

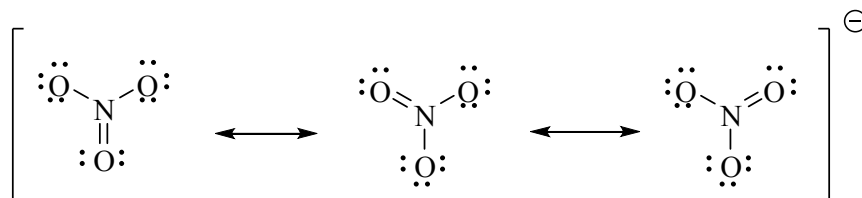
<ul style="list-style-type: none"> <li>In the spaces provided, explain the meanings of the following terms.</li> </ul>	<b>Marks</b> <b>3</b>
<p>(a) enzyme</p> <p><b>A biological catalyst. Like any catalyst, it acts by providing an alternative reaction pathway with a lower activation energy. Enzymes are typically highly efficient and specific.</b></p>	
<p>(b) cofactor</p> <p><b>The non-protein part of an enzyme, such as the haem group in haemoglobin, that is required for the enzymic activity.</b></p>	
<p>(c) peptide</p> <p><b>A sequence of amino acids linked by peptide bonds – a biological polymer formed by linking the carboxylic acid group of one amino acid and the amine group on another.</b></p>	
<ul style="list-style-type: none"> <li>Explain, in terms of chemical bonding and intermolecular forces, the following trend in melting points: <math>\text{CH}_4 &lt; \text{I}_2 &lt; \text{NaCl} &lt; \text{silica (SiO}_2)</math></li> </ul>	<b>2</b>
<p><b>The intermolecular forces in <math>\text{I}_2</math> and <math>\text{CH}_4</math> are weak dispersion forces. Iodine is a much larger atom than H or C and hence has more electrons and these are held further from the nucleus. The electron cloud in <math>\text{I}_2</math> is, therefore, much more polarisable leading to stronger dispersion forces in <math>\text{I}_2</math>. and a higher melting point.</b></p> <p><b><math>\text{NaCl}</math> has relatively strong ionic bonds between all of the <math>\text{Na}^+</math> and <math>\text{Cl}^-</math> ions in the lattice.</b></p> <p><b><math>\text{SiO}_2</math> is a covalent network compound with a very high melting point as strong covalent bonds need to be broken.</b></p>	

- What is the bond order of the nitrogen-oxygen bonds in the nitrate ion,  $\text{NO}_3^-$ ? Explain your answer.

Marks

2

Three equivalent Lewis structures can be drawn for the nitrate ion:



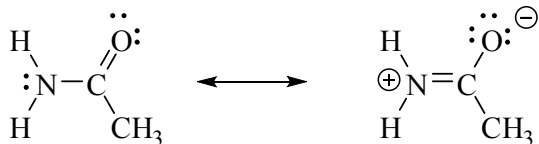
These *resonance* structures contribute equally and the real electron distribution is an average of them. The N-O bond order is an average of its bond order in the resonance structures:

$$\text{bond order} = \frac{1}{3} (1 + 1 + 2) = \frac{4}{3}$$

- The observed geometry of the atoms attached to the N atom in  $\text{H}_2\text{NCOCH}_3$  is trigonal planar. Explain this observation.

2

The molecule has two major resonance contributors as shown below:



Although the form on the left is more important, the contribution of the form on the right means that the C-N bond has partial double bond character.

This causes the peptide bond to be planar with restricted rotation. It also means that the amide nitrogen atom has low basicity and that the C-N bond is strong.

<ul style="list-style-type: none"> <li>Give the ground-state electron configuration of the aluminium atom.</li> </ul>	<b>Marks</b> 2
$1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne] $3s^2 3p^1$	
Provide one set of valid quantum numbers ( $n, l, m_l, m_s$ ) for the highest energy electron.	
<p>For the <math>3p^1</math> electron, there are six possible sets:</p> <ul style="list-style-type: none"> <li><math>n = 3, l = 1, m_l = 1, m_s = +\frac{1}{2}</math></li> <li><math>n = 3, l = 1, m_l = 1, m_s = -\frac{1}{2}</math></li> <li><math>n = 3, l = 1, m_l = 0, m_s = +\frac{1}{2}</math></li> <li><math>n = 3, l = 1, m_l = 0, m_s = -\frac{1}{2}</math></li> <li><math>n = 3, l = 1, m_l = -1, m_s = +\frac{1}{2}</math></li> <li><math>n = 3, l = 1, m_l = -1, m_s = -\frac{1}{2}</math></li> </ul>	
<ul style="list-style-type: none"> <li>The osmotic pressure of a solution containing <math>5.5 \text{ g L}^{-1}</math> of a polypeptide is <math>0.103 \text{ atm}</math> at <math>5^\circ \text{C}</math>. Calculate the molar mass of the polypeptide.</li> </ul>	2
<p>The osmotic pressure, <math>\Pi</math>, is related to the concentration, <math>c</math>, and the temperature, <math>T</math>:</p> $\Pi = cRT$ <p>where <math>R</math> is the gas constant. With <math>\Pi = 0.103 \text{ atm}</math> and <math>T = 5^\circ \text{C} = (273 + 5) \text{ K}</math>,</p> $0.103 \text{ atm} = c \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (278 \text{ K})$ $c = 0.00452 \text{ mol L}^{-1}$ <p>where <math>R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}</math> has been used to remove the need to convert the pressure in Pascals.</p> <p>As the solution contains <math>5.5 \text{ g L}^{-1}</math> of the polypeptide and this is equivalent to <math>0.00452 \text{ mol L}^{-1}</math>, <math>5.5 \text{ g}</math> must contain <math>0.00452 \text{ mol}</math>. Hence,</p> $\text{molar mass} = \frac{5.5 \text{ g}}{0.00452 \text{ mol}} = 1200 \text{ g mol}^{-1} = 1.2 \times 10^3 \text{ g mol}^{-1}$ <div style="border: 1px solid black; padding: 5px; width: fit-content; margin-left: auto; margin-right: auto;">         Answer: <math>1200 \text{ g mol}^{-1} = 1.2 \times 10^3 \text{ g mol}^{-1}</math> </div>	

THE REMAINDER OF THIS PAGE IS FOR ROUGH WORKING ONLY.

<ul style="list-style-type: none"><li>A galvanic cell is made of a <math>\text{Ni}^{2+}/\text{Ni}</math> half cell with <math>[\text{Ni}^{2+}] = 1.00 \times 10^{-3} \text{ M}</math> and a <math>\text{Ag}^+/\text{Ag}</math> half cell with <math>[\text{Ag}^+] = 5.00 \times 10^{-2} \text{ M}</math>. Calculate the electromotive force of the cell at <math>25^\circ\text{C}</math>.</li></ul>	<b>Marks 6</b>
<p><b>The reduction potentials for the two half cells are (from the data sheet):</b></p> $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s}) \quad E^\circ = -0.24 \text{ V}$ $\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s}) \quad E^\circ = +0.80 \text{ V}$ <p><b>The <math>\text{Ni}^{2+}(\text{aq}) / \text{Ni}(\text{s})</math> cell has the lower electrode potential and it is the one that is reversed. Hence, the cell reaction and the standard cell potential are</b></p> $2\text{Ag}^+(\text{aq}) + \text{Ni}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq}) \quad E^\circ = (+0.80 \text{ V}) + (+0.24 \text{ V}) = 1.04 \text{ V}$ <p><b>At non-standard concentrations, the electrode potential is given by the Nernst equation:</b></p> $E = E^\circ - \frac{RT}{nF} \ln Q$ <p><b>For this two electron reduction, <math>n = 2</math> and <math>Q = \frac{[\text{Ni}^{2+}(\text{aq})]}{[\text{Ag}^+(\text{aq})]^2}</math></b></p> <p><b><math>[\text{Ni}^{2+}(\text{aq})] = 1.00 \times 10^{-3} \text{ M}</math> and <math>[\text{Ag}^+(\text{aq})] = 5.00 \times 10^{-2} \text{ M}</math>. Hence, at <math>T = 25^\circ\text{C} = (25 + 273) \text{ K} = 298 \text{ K}</math>:</b></p> $E = (1.04 \text{ V}) - \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{(2 \times 96485 \text{ C mol}^{-1})} \ln\left(\frac{1.00 \times 10^{-3}}{(5.00 \times 10^{-2})^2}\right) = 1.06 \text{ V}$ <table border="1" style="width: 100%;"><tr><td style="text-align: right;">Answer: <b>1.06 V</b></td></tr></table>	
Answer: <b>1.06 V</b>	
Calculate the equilibrium constant of the reaction at $25^\circ\text{C}$ .	
<p><b>The equilibrium constant is related to the standard electrode potential:</b></p> $E^\circ = \frac{RT}{nF} \ln K$ <p><b>Hence, with <math>E^\circ = 1.04 \text{ V}</math> and <math>n = 2</math>:</b></p> $\ln K = E^\circ \times \frac{nF}{RT} = (1.04 \text{ V}) \times \frac{(2 \times 96485 \text{ C mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 81.0$ <p><b>so,</b></p> $K = 1.51 \times 10^{35}$ <table border="1" style="width: 100%;"><tr><td style="text-align: right;">Answer: <b><math>1.51 \times 10^{35}</math></b></td></tr></table>	Answer: <b><math>1.51 \times 10^{35}</math></b>
Answer: <b><math>1.51 \times 10^{35}</math></b>	

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the standard free energy change of the reaction at 25 °C.

The standard free energy change,  $\Delta G^\circ$ , is related to the standard electrode potential,  $E^\circ$ :

$$\Delta G^\circ = -nFE^\circ$$
$$= -(2) \times (96485 \text{ C mol}^{-1}) \times (1.04 \text{ V}) = -201000 \text{ J mol}^{-1} = 201 \text{ kJ mol}^{-1}$$

Alternatively, the free energy change is related to the equilibrium constant,  $K$ :

$$\Delta G^\circ = -RT \ln K$$
$$= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (1.51 \times 10^{35}) = -201 \text{ kJ mol}^{-1}$$

Answer: **-201 kJ mol<sup>-1</sup>**

Indicate whether the reaction is spontaneous or not. Give reasons for your answer.

- $E^\circ > 0$  so the reaction is spontaneous.
- $\Delta G^\circ < 0$  so the reaction is spontaneous.
- $K$  is much greater than 1 so the reaction is spontaneous.

Express the overall reaction in the shorthand voltaic cell notation.



- Calculate  $\Delta G^\circ$  for the following reaction at  $25^\circ\text{C}$ .



Data:	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	$\Delta_f H^\circ / \text{kJ mol}^{-1}$
$\text{SO}_3(\text{g})$	256.2	-395.2
$\text{NH}_3(\text{g})$	192.5	-46.19
$\text{NO}(\text{g})$	210.6	90.37
$\text{SO}_2(\text{g})$	248.5	-296.9
$\text{H}_2\text{O}(\text{g})$	188.7	-241.8

Marks  
4

Using  $\Delta_r H^\circ = \sum m \Delta_f H^\circ(\text{products}) - \sum m \Delta_f H^\circ(\text{reactants})$ , the enthalpy change for the reaction can be written as,

$$\begin{aligned} \Delta_r H^\circ &= [2\Delta_f H^\circ(\text{NO}(\text{g})) + 5\Delta_f H^\circ(\text{SO}_2(\text{g})) + 3\Delta_f H^\circ(\text{H}_2\text{O}(\text{g}))] \\ &\quad - [5\Delta_f H^\circ(\text{SO}_3(\text{g})) + 2\Delta_f H^\circ(\text{NH}_3(\text{g}))] \\ &= (2 \times 90.37 + 5 \times -296.9 + 3 \times -241.8) - [5 \times -395.2 + 2 \times -46.19] \text{ kJ mol}^{-1} \\ &= +44.2 \text{ kJ mol}^{-1} \end{aligned}$$

Similarly,  $\Delta_r S^\circ = \sum m S^\circ(\text{products}) - \sum m S^\circ(\text{reactants})$  so the entropy change for the reaction can be written as,

$$\begin{aligned} \Delta_r S^\circ &= [2S^\circ(\text{NO}(\text{g})) + 5S^\circ(\text{SO}_2(\text{g})) + 3S^\circ(\text{H}_2\text{O}(\text{g}))] \\ &\quad - [5S^\circ(\text{SO}_3(\text{g})) + 2S^\circ(\text{NH}_3(\text{g}))] \\ &= (2 \times 210.6 + 5 \times 248.5 + 3 \times 188.7) - [5 \times 256.2 + 2 \times 192.5] \text{ J K}^{-1} \text{ mol}^{-1} \\ &= +563.8 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Overall,  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ$  so at  $T = 25^\circ\text{C} = (25 + 273) \text{ K}$ :

$$\begin{aligned} \Delta_r G^\circ &= (+44.2 \times 10^3 \text{ J mol}^{-1}) - (298 \text{ K}) \times (+563.8 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -128000 \text{ J mol}^{-1} = -128 \text{ kJ mol}^{-1} \end{aligned}$$

Answer:  $-123.8 \text{ kJ mol}^{-1}$

Is the reaction spontaneous? Give a reason for your answer.

As  $\Delta_r G^\circ < 0$ , the reaction is spontaneous.

At what temperature does the spontaneity change?

The reaction is endothermic so becomes more favourable as the temperature is increased and less favourable as the temperature is lowered (Le Chatelier's principle).

The reaction becomes non-spontaneous when  $\Delta_r G^\circ = 0$ :

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The reaction is endothermic so becomes more favourable as the temperature is increased and less favourable as the temperature is lowered (Le Chatelier's principle).

The reaction becomes non-spontaneous when  $\Delta_r G^\circ = 0$ :

$$\Delta_r H^\circ - T\Delta_r S^\circ = 0 \quad \text{or} \quad T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ}$$

Assuming that  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  do not change over the temperature range:

$$T = \frac{\Delta_r H^\circ}{\Delta_r S^\circ} = \frac{(44.2 \times 10^3 \text{ J mol}^{-1})}{(563.8 \text{ J K}^{-1} \text{ mol}^{-1})} = 78.4 \text{ K}$$

Hence, the reaction is spontaneous at  $T > 78.4 \text{ K}$

Answer: **78.4 K**

	Marks
<p>• Explain why copper dissolves in dilute <math>\text{HNO}_3</math>, but not in dilute <math>\text{HCl}</math>?</p> <p><b>Copper does not dissolve in dilute <math>\text{HCl}(\text{aq})</math> it is not oxidized to <math>\text{Cu}^{2+}(\text{aq})</math> under these conditions:</b></p> $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \quad E^\circ_{\text{ox}} = -0.34 \text{ V}$ $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \quad E^\circ_{\text{red}} = 0 \text{ V}$ <p>The overall cell potential <math>E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (-0.34 + 0) = -0.34 \text{ V}</math>. The cell potential is negative and the reaction is not spontaneous.</p> <p><b>Copper does dissolve in dilute <math>\text{HNO}_3</math> due to oxidation by the <math>\text{NO}_3^-</math> ion:</b></p> $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \quad E^\circ_{\text{ox}} = -0.34 \text{ V}$ $\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3\text{e}^- \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O} \quad E^\circ_{\text{red}} = 0.96 \text{ V}$ <p>The overall cell potential <math>E^\circ = E^\circ_{\text{ox}} + E^\circ_{\text{red}} = (-0.34 + 0.96) = +0.62 \text{ V}</math>. The cell potential is positive and the reaction is spontaneous.</p>	<p>2</p>

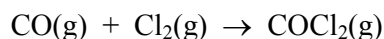
<p>• Nitrous oxide decomposes at 25 °C according to the following equation.</p> $2\text{N}_2\text{O}(\text{g}) \rightleftharpoons 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \quad K_{\text{p}} = 1.8 \times 10^{36}$ <p>What is the value for <math>K_{\text{p}}</math> at 40 °C?</p>	4
<p><b>Using <math>\Delta_{\text{r}}G^\circ = -RT\ln K_{\text{p}}</math>, at 25 °C (= 298 K):</b></p> $\Delta_{\text{r}}G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times \ln(1.8 \times 10^{36}) = -207 \text{ kJ mol}^{-1}$ <p><b>Assuming that <math>\Delta_{\text{r}}G^\circ</math> does not change over the temperature range, at 40 °C = 313 K:</b></p> $\ln K_{\text{p}} = \frac{\Delta_{\text{r}}G^\circ}{RT} = \frac{(210 \times 10^3 \text{ J mol}^{-1})}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})} = 79$ $K_{\text{p}} = 3.3 \times 10^{34}$ <div style="border: 1px solid black; padding: 2px; display: inline-block; margin-top: 10px;">Answer: <math>3.3 \times 10^{34}</math></div>	

Is the reaction endothermic or exothermic? Give a reason for your answer.

**The equilibrium constant decreases when the temperature increases. This is consistent with an exothermic reaction since these become less favourable as the temperature increases (Le Chatelier's principle).**



- Phosgene is a toxic gas prepared by the reaction of carbon monoxide with chlorine.



The following data were obtained in a kinetics study of its formation at 150 °C.

Experiment	Initial [CO] (mol L <sup>-1</sup> )	Initial [Cl <sub>2</sub> ] (mol L <sup>-1</sup> )	Initial rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	1.00	0.100	$1.29 \times 10^{-3}$
2	0.100	0.100	$1.33 \times 10^{-4}$
3	0.100	1.00	$1.30 \times 10^{-3}$
4	0.100	0.0100	$1.32 \times 10^{-5}$

Write the rate law for the formation of phosgene at 150 °C.

Between experiments (1) and (2), [Cl<sub>2</sub>] is constant and [CO] is increased by a factor of ten. This leads to a tenfold increase in the rate. The reaction is first order with respect to [CO].

Between experiments (2) and (3), [CO] is constant and [Cl<sub>2</sub>] is increased by a factor of ten. This leads to a tenfold increase in the rate. The reaction is also first order with respect to [Cl<sub>2</sub>].

Hence, the rate law is,

$$\text{rate} = k[\text{CO(g)}][\text{Cl}_2\text{(g)}]$$

Calculate the value of the rate constant at 150 °C.

In experiment (1), rate =  $1.29 \times 10^{-3}$  mol L<sup>-1</sup> s<sup>-1</sup> when [CO] = 1.00 mol L<sup>-1</sup> and [Cl<sub>2</sub>] = 0.100 mol L<sup>-1</sup>. Substituting into the rate law gives,

$$(1.29 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}) = k \times (1.00 \text{ mol L}^{-1}) \times (0.100 \text{ mol L}^{-1})$$

$$k = 1.29 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

The same method gives  $k = 1.33 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$ ,  $1.30 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$  and  $1.32 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$  for experiments (2), (3) and (4) respectively. The accuracy of the experiments suggests a value of  $1.3 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$ .

$$\text{Answer: } 1.3 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}$$

Marks

4

ANSWER CONTINUES ON THE NEXT PAGE

Calculate the rate of appearance of phosgene when  $[\text{CO}] = [\text{Cl}_2] = 1.3 \text{ M}$ .

**Using the rate law derived above.**

$$\begin{aligned}\text{rate} &= (1.3 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}) \times [\text{CO}] \times [\text{Cl}_2] \\ &= (1.3 \times 10^{-2} \text{ mol}^{-1} \text{ L s}^{-1}) \times (1.3 \text{ mol L}^{-1}) \times (1.3 \text{ mol L}^{-1}) \\ &= 2.2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}\end{aligned}$$

Answer:  $2.2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$

**Marks**  
2

- Codeine, a cough suppressant extracted from crude opium, is a weak base with a  $pK_b = 5.79$ . What is the pH of a 0.020 M solution of codeine?

As codeine, is a weak base and so  $[OH^-]$  must be calculated. for example using a reaction table:

	codeine	H <sub>2</sub> O	$\rightleftharpoons$	codeineH <sup>+</sup>	OH <sup>-</sup>
initial	0.020	large		0	0
change	-x	negligible		+x	+x
final	0.020 - x	large		x	x

The equilibrium constant  $K_b$  is given by:

$$K_b = \frac{[\text{codeineH}^+][\text{OH}^-]}{[\text{codeine}]} = \frac{x^2}{(0.020 - x)}$$

As  $pK_b = -\log_{10}K_b = 5.79$ ,  $K_b = 10^{-5.79}$ . Hence,

$$\frac{x^2}{(0.020 - x)} = 10^{-5.79}$$

As  $K_b$  is very small,  $0.020 - x \sim 0.020$  and hence:

$$x^2 = 0.020 \times 10^{-5.79} \quad \text{or} \quad x = 1.8 \times 10^{-4} \text{ M} = [\text{OH}^-(\text{aq})]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[\text{OH}^-] = -\log_{10}[1.8 \times 10^{-4}] = 3.74$$

Finally,  $pH + pOH = 14.00$  so

$$pH = 14.0 - 3.74 = 10.26$$

Answer: **10.26**

- A buffer solution is formed with 0.250 M CH<sub>3</sub>COOH and 0.350 M CH<sub>3</sub>COONa. What is the pH of this buffer solution? ( $K_a$  of acetic acid =  $1.8 \times 10^{-5}$  M.)

3

The pH of a buffer solution is given by the Henderson-Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{\text{base}}{\text{acid}}\right)$$

As  $pK_a = -\log_{10}K_a = -\log_{10}(1.8 \times 10^{-5}) = 4.74$ . With  $[\text{base}] = [\text{CH}_3\text{COONa}] = 0.350 \text{ M}$  and  $[\text{acid}] = [\text{CH}_3\text{COOH}] = 0.250 \text{ M}$ ,

ANSWER CONTINUES ON THE NEXT PAGE

$$\text{pH} = 4.74 + \log\left(\frac{0.350}{0.250}\right) = 4.89$$

As the buffer contains a higher concentration of base than acid, the  $\text{pH} > \text{p}K_{\text{a}}$ .

Answer: **4.89**

Calculate the pH of the solution formed when  $6.3 \times 10^{-2}$  mol of NaOH is added to 1.0 L of the buffer solution.

In a 1.0 L solution of the buffer, there is 0.250 mol of  $\text{CH}_3\text{COOH}$  and 0.350 mol of  $\text{CH}_3\text{COO}^-$ .

The  $\text{OH}^-$  will react with the  $\text{CH}_3\text{COOH}$  to produce  $\text{CH}_3\text{COO}^-$ . The concentration of the former will therefore decrease whilst the concentration of the latter will increase. After the  $\text{OH}^-$  is added:

$$\begin{aligned}\text{number of moles of } \text{CH}_3\text{COOH} &= (0.250 - 6.3 \times 10^{-2}) \text{ M} = 0.187 \text{ mol} \\ \text{number of moles of } \text{CH}_3\text{COO}^- &= (0.350 + 6.3 \times 10^{-2}) \text{ M} = 0.413 \text{ mol}\end{aligned}$$

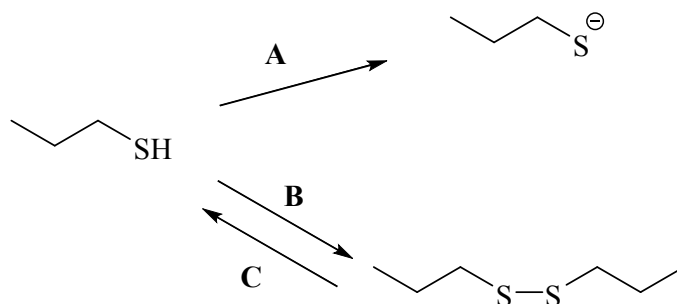
As the volume of solution does not change, these are also the new acid and base concentrations. Hence, the buffer now has:

$$\text{pH} = 4.74 + \log\left(\frac{0.413}{0.187}\right) = 5.09$$

As base has been added, there is an increase in the pH. As it is being added to a buffer system, this change is small. Addition of this quantity of base to water would increase the pH by 1.20 units.

Answer: **5.09**

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

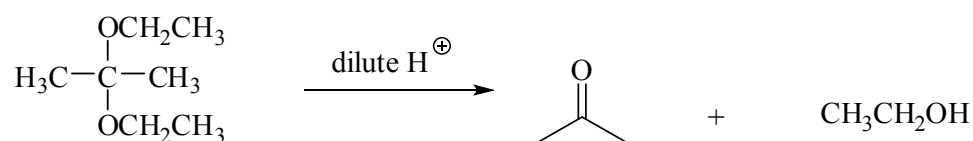
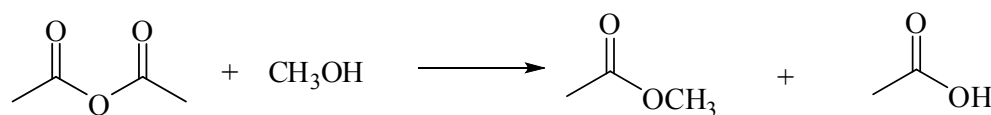
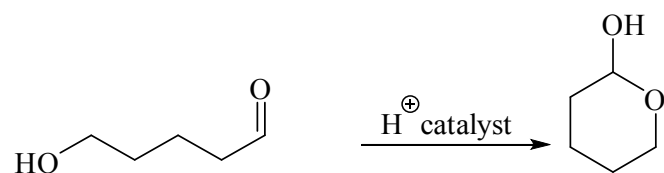
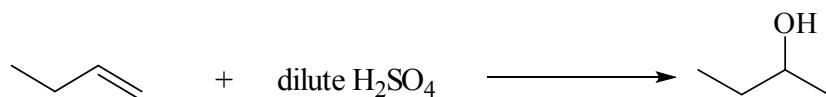
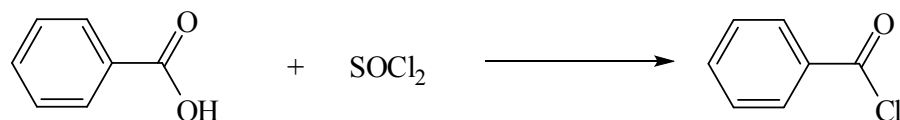


**A:** A strong base such as  $\text{NaOH}$ ,  $\text{Na}$  or  $\text{NaNH}_2$

**B:**  $\text{I}_2$

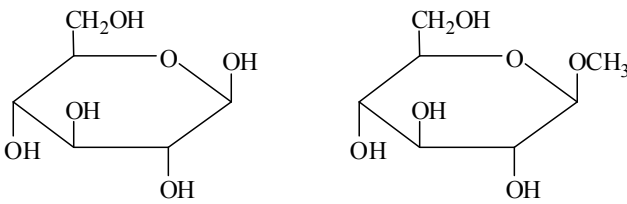
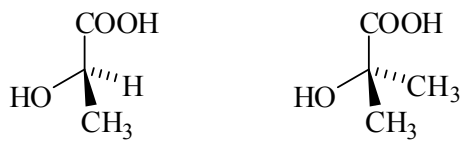

**C:**  $\text{Zn} / \text{H}^+$

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

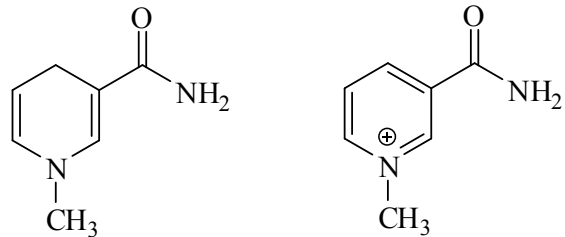


**Marks**  
**5**

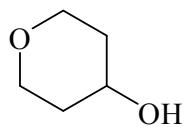
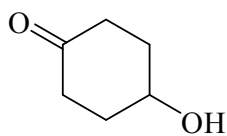
- Using a chemical test, how would you distinguish between the following pairs of compounds? Indicate the reagent you would use and the observations you would make.

Compounds	Reagent and observation
	<p><b>Tollens' reagent, <math>[\text{Ag}(\text{NH}_3)_2]/\text{OH}^-</math></b></p> <p><b>The first compound will cause a silver precipitate to form. No reaction with the second compound as it does not contain hemi-acetal group.</b></p>
	<p><b><math>\text{Cr}_2\text{O}_7^{2-}/\text{H}^+</math></b></p> <p><b>Orange reagent will go green with first compound. No reaction with the second compound.</b></p>
	<p><b><math>\text{Br}_2</math> solution.</b></p> <p><b>First compound will decolourise the orange/brown <math>\text{Br}_2</math> solution. No reaction with the second compound.</b></p>

Using a spectroscopic technique, how would you distinguish between the following pairs of compounds? Indicate the observations you would make.

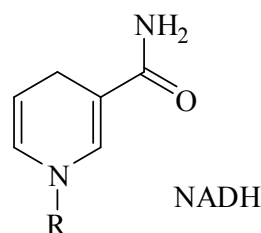
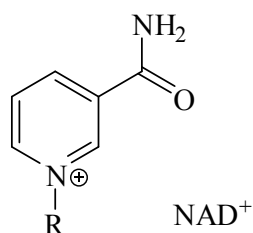
Compounds	Technique and observation
	<p><b><math>^1\text{H}</math> nmr will detect different numbers of H's attached to the ring. The first compound has 3 olefinic resonances (each 1H) and 1 aliphatic resonance (2H) whilst the second compound has 4 aromatic resonances (each 1H).</b></p>

**ANSWER CONTINUES ON THE NEXT PAGE**



**IR.** The first compound will give intense absorption at about  $1740\text{ cm}^{-1}$  due to the C=O group. The second compound will have no absorption in that region.

- $\text{NAD}^+/\text{NADH}$  is a biological redox system. The two species may be represented by the structures below.



What are the requirements for a compound to be aromatic? Indicate which of  $\text{NAD}^+$  and/or  $\text{NADH}$  fulfil these requirements.

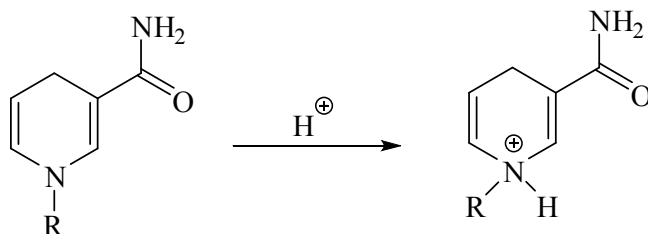
**An aromatic compound must be cyclic, planar, conjugated, and have  $4n+2$   $\pi$  electrons (with  $n$  being an integer).**

**$\text{NAD}^+$  is aromatic – there are  $2 \times \text{C}=\text{C}$  and  $1 \times \text{C}=\text{N}$  bond each of which contributes  $2 \pi$  electrons, giving a total of 6. This is aromatic with  $n = 1$ .**

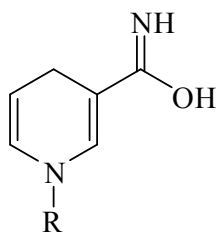
**$\text{NADH}$  is not aromatic. The presence of an  $sp^3$  carbon atom breaks the conjugation.**

Which of  $\text{NAD}^+$  and/or  $\text{NADH}$  will react with cold dilute  $\text{H}^+$  in an acid/base reaction? Using the structures above, give the chemical equation for the reaction and a brief explanation for your choice.

**Only  $\text{NADH}$  will react.**



Draw the structure of a tautomer of  $\text{NADH}$ .

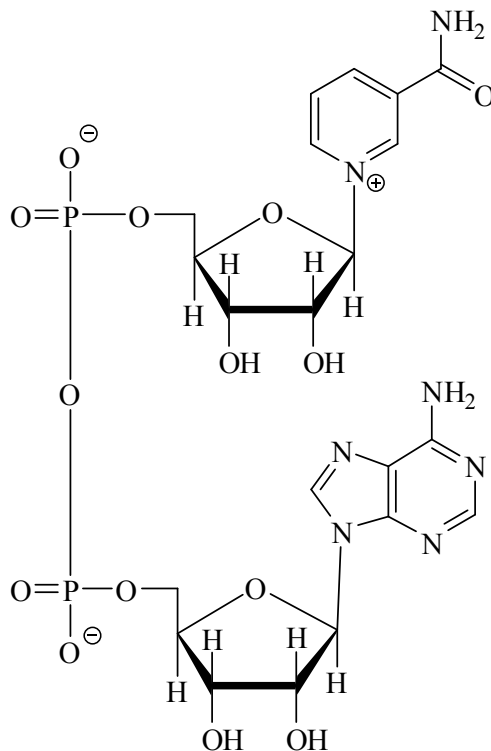


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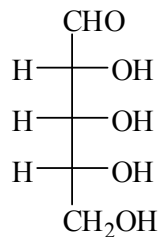


The full structure of  $\text{NAD}^+$  contains ribose, two phosphate groups and adenine.

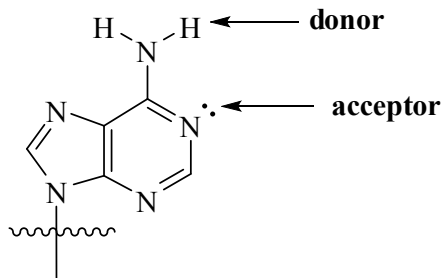
**Marks**  
**4**



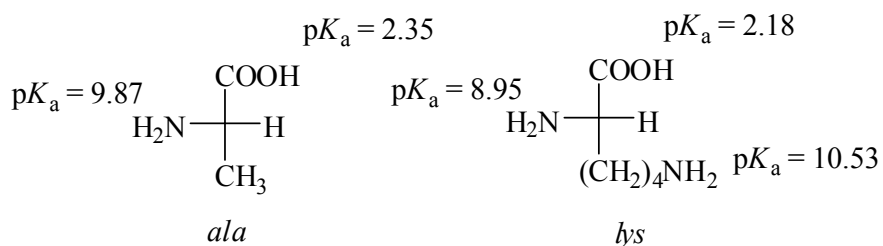
Draw ribose as a Fischer projection.



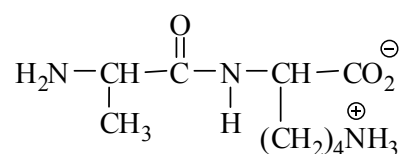
Adenine is also a component of DNA used in forming complementary strands by hydrogen bonding. Indicate the sites of hydrogen bonding on adenine that are used in forming complementary strands in DNA and differentiate between those sites that are hydrogen bond donors and those that are hydrogen bond acceptors.



- Alanine (*ala*) and lysine (*lys*) are two amino acids with the structures given below as Fischer projections. The  $pK_a$  values of the conjugate acid forms of the different functional groups are indicated.



Draw the structure of the dipeptide *ala-lys* in its zwitterionic form.



Would you expect the dipeptide to be soluble in water? Give a brief reason for your choice.

**The presence of oxygen and nitrogen atoms and O-H and N-H groups would lead to strong H-bonding and ion-dipole forces in water and so the dipeptide is likely to be water soluble.**

Would you expect the dipeptide to be acidic, neutral or basic? Give a brief reason for your choice.

**There is a basic  $-\text{NH}_2$  side chain on lysine. As there is a greater number of basic groups than acidic groups overall, it is likely to be basic.**

Estimate the isoelectric point of the dipeptide.

**The dipeptide has three ionizable groups – the amine function on the alanine ( $pK_a$  9.87), the carboxylic acid group on the lysine ( $pK_a$  2.18) and the amine group on the lysine side chain ( $pK_a$  10.53).**

**The fully protonated form of the dipeptide has the two  $-\text{NH}_2$  and the  $-\text{COOH}$  groups protonated and has a +2 charge. This form will exist at low pH. The fully deprotonated form, the amine functions are not protonated and the carboxylic acid is deprotonated ( $-\text{COO}^-$ ) giving the molecule a -1 charge.**

ANSWER CONTINUES ON THE NEXT PAGE

At low pH, the protonated (+2) form dominates. As the pH is raised the group with the lowest  $pK_a$  (the carboxylic acid group) will become steadily deprotonated. At a  $pK_a$  of 2.18, there is a 50:50 mixture of the +2 and +1 forms. The latter having the carboxylic acid group deprotonated.

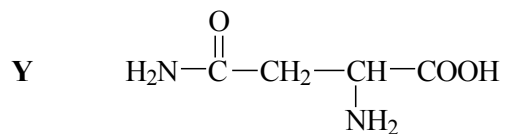
As the pH is raised further, the group with the next lowest  $pK_a$  (the alanine amine group) becomes steadily deprotonated. At a  $pK_a$  of 9.87, there is a 50:50 mixture of the +1 and neutral forms. The latter having the alanine mine group deprotonated.

As the pH is raised even more, the final group (lysine side-chain amine) becomes deprotonated. At a  $pK_a$  of 10.53, there is a 50:50 mixture of the neutral and -1 forms.

A pH of 9.87 gives a 50:50 mixture of +1 and neutral. A pH gives a 50:50 mixture of -1 and neutral. Hence, a pH intermediate between these values will give a solution predominately containing the neutral form. This is the isoelectric point:

$$pI = \frac{pk_{a1} + pk_{a2}}{2} = \frac{(10.53 + 9.87)}{2} = 10.2$$

- The amino acid, asparagine, was isolated from asparagus juice in 1806. The uncharged form, **Y**, is given below.



Draw the constitutional formula of the product(s) formed in the reaction of **Y** with the following reagents.

Cold, dilute hydrochloric acid  $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\oplus\text{NH}_3}{\text{CH}}-\text{COOH}$	Cold, dilute sodium hydroxide  $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CO}_2^\ominus$
Hot, 6 M hydrochloric acid  $\overset{\ominus}{\text{NH}}_4^+ + \text{HO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\oplus\text{NH}_3}{\text{CH}}-\text{COOH}$	Hot, 6 M sodium hydroxide  $\text{NH}_3 + \overset{\ominus}{\text{O}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\underset{\text{NH}_2}{\text{CH}}-\text{CO}_2^\ominus$

**Marks****4**