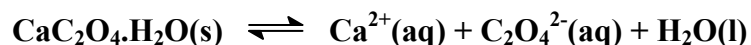


Marks
2

- Oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, found in rhubarb, causes muscle spasms by precipitating Ca^{2+} ions from the blood as calcium oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. Given the solubility product constant for calcium oxalate is $2.3 \times 10^{-9} \text{ M}^2$, calculate the concentration of calcium ions in g L^{-1} formed by dissolving $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ in water at 25°C to give a saturated solution.

The dissolution equilibrium for $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is:



Hence, the solubility product $K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{C}_2\text{O}_4^{2-}(\text{aq})]$

The chemical equation shows that dissolution of one mole of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}(\text{s})$ leads to one mole of $\text{Ca}^{2+}(\text{aq})$ and one mole of $\text{C}_2\text{O}_4^{2-}(\text{aq})$.

If $[\text{Ca}^{2+}(\text{aq})] = [\text{C}_2\text{O}_4^{2-}(\text{aq})] = x$,

$$K_{\text{sp}} = x^2 = 2.3 \times 10^{-9} \text{ so } x = 4.8 \times 10^{-5}.$$

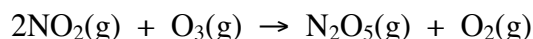
Ca^{2+} will be present at $4.8 \times 10^{-5} \text{ mol L}^{-1}$. As the atomic mass of Ca is 40.08, this corresponds to a mass of:

$$\begin{aligned} \text{mass of } \text{Ca}^{2+} \text{ ions} &= \text{number of moles} \times \text{atomic mass} \\ &= (4.8 \times 10^{-5}) \times 40.08 = 1.9 \times 10^{-3} \text{ g} \end{aligned}$$

Answer: $1.9 \times 10^{-3} \text{ g}$

Marks
4

- The following initial rate data have been obtained for the gas phase reaction of nitrogen dioxide, $\text{NO}_2(\text{g})$, and ozone, $\text{O}_3(\text{g})$, at 300 K.



$[\text{NO}_2(\text{g})] \text{ M}$	$[\text{O}_3(\text{g})] \text{ M}$	Rate M s^{-1}
0.65	0.80	2.61×10^4
1.10	0.80	4.40×10^4
1.10	1.60	8.80×10^4

What is the order of this reaction with respect to each reagent?

Between the first and second experiments, $[\text{O}_3(\text{g})]$ is kept constant and $[\text{NO}_2(\text{g})]$ increases by about 1.7. This leads to the rate also increasing by about 1.7. The reaction is therefore first order with respect to $[\text{NO}_2(\text{g})]$.

Between the second and third experiments, $[\text{NO}_2(\text{g})]$ is kept constant and $[\text{O}_3(\text{g})]$ is doubled. This also leads to a doubling of the rate. The reaction is therefore also first order with respect to $[\text{O}_3(\text{g})]$.

$$\text{rate} = k[\text{NO}_2(\text{g})][\text{O}_3(\text{g})]$$

What is the rate constant of the reaction?

Using the rate law $\text{rate} = k[\text{NO}_2(\text{g})][\text{O}_3(\text{g})]$, k can be worked out using any of the three experiments. For example, using the first experiment:

$$\text{rate} = 2.61 \times 10^4 = k[\text{NO}_2(\text{g})][\text{O}_3(\text{g})] = k \times (0.65) \times (0.80)$$

$$\text{Hence } k = \frac{2.61 \times 10^4}{(0.65)(0.80)} = 5.0 \times 10^4$$

The units of k are obtained by balancing those in the rate law: the rate has units of M s^{-1} and the concentrations both have units of M . Hence:

$$\text{Units of } k = \frac{\text{M s}^{-1}}{(\text{M})(\text{M})} = \text{M}^{-1} \text{ s}^{-1}$$

Answer: $5.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$

Marks
2

- Briefly explain why HF is a weaker Brønsted acid than HI and a stronger acid than H₂O.

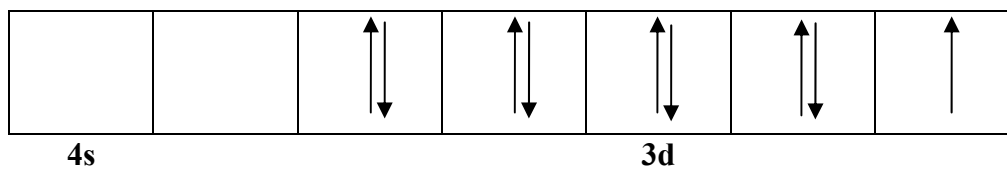
F is more electronegative than O, so the H–F is more polarised bond than the O–H. This facilitates dissociation into F[−] and H⁺ ions.

I is much larger atom than F, so the H–I bond is much longer and weaker than H–F, so HF is weaker acid than HI.

2

- Compounds of *d*-block elements are frequently paramagnetic. Using the box notation to represent atomic orbitals, account for this property in compounds of Cu²⁺.

As Cu is in group 11, it has 11 valence electrons. Cu²⁺ therefore has (11 – 2) = 9. These occupy the five 3d orbitals:



There is an unpaired electron and so Cu²⁺ is paramagnetic.

6

- Complete the following table.

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of <i>d</i> -electrons in the transition metal	Species formed upon dissolving in water
Na ₂ [CoCl ₄]	+2	4	7	Na ⁺ , [CoCl ₄] ^{2−}
[Ni(NH ₃) ₅ (H ₂ O)]SO ₄	+2	6	8	[Ni(NH ₃) ₅ (H ₂ O)] ²⁺ , SO ₄ ^{2−}
[Cr(en) ₃]Br ₃	+3	6	3	[Cr(en) ₃] ³⁺ , Br [−]

en = ethylenediamine = NH₂CH₂CH₂NH₂

Marks
8

- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid, HN_3 , at 25 °C. Calculate the pH of Solution A. The $\text{p}K_a$ of HN_3 is 4.63.

As $\text{p}K_a = -\log(K_a) = 4.63$, $K_a = 10^{-4.63} = 2.34 \times 10^{-5}$. The reaction table is:

	$\text{HN}_3(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	$\text{N}_3^-(\text{aq})$
t = 0	0.25		0	0
change	-x		+x	+x
equilibrium	0.25 - x		x	x

$$\text{Hence, } K_a = \frac{[\text{H}^+(\text{aq})][\text{N}_3^-(\text{aq})]}{[\text{HN}_3]} = \frac{(x)(x)}{(0.25-x)} = \frac{x^2}{(0.25-x)} = 2.34 \times 10^{-5}$$

As K_a is very small, very little HN_3 dissociates and x is tiny so $(0.25 - x) \sim 0.25$

$$\text{Hence, } \frac{x^2}{(0.25)} = 2.34 \times 10^{-5} \quad \text{or } x = [\text{H}^+(\text{aq})] = 2.42 \times 10^{-3} \text{ M}$$

As $\text{pH} = -\log[\text{H}^+(\text{aq})]$:

$$\text{pH} = -\log(2.42 \times 10^{-3}) = 2.62$$

Answer: **2.62**

(ANSWER CONTINUES ON THE NEXT PAGE)

At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide (NaN_3) dissolved in water. Calculate the pH of Solution B.

The relevant reaction is now: $\text{N}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HN}_3(\text{aq}) + \text{OH}^-(\text{aq})$

As N_3^- is the conjugate base of HN_3 , the equilibrium constant for this reaction is K_b where $\text{p}K_a + \text{p}K_b = 14.00$.

Hence, using $\text{p}K_a$ from above:

$$\text{p}K_b = 14.00 - 4.63 = 9.37 \text{ or } K_b = 10^{-9.37} = 4.27 \times 10^{-10}.$$

The molar mass of NaN_3 is $(22.99 (\text{Na})) + (3 \times 14.01 (\text{N})) = 65.02$. The number of moles in 13.0 g is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{13.0}{65.02} = 0.200 \text{ mol}$$

As this is dissolved in 1.00 L, $[\text{N}_3^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.200}{1.00} = 0.200 \text{ M}$

The relevant reaction table is now:

	$\text{N}_3^-(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{HN}_3(\text{aq})$	$\text{OH}^-(\text{aq})$
t = 0	0.200			0	0
change	-x			+x	+x
equilibrium	0.200 - x			x	x

$$\text{The equilibrium constant } K_b = \frac{[\text{HN}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{N}_3^-(\text{aq})]} = \frac{(x)(x)}{(0.200-x)} = \frac{x^2}{(0.200-x)}$$

K_b is small so the amount of $\text{N}_3^-(\text{aq})$ which is protonated is tiny and hence $0.200 - x \sim 0.200$.

$$\text{Hence, } \frac{x^2}{(0.200)} = 4.27 \times 10^{-10} \quad \text{or } x = [\text{OH}^-(\text{aq})] = 9.24 \times 10^{-6} \text{ M}$$

$$\text{As } \text{pOH} = -\log[\text{OH}(\text{aq})] = -\log(9.24 \times 10^{-6}) = 5.03$$

$$\text{As } \text{pH} + \text{pOH} = 14:$$

$$\text{pH} = 14 - 5.03 = 8.97$$

Answer: **8.97**

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Solution C is a buffer system as it contains both a weak acid (HN₃) and its conjugate base (N₃⁻(aq)). The pH can be obtained from the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

Using pK_a = 4.63, [HA(aq)] = [HN₃(aq)] = 0.25 M and [A⁻(aq)] = [N₃⁻(aq)] = 0.200 M:

$$\text{pH} = (4.63) + \log \frac{(0.200)}{(0.25)} = 4.53$$

Answer: **4.53**

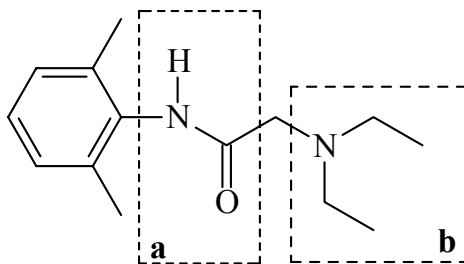
If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

**To lower the pH,
the acid
concentration
(HN₃) is increased**

<ul style="list-style-type: none">Define what is meant by an “allotrope”. Give an example of a pair of allotropes involving oxygen and a pair <i>not</i> involving oxygen.	Marks 3
<p>Allotropes are different structural forms of the same element.</p> <p>Examples include diamond and graphite for carbon; red and white phosphorus; oxygen O₂ and ozone O₃.</p>	

Marks
7

- The structure of lignocaine, a local anaesthetic, is given below.



Give the molecular formula of lignocaine.



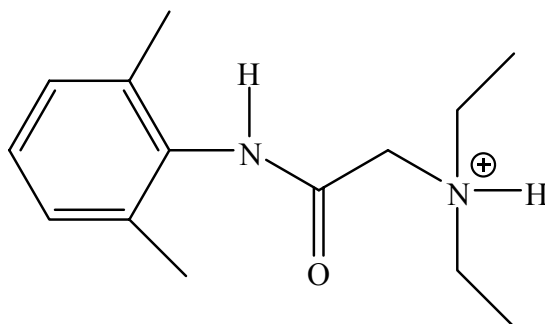
Name the functional groups in lignocaine indicated by boxes “a” and “b”.

a: amide

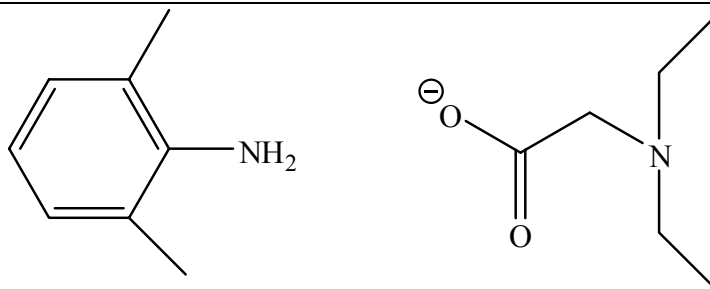
b: tertiary amine

Give the structure(s) of all organic products formed when lignocaine is treated with the following reagents. If no reaction occurs, write “NO REACTION”.

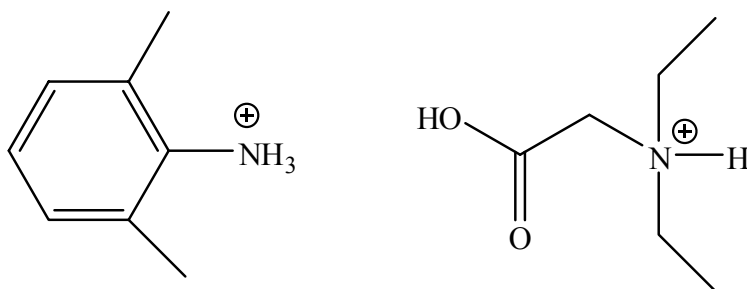
cold HCl (1 M)



hot NaOH (4 M)

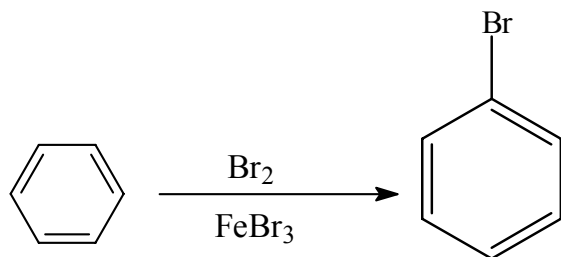
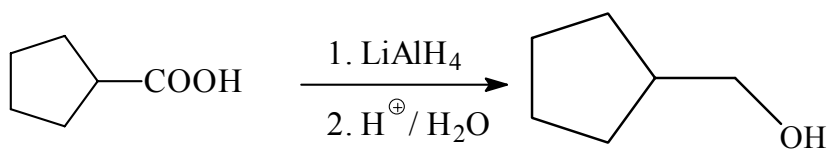
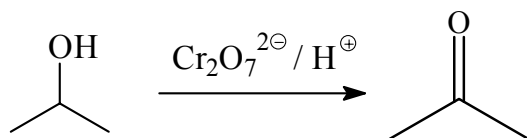
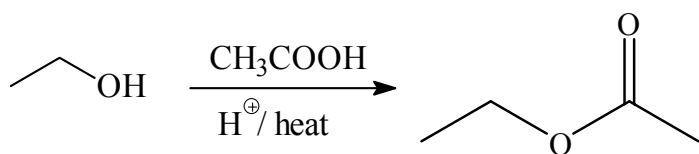
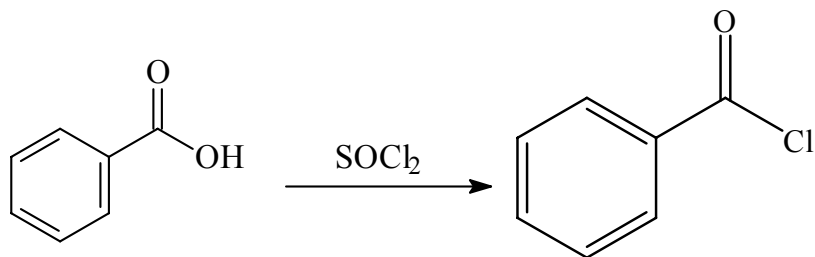
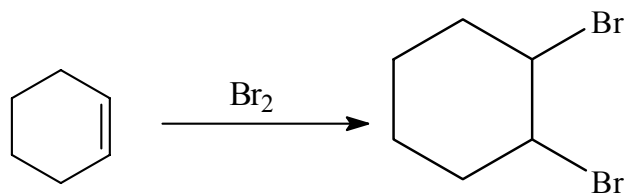


hot HCl (4 M)



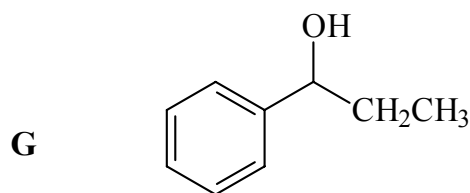
Marks
6

- Draw the constitutional formula of the major organic product formed in each of the following reactions.



Marks
5

- Propionaldehyde (propanal) is treated first with phenylmagnesium bromide in dry diethyl ether and then with dilute aqueous acid, to yield alcohol **G**.



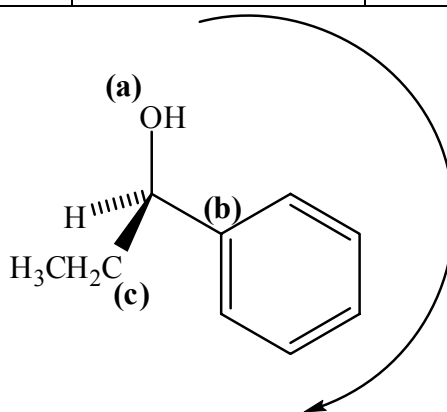
State whether **G** is obtained as the (*R*)-enantiomer, the (*S*)-enantiomer, a racemic mixture, or is achiral.

Racemic mixture

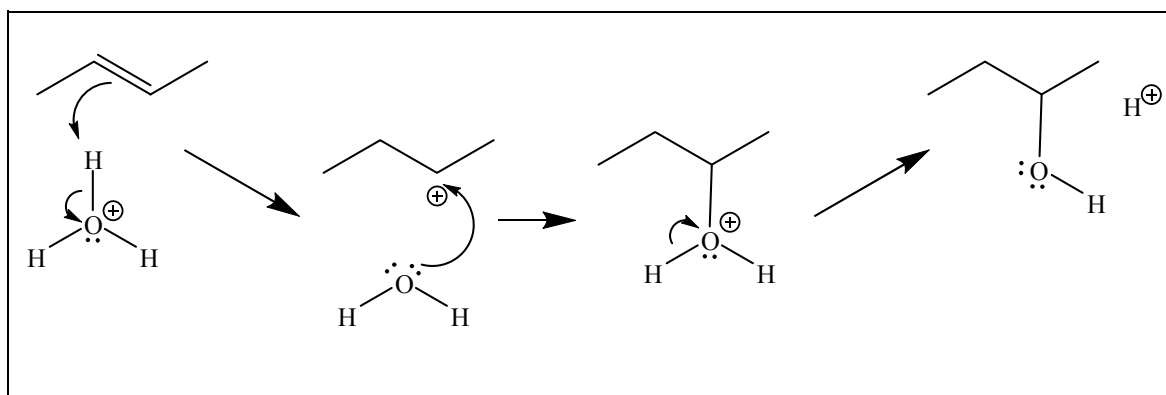
List below, the substituents on the stereogenic carbon atom in **G**, in decreasing priority (*i.e.* from highest to lowest priority), as determined by the sequence rules.

highest priority			lowest priority
-OH		-CH₂CH₃	-H

Draw the (*R*) enantiomer of **G**, showing the correct absolute stereochemistry.

**5**

- The incomplete proposed mechanism for the reaction of (*E*)-but-2-ene with aqueous acid is shown below. Complete the mechanism by adding curly arrows and relevant lone pairs to illustrate the bonding changes that take place.



What two-word description may be used for the name of this mechanism?

electrophilic addition

Marks
6

- Devise a synthesis of 2-phenyl-2-propanol, starting from propene and bromobenzene. Note that your synthetic route will require more than one step from each starting material. Show clearly the reagents you would use and draw constitutional formulas for all intermediate compounds.

