

A2 CHEM Mark scheme

Thermodynamics + Kinetics

Mark schemes

1

- (a) (i) $\Delta H = \Sigma(\text{enthalpies formation products}) - \Sigma(\text{enthalpies formation reactants})$
Or correct cycle with enthalpy changes labelled

1

$$= -111 - (-75 - 242)$$

1

$$= (+)206 \text{ (kJ mol}^{-1}\text{)}$$

-206 scores 1 only

Units not essential if ans in kJ mol⁻¹ but penalise incorrect units

1

- (ii) $\Delta S = \Sigma(\text{entropies of products}) - \Sigma(\text{entropies reactants})$

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

1

$$= (+) 216 \text{ (J K}^{-1} \text{ mol}^{-1}\text{)}$$

OR

$$0.216 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Units not essential but penalise incorrect units

1

- (b) When $\Delta G = 0$ OR $\Delta H = T\Delta S$

1

$$T = \Delta H / \Delta S$$

M2 also scores M1

1

$$= 206 \times 1000 / 216$$

Allow error carried forward from (a)(i) and (a)(ii)

Ignore unexplained change of sign from - to +

1

$$= 954 \text{ K}$$

Allow 953 - 955, Units of K essential, must be +ve

If values from (a)(i) and (a)(ii) lead to negative value in M3 allow M1

to M3 but do not allow negative temperature for M4

If negative value changed to positive for M4, allow M4

1

- (c) To speed up the rate of reaction OR wtte

Allow so that more molecules have energy greater than the activation energy

IF T in (b) > 1300 allow answers such as;

to reduce energy cost

to slow down reaction

do NOT allow to increase rate

1

(d) (i) **Method 1**
 $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -41 - (1300 \times -42 / 1000)$ (M1)
If 42 and not 42 / 1000 used can score M3 only
but allow $\Delta G = -41 \times 1000 - (1300 \times -42)$ (M1)

1

$= +13.6 \text{ kJ mol}^{-1}$
 $= 13600 \text{ J mol}^{-1}$ (M2)
Units essential

1

ΔG must be negative for the reaction to be feasible.

OR ΔG is positive so reaction is not feasible

1

Method 2

For reaction to be feasible ΔG must be negative or zero

1

T when $\Delta G = 0 = \Delta H / \Delta S = 976 \text{ K}$

1

ΔS is -ve so ΔG must be +ve at temperatures above 976 K / at 1300 K

1

(ii) If the temperature is lowered

(Ignore reference to catalyst and / or pressure)

Alternative mark scheme (if T is calculated)

Allow T reduced to 976 K or lower M1

1

ΔG will become (more) negative because

the $-T\Delta S$ term will be less positive / $T\Delta S > \Delta H$

At this temperature (the reaction becomes feasible because) $\Delta G < 0$ M2

1

[15]

2

(a) $\text{MgCl}_2(\text{s}) \rightarrow \text{Mg}^{2+}(\text{g}) + 2\text{Cl}^{-}(\text{g})$

1

(b) The magnesium ion is smaller / has a smaller radius / greater charge density (than the calcium ion)

If not ionic or if molecules / IMF / metallic / covalent / bond pair / electronegativity mentioned, CE = 0

1

Attraction between ions / to the chloride ion stronger

Allow ionic bonds stronger

Do not allow any reference to polarisation or covalent character

Mark independently

1

(c) The oxide ion has a greater charge / charge density than the chloride ion

If not ionic or if molecules / IMF / metallic / covalent / bond pair mentioned, CE = 0

Allow oxide ion smaller than chloride ion

1

So it attracts the magnesium ion more strongly

Allow ionic bonds stronger

Mark independently

1

(d) $\Delta H_{\text{solution}} = \Delta H_{\text{L}} + \Sigma \Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} + \Sigma \Delta H_{\text{hyd}} \text{Cl}^{-} \text{ ions}$

Allow correct cycle

1

$$-155 = 2493 + \Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} - 2 \times 364$$

$$\Delta H_{\text{hyd}} \text{Mg}^{2+} \text{ ions} = -155 - 2493 + 728$$

1

$$= -1920 \text{ (kJ mol}^{-1}\text{)}$$

Ignore units

Allow max 1 for +1920

Answer of + or -1610, CE = 0

Answer of -2284, CE = 0

1

(e) Water is polar / O on water has a delta negative charge

Allow Q (not water) has lone pairs (can score on diagram)

1

Mg^{2+} ion / +ve ion / + charge attracts (negative) O on a water molecule

Allow Mg^{2+} attracts lone pair(s)

M2 must be stated in words (QoL)

Ignore mention of co-ordinate bonds

CE = 0 if O^{2-} or water ionic or H bonding

1

(f) Magnesium oxide reacts with water / forms $\text{Mg}(\text{OH})_2$

Allow MgO does not dissolve in water / sparingly soluble / insoluble

1

[11]

3

- (a) Enthalpy change when 1 mol of an (ionic) compound/lattice (under standard conditions)

Allow heat energy change

1

Is dissociated/broken/separated into its (component) ions

1

The ions being in the gaseous state (at infinite separation)

Mark independently. Ignore any conditions.

1

- (b) There is an attractive force between the nucleus of an O atom and an external electron.

Allow any statement that implies attraction between the nucleus and an electron

1

- (c) $\text{Mg}^{2+}(\text{g}) + \text{O}(\text{g}) + 2\text{e}^{-}$

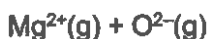
Ignore lack of state symbols

Penalise incorrect state symbols

1



1



1

First new level for Mg^{2+} and O above last on L

If levels are not correct allow if steps are in correct order with arrows in the correct direction and correct ΔH values

1

Next level for Mg^{2+} and O^{-} below that

Next level for Mg^{2+} and O^{2-} above that and also above that for Mg^{2+} and O

Allow +124

Allow M4 with incorrect number of electrons

- (d) $\text{LE MgO} = 602 + 150 + 736 + 1450 + 248 - 142 + 844$

Note use of 124 instead of 248 CE=0

1

$$= +3888 \text{ kJ mol}^{-1}$$

Allow 1 for -3888

Allow no units

Penalise wrong units

1

(e) Forms a protective layer/barrier of MgO / MgO prevents oxygen attacking Mg

Allow activation energy is (very) high

Allow reaction (very) slow

1

(f) $\Delta G = \Delta H - T\Delta S$

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

1

$$\Delta S = (-602 - (-570)) \times 1000 / 298$$

1

$$= -107 \text{ J K}^{-1} \text{ mol}^{-1} / -0.107 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

If units not correct or missing, lose mark

Allow -107 to -108

+107 with correct units scores max 1/3

1

(g) 1 mol of solid and 0.5 mol of gas reactants form 1 mol solid products

Decrease in number of moles (of gas/species)

Allow gas converted into solid

Numbers of moles/species, if given, must be correct

1

System becomes more ordered

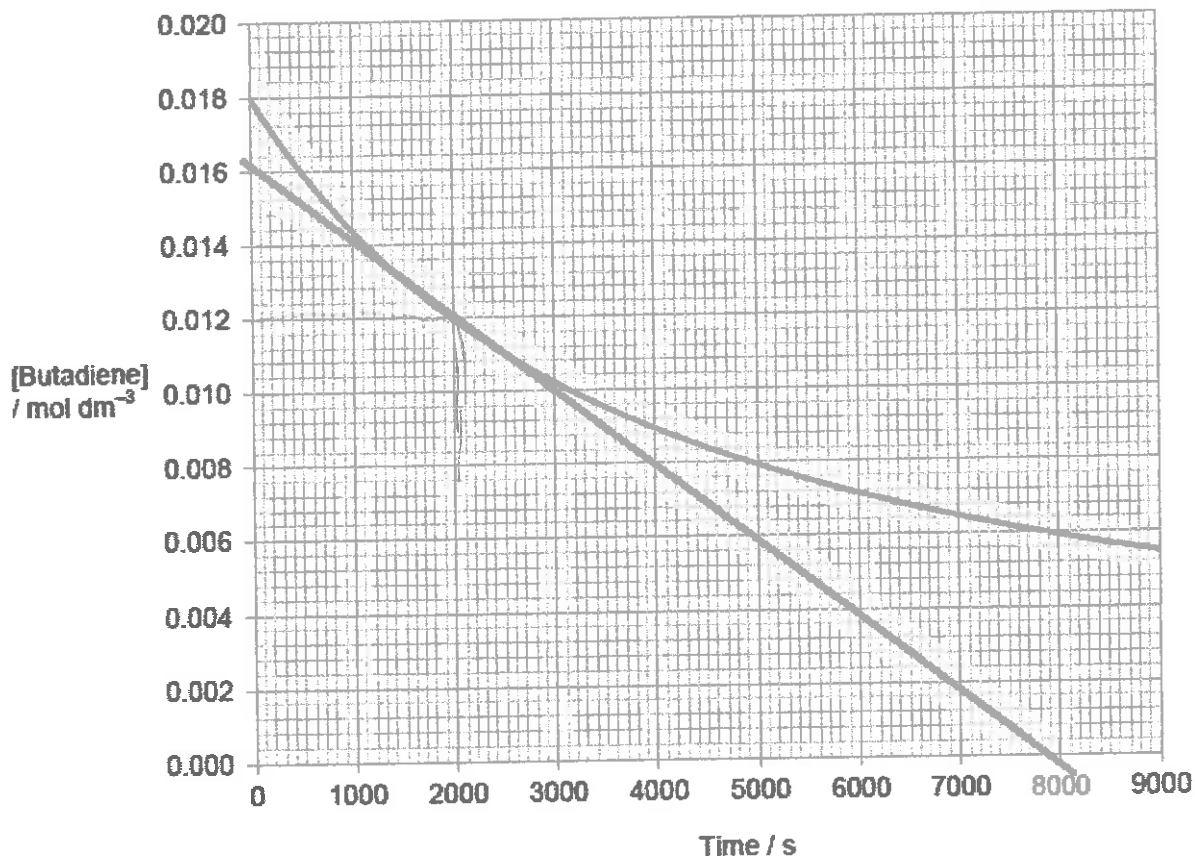
Allow consequential provided ΔS is -ve in 1(f)

If ΔS is +ve in 1(f) can only score M1

1

[16]

4 (a) Gradient drawn on graph



Line must touch the curve at 0.012 but must not cross the curve.

1

(b) Stage 1: Rate of reaction when concentration = 0.0120 mol dm⁻³

From the tangent

Change in [butadiene] = -0.0160 - 0 and change in time = 7800 - 0

Extended response

1

$$\text{Gradient} = -(0.0160 - 0) / (7800 - 0) = -2.05 \times 10^{-6}$$

$$\text{Rate} = 2.05 \times 10^{-6} \text{ (mol dm}^{-3} \text{ s}^{-1}\text{)}$$

1

Stage 2: Comparison of rates and concentrations

$$\text{Initial rate / rate at 0.0120} = (4.57 \times 10^{-6}) / (2.05 \times 10^{-6}) = 2.23$$

Marking points in stage 2 can be in either order

1

$$\text{Initial concentration / concentration at point where tangent drawn} = 0.018 / 0.012 =$$

1.5

1

Stage 3: Deduction of order

If order is 2, rate should increase by factor of $(1.5)^2 = 2.25$ this is approximately equal to 2.23 therefore order is 2nd with respect to butadiene

1

[6]

5

- (a) Exp 2 $14.(4) \times 10^{-3}$ OR $1.4(4) \times 10^{-2}$ or 0.014

Allow 2sf

1

Exp 3 0.1(0)

1

Exp 4 0.3(0)

If three wrong answers, check their value of k in 1(b).

They can score all 3 if they have used their (incorrect) value of k. see below.

Exp 2 rate = $0.096 \times k$

Exp 3 [Q] = $0.015/k$

Exp 4 [P] = $0.116/k$

1

(b)
$$K = \frac{1.8 \times 10^{-2}}{(0.20)^2 \times 0.30}$$

mark is for insertion of numbers into a correctly rearranged rate equ, k = etc

1

= 0.15 (min 2sfs) (allow $\frac{3}{20}$)

if upside down, score only units mark

AE (-1) for copying numbers wrongly or swapping two numbers

1

$\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$

Any order

If k calculation wrong, allow units conseq to their k

1

- (c) G

1

[7]

6

- (a) A mixture of liquids is heated to boiling point for a prolonged time

1

Vapour is formed which escapes from the liquid mixture, is changed back into liquid and returned to the liquid mixture

1

Any ethanal and ethanol that initially evaporates can then be oxidised

1



1

(c) Mixture heated in a suitable flask / container

A labelled sketch illustrating these points scores the marks

1

With still head containing a thermometer

1

Water cooled condenser connected to the still head and suitable cooled collecting vessel

1

Collect sample at the boiling point of ethanal

1

Cooled collection vessel necessary to reduce evaporation of ethanal

1

(d) Hydrogen bonding in ethanol and ethanoic acid or no hydrogen bonding in ethanal

1

Intermolecular forces / dipole-dipole are weaker than hydrogen bonding

1

(e) Reagent to confirm the presence of ethanal:

Add Tollens' reagent / ammoniacal silver nitrate / aqueous silver nitrate followed by 1 drop of aqueous sodium hydroxide, then enough aqueous ammonia to dissolve the precipitate formed

OR

Add Fehling's solution

1

Warm

M2 and M3 can only be awarded if M1 is given correctly

1

Result with Tollen's reagent:

Silver mirror / black precipitate

OR

Result with Fehling's solution:

Red precipitate / orange-red precipitate

1

Reagent to confirm the absence of ethanoic acid

Add sodium hydrogencarbonate or sodium carbonate

1

Result; no effervescence observed; hence no acid present

1

M5 can only be awarded if M4 is given correctly

OR

Reagent; add ethanol and concentrated sulfuric acid and warm

Result; no sweet smell / no oily drops on the surface of the liquid,

hence no acid present

[16]