ *1.55×10^x (where x is incorrect)* ✓✗✗

62 cm^3 / 0.062 dm^3 ✓✓✗ 6.2×10^x (where x is incorrect) ✓✗✗ [3]

[Total: 11]