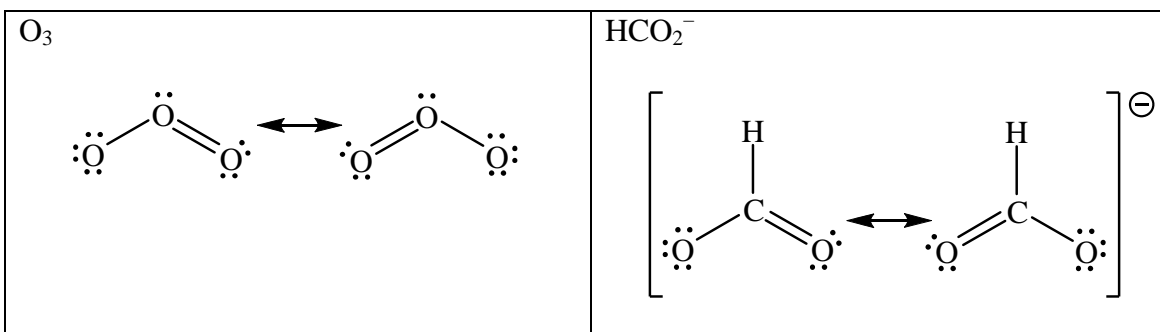


- Draw Lewis structures of ozone, O_3 , and the formate anion, HCO_2^- , including resonance hybrids where appropriate.

Marks
3



- Calculate the osmotic pressure of a solution of 1.0 g of glucose ($C_6H_{12}O_6$) in 1500 mL of water at 37 °C.

4

The osmotic pressure $\pi = cRT$ where c is the concentration.

The molar mass of glucose is:

$$(6 \times 12.01 \text{ (C)}) + (12 \times 1.008 \text{ (H)}) + (6 \times 16.00 \text{ (O)}) = 180.156$$

$$1.0 \text{ g of glucose corresponds to } \frac{\text{mass}}{\text{molar mass}} = \frac{1.0}{180.156} = 0.0056 \text{ mol}$$

The concentration when this amount is dissolved in 1500 mL = 1.5 L is:

$$c = \frac{\text{number of moles}}{\text{volume}} = \frac{0.0056}{1.5} = 0.0037 \text{ M}$$

$$\text{Hence, } \pi = cRT = (0.0037) \times (0.08206) \times (273 + 37) = 0.094 \text{ atm.}$$

Answer: **0.094 atm**

Explain why a drip for intravenous administration of fluids is made of a solution of NaCl at a particular concentration rather than pure water.

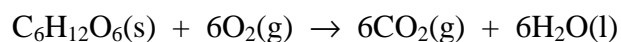
Blood plasma is isotonic with cells (same osmotic pressure). Using saline drip of same osmotic pressure as blood prevents haemolysis or crenation of red blood cells.

- Write down the ground state electron configuration of the iron atom.



1

- The balanced equation for the complete oxidation of glucose to carbon dioxide and water is given below.



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

The molar mass of glucose is:

$$(6 \times 12.01 (\text{C})) + (12 \times 1.008 (\text{H})) + (6 \times 16.00 (\text{O})) = 180.156$$

$$1.0 \text{ g of glucose corresponds to } \frac{\text{mass}}{\text{molar mass}} = \frac{1.00}{180.156} = 0.00555 \text{ mol}$$

From the chemical equation, oxidation of 1 mol of glucose leads 6 mol of CO₂. Hence the number of moles of CO₂ produced is 6 × 0.00555 = 0.0333 mol.

The molar mass of CO₂ is (12.01 (C)) + (2 × 16.00 (O)) = 44.01

Therefore, the number of mass of CO₂ produced is:

$$\text{mass} = \text{number of moles} \times \text{molar mass} = 0.0333 \times 44.01 = 1.47 \text{ g}$$

Answer: **1.47 g**

Calculate the volume of this mass of carbon dioxide at 0.50 atm pressure and 37 °C.

The ideal gas law gives PV = nRT, hence:

$$V = \frac{nRT}{P} = \frac{(0.0333) \times (0.08206) \times (273+37)}{(0.50)} = 1.69 \text{ L}$$

Answer: **1.69 L**

- Explain, in terms of chemical bonding and intermolecular forces, the following trend in melting points: CH₄ < I₂ < NaCl < silica (SiO₂)

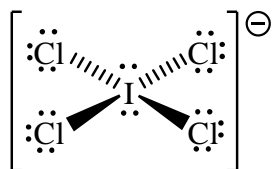
There are only dispersion forces between the molecules in CH₄ and I₂. The I atom is a large, many-electron atom so its electron cloud is more easily polarised than the C or H in CH₄ and therefore I₂ has stronger dispersion forces and the higher melting point. NaCl is an ionic compound with strong coulombic attraction between the Na⁺ ions and the Cl⁻ ions packed together in the solid. Silica is a covalent network solid. Melting it requires breaking of the very strong covalent Si–O bonds, so it has the highest melting point.

**Marks
3**

3

- Draw a Lewis structure and thus determine the geometry of the ICl_4^- ion. (The I is the central atom.)

Marks
2



There are two lone pairs and 4 bonds around the iodine: the geometry is based on an octahedron with the lone pairs located opposite to one another to minimise repulsion between them. The geometry of the actual molecule is therefore square planar.

- Explain briefly, in terms of intermolecular forces, why an analogue of DNA could not be made with phosphorus atoms replacing some nitrogen atoms, while still retaining a double-helical structure.

3

The double helical structure is held together by hydrogen bonding between the cytosine and guanine ($\text{C}\equiv\text{G}$) and the adenine and thymine ($\text{A}=\text{T}$) base pairs.

No H-bonding would occur if the electronegative N atoms in these bases were replaced with P atoms.

- The solubility of nitrogen in water at 25 °C and 1.0 atm is 0.018 g L^{-1} . What is its solubility at 0.50 atm and 25 °C?

1

The equilibrium of interest is $\text{N}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{aq})$ with equilibrium constant:

$$K = \frac{[\text{N}_2(\text{aq})]}{[\text{N}_2(\text{g})]}$$

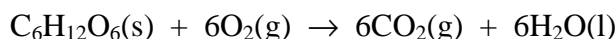
From the perfect gas law, $PV = nRT$ or concentration = $\frac{n}{V} = \frac{P}{RT}$.

As a result, doubling the pressure doubles the concentration of $\text{N}_2(\text{g})$. As the temperature is unchanged, the equilibrium constant does not change and so $[\text{N}_2(\text{aq})]$ must halve to ensure that K_p is constant.

The solubility is thus halved to $\frac{1}{2} \times 0.018 = 0.009 \text{ g L}^{-1}$

Answer: 0.009 g L^{-1}

- Glucose is a common food source. The net reaction for its metabolism in humans is:



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

$$\Delta H^\circ_f(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) = -1274 \text{ kJ mol}^{-1}, \quad \Delta H^\circ_f(\text{CO}_2(\text{g})) = -393 \text{ kJ mol}^{-1} \quad \text{and} \\ \Delta H^\circ_f(\text{H}_2\text{O}(\text{l})) = -285 \text{ kJ mol}^{-1}$$

Using $\Delta_{\text{rxn}}H^\circ = \sum m\Delta_fH^\circ(\text{products}) - \sum n\Delta_fH^\circ(\text{reactants})$:

$$\Delta_{\text{rxn}}H^\circ = [6 \times \Delta_fH^\circ(\text{CO}_2(\text{g})) + 6 \times \Delta_fH^\circ(\text{H}_2\text{O}(\text{l}))] - [\Delta_fH^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))] \\ = [(6 \times -393) + (6 \times -285)] - [-1274] = -2794 \text{ kJ mol}^{-1}$$

(Note that $\Delta_fH^\circ(\text{O}_2(\text{g})) = 0$ as it is an element in its standard state).

Answer: **-2794 kJ mol⁻¹**

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



As vaporising liquid water requires energy (+44 kJ mol⁻¹), the combustion enthalpy is reduced. Six moles of H₂O are produced in the combustion so the enthalpy of combustion is reduced to:

$$-2794 + (6 \times +44) = -2530 \text{ kJ mol}^{-1}$$

Answer: **-2530 kJ mol⁻¹**

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

As gaseous molecules have higher entropy than liquid phase molecules, oxidation to produce H₂O(g) will lead to a higher value for ΔS than oxidation to produce H₂O(l).

Marks
5

- Butyric acid, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$, is found in rancid butter and parmesan cheese. The $\text{p}K_a$ of butyric acid is 4.83.
(a) What is the pH of a 0.10 M water solution of butyric acid?

As $\text{p}K_a = -\log K_a = 4.83$, $K_a = 10^{-4.83}$. Denoting butyric acid as HA, the initial concentration of $[\text{HA}(\text{aq})] = 0.10 \text{ M}$. The reaction table is then:

	$[\text{HA}(\text{aq})]$	\rightleftharpoons	$[\text{H}^+(\text{aq})]$	$[\text{A}^-(\text{aq})]$
t = 0	0.10.		0	0
change	-x		+x	+x
equilibrium	$0.10 - x$		x	x

$$\text{Hence, } K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} = \frac{(x)(x)}{0.10-x} = \frac{x^2}{0.10-x}$$

As K_a is small, the amount of dissociation, x, is also small so $0.10 - x \sim 0.10$.

$$\text{Using this approximation, } K_a = \frac{x^2}{0.10} = 10^{-4.83} \text{ hence } x = 1.22 \times 10^{-3} \text{ M.}$$

$$\text{As } x = [\text{H}^+(\text{aq})], \text{ pH} = -\log[\text{H}^+(\text{aq})] = -\log(1.22 \times 10^{-3}) = 2.92$$

Answer: 2.92

- (b) Calculate the pH of the solution formed when 0.050 mol of NaOH(s) is added to 1.0 L of 0.10 M butyric acid.

As NaOH is a strong base, it will dissociate completely and each mole of OH^- will react with butyric acid to form one mole of $\text{A}^-(\text{aq})$.

1.0 L of 0.10 M HA contains 0.10 mol. After addition of 0.050 mol of OH^- , the number of moles of HA = $(0.10 - 0.050) = 0.05 \text{ mol}$ and the number of moles of $\text{A}^- = 0.050 \text{ mol}$.

As 1.0 L of solution is present, $[\text{HA}(\text{aq})] = 0.05 \text{ M}$ and $[\text{A}^-(\text{aq})] = 0.05 \text{ M}$. Substituting into the expression for K_a gives:

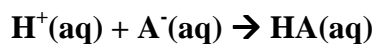
$$K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} = \frac{[\text{H}^+(\text{aq})] \times (0.05)}{(0.05)} = 10^{-4.83} \text{ so } [\text{H}^+(\text{aq})] = 1.5 \text{ M}$$

$$\text{Hence, pH} = -\log[\text{H}^+(\text{aq})] = 4.83$$

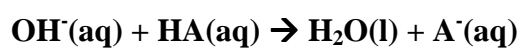
Answer: 4.83

(c) Using equations, comment on how the final solution in (b) will respond to additions of small amounts of acid or base in comparison to 1 L of water.

Solution (b) consists of a mixture of a weak acid and its conjugate base: it is a buffer system and will resist changes in pH. If acid is added, the system can respond by removing it using A^- :



If base is added, the system can respond by removing it using HA:



- Consider the reaction of $\text{H}_2(\text{g})$ with $\text{I}_2(\text{g})$ at 298 K to give $\text{HI}(\text{g})$.



If partial pressures of 0.20 atm of all three gases are mixed, in which direction will the reaction proceed?

$$\text{The reaction quotient } Q = \frac{(p_{\text{HI}})^2}{(p_{\text{H}_2})(p_{\text{I}_2})} = \frac{(0.20)^2}{(0.20)(0.20)} = 1.0$$

As $Q < K_p$, the reaction will proceed towards HI, to increase the partial pressure of HI and decrease the partial pressure of H_2 and I_2 , until $Q = K$.

Answer: **towards products**

Calculate ΔG° for this reaction at 298 K.

Using $\Delta G^\circ = -RT \ln K_p$:

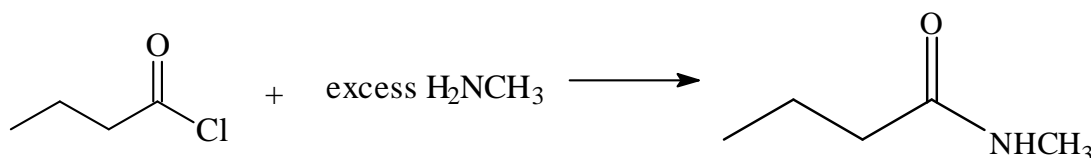
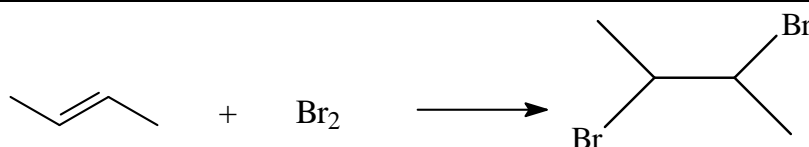
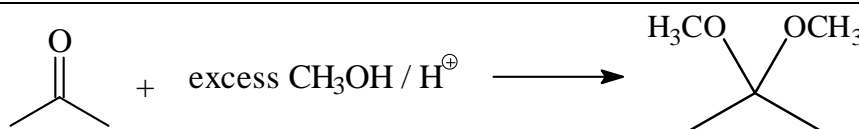
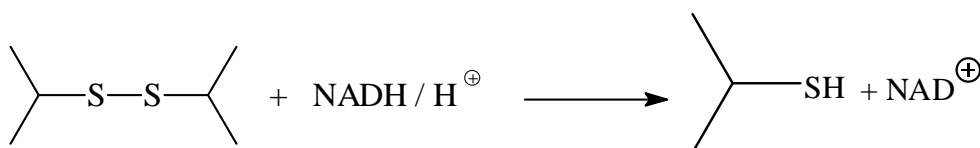
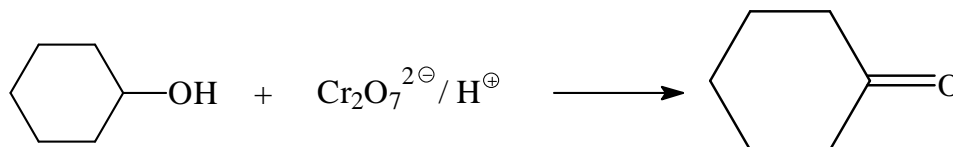
$$\Delta G^\circ = -(8.314) \times (298) \times \ln(2.24) = -2000 \text{ J mol}^{-1} = -2.00 \text{ kJ mol}^{-1}$$

Answer: **-2000 J mol⁻¹ = -2.00 kJ mol⁻¹**

Marks
3

- Draw the constitutional formula(s) of the major organic product(s) of the following reactions.

Marks
5

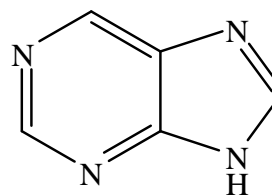
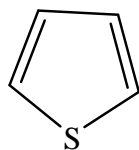
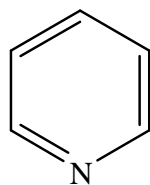


- What are the requirements for a molecule to be aromatic? Give one example of an aromatic heterocycle.

2

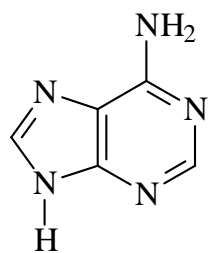
The molecule must be cyclic. The ring system must have a conjugated π bond system. The number of electrons in the π bond system must be $4n+2$ where n =integer. All atoms in the ring system must be sp^2 hybridised.

Examples of heterocyclic aromatic systems include:

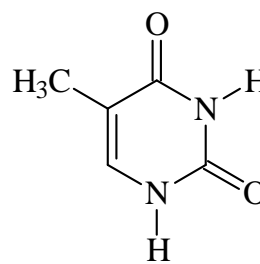


- Adenine and thymine have the structures shown below.

Marks
4

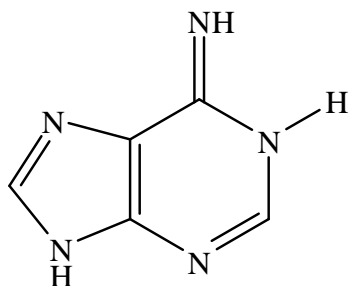


adenine



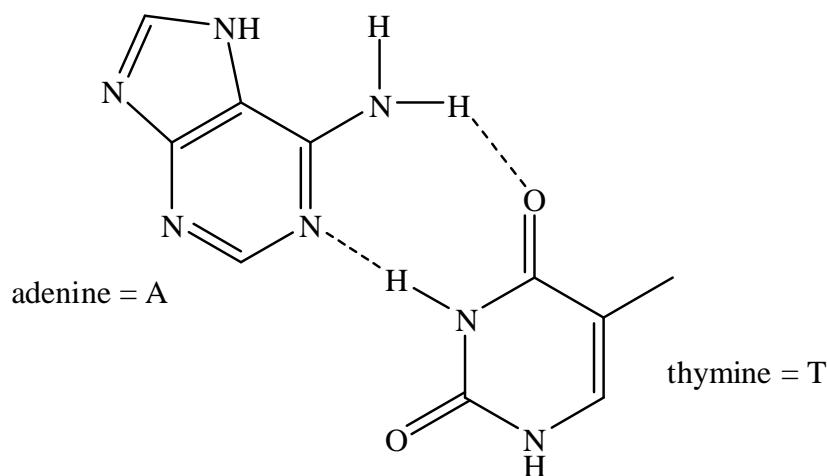
thymine

Draw a tautomer of the shown structure of adenine.

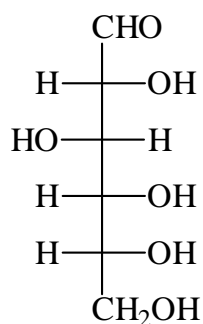


In DNA, adenine forms a “base pair” with thymine. Explain what is meant by “base pair” and indicate the point(s) of interaction between adenine and thymine.

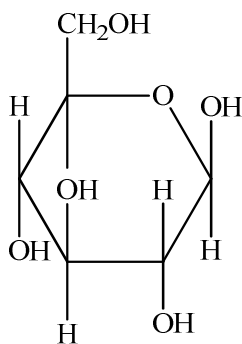
Four different bases are found in DNA chains. The two strands in the double helix are held together by 3 hydrogen bonds between guanine (G) and cytosine (C), and by 2 hydrogen bonds between adenine (A) and thymine (T). The complementary bases C and G are called a “base pair”. A and T are another “base pair”.



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

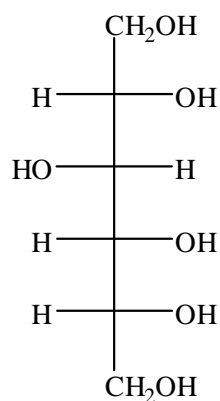


Draw the Haworth projection of β -D-glucopyranose.

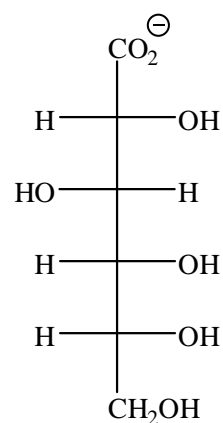


Draw the major organic product of the reaction of D-glucose with the following reagents.

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



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

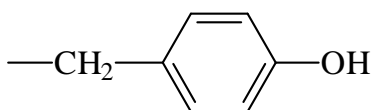


Would you expect D-glucose to be water soluble? Why?

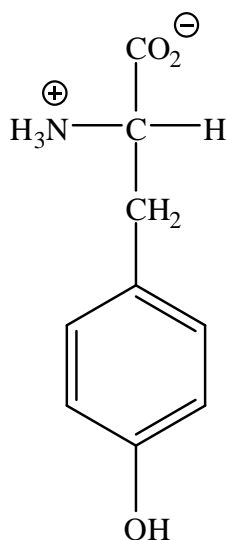
D-glucose will be water soluble as it has numerous alcohol functional groups which can hydrogen bond with the water molecules.

**Marks
5**

- L-Tyrosine is a naturally occurring amino acid with the following side-chain.



The pK_a values of tyrosine are 2.20 (α -COOH), 9.19 (α -NH₃[⊕]) and 10.47 (sidechain). Draw the Fischer projection of L-tyrosine indicating the correct charge state at physiological pH.



What is the absolute stereochemistry of L-tyrosine? Write (*R*) or (*S*).

S

What is the value of the pI of L-tyrosine?

$$pI = \frac{1}{2} (2.20 + 9.19) = 5.70$$

What does pI represent?

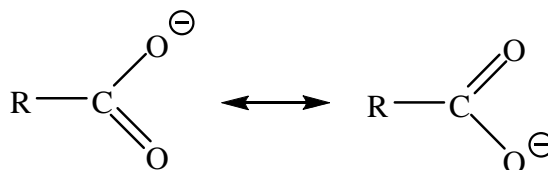
pI represents the isoelectric point - the pH at which there is no net charge on the molecule.

**Marks
6**

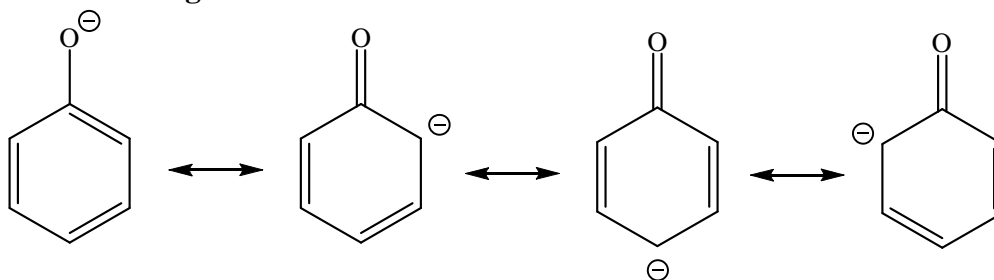
Account for the difference in acidity of the carboxylic acid group and the phenol.

Acid strength is dependent on the stability of the conjugate base.

The carboxylate anion is resonance stabilised, with the charge being spread over the electronegative O atoms:



The phenoxide anion is resonance stabilised also, but the charge in the resonance contributors is spread over the C atoms in the ring. C is not as electronegative as O, so these contributors are not as significant as that with the charge on the O.



Resonance stabilisation is not as great as for carboxylate and therefore phenol is weaker acid than carboxylic acid.

- Draw the products of acid hydrolysis of the following peptide, indicating the correct charge state under these conditions.

Marks
3

