

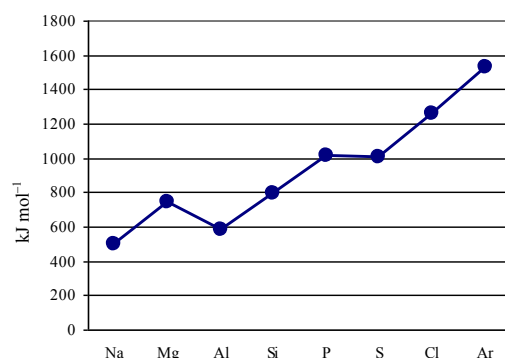
- In general terms, which elements in the periodic table are likely to be essential elements for living species and which ones are likely to be toxic. Explain.

Marks
2

Most of the lighter elements (at. no. up to 20) are essential elements. They are readily available in nature, so more likely to be utilised by organisms. Similarly most of the lighter *d*-block elements (Sc - Zn) are essential (utilised in redox and electron transport systems in the body) whereas the heavier transition metals are generally toxic.

- The diagram below shows the general trend for the first ionisation energy for some *s* and *p* block elements.

3

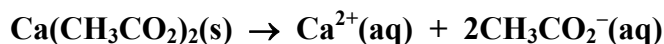


How will the general trend differ for the second ionisation energy of these elements (*i.e.* $X^+(g) \rightarrow X^{2+}(g) + e^-$)? Explain.

The second ionisation of Na will be off the scale as a core electron is ionised. (Actual value > 4500 kJ mol⁻¹)

Mg⁺ is isoelectronic with Na, Al⁺ is isoelectronic with Mg, *etc.*, so the second ionisations of the other elements follow the same trends as the first ionisations (for exactly the same reasons), but displaced one atomic number to the right and at a slightly higher energy (as Z_{eff} is greater).

- Write the balanced chemical equation for the dissolution of solid $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ in water.



What is the pH of a solution that has 158.2 g of $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ dissolved in 1.000 L of water? The $\text{p}K_a$ of acetic acid, CH_3COOH , is 4.76.

The molar mass of $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ is:

$$\begin{aligned} \text{molar mass} &= (40.08 (\text{Ca}) + 4 \times 12.01 (\text{C}) + 6 \times 1.008 (\text{H}) + 4 \times 16.00 (\text{O})) \text{ g mol}^{-1} \\ &= 158.168 \text{ g mol}^{-1} \end{aligned}$$

Thus, 158.2 g corresponds to:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{158.2 \text{ g}}{158.168 \text{ g mol}^{-1}} = 1.000 \text{ mol}$$

When $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ is dissolved, it produces $\text{Ca}^{2+}(\text{aq}) + 2\text{CH}_3\text{CO}_2^-$. Hence, if 1.000 mol of $\text{Ca}(\text{CH}_3\text{CO}_2)_2$ is dissolved in 1.0 L, $[\text{CH}_3\text{CO}_2^-]_{\text{initial}} = 2.000 \text{ M}$.

As CH_3CO_2^- is a weak base, $[\text{CH}_3\text{CO}_2^-]$ must be calculated by considering the equilibrium:

	CH_3CO_2^-	H_2O	\rightleftharpoons	$\text{CH}_3\text{CO}_2\text{H}$	OH^-
initial	2.000	large		0	0
change	-x	negligible		+x	+x
final	$2.000 - x$	large		x	x

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{CH}_3\text{CO}_2\text{H}][\text{OH}^-]}{[\text{CH}_3\text{CO}_2^-]} = \frac{x^2}{(2.000 - x)}$$

For an acid and its conjugate base:

$$\text{p}K_a + \text{p}K_b = 14.00 \text{ so } \text{p}K_b = 14.00 - 4.76 = 9.24$$

As $\text{p}K_b = 9.24$, $K_b = 10^{-9.24}$. K_b is very small so $2.000 - x \sim 2.000$ and hence:

$$x^2 = 2.000 \times 10^{-9.24} \text{ or } y = 0.0000393 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$\text{pOH} = -\log_{10}[\text{OH}^-] = \log_{10}[0.0000393] = 4.47$$

Finally, $\text{pH} + \text{pOH} = 14.00$ so

$$\text{pH} = 14.000 - 4.47 = 9.53$$

$$\text{pH} = 9.53$$

Calculate the pH of this solution after the addition of 0.250 mol of HCl gas?

The solution contain 2.000 mol of CH_3CO_2^- . This will react with 0.250 mol of $\text{HCl}(\text{g})$ to produce 0.250 mol of $\text{CH}_3\text{CO}_2\text{H}$, leaving $(2.000 - 0.250)$ mol = 1.750 mol of CH_3CO_2^- in unreacted.

As the solution has a volume of 1.000 L, $[\text{CH}_3\text{CO}_2\text{H}] = 0.250$ M and $[\text{CH}_3\text{CO}_2^-] = 1.750$ M.

The solution contains a weak acid and its conjugate base. The pH of this buffer solution can be calculated using the Henderson-Hasselbalch equation;

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{1.750}{0.250} = 5.61$$

$$\text{pH} = 5.61$$

Marks
2

- What physical state would water adopt under ambient conditions (1 atm and 25 °C) if it did not possess hydrogen bonding? Explain.

Water would be a gas.

The other hydrides of group 16 elements increase in boiling point as the molar mass increases, due to the increase in dispersion forces. H₂S is a gas. As the dispersion forces in water are weaker, it would be a gas too.

H₂O has an anomalously high boiling point due to its H-bonds. Without H-bonds it would have a boiling point below that of H₂S.

3

- Henry's law describes the solubility of a gas in a liquid phase. What methods are possible to ensure a patient receives enough oxygen during surgery? Which method is the most practical? Explain.

Henry's law states that the higher the pressure of gas above a liquid, the greater the solubility of the gas in that liquid:

$$c = kP$$

Normal air is 21% O₂. Anaesthetists can ensure a patient receives enough O₂ during surgery by increasing the % (*i.e.* partial pressure) of O₂ in the gas the patient breathes. This is the most practical and easy approach.

The alternative would be to get the patient to breathe a mixture of air at a pressure greater than 1 atm, but this would be more difficult to control and could lead to other problems (*e.g.* "the bends").

2

- A saline solution used to administer drugs intravenously is prepared by dissolving 0.90 g NaCl in 100.0 mL water. What mass of glucose (C₆H₁₂O₆) is required to prepare a 100.0 mL solution with the same osmotic pressure?

The formula mass of NaCl is (22.99 (Na) + 35.45 (Cl)) g mol⁻¹ = 58.55 g mol⁻¹. The number of moles in 0.90 g is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{formula mass}} = \frac{0.90 \text{ g}}{58.55 \text{ g mol}^{-1}} = 0.015 \text{ mol}$$

Dissolution of NaCl(s) produces Na⁺(aq) and Cl⁻(aq) so the total number of moles of ions present is 2 × 0.015 mol = 0.030 mol. The concentration of ions in a solution with volume 100.0 mL is thus:

$$\text{concentration} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.030 \text{ mol}}{0.1000 \text{ L}} = 0.30 \text{ mol L}^{-1} = 0.30 \text{ M}$$

The osmotic pressure is related to the concentration by $\Pi = cRT$. As glucose does not dissociate in solution, to produce the same concentration of particles in solution requires 0.030 mol of glucose.

ANSWER CONTINUES ON THE NEXT PAGE

The molar mass of glucose, $C_6H_{12}O_6$ is $(6 \times 12.01 \text{ (C)} + 12 \times 1.008 \text{ (H)} + 6 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} = 180.156 \text{ g mol}^{-1}$.

The mass of 0.030 mol of glucose is therefore:

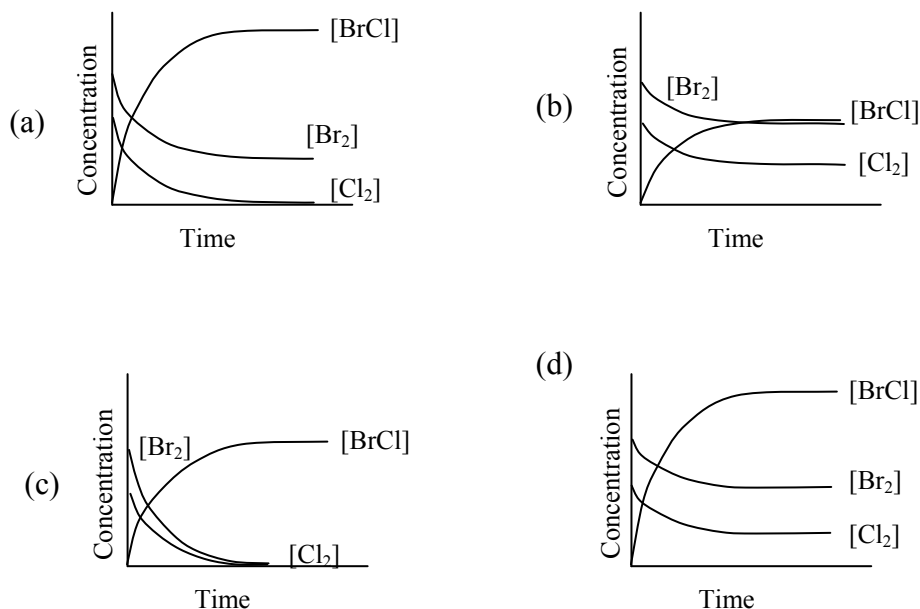
$$\begin{aligned} \text{mass} &= \text{number of moles} \times \text{molar mass} = (0.030 \text{ mol}) \times (180.156 \text{ g mol}^{-1}) \\ &= 5.4 \text{ g} \end{aligned}$$

Answer: 5.4 g

- In the reaction of Cl_2 with Br_2 in CCl_4 solution, BrCl forms according to the equation:



With initial concentrations of $[\text{Br}_2] = 0.6 \text{ M}$, $[\text{Cl}_2] = 0.4 \text{ M}$ and $[\text{BrCl}] = 0.0 \text{ M}$, which of the following concentration versus time graphs represents this reaction? Explain why you rejected each of the other three graphs.



Graph B is correct.

Graph A has $[\text{Cl}_2]$ tending to zero and graph C has both $[\text{Cl}_2]$ and $[\text{Br}_2]$ tending to zero. As $K_c = 2$, the reaction does not go anywhere near to completion.

In Graph C, the rates of change of $[\text{Br}_2]$ and $[\text{Cl}_2]$ are different. The chemical reaction shows that these react with a 1 : 1 stoichiometry and so their concentrations should decrease at the same rate.

As the initial concentration of $[\text{Cl}_2] > [\text{Br}_2]$ and these react with a 1 : 1 stoichiometry, $[\text{Cl}_2]$ is the limiting reagent. The maximum value of $[\text{BrCl}]$ is limited by the initial $[\text{Cl}_2]$. As $[\text{Cl}_2]_{\text{initial}} = 0.4 \text{ M}$ and the chemical equation shows that 2BrCl are made from each Cl_2 , $[\text{BrCl}]_{\text{final}} = 0.8 \text{ M}$. In graph D, $[\text{BrCl}]$ is larger than $2 \times [\text{Cl}_2]_{\text{initial}}$ so this graph can also be ruled out.

Marks
2

- The radioactive isotope ^{99m}Tc has a half life of 6.0 hours. How much time after production of the ^{99m}Tc isotope do radiologists have to examine a patient if at least 25 % of the original activity is required to get useful exposures?

As the half life is 6.0 hours, the activity will be reduced to 50 % of its original value after 6.0 hours.

After a further 6.0 hours, it will be reduced by another 50 % and so will be 25% of its original value. Therefore 2 half lives are required: 12 hours.

Alternatively, the activity decreases with time according to the equation:

$$\ln\left(\frac{A_0}{A_t}\right) = kt.$$

If the activity has decreased to 25 %, $\frac{A_0}{A_t} = \frac{100}{25} = 4$. As $t_{1/2} = 6.0$ hours, the activity coefficient = $\ln 2 / t_{1/2}$. Therefore:

$$\ln 4 = \left(\frac{\ln 2}{6.0 \text{ hours}}\right) \times t \text{ so } t = 12 \text{ hours}$$

Answer: 12 hours

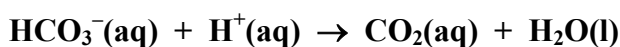
- Both $\text{HCO}_3^-(\text{aq})$ and $\text{CO}_2(\text{aq})$ are present in human blood. How does their presence ensure that the pH of blood is maintained at ~ 7.2 , even if $\text{H}^+(\text{aq})$ or $\text{OH}^-(\text{aq})$ are produced by processes in the body?

4

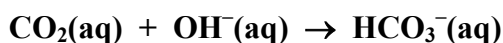
$\text{CO}_2(\text{aq})$ and $\text{HCO}_3^-(\text{aq})$ constitute a buffer system:



Excess H^+ is removed by:



Excess OH^- is removed by:



How does hyperventilation (very rapid breathing) interfere with this balance? What is the effect?

Hyperventilation removes CO_2 from the blood. This shifts the above buffer equilibrium to the left (Le Chatelier's principle), $[\text{H}^+(\text{aq})]$ decreases and the blood pH increases.

Marks
3

- Briefly explain the two factors necessary for a collision between two molecules to result in a reaction.

The molecules need to be orientated correctly and they need to have energy \geq the activation energy, E_a for a reaction to occur.

Briefly describe the relationship between the rate of a reaction and the activation energy for the reaction.

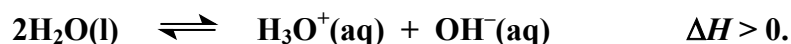
The relationships between the activation energy, E_a , the temperature, T , and the rate constant, k , are summarised by the Arrhenius equation, $k = Ae^{-E_a/RT}$.

This shows that the higher the activation energy, the lower the rate constant and the lower the reaction rate.

- The pH value of pure water at 25 °C is 7.00. How, if at all, does that value change when the temperature is changed to 37 °C (a person's body temperature)? Explain.

3

The auto-ionisation of water is an endothermic reaction



Increasing the temperature will push this reaction to the right (Le Chatelier's principle), so the $[\text{H}_3\text{O}^+(\text{aq})]$ will increase and the pH will therefore *decrease*.

Is pure water at 37 °C acidic, basic or neutral? Circle your choice.

acidic

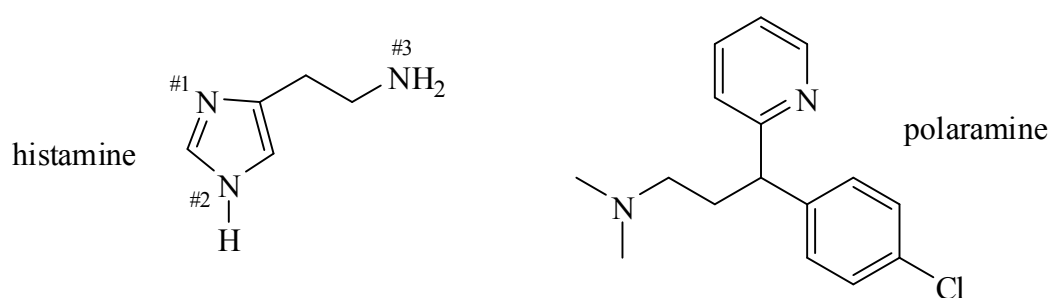
basic

neutral

(Pure water is neutral as $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$. This is the criterion for a neutral solution NOT pH = 7.)

Marks
6

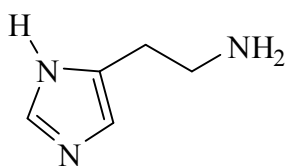
- The structures of histamine and polaramine are shown below.



Indicate the hybridisation and geometry of bonds around each of the nitrogen atoms in histamine.

	Hybridisation	Geometry of bonds
N #1:	sp^2	bent
N #2:	sp^2	trigonal planar
N #3:	sp^3	trigonal pyramidal

Draw a tautomer of histamine.



In histamine, only one of the nitrogen atoms in the ring is easily protonated (basic). Indicate which it is and explain why.

N#1 is basic. It has a lone pair directed away from the ring that is *not* involved in the π bonding of the aromatic ring. The lone pair can be used to accept a proton.

The "lone pair" on N#2 is part of the aromatic system.

Marks
3

The release of histamine in the body triggers nasal secretions and constriction of airways. Polaramine is one of many anti-histamine compounds used to treat allergies. Explain what structural features of polaramine might make it a suitable anti-histamine agent.

Polaramine has a basic aromatic N and an aliphatic N separated by 5 bonds, as does histamine.

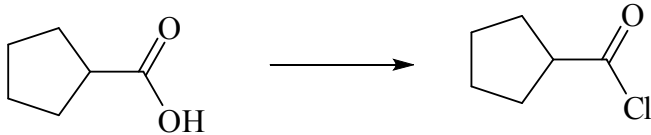
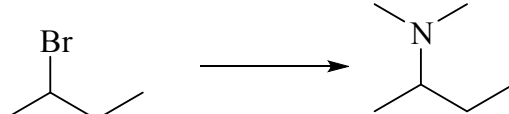
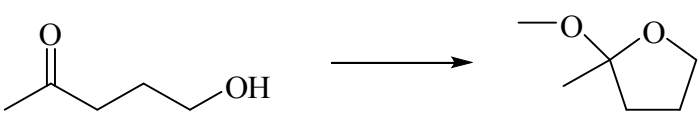
It is therefore likely that it will compete with histamine for the binding sites of certain enzymes in the body and thus block the effects of histamine.

(+)-2-[*p*-Chloro- α -[2-(dimethylamino)ethyl]benzyl]pyridine is another name for polaramine. What does the (+) in this name mean?

The molecule is chiral and rotates plane polarised light in a clockwise direction.

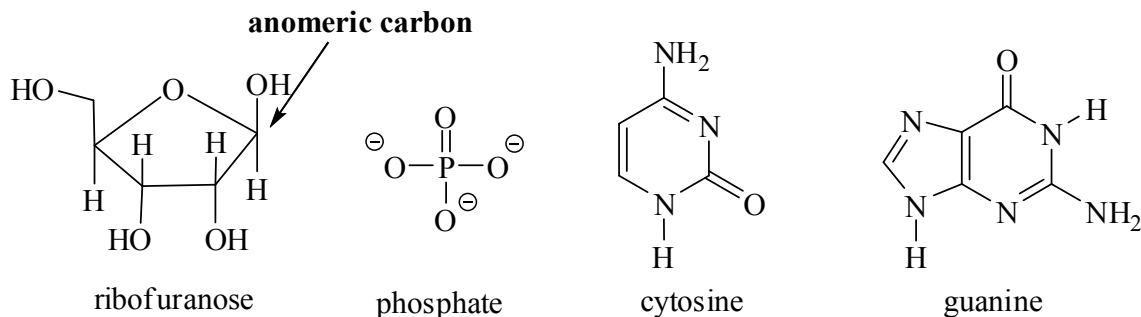
- Indicate the reagents used in the laboratory to effect the following transformations.

3

Reaction	Reagent
	SOCl ₂
	NaN(CH ₃) ₂ or (i) HN(CH ₃) ₂ (ii) OH ⁻
	excess CH ₃ OH / H ⁺ catalyst / heat

Marks
8

- The following species represent some of the building blocks of RNA.



Is the sugar depicted the α - or the β - form? Circle the one correct answer.

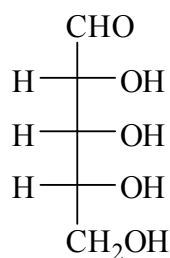
α	β
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Is the sugar depicted a reducing sugar or a non-reducing sugar? Circle the one correct answer.

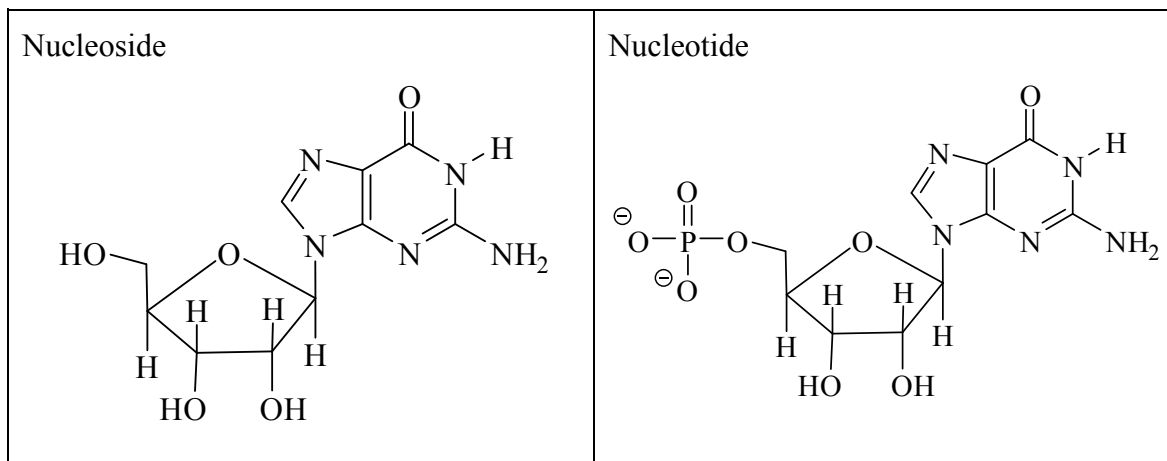
<u>reducing</u>	non-reducing
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Indicate on the above structure the 'anomeric' carbon atom that gives rise to the α or the β form.

Draw the Fischer projection of D-ribose.

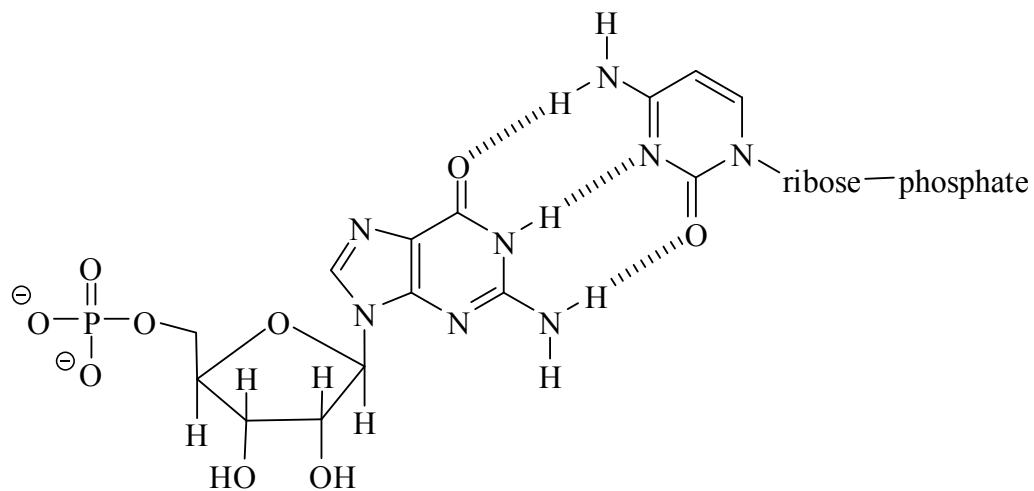


Using a selection of the species given, draw a nucleoside and a nucleotide.



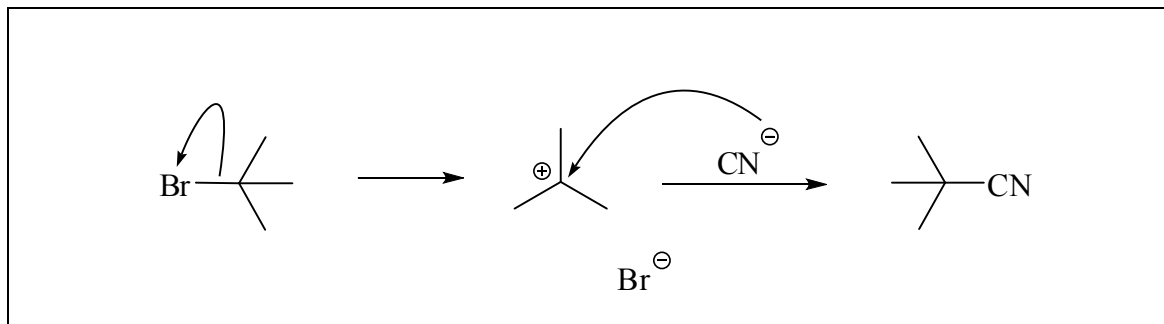
ANSWER CONTINUES ON THE NEXT PAGE

Indicate the likely hydrogen-bonding interactions between complementary strands of RNA containing cytosine and guanine.



Marks
1

- Add curly arrows to complete the following mechanism.

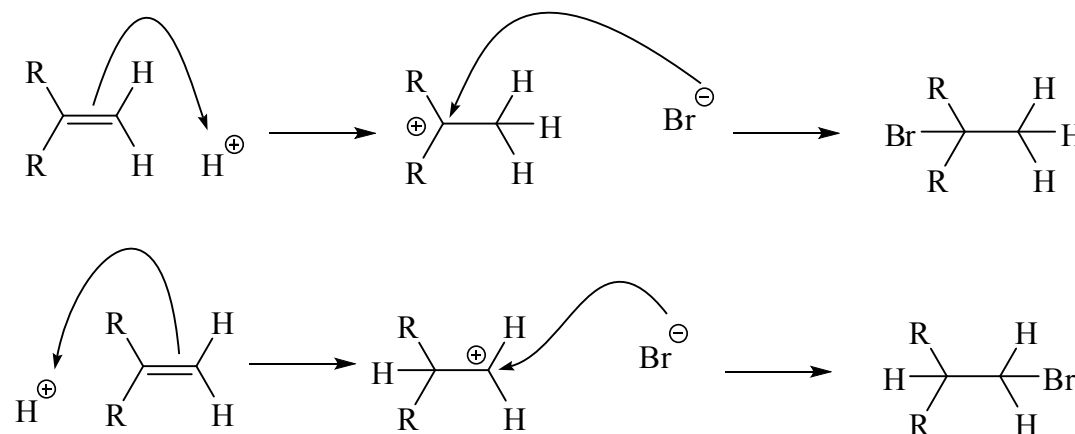

2

- Briefly explain Markovnikov's Rule in terms of the mechanism of electrophilic addition; *i.e.* why does Markovnikov's Rule work?

When HX adds across the double bond of an unsymmetrical alkene, the H goes to the carbon that already has the greater number of H's attached.

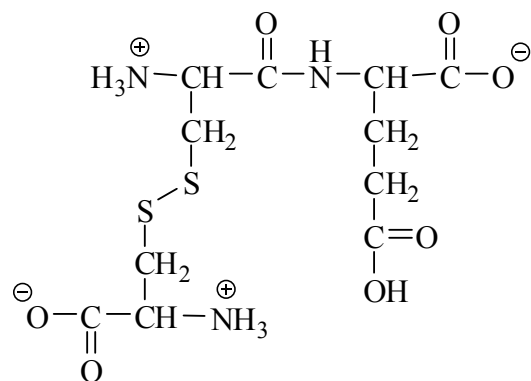
This occurs because the relative stabilities of the intermediate carbocations that can form in this reaction have the following order: tertiary > secondary > primary > CH₃⁺.

For example:



The tertiary carbocation produced in the top reaction is more stable than the primary carbocation produced in the bottom reaction, so the major pathway is the top reaction.

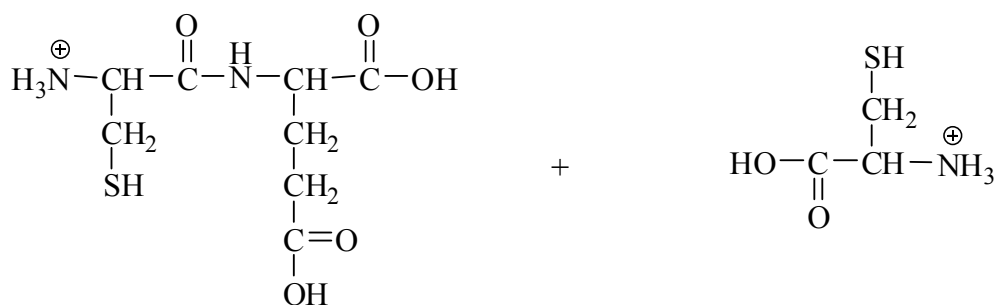
- A peptide has the following structure.



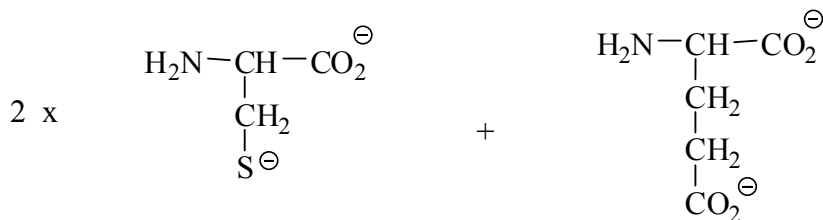
Would you expect this peptide to be soluble in water? Explain your answer.

Yes. It has a number of charged groups that will be solvated by water molecules due to ion-dipole interactions.

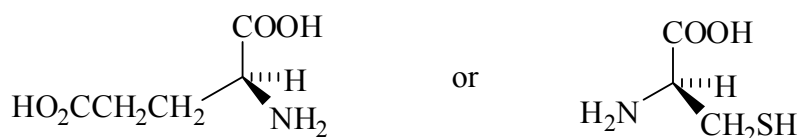
Give the products formed after treatment of the peptide with Zn/H^+ .



These products are then heated with excess aqueous OH^- . Draw the constitutional formulas of the different amino acids formed. Ensure you represent the amino acids in the correct charge state for the conditions.



Choose one of the amino acids produced on hydrolysis and draw the (S) configuration.



- Indicate the major organic product(s) in the following reactions.

