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# 2014 AUSTRALIAN SCIENCE OLYMPIAD EXAM

## CHEMISTRY – SECTIONS A & B

TO BE COMPLETED BY THE STUDENT. USE CAPITAL LETTERS

**Student Name:** .....

**Home Address:** .....

..... **Post Code:** .....

**Telephone:** (.....) ..... **Mobile:** .....

**E-Mail:** ..... **Date of Birth:** ...../...../.....

☐ Male ☐ Female

**Year 10** ☐ **Year 11** ☐ **Other:** .....

**Name of School:** ..... **State:** .....

To be eligible for selection for the Australian Science Olympiad Summer School, students must be able to hold an Australian passport by the time of team selection (March 2015).

The Australian Olympiad teams in Biology, Chemistry and Physics will be selected from students participating in the Australian Science Olympiad Science Summer School.

Please note - students in Yr12 in 2014 are not eligible to attend the 2015 Australian Science Olympiad Science Summer School

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## 2014 Australian Science Olympiad Exam

***Time Allowed:***

***Reading Time: 10 minutes***

***Examination Time: 120 minutes***

### INSTRUCTIONS

- Attempt *ALL* questions in *ALL* sections of this paper.
- Permitted materials: Non-programmable non-graphical calculator, pens, pencils, erasers and a ruler.
- Answer SECTION A on the Multiple Choice Answer Sheet provided. **Use a pencil.**
- Answer SECTION B in the spaces provided in this paper. Write in pen and use a pencil only for graphs.
- Ensure that your diagrams are clear and labelled.
- All numerical answers must have correct units.
- Marks will not be deducted for incorrect answers.
- Rough working must be done only on pages 27 to 28 of this booklet.
- Relevant data that may be required for a question will be found on page 3.
- Do not staple the multiple choice answer sheet to this booklet.

### MARKS

|           |                              |           |
|-----------|------------------------------|-----------|
| SECTION A | 15 multiple choice questions | 30 marks  |
| SECTION B | 3 short answer questions     | 90 marks  |
|           | Total marks for the paper    | 120 marks |

## DATA

|                                                                                                                                         |                                         |                                                                                                                                                                                                                                                                                           |                                      |
|-----------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|
| Avogadro constant (N)                                                                                                                   | $6.022 \times 10^{23} \text{ mol}^{-1}$ | Velocity of light (c)                                                                                                                                                                                                                                                                     | $2.998 \times 10^8 \text{ m s}^{-1}$ |
| 1 faraday                                                                                                                               | 96,486 coulombs                         | Density of water at 25°C                                                                                                                                                                                                                                                                  | $0.9971 \text{ g cm}^{-3}$           |
| 1 coulomb                                                                                                                               | $1 \text{ A s}^{-1}$                    | Acceleration due to gravity                                                                                                                                                                                                                                                               | $9.81 \text{ m s}^{-2}$              |
| Universal gas constant (R)<br>$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$<br>$8.206 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ |                                         | 1 newton (N)                                                                                                                                                                                                                                                                              | $1 \text{ kg m s}^{-2}$              |
| Planck's constant (h)                                                                                                                   | $6.626 \times 10^{-34} \text{ J s}$     | 1 pascal (Pa)                                                                                                                                                                                                                                                                             | $1 \text{ N m}^{-2}$                 |
| Standard temperature and pressure (STP)<br>273 K and 100 kPa<br>0°C and 100 kPa<br>0°C and 1 bar<br>0°C and 750 mm Hg                   |                                         | $\text{pH} = -\log_{10}[\text{H}^+]$<br>$\text{pH} + \text{pOH} = 14.00 \text{ at } 25^\circ\text{C}$<br>$K_a = \{[\text{H}^+][\text{A}^-]\} / [\text{HA}]$<br>$\text{pH} = \text{p}K_a + \log_{10}\{[\text{A}^-] / [\text{HA}]\}$<br>$\text{PV} = nRT$<br>$E = h\nu$<br>$c = \nu\lambda$ |                                      |
| Molar volume of ideal gas at STP                                                                                                        | 22.71 L                                 | Surface area of sphere $A = 4\pi r^2$                                                                                                                                                                                                                                                     |                                      |
| 1 bar = 100 kPa                                                                                                                         |                                         |                                                                                                                                                                                                                                                                                           |                                      |

## Periodic table of the Elements

|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
|-------|--|-------|--|----|--|----|--|----|--|----|--|----|--|-------|--|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|--|--|--|--|--|--|--|
| 1A    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       |       |       |       |       |       |       |       | 8A    |       |       |       |       |       |       |  |  |  |  |  |  |  |
| 1     |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       |       |       |       |       |       |       |       | 2     |       |       |       |       |       |       |  |  |  |  |  |  |  |
| H     |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       |       |       |       |       |       |       |       | He    |       |       |       |       |       |       |  |  |  |  |  |  |  |
| 1.008 |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       |       |       |       |       |       |       |       | 4.003 |       |       |       |       |       |       |  |  |  |  |  |  |  |
| 3     |  | 4     |  |    |  |    |  |    |  |    |  |    |  | 5     |  | 6     |       | 7     |       | 8     |       | 9     |       | 10    |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| Li    |  | Be    |  |    |  |    |  |    |  |    |  |    |  | B     |  | C     |       | N     |       | O     |       | F     |       | Ne    |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| 6.941 |  | 9.012 |  |    |  |    |  |    |  |    |  |    |  | 10.81 |  | 12.01 |       | 14.01 |       | 16.00 |       | 19.00 |       | 20.18 |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| 11    |  | 12    |  |    |  |    |  |    |  |    |  |    |  | 13    |  | 14    |       | 15    |       | 16    |       | 17    |       | 18    |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| Na    |  | Mg    |  | 3B |  | 4B |  | 5B |  | 6B |  | 7B |  | 8B    |  | 1B    |       | 2B    |       | 3A    |       | 4A    |       | 5A    |       | 6A    |       | 7A    |       | Ar    |       |       |       |  |  |  |  |  |  |  |
| 22.99 |  | 24.31 |  |    |  |    |  |    |  |    |  |    |  |       |  |       |       |       |       | 26.98 |       | 28.09 |       | 30.97 |       | 32.06 |       | 35.45 |       | 39.95 |       |       |       |  |  |  |  |  |  |  |
| 19    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 20    | 21    | 22    | 23    | 24    | 25    | 26    | 27    | 28    | 29    | 30    | 31    | 32    | 33    | 34    | 35    | 36    |  |  |  |  |  |  |  |
| K     |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Ca    | Sc    | Ti    | V     | Cr    | Mn    | Fe    | Co    | Ni    | Cu    | Zn    | Ga    | Ge    | As    | Se    | Br    | Kr    |  |  |  |  |  |  |  |
| 39.10 |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 40.08 | 44.96 | 47.88 | 50.94 | 52.00 | 54.94 | 55.85 | 58.93 | 58.69 | 63.55 | 65.38 | 69.72 | 72.59 | 74.92 | 78.96 | 79.90 | 83.80 |  |  |  |  |  |  |  |
| 37    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 38    | 39    | 40    | 41    | 42    | 43    | 44    | 45    | 46    | 47    | 48    | 49    | 50    | 51    | 52    | 53    | 54    |  |  |  |  |  |  |  |
| Rb    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Sr    | Y     | Zr    | Nb    | Mo    | Tc    | Ru    | Rh    | Pd    | Ag    | Cd    | In    | Sn    | Sb    | Te    | I     | Xe    |  |  |  |  |  |  |  |
| 85.47 |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 87.62 | 88.91 | 91.22 | 92.91 | 95.94 | (98)  | 101.1 | 102.9 | 106.4 | 107.9 | 112.4 | 114.8 | 118.7 | 121.8 | 127.6 | 126.9 | 131.3 |  |  |  |  |  |  |  |
| 55    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 56    | 57    | 72    | 73    | 74    | 75    | 76    | 77    | 78    | 79    | 80    | 81    | 82    | 83    | 84    | 85    | 86    |  |  |  |  |  |  |  |
| Cs    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Ba    | La    | Hf    | Ta    | W     | Re    | Os    | Ir    | Pt    | Au    | Hg    | Tl    | Pb    | Bi    | Po    | At    | Rn    |  |  |  |  |  |  |  |
| 132.9 |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 137.3 | 138.9 | 178.5 | 180.9 | 183.9 | 186.2 | 190.2 | 192.2 | 195.1 | 197.0 | 200.6 | 204.4 | 207.2 | 209.0 | (209) | (210) | (222) |  |  |  |  |  |  |  |
| 87    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 88    | 89    | 104   | 105   | 106   | 107   | 108   | 109   | 110   |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| Fr    |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Ra    | Ac    | Rf    | Db    | Sg    | Bh    | Hs    | Mt    | Ds    |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
| (223) |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 226.0 | (227) |       |       |       |       |       |       |       |       |       |       |       |       |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 58    | 59    | 60    | 61    | 62    | 63    | 64    | 65    | 66    | 67    | 68    | 69    | 70    | 71    |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Ce    | Pr    | Nd    | Pm    | Sm    | Eu    | Gd    | Tb    | Dy    | Ho    | Er    | Tm    | Yb    | Lu    |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 140.1 | 140.9 | 144.2 | (145) | 150.4 | 152.0 | 157.3 | 158.9 | 162.5 | 164.9 | 167.3 | 168.9 | 173.0 | 175.0 |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 90    | 91    | 92    | 93    | 94    | 95    | 96    | 97    | 98    | 99    | 100   | 101   | 102   | 103   |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | Th    | Pa    | U     | Np    | Pu    | Am    | Cm    | Bk    | Cf    | Es    | Fm    | Md    | No    | Lr    |       |       |       |  |  |  |  |  |  |  |
|       |  |       |  |    |  |    |  |    |  |    |  |    |  |       |  |       | 232.0 | (231) | 238.0 | (237) | (244) | (243) | (247) | (247) | (251) | (252) | (257) | (258) | (259) | (260) |       |       |       |  |  |  |  |  |  |  |

Atomic mass values given here are to four significant figures. A value given in parentheses denotes the mass of the longest-lived isotope.

## SECTION A: MULTIPLE CHOICE

### USE THE ANSWER SHEET PROVIDED

1. In which one of the following pairs is the radius of the second atom greater than that of the first?
  - (a) Na, Mg
  - (b) Sr, Ca
  - (c) Br, Cl
  - (d) Si, P
  - (e) N, P
  
2. Elements X and Y are in the same period of the Periodic Table and have 2 and 5 electrons respectively in the outer shell. What is the likely formula of the compound they form together?
  - (a)  $X_2Y_5$
  - (b)  $X_2Y_3$
  - (c) XY
  - (d)  $X_3Y_2$
  - (e)  $X_5Y_2$
  
3. In an analysis of a solution containing barium ions ( $Ba^{2+}$ ), 50.0 mL of the solution gave 0.244 g of barium sulfate ( $BaSO_4$ ) (molar mass =  $233 \text{ g mol}^{-1}$ ) upon addition of sufficient sulfuric acid to precipitate all the  $Ba^{2+}$  ions present. What is the concentration (in  $\text{mol L}^{-1}$ ) of the  $Ba^{2+}$  ions in the solution?
  - (a)  $\frac{1000}{50.0} \times \frac{0.244}{233}$
  - (b)  $\frac{50.0}{1000} \times \frac{0.244}{233}$
  - (c)  $\frac{1000}{50.0} \times \frac{233}{0.244}$
  - (d)  $\frac{1}{50.0} \times \frac{233}{0.244}$
  - (e)  $50.0 \times \frac{0.244}{233}$

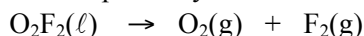
4. Which one of the following elements is likely to have an electronegativity most similar to that of aluminium?
- (a) barium
  - (b) beryllium
  - (c) calcium
  - (d) magnesium
  - (e) strontium
5. Which one of the following statements is correct about allotropes of an element?
- (b) they have the same chemical reactivity
  - (a) they have the same electrical conductivity
  - (c) they have the same heat of combustion
  - (d) they have the same interatomic distance
  - (e) they have the same isotopic composition
6. A small spacecraft of capacity  $10 \text{ m}^3$  is connected to another of capacity  $30 \text{ m}^3$ . Prior to connection, the pressure inside the smaller craft is 50 kPa and that inside the larger is 100 kPa. If all measurements are made at the same temperature, what is the pressure in the combined arrangement after connection?
- (a) 75.0 kPa
  - (b) 87.5 kPa
  - (c) 100 kPa
  - (d) 125 kPa
  - (e) 150 kPa
7. Which one of the following substances is composed of linear molecules at  $25^\circ\text{C}$  and 1 Bar?
- (a)  $\text{CO}_2$
  - (b)  $\text{H}_2\text{O}_2$
  - (c)  $\text{H}_2\text{S}$
  - (d)  $\text{NaCl}$
  - (e)  $\text{SO}_2$



12. Phosphotungstic acid has the formula  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  and is commonly used to stain cell specimens. It is made by the reaction of phosphoric acid ( $\text{H}_3\text{PO}_4$ ) and sodium tungstate ( $\text{Na}_2\text{WO}_4$ ) in concentrated hydrochloric acid. How many water molecules are produced for each phosphotungstic acid produced?

- (a) 0
- (b) 1
- (c) 1.5
- (d) 12
- (e) 40

13. Dioxygen difluoride ( $\text{O}_2\text{F}_2$ ) is a highly oxidising and unstable liquid. At 273 K, it slowly decomposes back to oxygen and fluorine, which are both gases at this temperature. The equation for the reaction is given below. 1.0 g of  $\text{O}_2\text{F}_2$  (molar mass =  $70.0 \text{ g mol}^{-1}$ ) was left for 24 hours and the 26 mL of gas mixture evolved was collected in a syringe at 273 K and 100 kPa. What percentage by mass of dioxygen difluoride has decomposed by this time?

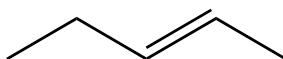


- (a) 2.6%
- (b) 4.0%
- (c) 8.0%
- (d) 16%
- (e) 40%

14. What is the correct Lewis (electron dot) structure for  $\text{OF}_2$ ?

- (a)  $\begin{array}{c} \text{:}\ddot{\text{F}}\text{---}\ddot{\text{O}}\text{---}\ddot{\text{F}}\text{:} \end{array}$
- (b)  $\begin{array}{c} \text{:}\ddot{\text{F}}\text{---}\ddot{\text{O}}\text{=}\ddot{\text{F}}\text{:} \end{array}$
- (c)  $\begin{array}{c} \text{:}\ddot{\text{F}}\text{=}\text{O}\text{=}\ddot{\text{F}}\text{:} \end{array}$
- (d)  $\begin{array}{c} \text{:}\ddot{\text{F}}\text{---}\ddot{\text{F}}\text{=}\ddot{\text{O}}\text{:} \end{array}$
- (e)  $\begin{array}{c} \text{:}\ddot{\text{F}}\text{=}\ddot{\text{F}}\text{---}\ddot{\text{O}}\text{:} \end{array}$

15. Which one of the following responses is the correct name for the structure below?



- (a) pent-2-ane
- (b) pent-3-ane
- (c) pent-2-ene
- (d) pent-3-ene
- (e) prop-2-ene

## ANSWER IN THE SPACES PROVIDED

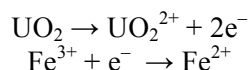
### Question 16

Australia is currently the world's third largest producer of uranium after Kazakhstan and Canada. Uranium is currently extracted from its ores at Olympic Dam and Beverley in South Australia and at Ranger in the Northern Territory, with more mines planning to open in the near future. This question concerns the chemistry of uranium extraction and analysis procedures.

Uranium forms a number of oxides, including  $\text{UO}_2$ ,  $\text{UO}_3$  and  $\text{U}_3\text{O}_8$ .  
 $\text{UO}_3$  reacts with  $\text{H}^+$  ions to produce  $\text{UO}_2^{2+}$  ions and water.

a) Write the balanced equation for this reaction.

$\text{UO}_2^{2+}$  is the most stable form of uranium in acidic aqueous solutions.  $\text{UO}_2^{2+}$  can also be produced from oxidation of  $\text{UO}_2$  by  $\text{Fe}^{3+}$  (which is often present in uranium ores). The two half-equations for this reaction are as follows:



b) Write the balanced equation for the reaction between  $\text{UO}_2$  and  $\text{Fe}^{3+}$ .

$\text{U}_3\text{O}_8$  can be thought of as  $\text{UO}_2 \cdot 2\text{UO}_3$ .

c) Write the full equation for the oxidation of  $\text{U}_3\text{O}_8$  to  $\text{UO}_2^{2+}$  by an acidified solution of  $\text{Fe}^{3+}$ .

The  $\text{Fe}^{3+}$  ions mentioned above need only be present in catalytic amounts if an oxidant that can oxidise  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  is also present in stoichiometric amounts.  $\text{H}_2\text{O}_2$  is frequently employed as a "green" oxidant as it produces only water as a product. The balanced equation for the regeneration of  $\text{Fe}^{3+}$  by oxidation with hydrogen peroxide is as follows:



d) Write the reduction half-equation for this reaction.



A standard solution of uranyl nitrate was prepared by dissolving 0.5000 g of uranyl nitrate hexahydrate ( $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) in a 500.0 mL volumetric flask.

e) Calculate the molar mass of uranyl nitrate hexahydrate.

f) Calculate the concentration of uranyl nitrate in the volumetric flask.

In general chemical practice, it is standard to report uranium concentrations not as concentrations of uranium, but as the  $\text{U}_3\text{O}_8$  equivalent concentration.

g) Calculate the  $\text{U}_3\text{O}_8$  equivalent concentration for the solution (that is, the amount of  $\text{U}_3\text{O}_8$  per litre of solution that would give rise to the  $\text{UO}_2^{2+}$  concentration in (f)).

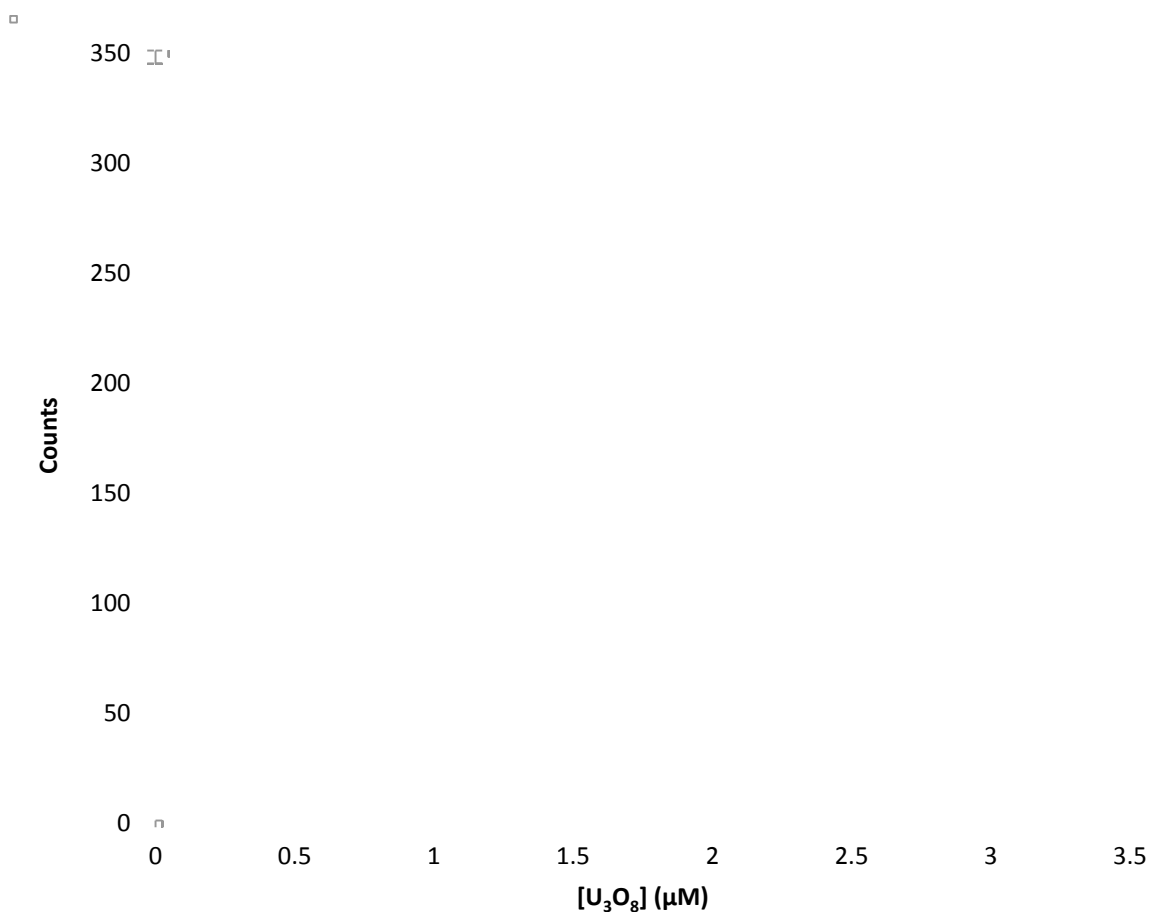
0.5000 mL of this standard uranyl nitrate solution is transferred to a 100.0 mL volumetric flask and made up to the mark with deionised water.

h) Calculate the  $\text{U}_3\text{O}_8$  equivalent concentration for this diluted solution.

Six 100.0 mL standard solutions of varying concentrations (labelled A to F) are produced from dilutions of the diluted standard solution. The uranium in the sample is extracted into ethyl acetate and aliquots of this extract are fused with NaF-LiF flux and analysed by fluorometry. The results are listed in the table below.

| Standard ID | $[\text{U}_3\text{O}_8]$ ( $\mu\text{M}$ ) | Fluorescence intensity (counts) |
|-------------|--------------------------------------------|---------------------------------|
| A           | 0.50                                       | 85                              |
| B           | 1.00                                       | 122                             |
| C           | 1.50                                       | 161                             |
| D           | 2.00                                       | 199                             |
| E           | 2.50                                       | 209                             |
| F           | 3.00                                       | 275                             |

i) Plot a graph of the fluorescence intensity against the  $\text{U}_3\text{O}_8$  equivalent concentration. Include a trendline.



1.000 mL of an ore sample solution, containing uranium, is added to each of the six standard solutions mentioned above (A to F) and the procedure repeated. The new count values are listed in the table below.

| Standard ID | [U <sub>3</sub> O <sub>8</sub> ] (μM) | Fluorescence intensity (counts) |
|-------------|---------------------------------------|---------------------------------|
| A           | 0.50                                  | 157                             |
| B           | 1.00                                  | 193                             |
| C           | 1.50                                  | 228                             |
| D           | 2.00                                  | 268                             |
| E           | 2.50                                  | 275                             |
| F           | 3.00                                  | 347                             |

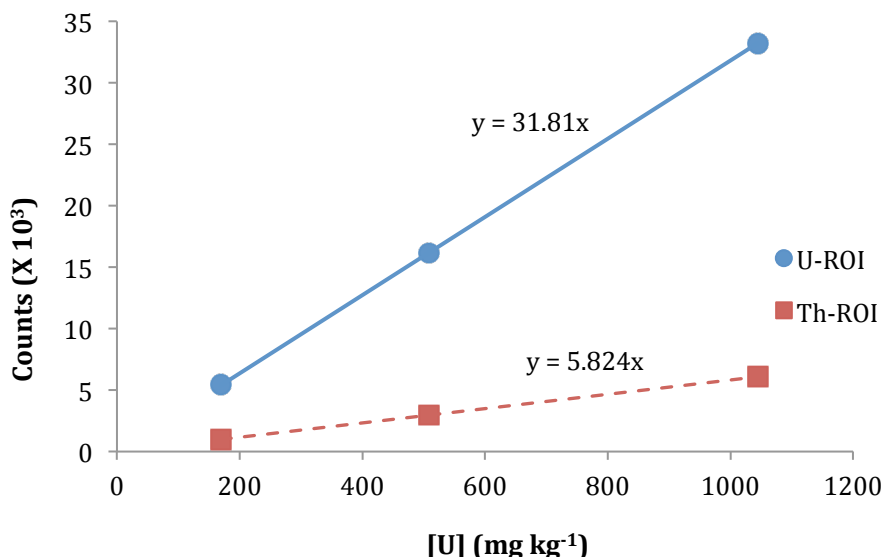
j) On the same graph as part (i) above, plot a graph of the new fluorescence intensity against U<sub>3</sub>O<sub>8</sub> equivalent concentration in the original standard solutions.

**Do this on the same graph as (i).**

k) Calculate the U<sub>3</sub>O<sub>8</sub> equivalent concentration of the ore sample solution.

The concentration of uranium and thorium in geological samples can be determined by gamma ray spectroscopy. The gamma rays emitted when nuclei decay have known energies, so the amount of uranium and thorium in a sample may be determined by counting the number of gamma rays emitted at certain energies, referred to as the uranium and thorium ‘ranges of interest’, or U-ROI and Th-ROI respectively.

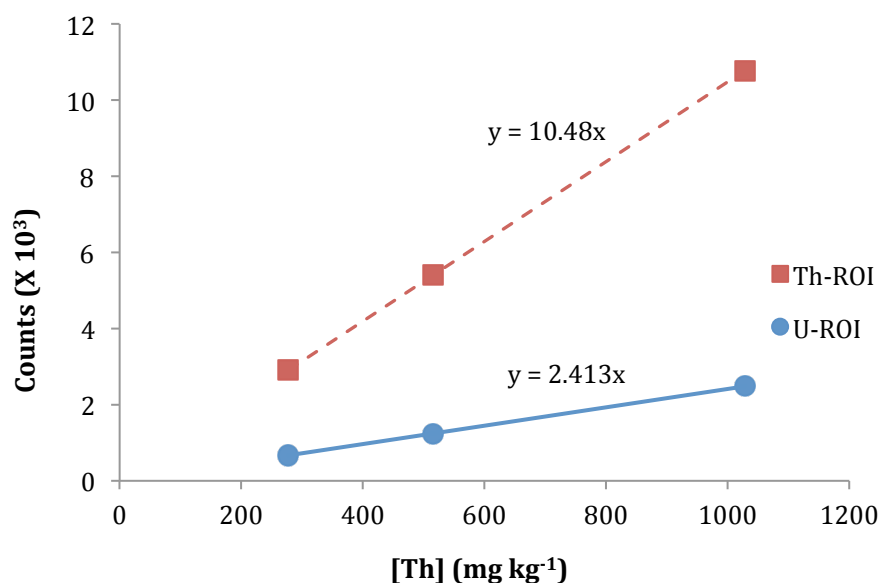
A standard uranium mixture (approximately  $1000 \text{ mg uranium kg}^{-1}$ ) was prepared and mixed with known masses of solid potassium carbonate to form two other standard mixtures of lesser concentration. When  $1.000 \text{ g}$  of each is analysed in a gamma ray spectrometer, the following results were obtained (note that these uranium mixtures contain no thorium, but nevertheless show some activity in the Th-ROI):



Analysis for thorium content is performed in the same way, but is different for three reasons:

1. Most standard thorium samples contain some uranium as well.
2. As previously mentioned, this uranium contributes activity in both the U-ROI and Th-ROI.
3. Thorium does not contribute to any activity in the U-ROI (that is, counts in the U-ROI are due only to uranium).

Standard thorium mixtures (approximately  $1000 \text{ mg thorium kg}^{-1}$ , but also containing some uranium) were prepared and analysed in the same way as previously described for the uranium mixtures, giving the following results:



A 1.000 g ore sample was analysed on the same instrument. It gives an average of 20080 counts in the U-ROI and 4200 in the Th-ROI.

l) Calculate the uranium concentration in the ore sample (in  $\text{mg kg}^{-1}$ ).

m) Calculate the number of counts in the Th-ROI resulting from the uranium concentration calculated in part l).

n) Calculate the ratio of [Th] to [U] in the **standard thorium mixtures**.

o) Calculate the thorium concentration in the ore sample (in  $\text{mg kg}^{-1}$ ).

### Question 17

In this question, the following units will be used:

eV: An electron-volt (eV) is a measure of energy equivalent to  $1.602 \times 10^{-19}$  J.

Å: An angstrom (Å) is a measure of length equivalent to  $1.000 \times 10^{-10}$  m.

In space, many unusual and high-energy reactions can occur. Many of these reactions involve hydrogen. One reaction is shown below:



a) What is the energy required for this reaction to occur called?

- A - electron affinity
- B - ionisation energy
- C - hydrogenation enthalpy
- D - van der Waals interaction

In fact, the energy input per atom of hydrogen is 13.6 eV.

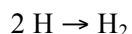
b) How much energy (in kJ) would be required to force 1.000 L of **atomic** hydrogen gas at STP (273 K, 100 kPa) to undergo this reaction?

Atomic hydrogen also turns out to be important because it fuels our sun. The mass of our sun is approximately  $2 \times 10^{30}$  kg.

c) Interstellar gas clouds have an average density of 1000 hydrogen atoms per millilitre. Consider a spherical gas cloud that has enough mass to collapse to form our sun. Calculate the volume (in cubic metres) and

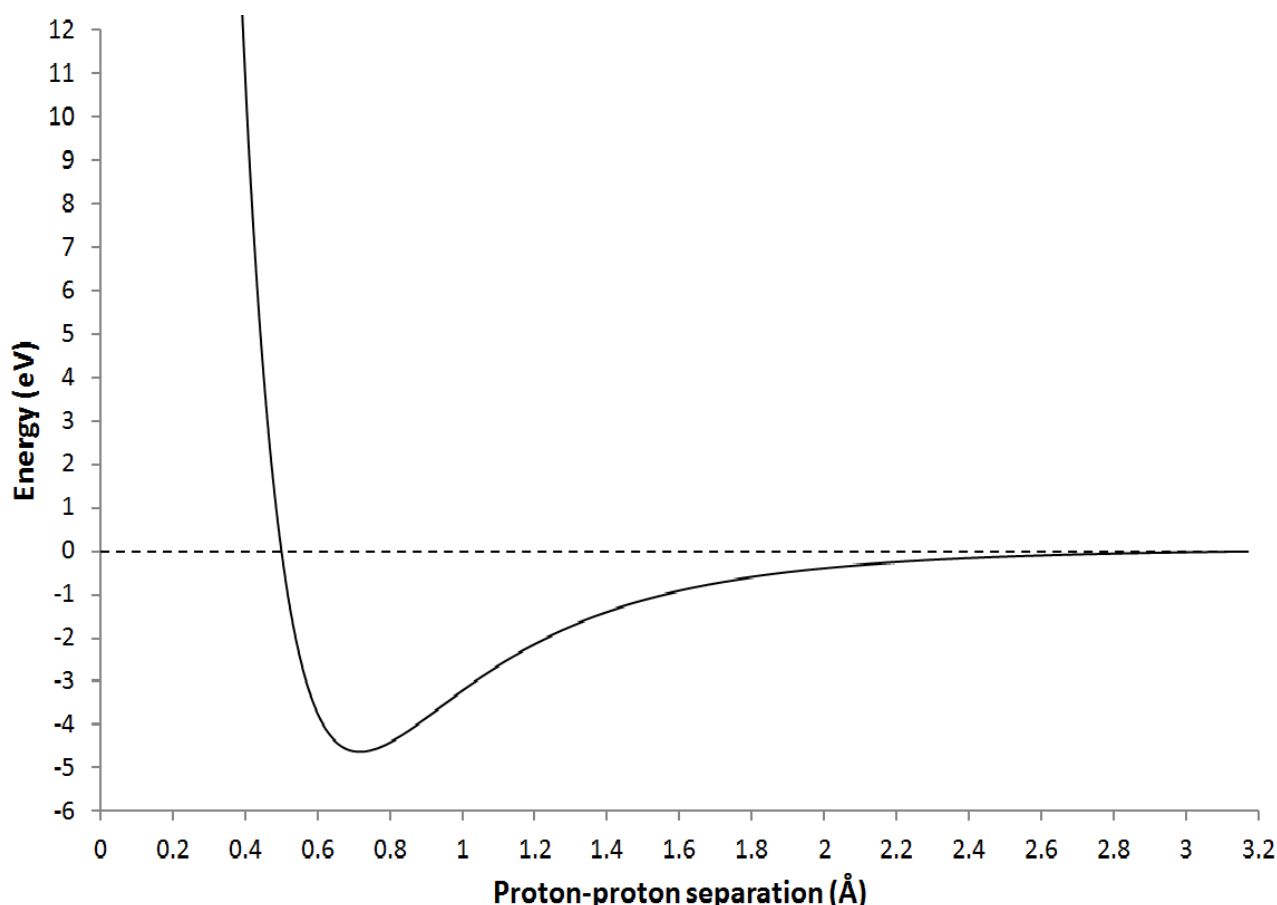
diameter (in metres) of this spherical gas cloud. The volume of a sphere:  $V = \frac{4}{3}\pi r^3$ .

Arguably the most important reaction in space is the production of diatomic hydrogen from two neutral atoms. One way this can happen is:



Shown below is the potential energy diagram for the hydrogen molecule as a function of the bond length. At infinite separation, we arbitrarily set the potential energy equal to 0, corresponding to the energy of two neutral hydrogen atoms.

A consequence of the second law of thermodynamics is that **a system will deform and move to the position that minimises its total potential energy**. For example, a ball will always roll down into the centre of any bowl it is placed in. The point at which it stops and rests is called the "**equilibrium position**".



d) Estimate the equilibrium bond length (in Å) of the hydrogen molecule from the graph. Explain why you have chosen this value.

e) The energy required to symmetrically break the hydrogen molecule at its equilibrium geometry into two neutral hydrogen atoms is called the **bond dissociation energy**. Estimate the bond dissociation energy for H<sub>2</sub> (in eV). Indicate this value on the graph above.



The shape of this curve can be loosely explained based on electrostatic interactions between protons (the nuclei) and electrons.

f) (i) Explain why the potential energy of the two hydrogen atoms decreases below zero as they move closer together (a favourable event). Diagrams may be helpful.

(ii) Explain why the potential energy curve increases rapidly as the atoms get too close (an unfavourable configuration). Diagrams may be helpful.

In the high-energy environment of outer space, we can find cosmic rays (c.r.). They are high energy particles that often ionise the hydrogen molecule, producing the dihydrogen cation,  $\text{H}_2^+$ . One cosmic ray may possess enough energy to ionise many hydrogen molecules before losing all its energy:



$\text{H}_2^+$  turns out to be an important species, because it reacts to produce a key reactive intermediate in interstellar chemistry. This intermediate was first suggested by experiments performed by Joseph Thomson in 1913, in which he subjected a mixture of  $\text{CO}_2$  and  $\text{H}_2$  to electrical discharges.

It turned out that the mass to charge ( $m/z$ ) ratio was a useful tool in investigating charged species. Thomson himself measured the  $m/z$  ratio relative to  $\text{H}^+$  which is assigned a  $m/z$  ratio of 1. **In this question, we will limit ourselves to integer  $m/z$  ratios.** For example,  $\text{He}^+$  would have a  $m/z$  ratio of 4, as  $\text{He}^+$  is four times heavier than  $\text{H}^+$ , but the same charge.

g) What is the mass to charge ratios of each of  $\text{He}^{2+}$  and  $\text{H}_2^+$ ? Tetrathiafulvalene has the molecular formula  $\text{C}_6\text{H}_4\text{S}_4$ . If tetrathiafulvalene loses two electrons, what is the mass to charge ratio of the resulting ion?

In Thomson's experiment, he found a species with a  $m/z$  ratio of 3. He called this species  $X_3$ .

h) Based on the elements present in his experiments, suggest two possible identities for  $X_3$ .

i)  $H_2^+$  reacts with another gaseous species to form  $X_3$ . The total volume of gas does not change during the reaction. Given this information, write down the most likely equation for the formation of  $X_3$ .

However, spectroscopic analysis of  $X_3$  is difficult because it has no dipole moment.

j) Draw two possible arrangements of atoms that satisfy this constraint for  $X_3$ . What is unusual about  $X_3$  when you attempt to draw bonds connecting the atoms?

$H_2^+$  can also be destroyed in a number of reactions. One molecule of  $H_2^+$  can be broken down into two products by two major processes: photodissociation and dissociative recombination.

In photodissociation,  $H_2^+$  interacts with high energy photons.

In dissociative recombination,  $H_2^+$  reacts with a free electron.

k) Write an equation for both of these processes.

l) What is the energy of the  $\text{H}_2^+$  molecule as the bond length approaches infinity, relative to zero representing two neutral hydrogen atoms?

Hint: Refer to your answer for (k) and the data for (b).

m) Would the equilibrium bond length of the  $\text{H}_2^+$  cation be shorter or longer than the  $\text{H}_2$  molecule? Why?

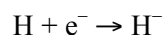
n) **In the space provided on the next page**, carefully sketch the following, showing clearly any differences. In particular indicate the bond-dissociation energies and equilibrium bond lengths for all appropriate species. Label each curve.

The potential energy curve for  $\text{H}_2$  (as shown in the previous figure)

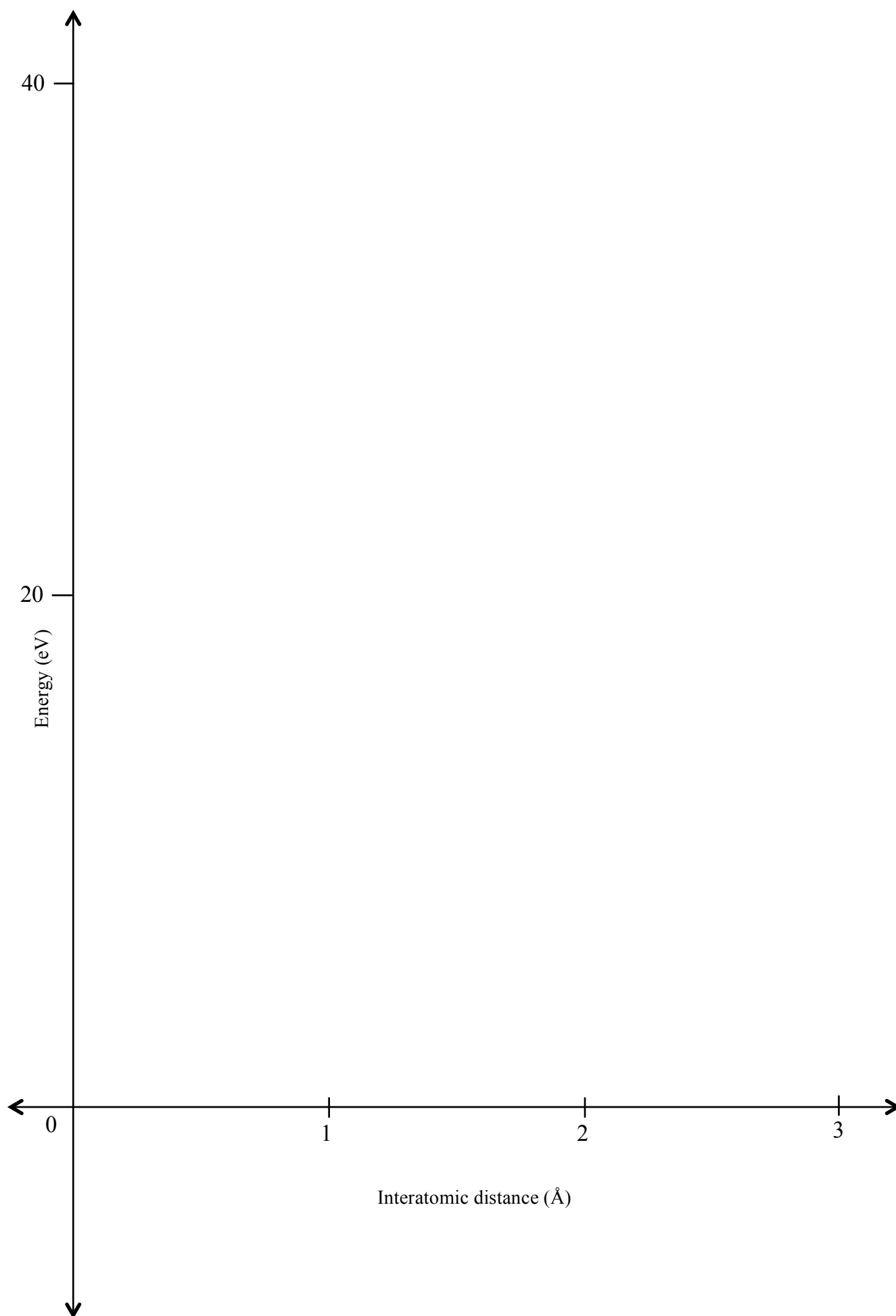
The potential energy curve for  $\text{H}_2^+$

The potential energy curve for the interaction of two protons ( $\text{H}^+$ ).

The following reaction releases 0.7 eV of energy:

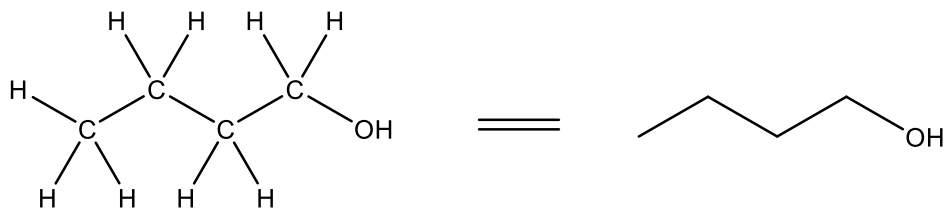


o) On your sketch, add a potential energy curve for the dissociation  $\text{H}_2 \rightarrow \text{H}^+ + \text{H}^-$ .

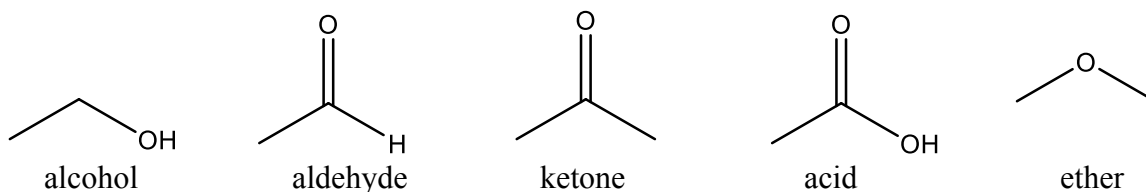


### Question 18

Organic molecules are often drawn in “skeletal form”; all hydrogen atoms are omitted and carbon atoms are represented by bends, such that:

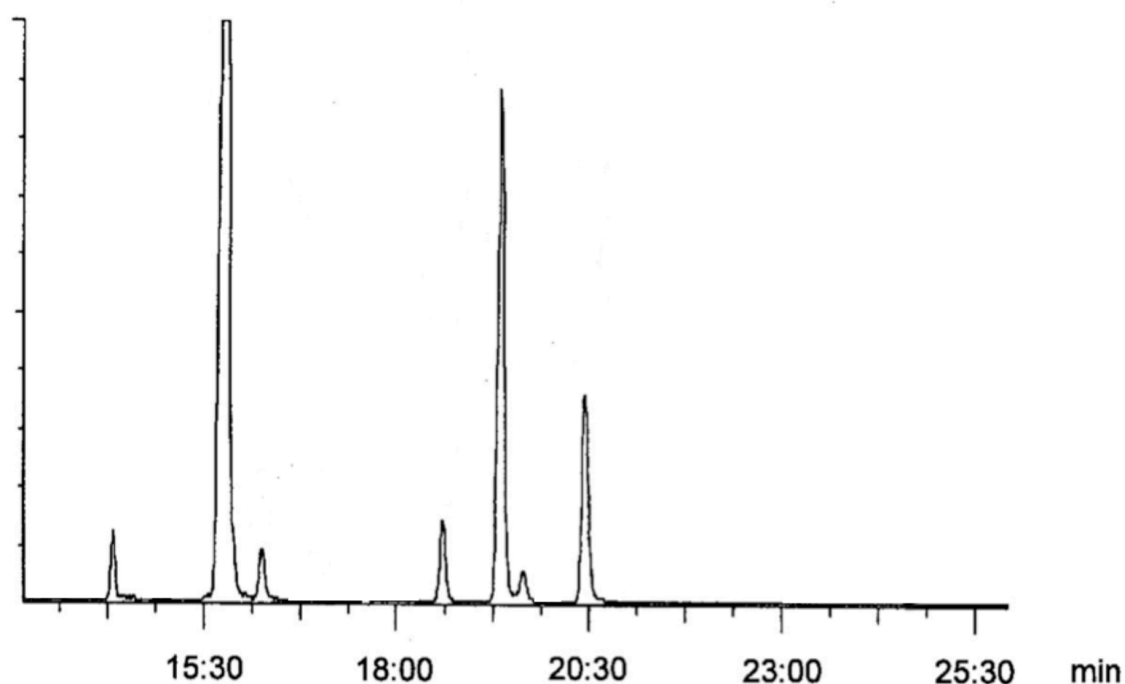


The polarity of organic compounds is largely affected by the nature of the functional groups. Functional groups are specific groups of atoms or bonds within molecules that are responsible for the characteristic chemical properties of those molecules. Common examples are shown below:



**Gas chromatography** is a common chemistry lab technique used for separating compounds that can be vaporised without decomposition. The components in a sample mixture pass through a flow-through tube (the “column”), carried by a stream of inert gas (the “mobile phase”) through the column filling (the “stationary phase”). These components flow through at different rates depending on their chemical and physical properties, separating based on their boiling points and their interaction with the stationary phase. The higher a component's affinity for the stationary phase, the slower it exits the column. As the compounds exit the end of the column, they are electronically detected, identified and represented as peaks on a “chromatogram”. The time taken for a particular compound to travel through the column to the detector is known as its “retention time”.

A gas chromatogram is shown below:

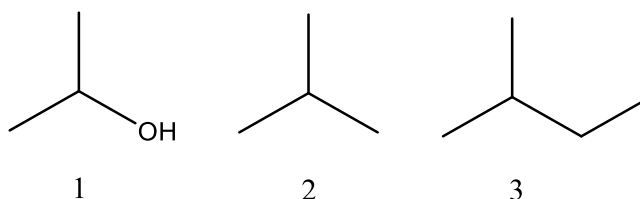


a) Identify the number of compounds in the mixture.

b) Will the retention time of a peak change if the column temperature is changed?  
Answer Yes or No.

c) What is the retention time of the compound with the highest boiling point?

d) Order the following compounds in the order (shortest retention time to longest retention time) they elute from the column.



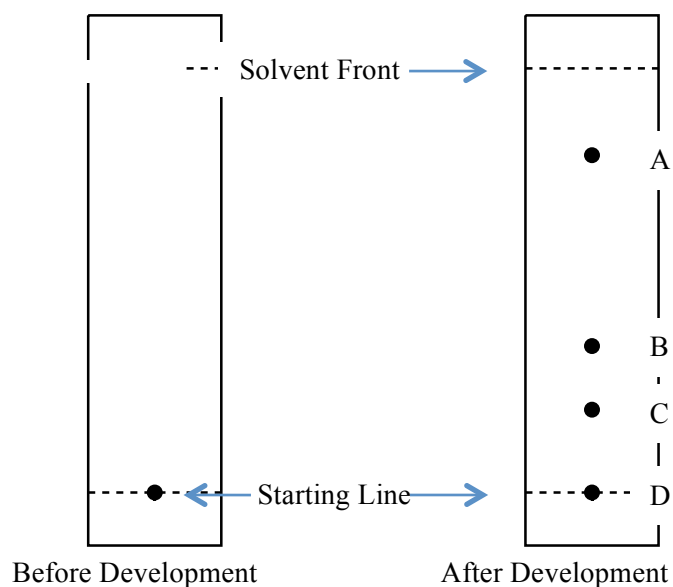
Shortest retention time

Longest retention time

**Thin layer chromatography (TLC)** is a common laboratory technique used for separation of *non-volatile* mixtures. In TLC, the mobile phase is a liquid solvent mixture and the stationary phase is usually a metal plate with a thin layer of adsorbent material such as silica gel, the surface of which contains silicon atoms that are attached to **polar –OH** groups.

After the sample is loaded onto a TLC plate, the solvent is drawn up the plate by capillary action. The different compounds in the sample mixture travel up the TLC plate at different rates due to the differences in their polarity and consequent attraction to the stationary phase. When the solvent gets close to the top of the plate, the plate is removed from the development tank and the final position of the solvent (the “solvent front”) is marked with a line before it has a chance to evaporate.

Below is the diagram of a TLC plate where the solvent used was 100% hexane. The bottom dotted horizontal line indicates starting point (where the mixture was originally adsorbed to the plate) and the top horizontal line indicates the solvent front.

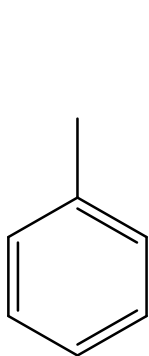


e) Identify the spot (A, B, C or D) corresponding to the most polar compound and justify your answer.

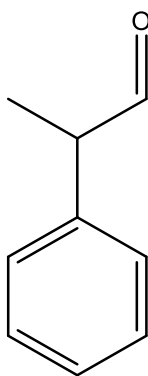
**Most polar compound:**

**Explanation:**

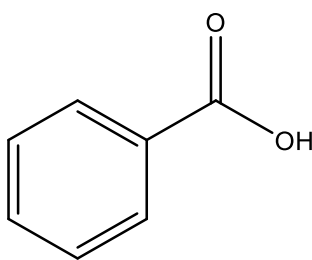
f) Assign each of the following compounds to a spot (A, B, C or D) on the above developed plate. Label 1, 2, 3 and 4 next the letters A, B, C and D.



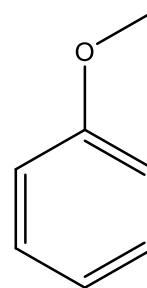
1



2



3



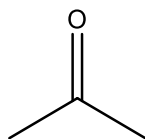
4

The retardation factors  $R_f$  can be calculated for each spot.  $R_f$  values are calculated using the following formula:

$$R_f = \frac{\text{distance from origin to spot}}{\text{distance from origin to solvent front}}$$

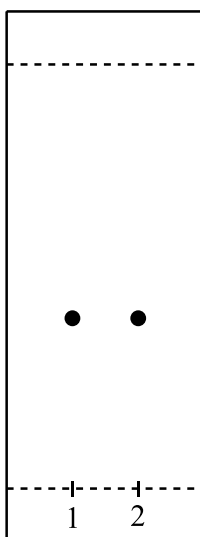
g) Give the  $R_f$  value for spot B.

h) Changing the solvent mixture can change the  $R_f$  values of compounds. As stated earlier, the previous TLC plates were run in 100% hexane. If the above compounds were run in 10% (v/v) acetone:90% (v/v) hexane) instead, would the  $R_f$  values be higher or lower? Justify your answer.



acetone

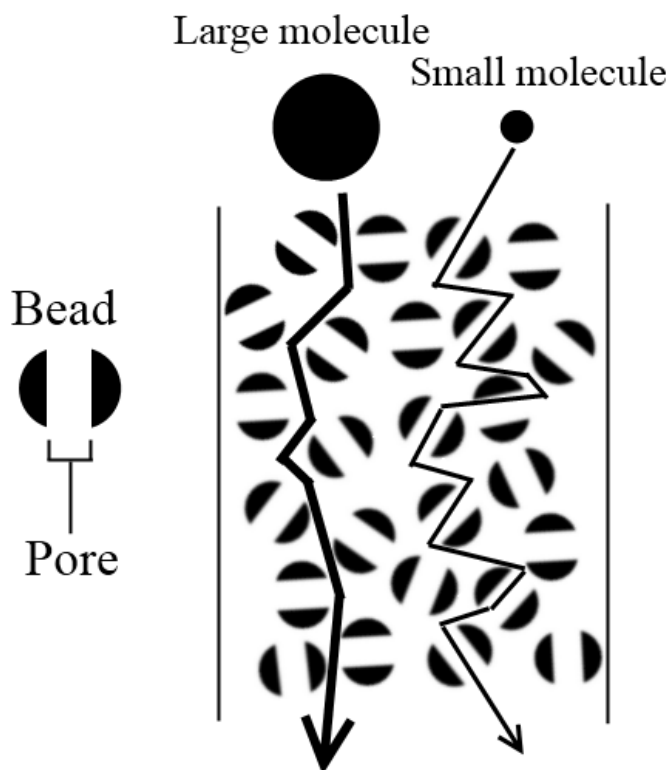
i) “If two samples run at the same time on the same TLC plate (see below) have the same  $R_f$  value, then they contain the same compound.” Is this statement true or false? Justify your answer.



j) Why is it important to remove the TLC plate from the development tank before the mobile phase reaches the top edge of the plate?



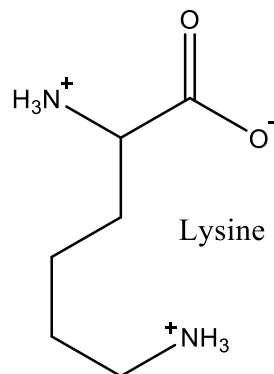
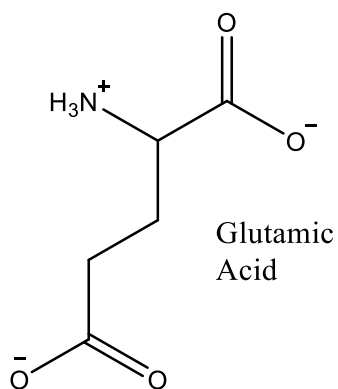
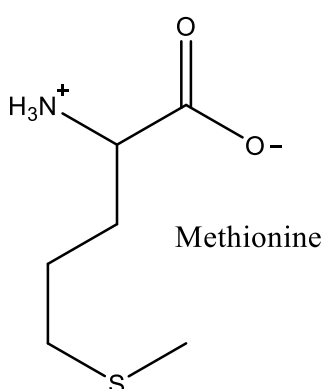
**Size-exclusion chromatography** separates organic compounds based on physical size, rather than polarity. The stationary phase used in size exclusion chromatography consists of beads of a certain pore size that allow compounds smaller than the pore size to enter into, and interact with, the pore of the beads. In this technique, the sample mixture is dissolved into a liquid mobile phase which is then passed through (“eluted”) a solid stationary phase containing the porous material in a supporting column as shown in the diagram below.



k) In this technique, would smaller or larger molecules elute first? Justify your answer.

Ion exchange chromatography uses a charged stationary phase to separate mixtures based on their respective charges.

Consider the following three amino acids. The charges are as follows at  $pH\ 7$ :



l) If the stationary phase was permanently positively charged, which amino acid would elute last? Justify your answer.

m) Following the elution of the first two amino acids, the last amino acid can be pushed off the column the adjusting the  $pH$ . Should the  $pH$  be increased or decreased? Justify your answer.

n) Another method for hastening the elution of the final amino acid is to push aqueous sodium chloride through the column. Why?

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***Integrity of Competition***

*If there is evidence of collusion or other academic dishonesty, students will be disqualified. Markers' decisions are final.*