

Thermodynamics and Kinetics Exam

Assessment Week 1

Name Model Answers

Total Marks 71

Time Allowed: 75 Minutes

1

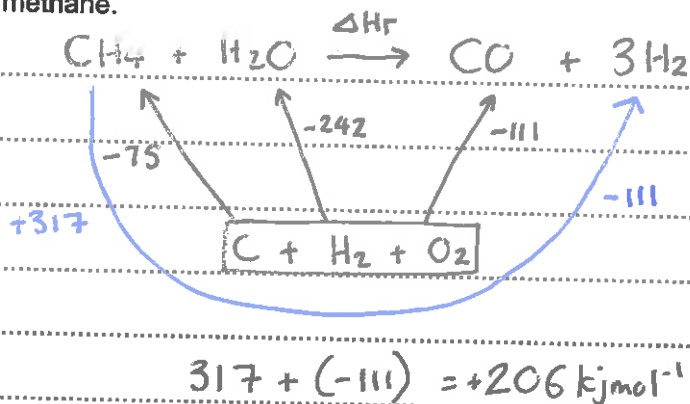
Hydrogen can be manufactured from the reaction of steam with methane.



(a) The table contains some enthalpy of formation and entropy data.

Substance	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$	$S^\ominus / \text{J K}^{-1} \text{mol}^{-1}$
$\text{CH}_4(\text{g})$	-75	186
$\text{H}_2\text{O}(\text{g})$	-242	189
$\text{CO}(\text{g})$	-111	198
$\text{H}_2(\text{g})$	0	131
$\text{CO}_2(\text{g})$	-394	214

(i) Use data from the table to calculate the enthalpy change, ΔH , for the reaction of steam with methane.



(3)

(ii) Use data from the table to calculate the entropy change, ΔS , for the reaction of steam with methane.

$$\Delta S = \text{product entropies} - \text{reactant entropies}$$

$$\Delta S = (198 + (3 \times 131)) - (186 + 189)$$

$$\Delta S = +216 \text{ J K}^{-1} \text{ mol}^{-1}$$

(2)

- (b) Use your values of ΔH and ΔS from parts (a)(i) and (a)(ii) to calculate the temperature above which this reaction is feasible.

$$\Delta G = \Delta H - T\Delta S \quad \text{if } \Delta G = 0 \text{ then:}$$

$$T = \frac{\Delta H}{\Delta S} \quad T = \frac{206 \times 1000}{216} \quad T = 954 \text{ K}$$

(4)

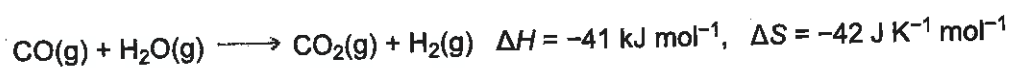
- (c) The temperature used for this manufacture of hydrogen is usually about 1300 K.

Suggest one reason, other than changing the position of equilibrium, why this temperature is used rather than the value that you calculated in part (b).

It speeds up the rate reaction.

(1)

- (d) Hydrogen can also be obtained by reaction of carbon monoxide with steam.



- (i) Explain, using a calculation, why this reaction should not occur at 1300 K.

$$\Delta G = \Delta H - T\Delta S \quad \frac{-42}{1000} = -0.042$$

$$\Delta G = -41 - (1300 \times -0.042) \quad \Delta G = +13.6 \text{ kJ mol}^{-1}$$

Not feasible @ 1300K as ΔG needs to be negative.

(3)

- (ii) Explain how the conditions for the reaction could be changed to allow this reaction to take place.

Temperature needs to be lowered. This will cause ΔG to become more negative as $-T\Delta S$ will become less positive.

$$T = \frac{\Delta H}{\Delta S} \quad T = \frac{-41}{(-42/1000)} \quad T = 976 \text{ K to be}$$

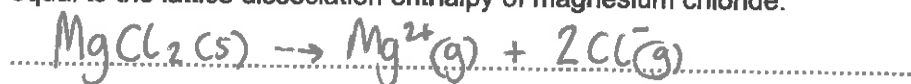
feasible or when $\Delta G = 0$ (2)
(Total 15 marks)

2

This table contains some values of lattice dissociation enthalpies.

Compound	MgCl ₂	CaCl ₂	MgO
Lattice dissociation enthalpy / kJ mol ⁻¹	2493	2237	3889

- (a) Write an equation, including state symbols, for the reaction that has an enthalpy change equal to the lattice dissociation enthalpy of magnesium chloride.



(1)

- (b) Explain why the lattice dissociation enthalpy of magnesium chloride is greater than that of calcium chloride.

This is because the magnesium ion is smaller and hence has a greater charge density. This means there is a greater attraction between the two ions (Mg²⁺ and Cl⁻).

(Extra space)

(2)

- (c) Explain why the lattice dissociation enthalpy of magnesium oxide is greater than that of magnesium chloride.

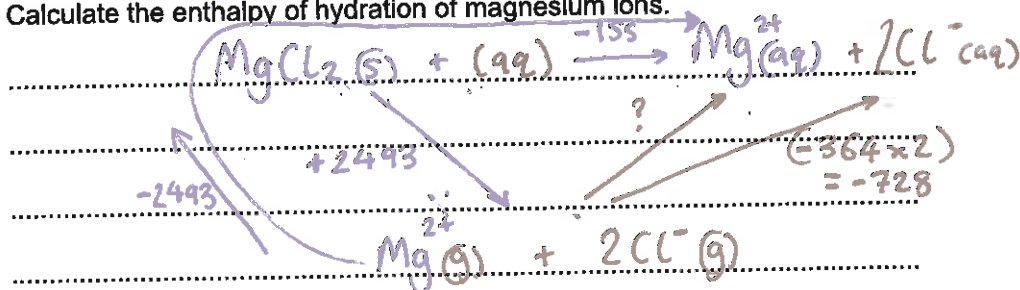
The oxide ion, O^{2-} has a greater charge than the Cl^- ion. This means it has a greater attraction to the Mg^{2+} ion.

(Extra space)

(2)

- (d) When magnesium chloride dissolves in water, the enthalpy of solution is -155 kJ mol^{-1} . The enthalpy of hydration of chloride ions is -364 kJ mol^{-1} .

Calculate the enthalpy of hydration of magnesium ions.



$$-2493 + (-155) = -2648$$

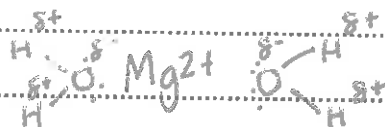
$$-2648 + 728 = -1920 \text{ kJ mol}^{-1}$$

(Extra space)

(3)

- (e) Energy is released when a magnesium ion is hydrated because magnesium ions attract water molecules.

Explain why magnesium ions attract water molecules.
You may use a labelled diagram to illustrate your answer.



water is polar and therefore has a delta negative charge on the oxygen. This is attracted to the positive charge on the Mg^{2+} ion.

(2)

- (f) Suggest why a value for the enthalpy of solution of magnesium oxide is **not** found in any data books.

Magnesium oxide is virtually insoluble.

(1)

(Total 11 marks)

3

This question is about magnesium oxide. Use data from the table below, where appropriate, to answer the following questions.

	$\Delta H^\ominus / \text{kJ mol}^{-1}$
First electron affinity of oxygen (formation of $\text{O}^-(\text{g})$ from $\text{O}(\text{g})$)	-142
Second electron affinity of oxygen (formation of $\text{O}^{2-}(\text{g})$ from $\text{O}^-(\text{g})$)	+844
Atomisation enthalpy of oxygen	+248

(a) Define the term *enthalpy of lattice dissociation*.

The enthalpy change when 1mol of an ionic lattice is dissociated into its ions in their gaseous states.

(3)

(b) In terms of the forces acting on particles, suggest **one** reason why the first electron affinity of oxygen is an exothermic process.

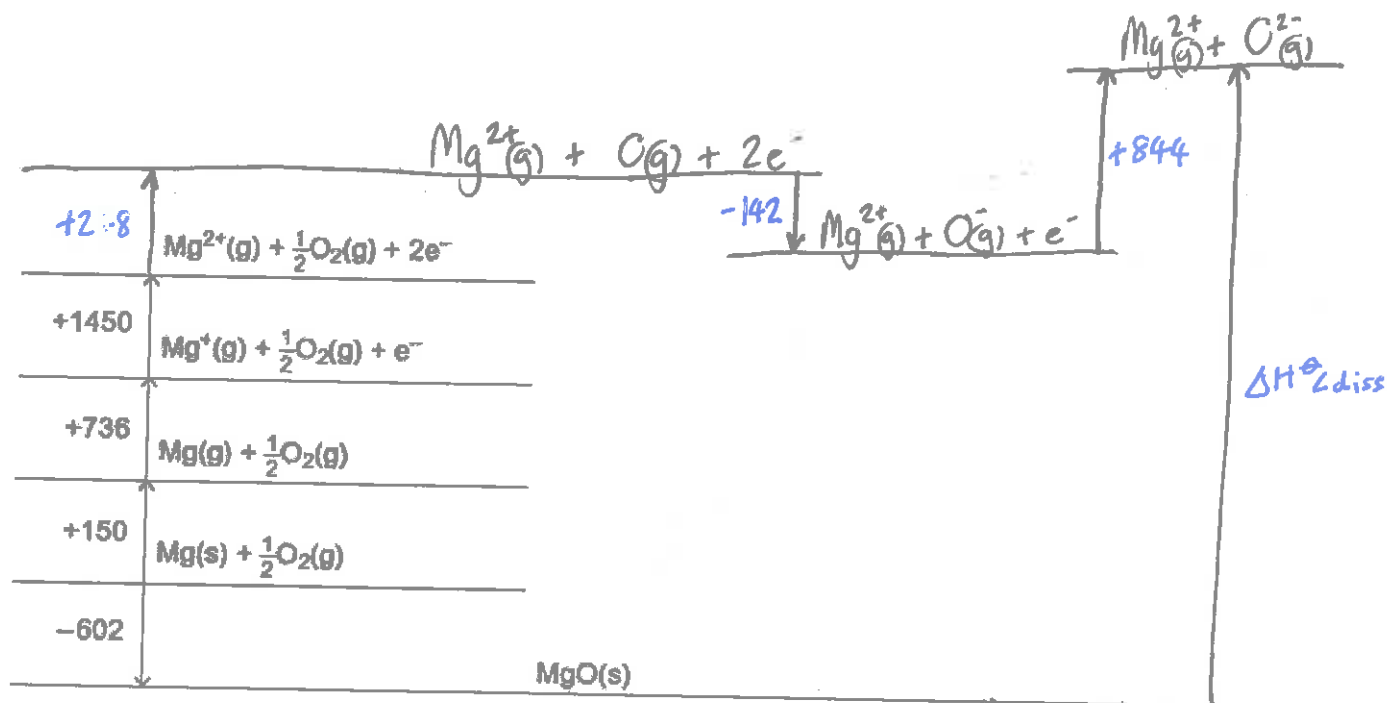
Because there is an attractive force between oxygen's positive nucleus and the negative electron.

(Extra space)

(1)

- (c) Complete the Born–Haber cycle for magnesium oxide by drawing the missing energy levels, symbols and arrows.

The standard enthalpy change values are given in kJ mol⁻¹.



(4)

- (d) Use your Born–Haber cycle from part (c) to calculate a value for the enthalpy of lattice dissociation for magnesium oxide.

$$602 + 150 + 736 + 1450 + 248 + 844 = 4030$$

$$4030 - 142 = \underline{\underline{3888 \text{ kJ mol}^{-1}}}$$

(2)

- (e) The standard free-energy change for the formation of magnesium oxide from magnesium and oxygen, $\Delta G_f^\ominus = -570$ kJ mol⁻¹.

Suggest **one** reason why a sample of magnesium appears to be stable in air at room temperature, despite this negative value for ΔG_f^\ominus .

As in air/oxygen it forms a MgO layer which prevents more oxygen attacking the Mg.

(Extra space)

(1)

- (f) Use the value of ΔG_f^\ominus given in part (e) and the value of ΔH_f^\ominus from part (c) to calculate a value for the entropy change ΔS^\ominus when one mole of magnesium oxide is formed from magnesium and oxygen at 298 K. Give the units of ΔS^\ominus .

$$\Delta G = \Delta H - T\Delta S \quad \Delta S = \frac{(\Delta H - \Delta G)}{T}$$

$$\Delta S = \frac{(-602 - (-570))}{298} \quad \Delta S = 0.107 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\text{or} \\ \times 1000 = -107 \text{ J K}^{-1} \text{ mol}^{-1}$$

(Extra space)

(3)

- (g) In terms of the reactants and products and their physical states, account for the sign of the entropy change that you calculated in part (f).

1 mol of solid and 0.5 mol of gas form 1 mol of solid. This means system becoming much more ordered.

(2)

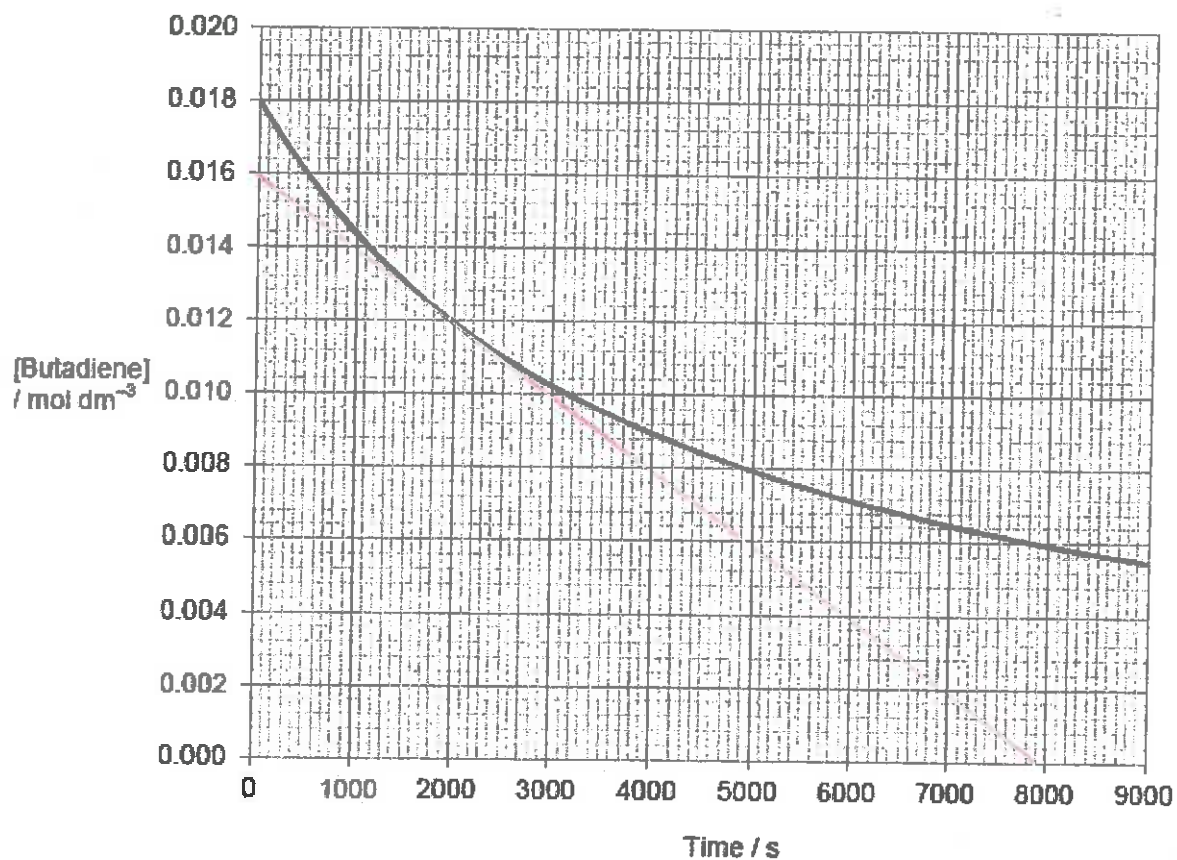
(Total 16 marks)

4

Butadiene dimerises according to the equation



The kinetics of the dimerisation are studied and the graph of the concentration of a sample of butadiene is plotted against time. The graph is shown below.



(a) Draw a tangent to the curve when the concentration of butadiene is $0.0120 \text{ mol dm}^{-3}$.

(1)

- (b) The initial rate of reaction in this experiment has the value $4.57 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}$.

Use this value, together with a rate obtained from your tangent, to justify that the order of the reaction is 2 with respect to butadiene.

$$\text{gradient} = \frac{dy}{dx} = \frac{0.016}{7800} = 2.05 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1} = \underline{\underline{\text{rate}}}$$

$$\text{If you compare the initial rate} : \left(\frac{4.57 \times 10^{-6}}{2.05 \times 10^{-6}} \right) = 2.23$$

to the calculated rate @ 0.012

$$\text{Now compare initial concentration} : \frac{0.018}{0.012} = 1.5$$

and concentration @ tangent

Therefore concentration changed by 1.5 but rate by 2.23. $(1.5)^2 = 2.25$ which shows this is second order with respect to butadiene.

(5)
(Total 6 marks)

5

The initial rate of the reaction between two gases P and Q was measured in a series of experiments at a constant temperature. The following rate equation was determined.

$$\text{rate} = k[\text{P}]^2[\text{Q}]$$

(a) Complete the table of data below for the reaction between P and Q.

Experiment	Initial [P] / mol dm ⁻³	Initial [Q] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.30	1.8×10^{-3}
2	0.40	0.60	a) 0.0144
3	0.60	b) 0.10	5.4×10^{-3}
4	c) 0.30	0.90	12.2×10^{-3}

(Space for working)

compare 1 and 2 → a) $0.2 \xrightarrow{\times 2} 0.4$ $0.3 \xrightarrow{\times 2} 0.6$ $= 1.8 \times 10^{-3} \times 2 \times (2)^2 = 0.0144$

compare 1 and 3 → b) $0.2 \xrightarrow{\times 3} 0.6$ $0.3 \xrightarrow{\div 3} 0.1$ $= 1.8 \times 10^{-3} \times 3^2 \div 3 = 5.4 \times 10^{-3}$

compare 1 and 4 → c) $0.2 \xrightarrow{\times 1.5} 0.3$ $0.3 \xrightarrow{\times 3} 0.9$ $= 1.8 \times 10^{-3} \times 3 \times (1.5)^2 = 12.2 \times 10^{-3}$

(3)

(b) Use the data from Experiment 1 to calculate a value for the rate constant k and deduce its units.

Calculation

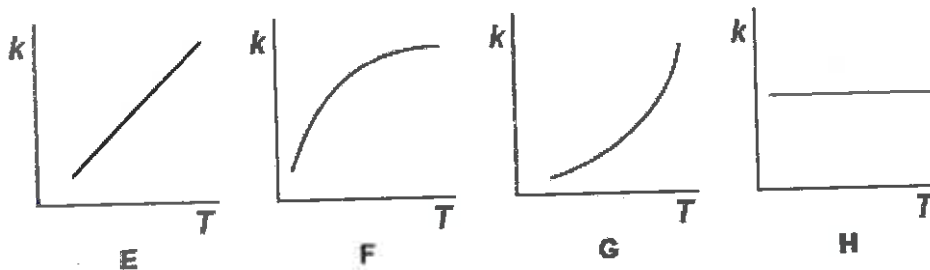
$$k = \frac{1.8 \times 10^{-3}}{(0.20)^2 \times 0.30} \quad k = 0.15$$

$$k = \frac{\text{mol dm}^{-3} \text{ s}^{-1}}{\text{mol dm}^{-3} \times \text{mol dm}^{-3} \times \text{mol dm}^{-3}} = \frac{\text{mol}^{-2} \text{ dm}^6 \text{ s}^{-1}}{\text{mol}^3 \text{ dm}^{-9}}$$

Units

(3)

(c) Consider the graphs E, F, G and H below.



Write in the box below the letter of the graph that shows how the rate constant k varies with temperature.

G

Remember for approx every 10K temperature rise, k doubles. Exponential growth like this gives rise to the curve shown in G.

(1)
(Total 7 marks)

6 Ethanol can be oxidised by acidified potassium dichromate(VI) to ethanoic acid in a two-step process.



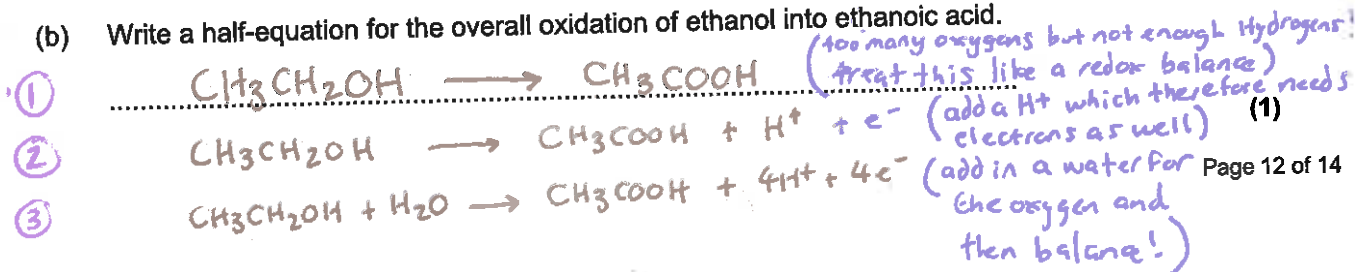
(a) In order to ensure that the oxidation to ethanoic acid is complete, the reaction is carried out under reflux.

Describe what happens when a reaction mixture is refluxed and why it is necessary, in this case, for complete oxidation to ethanoic acid.

A mixture of liquids undergoes constant boiling and condensation (reflux). This allows the ethanol to be completely oxidised into ethanoic acid.

(3)

(b) Write a half-equation for the overall oxidation of ethanol into ethanoic acid.



- (c) The boiling points of the organic compounds in a reaction mixture are shown in the following table.

Compound	ethanol	ethanal	ethanoic acid
Boiling point / °C	78	21	118

Use these data to describe how you would obtain a sample of ethanal from a mixture of these three compounds. Include in your answer a description of the apparatus you would use and how you would minimise the loss of ethanal. Your description of the apparatus can be either a description in words or a labelled sketch.

Heat the mixture in a pear shaped flask. Attach a condenser, not forgetting a thermometer which is placed near opening of the condenser. Allow water to flow through the condenser and turn heat source on under flask (Hot water bath around 70°C is suitable). Collect the ensuing distillate in a cooled vessel (beaker in an ice bath).

(5)

- (d) Use your knowledge of structure and bonding to explain why it is possible to separate ethanal in this way.

The strongest intermolecular bonding in ethanal is dipole-dipole, this is weaker than for ethanol and ethanoic acid which has hydrogen bonding. This means it is easier to boil the ethanal (lower b.p.).

(2)

- (e) A student obtained a sample of a liquid using the apparatus in part (c).

Describe how the student could use chemical tests to confirm that the liquid contained ethanal and did **not** contain ethanoic acid.

• Add tollens reagent to a small sample and warm. If ethanal a silver mirror would form.

• Add sodium carbonate to a second small sample of distillate, if any ethanoic acid present then CO_2 (fizzing) would be given off.

(5)
(Total 16 marks)