

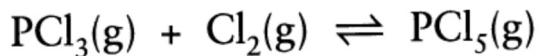
Kirkcaldy High School



Chemistry
Advanced Higher
Unit 2 - Physical Chemistry
TUTORIAL QUESTIONS

(a) Chemical Equilibrium

1. Consider the equilibrium below:

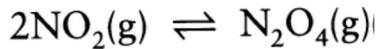


The equilibrium concentrations of the reagents involved, under certain conditions, are:

$$\begin{aligned} [\text{PCl}_3(\text{g})] &= 0.04 \text{ mol l}^{-1} \\ [\text{Cl}_2(\text{g})] &= 0.06 \text{ mol l}^{-1} \\ [\text{PCl}_5(\text{g})] &= 0.12 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , under the above conditions.

2. In the equilibrium:

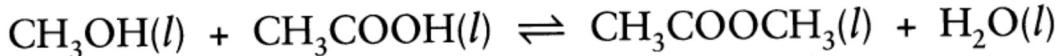


the concentrations of the gases present are:

$$\begin{aligned} [\text{NO}_2(\text{g})] &= 0.05 \text{ mol l}^{-1} \\ [\text{N}_2\text{O}_4(\text{g})] &= 0.4 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , for the reaction under the above conditions.

3. The esterification of methanol and ethanoic acid to form methyl ethanoate and water is represented by the equation below.



At equilibrium, the concentrations of the substances present are:

$$\begin{aligned} [\text{CH}_3\text{OH}(l)] &= 0.2 \text{ mol l}^{-1} \\ [\text{CH}_3\text{COOH}(l)] &= 0.5 \text{ mol l}^{-1} \\ [\text{CH}_3\text{COOCH}_3(l)] &= 1.2 \text{ mol l}^{-1} \\ [\text{H}_2\text{O}(l)] &= 0.8 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , for the reaction under the above conditions.

4. The decomposition of sulphur trioxide is represented by the following equation:

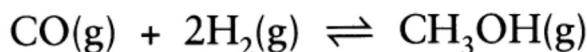


At equilibrium, under certain conditions, the concentrations of the gases are:

$$\begin{aligned} [\text{SO}_3(\text{g})] &= 2 \text{ mol l}^{-1} \\ [\text{SO}_2(\text{g})] &= 4 \text{ mol l}^{-1} \\ [\text{O}_2(\text{g})] &= 2 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , for the reaction under the above conditions.

5. The reaction of carbon dioxide with hydrogen to form methanol is given by the following equation:

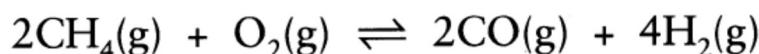


At equilibrium, the concentrations of the gases under certain conditions are:

$$\begin{aligned} [\text{CO(g)}] &= 2.5 \text{ mol l}^{-1} \\ [\text{H}_2(\text{g})] &= 2 \text{ mol l}^{-1} \\ [\text{CH}_3\text{OH(g)}] &= 5 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , for the reaction under the above conditions.

6. The partial oxidation of methane is shown by the equation below.



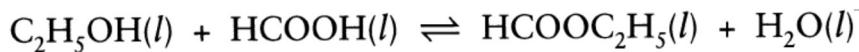
At equilibrium, under certain conditions, the concentrations of the gases are:

$$\begin{aligned} [\text{CH}_4(\text{g})] &= 0.5 \text{ mol l}^{-1} \\ [\text{O}_2(\text{g})] &= 0.6 \text{ mol l}^{-1} \\ [\text{CO(g)}] &= 0.3 \text{ mol l}^{-1} \\ [\text{H}_2(\text{g})] &= 0.2 \text{ mol l}^{-1} \end{aligned}$$

Calculate the equilibrium constant, K_c , for the reaction under the above conditions.

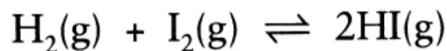
7. 0.2 mol $^{-1}$ of ethanol and 0.2 mol $^{-1}$ of methanoic acid are mixed with a few drops of concentrated sulphuric acid catalyst in an empty reaction vessel. After equilibrium is established, it is found that 0.15 mol $^{-1}$ of the ester, ethyl methanoate, has been formed.

The equation for the reaction taking place is:



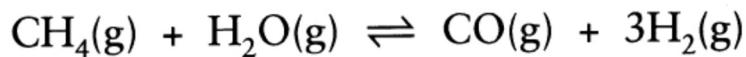
Calculate the equilibrium constant, K_c , for the reaction under these conditions.

8. 1 mol of H₂(g) and 1 mol of I₂(g) are introduced into an empty 1 l reaction chamber in which the following reaction takes place.



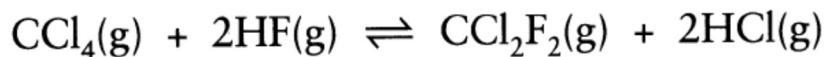
After some time, equilibrium is established and it is found that there is 0.6 mol of HI(g) present in the gas mixture. Calculate the equilibrium constant, K, for the reaction under the above conditions.

9. 0.5 mol of CH₄(g) and 0.5 mol of H₂O(g) are introduced into an empty, 1 litre, reaction chamber in which the reaction below takes place.



When equilibrium is established, it is found that there is 0.15 mol of CO(g) present. Calculate the equilibrium constant, K, for the reaction under these conditions.

10. The industrial production of 'freon', CCl₂F₂(g), is represented by the following equation.



1 mol of CCl₄(g) and 2 mol of HF(g) are introduced into an empty 1 l reaction chamber. When equilibrium is established, it is found that 0.75 mol of 'freon' has been formed. Calculate the equilibrium constant, K, for the reaction under these conditions.

11.

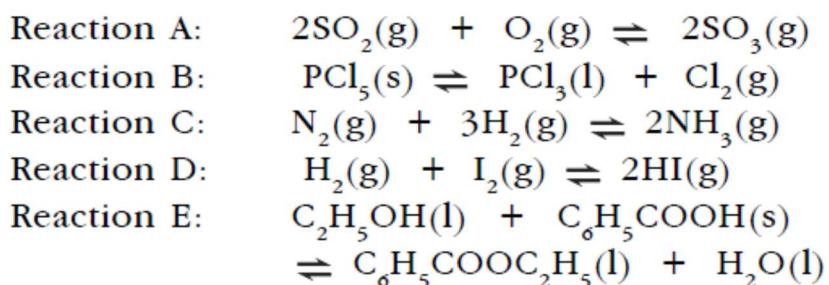
The value for the equilibrium constant, K, for a specific example of the following reaction is equal to 1:



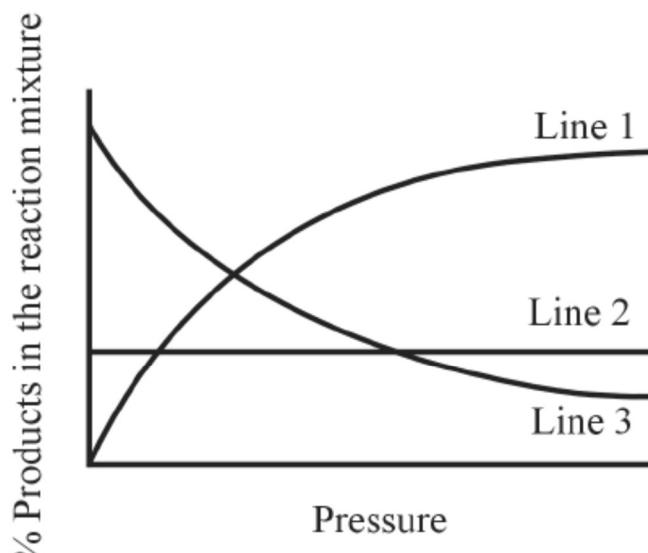
- (a) (i) Predict the maximum yield of ester, given this value of K. 1
(ii) Give **one** reason why this yield might not be achieved in practice. 1
- (b) A student suggested that a careful choice of catalyst could increase the yield of ester. Comment on this suggestion. 2
- (c) Another pupil suggested that increasing the concentration of the alcohol in the reaction mixture would increase the yield of ester by altering the value of K. Comment on this suggestion. 2

(6)

12.



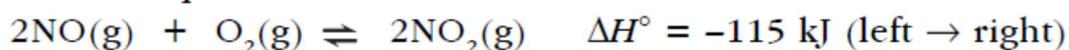
Each line on the graph below shows the effect of changing the pressure on the yield of products for each of the above reactions.



- (a) Allocate a line on the graph (by number) to each reaction (by letter). Explain your choice in each case. **5**
- (b) What effect would removing the catalyst have on the shape of line 1? **1**
- (6)**

13.

For the equilibrium:



established in a closed vessel at a fixed temperature, the equilibrium constant reaction has a value of 15 l mol^{-1} .

- (a) Write an expression for the equilibrium constant K . 2
- (b) What does the magnitude of K indicate? 1
- (c) What effect will increasing the temperature have on the value of the equilibrium constant K ?
Explain your answer. 2
- (d) Calculate the equilibrium concentration of NO_2 when the equilibrium concentrations of NO and O_2 are both 0.1 mol l^{-1} . 2

SY/90
(7)

14.

In the Data Booklet, the solubility of barium sulphate, shown by the equation:



is given as less than 1 g l⁻¹. In a more advanced textbook, it is noticed that an equilibrium constant, known as the solubility product K_{sp} , can be written to represent the dissolving process. K_{sp} is equal to the product of the concentrations of the ions in the solution:

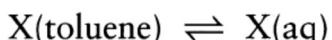
$$K_{\text{sp}} = [\text{Ba}^{2+}] \times [\text{SO}_4^{2-}]$$

- (a) At 298K, K_{sp} for barium sulphate is equal to 1×10^{-10} mol² l⁻². For a saturated solution of barium sulphate at 298K, calculate
- (i) the concentration of the barium ions dissolved in the solution **1**
 - (ii) the mass of barium sulphate dissolved in 1 litre of solution. **3**
- (b) A small quantity of the very soluble sodium sulphate is now added to the saturated solution of barium sulphate.
- (i) What will happen to the value of K_{sp} ? **1**
 - (ii) What will happen to the concentration of barium ions? **1**

SY/96
(6)

15.

Toluene is an organic liquid which is immiscible in water. A different organic substance, X, is soluble in both liquids. A sample of X is shaken up with toluene and water and given time for the equilibrium shown below to stabilise.



Samples of substance X in each of the layers were analysed. The concentration of X in the toluene layer was found to be 0.253 mol l^{-1} . The concentration of X in the aqueous layer was 0.201 mol l^{-1} . Calculate the partition coefficient for the above equilibrium in the ratio $[X(\text{aq})] / [X(\text{toluene})]$.

16.

A monoprotic organic acid, A, is soluble in both ethoxyethane and water. Ethoxyethane and water are immiscible.

The equilibrium relating to the acid between the two solvents is described in the equation below.



A 10 cm^3 sample of each solution was extracted by pipette and titrated with standard 0.10 mol l^{-1} sodium hydroxide solution, $\text{NaOH}(\text{aq})$.

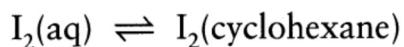
The sodium hydroxide titre of the ethoxyethane layer was 22.3 cm^3 . The titre of the aqueous layer was 14.8 cm^3 .

Calculate:

- the concentration of the organic acid in each of the two layers;
- the partition coefficient for this equilibrium, in the ratio $[A(\text{aq})] / [A(\text{ethoxyethane})]$, under the conditions of this analysis.

17.

Iodine is an element which can dissolve in aqueous potassium iodide solution and cyclohexane, but the two solvents are immiscible. A quantity of iodine was shaken with samples of the two solvents and given time for the equilibrium below to be established.



A 25 cm³ sample was taken from each layer and analysed by titration with standard 0.250 mol l⁻¹ sodium thiosulphate solution, Na₂S₂O₃(aq) using starch as an indicator. (At the endpoint of the titration the blue/black colour of the complex which iodine forms with starch disappears.)

The equation for the titration reaction is:



The titres were as below:

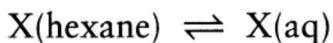
Aqueous layer:	12.4 cm ³
Cyclohexane layer:	18.6 cm ³

Calculate:

- the concentration of iodine in each layer;
- the partition coefficient in the ratio of [I₂(cyclohexane)] / [I₂(aq)].

18.

An organic substance, X, of molecular mass 60, can dissolve both in water and in hexane. The two solvents are immiscible. The equation for the equilibrium is given below.



The partition coefficient for this equilibrium, in the ratio $[X(\text{aq})] / [X(\text{hexane})]$, is 1.42.

A quantity of substance X is shaken up with 50 cm³ of water and 50 cm³ of hexane and left until equilibrium is established.

The concentration of X in the hexane layer is analysed and found to be 0.40 mol l⁻¹.

Calculate:

- the concentration of X in the aqueous layer;
- the mass of X in the aqueous layer.

19. 100 cm³ of a 10% (10g in 100cm³) solution of X in 100 cm³ water is to be extracted using chloroform.

The partition coefficient between water and chloroform is 0.125:

$$K = \frac{[X]_{\text{H}_2\text{O}}}{[X]_{\text{CHCl}_3}} = 0.125$$

Calculate how much more of the solute X can be extracted using 2 x 50 cm³ extractions rather than a 1 x 100 cm³ extraction.

20. Calculate the mass of an organic acid X which can be extracted from 200cm³ of aqueous solution containing 5.0g of X by shaking it with

- 200cm³ of a solvent in one portion.
- two 100cm³ portions of the solvent.

21. The partition coefficient between the solvent and water

$$K = \frac{[X]_{\text{org}}}{[X]_{\text{aq}}} = 3.0$$

Calculate the pH of a solution of a 0.20 mol l⁻¹ solution of hydrochloric acid, HCl.

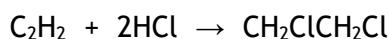
22. The concentration of hydrogen ions in a solution is $6.24 \times 10^8 \text{ mol l}^{-1}$. Calculate the pH of the solution.
23. A weak acid solution has a hydrogen ion concentration of $3.82 \times 10^{-5} \text{ mol l}^{-1}$. Calculate the pH of the solution.
24. Calculate the pH of a 0.182 mol l^{-1} solution of sulphuric acid, H_2SO_4 .
25. A solution of sulphuric acid, H_2SO_4 , has a concentration of 1.25 mol l^{-1} . Calculate the pH of the solution.
26. A solution of nitric acid, HNO_3 has a pH of 1.57. Calculate the concentration of hydrogen ions present.
27. A lactic acid solution has a pH of 4.87. Calculate the concentration of hydrogen ions in the solution.
28. Calculate the concentration of hydrogen ions in a solution with a pH of 9.8.
29. What is the concentration of hydrogen ions in an alkali solution with a pH of 12.97?
30. A hydrochloric acid solution has a pH of -0.152. Calculate the concentration of the solution.
31. A sodium hydroxide solution, NaOH , has a pH of 12.3. Calculate:
- (a) the concentration of hydrogen ions;
 - (b) the concentration of hydroxide ions.
32. An acid solution has a hydroxide ion concentration of $2.87 \times 10^{-13} \text{ mol l}^{-1}$. Calculate:
- (a) the concentration of hydrogen ions;
 - (b) the pH of the solution
33. A solution of sodium hydroxide, NaOH , has a concentration of 0.638 mol l^{-1} . Calculate:
- (a) the hydrogen ion concentration;
 - (b) the pH of the solution.
34. The pH of a hydrochloric acid solution is -0.253. Calculate:
- (a) the hydrogen ion concentration;
 - (b) the hydroxide ion concentration.
35. The pH of an ethanoic acid solution is 3.48. Calculate:
- (a) the hydrogen ion concentration;
 - (b) the hydroxide ion concentration.
36. Methanoic acid is a weak acid. Calculate the concentration of hydrogen ions in a 0.01 mol l^{-1} solution of methanoic acid.
37. Calculate the concentration of butanoic acid solution which would have a hydrogen ion concentration of $1.73 \times 10^{-3} \text{ mol l}^{-1}$.

38. Calculate the concentration of hydrogen ions in a 0.040 mol l^{-1} solution of propanoic acid.
39. Calculate the concentration of hydrofluoric acid solution which would have a hydrogen ion concentration of $0.0184 \text{ mol l}^{-1}$.
40. Calculate the concentration of hydrogen ions in a 0.35 mol l^{-1} solution of hydrocyanic acid.
41. Calculate the pH of a 0.100 mol l^{-1} solution of ethanoic acid.
42. Calculate the pH of a 0.200 mol l^{-1} solution of methanoic acid.
43. Calculate the pH of a 0.500 mol l^{-1} solution of hydrofluoric acid.
44. Calculate the pH of a $0.1500 \text{ mol l}^{-1}$ solution of benzoic acid.
45. Calculate the pH of a 0.240 mol l^{-1} solution of butanoic acid.
46. A solution of methanoic acid has a pH of 2.52. Calculate the concentration of the acid.
47. A solution of benzoic acid has a pH of 2.63. Calculate the concentration of the acid.
48. A solution of butanoic acid has a pH of 3.05. Calculate the concentration of the acid.
49. A solution of propanoic acid has a pH of 4.23. Calculate the concentration of the acid.
50. A solution of ethanoic acid has a pH of 3.48. Calculate the concentration of the acid.
51. A 0.1 mol l^{-1} solution of a monoprotic acid has a pH of 2.35. Calculate the pK_a of the acid.
52. A 0.05 mol l^{-1} solution of a monoprotic acid has a pH of 1.58. Calculate the pK_a of the acid.
53. A 0.2 mol l^{-1} solution of a monoprotic acid has a pH of 2.4. Calculate the pK_a of the acid.
54. A 0.15 mol l^{-1} solution of a monoprotic acid has a pH of 1.93. Calculate the pK_a of the acid.
55. A 0.5 mol l^{-1} solution of a monoprotic acid has a pH of 2.57. Calculate the pK_a of the acid.
56. Calculate the pH of a buffer comprising 0.20 mol l^{-1} ethanoic acid and 0.50 mol l^{-1} sodium ethanoate solution.
57. Calculate the pH of a buffer made from a mixture of 0.5 mol of butanoic acid and 0.2 mol of potassium butanoate dissolved to make 1 l of aqueous solution.
58. A buffer contains a mixture of benzoic acid and sodium benzoate at concentrations 0.10 and 0.4 mol l^{-1} respectively. Calculate the pH of the buffer.
59. A buffer is made from a mixture of propanoic acid and sodium propanoate solutions, both at concentrations of 0.1 mol l^{-1} . Calculate the pH of the buffer.
60. Calculate the pH of a buffer made from a mixture of 0.2 mol of methanoic acid and 0.5 mol of sodium methanoate in 1 l aqueous solution.
61. Calculate the pH of a buffer made by dissolving 6.00g of ethanoic acid, CH_3COOH and 4.10 g of sodium ethanoate CH_3COONa in 1 l aqueous solution.
62. A buffer solution is made by dissolving 2.76 g of methanoic acid HCOOH and 5.44 g of sodium methanoate HCOONa , in 1 l water. Calculate the pH of the buffer.
63. Calculate the pH of the buffer solution made by dissolving 24.4 g of benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$, and 7.20 g of sodium benzoate $\text{C}_6\text{H}_5\text{COONa}$, in 1 l water.
64. A buffer solution is made by dissolving 2.96 g of propanoic acid $\text{C}_2\text{H}_5\text{COOH}$ and 7.68 g of sodium propanoate $\text{C}_2\text{H}_5\text{COONa}$ in 1 l water. Calculate the pH of the buffer.

65. Calculate the pH of the buffer solution made by dissolving 2.40 g of ethanoic acid CH_3COOH and 1.64 g of sodium ethanoate, CH_3COONa , in 1 l water.
66. A buffer containing a solution of methanoic acid and sodium methanoate is made up to pH 3.42. Calculate the molar proportion of acid to salt which would be needed to obtain this pH.
67. A buffer containing ethanoic acid and the sodium salt of ethanoic acid, has a pH of 5.16. Calculate the molar proportion of acid to salt in this buffer.
68. A buffer solution with a pH of 4.76 contains a mixture of benzoic acid and sodium benzoate. Calculate the molar proportion of the acid to the salt present.
69. A solution containing a mixture of propanoic acid and potassium propanoate is a buffer with a pH of 4.32. What molar proportion of acid to salt would be needed to prepare this buffer?
70. A buffer is made from a solution containing a mixture of butanoic acid and sodium butanoate. What molar proportion of acid to salt required to produce a buffer solution with a pH of 4.47.

(b) Reaction Feasibility

1. 1,2-dichloroethane has been used as a solvent for lacquers and oils. One proposed method of production is the addition of hydrogen chloride to ethyne:



Compound	$S^\theta / \text{J K}^{-1} \text{ mol}^{-1}$	$\Delta H_{\text{ef}} / \text{kJ mol}^{-1}$
C_2H_2	201	227
HCl	187	-92.3
$\text{CH}_2\text{ClCH}_2\text{Cl}$	208	-166

(a) Using the data given in the table above,

- (i) calculate the standard entropy change, in J K mol^{-1} , for the reaction.
- (ii) calculate the standard enthalpy change, in kJ mol^{-1} , for the reaction.

(b) The reaction is thermodynamically feasible at room temperature. Above which temperature will this reaction no longer be feasible?

2. Consider the following reactions and their values for ΔG^θ and ΔH^θ at 298K:

	Reaction	$\Delta G^\theta / \text{kJmol}^{-1}$	$\Delta H^\theta / \text{kJmol}^{-1}$
(i)	$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g})$	-95	-92
(ii)	$2\text{Al}(\text{s}) + \frac{11}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3(\text{s})$	-1576	-1669
(iii)	$\text{NH}_4\text{Cl}(\text{s}) \rightarrow \text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$	-7	+16

- (a) Reaction ii) has the greatest difference in the values of ΔG^θ and ΔH^θ . Suggest a reason for this difference.
- (b) From the values given for reaction iii), it can be concluded that ammonium chloride dissolves spontaneously in water under standard conditions with a drop in temperature. Why can we come to these two conclusions?
- (c) Calculate the entropy change for reaction (i) at 298K.

3. In a catalytic reformer, straight-chain alkanes are converted to branched chains, cycloalkanes and aromatic hydrocarbons. Consider the sequence shown below.

Octane



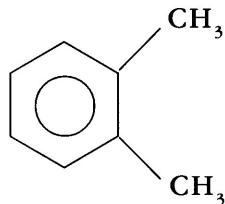
2,3-dimethylhexane



1,2-dimethylcyclohexane + hydrogen



1,2-dimethylbenzene (*o*-xylene) + hydrogen



- (a) Use the data in the table below to calculate ΔS^θ for the conversion of octane to *o*-xylene and hydrogen at 298K.

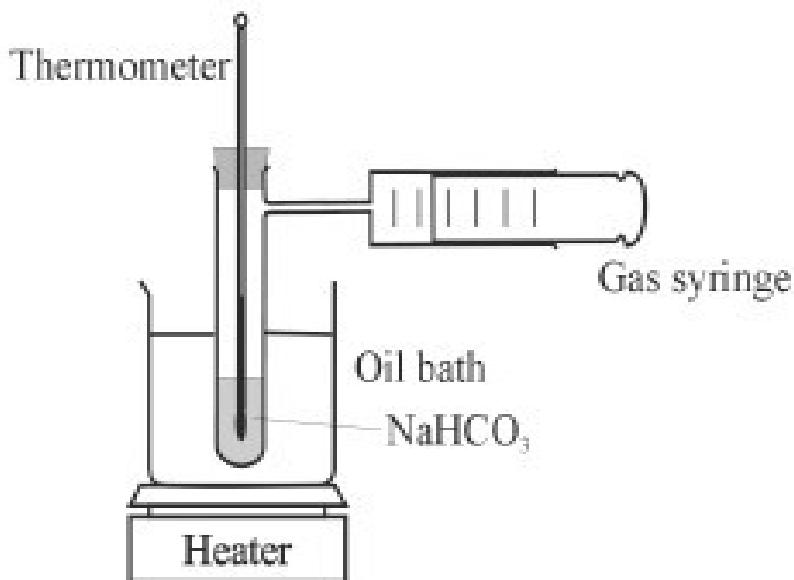
Compound	$S^\theta / \text{JK}^{-1}\text{mol}^{-1}$
Octane	463
<i>o</i> -xylene	352
Hydrogen	131

- (b) Calculate the minimum temperature at which the conversion in (a) becomes thermodynamically feasible, given that

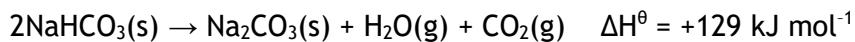
$$\Delta H^\theta = 227 \text{ kJ mol}^{-1}.$$

- (c) Explain why the conversion in (a) can be achieved at or above the temperature calculated in (b), despite the fact that the equilibrium constant for reaction A is very much less than 1 at this temperature.

4. The apparatus shown in the diagram below can be used to find the decomposition temperature of sodium hydrogencarbonate.



The equation for the decomposition is:



Substance	S ^θ /J K ⁻¹ mol ⁻¹
NaHCO ₃ (s)	102.1
Na ₂ CO ₃ (s)	136.0
H ₂ O(g)	188.7
CO ₂ (g)	213.6

- (a) Calculate ΔS^θ for the reaction.
(b) Calculate the temperature at which the decomposition becomes feasible.
(c) As the temperature of the oil bath is increased, the volume of gas in the syringe increases. Sketch the shape of the graph you would expect to obtain if the volume of gas is plotted against temperature. Graph paper is not required. Start at room temperature and mark clearly the decomposition temperature on your graph.

5.

SUBSTANCE	$\Delta G^\circ_{\text{FORMATION}} / \text{kJ mol}^{-1}$
CO_2	-394
MgO	-569
ZnO	-318
CuO	-130
All elements	0

(a) Use the information in the table to calculate the free energy change in the following reactions



(b) Explain whether these reactions are feasible at 298 K

6. The equation for the decomposition of magnesium carbonate is shown below



	$\text{MgCO}_3(\text{s})$	$\text{MgO}(\text{s}) +$	$\text{CO}_2(\text{g})$
$\Delta H^\circ_f / \text{kJ mol}^{-1}$	-1113	-602	-394
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	66	27	214

(a) Use the thermodynamic data to calculate the free energy change, in kJ mol^{-1} at 400 K.

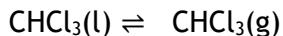
(b) Is the reaction feasible at this temperature?

7. Consider the thermodynamic data shown for the Haber process.

	$\text{N}_2(\text{g}) +$	$+ 3\text{H}_2(\text{g}) \rightleftharpoons$	$2\text{NH}_3(\text{g})$
$\Delta H^\circ_f / \text{kJ mol}^{-1}$	0	0	-46.4
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$?	?	193.2

Use the data given above, along with data book values to calculate the temperature at which the Haber process becomes feasible.

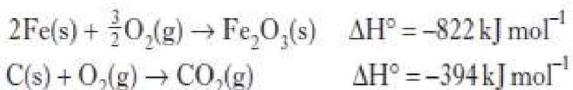
8. Chloroform was one of the first anaesthetics used in surgery. Use the thermodynamic data to calculate a boiling point for chloroform.



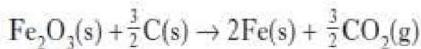
$$\Delta S = 94.2 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta H = 31.3 \text{ kJ mol}^{-1}$$

9.



Which of the following is the standard enthalpy change, in kJ mol^{-1} , for the reaction shown below?



- A +231
- B +428
- C +1216
- D +1413

10.

Which of the following reactions must be exothermic? One in which

- A ΔG° is negative
- B ΔS° is positive
- C both ΔG° and ΔS° are negative
- D both ΔG° and ΔS° are positive.

11.

Which line in the table is correct for the enthalpy change and entropy change when steam condenses?

	ΔH	ΔS
A	+ve	+ve
B	+ve	-ve
C	-ve	-ve
D	-ve	+ve

12.

Which of the following reactions results in a decrease in entropy?

- A $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
- B $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
- C $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- D $\text{C}(\text{s}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$

13. This table contains some thermodynamic data for hydrogen, oxygen and water.

	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{H}_2(\text{g})$	131	0
$\text{O}_2(\text{g})$	205	0
$\text{H}_2\text{O}(\text{g})$	189	-242
$\text{H}_2\text{O}(\text{l})$	70	

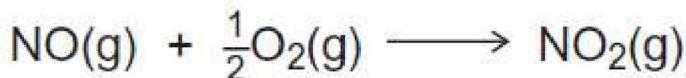
- (a) Calculate the temperature above which the reaction between hydrogen and oxygen to form gaseous water is **not** feasible.
- (b) State what would happen to a sample of gaseous water that was heated to a temperature higher than that of your answer to part a. Give a reason for your answer.

14. The oxides nitrogen monoxide (NO) and nitrogen dioxide (NO_2) both contribute to atmospheric pollution.

The table gives some data for these oxides and for oxygen.

	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{O}_2(\text{g})$	211	0
$\text{NO}(\text{g})$	205	+90
$\text{NO}_2(\text{g})$	240	+34

Nitrogen monoxide is formed in internal combustion engines. When nitrogen monoxide comes into contact with air, it reacts with oxygen to form nitrogen dioxide.



- (a) Calculate the enthalpy change for this reaction.
- (b) Calculate the entropy change for this reaction.
- (c) Calculate the temperature that this reaction becomes thermodynamically feasible.

(c) Kinetics

1.

The reaction $A + 2B \rightarrow C$ has a rate law of the form

Rate = $k [A] [B]$.

If the reaction proceeds by a two step process, then the rate-determining step might be

- A $A + B \rightarrow$ intermediate
- B $B + B \rightarrow$ intermediate
- C $A + B \rightarrow C$
- D $B + AB \rightarrow C$.

3.



The rate equation for this reaction is
Rate = $k[P] [Q]^2$.

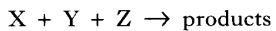
If the concentration of P and Q are both doubled, the rate will increase

- A 2 times
- B 4 times
- C 6 times
- D 8 times.

4.

2.

The following data refer to initial reaction rates obtained for the reaction



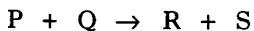
	RELATIVE CONCENTRATIONS			RELATIVE INITIAL RATE
	[X]	[Y]	[Z]	
Expt. 1	1·0	1·0	1·0	0·3
Expt. 2	1·0	2·0	1·0	0·6
Expt. 3	2·0	2·0	1·0	1·2
Expt. 4	2·0	1·0	2·0	0·6

These data fit the rate equation

- A Rate = $k [X]$
- B Rate = $k [X] [Y]$
- C Rate = $k [X] [Y]^2$
- D Rate = $k [X] [Y] [Z]$.

5.

The following reaction is first order with respect to P and second order with respect to Q.

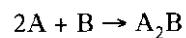


Which of the following statements is correct?

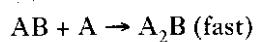
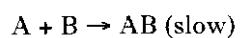
- A The reaction occurs by a simple one step mechanism.
- B The reaction is second order overall.
- C If the initial concentration of Q is doubled, the rate of the reaction will be doubled.
- D As the reaction proceeds its rate will decrease.

6.

A suggested mechanism for the reaction



is a two-step process



This mechanism is consistent with the rate equation

A rate = $k[A]^2 [B]$

B rate = $k[A] [B]$

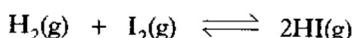
C rate = $k[A] [A_2B]$

D rate = $k[AB]$.

7.

Marks

The reaction



follows ***first order kinetics*** with respect to both iodine and hydrogen.

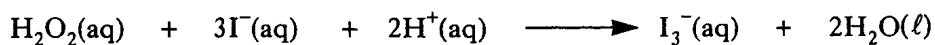
When studied at different temperatures, the data shown in the table below were obtained. The data could be used to determine the Activation Energy for the forward reaction.

Temperature/K	Rate Constant/ $\text{l mol}^{-1}\text{s}^{-1}$
556	4.45×10^{-5}
575	1.37×10^{-4}
629	2.52×10^{-3}
666	1.41×10^{-2}
700	6.43×10^{-2}
781	1.34

- (a) Write the rate equation for the reaction. 1
 - (b) Calculate the initial rate of reaction at 700 K, if the initial concentrations of both iodine and hydrogen are 0.5 mol l^{-1} . 2
 - (c) The data show that the rate constant increases with temperature. Explain this trend by sketching the distribution of kinetic energies among the reactant molecules at two different temperatures. Use the same set of axes for the two graphs and a single line to represent the energy of activation for the reaction. 3
- (6)**

8.

The following table of results was obtained for the reaction below.



Experiment	$[\text{H}_2\text{O}_2]/\text{mol l}^{-1}$	$[\text{I}^-]/\text{mol l}^{-1}$	$[\text{H}^+]/\text{mol l}^{-1}$	Initial rate/ $\text{mol l}^{-1}\text{s}^{-1}$
1	0.3	0.3	0.002	2.07×10^{-3}
2	0.6	0.3	0.002	4.14×10^{-3}
3	0.3	0.6	0.002	4.14×10^{-3}
4	0.3	0.3	0.004	2.07×10^{-3}

(a) Write the rate equation for the reaction.

1

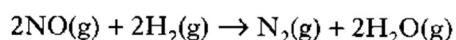
(b) Calculate the rate constant for this reaction giving the appropriate units.

3

(4)

9.

The table below refers to the reaction between nitrogen monoxide and hydrogen at a temperature of 1025 K.



Experiment number	Initial concentration of NO/mol l ⁻¹	Initial concentration of H ₂ /mol l ⁻¹	Initial rate of formation of N ₂ /mol l ⁻¹ s ⁻¹
1	0.03	0.005	0.012
2	0.03	0.010	0.024
3	0.03	0.015	0.036
4	0.01	0.015	0.004
5	0.02	0.015	0.016

- (a) Calculate the order of the reaction with respect to:
 - (i) hydrogen; 1
 - (ii) nitrogen monoxide. 1
 - (b) Write the rate equation for the reaction. 1
 - (c) Calculate the rate constant, showing appropriate units. 2
 - (d) Copy the axes given (no graph paper required) and sketch a graph to show how the rate of the reaction varies with concentration of nitrogen monoxide (at constant concentration of H₂). 1
- (6)

Initial rate of formation of N₂

Initial concentration of NO

10.

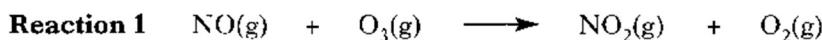
Ozone, O_3 , is one of the earth's key defences against damaging ultra-violet radiation.

- (a) Ozone can be described in terms of resonance structures.

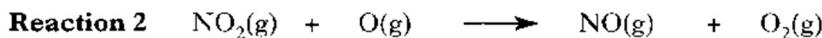
Draw the **two** resonance structures for ozone.

1

- (b) Ozone can be broken down by nitrogen monoxide gas produced by high flying aircraft.



The nitrogen dioxide formed can then react with oxygen atoms.



- (i) Write an equation for the overall reaction.

1

- (ii) From the equations, what part does the nitrogen monoxide play in the overall reaction?

1

- (c) The following table shows how the initial rate of **reaction 2** varies with changing concentrations of $\text{NO}_2(\text{g})$ and O(g) at a fixed temperature.

$[\text{O}]/\text{mol l}^{-1}$	$[\text{NO}_2]/\text{mol l}^{-1}$	Initial rate/ $\text{mol l}^{-1} \text{s}^{-1}$
9.20×10^{-15}	1.11×10^{-12}	6.10×10^{-17}
1.81×10^{-14}	1.11×10^{-12}	1.20×10^{-16}
1.81×10^{-14}	2.23×10^{-12}	2.41×10^{-16}

- (i) Determine the overall order of this reaction.

1

- (ii) Calculate a value for the rate constant, k , including appropriate units.

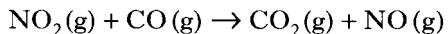
3

(7)

11.

Turner

Consider the reaction

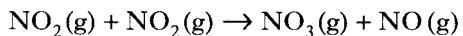


for which the rate equation has been shown by experiment to be

$$\text{Rate} = k[\text{NO}_2]^2$$

The first stage of this two stage reaction is the rate determining step (r.d.s.).

The equation for this stage is



- (a) Write the equation for the second stage which completes the reaction. 1

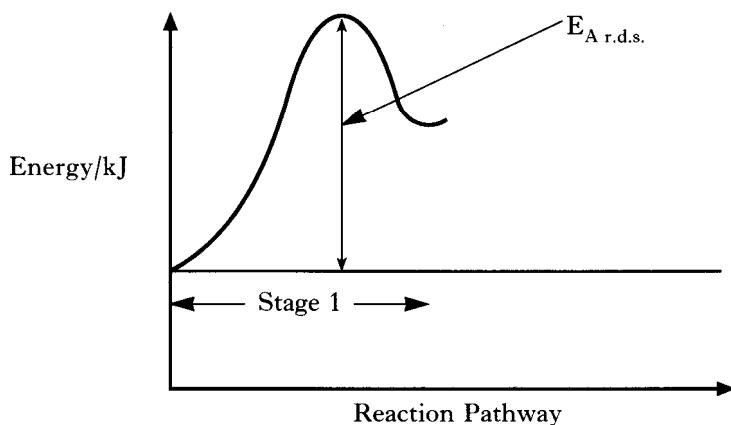
The table gives kinetic data for the above reaction at constant temperature.

Relative [NO ₂]	Relative [CO]	Relative Rate
1	1	1
2	1	<i>x</i>
2	2	<i>y</i>

- (b) Determine the values for *x* and *y* in the table. 2

The diagram below (not to scale) shows the energy change for the first stage of the reaction.

The enthalpy change, ΔH° , for the overall reaction is -226 kJ .



- (c) Copy the diagram into your answer book and complete it, with labels, to show:

(i) the completed energy diagram for the second stage; 1

(ii) the activation energy, E_A , for the second stage; 1

(iii) ΔH° for the overall reaction. 1

(6)