Topics in the November 2010 Exam Paper for CHEM1002

Click on the links for resources on each topic.

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- Intermolecular Forces and Phase Behaviour
- Physical States and Phase Diagrams

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- Crystal Structures

2010-N-4:

- Strong Acids and Bases
- Calculations Involving pK_a

2010-N-5:

- Solubility Equilibrium

2010-N-6:

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- Kinetics

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- Aldehydes and Ketones
- Alcohols
- Carboxylic Acids and Derivatives
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2010-N-8:

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- Representations of Molecular Structure
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2010-N-10:

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2010-N-11:

- Alcohols
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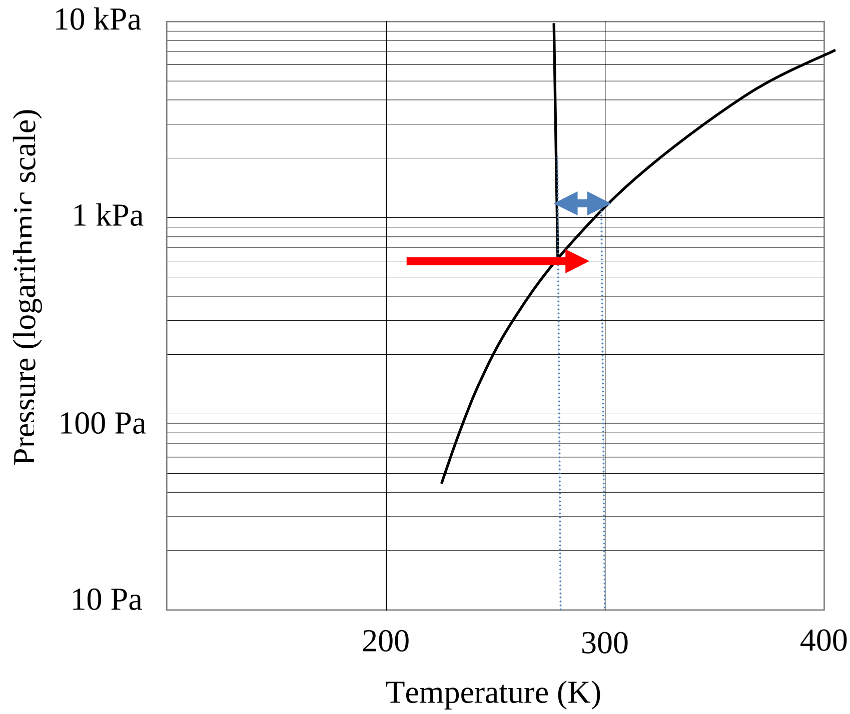
Marks
5

- The diagram below shows part of the phase diagram of water.



The average pressure on the surface of Mars is around 0.6 kPa. If the night time temperature is –60 °C and a summer day temperature is 20 °C, describe what happens to any water on the surface of Mars as the sun rises.

This process is illustrated by the red arrow in the phase diagram above. The process occurs just *below* the triple point so the phase changes from solid (at –60 °C) to gas (at 20 °C).

Water sublimes as the sun rises on Mars.

(Note the logarithmic scale on the graph. Each horizontal line between 100 Pa (0.1 kPa) and 1 kPa (1000 Pa) represents an increase of 100 Pa (0.1 kPa).)

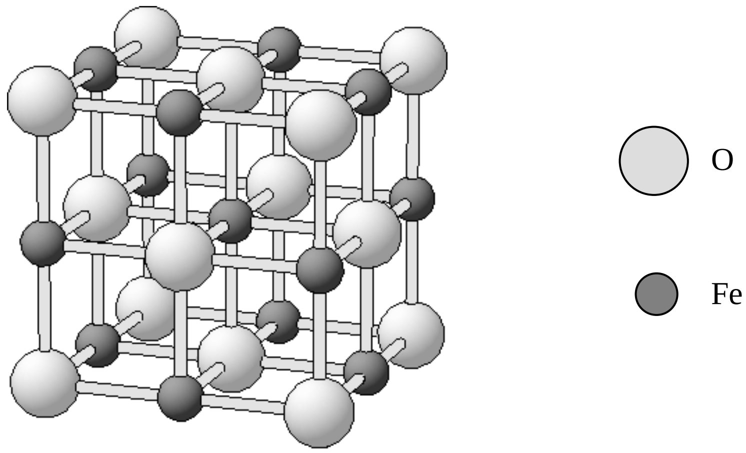
The highest surface pressure on Mars is thought to occur at the Hellas Basin, a low-lying area created by the impact of a large asteroid. If the pressure in this region is 1.2 kPa, use the phase diagram to estimate the temperature range in which liquid water will occur. Show your working on the phase diagram.

At 1.2 kPa, water is a liquid in the temperature range covered by the double-headed blue arrow in the phase diagram above.

Within the accuracy possible on the diagram, this corresponds to the temperature range 272 – 305 K.

Marks 8

- Iron forms three common oxides, FeO, Fe_3O_4 and Fe_2O_3. The unit cell for one of these oxides is shown below.



Explain which oxide the structure represents and describe the nature of the packing of the ions and their coordination numbers.

The structure contains 1 Fe atom at the centre and 12 Fe atoms on the edges. The atoms on the edges are shared between 4 cells and so contribute 1/4 to each:

number of Fe atoms = 1 (centre) + 12 × 1/4 (edges) = 4

The structure contains 8 O atoms on the corners and 6 O atoms on the faces. The atoms on the corners are shared between 8 cells and so contribute 1/8 to each and the atoms on the faces are shared between 2 cells and so contribute 1/2 to each:

number of O atoms = 8 × 1/8 (corners) + 6 × 1/2 = 4

There are 4 Fe atoms and 4 O atoms in the unit cell: the stoichimetry is Fe_4O_4 or FeO.

The coordination number is 6 for both Fe and O. The structure can be described as the cubic close packed arrangement of O atoms, with Fe in all of the octahedral holes.

The mineral magnetite, Fe_3O_4, is found in the beaks of homing pigeons. It contains a mixture of Fe^{2+} and Fe^{3+} ions. What is the ratio of Fe^{2+} to Fe^{3+} in Fe_3O_4?

As each O has an oxidation number of -2 and there are 4 of them in the formula, the 3 Fe atoms must together have a charge of +8. This is consistent with their being two Fe^{3+} ions and one Fe^{2+} per formula unit.

The ratio of Fe^{3+} to Fe^{2+} is 2 to 1.

ANSWER CONTINUES ON THE NEXT PAGE

How many unpaired electrons are there in an Fe^{2+} ion and in an Fe^{3+} ion? Explain your answer using the box notation.

Fe is in Group 8 so Fe^{2+} has a d^6 configuration and Fe^{3+} has a d^5 configuration. These electrons arrange in the five *d*-orbitals to minimise the repulsion between them by maximising the number of unpaired electrons:

Fe^{2+}	↑↓	↑	↑	↑	↑
Fe^{3+}	↑	↑	↑	↑	↑

Fe^{2+} has 4 unpaired electrons and Fe^{3+} has 5 unpaired electrons.

Fe^{2+}: **4**	Fe^{3+}: **5**

Marks 8

- Hydrochloric acid in a healthy human stomach leads to a pH in the range 1-2. What is the concentration of hydrochloric acid in the stomach?

As pH = -log$_{10}$[H_3O^+(aq)] and HCl is a strong acid, these pH values correspond to:

[H_3O^+(aq)] = 10^{-pH} = 0.1 M at pH = 1

[H_3O^+(aq)] = 10^{-pH} = 0.01 M at pH = 2

Answer: **0.01 – 0.1 M**

The stomach also contains considerable amounts of chloride ions, the conjugate base of hydrochloric acid, in the form of dissolved KCl and NaCl. Is this solution a buffer? Explain your answer.

No. A buffer contains a mixture of a *weak* acid and its conjugate base. HCl is a very, very strong acid and so Cl^- is a very, very weak base.

If acid is added to the stomach, there is no base for it to react with and so the pH will lower considerably.

If base is added to the stomach, it will react with the H_3O^+ present and the pH will rise considerably.

This is *not* the action of a buffer.

Milk of magnesia is often taken to reduce the discomfort of acid stomach. A teaspoon of milk of magnesia, containing 0.400 g of $Mg(OH)_2$, is added to a 0.300 L stomach solution with a pH of 1.3. What is the final pH of the solution?

The molar mass of $Mg(OH)_2$ is (24.31 (Mg) + 2 × 16.00 (O) + 2 × 1.008 (H)) g mol^{-1} = 58.326 g mol^{-1}.

The number of moles in 0.400 g is therefore:

number of moles = mass / molar mass
= (0.400 g) / (58.326 g mol^{-1}) = 0.00686 mol

The number of moles of OH^- added to the stomach is therefore:

number of moles of OH^- = 2 × 0.00686 mol = 0.0137 mol

ANSWER CONTINUES ON THE NEXT PAGE

If the pH is originally 1.3, $[H_3O^+(aq)] = 10^{-pH} = 10^{-1.3} = 0.050$ M. The number of moles originally present in 0.300 L is therefore:

number of moles of H_3O^+ = concentration × volume
= (0.050 mol L^{-1}) × (0.300 L) = 0.0150 mol

This will react with the added OH^-, leaving:

number of moles of H_3O^+ = (0.0150 – 0.0137) mol = 0.0013 mol

Hence, the final concentration of H_3O^+ is

$[H_3O^+(aq)]$ = number of moles / volume
= (0.0013 mol) / (0.300 L) = 0.0043 M

Finally,

$pH = -\log_{10}[H_3O^+(aq)] = 2.4$

Answer: **2.4**

Marks 5

- Nickel metal can be extracted and recycled from mobile phone batteries. This process leads to solutions containing both Cu^{2+}(aq) and Ni^{2+}(aq) ions. Separation of these ions is achieved by adding tiny amounts of sulfide ions as the metal sulfides have low and very different solubilities: $K_{sp}(CuS) = 8 \times 10^{-34}$ and $K_{sp}(NiS) = 3 \times 10^{-19}$.

  An aqueous solution has $[Ni^{2+}(aq)] = 0.0100$ M and an unknown concentration of Cu^{2+}(aq) ions. S^{2-}(aq) ions are added in small increments. CuS begins to precipitate when $[S^{2-}(aq)] = 8 \times 10^{-32}$ M. What was the original value of $[Cu^{2+}(aq)]$?

The solubility of CuS is *much* lower than NiS as its K_{sp} value is *much* smaller. When CuS begins to precipitate, virtually none will be left in solution.

CuS(s) dissolves to give Cu^{2+}(aq) and S^{2-}(aq), so $K_{sp}(CuS) = [Cu^{2+}(aq)][S^{2-}(aq)]$.

As $K_{sp} = 8 \times 10^{-34}$ and precipitation occurs when $[S^{2-}(aq)] = 8 \times 10^{-32}$ M,

$$[Cu^{2+}(aq)] = K_{sp}(CuS) / [S^{2-}(aq)] = (8 \times 10^{-34}) / (8 \times 10^{-32}) = 0.01 \text{ M}$$

Answer: **0.01 M**

At what $[S^{2-}(aq)]$ will NiS precipitate?

NiS(s) dissolves to give Ni^{2+}(aq) and S^{2-}(aq), so $K_{sp}(NiS) = [Ni^{2+}(aq)][S^{2-}(aq)]$.

As $K_{sp} = 3 \times 10^{-19}$ and $[Ni^{2+}(aq)] = 0.0100$ M,

$$[S^{2-}(aq)] = K_{sp}(NiS) / [Ni^{2-}(aq)] = (3 \times 10^{-19}) / (0.0100) = 3 \times 10^{-17} \text{ M}$$

Answer: **3×10^{-17} M**

If the CuS formed is filtered off before any NiS precipitates, how pure will the NiS precipitate be?

From above, NiS precipitates when $[S^{2-}(aq)] = 3 \times 10^{-17}$ M. At this concentration,

$$[Cu^{2+}(aq)] = K_{sp}(CuS) / [S^{2-}(aq)] = (8 \times 10^{-34}) / (3 \times 10^{-17}) = 3 \times 10^{-17} \text{ M}$$

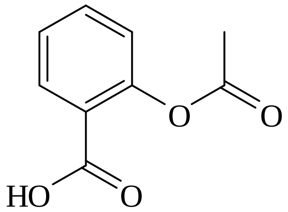
When NiS starts to precipitate, $[Ni^{2+}(aq)] = 0.0100$ M and $[Cu^{2+}(aq)] = 3 \times 10^{-17}$ M.

The NiS that precipitates will contain *very* little Cu^{2+}: it will be *very* pure.

Answer: **100%**

Marks 8

- The structure of common aspirin, acetylsalicylic acid, is shown below. It has a pK_a value of 3.5.



Calculate the pH of a solution in which one normal adult dose (0.65 g) is dissolved in 250 mL of water.

The chemical formula of acetylsalicylic acid is $C_9H_8O_4$. It has a molar mass of (9 × 12.01 (C) + 8 × 1.008 (H) + 4 × 16.00 (O)) g mol^{-1} = 180.154 g mol^{-1}.

The number of moles present corresponds to:

number of moles = mass / molar mass
= (0.65 g) / (180.154 g mol^{-1}) = 0.00361 mol

The concentration when this amount is dissolved in 250 mL of water is therefore:

[aspirin] = number of moles / volume
= (0.00361 mol) / (0.25 L) = 0.0144 M

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

	$C_9H_8O_4$	H_2O	$\rightleftharpoons$	H_3O^+	$C_9H_7O_4^-$
initial	**0.0144**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.144 –x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][C_9H_7O_4^-]}{[C_9H_7O_4]} = \frac{x^2}{0.0144 - x}$$

As pK_a = -log$_{10}K_a$, K_a = 10$^{-3.5}$ and is very small, 0.0144 – x ~ 0.0144 and hence:

$x^2 = 0.0144 \times 10^{-3.5}$ or $x = 2.1 \times 10^{-3}$ M = [H_3O^+]

Hence, the pH is given by:

pH = $-\log_{10}[H_3O^+] = -\log_{10}(2.1 \times 10^{-3}) = 2.7$

Answer: **2.7**

If blood has a pH of 7.4, what percentage of aspirin is present in the deprotonated form in a solution consisting of one normal adult dose in 250 mL of blood?

Using the Henderson – Hasselbalch equation,

$$\mathbf{pH = p}\boldsymbol{K}_\mathbf{a}\mathbf{ + log}\frac{[\mathbf{base}]}{[\mathbf{acid}]}$$

At a pH of 7.4

$$\mathbf{7.4 = 3.5 + log}\frac{[\mathbf{base}]}{[\mathbf{acid}]} \quad \mathbf{so} \quad \frac{[\mathbf{base}]}{[\mathbf{acid}]} = \mathbf{10^{3.9} = 7900}$$

The deprotonated, conjugate base form completely dominates at this pH.

Answer: **100% base**

Solutions of aspirin are unstable due to hydrolysis. If 0.26 g of a normal adult dose remains after 4 hours, what is the half-life of aspirin?

The number of moles present after 4 hours corresponds to:

number of moles = mass / molar mass
= (0.26 g) / (180.154 g mol^{-1}) = 0.00144 mol

The concentration when this amount is dissolved in 250 mL of water is therefore:

[aspirin] = number of moles / volume
= (0.00144 mol) / (0.25 L) = 0.00577 M

The amount present after time *t* is related to the amount initially present through the equation:

$$\mathbf{ln[A] = ln[A]_0 - }\boldsymbol{kt}$$

From above, $[A]_0$ = 0.0144 M. As [A] = 0.00577 M with *t* = 4 hours:

$$\mathbf{ln(0.00577) = ln(0.0144) -} \boldsymbol{k} \times \mathbf{4}$$

$$\boldsymbol{k}\mathbf{ = 0.23}$$

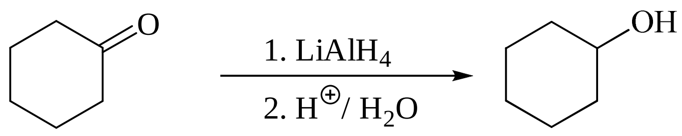
Finally, the half life, $t_{1/2}$, is given by

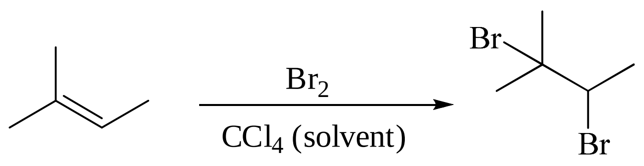
$$t_{1/2} = \mathbf{ln2} / k = \mathbf{3\ hours}$$

Answer: **3 hours**

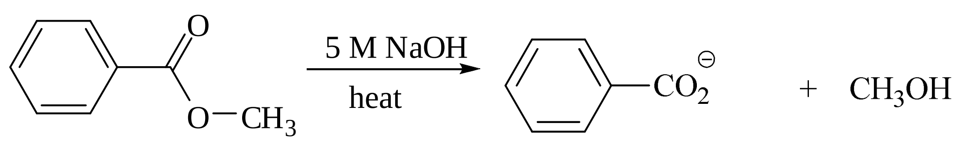
Marks
9

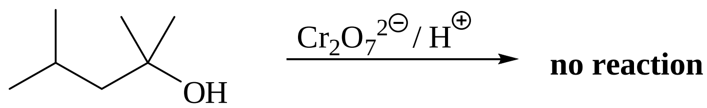
- Give the name of the starting material where indicated and the constitutional formula(s) of the major organic product(s) formed in each of the following reactions. NB: if there is no reaction, write "no reaction".



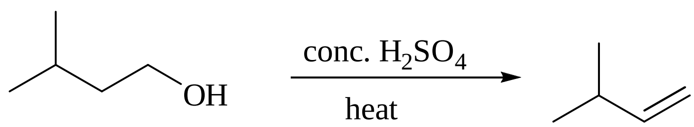


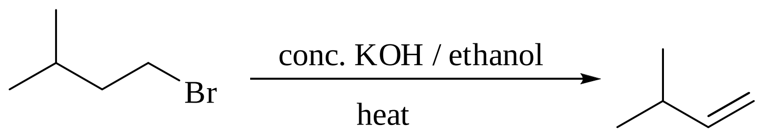
Name: 2-methyl-2-butene





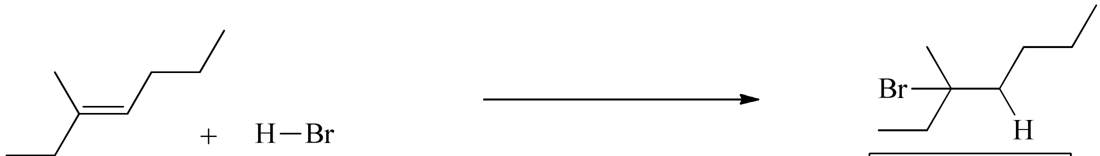
Name: 2,4-dimethylpentan-2-ol





Marks
5

- Classify the starting materials for each of the following reactions as nucleophile or electrophile in the boxes provided. Classify the products of the reactions as primary (1°), secondary (2°), tertiary (3°) or quaternary (4°) in the boxes provided.



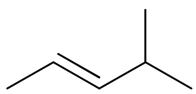
nucleophile | **electrophile** | **tertiary (3°)**

nucleophile | **electrophile** | **quaternary (4°)**

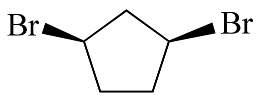
- Draw the constitutional formula for each of the following compounds.

3

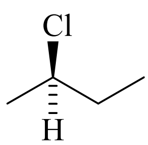
(E)-4-methylpent-2-ene



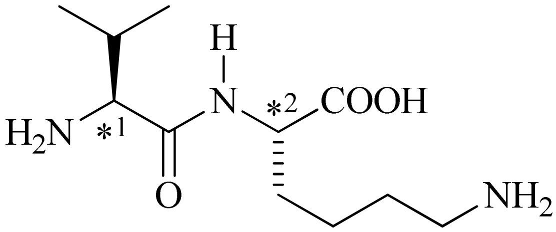
cis-1,3-dibromocyclopentane



(*R*)-2-chlorobutane



- Consider the following molecule (**M**) isolated from a natural source.



(**M**)

Indicate on the above structure all stereogenic centres in molecule (**M**).
Use numbered asterisks (∗1, ∗2, *etc*.).

Select one of these stereogenic centres and determine its absolute configuration.
Show your working.

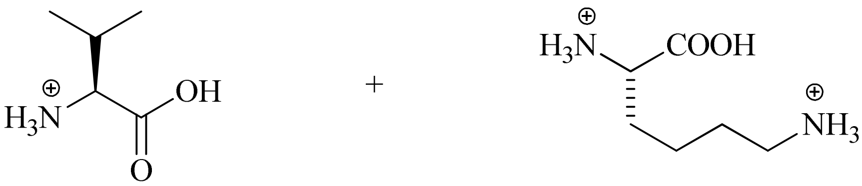
Priorities at *1: –NH_2 > –CONHR > –$CH(CH_3)_2$ > –H

With H at back these groups go anticlockwise. Therefore (*S*)- configuration about *1.

Priorities at *2: –NHCOR > –COOH > –$(CH_2)_4NH_2$ > –H

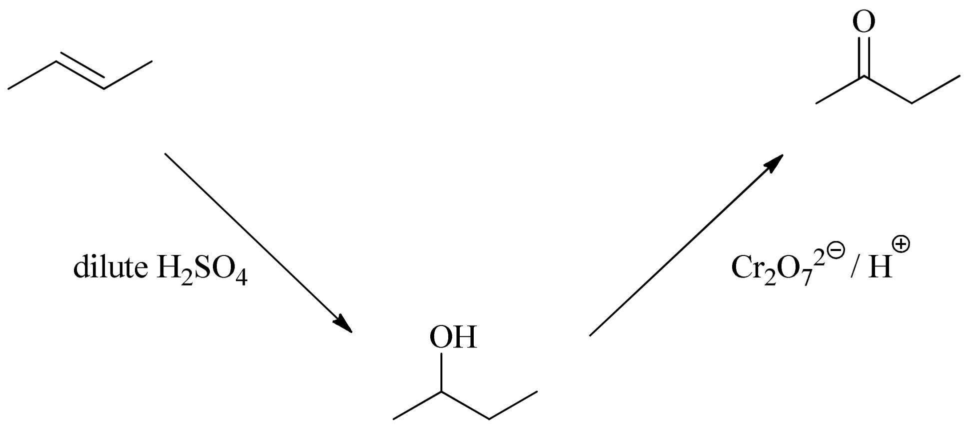
With H at front these groups go clockwise. Therefore, with H at back, they would go anticlockwise. Therefore (*S*)- configuration about *2.

Give the products when molecule (**M**) is hydrolysed by heating it with 6 M HCl.
Make sure you show the products in their correct ionisation states.



Marks
8

- Show clearly the reagents you would use to carry out the following chemical conversion. Two steps are required. Give the structure of the intermediate compound.



How can IR spectroscopy distinguish between the starting material, the intermediate and the product?

The product absorbs strongly in the 1650-1800 cm^{-1} region.

The intermediate alcohol absorbs strongly in the 3000-3300 cm^{-1} region.

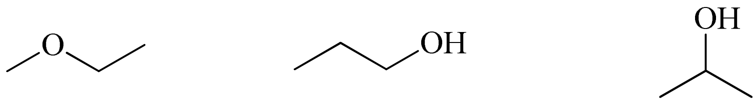
The starting material does not absorb strongly in either of these regions.

How can ^{13}C NMR spectroscopy distinguish between the starting material and the product?

The starting material is symmetrical and has only 2 resonances whilst the product has 4 resonances.

Marks
5

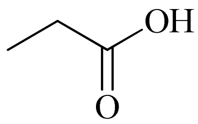
- Compound **X** is known to have the molecular formula C_3H_8O. Draw the constitutional formulas of the three possible isomers that could be compound **X**.



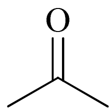
Compound **X** reacts with acidified potassium dichromate solution to give compound **Y**. Give the possible structure(s) of compound **Y**.

$\downarrow$ $\downarrow$ $\downarrow$

no reaction



propionic acid
(or propanoic acid)



acetone

Describe a simple **chemical test** that could be used to identify compound **Y**. Give the reagent(s) used and any expected observation(s).

Propionic acid is an acid and acetone is not. Any reaction that detects the presence of an acid – such as simple addition of universal indicator – would be able to identify whether propionic acid or acetone is present.

An alternative is addition of $NaHCO_3(aq)$. The propionic acid will react to produce bubbles of CO_2. Acetone will not react.