Marks
4

- Limestone caves can be found near Sydney. How have these caves been formed? Use appropriate chemical equations in your explanation.

Limestone has a very low solubility in water. The equilibrium,

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$$

greatly favours the solid.

However, limestone is much more soluble in water that contains dissolved carbon dioxide due to the reaction,

$$CaCO_3(s) + CO_2(aq) + H_2O \rightleftharpoons Ca^{2+}(aq) + 2HCO_3^{-}(aq)$$

Caves form where the limestone has dissolved away.

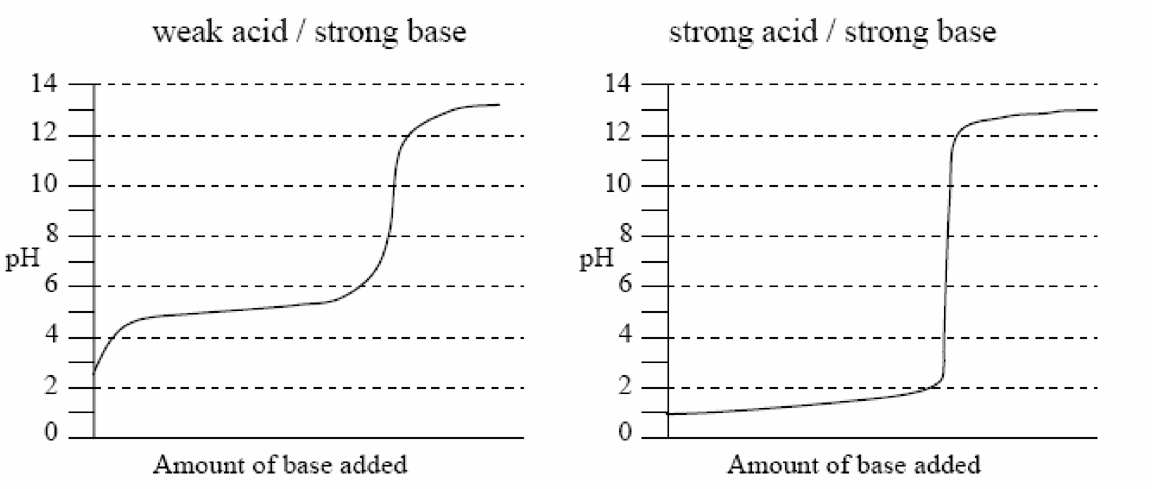
Stalactites and stalagmites can be found in many limestone caves. How do these form? Use appropriate chemical equations in your explanation.

When the water rich in Ca^{2+} and HCO_3^{-} ions from the formation of caves (see above) percolates through the cave, the water evaporates and the $CO_2(g)$ escapes into the atmosphere.

This pushes the equilibrium of the above reaction to the left and the $CaCO_3$ reprecipitates as limestone forming the stalagmites and stalactites.

Marks
7

- The titration curves for a titration of a weak acid with a strong base and for a strong acid with a strong base are distinctly different. Draw a diagram for each case.



List the main differences.

(i) **The initial starting pH is higher than for the strong acid than for the weak acid.**

(ii) **The equivalence point, where the moles of added base is the same as the initial moles of acid, is at pH = 7 for the strong acid/strong base case but it is at pH >7 for the weak acid/strong base.**

(iii) **The weak acid/strong base curve has an inflexion point at the half equivalence point. No such point is seen on the strong base/strong acid curve.**

Explain these differences.

(i) **This is because the strong acid dissociates completely but the weak acid dissociates only to a small extent. Thus, assuming equal concentrations of strong and weak acid, $[H_3O(aq)]^+$ is thus larger for the strong acid and the pH is lower.**

(ii) **At the equivalence point, the conjugate base of the acid is present. For the strong acid, the conjugate base is an extremely weak base and the solution is neutral. For the weak acid, the conjugate base is a weak base and the solution thus has pH > 7.**

(iii) **At the half-equivalence point, the weak acid and its conjugate base have equal concentrations and the pH is equal to pK_a. as given by the Henderson-Hasselbalch equation. This is the point of maximum buffering so that addition of extra base has limited effect on the pH.**

ANSWER CONTINUES ON THE NEXT PAGE

- What is the difference between the ‘end point’ and the ‘equivalence point’ in a titration.

2

The end point is the first permanent change of the indicator – it is when you see that the reaction has finished.

The equivalence point is when the stoichiometrically correct amount of reactant has been added.

Marks

- What is the pH of a 0.020 M solution of HF? The pK_a of HF is 3.17.

2

As HF is a weak acid, [H_3O^+] must be calculated using a reaction table:

	HF	H_2O	$\rightleftharpoons$	H_3O^+	F^-
initial	**0.020**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.020 – x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = \frac{x^2}{0.020 - x}$$

As pK_a = -log$_{10}$(K_a), K_a = $10^{-3.17}$ and is very small. Hence, 0.020 – x ~ 0.020 and hence:

$$x^2 = 0.020 \times 10^{-3.17} \quad \text{or} \quad x = 3.68 \times 10^{-3}\ \text{M} = [H_3O^+]$$

Hence, the pH is given by:

$$\text{pH} = -\log_{10}[H_3O^+] = -\log_{10}[(3.68 \times 10^{-3})] = 2.43$$

pH = **2.43**

- What is the pH of a solution that is 0.075 M in acetic acid and 0.150 M in sodium acetate? The pK_a of CH_3COOH is 4.76.

2

This solution containing a weak acid (CH_3COOH) and its conjugate base (CH_3COO^-) is a buffer and the Henderson-Hasselbalch equation can be used to calculate the pH:

$$\text{pH} = \text{p}K_a + \log_{10}\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \text{p}K_a(CH_3COOH) + \log_{10}\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$\text{pH} = 4.76 + \log_{10}\left(\frac{0.150}{0.075}\right) = 5.06$$

pH = **5.06**

THE ANSWER CONTINUES ON THE NEXT PAGE

- What is the pH of a 0.010 M solution of $Ba(OH)_2$?

2

$Ba(OH)_2$ is a strong base and dissociates completely according to the equation:

$$Ba(OH)_2(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

Hence a 0.010 M solution has $[OH^-(aq)] = 2 \times 0.010 = 0.020$ M.

As $pOH = -\log_{10}([OH^-(aq)])$, $pOH = -\log_{10}(0.020) = 1.70$.

In aqueous solution, $pH + pOH = 14.00$ so $pH = (14.00 – 1.70) = 12.30$

pH = **12.30**

Marks
6

- Complete the following table.

Formula	Oxidation state of transition metal	Coordination number of transition metal	Number of *d*-electrons in transition metal	Species formed upon dissolving in water
$Na_2[Ni(CN)_4]$	**II**	**4**	**8**	**$Na^+(aq)$,** **$[Ni(CN)_4]^{2-}(aq)$**
$[Cr(NH_3)_5Cl]Cl_2$	**III**	**6**	**3**	**$[Cr(NH_3)_5Cl]^+(aq)$,** **$Cl^-(aq)$**
$[Cu(en)_3]Br_2$	**II**	**6**	**9**	**$[Cu(en)_3]^{2+}(aq)$,** **$Br^-(aq)$**

en = ethylenediamine = $NH_2CH_2CH_2NH_2$

- Give the name of the starting material where indicated and the constitutional formula of the major organic product formed in each of the following reactions.

Marks
8

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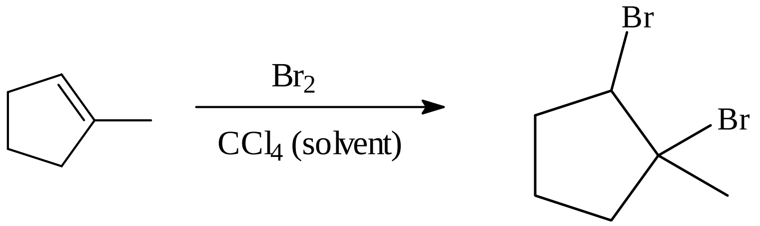
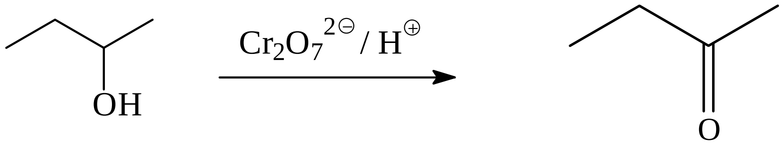
Marks
8

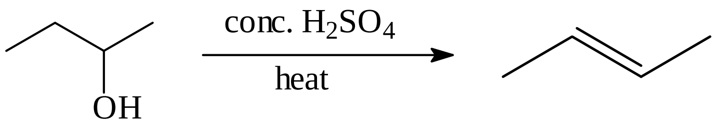


Name: 1-methylcyclopentene

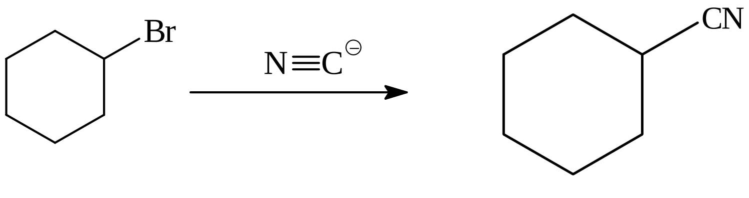
(Markovnikov addition of H_2O with H adding to the less substituted end of the double bond)



Name: 2-butanol



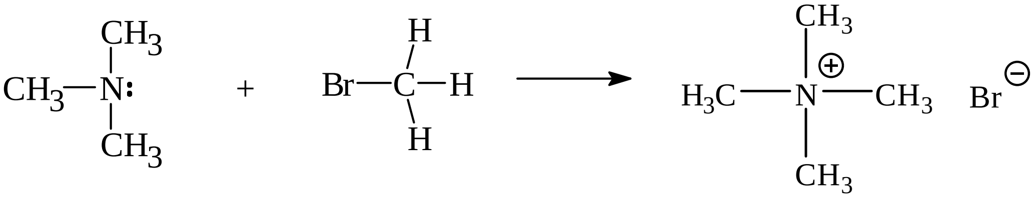
(Dehydration leading to more substituted double bond: Zeitsev's rule)



Name: bromocyclohexane

Marks
3

- Classify the starting materials for the following reaction as nucleophile or electrophile in the boxes provided and draw the structure of the product.



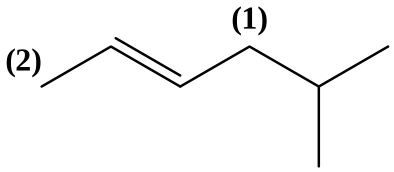
nucleophile

electrophile

2

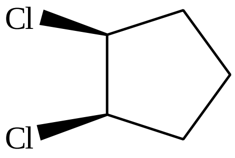
- Draw the constitutional formula for each of the following compounds.

(E)-5-methylhex-2-ene



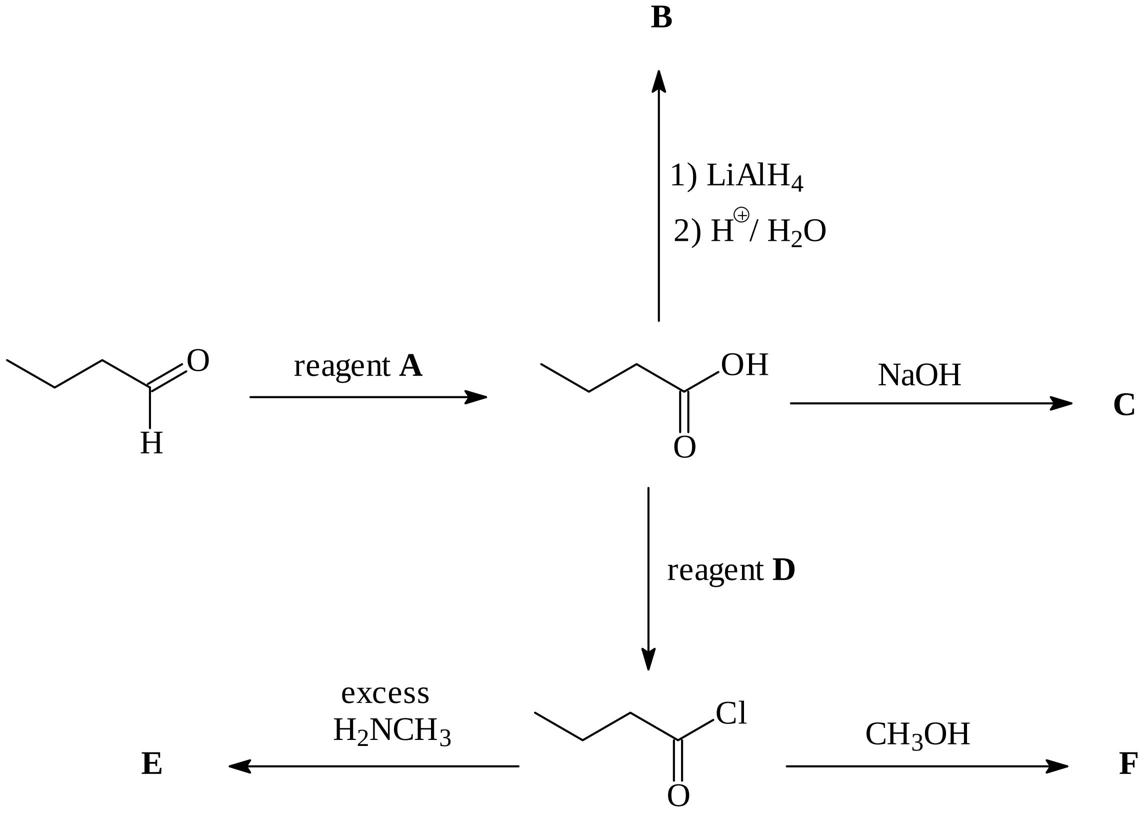
(Highest priority substituents on opposite sides of the double bond: (*E*))

cis-1,2-dichlorocyclopentane

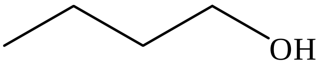
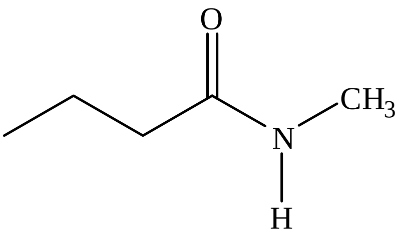
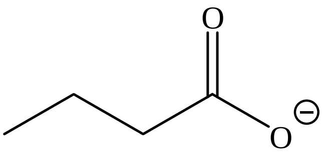
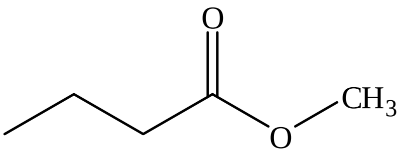


Marks
6

- Consider the following reaction sequence.



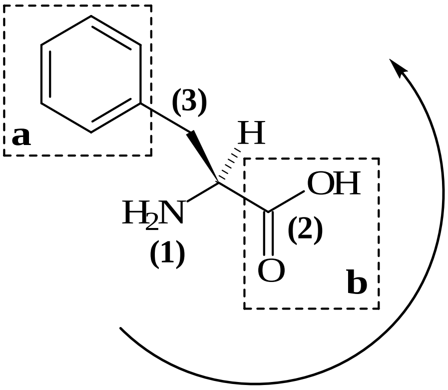
Give the reagents **A** and **D** and draw the structures of the major organic products, **B**, **C**, **E** and **F**, formed in these reactions.

A	**D**
$Cr_2O_7^{2-}$ / H^+	$SOCl_2$
B	**E**
	
C	**F**
	

Marks
6

- Phenylalanine is a naturally occurring amino acid. Only the enantiomer (**X**) is commonly produced in nature.

(X)

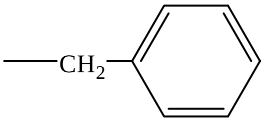


(Anticlockwise: (*S*))

What is the molecular formula of (**X**)? **$C_9H_{11}O_2N$**

List the substituents attached to the stereogenic centre in descending order of priority according to the sequence rules.

highest priority lowest priority

$-NH_2$	**-COOH**		**-H**

What is the absolute stereochemistry of (**X**)? Write (*R*) or (*S*). **(*S*)**

Name the functional groups, highlighted by the boxes **a** and **b**, present in (**X**).

a = arene (aromatic ring)	**b = carboxylic acid**