Ammonia Decomposition

A Level

In an experiment, the decomposition of gaseous ammonia to N_2 and H_2 on a hot tungsten wire was studied by monitoring the change in pressure with time. The rate equation for this reaction may be written in terms of either the concentration or the partial pressure of ammonia. In terms of the partial pressure of ammonia, p_{NH_3}, it is:

$$\text{rate} = -k(p_{NH_3})^\alpha,$$

where α is the order of the reaction and k is the rate constant.

At the start of the reaction, the only gas present was ammonia at an initial pressure of $200\,\mathrm{mmHg}$. The table below shows how the total pressure varied with time.

Time / s	**Total pressure** / mmHg
100	214
200	227
300	238
400	249
500	259
600	270
800	292

Part A Equation

Write a balanced equation, including state symbols, for the decomposition of one mole of ammonia.

Part B Pressure vs concentration

Using the ideal gas law, we can show that pressure is directly proportional to concentration at constant temperature. What is the proportionality constant we need to multiply concentration by to get the pressure?

The following symbols may be useful: `R, T, V, n, p`

Part C Total pressure

The initial partial pressure of ammonia is $p_0\,\mathrm{mmHg}$. After a time t it is $(p_0 - x)\,\mathrm{mmHg}$. Find an expression for the *total* pressure of reactants and products, p_T, at time t, expressed in mmHg (don't include the unit in your expression).

The following symbols may be useful: `p_0, t, x`

Part D Partial pressure

Find an expression for the *partial pressure of ammonia* at time t as a function of p_0 and p_T, expressed in mmHg (don't include the unit in your expression).

The following symbols may be useful: `p_0, p_T`

Part E Graph

Which of the following statements are true about the graph of the partial pressure of ammonia against time?

- [ ] It appears to be approximately a straight line.
- [ ] It appears to be approximately a parabola
- [ ] It appears to be approximately S-shaped
- [ ] It has a positive gradient throughout
- [ ] It has zero gradient throughout
- [ ] It has a negative gradient throughout
- [ ] It has both a positive and a negative gradient over different intervals.
- [ ] The graph is steepest at around $t = 400\,\mathrm{s}$
- [ ] The graph gets steeper at higher times

Part F Order

What is the order of the reaction, α?

Part G Rate constant

What is the rate constant of the reaction? Give your answer to 2 s.f.

Adapted with permission from OCR, STEP Chemistry, Jun 1999, Question 2

Life on Mars

A Level
C C C

Is there life on Mars? In 1976, two spacecraft landed on the planet. They were equipped with apparatus for carrying out experiments to try to find out the answer.

Three experiments were performed; two showed no evidence for life, but some scientists think the third experiment did. This experiment was designed to detect the presence of micro-organisms in Martian soil.

A solution of compounds, known to be used in metabolism by micro-organisms on Earth, was added to a sample of Martian soil. The compounds were labelled with $^{14}\mathrm{C}$, a radioactive isotope of carbon.

The chemists who designed the experiment argued that, if micro-organisms were present in the soil sample, there was a chance that they would metabolise the labelled compounds and break them down into small molecules, some of which would contain labelled carbon atoms, and might be released as gas. The experiment therefore included a Geiger counter to measure the radioactivity of the gas contained in the apparatus.

Part A 2-hydroxypropanoic acid

One of the compounds used in this experiment was sodium 2-hydroxypropanoate (sodium lactate). This was made from a sample of 2-hydroxypropanoic acid in which each molecule contained a ^{14}C atom.

Molecules of this kind were not already available and had to be prepared from a source of ^{14}C by appropriate chemical reactions. One such source is ^{14}C-labelled cyanide ions, $^{14}CN^-$. A list of potentially useful reactions is given below; in these reactions, R represents an alkyl group.

$$RBr \xrightarrow{NH_3} RNH_2 \quad (1)$$
$$RBr \xrightarrow{OH^-} ROH \quad (2)$$
$$RBr \xrightarrow{CN^-} RCN \quad (3)$$
$$RNH_2 \xrightarrow{H^+ / NO_2^-} RCN \quad (4)$$
$$RCN \xrightarrow{H_2 / \text{Pt catalyst}} RCH_2NH_2 \quad (5)$$
$$RCN \xrightarrow{H^+ / H_2O} RCOOH \quad (6)$$
$$RCHO \xrightarrow{CN^- / OH^-} RCH(OH)CN \quad (7)$$
$$RCHO \xrightarrow{H^+ / Cr_2O_7^{2-}} RCOOH \quad (8)$$
$$RCH_2OH \xrightarrow{H^+ / Cr_2O_7^{2-}} RCHO \quad (9)$$

Choose reactions from this list to suggest a two-step route which could be used to prepare 2-hydroxypropanoic acid. Record your chosen route by completing the sequence below.

$$? \longrightarrow ? \longrightarrow CH_3CH(OH)COOH$$

Available items

- (1) $RBr \xrightarrow{NH_3} RNH_2$
- (2) $RBr \xrightarrow{OH^-} ROH$
- (3) $RBr \xrightarrow{CN^-} RCN$
- (4) $RNH_2 \xrightarrow{H^+ / NO_2^-} RCN$
- (5) $RCN \xrightarrow{H_2 / \text{Pt catalyst}} RCH_2NH_2$
- (6) $RCN \xrightarrow{H^+ / H_2O} RCOOH$
- (7) $RCHO \xrightarrow{CN^- / OH^-} RCH(OH)CN$
- (8) $RCHO \xrightarrow{H^+ / Cr_2O_7^{2-}} RCOOH$
- (9) $RCH_2OH \xrightarrow{H^+ / Cr_2O_7^{2-}} RCHO$

Part B ^{1}H NMR

The proton NMR spectrum of the product of the reaction sequence was recorded and is shown in **Figure 1**.

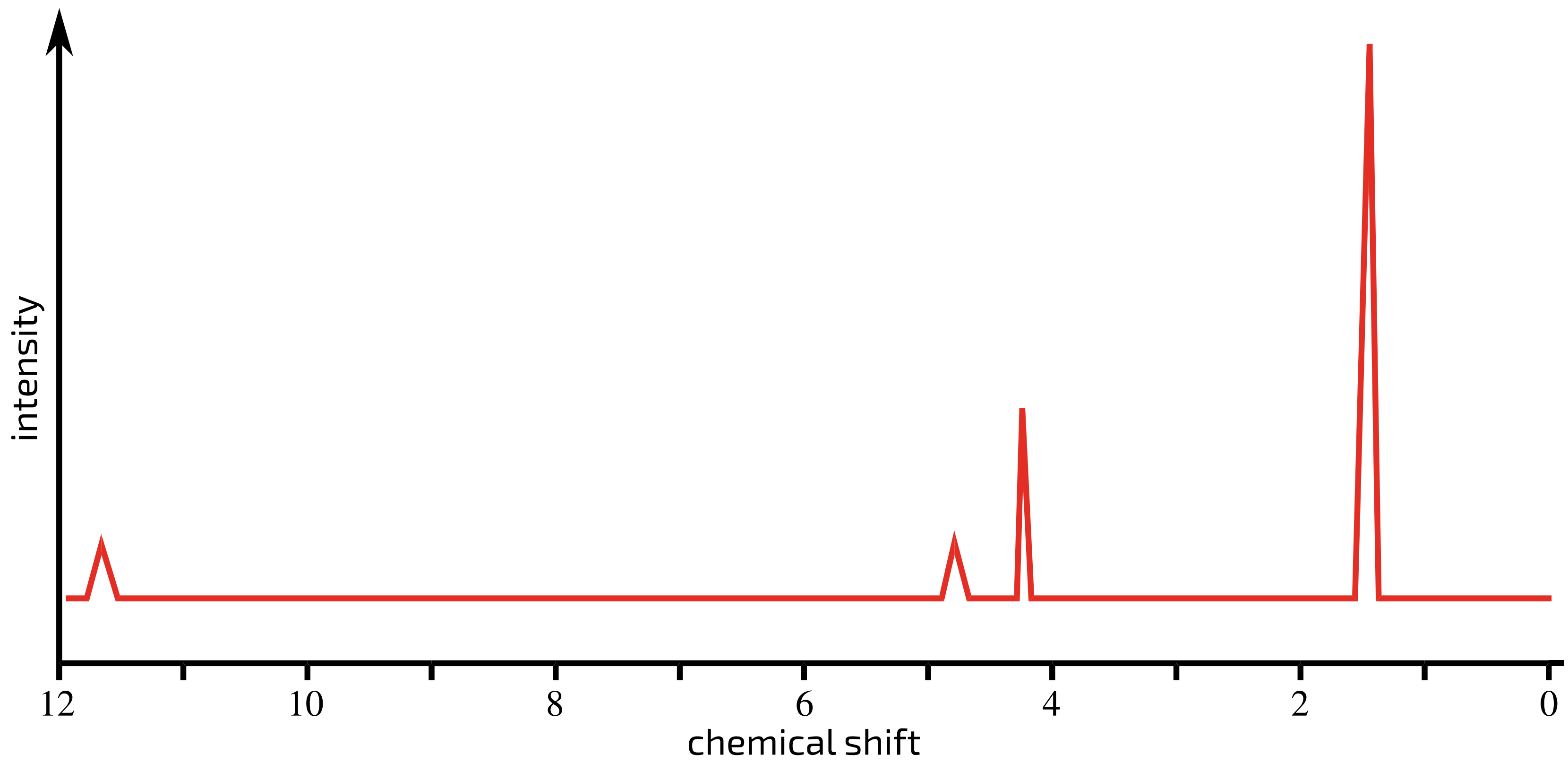

Figure 1: Proton NMR spectrum of the product, with chemical shift in ppm.

As well as showing that 2-hydroxypropanoic acid has been obtained, the NMR spectrum also shows that the reaction product is free from traces of starting material. Give a value for the chemical shift of one signal which is absent from this spectrum but which would be seen if traces of starting material were present.

- 0 - 2 ppm
- 2 - 4 ppm
- 4 - 6 ppm
- 6 - 8 ppm
- 8 - 10 ppm
- 10 - 12 ppm

Part C Type of proton

State the type of proton which would give rise to the signal you have chosen.

Adapted with permission from OCSEB, A-Level Chemistry (Salters), June 1996, Paper 2, Question 4.

Gameboard:
STEM SMART Chemistry Week 51 (extension)

Modelling Balloons

A Level

Due to the properties of the rubber that cylindrical modelling balloons are made from, they have two stable radii for the same value of internal pressure. If the pressure is high because the balloon is fully inflated, the whole cylindrical balloon will have a large radius.

As air is released, the balloon can remain at a fixed length, but a section of it can reduce to a lower radius, with the rest of the balloon remaining at a larger radius, looking rather like a snake that has swallowed an animal whole. Such a cylindrical balloon is inflated to a volume of $1.00\,\mathrm{dm}^3$ at room temperature ($25.0\,^\circ\mathrm{C}$).

The balloon is then heated up to $40.0\,^\circ\mathrm{C}$ at atmospheric pressure. The pressure due to the tension in the surface can be neglected.

Part A New volume

What is the volume of the balloon at the new temperature?

Part B Small radius section

The volume of air is sufficient that a section of the balloon is at one radius and the rest is at a larger radius. At this higher temperature, the two stable radii of the balloon are $2.00\,\mathrm{cm}$ and $5.00\,\mathrm{cm}$ and its overall length is $60.0\,\mathrm{cm}$. How long is the small radius section of the balloon?

Created for isaacphysics.org by Maria-Andreea Filip and Richard Simon

Gameboard:
STEM SMART Chemistry Week 51 (extension)

pH in Ester Hydrolysis

A Level

The hydrolysis of an ester can be carried out in both alkaline and acidic conditions.

Part A Equations

Fill in the gaps to complete the reaction equations for hydrolysis of ethyl ethanoate under acidic and alkaline conditions respectively.

$$CH_3C(=O)OCH_2CH_3 + H_2O \xrightarrow{\text{acid}} \square + \square$$

$$CH_3C(=O)OCH_2CH_3 + NaOH \xrightarrow{\text{alkali}} \square + \square$$

Items:

H_2O CH_3OH CH_3CH_2OH $HCOOH$ CH_3COOH $HCOONa$ CH_3COONa

Part B   pH rate profile

A study of the rate of hydrolysis of ethyl ethanoate in buffered solutions gave the following pH rate profile:

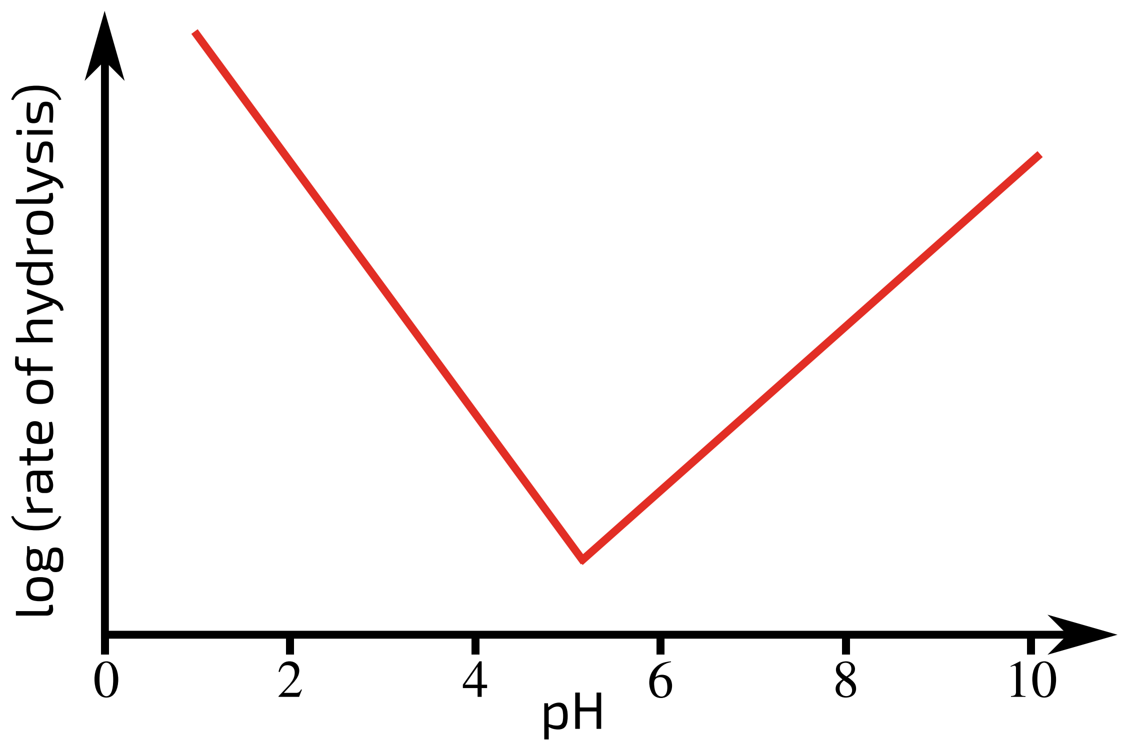

Figure 1: pH rate profile for ester hydrolysis

Which of the following statements help explain the trends seen in this profile?

- [ ] at higher pH, the H^+ concentration is higher, speeding up acid-catalysed hydrolysis
- [ ] at higher pH, the OH^- concentration is higher, speeding up base-catalysed hydrolysis
- [ ] at lower pH, the H^+ concentration is higher, speeding up acid-catalysed hydrolysis
- [ ] at lower pH the OH^- concentration is higher, speeding up base-catalysed hydrolysis

Part C pH 5.5

At pH 5.5, the rate for the acid hydrolysis reaction is the same as the rate for the alkaline hydrolysis reaction. What are the concentrations of H^+ and OH^- at this pH?

Give your answers to 2 sf.

Concentration of H^+:

Concentration of OH^-:

Part D Rate constant comparison

Which of the following statements about the rate constants for the two hydrolysis processes is/are correct?

- ☐ The rate constants for the acid and alkaline hydrolysis are equal, as the rate for both processes can be made equal under certain conditions.
- ☐ The rate constant for the acid hydrolysis is higher than the rate constant for the alkaline hydrolysis, as the rate for both processes is equal when the H^+ concentration is higher than the OH^- concentration.
- ☐ The rate constant for the alkaline hydrolysis is higher than the rate constant for the acid hydrolysis, as the rate for both processes is equal when the H^+ concentration is higher than the OH^- concentration.
- ☐ The rate constant for the acid hydrolysis is higher than the rate constant for the alkaline hydrolysis, as the acid hydrolysis dominates at neutral pH when the H^+ and OH^- concentrations are equal.
- ☐ The rate constant for the alkaline hydrolysis is higher than the rate constant for the acid hydrolysis, as the alkaline hydrolysis dominates at neutral pH when the H^+ and OH^- concentrations are equal.

Adapted with permission from OCSEB, STEP Chemistry, June 1991, Question 1.

Gameboard:
STEM SMART Chemistry Week 51 (extension)

Physics. You work it out.

Silane Reactions

A Level

When mixed with an excess of chlorine in the dark, silane, SiH_4, catches fire and gives silicon tetrachloride and hydrogen chloride. If the chlorine is diluted with argon and the silane is in excess, a compound **A**, with a boiling point of $-30\,°C$, can be isolated. **A** contains $53.3\,\%$ of chlorine by mass.

When **A** is passed over metallic sodium, a compound **B** with a relative molecular mass of 62 is formed. **B** catches fire when exposed to air, giving silicon(IV) oxide (silicon dioxide) and water only. When **A** is mixed with water vapour, a compound **C** with composition Si $71.8\,\%$, H $7.7\,\%$, by mass, is formed.

When $240\,cm^3$ of silane, at room temperature and pressure, are passed into aqueous sodium hydroxide, $960\,cm^3$ of hydrogen are formed and the solution is found to contain a compound **D** as well as sodium hydroxide. In this reaction, $0.020\,mol$ of sodium hydroxide was used.

Part A Compound A

Identify **A**.

Part B Compound B

Identify **B**.

Part C Compound C

Identify **C**.

Part D Compound D

Identify **D**.