



Oxford Cambridge and RSA

Monday 20 June 2022 – Morning

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Advanced Notice Article

Time allowed: 2 hours 15 minutes



INSTRUCTIONS

- Do **not** send this Advanced Notice Article for marking. Keep it in the centre or recycle it.

INFORMATION

- This is a clean copy of the Advance Notice Article you have already seen.
- This document has **8** pages.

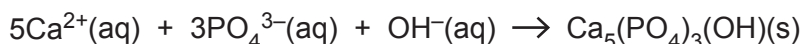
Fluoride compounds in dental hygiene

Extracted from 'The Chemistry of Dental Care' Parts 1 and 3 by Matthias Epple and Joachim Enax in *Chemistry Views* magazine, 2018.

Dental enamel is the hardest material in the human body. However, it is still possible for teeth to be damaged, for example, through cavities or consuming acidic foods. Therefore, modern dental hygiene is an important aspect of health care in general. In this article, we take a closer look at why fluoride is good for your teeth.

Enamel

The mineral phase of our teeth is based on calcium phosphate hydroxylapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$. This is precipitated under basic conditions according to the following equation:



Dental enamel consists of micrometer-sized, needle-like hydroxylapatite crystallites organized parallel to one another in crystallite bundles. It contains almost exclusively mineral components and only a small amount of protein. Due to its high mineral content and its specific microstructure, dental enamel is the hardest substance in the human body. Compared to a ceramic, dental enamel also possesses especially high resistance to breakage; that is to say, it is less brittle than tough. The outer surface of the enamel is coated with a thin protein layer (the pellicle).

Tooth decay (caries, cavities)

The most important dental disease worldwide is tooth decay.

A continuous process of de- and re-mineralization occurs within the oral cavity, on the surface of the tooth enamel. Upon consumption of acidic foods, the outer-most layer of the enamel becomes solvated and thus softened (demineralization). Fortunately, saliva is supersaturated with calcium phosphate, the result being a constant redeposition of calcium phosphate from this source (remineralization). Diseases are largely caused by bacterial biofilms (plaque). In the case of tooth decay (caries), bacteria such as *Streptococcus mutans* transform food components—mostly sugar—into acids (among others, lactic acid), which can then attack the teeth. For this reason, thoroughly cleaning the teeth is the chief goal of modern dental hygiene, in order to efficiently and effectively remove plaque deposits. If plaque is not effectively removed, calcium phosphate from saliva can be embedded within it, leading to the formation of tartar (a hardened form of dental plaque). Caries problems depend on the diet. The lower the sugar consumption, the lower the risk of caries. If acid attacks the hard material of teeth in the absence of bacteria (i.e., because of acidic dietary components such as soft drinks, fruit juice, or citrus fruits), or from gastric acid, one speaks of "acid erosion".

Fluoride compounds

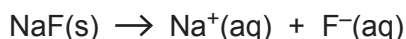
The use of fluoride-containing home tooth-care preparations is considered responsible for the considerable decrease in cases of cavities in recent decades. In Europe, however, oral hygiene agents are legally classified as cosmetic resources, and are thus subject to the European Cosmetic Ordinance. This, in turn, specifies a maximum allowed concentration of fluoride. Thus, the highest permitted fluoride level in toothpaste is 0.15% (calculated on the basis of F^-).

The amount actually present is made clear on the packaging of a fluoride toothpaste intended for adults; a typical value is 1450 ppm fluoride (i.e., 0.145%). Care is particularly called for with respect to children, since excessive fluoride levels can lead to fluorosis, a condition in which excess fluoride is incorporated into the teeth, leading to a yellowish discoloration.

Fluoride is the base corresponding to the moderately strong acid HF (hydrofluoric acid; $pK_a = 3.14$). Under the conditions normally present in the oral cavity ($pH = ca. 7$) the equilibrium lies fully on the side of the free fluoride ion. Even under acidic conditions, which can be encountered in plaque ($pH = ca. 5$), fluoride is present predominantly as the free anion, not in the form of HF. The fluoride in domestic products for dental hygiene may be introduced in the form of various compounds. In Germany, the most common fluoride source at present is sodium fluoride.

Sodium fluoride

The salt NaF is very water-soluble. In aqueous solution it dissociates into ions:



The nature of the counter-ion (sodium, potassium) here plays no significant role. Dissociation occurs immediately upon dissolution in water.

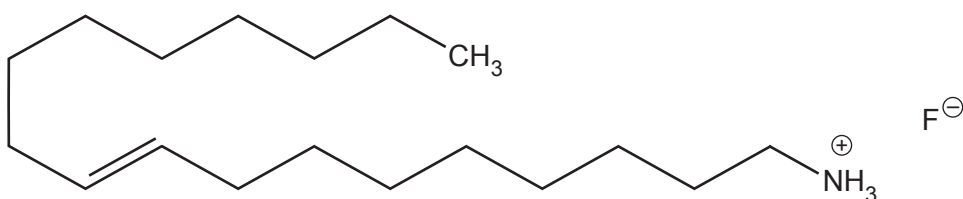
Tin difluoride

SnF_2 is a covalent material (i.e., not an ionic salt). The release of fluoride ions, in this case, requires hydrolysis.

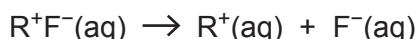
This occurs more rapidly at higher pH and higher temperature. Fluoride release here is clearly less rapid than with sodium fluoride, which dissociates into ions immediately upon dissolving.

Amine hydrofluorides

These are salts comprised of a cationic surfactant (ammonium salt) and the fluoride ion. A typical example is dactaflur:



Dissolution in water leads to immediate and complete dissociation, corresponding to:



This dissociation is independent of the nature of the ions, i.e., the same occurs with chloride instead of fluoride as the counterion.

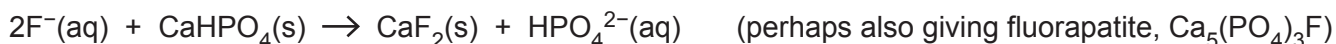
Effect of fluorine

Fluoride has a prophylactic effect against caries. The cationic surfactant plays a bacteriocidal role. Here, the bacteriocidal effect is not a function of the fluoride, as can be shown by the use of the corresponding amine hydrochloride.

It is also important to note that fluoride ions can be deactivated by calcium-containing cleansers, i.e., calcium carbonate:



or calcium hydrogen phosphate:



Solution and precipitation equilibria in the oral cavity

The mode of action of fluoride can be readily understood from a chemical standpoint in terms of the solid phases present and their solubility products. The source of the fluoride is irrelevant, incidentally; what is instead always important is fluoride ions in solution.

In what follows, we provide various calculations related to both dissolved and solid phases in the presence of fluoride in saliva. It is important to us in this context that these calculations – without complex numeric solution procedures – suffice for taking into account subsequent precipitation, protolysis, and complex-formation equilibria. They will, thus, rely on a few simplifying assumptions, but for this reason remain readily intelligible.

We assume in what follows that all ions are present in pure water. The following numerical values are thus employed in the calculations.

Compound	K_{sp} (M = mol dm ⁻³)
hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$	$1.58 \times 10^{-59} \text{M}^9$
fluorapatite $\text{Ca}_5(\text{PO}_4)_3\text{F}$	$9 \times 10^{-61} \text{M}^9$
calcium fluoride CaF_2	$3.9 \times 10^{-11} \text{M}^3$

Table 1.1

Ion	Concentration in saliva (M = mol dm ⁻³)
$[\text{Ca}^{2+}]$	$1.43 \times 10^{-3} \text{M}$
$[\text{PO}_4^{3-}]$	$2.55 \times 10^{-8} \text{M}$
$[\text{F}^{-}]$ after brushing with toothpaste containing 1500 ppm of fluoride, diluted ca. 1:10	150 ppm = $7.9 \times 10^{-3} \text{M}$

Table 1.2

The pH of saliva is assumed to be 7.0.

Let us consider the solubility equilibrium in saliva for **hydroxylapatite**, $\text{Ca}_5(\text{PO}_4)_3\text{OH}$; the mineral substance in teeth.

For the ion product, IP, the following applies:

$$\text{IP} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{OH}^-] = (1.43 \times 10^{-3})^5 \times (2.55 \times 10^{-8})^3 \times 10^{-7} \text{M}^9 = 9.9 \times 10^{-45} \text{M}^9$$

$$K_{\text{sp}} = 1.58 \times 10^{-59} \text{M}^9$$

Supersaturation, as opposed to precipitation, can be calculated using:

$$\sqrt[9]{\frac{\text{IP}}{K_{\text{sp}}}} = \sqrt[9]{6.3 \times 10^{14}} = 44$$

At pH 7, saliva is therefore highly supersaturated with respect to hydroxylapatite. This is to be expected, since teeth do not dissolve under neutral conditions. However, it illustrates the possibility for remineralization of tooth enamel after attack by acid.

Consider now the solubility equilibrium for **fluorapatite**, $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

For saliva containing 150 ppm fluoride after brushing, it remains true that:

$$\text{IP} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 [\text{F}^-] = (1.43 \times 10^{-3})^5 \times (2.55 \times 10^{-8})^3 \times 7.9 \times 10^{-3} \text{M}^9 = 7.8 \times 10^{-40} \text{M}^9$$

$$K_{\text{sp}} = 9 \times 10^{-61} \text{M}^9$$

with a supersaturation of:

$$\sqrt[9]{\frac{\text{IP}}{K_{\text{sp}}}} = \sqrt[9]{8.7 \times 10^{20}} = 212$$

In the presence of fluoride, saliva is thus very highly supersaturated relative to the precipitation of fluorapatite.

Finally, we consider the solution equilibrium of **calcium fluoride**, CaF_2 , in the presence of fluoride-containing saliva. Saliva containing 150 ppm fluoride ($7.9 \times 10^{-3} \text{M}$) after brushing can be shown to have a calcium fluoride supersaturation in double figures but much lower than fluorapatite.

After brushing with fluoride-containing toothpaste, it is thus possible that there will be precipitation of CaF_2 . But the supersaturation of fluorapatite is much greater.

The protective effect of fluoride against caries

Various mechanisms of action have been discussed with respect to the anticavity (anticaries) effect of fluoride (see **Table 1.3** below). The central point in this context is the accelerated crystallization (nucleation) of calcium phosphate during remineralization. However, the incorporation of fluoride into the enamel during routine daily tooth care is extremely limited (fluoride content of 500–1,000 ppm in the outer layer of solid tooth enamel; a stoichiometric fluorapatite would have a much higher ppm). There is also no detectable evidence for an acid-insoluble protective layer of calcium fluoride or fluorapatite. As a result, the activity of fluoride is apparently due to the effects of dental hygiene itself.

The discovery that the fluoride concentration is very low in the outermost enamel layer of the teeth, and that no crystalline calcium fluoride is detectable, indicates substoichiometric inclusion of fluoride in the hydroxyapatite lattice. Fluorapatite and hydroxylapatite are hardly distinguishable crystallographically, especially in the presence of extraneous ions. One can conclude that, due to its higher degree of supersaturation, fluorapatite crystallizes first, and acting as a seed, accelerates the further deposition of hydroxylapatite, without the incorporation of large amounts of fluoride.

Fluoride thus functions as a “catalyst” for the natural remineralization process from the saliva. Furthermore, the active agent fluoride requires saliva (i.e., the presence of calcium and phosphate ions) to be effective.

It is interesting to compare human teeth with shark teeth. The enamel of the shark tooth (enameloid) consists of almost stoichiometric amounts of fluorapatite, $\text{Ca}_5(\text{PO}_3)_3\text{F}$. Studies have shown that shark teeth, despite their high fluoride content, are subject to attack by acid. Shark teeth are just as hard as human teeth, so that one cannot assume hardening of the enamel through an integration of fluoride after use of a fluoride-containing oral-care product. The antibacterial effect of fluorides is due mainly to the counterion (with amine hydrofluorides, the cationic amine, with tin fluoride the $\text{Sn}(\text{II})$), and not to fluoride itself. The fluoride concentration is too low to produce an effective antibacterial activity. The table below summarizes these findings.

Postulated mechanism of action for fluorides in home dental care, with comments from a chemical point of view:

Postulated mechanism	Comments
Improved remineralization	Yes, due to improved nucleation through precipitation of fluorapatite
Formation of a protective layer of fluorapatite and/or calcium fluoride to protect against erosion as a fluoride reservoir	No, because fluorapatite and calcium fluoride are both acid-soluble, i.e. no acid-stable shell forms around the tooth
Inclusion of fluoride in the enamel	Only on the surface to a very limited extent
Hardening of the enamel	Scarcely, even in the case of stoichiometric fluoride incorporation; even shark tooth enamel (fluorapatite) is not significantly harder than human tooth enamel
Antibacterial effects	At least with toothpaste, fluoride concentrations are too low; fluoride antibacterial activity is due mostly to the counterion (i.e. amine or tin), not to the fluoride

Table 1.3

END OF ADVANCE NOTICE ARTICLE

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Monday 20 June 2022 – Morning

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Time allowed: 2 hours 15 minutes

You must have:

- a clean copy of the Advance Notice Article (inside this document)
- the Data Sheet for Chemistry B

You can use:

- a scientific or graphical calculator
- an HB pencil



Please write clearly in black ink. **Do not write in the barcodes.**

Centre number

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Candidate number

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First name(s)

Last name

INSTRUCTIONS

- Use black ink. You can use an HB pencil, but only for graphs and diagrams.
- Write your answer to each question in the space provided. If you need extra space use the lined pages at the end of this booklet. The question numbers must be clearly shown.
- Answer **all** the questions.
- Where appropriate, your answer should be supported with working. Marks might be given for using a correct method, even if your answer is wrong.

INFORMATION

- The total mark for this paper is **100**.
- The marks for each question are shown in brackets [].
- Quality of extended response will be assessed in questions marked with an asterisk (*).
- This document has **20** pages.

ADVICE

- Read each question carefully before you start your answer.

Answer **all** the questions.

- 1 Portland cement is a powder that 'sets' to a strong solid when water is added. The cement is usually mixed with gravel so that it sets to make concrete.

The typical ingredients of Portland cement are shown in the table.

Ingredients (solids)	% by mass
CaO	61 – 67
SiO ₂	19 – 23
Al ₂ O ₃	2.5 – 6
Fe ₂ O ₃	0 – 6
SO ₃	1.5 – 4.5

- (a) Give the systematic name for Fe₂O₃.

..... [1]

- (b) (i) A hazard warning for Portland cement states that it is alkaline.

One of the ingredients in the table reacts with water to form an alkaline solution.

Write an equation for the reaction of this ingredient with water including any ions that are formed.

[2]

- (ii) When Portland cement sets, the calcium oxide absorbs carbon dioxide from the air.

Suggest an equation for the reaction that occurs.

[1]

- (c) One way of testing for the presence of calcium in the cement would be a flame test, though any iron present would interfere.

- (i) What is the flame colour of calcium?

..... [1]

- (ii) The flame colour is caused by bright lines in the atomic emission spectrum of calcium.

Explain how these lines are formed.

.....

.....

.....

..... [2]

- (iii) Calculate the frequency of a line of wavelength 6.16×10^{-7} m.

frequency = Hz [2]

- (d) Fe_2O_3 and CaO are present in Portland cement.

- (i) In which 'blocks' of the periodic table are these elements found?

Ca

Fe [1]

- (ii) The electron configuration of a calcium **ion** is $1s^2 2s^2 2p^6 3s^2 3p^6$.

How does the electron configuration of the **cation** in Fe_2O_3 differ from this?

.....

..... [1]

- (iii) Explain why iron can form two stable cations.

.....

..... [1]

- (e) Fe_2O_3 is soluble in concentrated hydrochloric acid.

Excess sodium hydroxide is added to this solution.

Name the precipitate formed and describe its colour.

name:

colour: [1]

- (f) (i) A student has a solution containing Fe³⁺(aq) and reads that it will react with iodide ions to form iodine. The iodine can then be titrated with sodium thiosulfate.

Describe a method to measure the volume of sodium thiosulfate solution required to react with the iodine from 25 cm³ of Fe³⁺(aq).

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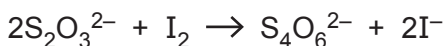
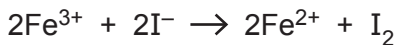
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[5]

- (ii) The student finds that 25.0 cm³ of Fe³⁺(aq) requires 3.2 cm³ of 0.510 mol dm⁻³ sodium thiosulfate.

Calculate the concentration of the Fe³⁺(aq).



Give your answer to an **appropriate** number of significant figures.

[Fe³⁺] = mol dm⁻³ [3]

- (iii) The student decides to repeat the experiment using $0.0510 \text{ mol dm}^{-3}$ sodium thiosulfate.

Suggest why the student does this.

.....

 [2]

- (g) Iron is formed in stars by fusion reactions.

Complete the nuclear equation for one such reaction.



- (h) The table shows the stable isotopes of iron and their abundances.

Mass number	Abundance / %
54	5.85
56	91.75
57	2.12
58	0.28

- (i) What is meant by the term **mass number**?

.....
 [1]

- (ii) Explain, without doing a calculation, how this data shows that the relative atomic mass of iron is below 56.

.....

 [1]

2 'Polybutene' is used in lip gloss.

The monomers for polybutene are the three isomers of butene, which are 2-methylpropene, but-2-ene and isomer **A**.

(a) Draw the **skeletal** formula of isomer **A** and name it.

skeletal formula:

name: [1]

(b) Give the number of π bonds and σ bonds in but-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$.

π bonds σ bonds [1]

(c) But-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$, exists as *E* and *Z* isomers.

(i) Draw the structure of the *E* isomer of but-2-ene.

[1]

(ii) Does 2-methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$, have *E* and *Z* isomers?

Explain your answer.

.....
 [1]

(d) Draw the repeating unit of the polymer of 2-methylpropene, $(\text{CH}_3)_2\text{C}=\text{CH}_2$.

[1]

(e) The presence of the three isomers as monomers in 'polybutene' means that different side-chains are present that do not allow the polymer chains to get close together. This causes the polymer to be a liquid suitable for lip gloss.

Name the intermolecular bonds that hold the chains together in polybutene.

..... [1]

- (f) But-2-ene, $\text{CH}_3\text{CH}=\text{CHCH}_3$, reacts with hydrogen bromide.

Draw the mechanism for this reaction.

Show curly arrows, full charges and the product.

[3]

- (g) But-2-ene reacts with hydrogen to form butane.

Name a catalyst and the corresponding conditions for this reaction.

catalyst:

conditions: [1]

- (h) But-2-ene is formed industrially by cracking alkanes from crude oil.

- (i) Complete the equation for a cracking reaction.

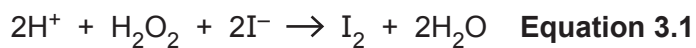


- (ii) Cracking is an example of heterogeneous catalysis.

Name the **first** step in the mechanism of heterogeneous catalysis.

..... [1]

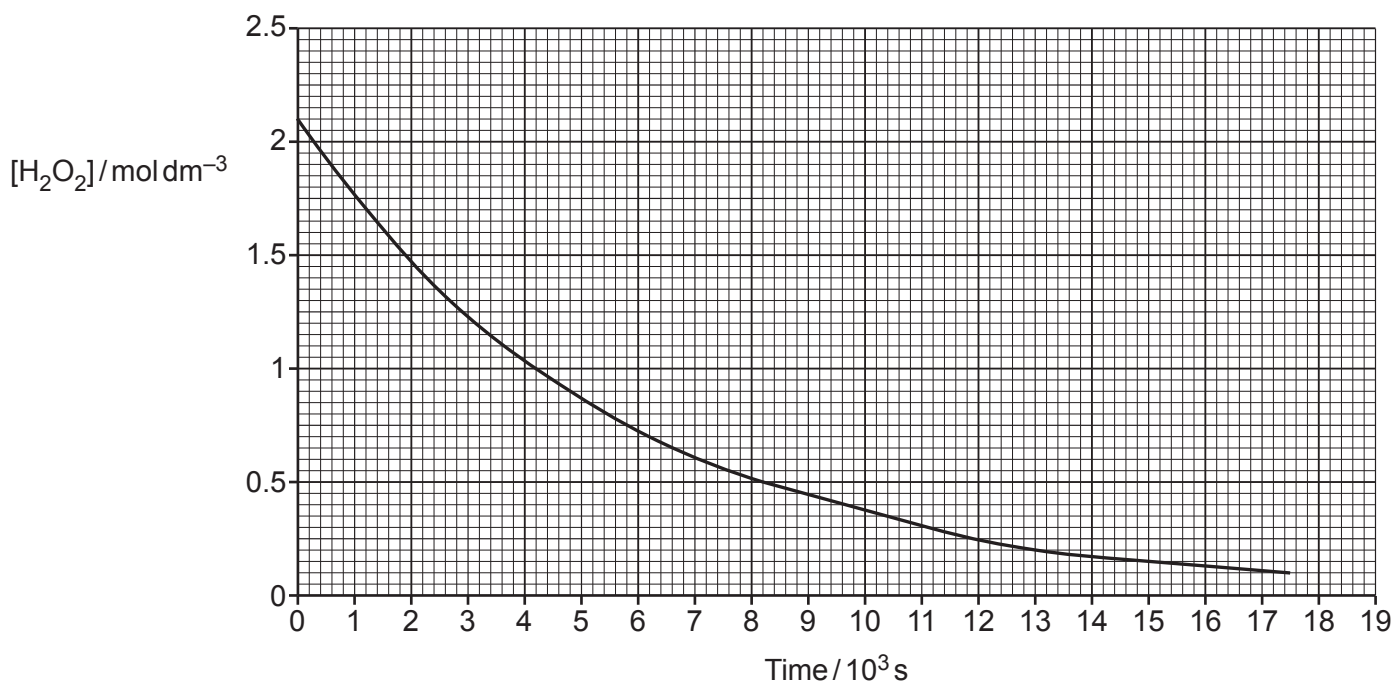
- 3 Some students read about the reaction between hydrogen peroxide and iodide ions as shown in equation 3.1.



- (a) The students find the results of an experiment which measures the concentration of hydrogen peroxide at various times.

Large excesses of acid and iodide ions are present.

The students plot a graph of these results as shown below.



- (i) Use the graph to measure two half-lives to show that the kinetics are first order.

Show your working on the graph.

first half-life =

second half-life = [3]

- (ii) Use the graph to measure the initial rate of the reaction in mol dm⁻³ s⁻¹.

initial rate = mol dm⁻³ s⁻¹ [1]

- (iii) The graph shows that the reaction in **equation 3.1** is first order with respect to hydrogen peroxide.

Explain why the orders with respect to the other reagents cannot be determined from this experiment.

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

- (b) The students then set up some experiments to find the orders of reaction with respect to iodide and hydrogen ions.

At the starting time they mix the hydrogen peroxide, acid and iodide ions together with a fixed volume of sodium thiosulfate and starch solutions.

They measure the time for the colourless solutions suddenly to go dark blue as iodine is formed.

- (i) Suggest why the tubes go dark blue after a period of time rather than gradually from the start.

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

- (ii) How can the relative rates of reaction be found from the students' results?

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

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.....

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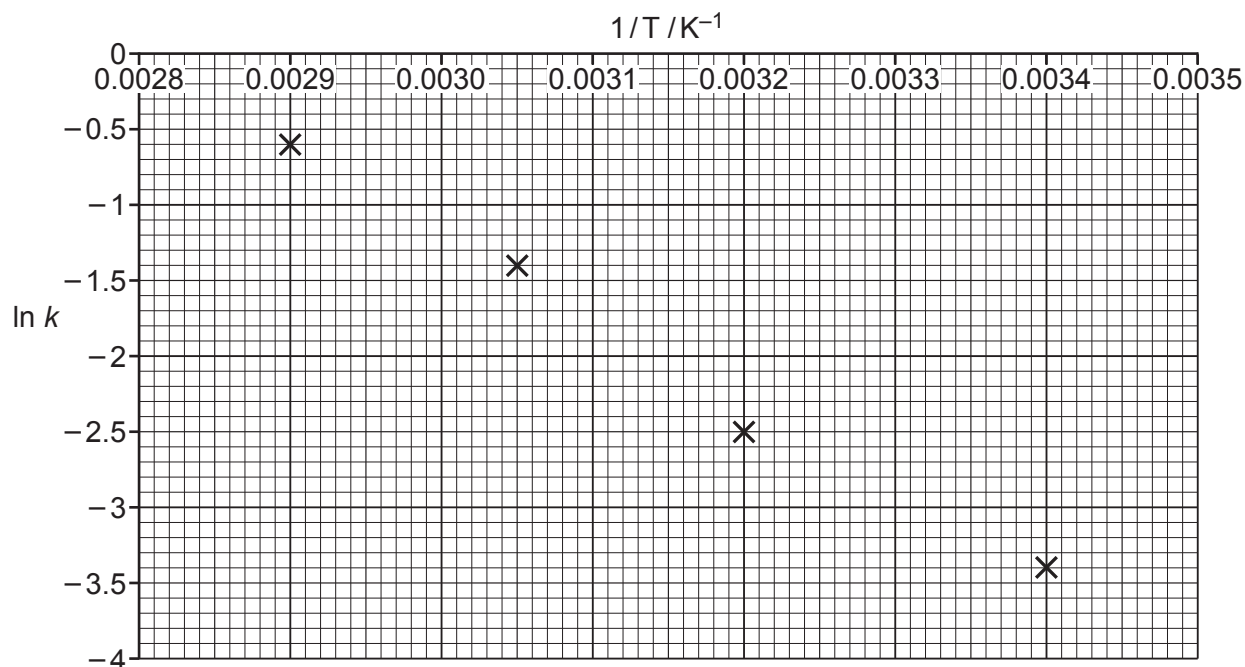
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- (d) The students find data for the variation of the rate constant, k , with temperature. From their data they plot the graph below.



Use the graph to calculate E_a in kJ mol^{-1} for the reaction in **equation 3.1**.

$$E_a = \dots\dots\dots \text{kJ mol}^{-1} \text{ [4]}$$

4 Chymotrypsin is an enzyme present in the small intestine.

One of the amino acids in chymotrypsin is serine, which can be represented as HOOCCHRNH_2 .

(a) (i) A molecule of serine has a chiral centre and two enantiomers.

Draw and label **two** serine molecules below to illustrate the meaning of the terms **chiral centre** and **enantiomer**.



[3]

(ii) Glycine $\text{HOOCCH}_2\text{NH}_2$ is another amino acid.

In solution, glycine exists as a zwitterion.
Draw the structure of this zwitterion.

[1]

(b) Serine reacts with glycine to form two dipeptides.

(i) In the boxes below, draw the structural formulae for the two dipeptides.

--	--

[2]

- (ii) Explain, with a reason, whether the reaction to form the dipeptides is condensation or addition.

.....
 [1]

- (c) Chymotrypsin is a protein with a definite amino acid sequence and parts that have an α -helical structure.

- (i) What name is given to the amino acid sequence of a protein?

..... [1]

- (ii) What name is given to the α -helical structure and how is it held together?

.....

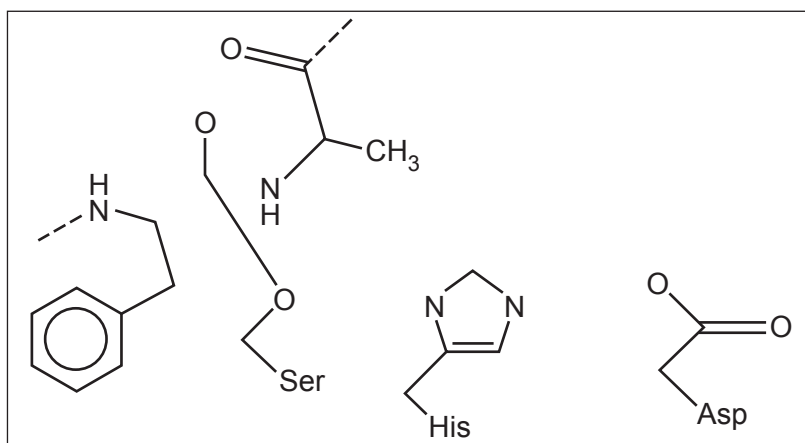
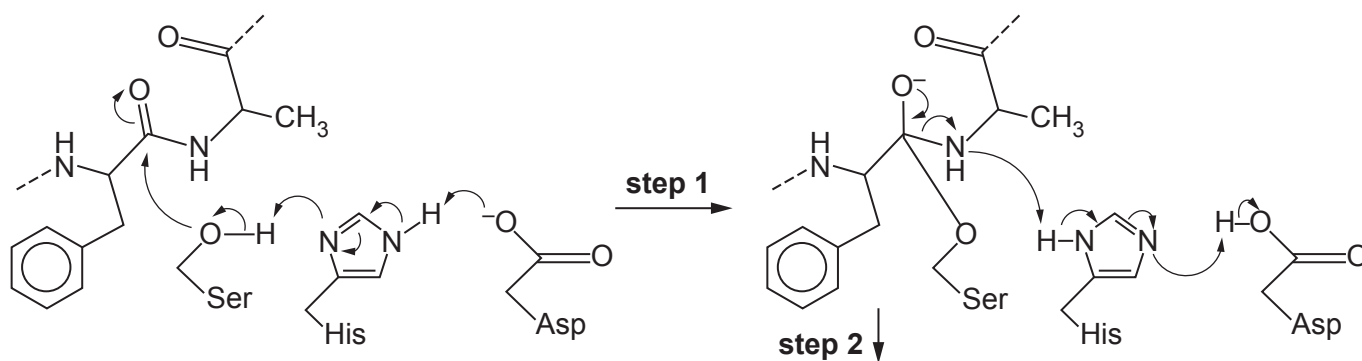
 [2]

- (d) Chymotrypsin catalyses the hydrolysis of proteins in the small intestine.

The active site of chymotrypsin consists of the amino acids serine, histidine and aspartic acid. These occur on different parts of the chain that are brought together by the folding of the structure.

The start of the hydrolysis mechanism is shown below. The protein being hydrolysed is at the top left.

Complete the diagram in the box below to show the results of the electron movements in step 2.



(e) (i) Explain why warming a solution of chymotrypsin will destroy its activity as an enzyme.

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

(ii) Chymotrypsin has an optimum pH = 8.

Draw a sketch to suggest the shape of the graph of chymotrypsin activity against pH.

Explain the shape of your graph.

.....
..... [3]

(iii) A student says that the rate of an enzyme reaction is proportional to the substrate concentration.

Comment on the student's statement, correcting any errors.

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

5 This question concerns the Advanced Notice Article 'Fluoride compounds in dental hygiene' that is included as an insert with this paper.

(a) Hydrofluoric acid (HF) is described in the article as 'moderately strong' with a pK_a of 3.14.

(i) Write the expression for K_a for HF and give its units.

$$K_a =$$

units [2]

(ii) Calculate the $\frac{[F^-]}{[HF]}$ ratio in hydrofluoric acid under the acidic conditions in plaque at pH 5.0.

$$\frac{[F^-]}{[HF]} = \dots\dots\dots [3]$$

(b) The HPO_4^{2-} ion is mentioned in the article.

Write the formula of the conjugate base of the HPO_4^{2-} ion and explain your answer.

.....

 [2]

(c) SnF_2 is said in the article to hydrolyse at 'higher pH'.

Suggest an equation for the reaction between SnF_2 and hydroxide ions.

[1]

(d) Name the shape around the N atom in the $-NH_3^+$ group in dectafur.

..... [1]

- (e) (i) Explain the relationship between the ion product, IP, and the solubility product, K_{sp} , for an ionic substance.

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

- (ii) Calculate the supersaturation of calcium fluoride in saliva after brushing.

Give your answer to the **nearest whole number**.

supersaturation = [3]

- (f) Calculate the ppm by mass of fluorine in pure fluoroapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$.

ppm by mass = [2]

ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).

A large area of lined paper for writing answers. It features a vertical margin line on the left side and horizontal dotted lines for writing. The lines are evenly spaced and extend across the width of the page.

A series of 24 horizontal dotted lines for writing, with a vertical solid line on the left side.

A large area of the page is reserved for writing, featuring a vertical solid line on the left side and horizontal dotted lines extending across the page.

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