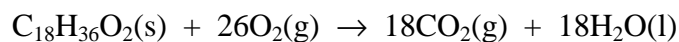


<ul style="list-style-type: none">Explain what is meant by hybridisation of atomic orbitals.	Marks 1
<p>The mathematical combining of atomic orbitals to produce equivalent orbitals which point in the direction of the bonds and lone pairs.</p> <p>There is no energy gain in this process, but the overlap of the hybridised orbitals to form bonds results in a lower energy situation because of reduced repulsion of the electron pairs.</p>	
<ul style="list-style-type: none">Carbon has atomic number $Z = 6$. What is the ground state electron configuration for an atom of carbon?	5
$1s^2 2s^2 2p^2$	
What compound would you expect to form between a carbon atom with that electron configuration and hydrogen, <i>i.e.</i> what is the value of x in the formula CH_x ? Explain.	
<p>CH_2 <i>i.e.</i> $x = 2$.</p> <p>The bonds would form using the unpaired electrons in the p orbitals. These orbitals would overlap with the $1s$ orbitals of the H atoms.</p> <p>As there are only 2 unpaired electrons, only 2 bonds would form.</p>	
What shape would that molecule have? Explain.	
<p>The molecule would be bent with approx 90° bond angle as the p orbitals are at right angles to each other.</p>	
What molecule forms instead? Explain.	
<p>CH_4 - methane.</p> <p>The s orbital and the three $2p$ orbitals of carbon undergo hybridisation to form 4 equivalent sp^3 orbitals that point to the corners of a tetrahedron.</p> <p>Overlap of these orbitals with the $1s$ orbital of each H atom results in the formation of the tetrahedral molecule, methane.</p>	

- Stearic acid, $C_{18}H_{36}O_2$, is a fatty acid common in animal fats and vegetable oils and is a valuable energy source for mammals. The net reaction for its metabolism in humans is:



Calculate ΔH° for this reaction given the following heats of formation.

Compound	$C_{18}H_{36}O_2(s)$	$CO_2(g)$	$H_2O(l)$
$\Delta_f H^\circ / \text{kJ mol}^{-1}$	-948	-393	-285

Using $\Delta_{\text{rxn}} H^\circ = \sum m \Delta_f H^\circ(\text{products}) - \sum n \Delta_f H^\circ(\text{reactants})$, the enthalpy of the combustion of the reaction with excess O_2 is:

$$\begin{aligned} \Delta H^\circ &= (18\Delta_f H^\circ(CO_2(g)) + 18\Delta_f H^\circ(H_2O(l)) - (\Delta_f H^\circ(C_{18}H_{36}O_2(s))) \\ &= [(18 \times -393 + 18 \times -285) - (-948)] \text{ kJ mol}^{-1} = -11300 \text{ kJ mol}^{-1} \end{aligned}$$

As $O_2(g)$ is an element in its standard state, its $\Delta_f H^\circ$ is zero.

$$\Delta H^\circ = -11300 \text{ kJ mol}^{-1}$$

If the combustion of stearic acid is carried out in air, water is produced as a vapour. Calculate the ΔH° for the combustion of stearic acid in air given that:



The reaction now needs vapourisation of $18H_2O(l)$ which requires *input* of $(18 \times 44) \text{ kJ mol}^{-1}$. The combustion enthalpy is reduced to:

$$\Delta H^\circ = (-11300 \text{ kJ mol}^{-1}) + (18 \times 44 \text{ kJ mol}^{-1}) = -10500 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ = -10500 \text{ kJ mol}^{-1}$$

Will ΔS be different for the two oxidation reactions? If so, how will it differ and why?

ΔS will be greater for the air-oxidation as the product $H_2O(g)$ has a much greater entropy than the product $H_2O(l)$ - gases are much more disordered than liquids.

Calculate the mass of carbon dioxide produced by the complete oxidation of 1.00 g of stearic acid.

The molar mass of stearic acid, $C_{18}H_{36}O_2$, is:

$$\begin{aligned} \text{molar mass} &= (18 \times 12.01 \text{ (C)}) + (36 \times 1.008 \text{ (H)}) + (2 \times 16.00 \text{ (O)}) \text{ g mol}^{-1} \\ &= 284.47 \text{ g mol}^{-1} \end{aligned}$$

ANSWER CONTINUES ON THE NEXT PAGE

The number of moles in 1.00 g is therefore:

$$\begin{aligned}\text{number of moles} &= \text{mass} / \text{molar mass} \\ &= (1.00 \text{ g}) / (284.47 \text{ g mol}^{-1}) = 0.00353 \text{ mol}\end{aligned}$$

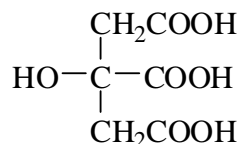
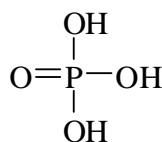
The chemical equation shows that 18 mol of CO₂(g) are produced from every 1 mol of C₁₈H₃₆O₂(s). The number of moles of CO₂(g) produced is therefore (18 × 0.00353 mol) = 0.06328 mol.

The molar mass of CO₂ is (12.01 (C) + 2 × 16.00 (O)) g mol⁻¹ = 44.01 g mol⁻¹. The mass of CO₂ produced is therefore:

$$\begin{aligned}\text{mass of CO}_2 &= \text{number of moles} \times \text{molar mass} \\ &= (0.06328 \text{ mol}) \times (44.01 \text{ g mol}^{-1}) = 2.78 \text{ g}\end{aligned}$$

Answer: **2.78 g**

- Consider the two triprotic acids, phosphoric acid and citric acid.



Acid	Formula	K_{a1}	K_{a2}	K_{a3}
phosphoric	H_3PO_4	7.1×10^{-3}	6.3×10^{-8}	4.5×10^{-13}
citric	$\text{C}_6\text{H}_8\text{O}_7$	7.1×10^{-4}	1.7×10^{-5}	6.4×10^{-6}

Explain why $K_{a1} > K_{a2} > K_{a3}$ for both acids.

It is more difficult to remove a proton from a negatively charged species, so $K_{a1} > K_{a2} > K_{a3}$ for all acids. *i.e.* K_{a1} , K_{a2} and K_{a3} correspond to removal of H^+ from H_3PO_4 , H_2PO_4^- and HPO_4^{2-} respectively. This process gets harder and harder because a positively charged proton is having to be removed from a negatively charged molecule.

For phosphoric acid, the K_a values differ by about 5 orders of magnitude while for citric acid there is a much smaller difference. Explain.

The number of resonance structures for the various conjugate bases are:

**2 for H_2PO_4^- ; 3 for HPO_4^{2-} ; and 4 for PO_4^{3-}
2 for $\text{C}_6\text{H}_7\text{O}_7^-$; 4 for $\text{C}_6\text{H}_6\text{O}_7^{2-}$; and 8 for $\text{C}_6\text{H}_5\text{O}_7^{3-}$**

The conjugate bases for citric acid are more stable (because they have greater resonance stabilisation) so the corresponding acids are all stronger.

Alternatively, the increasing negative charges in the conjugate bases are being formed in different parts of the molecule in the case of citric acid, whereas they are all very close to each other in phosphoric acid. Again, the formation of the conjugate base series of citric acid is therefore easier and the acids are therefore stronger.

Marks
4

- Henry's law relates the solubility of a gas to its pressure. *i.e.* $c = kp$

The Henry's law constant for $N_2(g)$ at 298 K is $6.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}$. A diver descends to a depth where the pressure is 5 atm. If the diver's body contains about 5 L of blood, calculate the maximum amount of nitrogen gas dissolved in the diver's blood at 1 atm and at 5 atm. (Assume solubility of nitrogen in water and blood to be the same.)

At the surface, $p = 1 \text{ atm}$ and so:

$$c = kp = (6.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}) \times (1 \text{ atm}) = 6.8 \times 10^{-4} \text{ mol L}^{-1}$$

Hence, the amount of N_2 in 5 L is

$$\begin{aligned} \text{number of moles} &= \text{concentration} \times \text{volume} \\ &= (6.8 \times 10^{-4} \text{ mol L}^{-1}) \times (5 \text{ L}) = 0.003 \text{ mol} \end{aligned}$$

When $p = 5 \text{ atm}$ and so:

$$c = (6.8 \times 10^{-4} \text{ mol L}^{-1} \text{ atm}^{-1}) \times (5 \text{ atm}) = 3.4 \times 10^{-3} \text{ mol L}^{-1}$$

Hence, the amount of N_2 in 5 L is

$$\text{number of moles} = (3.4 \times 10^{-3} \text{ mol L}^{-1}) \times (5 \text{ L}) = 0.02 \text{ mol}$$

1 atm: $3 \times 10^{-3} \text{ mol}$

5 atm: $2 \times 10^{-2} \text{ mol}$

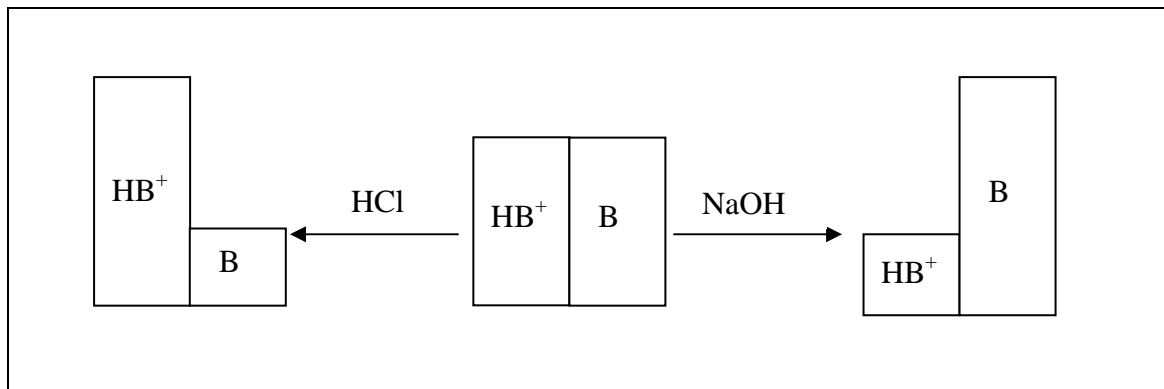
If all the gas dissolved at 5 atm were suddenly released, what volume would it occupy at 1 atm and 298 K?

Using the ideal gas law, $PV = nRT$, with $n = 2 \times 10^{-2} \text{ mol}$:

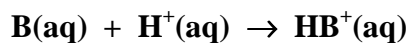
$$V = nRT / P = (2 \times 10^{-2} \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K}) / (1 \text{ atm}) = 0.4 \text{ L}$$

Answer: **0.4 L**

- A buffer system with a weak base B and its conjugate acid HB^+ is shown in the diagram below with equal concentrations. Complete the diagram by showing the relative concentrations after the addition of some HCl or NaOH.



Write down the balanced net ionic equations for both these reactions.



Calculate the pH of a buffer if it contains 0.200 mol of NaNO_2 and 0.300 mol of HNO_2 in 1.00 L of water. The $\text{p}K_a$ of HNO_2 is 3.15.

The concentrations of acid (HNO_2) and base (NO_2^-) are:

$$\begin{aligned} \text{concentration of acid} &= \text{number of moles} / \text{volume} \\ &= (0.300 \text{ mol} / 1.00 \text{ L}) = 0.300 \text{ mol L}^{-1} \end{aligned}$$

$$\text{concentration of base} = (0.200 \text{ mol} / 1.00 \text{ L}) = 0.200 \text{ mol L}^{-1}$$

The pH of this buffer can then be calculated using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log \frac{0.200}{0.300} = 2.97$$

$$\text{pH} = 2.97$$

What is the pH if (a) 0.05 mol of $\text{HCl}(\text{g})$ and (b) 0.25 mol of $\text{HCl}(\text{g})$ is added?

HCl will react with the NO_2^- to form HNO_2 .

(a) 0.05 mol of $\text{HCl}(\text{g})$ will react with 0.05 mol of the NO_2^- present to form an additional 0.05 mol of HNO_2 . The amount of NO_2^- will decrease by 0.05 mol:

$$\text{concentration of acid} = (0.35 \text{ mol} / 1.00 \text{ L}) = 0.35 \text{ mol L}^{-1}$$

$$\text{concentration of base} = (0.15 \text{ mol} / 1.00 \text{ L}) = 0.15 \text{ mol L}^{-1}$$

ANSWER CONTINUES ON THE NEXT PAGE

Hence:

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{base}]}{[\text{acid}]} = 3.15 + \log \frac{0.15}{0.35} = 2.78$$

(b) 0.25 mol of HCl(g) will react *all* of the NO₂⁻. As there is only 0.200 mol of NO₂⁻ present, 0.05 mol of HCl will remain unreacted. As HCl is a strong acid, this will completely ionize to give [H⁺(aq)] = 0.05 mol L⁻¹. Hence:

$$\text{pH} = -\log_{10}[\text{H}^{+}(\text{aq})] = -\log_{10}(0.05) = 1.30$$

(a) pH = 2.78

(b) pH = 1.30

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 35 % of the original activity is required to get useful exposures?

If the half life is 6.0 hours, the activity coefficient, λ , is:

$$\lambda = \ln 2 / t_{1/2} = \ln 2 / (6.0 \text{ hours}) = 0.116 \text{ hours}^{-1}$$

As the activity is proportional to the number of nuclei present, the activity at a time t is related to the original activity by:

$$\ln(A_0 / A_t) = \lambda t$$

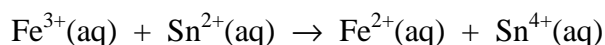
If $A_t = 0.35 \times A_0$ then:

$$\ln(1/0.35) = (0.116 \text{ hours}^{-1})t$$

$$t = 9.1 \text{ hours}$$

Answer: **9.1 hours**

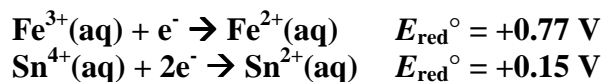
- Consider the following *unbalanced* reaction at 25 °C:



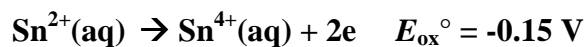
Calculate the standard cell potential.

3

The two half cells and the standard reduction potentials are:



As the $\text{Sn}^{4+} / \text{Sn}^{2+}$ cell has the least positive reduction potential, it is reversed and becomes the oxidation half cell:



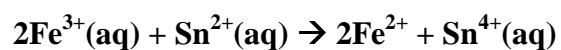
Hence, the standard cell potential is:

$$E^\circ = (+0.77 \text{ V}) + (-0.15 \text{ V}) = +0.62 \text{ V}$$

Answer: **+0.62 V**

Calculate the equilibrium constant, K , for the reaction at 25 °C.

Using the half cell reactions above, the balanced equation is:



It involves the transfer of 2 electrons. The equilibrium constant for this 2 electron reaction is therefore given by:

$$E^{\circ} = (RT/nF)\ln K$$

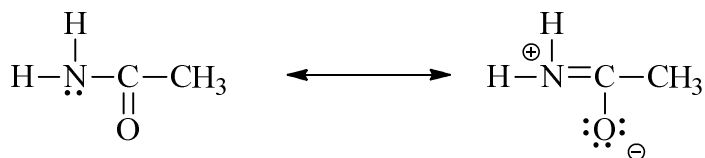
$$\ln K = E^{\circ} \times (nF / RT) = (0.62) \times (2 \times 96485) / (8.314 \times 298) = 48.3$$

$$K = 9.4 \times 10^{20}$$

Answer: 9.4×10^{20}

Marks
2

- The observed geometry of the N atom in H_2NCOCH_3 is trigonal planar. Draw a Lewis structure consistent with this observation and explain this observation.



The canonical form on the right is a significant contributor to the resonance stabilised molecule. The N atom in this structure is sp^2 hybridised with trigonal planar geometry.

This hybridisation means that the 'lone pair' is in a p -orbital on N and is able to become involved in π bonding with the $\text{C}=\text{O}$. This resonance acts to strengthen the N-C bond.

- The reaction $2\text{A} + \text{B} \rightarrow \text{C} + 3\text{D}$ has reached equilibrium. What is the expression for the equilibrium constant, K_c ?

2

$$K_c = \frac{[\text{C}][\text{D}]^3}{[\text{A}]^2[\text{B}]}$$

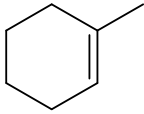
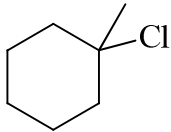
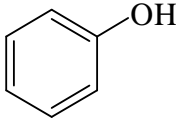
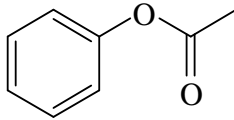
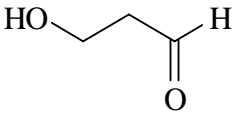
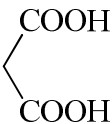
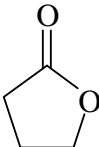
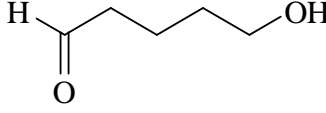
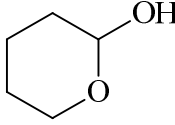
Explain how the equilibrium constant, K_c , changes when more C is added to the reaction mixture.

K_c is the equilibrium constant: it does not change.

K_c changes only with temperature.

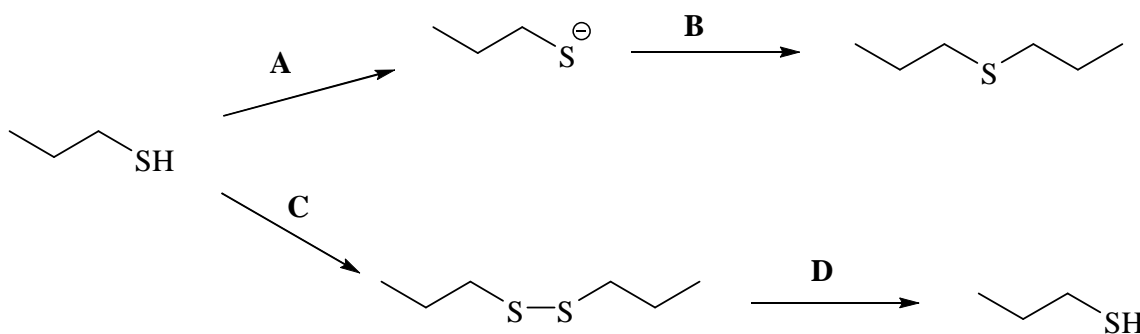
Marks
6

- Complete the following table.

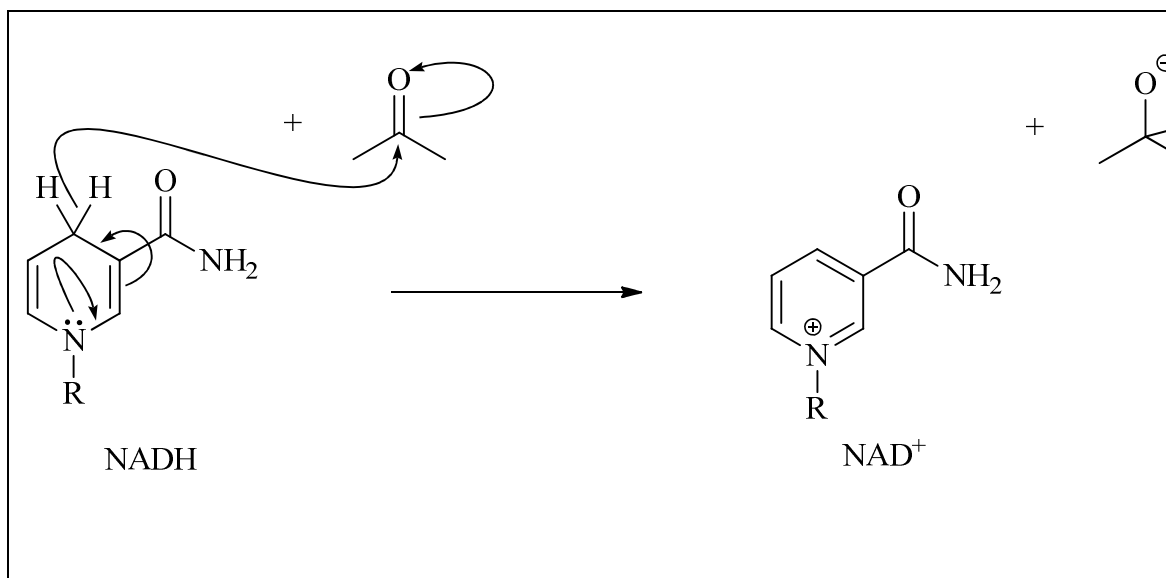
STARTING MATERIAL	REAGENTS/ CONDITIONS	CONSTITUTIONAL FORMULA(S) OF MAJOR ORGANIC PRODUCT(S)
	HCl / CCl ₄ solvent	
	CH ₃ COCl	
CH ₃ CH ₂ CH(Br)CH ₂ CH ₃	N(CH ₃) ₃	CH ₃ CH ₂ CH [⊖] (Br)CH ₂ CH ₃ ⊕N(CH ₃) ₃
	Cr ₂ O ₇ ^{2⊖} / H [⊕]	
	3 M NaOH / heat	HO-CH ₂ -CH ₂ -CH ₂ -CO ₂ [⊖]
	catalytic H [⊕]	

Marks
4

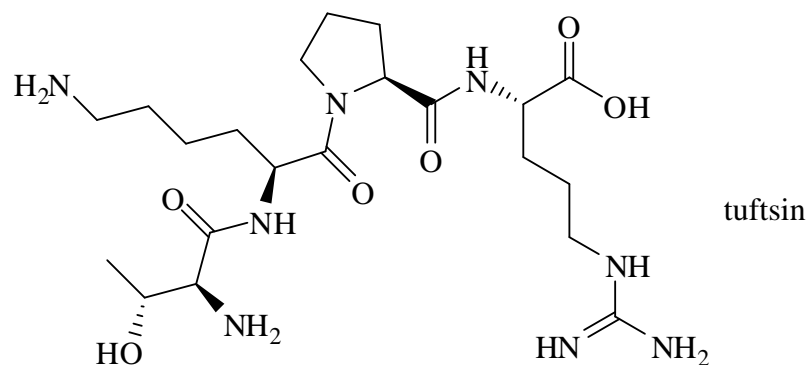
- Indicate the reagents used in the laboratory to undertake the following transformations.


A: **NaOH**
B: **CH₃CH₂CH₂Br**
C: **H₂O₂**
D: **Zn / H⁺**
3

- NADH is the most important reducing agent in Nature. It is itself oxidised to NAD⁺. Complete the scheme below by:
 - drawing in curly arrows to show the movement of electrons during the first step in the reduction of acetone with NADH, and
 - drawing the structure of NAD⁺.



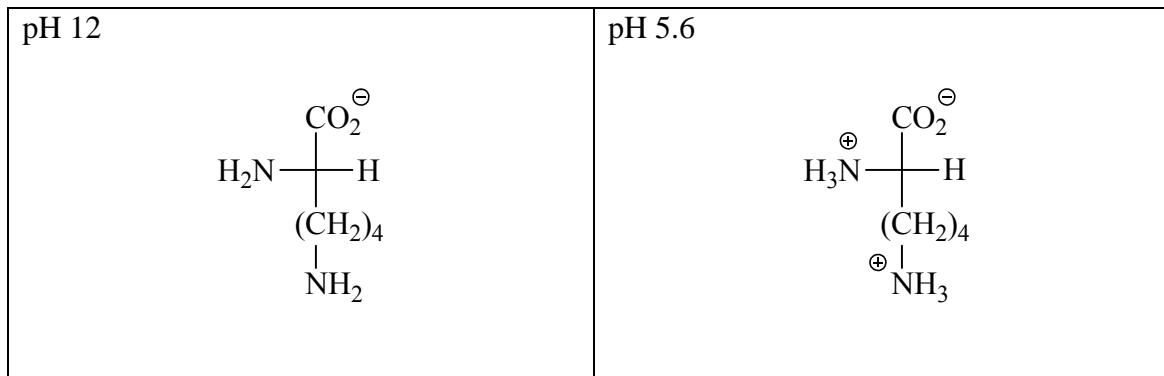
- Tuftsins is a tetrapeptide (Thr-Lys-Pro-Arg) produced by enzymatic cleavage of the Fc-domain of the heavy chain of immunoglobulin G. It is mainly produced in the spleen and its activity is related primarily to immune system function.



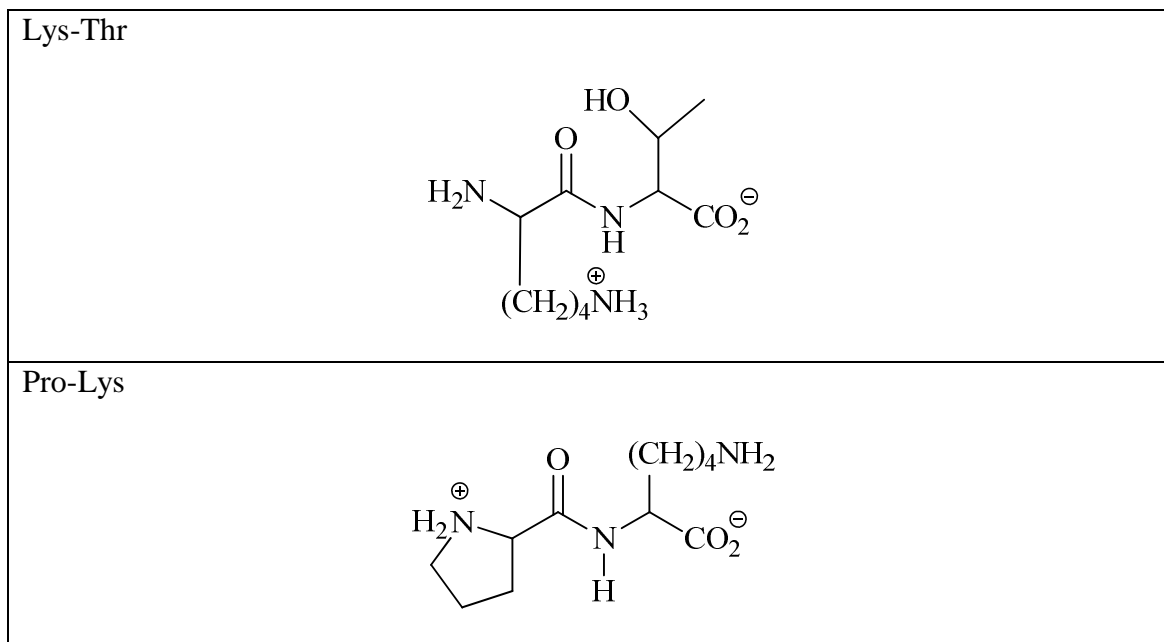
Draw the Fischer projections of the four L-amino acids that result from the acid hydrolysis of tuftsins.

Marks
4

What is the major species present when lysine (Lys) is dissolved in water at pH 12 and pH 5.6. The pK_a values of lysine are 1.82 (α -COOH), 8.95 (α -NH₃[⊕]) and 10.53 (side chain).



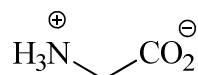
Give the constitutional formulas for the following dipeptides in their zwitterionic states. The pK_a values of proline are 1.95 and 10.64.



2

- Glycine, NH₂CH₂COOH, is the simplest of the naturally occurring amino acids. It has a melting point of 238 °C, while CH₃CH₂COOH has a melting point of -21 °C. Give one reason for this difference.

Glycine is an amino acid and has the following zwitterionic structure.



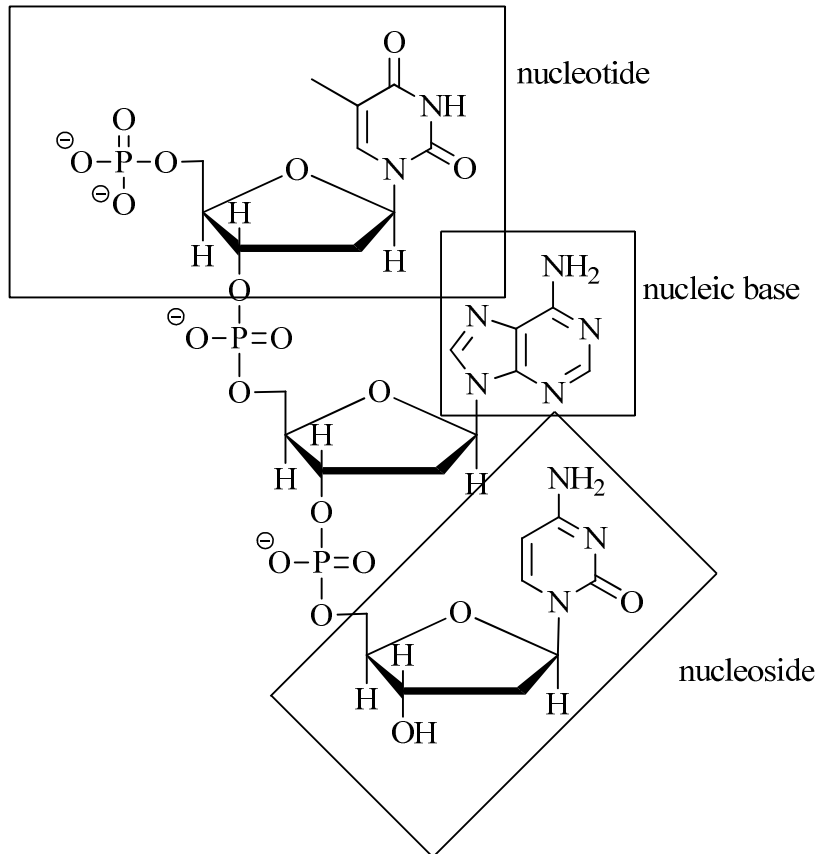
Propionic acid has strong hydrogen bonds, giving it a relatively high m.p. However, glycine has very strong ionic bonds between the NH₃⁺ and CO₂⁻ groups giving it very high melting point.

- Is the following structure a fragment of DNA or RNA? Give two reasons.

Marks
5

It is a DNA fragment:

- The sugar is deoxyribose (RNA has ribose as the sugar).**
- The topmost nucleic base is thymine (RNA utilises uracil instead of thymine).**



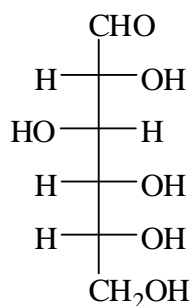
Clearly identify on the above structure one example of each of the following subunits.

nucleic base – **see above**

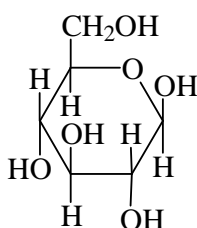
nucleoside – **see above**

nucleotide - **see above**

- The open chain form of D-glucose has the structure shown.

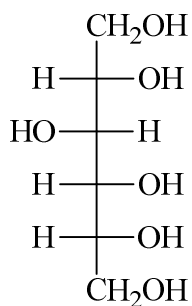


Draw the Haworth projection of β -D-glucopyranose.

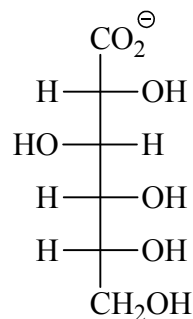


Draw the major organic product of the reaction of D-glucose with the following reagents.

1. NaBH_4 2. $\text{H}^+ / \text{H}_2\text{O}$



$[\text{Ag}(\text{NH}_3)_2]^+ / \text{OH}^-$



Would you expect D-glucose to be water soluble? Why?

Yes - it contains a large number of alcohol groups which will form hydrogen bonds with water.