

Find the pattern – alcohols

Introduction

Teachers who have not used the problems before should read the section Using the problems before starting.

Prior knowledge

Mole concept. A detailed knowledge is unnecessary as students are encouraged to consult textbooks and data books during the exercise.

Resources

Scientific calculators; data books and textbooks should be available for reference.

Group size

3.

Possible solutions

(i) Densities are quoted in g cm^{-3} . The pattern emerges when molar values are considered. The molar volumes for the alcohols are given in the table below.

Alcohol	Density at 20 °C (g cm^{-3})	Calculated molar volume (cm^3)	Difference (cm^3)
Methanol			
Ethanol	0.7893	58.4	
Propan-1-ol	0.8035	74.8	16.4
Butan-1-ol	0.8098	91.5	16.7
Pentan-1-ol	0.8144	108.3	16.8
Hexan-1-ol	0.8188	124.8	16.5
Heptan-1-ol	0.8219	141.4	16.6

(ii) The molar volumes increase regularly because there are the same number of molecules each time, and each step down in the table represents the addition of one CH_2 group to each molecule.

(iii) The volume taken up by one mole of CH_2 groups is the average of the figures in the last column, 16.6 cm^3 . Thus the expected molar volume of methanol is $58.4 - 16.6 \text{ cm}^3$, ie 41.8 cm^3 . This is the volume of one mole of molecules: to obtain the volume occupied by one molecule this figure is divided by Avogadro's number, ie
Volume of one methanol molecule = $41.8 / (6.02 \times 10^{23})$
= $6.9 \times 10^{-23} \text{ cm}^3$.

This volume represents the volume of the molecules including the spaces between them, so the actual volume of one molecule must be less than this.

(iv) The following are two possible solutions but students may think of others that are equally good. Both methods use atomic radii (or bond lengths).

- Consider the 'volume' of a methanol molecule as the volume of a sphere with diameter equal to the distance H-C-O-H .

Radius = $0.5 \{ (2 \times \text{diameter of H}) + \text{diameter of C} + \text{diameter of O} \}$
 = $0.074 + 0.077 + 0.074 \text{ nm}$
 = 0.225 nm
 = $2.25 \times 10^{-10} \text{ m}$
 Volume of this sphere = $\frac{4}{3} \pi r^3$
 = $47 \times 10^{-30} \text{ m}^3$
 = $4.7 \times 10^{-23} \text{ cm}^3$
 Compare this with the figure of $6.9 \times 10^{-23} \text{ cm}^3$ calculated from the molar volume in (iii) above.

b. Consider the 'volume' of a methanol molecule as made up of two parts, CH₃ and OH. The total volume is taken as the volume of two spheres touching one another – one (the CH₃ group) swept out by the C–H bonds, the other (the OH group) the volume of an oxygen atom.

Radius of CH sphere = radius of C + (2 x radius of H)
 = $0.077 + 0.074 \text{ nm}$
 = 0.151 nm
 = $1.51 \times 10^{-10} \text{ m}$
 Volume of sphere = $\frac{4}{3} \pi r^3$
 = $14.4 \times 10^{-30} \text{ m}^3$
 = $1.4 \times 10^{-23} \text{ cm}^3$
 Radius of OH sphere = radius of O + 2 x radius of H
 = $0.074 + 0.074 \text{ nm}$
 = 0.148 nm
 Volume of sphere = $1.4 \times 10^{-23} \text{ cm}^3$
 Total volume = $1.4 \times 10^{-23} + 1.4 \times 10^{-23} \text{ cm}^3$
 = $2.8 \times 10^{-23} \text{ cm}^3$

ie Volume of one methanol molecule is $6.9 \times 10^{-23} \text{ cm}^3$ from molar volumes ((iii) above); $4.7 \times 10^{-23} \text{ cm}^3$ from atomic radii assuming a spherical molecule ((iv)a. above); $2.8 \times 10^{-23} \text{ cm}^3$ from atomic radii assuming two spheres touching ((iv)b. above).

The first estimate is larger than the other two because it includes the space between the molecules.

Dulong and Petit' s Law

It is interesting to compare the pattern in these figures with those in 'Find the pattern – metals' (Dulong and Petit's Law). In the latter case, the heat required to raise the temperature of a metal is proportional to the number of atoms and does not depend on what these species are, ie the molar heat capacity for the metals is roughly constant ($26 \text{ J mol}^{-1} \text{ K}^{-1}$). In this case the molar volumes increase regularly and it is the differences between the values for homologues (16.6 cm^3) that are roughly constant.

Suggested approach

During trialling the following instructions were given to students and proved to be extremely effective:

1. Working as a group discuss the first task and carry out the calculations. If you wish you can divide the calculations amongst yourselves and then gather the results together.

Such discussion can play a vital part in working out a solution to an open-ended problem like this. Several minds working together on a problem can stimulate ideas that one on its own could not manage. A few minutes should be spent at the start discussing all the tasks with further discussion as required. Ask for help if you get stuck.

2. Carry out the second task, discuss your findings and write a brief account of them.
3. Repeat this process for the third and fourth tasks.
4. Working as a group, prepare a short (ca 5-minute maximum) presentation to give to the rest of the class. If possible all group members should take part: any method of presentation (such as a blackboard, overhead projector, etc) can be used.

Outline the problems and describe what you did. Do not go through the detailed calculations but outline your conclusions and explain how you arrived at them. After the presentation, be prepared to accept and answer questions and to discuss what you did with the rest of the class.

Possible extension

If students have tackled both 'Find the pattern' problems they could be asked to explain the difference and to predict what pattern molar enthalpies of combustion of these alcohols are likely to follow.

Notes

1. The figures were originally obtained from the 72nd edition (1991–92) of the 'Rubber Handbook', properly called the CRC Handbook of Chemistry and Physics. The quoted density of hexan-1-ol (0.8136) was inconsistent with the other alcohols: on investigation, it was found that the accepted IUPAC value is 0.8188 and this was used. This value is published in Proceedings of the Sixth International IUPAC Workshop in Liblice, Czechoslovakia 1991 – Fluid Phase Equilibria, Special Issue 1992 – paper by I. Cibulka. This gives a large number of references to the original literature – the figure for hexan-1-ol was obtained from Findenegg Monatsh. Chem., 1973, 104, 998. It is worth pointing out to students that values given in reference books should be treated with caution and original references used where possible.
2. The actual value calculated from the density of methanol (0.7914 g cm⁻³) is $32.04/0.7914 = 40.5$ cm³ to three significant figures.
3. For simplicity the four atoms are assumed to be in a straight line – an incorrect assumption which makes the estimate larger than the actual volume.

Find the pattern – alcohols

Consider the data on the densities of six primary alcohols given below.

- I. Calculate the molar volume of each alcohol in the list.
- II. Find a pattern in the variation of the molar volumes and then propose an explanation for the pattern.
- III. On the basis of the pattern in the values of the molar volumes, estimate the volume of a single molecule of methanol. Explain how this estimate is likely to compare with the actual volume of a single molecule of methanol.
- IV. Estimate the volume of a single molecule of methanol by using other data and compare this value with the one calculated in (iii).

You should refer to any sources of information that you think might help such as your notebooks, textbooks and data books. Ask for assistance if you get stuck.

Alcohol	Density at 20°C (g cm ⁻³)
Methanol	—
Ethanol	0.7893
Propan-1-ol	0.8035
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