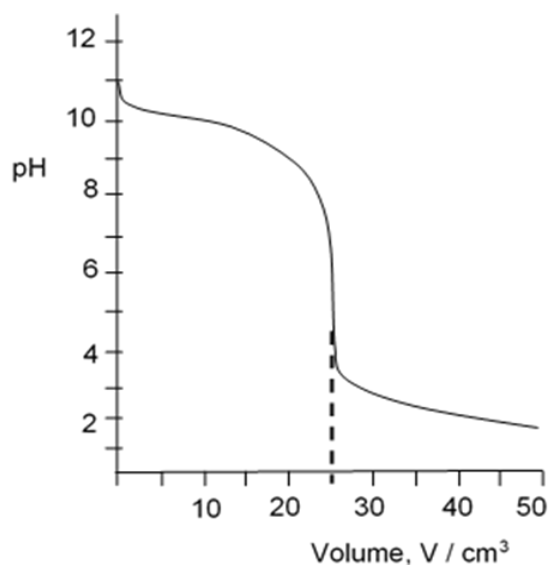


ACID-BASE EQUILIBRIA MCQ PART 1

- 1 Which solution will solid silver phosphate, Ag_3PO_4 , be the least soluble in, at 25°C ?
The numerical value of K_{sp} (Ag_3PO_4) is 8.89×10^{-17}
- A pure water
B $2.0 \text{ mol dm}^{-3} \text{ AgNO}_3 (\text{aq})$
C $2.0 \text{ mol dm}^{-3} \text{ NH}_3 (\text{aq})$
D $2.0 \text{ mol dm}^{-3} \text{ K}_3\text{PO}_4 (\text{aq})$
- 2 In an acid-base titration, 0.10 mol dm^{-3} solution of an acid is added to 25 cm^3 of 0.10 mol dm^{-3} solution of a base.
The pH value of the solution is plotted against the volume, V , of acid added as shown in the diagram.

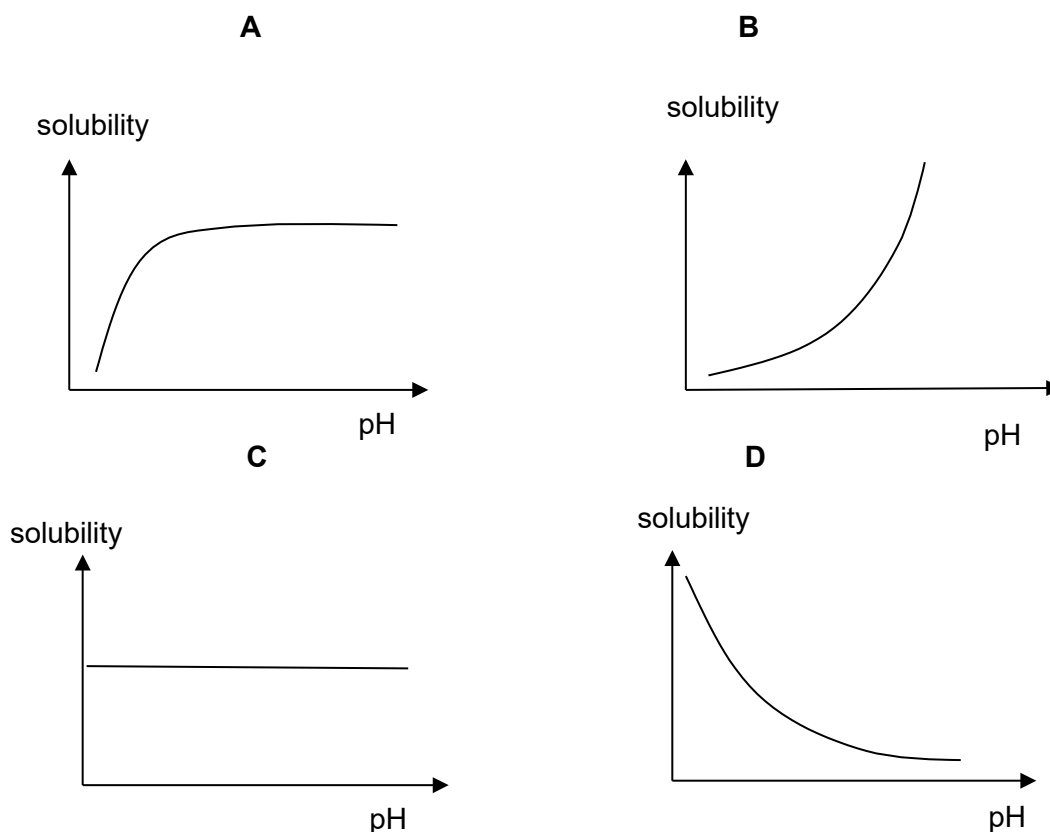


Which statement is incorrect?

- A Maximum buffering capacity occurs at $V = 12.5 \text{ cm}^3$
B The pair of solutions could have been $\text{HCl}(\text{aq})$ and $\text{CH}_3\text{NH}_2 (\text{aq})$.
C Methyl orange is suitable indicator for the above titration.
D When the concentration of the acid is doubles, the pH at equivalence point remains unchanged.

3 Aqueous HF is a weak acid. Magnesium fluoride is sparingly soluble.

Which graph below shows how the solubility of MgF_2 in water will vary with pH at constant temperature?



4 The variation of the ionic product of water, K_w , with the temperature is given in the table.

Temperature/ °C	$K_w/\text{mol}^2\text{dm}^{-6}$
25	1.00×10^{-14}
50	5.50×10^{-14}
62	1.00×10^{-13}

What can be deduced from this information?

- A The ionization of water is an exothermic process.
- B $[\text{H}^+]$ is more than $[\text{OH}^-]$ as temperature increases.
- C pH of water at 10°C is higher than at 25°C
- D The equilibrium position lies furthest to the right at 25°C

- 5 Aqueous ethanenitrile, CH_3CN , has no effect on litmus but aqueous ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, turns litmus blue.

Which statements below can be used to explain this observation?

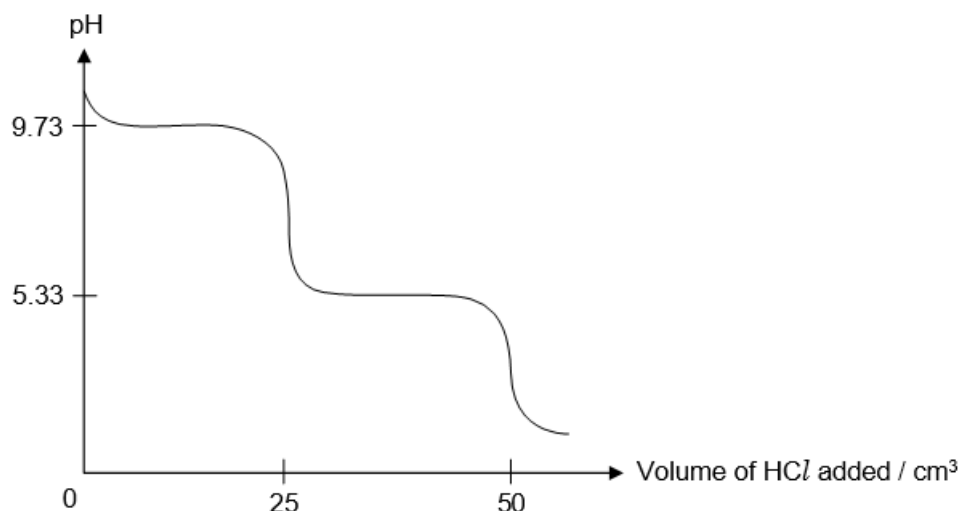
- 1 Delocalisation of the lone pair of electrons on the nitrogen atom of CH_3CN over the $\text{C}=\text{N}$ group strengthens the $\text{C}-\text{N}$ bond.
- 2 Lone pair of electrons on the nitrogen atom of $\text{C}=\text{N}$ are in an sp hybridized orbital which is closer to the nucleus than the lone pair of electrons on the sp^3 hybridised nitrogen atom of the NH_2 group.
- 3 The ethyl group in ethylamine is a stronger electron donating group than the methyl group in ethanenitrile as it has one more carbon atom.

A 1, 2 and 3 **B** 1 only **C** 2 and 3 **D** 2 only

- 6 What is the pH of the final solution when $V \text{ cm}^3$ of dilute nitric acid of pH 2.0 is mixed with $V \text{ cm}^3$ of dilute nitric acid of pH 4.0 followed by the addition of $2V \text{ cm}^3$ of water?

A 2.3 **B** 2.6 **C** 3.0 **D** 3.6

- 7 The pH change when 1.00 mol dm^{-3} hydrochloric acid was added dropwise to 25 cm^3 of 1.00 mol dm^{-3} piperazine ($\text{C}_4\text{H}_{10}\text{N}_2$) is shown below.

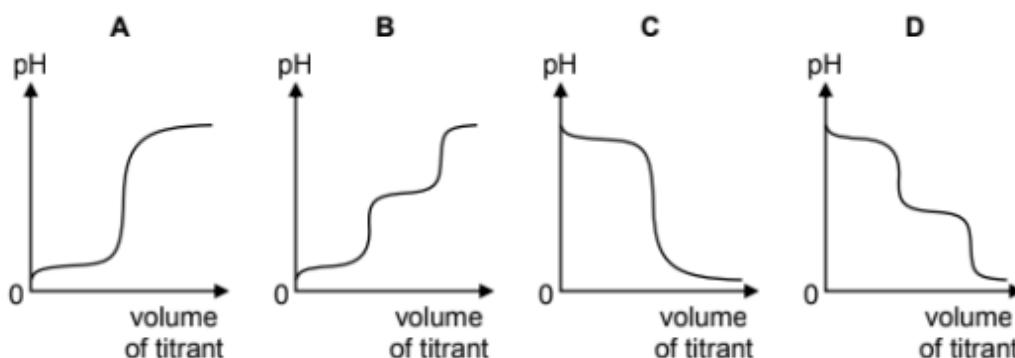


From the table below, which pair of indicators can be used consecutively to detect the end-points of the titration?

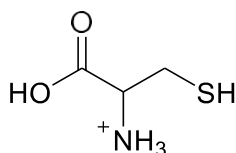
indicator	range
bromothymol blue	6.0 – 7.6
ethyl orange	3.4 – 4.8
methyl red	4.8 – 6.0
thymolphthalein	9.4 – 10.6

- A** Bromothymol blue followed by ethyl orange
B Bromothymol blue followed by methyl red
C Thymolphthalein followed by ethyl orange
D Thymolphthalein followed by methyl red

- 8 Which of the following titration curves is obtained when HCl(aq) is titrated against standard Na₂CO₃(aq)?



- 9 A solution of cysteine in its fully protonated form is titrated against a standard solution of potassium hydroxide. The structure of fully protonated cysteine is shown below and its three pK_a values are 10.3 (for –SH), 8.1 and 1.9.



The isoelectric point is the pH value at which the net electric charge of a molecule is zero, and in the case of cysteine, can be estimated by taking the average of two appropriate pK_a values.

Which of the following indicators can be used to detect the isoelectric point of

cysteine? indicator working range

- | | | |
|----------|------------------|-----------|
| A | methyl orange | 3.2 – 4.4 |
| B | methyl red | 4.1 – 6.1 |
| C | bromothymol blue | 6.0 – 8.0 |
| D | phenol red | 6.9 – 8.9 |

- 10 Use of the Data Booklet is relevant to this question.

Water dissociates as shown.



At 25° C, the equilibrium value of [H⁺] is 10⁻⁷ mol dm⁻³; [H₂O] = 55.6 mol dm⁻³.

What is the order of increasing numerical value of pH, pK_a and pK_w for this equilibrium at this temperature?

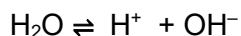
	smallest		Largest
A	pH	pK _a	pK _w
B	pH	pK _w	pK _a
C	pK _a	pK _w	pH
D	pK _w	pK _a	pH

- 11 Which combinations of substances would result in a buffer solution?
- A 25.0 cm³ of 0.100 mol dm⁻³ HCl(aq) and 20.0 cm³ of 0.100 mol dm⁻³ NaCl(aq)
 B 25.0 cm³ of 0.100 mol dm⁻³ HCl(aq) and 25.0 cm³ of 0.200 mol dm⁻³ NH₃(aq)
 C 25.0 cm³ of 0.100 mol dm⁻³ H₂CO₃(aq) and 50.0 cm³ of 0.100 mol dm⁻³ NaOH(aq)
 D 20.0 cm³ of 0.100 mol dm⁻³ CH₃CO₂H(aq) and 25.0 cm³ of 0.100 mol dm⁻³ NaOH(aq)

- 12 Aqueous solutions of aluminium salts are acidic. They contain [Al(H₂O)₆]³⁺ ions.
 K_a for [Al(H₂O)₆]³⁺ = 1.0 × 10⁻⁵ mol dm⁻³

What is the pH of 0.01 mol dm⁻³ AlCl₃?

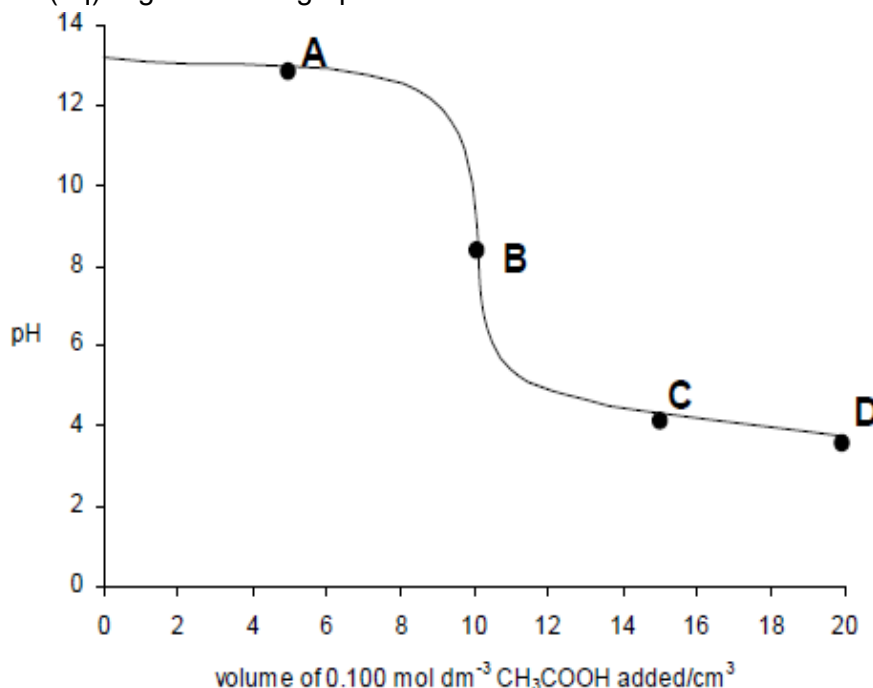
- A 2.5 B 3.5 C 5.0 D 6.0
- 13 Pure water undergoes dissociation as shown in the equation below.



At 40°C, the [H⁺] is found to be 10^{-6.8} mol dm⁻³.

Which of the following statements is **incorrect**?

- A The dissociation of water is an endothermic process.
 B Water is acidic at 40°C
 C At 40°C, the value of pK_w is 13.6.
 D Both H⁺ and OH⁻ ions are of the same concentration for pure water at 40°C
- 14 The pH change when 0.100 mol dm⁻³ CH₃CO₂H is added dropwise to 10.0 cm³ of 0.100 mol dm⁻³ KOH(aq) is given in the graph below.



At which point on the graph does pH = pK_a, where K_a is the acid dissociation constant of the weak acid?

- 15 Four solutions, each of concentration 0.1 mol dm^{-3} , were tested with a pH meter. The results are shown

solution	pH
$\text{CH}_3\text{CO}_2\text{H}$	4
HNO_3	1
CH_3NH_2	11
NaOH	14

Which statement is **incorrect**?

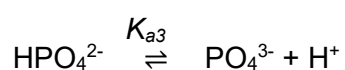
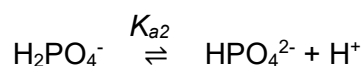
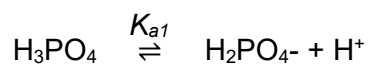
- A Conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is less stable than that of HNO_3
- B HNO_3 has a lower pH than $\text{CH}_3\text{CO}_2\text{H}$ because it is more soluble.
- C NaOH has a higher concentration of hydroxide ions in solution than CH_3NH_2 .
- D Mixing equal volume of CH_3NH_2 and HNO_3 form a solution with pH less than 7.
- 16 The ionic product of water, K_w , is affected by temperature. The table gives the $\text{p}K_w$ of pure water at different temperatures.

temperature / °C	$\text{p}K_w$
10	14.5
40	13.5

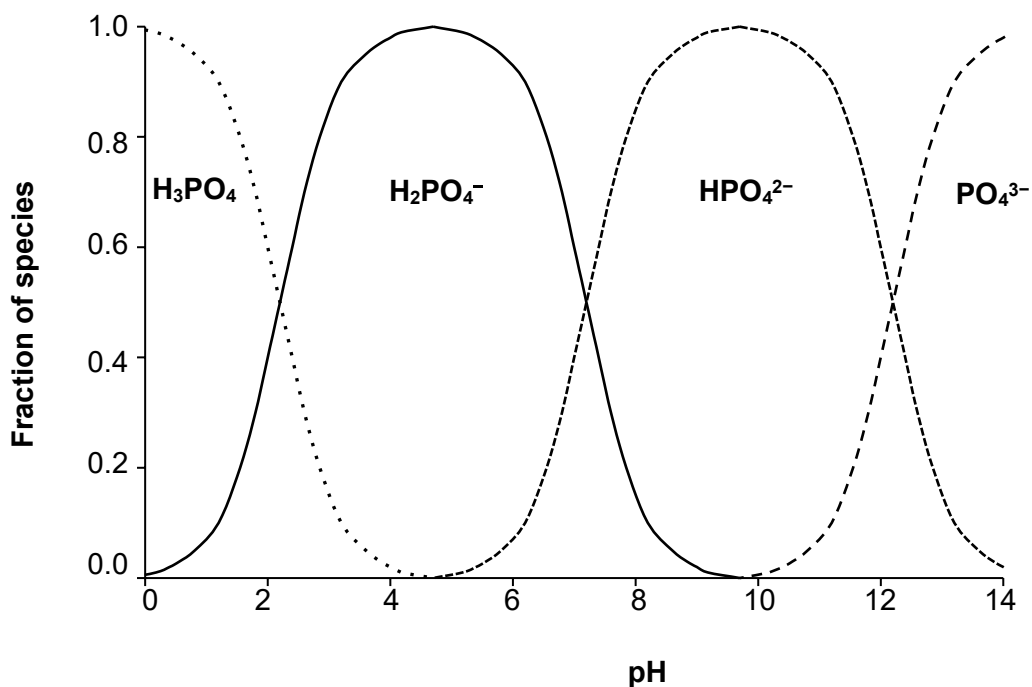
Solutions of acids and alkalis are prepared by dissolving HCl or NaOH in pure water at 10°C and at 40°C .

Which solution has the highest ionic concentration?

- A $\text{HCl}(\text{aq})$ at pH 1 at 40°C .
- B $\text{HCl}(\text{aq})$ at pH 1 at 10°C
- C $\text{NaOH}(\text{aq})$ at pH 13 at 40°C
- D $\text{NaOH}(\text{aq})$ at pH 13 at 10°C .
- 17 Phosphoric acid is a tribasic acid.



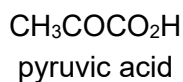
The graph shows the fraction of each species at different pH.



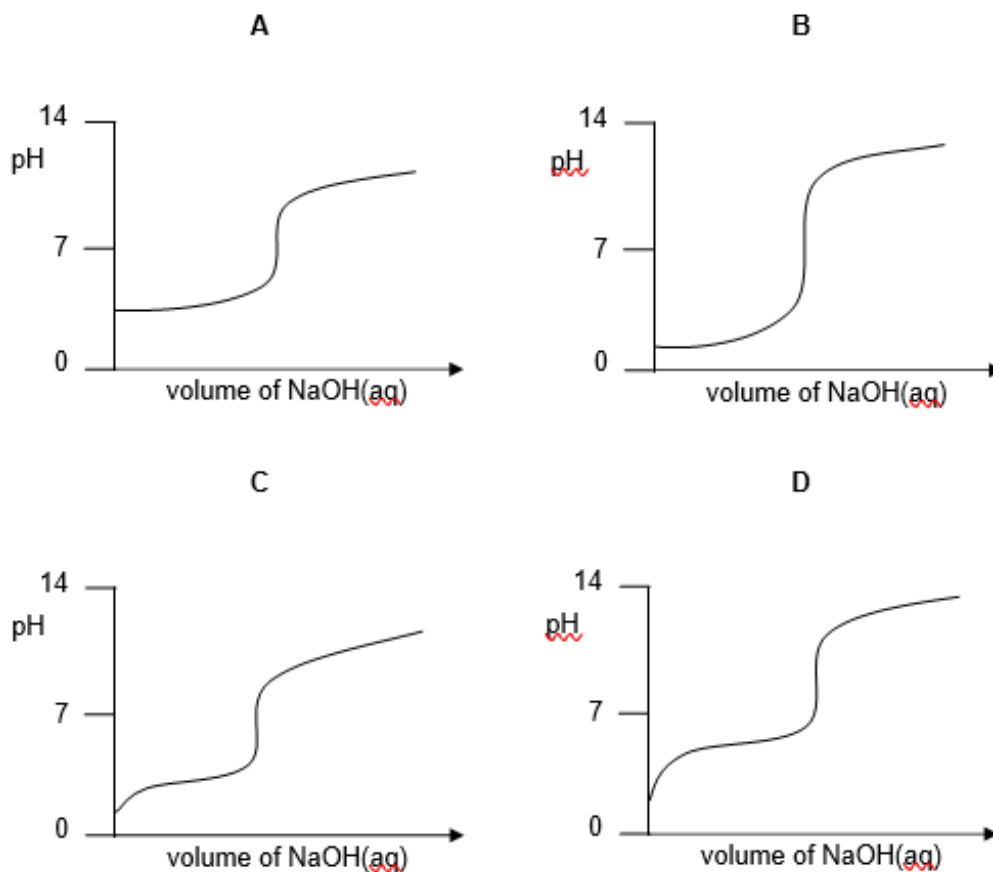
What is the numerical value of K_{a2} ?

- A** 6.3×10^{-3} **B** 2.0×10^{-5} **C** 6.3×10^{-8} **D** 2.0×10^{-10}

- 18** Pyruvic acid is a weak acid that is an important intermediate in many biochemical processes.



Which graph best represents the change in pH that occurs when a sample of pyruvic acid is titrated against $\text{NaOH}(\text{aq})$?



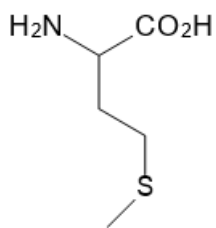
19 The K_a of lactic acid is $1.4 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K.

A buffer solution contains 1.5 mol dm^{-3} lactic acid and 0.5 mol dm^{-3} sodium lactate.

Which statement correctly describes the buffer solution?

- A** The pH of the buffer solution is 4.33.
- B** The pH of the buffer solution decreases upon dilution with water.
- C** The buffering capacity of the buffer solution increases upon dilution with water.
- D** The buffer solution has a greater buffering capacity against a base compared to an acid.

- 2 (a) Methionine is an essential amino acid in humans. It plays a critical role in the metabolism and health of humans because it is the precursor of other amino acids such as cysteine and taurine.



Methionine

The pK_a values associated with methionine are 2.28 and 9.21.

- (i) Calculate the pH of 0.15 mol dm^{-3} solution of methionine, ignoring the effect of the second pK_a value.

- (ii) Draw the structure of the zwitterionic form of methionine

- (iii) Write two equations to describe how a solution containing the zwitterionic form of methionine can act as a buffer.

- (iv) When 10 cm^3 of 0.15 mol dm^{-3} of **protonated** methionine was titrated against aqueous sodium hydroxide, the first equivalence point was reached when 15 cm^3 of the 0.10 mol dm^{-3} NaOH was added.

At the first equivalence point, only the zwitterionic form of methionine exists.

With the use of relevant equilibrium constant values, explain if the pH of the solution at the first equivalence point is less than, equal to or more than 7.

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- (v) Using the value and information from **(a)(i)** and **(a)(iv)**, as well as the pK_a values provided, sketch the pH–volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.15 mol dm^{-3} **protonated** methionine.

- (vi) Suggest a suitable indicator for the equivalence point in the above titration.

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- (b) Fig. 3.1 shows the four-step synthesis of an amino acid from an aldehyde, via an intermediate **G**.

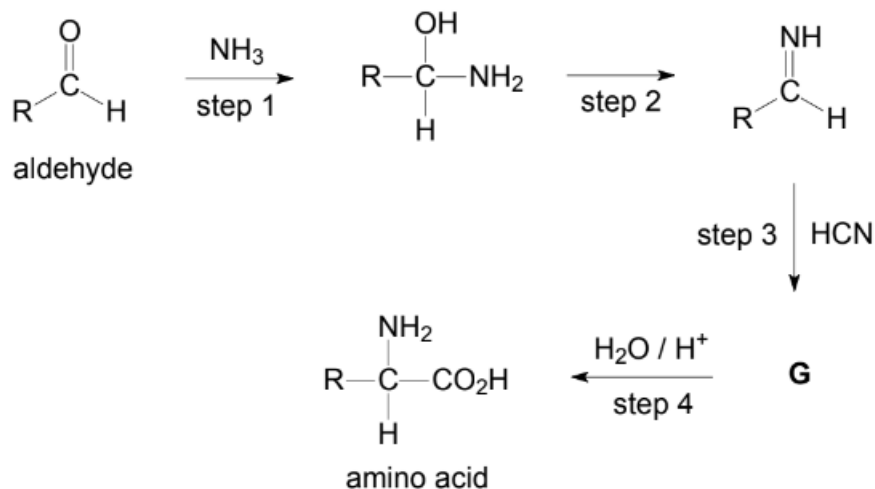


Fig. 3.1

- (i) States the types of reaction that occur during each of the steps 1 and 2.

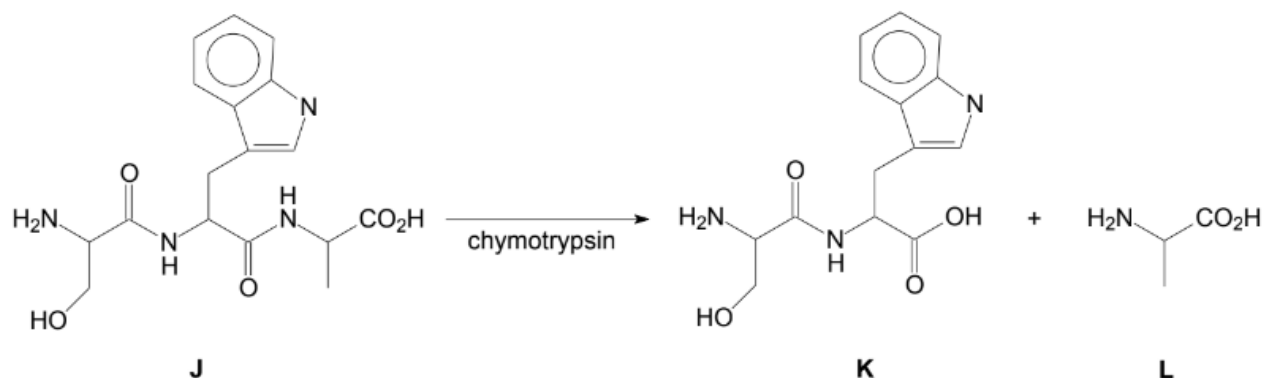
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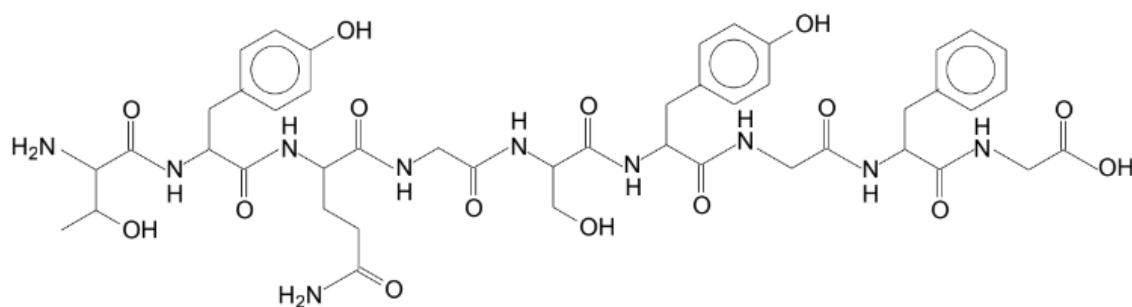
- (ii) Suggest the structure of compound **G**.

- (iii) Draw the displayed formula of a suitable starting aldehyde that can be used to synthesise methionine

- (c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide **J** produces two compounds **K** and **L** as shown.

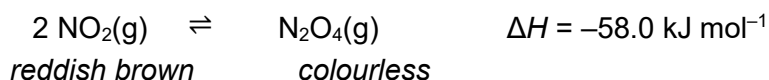


The following shows part of a short amino acid sequence found in human protein.



Draw the two dipeptides formed when the above amino acid sequence is hydrolysed by chymotrypsin.

- (b) At room temperature, reddish brown nitrogen dioxide, NO_2 , dimerises into colourless nitrogen tetroxide, N_2O_4 . The two gases are in dynamic equilibrium as shown.



- (i) Using your answer in (a)(i), explain why the dimerisation of NO_2 to form N_2O_4 is an exothermic process. [1]

The graph in Fig. 1.1 shows the pressure-temperature (p - T) relationship of two separate gaseous samples in an enclosed volume.

At 273 K, the first sample contains 1 mole of helium gas and the second sample contains 1 mole of gaseous N_2O_4 . As temperature increases, it is observed that the second sample behaves differently from the helium gas in the first sample.

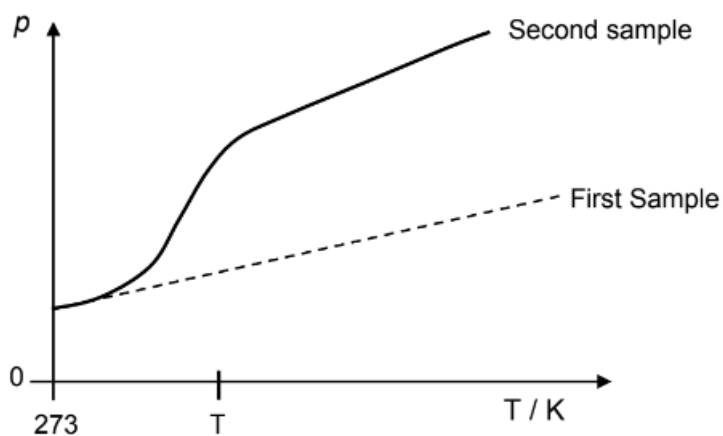


Fig. 1.1

- (ii) Explain the shape of p - T graph for the second sample in Fig. 1.1.

- The steeper slope as temperature increases from 273 K to T K.
- The gentler slope as temperature increases after temperature T K.

[3]

- (iii) State the visible observation that would be made for the second sample as the temperature increases.

[1]

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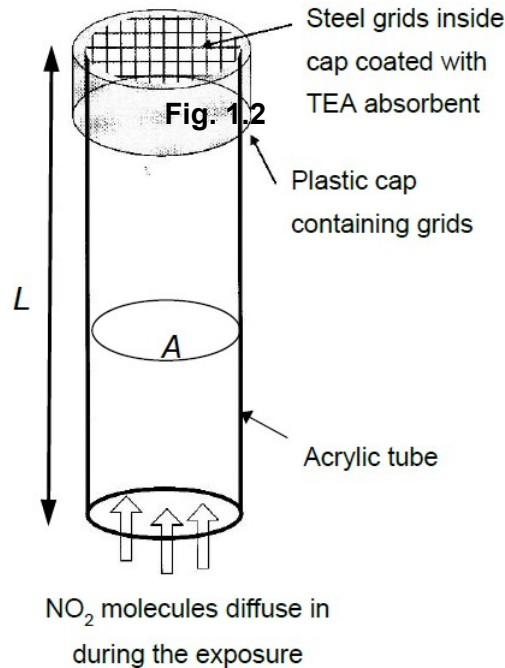
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As NO₂ has detrimental impacts on human health, it is important to monitor the level of ambient NO₂ in the atmosphere. One method to detect and measure ambient NO₂ involves the use of open tube diffusion sampler to collect air samples and measure the concentration of NO₂ in the air.

The process of determination of NO₂ can take place in three main stages:

(c) Stage 1: Collection of gas sample using a diffusion tube

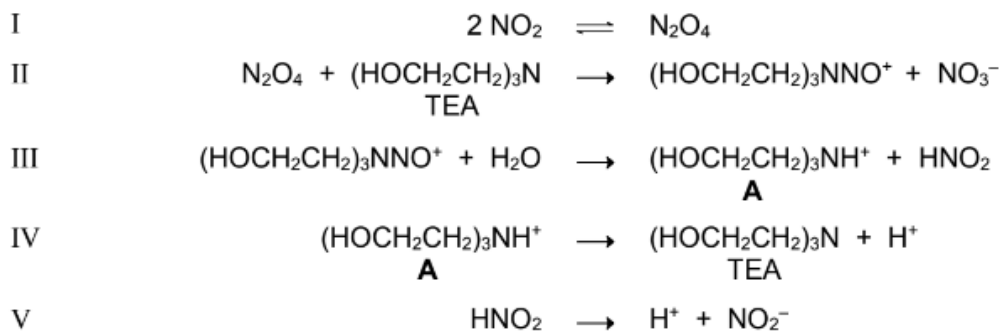
Fig. 1.2 shows a typical diffusion tube used for sample collection. It has a length (*L*) of 7.1 cm and cross-sectional area (*A*) of 0.91 cm².



The air sample to be analysed diffuses into the tube through an opening at the bottom. Triethanolamine (TEA), (HOCH₂CH₂)₃N, which is coated on the steel mesh grid, absorbs and converts NO₂ to produce nitrite NO⁻ in Stage 2.

Stage 2: Conversion of NO₂ to NO⁻

The following mechanism, consisting of steps I to V, has been proposed for the conversion of NO₂ to NO₂⁻ by TEA.



(d) Stage 3: Analysis and determination of the concentration of NO₂

The NO₂ produced is treated with suitable reagents to form a purple-coloured azo dye before it is placed in a colorimeter. The absorbance of light by the dye, measured at fixed wavelength, is proportional to the concentration of NO₂.

The average concentration of nitrogen dioxide in the air, [NO₂]_{av}, in µg m⁻³, can be determined using the expression given below.

$$[\text{NO}_2]_{\text{av}} = \frac{QL}{ADt}$$

- where
- Q is the amount of NO₂ (µg),
 - L is the length of the diffusion tube (m),
 - A is the cross-sectional area of the diffusion tube (m²),
 - D is the diffusion coefficient for NO₂ in the air at room temperature = 1.56 × 10⁻⁵ m² s⁻¹,
 - t is the duration of exposure (s).

The World Health Organisation (WHO) guideline states that ambient air quality is good when the concentration of NO₂ is below 25 µg m⁻³ (24-hour mean).

To monitor the quality of ambient air in a school compound, a diffusion tube with dimensions as shown in Fig. 1.2 was installed in the classroom for 10 days. The amount of NO₂ was found to be 4.13 × 10⁻³ µg.

Hence, determine the average concentration of NO₂, in µg m⁻³, in the ambient air of the school compound and use this to comment on the quality of air in terms of NO₂ level, during the 10-day monitoring.

(1 µg = 10⁻⁶ g) [2]

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- (b) Cis–trans isomers of transition metal complexes differ from each other in the arrangement of the ligands around the central metal ion or atom.

Cis isomers have two of the same ligands 90° apart from one another in relation to the central metal ion or atom, whereas trans isomers have two of the same ligands 180° apart.

Propose the structures of the cis and trans isomers of tetraaquadichlorochromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. Label your structures clearly. [2]

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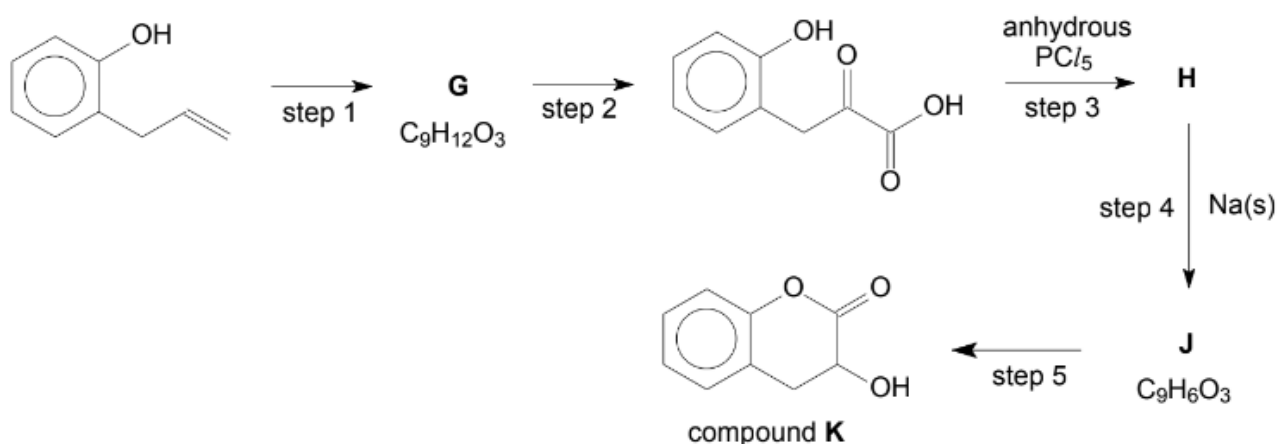
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- c) Compound **K** can be synthesised using the following reaction scheme shown in Fig. 4.1.



- (i) Suggest structures for the compounds **G**, **H** and **J**. [3]
- (ii) Suggest reagents and conditions for each of the steps 1, 2 and 5. [3]

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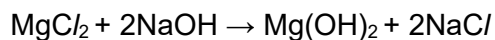
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- (d) Magnesium chloride gives a weakly acidic solution when dissolved. It can be titrated with a strong base to give a rapid pH change upon complete reaction at the equivalence volume.



In an experiment, 50.0 cm³ of aqueous magnesium chloride was titrated with 1.00 mol dm⁻³ sodium hydroxide. The pH of the solution changed as shown in Fig 4.2.

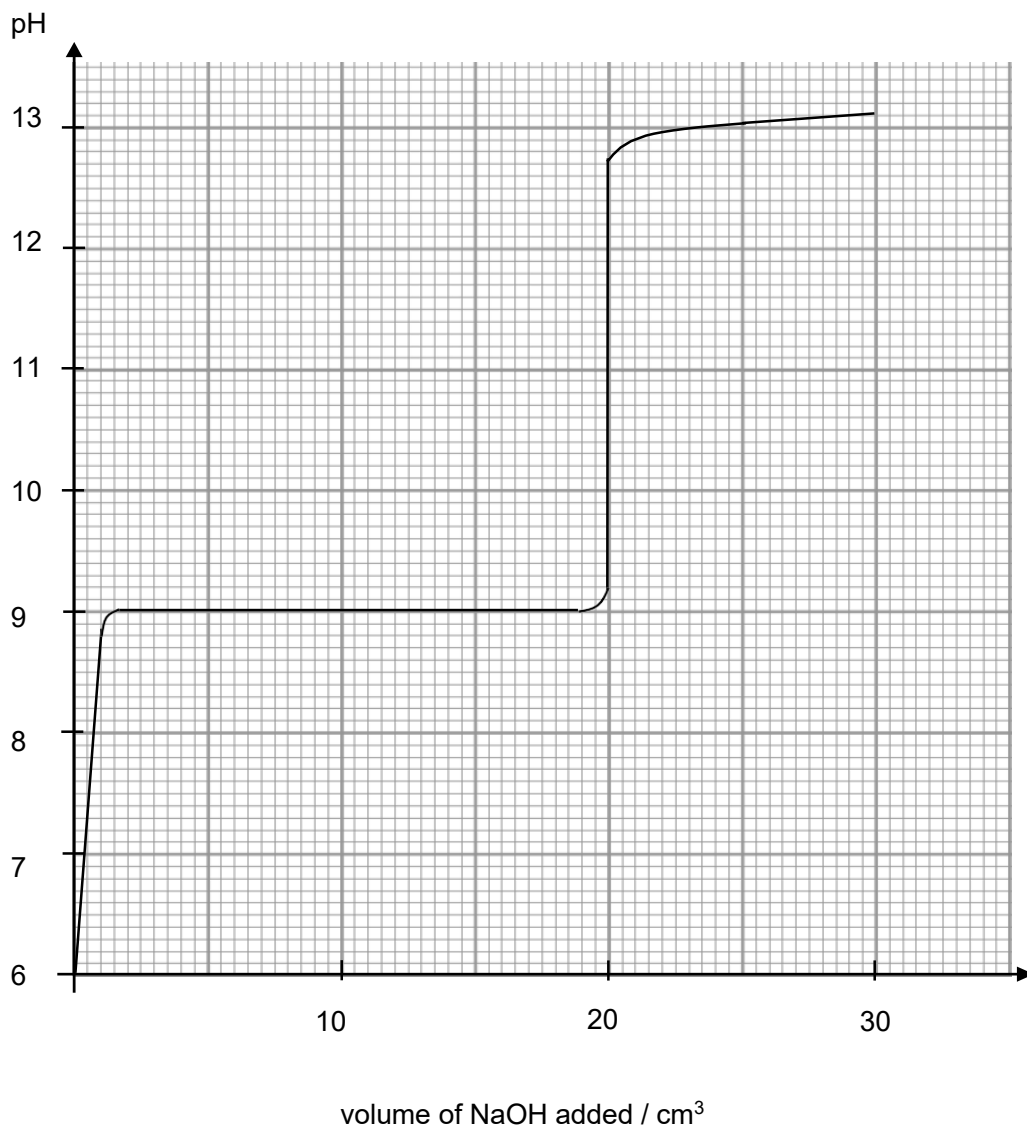


Fig. 4.2

- (i) Explain, with the aid of equations, why aqueous MgCl₂ has an initial pH of about 6. [2]
- (ii) Determine the concentration of aqueous MgCl₂ used in the above titration. [1]
- (iii) Write an expression for the solubility product, K_{sp} , of magnesium hydroxide. [1]
- (iv) When 10 cm³ of NaOH was added, the concentration of Mg²⁺(aq) is found to be half of the value in (d)(ii).

5 (a) Liquid ammonia, like aqueous ammonia is a conductor of electricity, but a very weak one. Liquid ammonia can exhibit this property as it can undergo self-ionisation.

(i) Write an equation between two ammonia molecules to show this property of liquid ammonia.

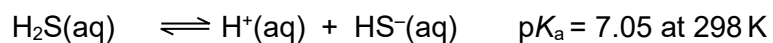
.....[1]

(ii) Identify the two different conjugate acid-base pairs in the reaction occurring in **(a)(i)**.

.....

.....[1]

(b) Hydrogen sulfide can act as a weak acid.



(i) NaHS is a basic salt that undergoes salt hydrolysis. Calculate the pH of 0.100 mol dm⁻³ NaHS(aq).

- (ii) The pK_a for C_6H_5SH is 6.5. Suggest an explanation for the different pK_a values for H_2S and C_6H_5SH .

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.....[1]

- 6 (c) A solution containing hydrogensulfite ions, $HSO_3^-(aq)$, and sulfite ions, $SO_3^{2-}(aq)$, can act as a buffer. The K_a of $HSO_3^-(aq)$ is $6.73 \times 10^{-8} \text{ mol dm}^{-3}$ at 298 K. A buffer solution is prepared by mixing 50.0 cm^3 of $0.500 \text{ mol dm}^{-3} \text{ NaHSO}_3$ and 25.0 cm^3 of $0.600 \text{ mol dm}^{-3} \text{ NaOH}$. By finding $[SO_3^{2-}]$ and $[HSO_3^-]$ after mixing $NaHSO_3$ and $NaOH$, calculate the pH of the buffer solution formed at 298 K. Show your working clearly.

[2]

- (d) Calcium fluoride, CaF_2 , occurs naturally in the mineral *fluorspar*. It is the major sources of fluorine for the chemical industry, for making polymers (PTFE), freons and fire retardants. It is also sparingly soluble in water. In its saturated solution, the concentration of CaF_2 is $2.30 \times 10^{-4} \text{ mol dm}^{-3}$.

(i) Write an expression for the solubility product, K_{sp} , of calcium fluoride, and calculate its value.

[2]

- 6 (d) (ii) Use only the relevant data provided below to calculate a value for the enthalpy change of solution of calcium fluoride.

enthalpy change of formation of $\text{CaF}_2(\text{s})$	$-1220 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $\text{Ca}(\text{s})$	$+178 \text{ kJ mol}^{-1}$
enthalpy change of formation of $\text{Ca}^{2+}(\text{aq})$	-543 kJ mol^{-1}
electron affinity of fluorine atoms	-328 kJ mol^{-1}
enthalpy change of formation of $\text{F}^{-}(\text{aq})$	-333 kJ mol^{-1}

[2]

- (iii) Hence, predict whether CaF_2 will be more, or less, soluble in hot water than in cold water.

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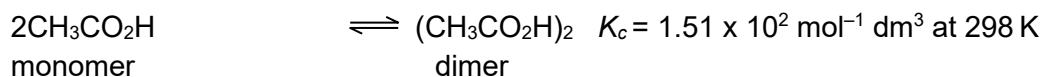
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.....[1]

6 (d) (iv) Describe and explain how the solubility of CaF_2 , is affected when $\text{CaCl}_2(\text{aq})$ is added.

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.....[1]

(v) In non-polar solvents, ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, can form a dimer containing two hydrogen bonds.



I A solution of $0.100 \text{ mol dm}^{-3}$ $\text{CH}_3\text{CO}_2\text{H}$ is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is

$0.0417 \text{ mol dm}^{-3}$. Calculate the $\frac{[(\text{CH}_3\text{CO}_2\text{H})_2]}{[\text{CH}_3\text{CO}_2\text{H}]}$ ratio at equilibrium. Quote your answer to 3

.

[1]

II Suggest how the ΔG for this equilibrium in an aqueous solution would differ from the ΔG in a non-polar solvent. Explain your answer.

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..... [1]

[Total: 15]

7 (a) Baryta water, barium hydroxide, $\text{Ba}(\text{OH})_2(\text{aq})$ is a Bronsted base.

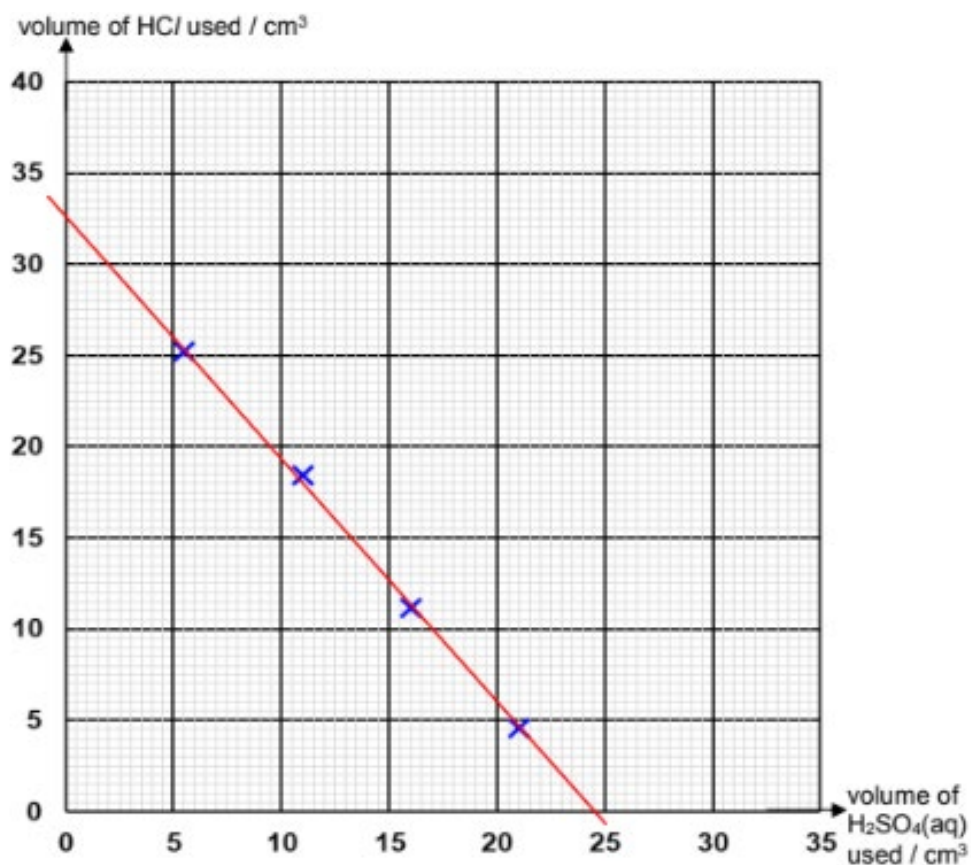
Define what is meant by a Bronsted base.

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[1]

(b) $\text{Ba}(\text{OH})_2(\text{aq})$ neutralises both H_2SO_4 and HCl acid. In an experiment, a student prepared 4 mixtures, each containing the same volume of 25.0 cm^3 of $\text{Ba}(\text{OH})_2$ solution, but with different volumes of sulfuric acid added.

In each mixture, neutralisation has not been completed, the solution remains alkaline and is neutralised by titration with $0.150 \text{ mol dm}^{-3}$ HCl acid. A graph of volume of HCl on the y-axis was plotted against volume of H_2SO_4 for each of the 4 mixtures. The graph is extrapolated until it touches both axes.



- (i) Read from the graph, and record the volume of HCl (Vol.HCl (max), required to exactly neutralise 25.0 cm³ of Ba(OH)₂.

.....

.....

[1]

[Total: 5]

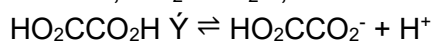
- (ii) Calculate the concentration of Ba(OH)₂.

[2]

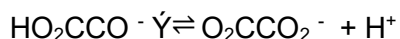
- (iii) Explain in terms of the chemistry involved, why the direction of the slope of the graph is negative

[2]

8 (a) Oxalic acid, HO₂CCO₂H, is a weak diprotic acid.



$$pK_{a1} = 1.27$$



$$pK_{a2} = 4.28$$

(i) 10 cm³ of 0.100 mol dm⁻³ HO₂CCO₂H was mixed with 10 cm³ of 0.150 mol dm⁻³ HO₂CCO₂Na.

Write an equation to show how this solution is able to maintain pH upon addition of alkali.

..... [1]

(ii) 14.0 cm³ of 0.100 mol dm⁻³ KOH was added to the solution in (a)(i). Calculate the pH of the resultant solution after adding KOH(aq).

[3]

(b) Rare earth ions in the oxidation state of +3, such as cerium(III) ions, Ce³⁺, are used in the production of luminescent materials.

Solutions containing Ce³⁺ ions may sometimes be contaminated by other cations such as Ca²⁺. The recovery of Ce³⁺ ions from such solutions can be achieved through selective precipitation using oxalic acid as the precipitating agent. After adding oxalic acid to a solution containing Ce³⁺ ions contaminated with Ca²⁺ ions, the pH of the solution is adjusted through the addition of a strong mineral acid. The purpose is to control the concentration of the oxalate anion, C₂O₄²⁻ in the solution and hence ensure that maximum amount of Ce³⁺ ion is precipitated to achieve an effective separation from the contaminant cation.

Table 2.1 contains the values of the logarithm to the base 10 of the equilibrium constant, *K*, for some of the equilibrium reactions.

Table 2.1

Equilibrium equations	lg <i>K</i>
Ca ²⁺ (aq) + C ₂ O ₄ ²⁻ (aq) ⇌ CaC ₂ O ₄ (s)	8.63
2Ce ³⁺ (aq) + 3C ₂ O ₄ ²⁻ (aq) ⇌ Ce ₂ (C ₂ O ₄) ₃ (s)	30.18
HO ₂ CCO ₂ H(aq) ⇌ 2H ⁺ (aq) + C ₂ O ₄ ²⁻ (aq)	-5.06

The numerical values for the solubility product of CaC₂O₄ and Ce₂(C₂O₄)₃ are 2.34 × 10⁻⁹ and 6.60 × 10⁻³¹ respectively.

(i) Using data from Table 2.1, prove that the numerical value of K_{sp} of CaC_2O_4 is 2.34×10^{-9} .

[1]

(ii) Solution A contains $0.010 \text{ mol dm}^{-3}$ of Ca^{2+} , $0.010 \text{ mol dm}^{-3}$ of Ce^{3+} and 1.0 mol dm^{-3} of oxalic acid. Calculate the minimum concentration of $\text{C}_2\text{O}_4^{2-}$ needed for the precipitation of Ca^{2+} and Ce^{3+} respectively.

[2]

(iii) Using your answers in (b)(ii) and data from Table 2.1, calculate the pH of solution A that is required to precipitate the maximum amount of Ce^{3+} .

[3]

[Total: 10]

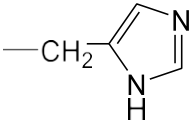
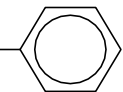
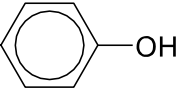
- 9 COVID-19 is an illness caused by the virus SARS-CoV-2, which was first identified amid an outbreak of respiratory illness cases in 2019.

In November 2021, a new Omicron variant was found to be the most transmissible variant compared to the previous variants, such as the Delta variant.

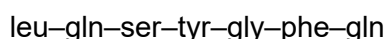
- a. The differences in the transmissibility of the variants are due to their varying amino acid sequences in a specific region **X** of their peptide chains.

Some of the amino acids present in the variants are listed in Table 3.1.

Table 3.1

name	abbreviation	formula of side chain (R in R-CH(NH ₂)CO ₂ H)
arginine	arg	
glutamine	gln	-CH ₂ CH ₂ CONH ₂
glutamic acid	glu	-CH ₂ CH ₂ COOH
glycine	gly	-H
leucine	leu	-CH ₂ CH(CH ₃) ₂
phenylalanine	phe	-CH ₂ - 
serine	ser	-CH ₂ OH
tyrosine	tyr	-CH ₂ - 

A heptapeptide found in region **X** of the Delta variant has the sequence shown below.



The heptapeptide was partially hydrolysed by heating with a concentrated solution of sodium hydroxide. The partial hydrolysis produced a mixture of dipeptides.

- i. Upon acidification of the dipeptides, leu-glu and phe-glu were obtained instead of leu-gln and phe-gln.

By referring to Table 3.1, suggest why this is so.

.....

(ii) Ser-tyr was also one of the dipeptides formed.

Draw the structure of this dipeptide at pH 13.

[1]

Another heptapeptide found in region X of the Omicron variant was also subjected to hydrolysis under the same conditions.

The initial partial hydrolysis of this heptapeptide produced the tetrapeptides shown below.

tyr-ser-phe-arg, arg-ser-tyr-ser, leu-arg-ser-tyr

(iii) Deduce the sequence of amino acids in this heptapeptide.

..... [1]

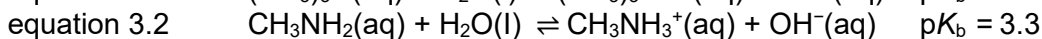
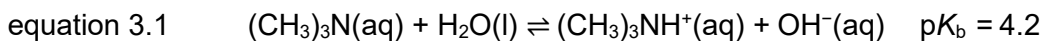
Increasing evidence suggests that gut health may be compromised in COVID-19 patients. One indicator of bad gut health is high levels of trimethylamine.

Both trimethylamine, $(\text{CH}_3)_3\text{N}$, and methylamine, CH_3NH_2 , behave as bases in the gaseous and aqueous phases.

(c) Explain why, in the gaseous phase, $(\text{CH}_3)_3\text{N}$ is a stronger base than CH_3NH_2 .

.....
.....
.....

In aqueous solution, the following equilibria are established.



(ii) State the predominant interaction, other than hydrogen bonding, between $(\text{CH}_3)_3\text{NH}^+$ and water.

.....

(iii) Compared to $(\text{CH}_3)_3\text{NH}^+$, CH_3NH_3^+ has a stronger interaction with water.

With reference to your answer in (b)(ii), explain why this is so.

.....
.....
.....[1]

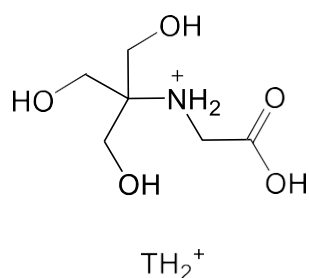
(iv) Hence, suggest why the $\text{p}K_{\text{b}}$ of CH_3NH_2 is lower than that of $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

.....
.....
..... [1]

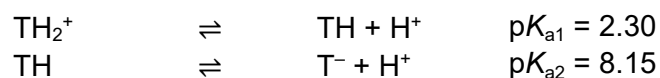
Antigen-based rapid diagnostic test kits have been used to detect the SARS-CoV-2 virus.

(c) The test kit includes a vial containing a buffer solution prepared from tricine, TH.

The structure of protonated tricine, TH_2^+ , is shown below.



The acid dissociation involving TH_2^+ and TH and their corresponding $\text{p}K$ values at 25 °C are shown below.



(i) TH exists as a solid at room temperature.

Draw the structure of TH and explain why it has a high melting point.

.....

.....

.....

.....

[2]

The buffer solution is prepared by dissolving 0.1 mol of solid tricine, TH, in 1.0 dm³ of aqueous sodium hydroxide. The pH of this buffer is 8.78.

(ii) Calculate the concentration of aqueous sodium hydroxide used in the preparation of this buffer solution. [2]

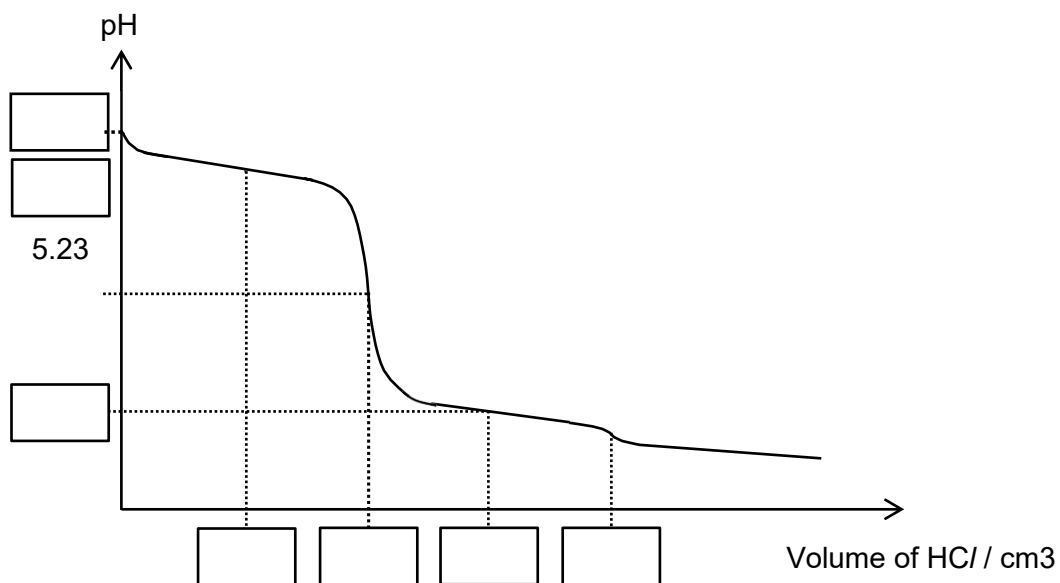
(iii) Explain how a more dilute buffer solution of the same volume will compare in terms of buffering capacity.

.....
.....
..... [1]

d) 10 cm³ of 0.1 mol dm⁻³ of the deprotonated tricine, T⁻, was titrated against 0.1 mol dm⁻³ of HCl from a burette.

(i) Calculate the pH of 0.1 mol dm⁻³ of T⁻ solution at 25 °C. [2]

(ii) Using your answer in (d)(i) and information in (c), fill in the boxes below with the correct pH values and HCl volumes [2]



(iii) Methyl red is used as the indicator for determining the first end-point for this titration. It changes colour from red at pH 4.4 to yellow at pH 6.2.

Explain why methyl red is suitable for determining the first end-point. Hence, state the colour change at the first end-point of the titration.

.....
.....
.....
..... [2]

(iv) Suggest why the second end-point cannot be determined by titration.

.....
..... [1]

ANSWERS FOR ACID-BASE EQUILIBRIA MCQ PART 1

- 1 Which solution will solid silver phosphate, Ag_3PO_4 , be the least soluble in, at 25°C ?
The numerical value of K_{sp} (Ag_3PO_4) is 8.89×10^{-17}

- A pure water
B 2.0 mol dm^{-3} AgNO_3 (aq)
C 2.0 mol dm^{-3} NH_3 (aq)
D 2.0 mol dm^{-3} K_3PO_4 (aq)

Let the solubility of Ag_3PO_4 be s mol dm^{-3}

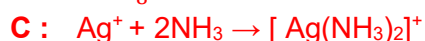
$$K_{\text{sp}} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

A : $K_{\text{sp}} = (3s)^3 (s) \Rightarrow 27s^4 = K_{\text{sp}}$

$$s = \sqrt[4]{\frac{K_{\text{sp}}}{27}} = 4.26 \times 10^{-5}$$

B : $K_{\text{sp}} = (3s + 2)^3 (s) \approx 2^3 s$

$$s = \frac{K_{\text{sp}}}{8} = 1.11 \times 10^{-17}$$



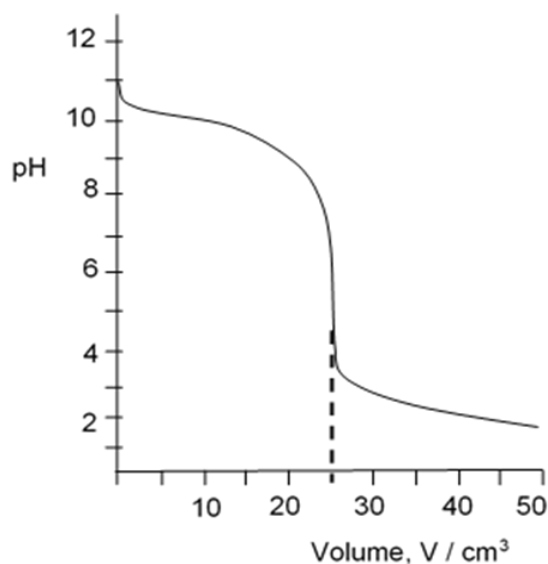
Formation of complex increases solubility of Ag_3PO_4 as the concentration of Ag^+ decreases.

D : $K_{\text{sp}} = (3s)^3 (s + 2) \approx (3s)^3 \cdot 2$

$$s = \sqrt[3]{\frac{K_{\text{sp}}}{54}} = 1.18 \times 10^{-6}$$

- 2 In an acid-base titration, 0.10 mol dm^{-3} solution of an acid is added to 25 cm^3 of 0.10 mol dm^{-3} solution of a base.

The pH value of the solution is plotted against the volume, V , of acid added as shown in the diagram.



Which statement is incorrect?

- A Maximum buffering capacity occurs at $V = 12.5 \text{ cm}^3$
- B The pair of solutions could have been $\text{HCl}(\text{aq})$ and $\text{CH}_3\text{NH}_2(\text{aq})$.
- C Methyl orange is suitable indicator for the above titration.
- D When the concentration of the acid is doubles, the pH at equivalence point remains unchanged.

A: pH at equivalence point < 7 ; implies presence of acidic salt. Hence strong acid-weak base titration has occurred. When a strong acid is added to the weak base, an acidic salt is formed (conjugate acid of the weak base). As the conjugate acid is present together with the weak base in the solution, a buffer is formed. The solution is at its maximum buffering capacity at half the volume needed for complete neutralisation of the base. Option A is correct.

B: 25 cm^3 of base required 25 cm^3 of acid at equivalence point. As the concentrations of both solutions are the same, it indicates that the stoichiometry of acid:base is 1:1, hence the solutions involved should be a monoprotic base and a monobasic acid.

Since the equivalence point occurs at $\text{pH} < 7$, it indicates that the salt is acidic and that the base is used in the titration is a weak base. Option B is correct.

C: For strong acid-weak base titration, methyl orange is a suitable indicator as the equivalence point lies below 7 and coincides with the working range of the indicator (approximately 3 to 4). Option C is correct.

D: When the concentration of the acid is doubled, the amount of salt formed at equivalence point is the same, though total volume of the solution is now lower.

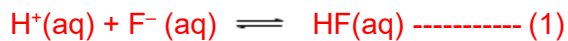
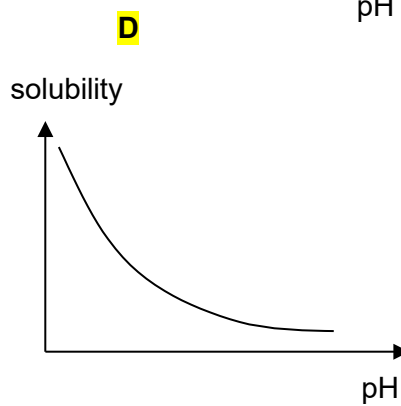
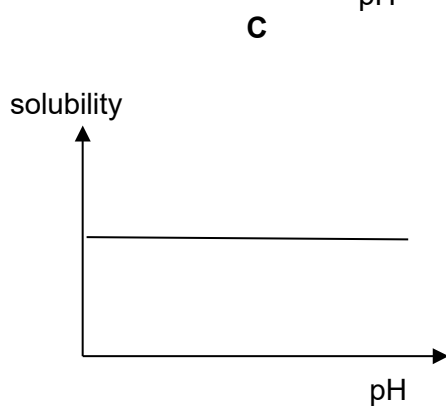
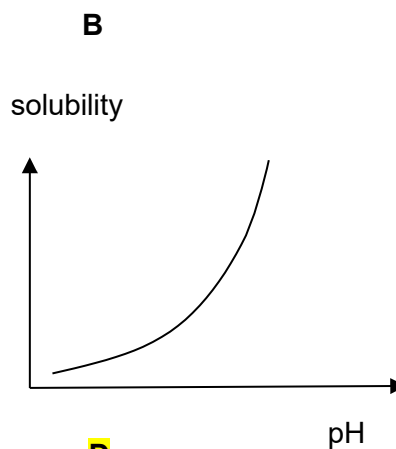
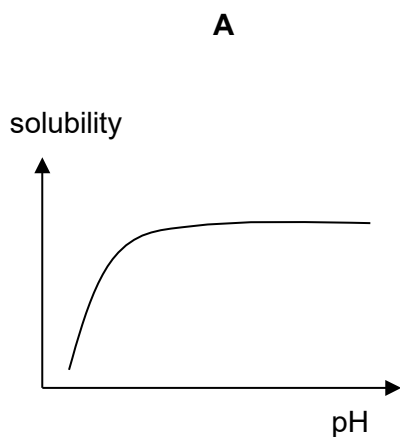
$$\text{Compared to } [\text{salt}]_{\text{original}} = 25.0 \times 0.1 / (25 + 25) = 0.05 \text{ mol dm}^{-3}$$

$$[\text{salt}]_{\text{new}} = 12.5 \times 0.2 / (12.5 + 25) = 0.0667 \text{ mol dm}^{-3} \text{ So } [\text{H}^+] = \sqrt{K_a} \times [\text{salt}]$$

when $[\text{salt}]$ is higher, new $[\text{H}^+]$ be higher, hence new equivalence pH will decrease.

3 Aqueous HF is a weak acid. Magnesium fluoride is sparingly soluble.

Which graph below shows how the solubility of MgF_2 in water will vary with pH at constant temperature?



Towards lower pH as $[\text{H}^+]$ increases, POE for equation (1) shifts right. This results in a decrease in $[\text{F}^-]$ in equation (2).

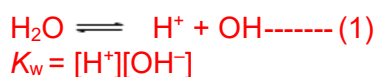
By LCP, POE for equation (2) shifts right to increase $[\text{F}^-]$, thus increasing the solubility of MgF_2 .

- 4 The variation of the ionic product of water, K_w , with the temperature is given in the table.

Temperature/ °C	$K_w/\text{mol}^2\text{dm}^{-6}$
25	1.00×10^{-14}
50	5.50×10^{-14}
62	1.00×10^{-13}

What can be deduced from this information?

- A The ionization of water is an exothermic process.
B $[\text{H}^+]$ is more than $[\text{OH}^-]$ as temperature increases.
C pH of water at 10°C is higher than at 25°C
D The equilibrium position lies furthest to the right at 25°C



When temperature increases, K_w increases, indicating POE for (1) shifts right to absorb additional heat. Thus the ionization of water is endothermic.

As POE shifts right, $[\text{H}^+]$ and $[\text{OH}^-]$ increases to the same amount.

K_w at 10°C is lower than $1.00 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$. $[\text{H}^+]$ at 10°C will be less than $\sqrt{(1 \times 10^{-14})}$, pH will be higher than at 25°C.

- 5 Aqueous ethanenitrile, CH_3CN , has no effect on litmus but aqueous ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$, turns litmus blue.

Which statements below can be used to explain this observation?

- 1 Delocalisation of the lone pair of electrons on the nitrogen atom of CH_3CN over the C=N group strengthens the C-N bond.
- 2 Lone pair of electrons on the nitrogen atom of C=N are in an sp hybridized orbital which is closer to the nucleus than the lone pair of electrons on the sp^3 hybridised nitrogen atom of the NH_2 group.
- 3 The ethyl group in ethylamine is a stronger electron donating group than the methyl group in ethanenitrile as it has one more carbon atom.

- A 1, 2 and 3 B 1 only C 2 and 3 D 2 only

Statement 1 is incorrect as the lone pair is NOT delocalised; the lone pair is localised on the sp hybridised N atom of the nitrile group. Furthermore, the strength of the C-N bond does not impact the availability of the lone pair for donation to a proton.

Statement 2 is correct. Observing the nitrile is neutral, while the amine is basic indicates that the lone pair on the N of nitrile is not available for donation to a proton. This is due to the sp hybridised state of N in nitrile has higher s character than the sp^3 hybridised state of N in amine. This results in stronger attraction of the nucleus on the lone pair, making it less available to accept proton.

Statement 3 is incorrect. The **size** of the alkyl group does **not** affect the extent of electron donating effects significantly.

You may have thought that statement 3 is correct because of what you read in the Hydroxy Compounds lecture notes pg 25. However, please note that the difference in electron donating effect between alkyl groups of different sizes is insignificant (in fact you will only see very slight difference in pK_a values of ethanoic acid vs propanoic acid) and it has never been mentioned as a reason to significantly impact basicity of organic compounds such that one compound is basic while the other is neutral.

If you are interested to read up more, you may see this website that is related to our syllabus:

<https://www.chemguide.co.uk/basicorg/acidbase/acids.html>

- 6 What is the pH of the final solution when $V \text{ cm}^3$ of dilute nitric acid of pH 2.0 is mixed with $V \text{ cm}^3$ of dilute nitric acid of pH 4.0 followed by the addition of $2V \text{ cm}^3$ of water?

A 2.3

B 2.6

C 3.0

D 3.6

Topic: Chemistry of aqueous solutions

Concept: Calculation of pH of acidic solutions

Total volume of final solution = $V + V + 2V = 4V \text{ cm}^3$

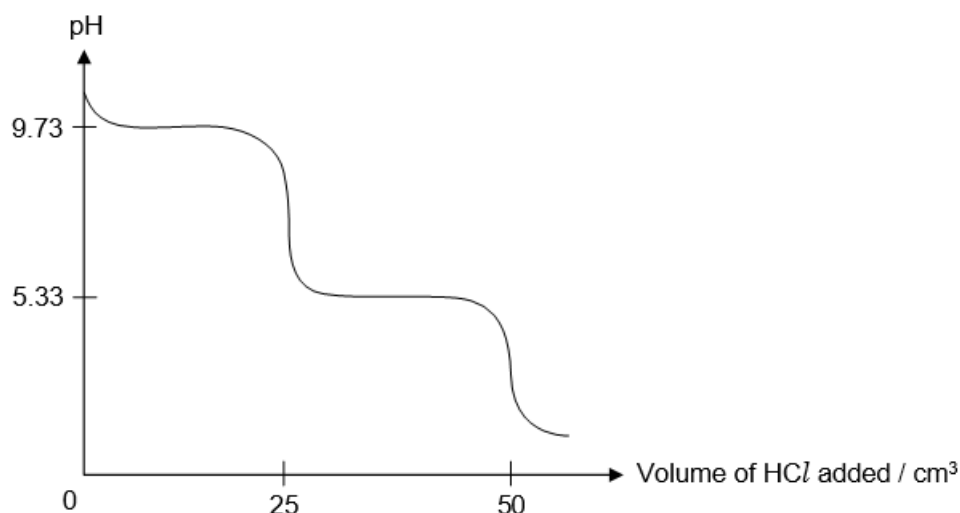
Total amount of H^+ ions in final solution = $(10^{-2} \times \frac{V}{1000}) + (10^{-4} \times \frac{V}{1000}) \text{ mol}$

$$[\text{H}^+] \text{ in final solution} = \frac{(10^{-2} \times \frac{V}{1000}) + (10^{-4} \times \frac{V}{1000})}{\frac{4V}{1000}} = 0.002525 \text{ mol dm}^{-3}$$

pH of final solution = $-\log(0.002525) = 2.6$

Answer: B

- 7 The pH change when 1.00 mol dm^{-3} hydrochloric acid was added dropwise to 25 cm^3 of 1.00 mol dm^{-3} piperazine ($\text{C}_4\text{H}_{10}\text{N}_2$) is shown below.



From the table below, which pair of indicators can be used consecutively to detect the end-points of the titration?

indicator	range
bromothymol blue	6.0 – 7.6
ethyl orange	3.4 – 4.8
methyl red	4.8 – 6.0
thymolphthalein	9.4 – 10.6

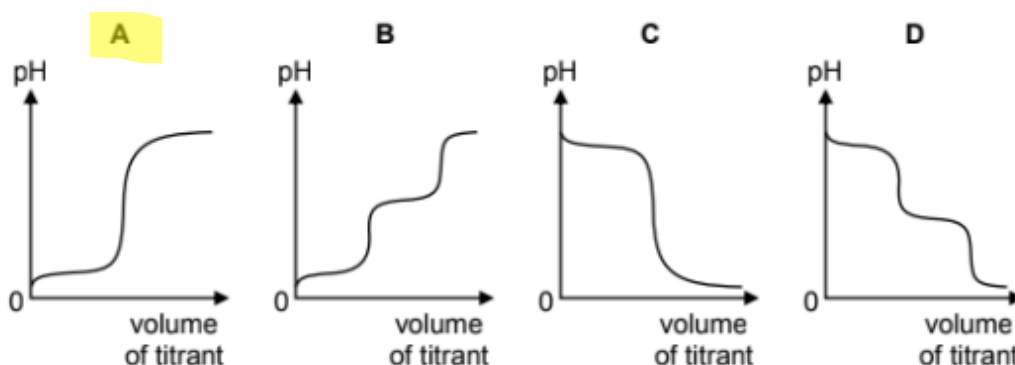
- A** Bromothymol blue followed by ethyl orange
B Bromothymol blue followed by methyl red
C Thymolphthalein followed by ethyl orange
D Thymolphthalein followed by methyl red

In order for end-point to be determined, the transition range of the indicator should fall within the region of sharp pH change.

For the first end-point, the sharp pH change occurs between 5.33 and 9.73. Hence, a suitable indicator would be bromothymol blue. Thymolphthalein will not be suitable as its colour would have changed before the first equivalence point is reached.

For the second end-point, the ethyl orange would be a suitable indicator as its pH range is below 5.33. Methyl red will not be suitable since its colour would have changed before the second equivalence point is reached.

- 8 Which of the following titration curves is obtained when HCl(aq) is titrated against standard Na₂CO₃(aq)?

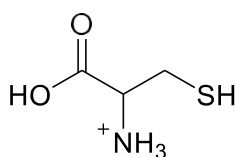


As HCl is titrated against Na₂CO₃, Na₂CO₃ is added from the burette into HCl in the conical flask, the pH increases with the volume of titrant. HCl will completely react with any Na₂CO₃ added



Hence there will be only one end-point.

- 9 A solution of cysteine in its fully protonated form is titrated against a standard solution of potassium hydroxide. The structure of fully protonated cysteine is shown below and its three pK_a values are 10.3 (for -SH), 8.1 and 1.9.

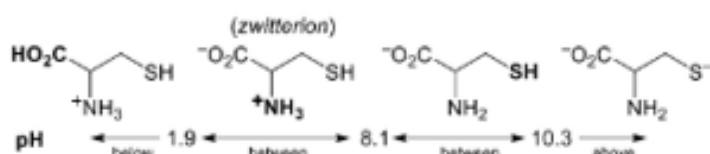


The isoelectric point is the pH value at which the net electric charge of a molecule is zero, and in the case of cysteine, can be estimated by taking the average of two appropriate pK_a values.

Which of the following indicators can be used to detect the isoelectric point of cysteine?
Indicator working range

- | | | |
|----------|------------------|-----------|
| A | methyl orange | 3.2 – 4.4 |
| B | methyl red | 4.1 – 6.1 |
| C | bromothymol blue | 6.0 – 8.0 |
| D | phenol red | 6.9 – 8.9 |

11 Considering the species present:



$$pI \approx \frac{1.9 + 8.1}{2} = 5.0 \text{ (zwitterion is neutral)}$$

10 Use of the Data Booklet is relevant to this question.

Water dissociates as shown.



At 25° C, the equilibrium value of $[\text{H}^+]$ is $10^{-7} \text{ mol dm}^{-3}$; $[\text{H}_2\text{O}] = 55.6 \text{ mol dm}^{-3}$.

What is the order of increasing numerical value of pH, $\text{p}K_{\text{a}}$ and $\text{p}K_{\text{w}}$ for this equilibrium at this temperature?

	smallest		Largest
A	pH	$\text{p}K_{\text{a}}$	$\text{p}K_{\text{w}}$
B	pH	$\text{p}K_{\text{w}}$	$\text{p}K_{\text{a}}$
C	$\text{p}K_{\text{a}}$	$\text{p}K_{\text{w}}$	pH
D	$\text{p}K_{\text{w}}$	$\text{p}K_{\text{a}}$	pH

$$\text{pH} = -\lg[\text{H}^+] = 7$$

$$\text{p}K_{\text{w}} = -\lg[\text{H}^+][\text{OH}^-] = 14$$

$$\text{p}K_{\text{a}} = -\lg \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = -\lg((10^{-7})^2 / (55.6)) = 15.7$$

11 Which combinations of substances would result in a buffer solution?

- A 25.0 cm³ of 0.100 mol dm⁻³ HCl(aq) and 20.0 cm³ of 0.100 mol dm⁻³ NaCl(aq)
- B 25.0 cm³ of 0.100 mol dm⁻³ HCl(aq) and 25.0 cm³ of 0.200 mol dm⁻³ NH₃(aq)
- C 25.0 cm³ of 0.100 mol dm⁻³ H₂CO₃(aq) and 50.0 cm³ of 0.100 mol dm⁻³ NaOH(aq)
- D 20.0 cm³ of 0.100 mol dm⁻³ CH₃CO₂H(aq) and 25.0 cm³ of 0.100 mol dm⁻³ NaOH(aq)

Recall that a buffer should be made up of a weak acid and its conjugate base or a weak base and its conjugate acid.

Option	Explanation
A	This mixture consists of NaCl(aq) (a salt) and HCl(aq) (a strong acid). Thus this is not a buffer solution.
B	$\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$ Since the same volume but a higher concentration of NH ₃ (aq) is used, NH ₃ (aq) is added in excess. The resulting mixture consists of NH ₃ (a weak base) and NH ₄ Cl (its conjugate acid) which makes up a buffer solution.
C	H ₂ CO ₃ is a dibasic acid. Twice the volume of NaOH(aq) (a monoacidic strong base) is added to H ₂ CO ₃ (aq) of the same concentration. Hence, H ₂ CO ₃ and NaOH are completely neutralised to give Na ₂ CO ₃ and H ₂ O. This is not a buffer solution.
D	$\text{CH}_3\text{CO}_2\text{H} + \text{NaOH} \rightarrow \text{CH}_3\text{CO}_2\text{Na} + \text{H}_2\text{O}$

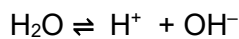
12 Aqueous solutions of aluminium salts are acidic. They contain $[Al(H_2O)_6]^{3+}$ ions.

$$K_a \text{ for } [Al(H_2O)_6]^{3+} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

What is the pH of $0.01 \text{ mol dm}^{-3} AlCl_3$?

- A 2.5 **B 3.5** C 5.0 D 6.0

13 Pure water undergoes dissociation as shown in the equation below.

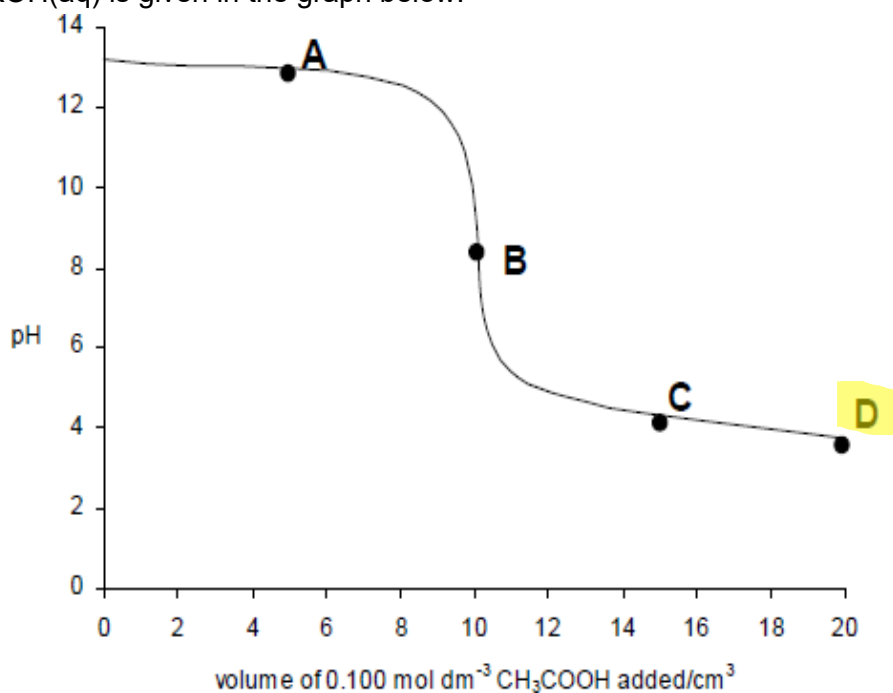


At $40^\circ C$, the $[H^+]$ is found to be $10^{-6.8} \text{ mol dm}^{-3}$.

Which of the following statements is **incorrect**?

- A The dissociation of water is an endothermic process.
B Water is acidic at $40^\circ C$
C At $40^\circ C$, the value of pK_w is 13.6.
D Both H^+ and OH^- ions are of the same concentration for pure water at $40^\circ C$

14 The pH change when $0.100 \text{ mol dm}^{-3} CH_3CO_2H$ is added dropwise to 10.0 cm^3 of $0.100 \text{ mol dm}^{-3} KOH(aq)$ is given in the graph below.



At which point on the graph does $pH = pK_a$, where K_a is the acid dissociation constant of the weak acid?

- 15 Four solutions, each of concentration 0.1 mol dm^{-3} , were tested with a pH meter. The results are shown

solution	pH
$\text{CH}_3\text{CO}_2\text{H}$	4
HNO_3	1
CH_3NH_2	11
NaOH	14

Which statement is **incorrect**?

- A Conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is less stable than that of HNO_3
- B HNO_3 has a lower pH than $\text{CH}_3\text{CO}_2\text{H}$ because it is more soluble.**
- C NaOH has a higher concentration of hydroxide ions in solution than CH_3NH_2 .
- D Mixing equal volume of CH_3NH_2 and HNO_3 form a solution with pH less than 7.

Option A: Correct

HNO_3 and $\text{CH}_3\text{CO}_2\text{H}$ are of same concentration. Given that $\text{CH}_3\text{CO}_2\text{H}$ has pH 4, implies that there is less dissociation for $\text{CH}_3\text{CO}_2\text{H}$. i.e. Conjugate base of $\text{CH}_3\text{CO}_2\text{H}$ is less stable than that of HNO_3 .

Option B: Incorrect

HNO_3 has a lower pH than $\text{CH}_3\text{CO}_2\text{H}$ **because** HNO_3 dissociates fully while $\text{CH}_3\text{CO}_2\text{H}$ partially dissociates.

Option C: Correct

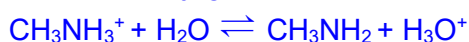
NaOH has a higher concentration of hydroxide ions in solution than CH_3NH_2 , hence NaOH has a higher pH.

Option D: Correct

Mixing equal volumes of CH_3NH_2 and HNO_3 gives salt $\text{CH}_3\text{NH}_3^+\text{NO}_3^-$ only. $\text{CH}_3\text{NH}_2 + \text{HNO}_3 \rightarrow \text{CH}_3\text{NH}_3^+\text{NO}_3^-$

$\text{CH}_3\text{NH}_3^+\text{NO}_3^-$ dissociates to give CH_3NH_3^+ and NO_3^-

CH_3NH_3^+ , conjugate acid of CH_3NH_2 , undergoes hydrolysis to give H_3O^+ , hence $\text{pH} < 7$.



- 16 The ionic product of water, K_w , is affected by temperature. The table gives the pK_w of pure water at different temperatures.

temperature / °C	pK_w
10	14.5
40	13.5

Solutions of acids and alkalis are prepared by dissolving HCl or NaOH in pure water at 10 °C and at 40 °C.

Which solution has the highest ionic concentration?

- A HCl(aq) at pH 1 at 40 °C.
- B HCl(aq) at pH 1 at 10 °C
- C NaOH(aq) at pH 13 at 40 °C**
- D NaOH(aq) at pH 13 at 10 °C.

$pK_w = pH + pOH$

A: pH = 1. $[H_3O^+] = 0.1 \text{ mol dm}^{-3}$.

$[HCl] = 0.1 \text{ mol dm}^{-3}$

B: pH = 1. $[H_3O^+] = 0.1 \text{ mol dm}^{-3}$

$[HCl] = 0.1 \text{ mol dm}^{-3}$

C: pH = 13. pOH = 13.5 - 13 = 0.5

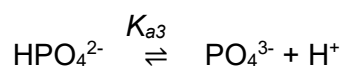
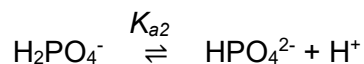
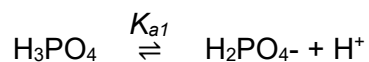
$[NaOH] = 10^{-0.5} = 0.316$

D: pH = 13. pOH = 14.5 - 13 = 1.5

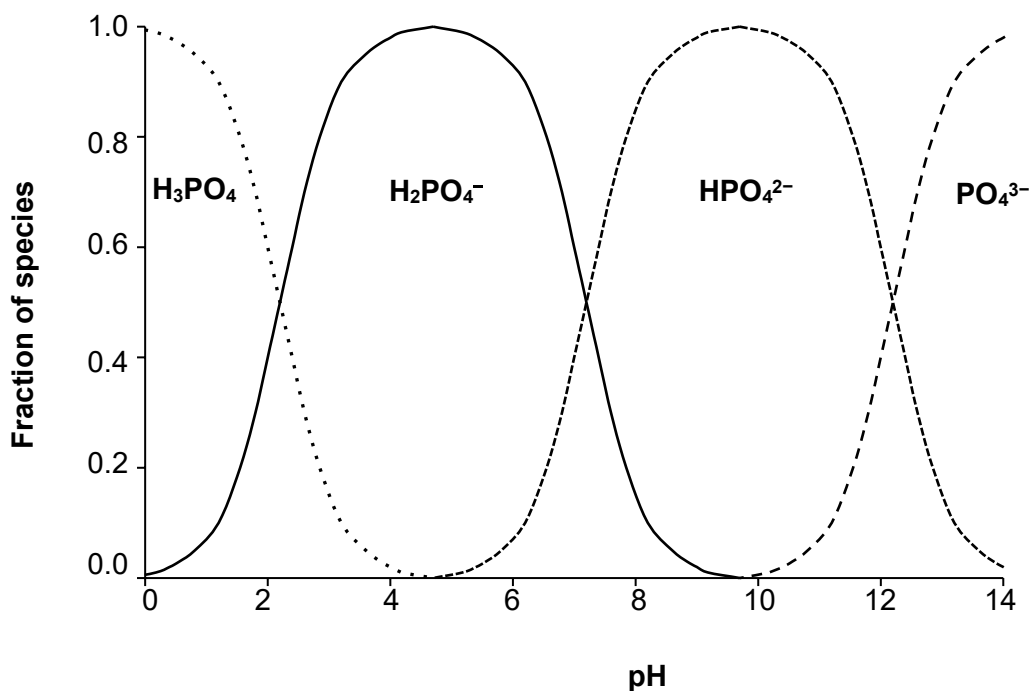
$[NaOH] = 10^{-1.5} = 0.0316$

Hence, C has the highest concentration of ions.

- 17 Phosphoric acid is a tribasic acid.



The graph shows the fraction of each species at different pH.



What is the numerical value of K_{a2} ?

- A** 6.3×10^{-3} **B** 2.0×10^{-5} **C** 6.3×10^{-8} **D** 2.0×10^{-10}

First, calculate the pKa values.

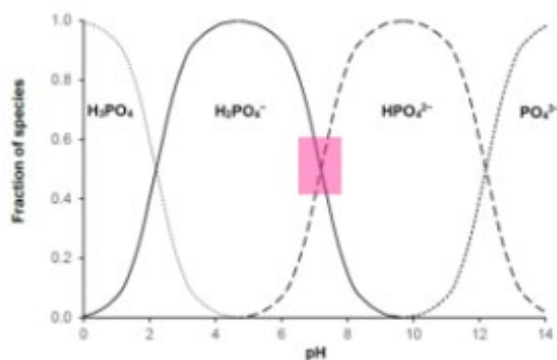
	Ka	pKa
A	6.3×10^{-3}	2.2
B	2.0×10^{-5}	4.7
C	6.3×10^{-8}	7.2
D	2.0×10^{-10}	9.7

To determine K_{a2} , use the H-H equation.

$$\text{pH} = \text{p}K_{a2} + \lg \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

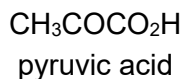
At maximum buffer capacity, $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$, $\text{pH} = \text{p}K_{a2}$.

Hence, we need to find the point in the graph where $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$.

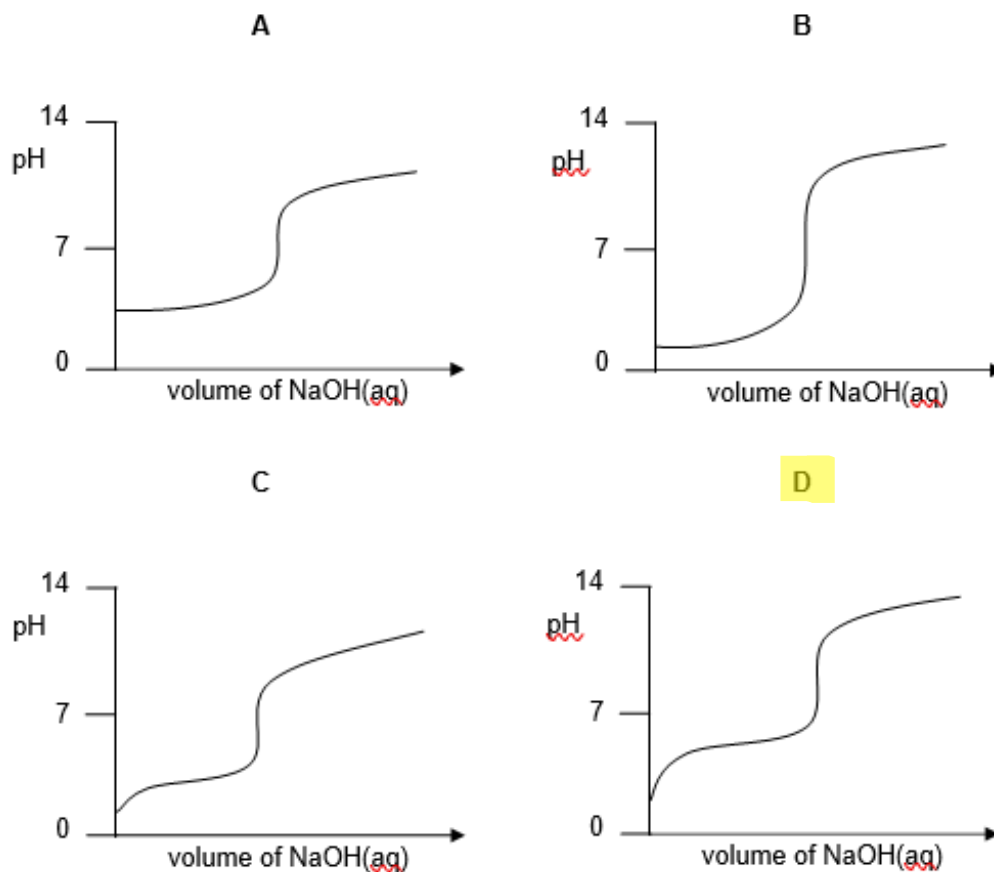


From graph, when $[\text{HPO}_4^{2-}] = [\text{H}_2\text{PO}_4^-]$, $\text{pH} \sim 7.2$.

- 18 Pyruvic acid is a weak acid that is an important intermediate in many biochemical Processes.



Which graph best represents the change in pH that occurs when a sample of pyruvic acid is titrated against NaOH(aq)?



At equivalence point, a weakly alkaline solution where $\text{pH} > 7$ is formed.
Hence answer is D.

- 19 The K_a of lactic acid is $1.4 \times 10^{-4} \text{ mol dm}^{-3}$ at 298 K.

A buffer solution contains 1.5 mol dm^{-3} lactic acid and 0.5 mol dm^{-3} sodium lactate.

Which statement correctly describes the buffer solution?

- A The pH of the buffer solution is 4.33.
- B The pH of the buffer solution decreases upon dilution with water.
- C The buffering capacity of the buffer solution increases upon dilution with water.
- D The buffer solution has a greater buffering capacity against a base compared to an acid.**

Option A	<p>Incorrect. The correct pH of the buffer solution is:</p> $\text{pH} = \text{p}K_a + \lg \frac{[\text{lactate}]}{[\text{lactic acid}]} = -\lg(1.4 \times 10^{-4}) + \lg \frac{0.5}{1.5} = 3.38$
Option B	<p>Incorrect. Upon dilution with some water, the pH of the buffer solution should remain the same as the amount of lactic acid and sodium lactate in the buffer solution remains unchanged (although their concentrations decrease).</p> $\text{pH} = \text{p}K_a + \lg \frac{[\text{lactate}]}{[\text{lactic acid}]} = \text{p}K_a + \lg \frac{n(\text{lactate}) / V_{\text{buffer}}}{n(\text{lactic acid}) / V_{\text{buffer}}} = \text{p}K_a + \lg \frac{n(\text{lactate})}{n(\text{lactic acid})}$ <p><i>(If the buffer solution is infinitely diluted with water, the $[H^+]$ in the buffer solution tends towards that of pure water (i.e. $10^{-7} \text{ mol dm}^{-3}$) and pH increases and approaches 7.)</i></p> <p>Hence, pH of the buffer solution will not decrease upon dilution with water.</p>
Option C	<p>Incorrect. For a given volume, a more diluted buffer solution will have a lower buffering capacity due to smaller amount of the lactic acid and lactate ions to remove any added OH^- and H^+ ions respectively.</p>
Option D	<p>Correct. Since the buffer solution has a greater amount of lactic acid (weak acid) than the lactate ions (conjugate base), the buffer solution is more effective in buffering the effect of addition of small amounts of base than acid.</p>

ANSWERS FOR ACID- BASE EQUILIBRIA STRUCTURED QUESTIONS PART 1

- 1 (a) Explain what is meant by the term *Lewis acid* [1]

Lewis acid is a substance that accepts an electron pair from a base via a dative covalent bond (i.e. an electron-pair acceptor)

- (b) The water molecule can react in various ways: as an acid, as a base, as a nucleophile, as an oxidising agent and as a reducing agent.

Study the following reactions and decide in which way water is reacting in each case.

Explain your answers fully.

- (i) $2\text{F}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{HF} + \text{O}_2$ [1]

Reducing agent as itself is being oxidised. The oxidation number of O increases from -2 in H_2O to 0 in O_2 .

Or water reduces F_2 to HF as the oxidation number of F decreases from 0 in F_2 to -1 in HF .

- (ii) $\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$ [1]

Nucleophile. The carbon of the acyl chloride functional group is electron deficient and is susceptible to nucleophilic attack by water, which has a lone pair of electrons on its oxygen atom.

- (iii) $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$ [1]

Base. H_2O accepts a proton from H_2PO_4^- to form H_3O^+ and HPO_4^{2-} .

- (iv) $\text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2$ [1]

Oxidising agent. Water oxidises Li to Li^+ as the oxidation number of Li increases from 0 in Li to $+1$ in LiOH

- (v) $\text{NO}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^-$ [1]

Acid. H_2O donates a proton to NO_2^- to form OH^- and HNO_2 .

- (c) The pK_a values of three acids are listed in Table 1.1.

Table 1.1

acid	formula	pK_a
1	$\text{CH}_3\text{CH}_2\text{COOH}$	4.9
2	$\text{CH}_3\text{CHClCOOH}$	2.8
3	$\text{CH}_2\text{ClCH}_2\text{COOH}$	Z

- (i) Explain the difference in pK_a values between acid 1 and acid 2 [2]

The presence of the electron withdrawing chlorine group in acid 2 disperses the negative charge on the conjugate base, $\text{CH}_3\text{CHClCOO}^-$, hence making it a more stable conjugate base than $\text{CH}_3\text{CH}_2\text{COO}^-$.

Therefore, acid 2 has a lower pK_a as this increases the acid strength of $\text{CH}_3\text{CHClCOOH}$

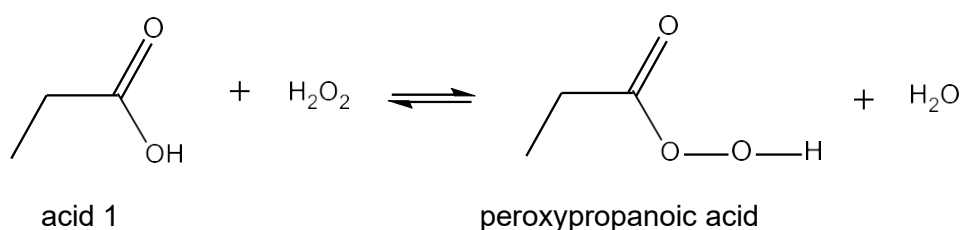
- (ii) Suggest a value for z and explain your answer. [1]

4.0 (accept any value between 2.8 and 4.9)

As the distance between the $-\text{COOH}$ group and the Cl atom increases, the negative charge on the conjugate base is less dispersed. The conjugate base becomes less stable and hence acid strength decreases.

However, acid 3 should still be more acidic than acid 1 due to the presence of the electron withdrawing Cl group.

- (iii) Peroxyacids are weak acids. One way to prepare peroxypropanoic acid is to treat the corresponding carboxylic acid with hydrogen peroxide.



- Suggest why the pK_a of peroxypropanoic acid is higher than that of acid 1. [1]

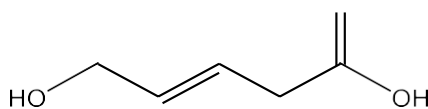
$\text{CH}_3\text{CH}_2\text{CO}_3\text{H}$ is less acidic than CH_3COOH as $\text{CH}_3\text{CH}_2\text{CO}_3^-$ is less stable than $\text{CH}_3\text{CH}_2\text{CO}_2^-$ because the negative charge on $\text{CH}_3\text{CH}_2\text{CO}_3^-$ cannot be delocalised over the $\text{C}=\text{O}$ group due to the additional oxygen atom, hence the resonance stabilisation of the conjugate base is lost.

(d) **A**, **B** and **C** are isomers with the molecular formula $C_5H_6O_2$. All three compounds decolourise bromine water in the dark.

A produces effervescence in the presence of $Na_2CO_3(aq)$ whereas **B** and **C** do not. **A** also reacts with hot acidified $KMnO_4$ to form **D**, $C_3H_4O_5$

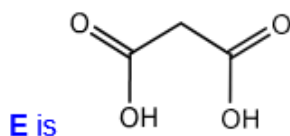
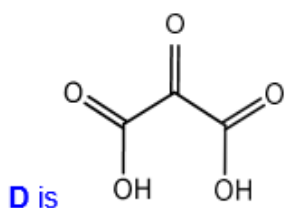
B forms a brick-red precipitate when heated with Fehling's solution

C reacts with hot aqueous sodium hydroxide. Upon acidification, it forms $C_5H_8O_3$.



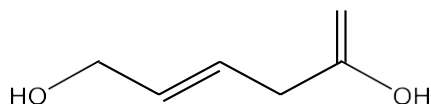
When **B** and **C** are separately reacted with hot acidified $KMnO_4$, they form the same mixture of **E**, $C_3H_4O_4$, and **F**, $C_2H_2O_4$. **F** undergoes further oxidation to give effervescence.

(i) Draw the structures of **D**, **E** and **F**. [3]



F is $HOOC-COOH$

(ii) Deduce the structures of **A**, **B** and **C** with reasoning. [7]



A, **B** and **C** have 3 degrees of unsaturation.

A, **B** and **C** have alkene functional group that undergoes electrophilic addition with bromine water.

A, **B** and **C** undergoes vigorous oxidation / oxidative cleavage of the alkene functional group.

A has the carboxylic acid functional group that undergoes acid-carbonate / acid- base reaction with carbonate.

B has the aldehyde functional group that undergoes oxidation in the presence of Fehling's solution.

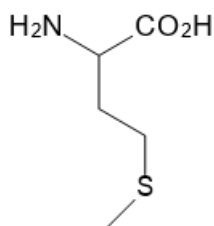
C undergoes alkaline hydrolysis, so it has an ester functional group.

O

A **B** **C**

[Total: 20]

- 2 (a) Methionine is an essential amino acid in humans. It plays a critical role in the metabolism and health of humans because it is the precursor of other amino acids such as cysteine and taurine.



Methionine

The pK_a values associated with methionine are 2.28 and 9.21.

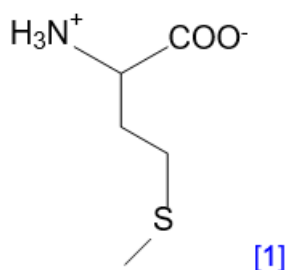
- (ii) Calculate the pH of 0.15 mol dm^{-3} solution of methionine, ignoring the effect of the second pK_a value.

$$[H^+] = \sqrt{10^{-2.28} \times 0.15} = 0.0281 \text{ mol dm}^{-3}$$

$$\text{pH} = -\lg 0.0281 = \mathbf{1.55 [1]}$$

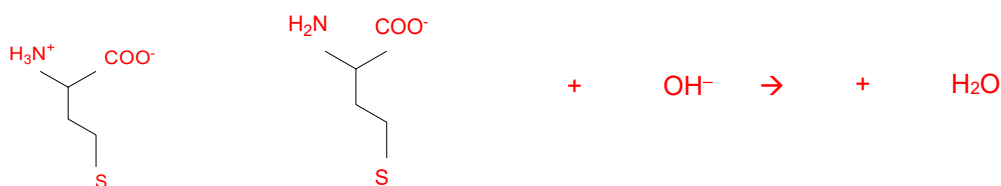
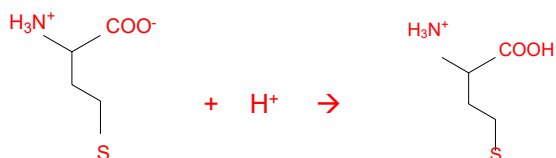
Comments: This question was done well. Only a small minority did not attempt the question or used the given concentration directly to calculate pH, incorrectly treating methionine as a strong acid.

- (ii) Draw the structure of the zwitterionic form of methionine



[1]

- (iii) Write two equations to describe how a solution containing the zwitterionic form of methionine can act as a buffer.



[1] for each equation

Comments:

Many students gave the correct equations. Common error was to leave out water as the product for the equation where OH^- was added. Those who represented the structure of methionine other than how it was given in the question, often wrote incorrect structures with missing atoms.

- (iv) When 10 cm^3 of 0.15 mol dm^{-3} of **protonated** methionine was titrated against aqueous sodium hydroxide, the first equivalence point was reached when 15 cm^3 of the 0.10 mol dm^{-3} NaOH was added.

At the first equivalence point, only the zwitterionic form of methionine exists.

With the use of relevant equilibrium constant values, explain if the pH of the solution at the first equivalence point is less than, equal to or more than 7.

The zwitterion is amphoteric and can act as both acid and base.

$$\text{p}K_{\text{b}1} = 14 - 2.28 = 11.72$$

$$K_{\text{b}1} = 10^{-11.72} = 1.905 \times 10^{-12} \text{ [1]}$$

$$\text{p}K_{\text{a}2} = 9.21$$

$$K_{\text{a}2} = 10^{-9.21} = 6.166 \times 10^{-10}$$

Since $K_{\text{a}}(-\text{NH}_3^+) > K_{\text{b}}(-\text{COO}^-)$, the solution will be acidic. [1]

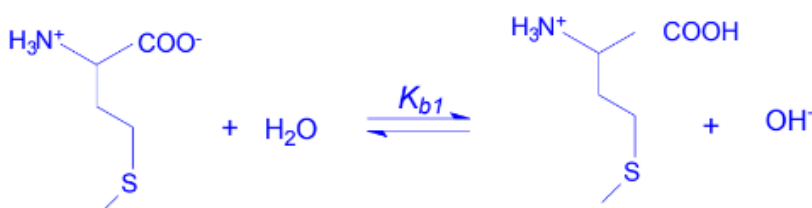
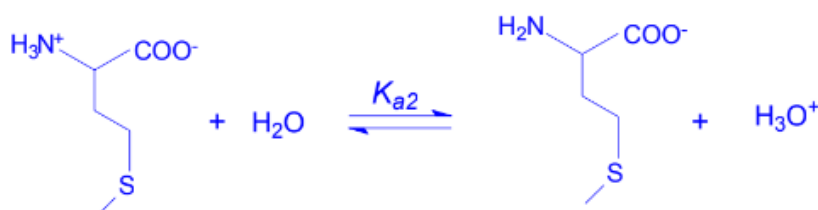
1 mark for calculating K_{b} and using the correct K_{a} for comparison

1 mark for correct conclusion of pH based on comparison

Comments:

This proved to be a difficult question.

At first equivalence point, only the zwitterion is present. Both the acidic group ($-\text{NH}_3^+$) and a basic group ($-\text{COO}^-$) can undergo hydrolysis to give H_3O^+ or OH^- respectively. The pH of the resulting solution then depends on which hydrolysis reaction occurs to a greater extent. This can be determined by comparing which value, $K_{\text{b}1}$ (calculated from $K_{\text{a}1}$) or $K_{\text{a}2}$ is larger



Students can also refer to the Acid-Base Equilibria Tutorial Q16 for a similar question.

Common misconceptions:

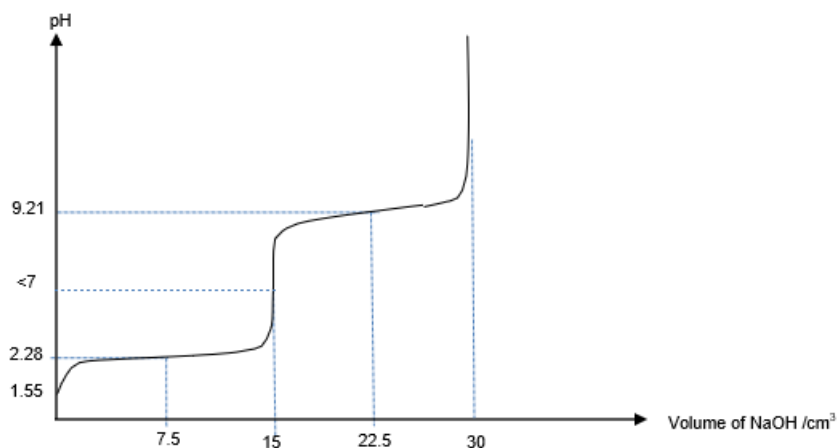
- Many students know that at first equivalence point, the zwitterion is present. However, they then wrongly concluded that since an acidic group ($-\text{NH}_3^+$) and a basic group ($-\text{COO}^-$) are present, the pH is then equal to 7.
- Others looked at the volumes and concentrations of methionine and NaOH given in the question to conclude that there was no limiting reagent / excess acid or base so the resulting solution would be neutral.
- A handful assumed that the hydrolysis of the $-\text{NH}_3^+$ group occurred to a greater extent but did not provide explanation and were not given full credit

- (v) Using the value and information from (a)(i) and (a)(iv), as well as the pK_a values provided, sketch the pH–volume added curve you would expect to obtain when 30 cm^3 of 0.10 mol dm^{-3} NaOH is added to 10 cm^3 of 0.15 mol dm^{-3} **protonated** methionine.

At 7.5 cm^3 , 1st maximum buffering capacity point
 $\text{pH} = pK_{a1} = 2.28$

At 15 cm^3 , 1st equivalence point, $\text{pH} = 5.22$ or 5.75 [check part (iv)]

At 22.5 cm^3 , 2nd maximum buffering capacity point $\text{pH} = pK_{a2} = 9.21$



- [1] labelled axes and correct shape of graph with the flattening at the buffer regions
[1] labelled points (0, 1.55), (7.5, 2.28), (15, <7) and (22.5, 9.21)

Comments:

Many students were able to draw an appropriate sketch, though quite a number did not show a sharp increase in pH initially when NaOH was first added. Many did not label all the required values on their graph. The volumes where $\text{pH} = pK_a$ were often missing.

- (vi) Suggest a suitable indicator for the equivalence point in the above titration.

Methyl orange. [1]

Comments:

Most students suggested a suitable indicator, based on the pH proposed in part (iv).

- (b) Fig. 3.1 shows the four-step synthesis of an amino acid from an aldehyde, via an intermediate **G**.

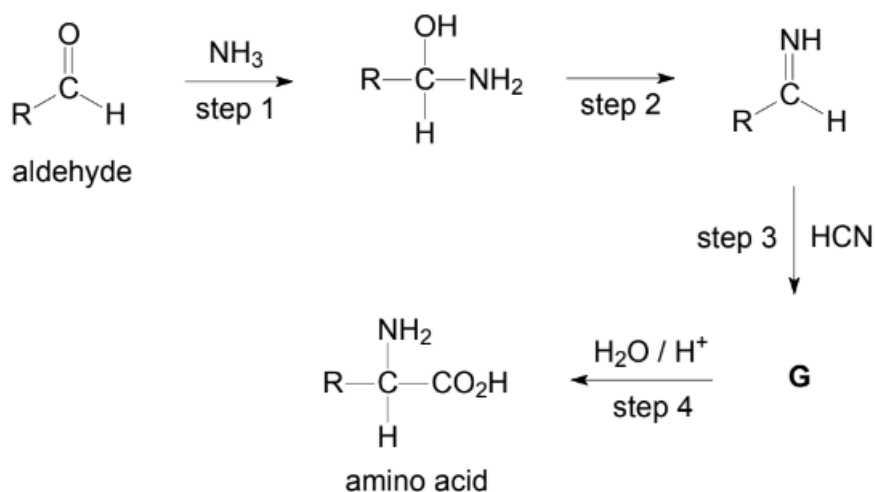


Fig. 3.1

- (i) States the types of reaction that occur during each of the steps 1 and 2.

Step 1: Nucleophilic addition [1]

Step 2: Elimination (of H₂O) [1]

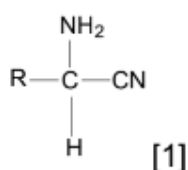
Comments:

Common wrong answers for Step 2 are condensation/hydrolysis/reduction.

The technique here is to compare the difference in molecular formulae of reactant and product of step 2 (there is loss of 2H and 1O, hence elimination of 1 H₂O).

Students must INDICATE clearly the step in which each answer is for!

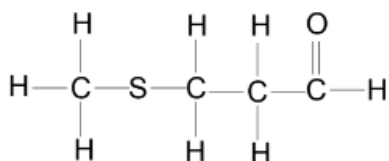
- (ii) Suggest the structure of compound G.



Comments:

Students often carelessly omitted the 2 in -NH₂. Students must work backwards from step 4 to see that the reagents suggest that of hydrolysis (of -CN group). So the -NH₂ group must be present in compound G.

- (iii) Draw the displayed formula of a suitable starting aldehyde that can be used to synthesise methionine

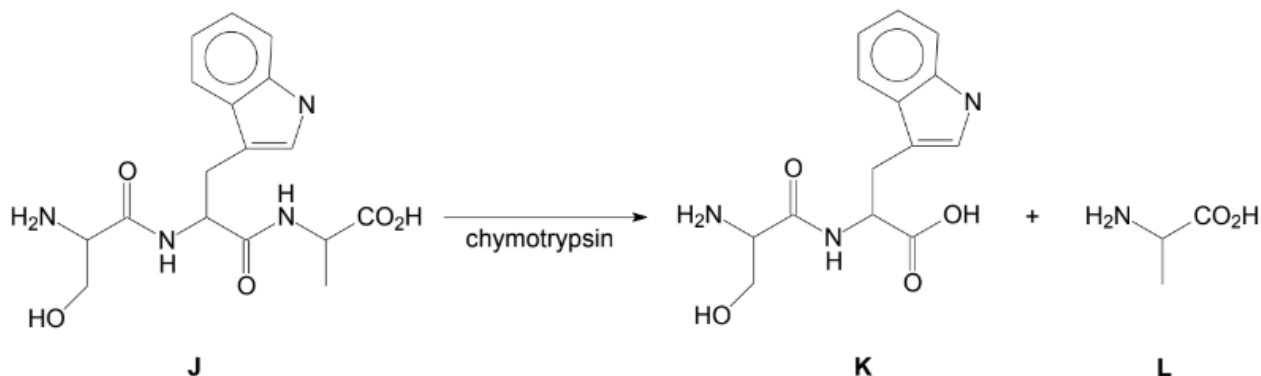


[1] for correct displayed structure

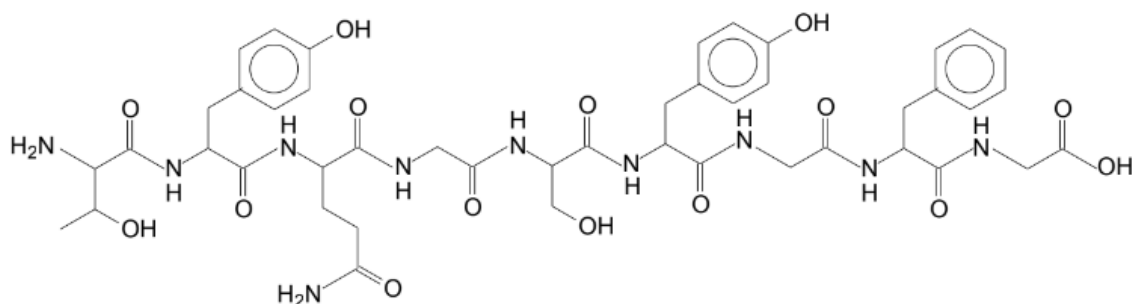
Comments:

Most students who arrived at the correct structure were careless to have overlooked the keywords 'displayed formula' in the question. There is a handful of students who thought that there were 2 S-H bonds. Remember that in writing the skeletal formula, only C-H and C-C bonds are abbreviated. A molecule that contains a S-H will still have the bond shown in the skeletal formula.

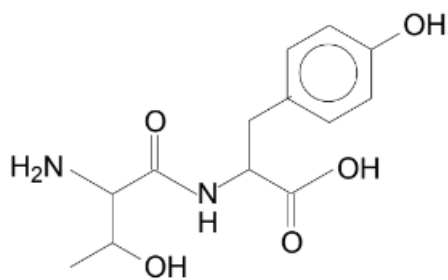
- (c) Chymotrypsin is an enzyme that hydrolyses proteins into smaller peptides and amino acids. It specifically hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring. For example, the tripeptide **J** produces two compounds **K** and **L** as shown.



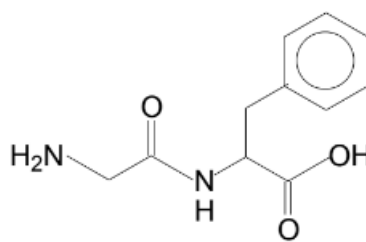
The following shows part of a short amino acid sequence found in human protein.



Draw the two dipeptides formed when the above amino acid sequence is hydrolysed by chymotrypsin.



[1]



[1]

Comments:

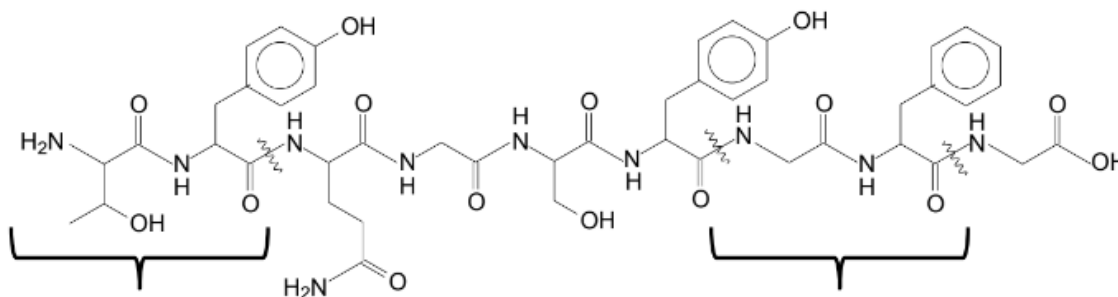
Students need to know that a **dipeptide is a molecule that consists of two amino acids joined together by a peptide bond.**

To solve this question, you need to follow the instructions "hydrolyses the peptide bond on the carboxyl side of a residue that contains an aromatic ring".

1) identify the aromatic ring in the R group (side chain) and

2) cleave at the C-O amide bond on the carboxyl side in response to the pattern given

3) look for fragments with 2 amino acids joined together (see below).

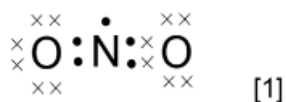


gives dipeptide fragment

gives dipeptide fragment

- 3 NO₂ has been identified as a pollutant with strong evidence for public health concern. Exposure to NO₂ can irritate airways and aggravate respiratory diseases.

(a) (i) Draw a dot-and-cross diagram to show the bonding in a molecule of NO₂. [1]



[1]

- (ii) The 2s and 2p orbitals of nitrogen atoms can hybridise in the same way as the 2s and 2p orbitals of carbon atoms.
State the shape with respect to the nitrogen atom in NO₂. Hence, suggest the hybridisation state of nitrogen in NO₂. [1]

Table 1.1 shows the bond lengths of two nitrogen–oxygen bonds.

Table 1.1

Bond	N–O	N=O
Bond length (pm)	136	115

The observed bond length of each nitrogen–oxygen bond in the NO₂ is 119 pm.

bent, sp² [1]

Comments:

(i) Many students did not know that in some molecules (eg NO₂), the **total number of valence electrons is an odd number**. You can easily check by summing the total number of valence electrons before drawing the dot-and-cross diagram. In this case NO₂ has 5+6+6=17 valence electrons. This means that there will be at least one unpaired electron in the molecule! You can see this in your Chemical Bonding lecture notes, Pg 20 for more example and details.

$\cdot \ddot{\text{O}} : \overset{\times}{\underset{\times}{\text{N}}} : \ddot{\text{O}} :$ is incorrect as there are 9 electrons around N. N, in period 2, CANNOT expand octet. It will only have a maximum of 8 electrons.

(ii) In counting the number of bond pairs, each double bond or dative bond is counted as one bond pair. One lone electron is also counted as one lone pair as it also exerts repulsion, though less than a full 2-electron lone pair. This concept has been covered in our JC1 Chemical Bonding tutorial question 8!

When writing the hybridisation state such as sp², 'sp' is written in small letters and '2' is written in superscript (raised).

- (iii) What do you understand by the term *bond length*? [1]

Bond length is the distance between the nuclei of the two atoms in the bond. [1]

- (iv) With reference to your answers to (a)(i) and (a)(ii), explain the observed bond length in NO₂. [2]

The 2p orbital of N overlaps with the 2p orbital of the singly bonded O atom allows the lone pair of electrons on the O atom to be delocalised into the N=O bond. [1]

As a result, both the N–O bonds have partial double bond character. And the observed bond length is intermediate between a single and double bond. [1]

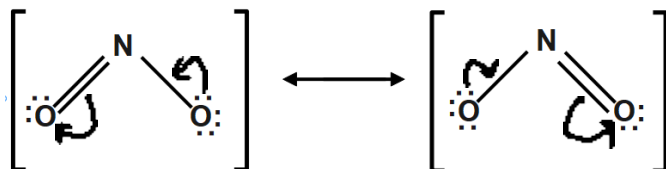
- Mention delocalization of electron pair of O into the N=O bond
- Leading to partial double bond character

Comments:

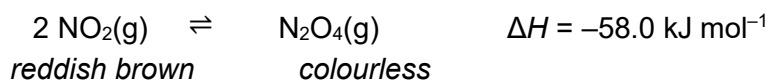
(iii) The words 'nuclei' and 'bond' are often missing.

(iv) Many students attempted to explain the difference in bond length/bond strength of N=O and N-O instead of answering to the question on why the N-O in NO₂ is intermediate between a single and double bond.

(FYI) Delocalisation of lone pair on O in N=O bond:



(b) At room temperature, reddish brown nitrogen dioxide, NO₂, dimerises into colourless nitrogen tetroxide, N₂O₄. The two gases are in dynamic equilibrium as shown.



(i) Using your answer in (a)(i), explain why the dimerisation of NO₂ to form N₂O₄ is an exothermic process. [1]

Energy is released as a N-N covalent bond is formed using the single unpaired electron of each of the N atoms of two NO₂ radicals, thus forming N₂O₄.



[1] mention energy released due to bond formation between 2 N atoms or it is N-N bond.

Comments:

Common misconceptions observed:

- N of one NO₂ radical forms a bond with O of another NO₂ radical
- The bond formed between N of one NO₂ radical and N of another NO₂ radical is dative
- Energy is absorbed during bond formation

The graph in Fig. 1.1 shows the pressure-temperature (p - T) relationship of two separate gaseous samples in an enclosed volume.

At 273 K, the first sample contains 1 mole of helium gas and the second sample contains 1 mole of gaseous N_2O_4 . As temperature increases, it is observed that the second sample behaves differently from the helium gas in the first sample.

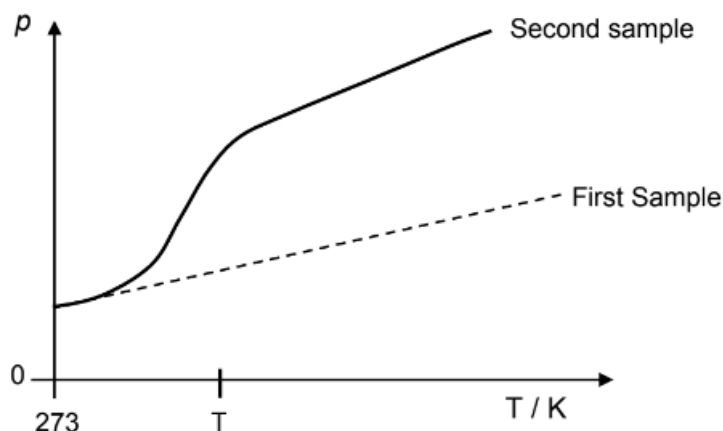


Fig. 1.1

(ii) Explain the shape of p - T graph for the second sample in Fig. 1.1.

- The steeper slope as temperature increases from 273 K to T K.
 - The gentler slope as temperature increases after temperature T K. [3]
- $$2 \text{ NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g}) \quad \Delta H = -58.0 \text{ kJ mol}^{-1}$$
- reddish brown* *colourless*

As temperature increases from 273K, POE shifts to the left to decrease the temperature by absorbing the excess heat, favouring the endothermic reaction. [1]

This POE shift is accompanied by increase in number of gaseous particles (2 vs 1), which contributes to increase in pressure. Hence the gradual increase in pressure as observed. [1]

At temperature T, $N_2O_4(\text{g})$ has completely converted to NO_2 molecules. As temperature increases from T, the number of moles of NO_2 molecules does change. The pressure of the gaseous sample then increases proportionally with increase in temperature. [1] } ther.

Comments:

Some students did not apply the concept of Le Chatelier's Principle to the reversible reaction to explain the increase in pressure from 273 K to T K. It is insufficient to just write that position of equilibrium shifts left. The full explanation as above should be given in your answer.

Students did not realise that at temperature T, all the N_2O_4 molecules has been converted to NO_2 molecules. The position of equilibrium lies fully to the right then and there is no further increase in the amount of gas particles.

- (iii) State the visible observation that would be made for the second sample as the temperature increases.

[1]

Observation:

light brown/yellow gaseous mixture becomes darker brown, OR [1]
the colour of the gaseous mixture becomes darker brown

Comments:

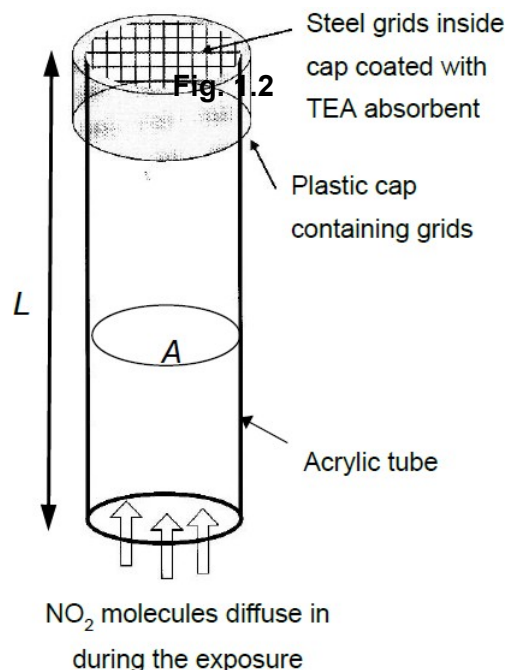
This part is well-done. As the question is about noting visible changes to the system, answers which discussed about the change to the gradient (or shape) of the graph or the pressure of the container were not accepted.

As NO_2 has detrimental impacts on human health, it is important to monitor the level of ambient NO_2 in the atmosphere. One method to detect and measure ambient NO_2 involves the use of open tube diffusion sampler to collect air samples and measure the concentration of NO_2 in the air.

The process of determination of NO_2 can take place in three main stages:

(c) **Stage 1: Collection of gas sample using a diffusion tube**

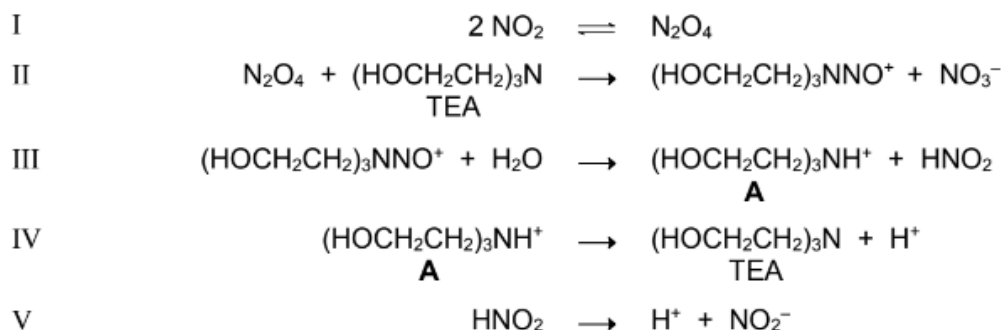
Fig. 1.2 shows a typical diffusion tube used for sample collection. It has a length (L) of 7.1 cm and cross-sectional area (A) of 0.91 cm^2 .



The air sample to be analysed diffuses into the tube through an opening at the bottom. Triethanolamine (TEA), $(\text{HOCH}_2\text{CH}_2)_3\text{N}$, which is coated on the steel mesh grid, absorbs and converts NO_2 to produce nitrite NO_2^- in Stage 2.

Stage 2: Conversion of NO₂ to NO₂⁻

The following mechanism, consisting of steps I to V, has been proposed for the conversion of NO₂ to NO₂⁻ by TEA.



- (i) Write an overall equation for the reaction between NO₂ and TEA. Hence, state the type of reaction that has taken place. [2]



Disproportionation [1]

Comments

While students showed confidence in cancelling out common terms to arrive at the correct equation, many incorrectly stated the equation as simply redox. Disproportionation is a more specific answer to this context as the same element (N) is both reduced and oxidised

- (ii) The species in the reaction mechanism have various roles. They can be reactants, products, catalysts or intermediates.

Suggest, with a reason for each case, the roles of TEA and species A. [2]

TEA: catalyst as it is reacted/consumed in Step II and regenerated in Step IV. [1]

A: intermediate as it is produced/formed in in Step III and reacted in Step IV. [1]

State role + reason

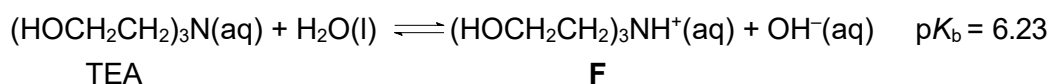
Comments:

Good effort there in including the details of both species observed in the specific steps of the mechanism in relation to the roles.

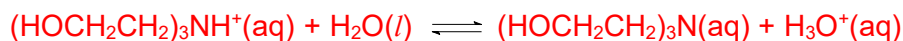
Answers which explained that they have identified catalyst as it is chemically unchanged after the reaction or intermediate as it does not appear in the overall equation are not given credit as these answers do not clearly explain how the answer was derived based on the mechanism.

Ambiguous answers such as Stage II or Step 2 were accepted this time even though they differ from the labelling used by the question. Please be more mindful in A levels.

(iii) TEA dissociates in water forming its conjugate acid **F** as shown.



Calculate the pH of an aqueous solution containing $6.00 \times 10^{-2} \text{ mol dm}^{-3}$ of species **F**. [2]



$$pK_a = 14 - 6.23 = 7.77$$

$$\therefore K_a = 10^{-7.77} = 1.70 \times 10^{-8} \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{H}_3\text{O}^+] &= \sqrt{(1.70 \times 10^{-8})(6.00 \times 10^{-2})} \\ &= 3.19 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned} \quad [1]$$

$$\begin{aligned} \text{pH} &= -\log(3.19 \times 10^{-5}) \\ &= 4.50 \end{aligned} \quad [1]$$

Comments:

*This question was badly done. Many students tried to solve in terms of K_b which will not work as **F** is an (conjugate) acid. Students should have solved in terms of K_a for this weak acid. Many students fumbled in this question evidently from their weird assumptions such as $[\text{OH}^-] = [\text{F}]$ or $[\text{F}] = [\text{TEA}]$.*

(d) Stage 3: Analysis and determination of the concentration of NO_2

The NO_2 produced is treated with suitable reagents to form a purple-coloured azo dye before it is placed in a colorimeter. The absorbance of light by the dye, measured at fixed wavelength, is proportional to the concentration of NO_2 .

The average concentration of nitrogen dioxide in the air, $[\text{NO}_2]_{av}$, in $\mu\text{g m}^{-3}$, can be determined using the expression given below.

$$[\text{NO}_2]_{av} = \frac{QL}{ADt}$$

where

Q	is the amount of NO_2 (μg),
L	is the length of the diffusion tube (m),
A	is the cross-sectional area of the diffusion tube (m^2),
D	is the diffusion coefficient for NO_2 in the air at room temperature $= 1.56 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$,
t	is the duration of exposure (s).

The World Health Organisation (WHO) guideline states that ambient air quality is good when the concentration of NO_2 is below $25 \mu\text{g m}^{-3}$ (24-hour mean).

To monitor the quality of ambient air in a school compound, a diffusion tube with dimensions as shown in Fig. 1.2 was installed in the classroom for 10 days. The amount of NO_2 was found to be $4.13 \times 10^{-3} \mu\text{g}$.

Hence, determine the average concentration of NO₂, in µg m⁻³, in the ambient air of the school compound and use this to comment on the quality of air in terms of NO₂ level, during the 10-day monitoring.

Answer:

$$[\text{NO}_2]_{av} = \frac{(4.13 \times 10^{-3})(7.1 \times 10^{-2})}{(0.91 \times 10^{-4})(1.56 \times 10^{-5})(10 \times 24 \times 60 \times 60)}$$

$$= \underline{0.239 \mu\text{g m}^{-3}} \quad [1] \text{ for correct answer}$$

Since the [NO₂]_{av} is below / less than / does not exceed 25 µg m⁻³, the quality of air in terms of NO₂ level is good / satisfactory / acceptable. [1] allow ecf

(accept words to the same effect)

Comments:

A handful of students struggled with the unit conversion from cm² to m². Others who did not obtain full credit for this part often left out the basis on their comment on air quality.

[Total: 18]

- 4 (a) When potassium dichromate (VI), K₂Cr₂O₇, is dissolved in 6 mol dm⁻³ of hydrobromic acid, HBr, and cooled, orange crystals of a potassium salt **A** are precipitated.

A has a formula mass of 219.0 and the following composition by mass: K, 17.9%; Cr, 23.7%; Br, 36.5% O, 21.9% and the oxidation state of the chromium in salt **A** is the same as that of K₂Cr₂O₇.

When aqueous silver nitrate was added to a solution of **A**, an acidic solution is produced and a cream-coloured precipitate **B** is formed. An initial yellow solution **C** is also observed which rapidly turns to an orange solution, **D**.

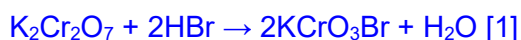
On addition of sulfur dioxide to solution **D**, a green solution **E** is obtained.

- (i) Show that the formula of **A** is KCrBrO₃ and hence write a balanced equation showing its formation from potassium dichromate (VI), K₂Cr₂O₇. [2]

	K	Cr	Br	O
No. of moles	$\frac{17.9}{39.1} = 0.4578$	$\frac{23.7}{52} = 0.4558$	$\frac{36.5}{79.9} = 0.4568$	$\frac{21.9}{16} = 1.369$
Simplest ratio	1	1	1	3

Empirical formula of **A** = KCrO₃Br (accept KCrBrO₃) [1]

mass of empirical formula = 219.0
therefore, n=1



Comments:

*The method shown in the answer is especially useful if the question is asking to state the empirical formula, followed by the formula of **A** (also note that it is not molecular formula as **A** is not a molecule).*

(ii) Identify species **B**, **C**, **D** and **E**.

Hence, state the type of reaction for the formation of solution **E** from solution **D**, giving a balanced equation for the reaction. [4]

Cream coloured ppt is **B** is silver bromide, AgBr

Yellow solution **C** contains CrO_4^{2-} (ignore cation if stated)

Orange solution **D** contains $\text{Cr}_2\text{O}_7^{2-}$

E, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ (accept Cr^{3+})

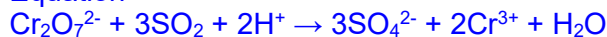
[1] 1 mark for any two unknowns **B**, **C**, **D**, **E**

not required, FYI: $\text{CrO}_3\text{Br}^- + \text{Ag}^+ + \text{H}_2\text{O} \rightarrow \text{AgBr} + \text{CrO}_4^{2-} + 2\text{H}^+$

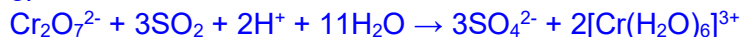
not required, FYI: $2\text{CrO}_4^{2-} + 2\text{H}^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}$

D undergoes redox reaction with SO_2 to form **E** [1]

Equation



or



[1] type of reaction for the formation of solution **E** from solution **D**

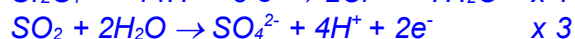
[1] balanced equation

Comments:

*Many students wrote "reduction" without any indication if it is **D** or **E** or SO_2 that was reduced. Some students incorrectly wrote it as **D** is reduced from **E**.*

As for the balanced equation, do remember there should not be any electrons appearing on either side of the arrow.

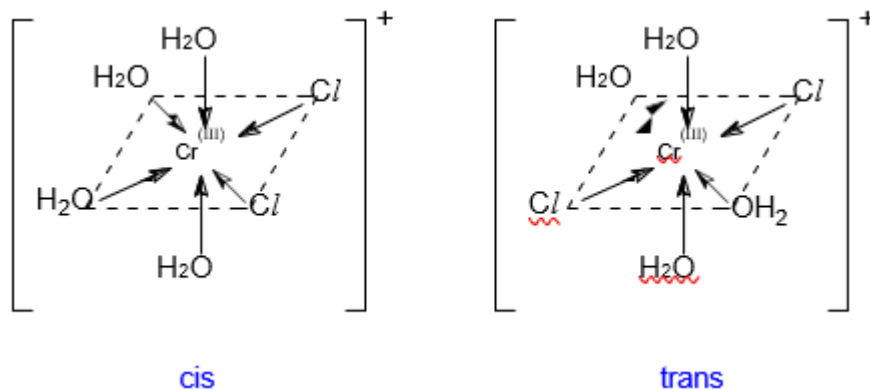
The 2 half equations can be obtained from the Data Booklet:



- (b) Cis–trans isomers of transition metal complexes differ from each other in the arrangement of the ligands around the central metal ion or atom.

Cis isomers have two of the same ligands 90° apart from one another in relation to the central metal ion or atom, whereas trans isomers have two of the same ligands 180° apart.

Propose the structures of the cis and trans isomers of tetraaquadichlorochromium(III) ion, $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$. Label your structures clearly. [2]

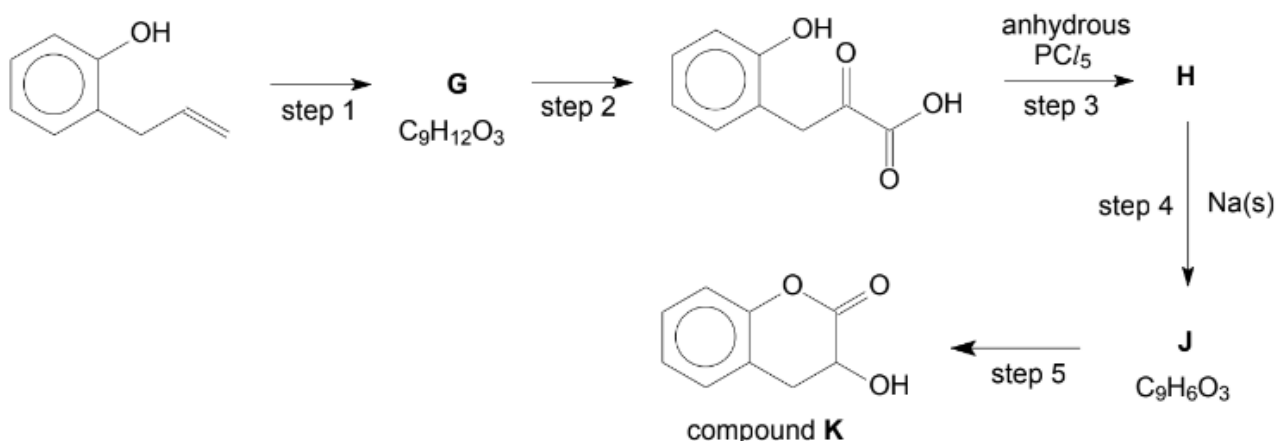


[1] for each isomer

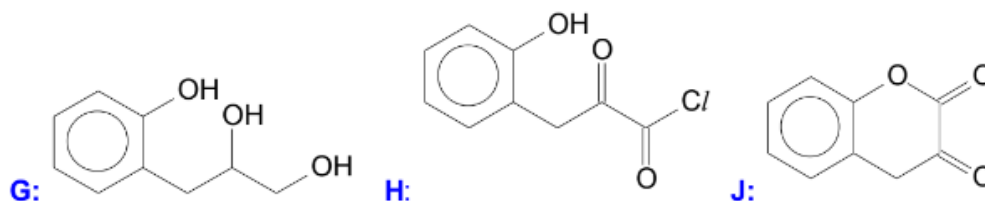
Comments:

Many students did not draw the octahedral shape and hence could not show how the cis and trans isomer will look like. They also forgot to include the "III" on Cr, or the charge outside the square bracket, or the arrows were drawn pointing towards the ligands which is incorrect. Some students wrote the negative charge on the Cl even though there was an overall charge already indicated outside the square brackets.

- (c) Compound **K** can be synthesised using the following reaction scheme shown in Fig. 4.1.



- (i) Suggest structures for the compounds **G**, **H** and **J**. [3]



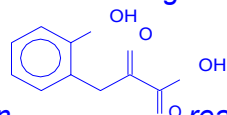
1 mark each

Comments:

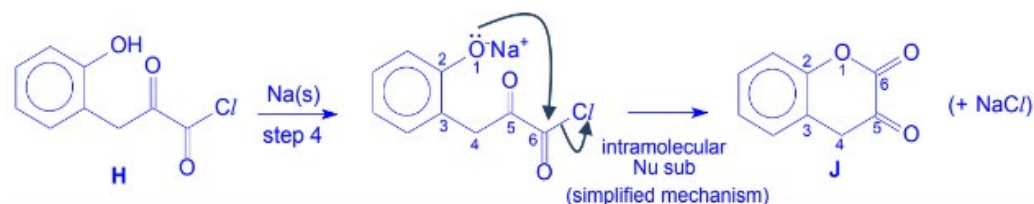
Most students could draw the structures for G and H, but could not determine the structure of J.

To work out the structure for G, we observe that the molecular formula in step 1 increased by 2H and 2O

atoms (from $C_9H_{10}O$ to $C_9H_{12}O_3$) so likely the alkene group has undergone mild oxidation to form a diol (2 -OH groups added). Looking at the product of step 2 also shows that the alkene group is no longer present, and in place of the alkene, a ketone and a carboxylic acid are formed. Oxidation of the secondary and primary alcohols in G will give these two functional groups. Only the carboxylic



acid group in H reacts with anhydrous PCl_5 to form the acid chloride in H. Phenol group does not react with PCl_5 as the C-O bond of the phenol group has partial double bond character due to resonance and do not participate in nucleophilic substitution reactions. Addition of Na(s) causes a redox reaction with the phenol group in H, to form a phenoxide ion (a stronger nucleophile than phenol), which then undergoes intramolecular nucleophilic acyl substitution reaction with the acid chloride group, forming cyclic compound J.



(ii) Suggest reagents and conditions for each of the steps 1, 2 and 5. [3]

Step 1: $KMnO_4$, dilute H_2SO_4 , cold [1]

Step 2: $K_2Cr_2O_7$, dilute H_2SO_4 , heat under reflux [1] (cannot accept $KMnO_4$)

Step 3: $NaBH_4$ (in methanol/ethanol), r.t./ H_2 with Ni, heat / H_2 with Pd/Pt, r.t.p.[1]

Comments:

Many students could give the correct reagent and condition for step 1 but had more trouble with steps 2 and 3.

Common errors:

Step 1

Use $K_2Cr_2O_7$. Alkenes can only be oxidised by $KMnO_4$ Use heat under reflux instead of cold for mild oxidation

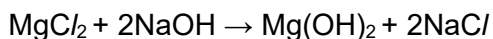
Step 2

Use $KMnO_4$. Note that the presence of benzylic hydrogen in G will cause side-chain oxidation to occur.

Step 3

Using $LiAlH_4$. The ester group present in J will be reduced by $LiAlH_4$.

(d) Magnesium chloride gives a weakly acidic solution when dissolved. It can be titrated with a strong base to give a rapid pH change upon complete reaction at the equivalence volume.



In an experiment, 50.0 cm³ of aqueous magnesium chloride was titrated with 1.00 mol dm⁻³ sodium hydroxide. The pH of the solution changed as shown in Fig 4.2.

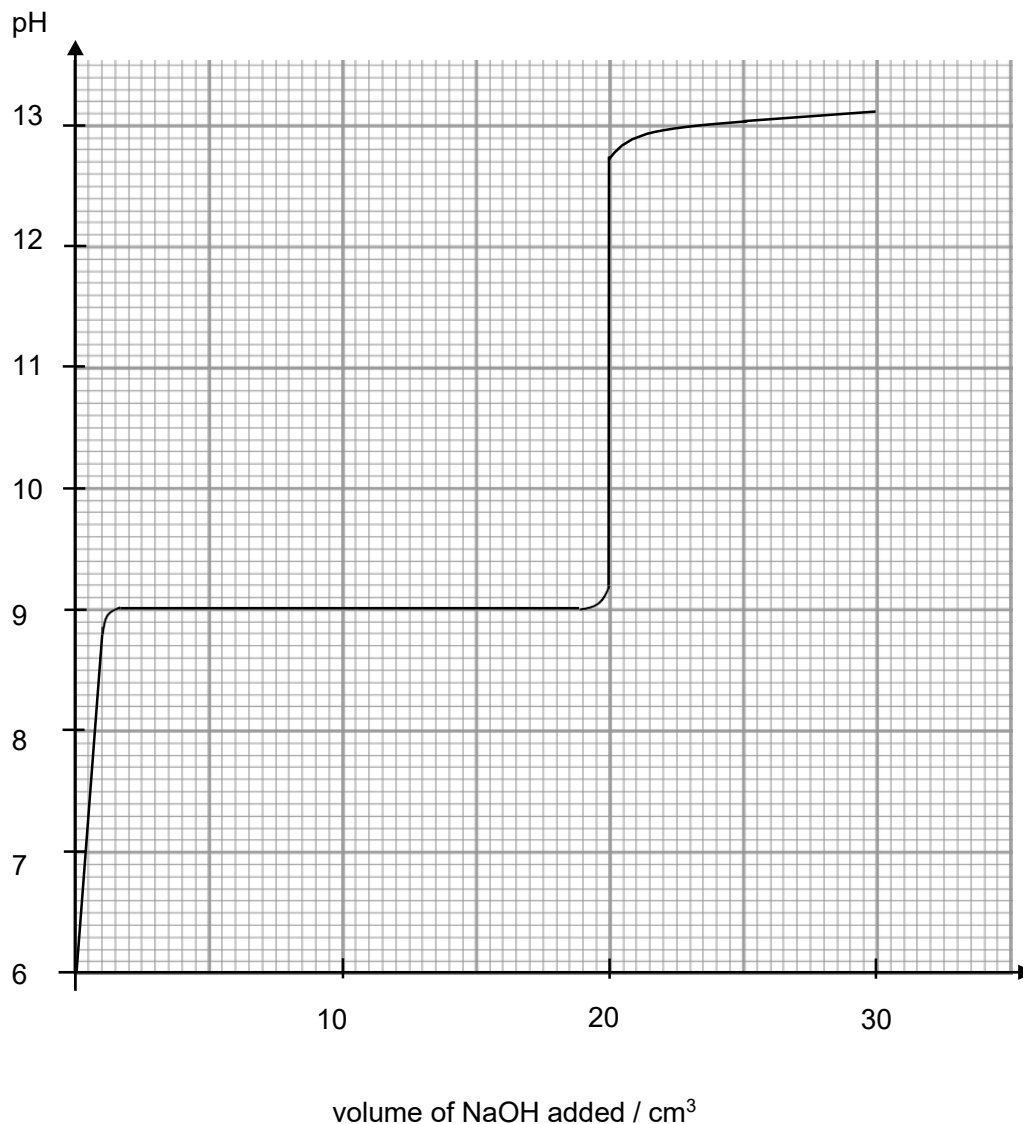
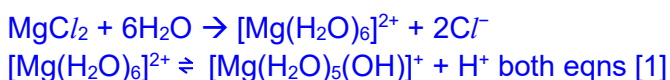


Fig. 4.2

- (i) Explain, with the aid of equations, why aqueous MgCl₂ has an initial pH of about 6.
[2]

Due to the small cationic size and a large positive charge, and hence a high charge density of Mg²⁺. After dissolving, the hydrated magnesium ion undergoes slight hydrolysis[1] to form a slightly acidic solution of pH 6.



Comments:

Many students could explain the pH value in terms of the hydrolysis of Mg²⁺ but fewer students explained hydrolysis occurred due to the high charge density of Mg²⁺. Quite a number of students wrote an incorrect equation where both Mg(OH)₂ or MgO and HCl were formed as products together.

- (ii) Determine the concentration of aqueous MgCl_2 used in the above titration. [1]

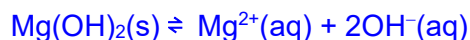
$$n\text{MgCl}_2 = \frac{1}{2} \times n\text{NaOH} = \frac{1}{2} \left(\frac{20}{1000} \times 1.00 \right) = 0.0100 \text{ mol}$$

$$[\text{MgCl}_2] = \frac{1000}{50} \times 0.0100 = 0.200 \text{ mol dm}^{-3} \text{ [1]}$$

Comments:

Most students who attempted scored the mark here. Most common errors were to use the wrong volume of NaOH or the wrong mole ratio ($n\text{MgCl}_2 = n\text{NaOH}$) for calculations.

- (iii) Write an expression for the solubility product, K_{sp} , of magnesium hydroxide. [1]



$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^{-}]^2 \text{ [1]}$$

Comments:

Most students scored the mark here, though a few wrote the expression wrongly in terms of soluble MgCl_2 instead. A handful also wrote the K_c expression for the reaction of MgCl_2 with NaOH as the answer.

- (iv) When 10 cm^3 of NaOH was added, the concentration of $\text{Mg}^{2+}(\text{aq})$ is found to be half of the value in (d)(ii).

Use information from Fig. 4.2 to calculate the K_{sp} value for Mg(OH)_2 . [2]

pH = 9 when 10 cm^3 of NaOH was added

$$[\text{OH}^{-}] = 10^{-(14-9)} = 1.00 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{Mg}^{2+}] = \frac{1}{2} (0.200) = 0.100 \text{ mol dm}^{-3} \text{ both conc [1]}$$

$$K_{sp} = (0.100)(1.00 \times 10^{-5})^2 = 1.00 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9} \text{ [1] for correct value.}$$

Comments:

This question was poorly done.

Students need to be able to see the similarities in the typical acid-base titration graph that they are familiar with and apply to this new context (e.g. in this graph, at 20 cm³ of NaOH, all the MgCl₂ has been reacted away similar to equivalence point in acid-base graph).

To find the K_{sp} value, we need to use the information given in the question including the information from Fig 4.2.

When 10 cm³ of NaOH was added,

- the [Mg²⁺(aq)] halved as some Mg²⁺(aq) is precipitated as Mg(OH)₂.*
- the pH of the solution is 9 (from Fig. 4.2) due to the [OH⁻] present from the equilibrium: Mg(OH)₂(s) ⇌ Mg²⁺(aq) + 2OH⁻(aq) ---eqm 1*

Common errors:

- Halving the [Mg²⁺] calculated from (d)(ii) and using mole ratio to determine [OH⁻]. This method is not valid since [Mg²⁺(aq)] present in the solution comes from both the MgCl₂ remaining and the Mg²⁺(aq) from the eqm 1.*
- Finding the [OH⁻] in the solution by taking nNaOH added / total volume. This method is incorrect as the 10 cm³ of NaOH added is the limiting reagent and would have all reacted to form Mg(OH)₂. So the amount of OH⁻ present is due to partial solubility of the Mg(OH)₂ formed.*
- Incorrectly reading the graph or taking pH = 9 to be pOH to calculate [OH⁻].*

[Total :20]

5 (a) Liquid ammonia, like aqueous ammonia is a conductor of electricity, but a very weak one. Liquid ammonia can exhibit this property as it can undergo self-ionisation.

(i) Write an equation between two ammonia molecules to show this property of liquid ammonia.



.....[1]

(ii) Identify the two different conjugate acid-base pairs in the reaction occurring in **(a)(i)**.

Acid: NH₃ conjugate base: NH₂⁻

.....

Base: NH₃ conjugate acid: NH₄⁺

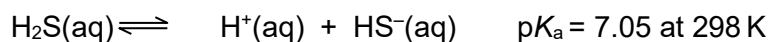
.....[1]

EXAMINER'S COMMENTS

Many candidates thought wrongly that the equation was meant for NH₃(aq) rather than NH₃(l)! Therefore, **no water** must be included. Many gave NH₂⁺ as the conjugate base rather than NH₂⁻.

For (ii), candidates need to specify which is the acid and its associated conjugate base or which is the base and its associated conjugate acid. Failure to do so that would result in penalty.

(b) Hydrogen sulfide can act as a weak acid.



(i) NaHS is a basic salt that undergoes salt hydrolysis. Calculate the pH of 0.100 mol dm⁻³ NaHS(aq).



The anion is then hydrolysed in water (salt hydrolysis).



$$\begin{aligned} [\text{OH}^-] &= \sqrt{K_b \times 0.100} \\ &= \sqrt{\frac{K_w}{K_a} \times 0.100} \\ &= \left(\frac{10^{-14}}{10^{-7.05}} \right) \times 0.100^{1/2} \\ &= 1.059 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \\ &= 14 - [-\log(1.059 \times 10^{-4})] \\ &= 10.0 \end{aligned}$$

EXAMINER'S COMMENTS

Surprisingly, many candidates failed to recognise that the Q asked for salt hydrolysis (anion hydrolysis in this case). Therefore, a basic pH was to be expected!

[2]

(ii) The pK_a for C₆H₅SH is 6.5. Suggest an explanation for the different pK_a values for H₂S and C₆H₅SH.

For the anion or the conjugate base, C₆H₅S⁻, the lone pair of electrons on S atom can be delocalised into the benzene ring, dispersing the negative charge on the anion and so stabilises it. This makes it less ready to accept protons. Therefore, C₆H₅SH is more acidic than H₂S and so has a lower pK_a value than H₂S

[1]

EXAMINER'S COMMENTS

Failure by candidates to indicate the lone pair of electrons on S atom specifically, rather than just electrons that could be delocalised into the benzene ring and therefore dispersing the negative charge on the conjugate base, anion C₆H₅S⁻, resulted in penalty.

- 6 (c) A solution containing hydrogensulfite ions, $\text{HSO}_3^- (\text{aq})$, and sulfite ions, $\text{SO}_3^{2-} (\text{aq})$, can act as a buffer. The K_a of $\text{HSO}_3^- (\text{aq})$ is $6.73 \times 10^{-8} \text{ mol dm}^{-3}$ at 298 K. A buffer solution is prepared by mixing 50.0 cm^3 of $0.500 \text{ mol dm}^{-3} \text{ NaHSO}_3$ and 25.0 cm^3 of $0.600 \text{ mol dm}^{-3} \text{ NaOH}$. By finding $[\text{SO}_3^{2-}]$ and $[\text{HSO}_3^-]$ after mixing NaHSO_3 and NaOH , calculate the pH of the buffer solution formed at 298 K. Show your working clearly.

$$\text{HSO}_3^- + \text{OH}^- \rightarrow \text{SO}_3^{2-} + \text{H}_2\text{O}$$

$$\text{Amount of HSO}_3^- = \left(\frac{50.0}{1000} \times 0.500 \right) = 0.0250 \text{ mol}$$

$$\text{Amount of OH}^- = \left(\frac{25.0}{1000} \times 0.600 \right) = 0.0150 \text{ mol}$$

$$\text{Amount of HSO}_3^- \text{ left after reaction} = (0.0250 - 0.0150) = 0.0100 \text{ mol}$$

$$\text{Amount of SO}_3^{2-} \text{ formed} = 0.0150 \text{ mol}$$

$$[\text{SO}_3^{2-}] = \left(0.0150 \times \frac{1000}{75.0} \right) = 0.200 \text{ mol dm}^{-3}$$

$$[\text{HSO}_3^-] = \left(0.0100 \times \frac{1000}{75.0} \right) = 0.133 \text{ mol dm}^{-3}$$

$$\text{pH} = \text{p}K_a + \lg \left(\frac{[\text{salt}]}{[\text{acid}]} \right)$$

$$= -\lg (6.73 \times 10^{-8}) + \lg \left(\frac{0.200}{0.133} \right)$$

$$= 7.35$$

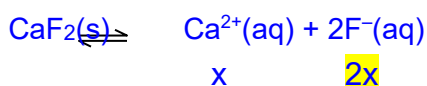
[2]

EXAMINER'S COMMENTS

A majority of candidates were not able to calculate the $[\text{HSO}_3^-]$ and $[\text{SO}_3^{2-}]$ correctly! And surprisingly, though the Q stated that the resulting mixture is a buffer solution three times (!), still, a majority of candidates failed to use the buffer equation to calculate the pH of the solution!

- (d) Calcium fluoride, CaF_2 , occurs naturally in the mineral *fluorspar*. It is the major sources of fluorine for the chemical industry, for making polymers (PTFE), freons and fire retardants. It is also sparingly soluble in water. In its saturated solution, the concentration of CaF_2 is $2.30 \times 10^{-4} \text{ mol dm}^{-3}$.

- (i) Write an expression for the solubility product, K_{sp} , of calcium fluoride, and calculate its value.



where $x = 2.30 \times 10^{-4} \text{ mol dm}^{-3}$

$$K_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2$$

$$= (x)(2x)^2 = 4x^3$$

$$= 4(2.30 \times 10^{-4})^3$$

$$= 4.87 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

EXAMINER'S COMMENTS

A rather basic and straight forward Q! However, many students were not able to calculate a value for the K_{sp} ! Failure to multiply the concentration of F^- by 2 was common! And this resulted in the wrong calculated value of the K_{sp} ! Worse still, quite a number of candidates could not give the correct expression for the K_{sp} of CaF_2 !

Expression such as $K_{sp} = [Ca^{2+}][2F^-]^2$ or $K_{sp} = [Ca^+][F^-]^2$ or $K_{sp} = [Ca^{2+}][F^-]^2$ given $[CaF_2]$

by candidates were not uncommon! It was simply amazing!

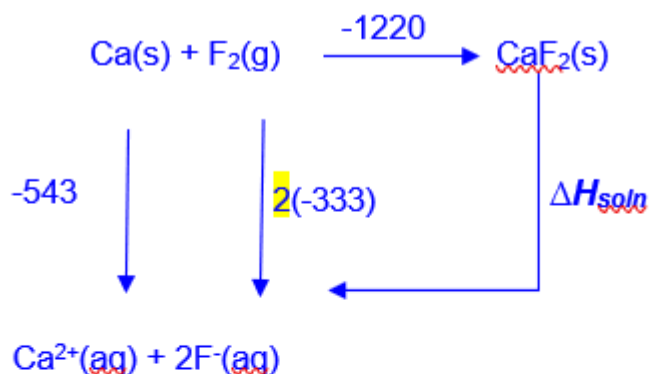
[2]

- 6 (d) (ii) Use only the relevant data provided below to calculate a value for the enthalpy change of solution of calcium fluoride.

enthalpy change of formation of $CaF_2(s)$	$-1220 \text{ kJ mol}^{-1}$
enthalpy change of atomisation of $Ca(s)$	$+178 \text{ kJ mol}^{-1}$
enthalpy change of formation of $Ca^{2+}(aq)$	-543 kJ mol^{-1}
electron affinity of fluorine atoms	-328 kJ mol^{-1}
enthalpy change of formation of $F^-(aq)$	-333 kJ mol^{-1}

[2]

Students can use either use the energy cycle method or direct application of formula to solve this question but only making use of the relevant data given. Full credit should be given for both methods.



By Hess' Law,

$$(-1220) + \Delta H_{soln} = (-543) + 2(-333)$$
$$\Delta H_{soln} = +11.0 \text{ kJ mol}^{-1}$$

OR



$$\Delta H_{soln} = \sum(\Delta H_f(\text{products})) - \sum(\Delta H_f(\text{reactants}))$$
$$= [-543 + 2(-333)] - [-1220]$$
$$= +11.0 \text{ kJ mol}^{-1}$$

EXAMINER'S COMMENTS

A common mistake made by candidates was to use **ALL** the data provided though the Q asked for the use of only the **relevant data** provided! Worse, many candidates also used even more data from the DB! As a result, the energy cycle drawn were irrelevant and confusing! No credit given here. This part of the Q was poorly done! Candidates must be informed and made aware of the use of **relevant information** only, based on the context of the Q asked!

- (iii) Hence, predict whether CaF_2 will be more, or less, soluble in hot water than in cold water.

Since the enthalpy change of solution of CaF_2 is endothermic, it follows

that the solubility will increase at a higher temperature; so it will be more

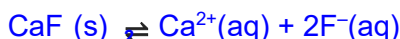
soluble in hot water

[1]

EXAMINER'S COMMENTS

Failure of candidates to provide reasons for the solubility of CaF_2 was penalised. Candidates have to take note of the words predict and hence! Predict is associated with giving a reason or explanation for the answer given and hence means based on the answer given in (ii). The expression, **endothermic** was required to obtain a mark!

- 6 (d) (iv) Describe and explain how the solubility of CaF_2 , is affected when $\text{CaCl}_2(\text{aq})$ is added. [1]



Adding CaCl_2 increases $[\text{Ca}^{2+}]$, so that the position of equilibrium

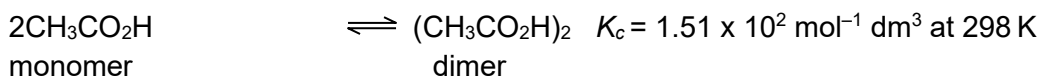
(POE) above (first equation) shifts to left due to the common ion effect. [1]

The solubility will decrease.

EXAMINER'S COMMENTS

Practically, almost all candidates failed to indicate the equation, **$\text{CaF}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2\text{F}^{-}(\text{aq})$** , when they wrote the position of equilibrium shifted to the left! No credit awarded here for their failure to do so!

- (v) In non-polar solvents, ethanoic acid, $\text{CH}_3\text{CO}_2\text{H}$, can form a dimer containing two hydrogen bonds.



- I. A solution of $0.100 \text{ mol dm}^{-3}$ $\text{CH}_3\text{CO}_2\text{H}$ is allowed to reach equilibrium in a non-polar solvent at 298 K. The equilibrium concentration of the dimer is $0.0417 \text{ mol dm}^{-3}$. Calculate the $\frac{[(\text{CH}_3\text{CO}_2\text{H})_2]}{[\text{CH}_3\text{CO}_2\text{H}]}$ ratio at equilibrium. Quote your answer to 3

	$2\text{CH}_3\text{CO}_2\text{H}$	$(\text{CH}_3\text{CO}_2\text{H})_2$
Initial / mol dm^{-3}	0.100	0
Change / mol dm^{-3}	$-2(0.0417)$	$+0.0417$
Equilibrium/ mol dm^{-3}	$0.100 - 2(0.0417)$ $= 0.0166$	0.0417

$$\frac{[(\text{CH}_3\text{CO}_2\text{H})_2]}{[\text{CH}_3\text{CO}_2\text{H}]} = \frac{0.0417}{0.0166} = 2.51$$

[1]

EXAMINER'S COMMENTS

Poorly done by candidates! The use of the K_c value provided to arrive at the answer of the ratio asked **was not necessary!** Again, it had to be emphasised as in (d)(ii) that not all data given had to use! However, some candidates did use the K_c value to calculate for the ratio. Full credit was given to those candidates too!

- II. Suggest how the ΔG for this equilibrium in an aqueous solution would differ from the ΔG in a non-polar solvent. Explain your answer. [1]

In an aqueous solution (polar water), ethanoic acid can dissociate partially into ions. In addition, hydrogen bonds can be formed between water and ethanoic acid, so decreases the feasibility of dimerisation. Therefore, ΔG will be less negative or even positive in an aqueous solution. The POE above is very much to the left.

EXAMINER'S COMMENTS

Also, poorly done by candidates! A variety of answers were given by candidates, mostly vague and unconvincing! A mere mention that in an aqueous solution (polar solvent), there is possibility of ethanoic acid dissociating into its ions or that H-bonding between it and water takes place and as a result, dimerisation of the monomer is limited, would suffice! And the corresponding effect on ΔG .

Many candidates thought incorrectly that if a reaction was **spontaneous** then ΔG should be **positive!**

[Total: 15]

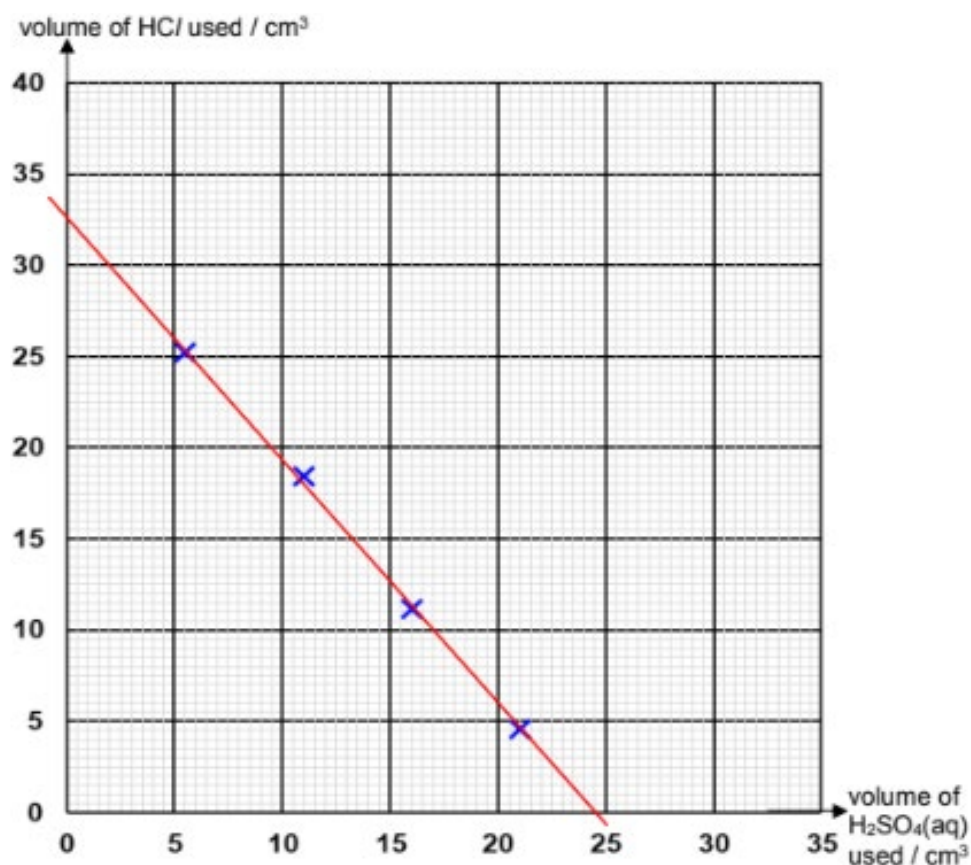
7 (a) Baryta water, barium hydroxide, $\text{Ba}(\text{OH})_2(\text{aq})$ is a Bronsted base.

Define what is meant by a Bronsted base.

Bronsted base is H^+ or proton acceptor. [1]

(b) $\text{Ba}(\text{OH})_2(\text{aq})$ neutralises both H_2SO_4 and HCl acid. In an experiment, a student prepared 4 mixtures, each containing the same volume of 25.0 cm^3 of $\text{Ba}(\text{OH})_2$ solution, but with different volumes of sulfuric acid added.

In each mixture, neutralisation has not been completed, the solution remains alkaline and is neutralised by titration with $0.150 \text{ mol dm}^{-3}$ HCl acid. A graph of volume of HCl on the y-axis was plotted against volume of H_2SO_4 for each of the 4 mixtures. The graph is extrapolated until it touches both axes.



(i) Read from the graph, and record the volume of HCl (Vol. HCl (max)), required to exactly neutralise 25.0 cm^3 of $\text{Ba}(\text{OH})_2$.

$\text{V}_{\text{HCl}}(\text{max}) = 32.50 \text{ cm}^3$ read correctly from the graph to $\pm \frac{1}{2}$ small square

[1]
[Total: 5]

(ii) Calculate the concentration of Ba(OH)₂. [2]

Using [HCl] and Vol. HCl/(max):

$$n(\text{HCl}) \text{ used} = 0.150 \times \frac{32.50}{1000} = 0.004875 \text{ mol}$$

Since 1 Ba(OH)₂ ≡ 2HCl,

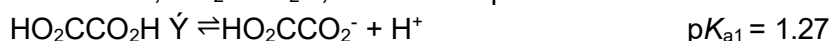
$$n\text{Ba(OH)}_2 \text{ in } 25.0 \text{ cm}^3 = \frac{1}{2} \times 0.004875 = 0.002438 \text{ mol}$$

$$[\text{Ba(OH)}_2] = 0.002438 \div \frac{25.0}{1000} = 0.0975 \text{ mol dm}^{-3}$$

(iii) Explain in terms of the chemistry involved, why the direction of the slope of the graph is negative [2]

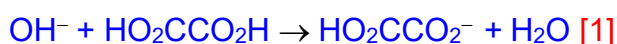
Negative gradient because the more sulfuric acid is added to 25.0 cm³ of sodium carbonate, the less sodium carbonate remaining, the less hydrochloric acid is required for neutralisation (or words to that effect).

8 (a) Oxalic acid, HO₂CCO₂H, is a weak diprotic acid.



(i) 10 cm³ of 0.100 mol dm⁻³ HO₂CCO₂H was mixed with 10 cm³ of 0.150 mol dm⁻³ HO₂CCO₂Na.

Write an equation to show how this solution is able to maintain pH upon addition of alkali.



(ii) 14.0 cm³ of 0.100 mol dm⁻³ KOH was added to the solution in (a)(i). Calculate the pH of the resultant solution after adding KOH(aq).

	OH ⁻ +	HO ₂ CCO ₂ H →	HO ₂ CCO ₂ ⁻ +	H ₂ O
I	0.0014	0.001	0.0015	
C	-0.001	-0.001	+0.001	
F	<u>0.0004</u>	0	<u>0.0025</u>	

1 mark for the amount of OH⁻ and O₂CCO₂⁻ There is still excess alkali.

	OH ⁻ +	HO ₂ CCO ₂ ⁻ →	⁻ O ₂ CCO ₂ ⁻ +	H ₂ O
I	0.0004	0.0025	0	
C	-0.0004	-0.0004	+0.0004	
F	0	<u>0.0021</u>	<u>0.0004</u>	

1 mark for the final amount of the oxalates

Another buffer has been formed.

$$\text{New total volume} = 14.0 + 10 + 10 = 34.0 \text{ cm}^3$$

$$\text{pH} = 4.28 + \lg \left[\frac{(0.0004 / 0.034)}{(0.0021 / 0.034)} \right] = \mathbf{3.56} \quad [1]$$

[3]

- (b) Rare earth ions in the oxidation state of +3, such as cerium(III) ions, Ce^{3+} , are used in the production of luminescent materials.

Solutions containing Ce^{3+} ions may sometimes be contaminated by other cations such as Ca^{2+} . The recovery of Ce^{3+} ions from such solutions can be achieved through selective precipitation using oxalic acid as the precipitating agent. After adding oxalic acid to a solution containing Ce^{3+} ions contaminated with Ca^{2+} ions, the pH of the solution is adjusted through the addition of a strong mineral acid. The purpose is to control the concentration of the oxalate anion, $\text{C}_2\text{O}_4^{2-}$ in the solution and hence ensure that maximum amount of Ce^{3+} ion is precipitated to achieve an effective separation from the contaminant cation.

Table 2.1 contains the values of the logarithm to the base 10 of the equilibrium constant, K , for some of the equilibrium reactions.

Table 2.1

Equilibrium equations	lgK
$\text{Ca}^{2+}(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq}) \rightleftharpoons \text{CaC}_2\text{O}_4(\text{s})$	8.63
$2\text{Ce}^{3+}(\text{aq}) + 3\text{C}_2\text{O}_4^{2-}(\text{aq}) \rightleftharpoons \text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{s})$	30.18
$\text{HO}_2\text{CCO}_2\text{H}(\text{aq}) \rightleftharpoons 2\text{H}^+(\text{aq}) + \text{C}_2\text{O}_4^{2-}(\text{aq})$	-5.06

The numerical values for the solubility product of CaC_2O_4 and $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ are 2.34×10^{-9} and 6.60×10^{-31} respectively.

- (i) Using data from Table 2.1, prove that the numerical value of K_{sp} of CaC_2O_4 is 2.34×10^{-9} .

$$K_{\text{sp}} \text{ of } \text{CaC}_2\text{O}_4 = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = \frac{1}{\frac{1}{[\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}]}} = \frac{1}{K} = \frac{1}{10^{\text{lg}K}} = \frac{1}{10^{8.63}}$$

$$= 2.34 \times 10^{-9} [1]$$

1 mark for establishing the relationship between K_{sp} and lg K and calculating the value of the K_{sp} of MgC_2O_4 correctly

[1]

- (ii) Solution A contains $0.010 \text{ mol dm}^{-3}$ of Ca^{2+} , $0.010 \text{ mol dm}^{-3}$ of Ce^{3+} and 1.0 mol dm^{-3} of oxalic acid. Calculate the minimum concentration of $\text{C}_2\text{O}_4^{2-}$ needed for the precipitation of Ca^{2+} and Ce^{3+} respectively.

$$K_{\text{sp}} \text{ of } \text{CaC}_2\text{O}_4 = [\text{Ca}^{2+}][\text{C}_2\text{O}_4^{2-}] = (0.010) [\text{C}_2\text{O}_4^{2-}] = 2.34 \times 10^{-9}$$

minimum concentration of $\text{C}_2\text{O}_4^{2-}$ needed for the precipitation of Ca^{2+}

$$= \frac{2.34 \times 10^{-9}}{0.010}$$

$$= 2.34 \times 10^{-7} [1]$$

K_{sp} of $Ce_2(C_2O_4)_3 = [Ce^{3+}]^2[C_2O_4^{2-}]^3 = (0.010)^2[C_2O_4^{2-}]^3 = 6.60 \times 10^{-31}$
minimum concentration of the oxalate ion, $C_2O_4^{2-}$ needed for the precipitation of Ce^{3+}

$$= \sqrt[3]{\frac{6.60 \times 10^{-31}}{(0.010)^2}}$$
$$= 1.88 \times 10^{-9} [1]$$

(iii) Using your answers in (b)(ii) and data from Table 2.1, calculate the pH of solution A that is required to precipitate the maximum amount of Ce^{3+} .

To prevent Ca^{2+} from precipitating as CaC_2O_4 , the solution must contain enough H^+ to give a maximum $[C_2O_4^{2-}]$ of $2.34 \times 10^{-7} \text{ mol dm}^{-3}$. [1]

Using the equilibrium constant for the dissociation of oxalic acid from Table 2.1, we can then calculate the required $[H^+]$ in solution A.

$$10^{-5.06} = \frac{[H^+]^2[C_2O_4^{2-}]^{2-}}{[HO_2CCO_2H]} = \frac{[H^+]^2(2.34 \times 10^{-7})}{1.0}$$

$$[H^+] = 6.095 [1]$$

$$pH = -\lg(6.095) = -0.785 [1], \text{ ecf allowed}$$

[3]

[Total: 10]

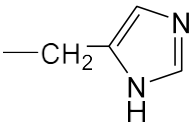
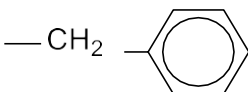
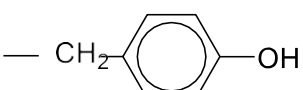
- 9 COVID-19 is an illness caused by the virus SARS-CoV-2, which was first identified amid an outbreak of respiratory illness cases in 2019.

In November 2021, a new Omicron variant was found to be the most transmissible variant compared to the previous variants, such as the Delta variant.

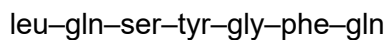
- a. The differences in the transmissibility of the variants are due to their varying amino acid sequences in a specific region X of their peptide chains.

Some of the amino acids present in the variants are listed in Table 3.1.

Table 3.1

name	abbreviation	formula of side chain (R in R-CH(NH ₂)CO ₂ H)
arginine	arg	
glutamine	gln	-CH ₂ CH ₂ CONH ₂
glutamic acid	glu	-CH ₂ CH ₂ COOH
glycine	gly	-H
leucine	leu	-CH ₂ CH(CH ₃) ₂
phenylalanine	phe	
serine	ser	-CH ₂ OH
tyrosine	tyr	

A heptapeptide found in region **X** of the Delta variant has the sequence shown below.



The heptapeptide was partially hydrolysed by heating with a concentrated solution of sodium hydroxide. The partial hydrolysis produced a mixture of dipeptides.

- i. Upon acidification of the dipeptides, leu-glu and phe-glu were obtained instead of leu-gln and phe-gln.

By referring to Table 3.1, suggest why this is so.

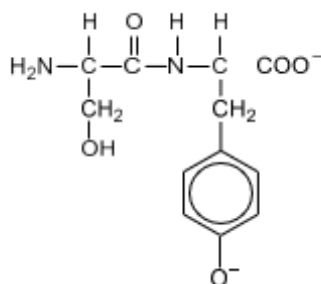
.....

.....

[1]

(ii) Ser-tyr was also one of the dipeptides formed.

Draw the structure of this dipeptide at pH 13.



[1]

Another heptapeptide found in region X of the Omicron variant was also subjected to hydrolysis under the same conditions.

The initial partial hydrolysis of this heptapeptide produced the tetrapeptides shown below.

tyr-ser-phe-arg, arg-ser-tyr-ser, leu-arg-ser-tyr

(iii) Deduce the sequence of amino acids in this heptapeptide.

leu-arg-ser-tyr
arg-ser-tyr-ser
_____ tyr-ser-phe-arg
leu-arg-ser-tyr-ser-phe-arg [1]

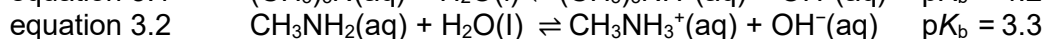
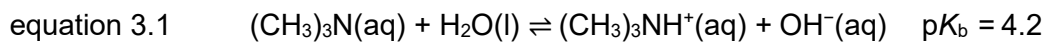
Increasing evidence suggests that gut health may be compromised in COVID-19 patients. One indicator of bad gut health is high levels of trimethylamine.

Both trimethylamine, $(\text{CH}_3)_3\text{N}$, and methylamine, CH_3NH_2 , behave as bases in the gaseous and aqueous phases.

(b) (i) Explain why, in the gaseous phase, $(\text{CH}_3)_3\text{N}$ is a stronger base than CH_3NH_2 .

$(\text{CH}_3)_3\text{N}$ is more basic as it has 2 more electron-donating alkyl groups, which increase the electron density on the N atom, making the lone pair of electrons on N more available for coordination to an electron deficient species / a proton.

In aqueous solution, the following equilibria are established.



(ii) State the predominant interaction, other than hydrogen bonding, between $(\text{CH}_3)_3\text{NH}^+$ and water.

ion-dipole interactions

(iii) Compared to $(\text{CH}_3)_3\text{NH}^+$, CH_3NH_3^+ has a stronger interaction with water.

With reference to your answer in (b)(ii), explain why this is so.

Due to its smaller ionic radius/size, CH_3NH_3^+ has a higher charge density compared to $(\text{CH}_3)_3\text{NH}^+$. Hence, CH_3NH_3 forms stronger ion-dipole interactions with water. [1]

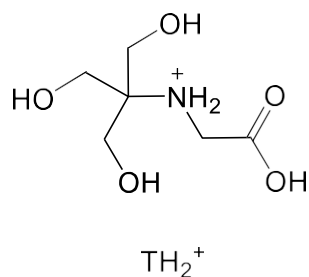
(iv) Hence, suggest why the pK_b of CH_3NH_2 is lower than that of $(\text{CH}_3)_3\text{N}$ in an aqueous solution.

The stronger interaction between CH_3NH_3^+ and water leads to greater stability and [1] causes the position of equilibrium of equation 3.2 to lie more to the right / greater extent of ionisation of CH_3NH_2 as compared to $(\text{CH}_3)_3\text{N}$. Hence, CH_3NH_2 is a stronger base with a lower pK_b .

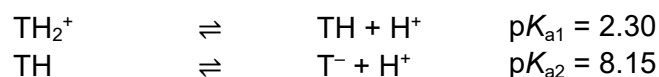
Antigen-based rapid diagnostic test kits have been used to detect the SARS-CoV-2 virus.

(c) The test kit includes a vial containing a buffer solution prepared from tricine, TH.

The structure of protonated tricine, TH_2^+ , is shown below.

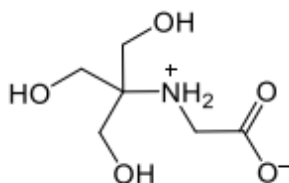


The acid dissociation involving TH^+ and TH and their corresponding pK values at 25 °C are shown below.



(i) TH exists as a solid at room temperature.

Draw the structure of TH and explain why it has a high melting point.



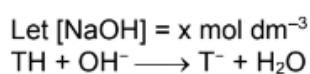
TH exists as a zwitterion with oppositely charged ends. It has a giant ionic lattice structure consisting of strong ionic bonds between the oppositely charged ends of neighbouring zwitterions. The strong ionic bonds require a large amount of heat energy to overcome. Hence, TH has a high melting point and exists as a solid at room temperature. [2]

The buffer solution is prepared by dissolving 0.1 mol of solid tricine, TH, in 1.0 dm³ of aqueous sodium hydroxide. The pH of this buffer is 8.78.

(ii) Calculate the concentration of aqueous sodium hydroxide used in the preparation of this buffer solution. [2]

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{T}^-]}{[\text{TH}]}$$

$$8.78 = 8.15 + \lg \frac{[\text{T}^-]}{[\text{TH}]}$$



$$\frac{[\text{T}^-]}{[\text{TH}]} = 10^{0.63} = \frac{x}{0.1-x}$$

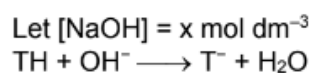
$$x = 0.08101$$

$$[\text{NaOH}] = \underline{0.0810 \text{ mol dm}^{-3}}$$

$$\text{pOH} = \text{pK}_b + \lg \frac{[\text{TH}]}{[\text{T}^-]}$$

$$\text{pK}_b = 14 - 8.15 = 5.85$$
$$\text{pOH} = 14 - 8.78 = 5.22$$

$$5.22 = 5.85 + \lg \frac{[\text{TH}]}{[\text{T}^-]}$$



$$\frac{[\text{TH}]}{[\text{T}^-]} = 10^{-0.63} = \frac{0.1-x}{x}$$

$$x = 0.08101$$

$$[\text{NaOH}] = \underline{0.0810 \text{ mol dm}^{-3}}$$

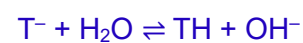
OR

- (iii) Explain how a more dilute buffer solution of the same volume will compare in terms of buffering capacity.

With lower concentrations of T^- and TH , the buffering capacity will decrease as there is less amount of T^- and TH to react with added H^+ or OH^- respectively. [1]

- (d) 10 cm^3 of 0.1 mol dm^{-3} of the deprotonated tricine, T^- , was titrated against 0.1 mol dm^{-3} of HCl from a burette.

- (i) Calculate the pH of 0.1 mol dm^{-3} of T^- solution at $25\text{ }^\circ\text{C}$. [2]



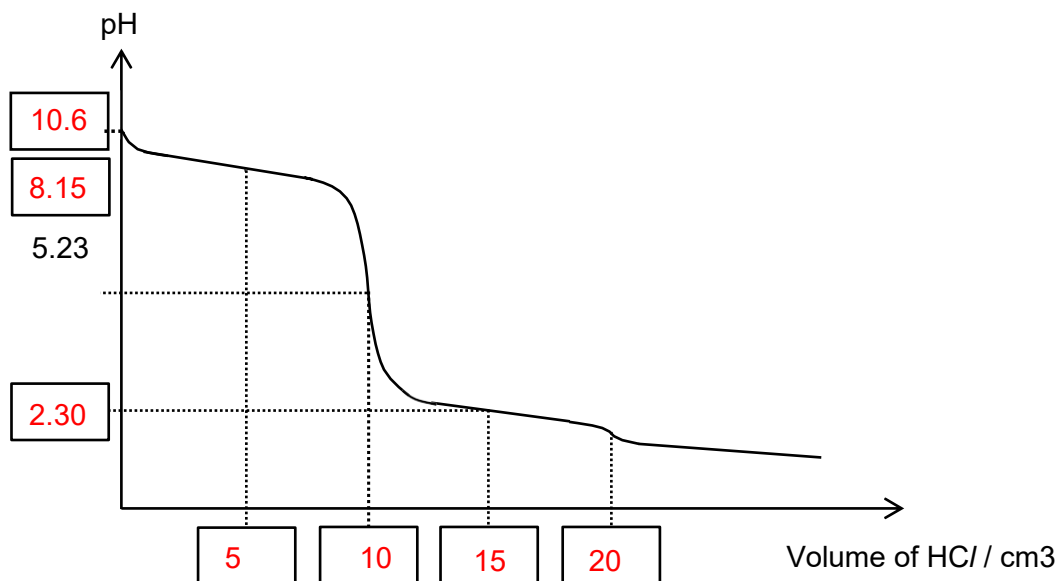
$$pK_{b2} = 14 - 8.15 = 5.85$$

$$[OH^-] = \sqrt{10^{-5.85} \times 0.1} = 3.758 \times 10^{-4}\text{ mol dm}^{-3}$$

$$pOH = -\lg(3.758 \times 10^{-4}) = 3.425$$

$$pH = 14 - 3.425 = \underline{10.6}$$

- (ii) Using your answer in (d)(i) and information in (c), fill in the boxes below with the correct pH values and HCl volumes [2]



- (iii) Methyl red is used as the indicator for determining the first end-point for this titration. It changes colour from red at pH 4.4 to yellow at pH 6.2.

Explain why methyl red is suitable for determining the first end-point. Hence, state the colour change at the first end-point of the titration.

The pH range of methyl red coincides with the region of rapid pH change in the first equivalence point. At the first end-point, the colour change is from yellow to orange. [2]

- (iv) Suggest why the second end-point cannot be determined by titration.

There is no region of rapid pH change at the second equivalence point. [1]

[Total: 19]