

# Answers

## Chapter 11

### Exercises

- 1 The smallest division is 1 so the uncertainty is  $\pm 0.5$ .
- 2 The missing diamond has a mass of between 9.87 and 9.97 g.  
The found diamond has a mass between 9.9 and 10.3 g.  
As the ranges overlap, it **could** be the missing diamond.
- 3 (a)  $4 \times 10^{-2}$  g                      (b)  $2.22 \times 10^2$  cm<sup>3</sup>  
(c)  $3.0 \times 10^{-2}$  g  
(d)  $3 \times 10$  or  $3.0 \times 10$  °C (unspecified)
- 4 (a) 4    (b) unspecified  
(c) 3    (d) 4
- 5 A                      6 A                      7 D                      8 A
- 9 A                      10 D                      11 C
- 12 The average value = 49.0 s  
The uncertainty in the measurements is given as  $\pm 0.1$  s but the results show that there is additional uncertainty, suggesting that the value could be anywhere between 48.8 and 49.2 s. So the value could be quoted as  $49.0 \text{ s} \pm 0.2 \text{ s}$ .
- 13 Note that the correct solution to this question is not one of the possible answers listed.  
The temperature change expressed to the appropriate precision is  $2.050 \pm 0.050$  K.
- 14 D                      15 B                      16 B                      17 C
- 18 A                      19 C
- 20 Number of moles = concentration  $\times$  volume/1000  
 $= 1.00 \times 10.0/1000 = 0.0100$  mol  
% uncertainty in concentration =  $(0.05/1.00) \times 100 = 5\%$   
% uncertainty in volume =  $(0.1/10.0) \times 100 = 1\%$   
% uncertainty in number of moles =  $5\% + 1\% = 6\%$   
Absolute uncertainty in number of moles =  $(6/100) \times 0.0100 = 0.0006$   
Number of moles =  $0.0100 \pm 0.0006$  mol
- 21 (a)  $\Delta T = 43.2 - 21.2^\circ\text{C} = 22.0^\circ\text{C}$   
absolute uncertainty =  $(\pm)0.2^\circ\text{C}$   
(b) % uncertainty =  $0.2/22.0 \times 100\% \approx 1\%$   
(c)  $\Delta H = -4.18 \times 22.0/0.500 = -184 \text{ kJ mol}^{-1}$   
(d) 1%  
(e) Absolute uncertainty =  $1/100 \times 184 = (\pm) 2 \text{ kJ mol}^{-1}$   
(f) Experimental value for  $\Delta H = -184 (\pm) 2 \text{ kJ mol}^{-1}$   
The literature value is outside this range.  
The random errors involved in reading the thermometer do not account for this difference.  
There are systematic errors. The assumptions on which the calculation is based are not strictly valid. Some of the heat of reaction passes into the surroundings and the other uncertainties in the measurements cannot be ignored. It should also be noted that the standard value for  $\Delta H$  refers to standard conditions of 298 K and 100 kPa.
- 22 B
- 23 The scale of the graph does not allow us to distinguish whether A or B is the best answer and both are acceptable.
- 24 B
- 25 Concentration of chromium (from graph for absorbance of 0.215) =  $3.34 \mu\text{g dm}^{-3}$
- 26 B                      27 C                      28 C
- 29 A (the spectrum on the left) corresponds to  $\text{CH}_3\text{CH}_2\text{CHO}$   
B (the spectrum on the right) corresponds to  $\text{CH}_3\text{COCH}_3$

### Similarities

Both have a molecular ion corresponding to 58.

### Differences

A has peaks corresponding to 29 ( $\text{CH}_3\text{CH}_2^+$ ) and 28 (loss of  $\text{CH}_3\text{CH}_2$ ).

B has a peak corresponding to 43 (loss of  $\text{CH}_3$ ).

30 (a)

| Mass / charge | Fragment  |
|---------------|---|
| 15            | $\text{CH}_3^+$                                   |
| 29            | $\text{C}_2\text{H}_5^+$                          |
| 43            | $\text{C}_3\text{H}_7^+$ (loss of $\text{CH}_3$ ) |
| 58            | $\text{C}_4\text{H}_{10}^+$                       |

(b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

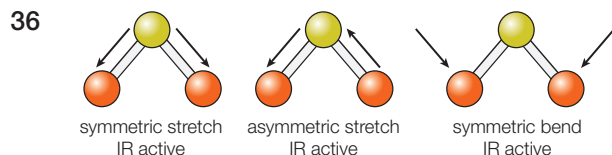
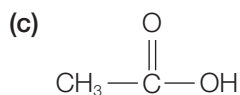
31

| Molecule                            | Corresponding saturated non-cyclic molecule | IHD |
|-------------------------------------|---|-----|
| $\text{C}_6\text{H}_6$              | $\text{C}_6\text{H}_{14}$                   | 4   |
| $\text{CH}_3\text{COCH}_3$          | $\text{C}_3\text{H}_8\text{O}$              | 2   |
| $\text{C}_7\text{H}_6\text{O}_2$    | $\text{C}_7\text{H}_{16}\text{O}$           | 5   |
| $\text{C}_2\text{H}_3\text{Cl}$     | $\text{C}_2\text{H}_5\text{Cl}$             | 1   |
| $\text{C}_4\text{H}_9\text{N}$      | $\text{C}_4\text{H}_9\text{NH}_2$           | 1   |
| $\text{C}_6\text{H}_{12}\text{O}_6$ | $\text{C}_6\text{H}_{14}\text{O}_6$         | 1   |

32 B      33 D      34 B

35 (a) Empirical formula  $\text{CH}_2\text{O}$ . Molecular formula  $\text{C}_2\text{H}_4\text{O}_2$ .

(b) IHD = 1



37 B

38 The polarity (of bond or molecule) changes as the bonds are bent or stretched.

39 Hex-1-ene shows an absorption in the range  $1610\text{--}1680\text{ cm}^{-1}$  due to the presence of the  $\text{C}=\text{C}$  bond.

40 C—H bond

41  $\text{CH}_3\text{OCH}_3$

42 C      43 A

44 (a) 2      (b) 1

(c) 1      (d) 2

45 The H atoms are in three different environments so there will be three peaks in the  $^1\text{H}$  NMR spectrum with integrated areas in the ratio 3:2:1.

46 (a)  $\text{CH}_3\text{COCH}_2\text{CH}_3$

(b)

| Type of hydrogen atom      | Chemical shift / ppm | No. of H atoms | Splitting pattern |
|----------------------------|----------------------|----------------|-------------------|
| $\text{CH}_3\text{CO}$     | 2.2–2.7              | 3              | 1                 |
| $\text{COCH}_2\text{CH}_3$ | 2.2–2.7              | 2              | 4                 |
| $\text{CH}_2\text{CH}_3$   | 0.9–1.0              | 3              | 3                 |

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| Compound                   | Number of peaks | Chemical shift / ppm | No. of H atoms | Splitting pattern |
|----------------------------|-----------------|----------------------|----------------|-------------------|
| $\text{CH}_3\text{CHO}$    | 2               | 2.2–2.7              | 3              | 2                 |
|                            |                 | 9.4–10.0             | 1              | 4                 |
| $\text{CH}_3\text{COCH}_3$ | 1               | 2.1                  | 6              | 1                 |

48 Possible structures:  $\text{CH}_3\text{CH}_2\text{COOH}$ ,  $\text{CH}_3\text{COOCH}_3$ ,  $\text{HCOOCH}_2\text{CH}_3$ .

The peak at 8.0 ppm corresponds to R—COOH. There is no splitting as there are no hydrogen atoms bonded to neighbouring carbon atoms.

The peak at 1.3 ppm corresponds to a  $\text{CH}_3$  group. The peak is split into a triplet because there is a neighbouring  $\text{CH}_2$  group.

The peak at 4.3 ppm corresponds to the R— $\text{CH}_2$ —COO group. The peak is split into a quartet as there is a neighbouring  $\text{CH}_3$  group. Molecular structure:  $\text{CH}_3\text{CH}_2\text{COOH}$

49 X-ray crystallography.

50 Monochromatic means all the X-rays have the same wavelength.

The angle of diffraction depends on the wavelength. If the X-rays have different wavelengths, different diffraction angles/pattern would be obtained. It would be impossible to match the angles with the wavelengths.

- 51 Hydrogen atoms have a low electron density.
- 52 The atoms must have a regular arrangement if an ordered diffraction pattern is to be produced.
- 53 (a)  $C_6H_5CH_3$
- (b) Hydrogen atoms do not appear because of their low electron density
- (c) The saturated non-cyclic compound is  $C_7H_{16}$   
 $IHD = \frac{1}{2}(16 - 8) = 4$  (the IHD of a benzene ring = 4)

## Practice questions

For advice on how to interpret the marking below please see Chapter 1.

1 B      2 C      3 C      4 A

- 5 (a) *Compound:*  
 $CH_3-CH_2-CHO$   
*Explanation: [1 max]*  
 only this compound would give 3 peaks / OWTTE  
 only this compound has H atoms in 3 different chemical environments / OWTTE  
 only this compound has protons in ratio 3:2:1 in each environment / OWTTE  
 only this compound would give a peak in the 9.4–10 ppm region / OWTTE [2 max]
- (b) 2.5 ppm peak  
 $CH_3-CO-CH_3$  also has hydrogen atoms on a carbon next to the  $>C=O$  group [2]
- (c) (i) 1700–1750  $cm^{-1}$  ( $>C=O$ ) [1]  
 (ii) 1610–1680  $cm^{-1}$  ( $>C=C<$ ) / 3200–3600  $cm^{-1}$  ( $-O-H$ ) [1]
- (d)  $C_3H_6O^+$  and  $m/z = 58$

$C_2H_5^+$  and  $m/z = 29$   
 $CHO^+$  and  $m/z = 29$   
 $CH_3^+$  and  $m/z = 15$  [2 max]

*Penalize missing + sign once only.*

- 6 (a) (stretches/vibrations in) HBr involve change in bond dipole / (stretches/vibrations in)  $Br_2$  do not involve change in bond dipole [1]
- (b) (i) I: O—H  
 II: C—H  
 III: C=O [3]  
*Award [2] for C—H for I and O—H for II.*
- (ii)  $m/z$  102: molecular ion peak /  $(CH_3)_3CCOOH^+$  /  $C_5H_{10}O^+$  /  $M^+$   
 $m/z$  57:  $(CH_3)_3C^+$  /  $(M-COOH)^+$  /  $C_4H_9^+$   
 $m/z$  45:  $COOH^+$  [3]  
*Penalize missing + once only.*
- (iii) (H of) COOH group [1]
- (iv) nine hydrogens in the same environment /  $(CH_3)_3C-$  (group) [1]

(v)  $(CH_3)_3CCOOH$  /  $(CH_3)_3CCO_2H$  /  $H_3C-C(CH_3)(OH)-C(=O)OH$  [1]

- (vi) no peak at 11.5 ppm in spectrum of isomer / different chemical shift values  
 four peaks (instead of two) / different number of peaks;  
*Three of these peaks can be split in actual spectrum, so allow for this in answers if exactly four peaks is not stated.*  
 different integration trace / different areas under the peaks / integration trace would have a 3:2:2:3 peak area ratio [2 max]  
*Do not award mark if incorrect peak area ratios are given for the structure drawn in (v).*

- 7 change in bond length / bond stretching / asymmetric stretch  
 change in bond angle / bending (of molecule)  
*Allow [1 max] for only stating vibrations.*

induces molecular polarity / dipole moment /  
OWTTE [3]

- 8 (a) A: O—H  
B: C=O  
C: C—O

Award [2] for three correct, [1] for two correct. [2]

- (b)  $m/z = 74$ :  $C_2H_5COOH^+$  /  $C_3H_6O_2^+$

$m/z = 45$ :  $COOH^+$

$m/z = 29$ :  $C_2H_5^+$

Penalize missing + charge once only.

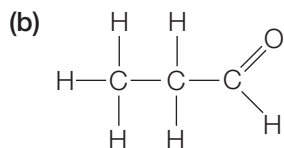
Do not award mark for  $m/z = 29$ :  $CHO^+$ . [3]

- (c) —COOH [1]

- (d)  $CH_3CH_2COOH$  /  $CH_3CH_2CO_2H$

More detailed structural formula may be given. [1]

- 9 (a) absence of peak between 3200 and 3600  $cm^{-1}$  / above 3000  $cm^{-1}$  / peak for OH  
presence of peak between 1700 and 1750  $cm^{-1}$  / peak for C=O  
absence of peak between 1610 and 1680  $cm^{-1}$  / peak for C=C [2 max]



Accept  $CH_3CH_2CHO$ .

3:2:1

Ignore order.

ECF if structure is incorrect only if its NMR spectrum contains three peaks. [2]

- 10 (a) (i) (2-)methylpropan-2-ol  
the (H atoms in the three) — $CH_3$  groups are responsible for the peak at 1.3 ppm  
the —OH hydrogen atom is responsible for the peak at 2.0 ppm  
Accept explanations with suitable diagram. [3]

- (ii) (2-)methylpropan-1-ol  
the first peak (at 0.9 ppm) is due to the (H atoms in the) two — $CH_3$  groups

(bonded to the second carbon atom) /  
 $(CH_3)_2CHCH_2OH$

the peak at 3.4 ppm is due to the (H atoms in the) — $CH_2$ — group /  
 $(CH_3)_2CHCH_2OH$

Accept explanations with suitable diagram. [3]

- (b) (i) butan-1-ol and butan-2-ol  
 $74$ :  $M^+$  /  $C_4H_{10}O^+$  /  $CH_3CH_2CH_2CH_2OH^+$   
and  $CH_3CH_2CH(OH)CH_3^+$

$59$ :  $C_3H_7O^+$  /  $(M - CH_3)^+$  /  
 $CH_2CH_2CH_2OH^+$  and  $CH_2CH(OH)CH_3^+$  /  
 $CH_3CH_2CH(OH)^+$

$45$ :  $C_2H_5O^+$  /  $(M - C_2H_5)^+$  /  $CH_2CH_2OH^+$   
and  $CH(OH)CH_3^+$   
Accept explained answers instead of formulas. [4]

- (ii) butan-1-ol  
 $CH_2OH^+$  /  $(M - C_3H_7)^+$   
Penalize missing + signs once only in parts (b)(i) and (ii). [2]

- (c) they all contain O—H  
they all contain C—H  
they all contain C—O  
Award [1 max] for same functional groups/bonds. [2 max]

- 11 D could be  $CH_3CH_2COOCH_3$  or  $CH_3COOCH_2CH_3$   
this is because there are 3 peaks / 3:2:3 ratio  
explanation of splitting into a singlet, a triplet and a quartet  
methyl propanoate /  $CH_3CH_2COOCH_3$  is correct isomer because of higher chemical shift value of singlet (3.6 instead of 2.0–2.5) [4]

- 12 (a) (i) 88  
Do not award mark if units are given.  
 $C_4H_8O_2^+$  [2]  
(ii)  $CH_3CH_2^+$  /  $C_2H_5^+$  /  $CHO^+$   
Only penalize once for missing charge in (a)(i) and (ii). [1]

- (iii)  $C_2H_3O_2$  produced has no charge / fragment produced after loss of  $C_2H_5$  from molecular ion has no charge

Accept fragment(s) too unstable, fragment breaks up etc.

Do not accept answers with reference to  $^{13}C/^{14}C$  isotopes and peak at  $m/z = 61$ .

Do not accept  $C_2H_3O_2^+ / C_3H_7O^+$  does not exist. [1]

- (b) (i) A: C=O and B: C—O

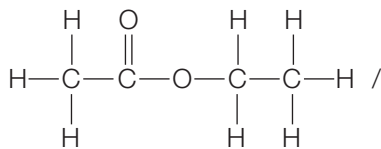
No mark if two bonds are given for A or B.

Ignore names if incorrect. [1]

- (ii) ester

Do not accept COO. [1]

- (c) (i)



- (ii)

| Peak   | Chemical shift / ppm | Relative peak area | Splitting pattern |
|--------|----------------------|--------------------|-------------------|
| first  | 2.0                  | 3                  | singlet           |
| second | 4.1                  | 2                  | quartet           |
| third  | 0.9–1.0              | 3                  | triplet           |

- (iii) (quartet means) neighbouring C:

has 3 H atoms [2]

3  $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2 \times (-2)) + (-1 \times 2) + 0 + (1 \times 1) + (2 \times (-1))}{2^2 + 1^2 + 0^2 + 1^2 + 2^2}$$

$$= \frac{4 - 2 + 1 - 2}{10} = 0.10$$

- 4 Saturated hydrocarbons have the general formula  $C_nH_{2n+2}$

For  $C_nH_p$ :

H atoms needed =  $2n + 2 - p$

$H_2$  molecules needed = IHD =  $\frac{1}{2}(2n + 2 - p)$

For  $C_nH_pO_q$ :

Oxygen forms two covalent bonds. Comparing ethane,  $C_2H_6$ : C—H, to ethanol,  $C_2H_5OH$ : C—O—H, we see that the presence of O has no impact on the IHD:

$$IHD = \frac{1}{2}(2n + 2 - p)$$

For  $C_nH_pO_qN_r$ :

Nitrogen forms three covalent bonds. Comparing C—H to C—N—H, we see that the presence of one N increases the IHD by 1:

$$IHD = \frac{1}{2}(2n + 2 - p + r)$$

For  $C_nH_pO_qN_rX_s$ :

A halogen, X, forms one bond, like hydrogen, so can be treated in the same way:

$$IHD = \frac{1}{2}(2n + 2 - p + r - s)$$

- 5  $E = hv$

$$E = 6.63 \times 10^{-34} \text{ J s} \times 3.0 \times 10^{14} \text{ s}^{-1} = 2.0 \times 10^{-19} \text{ J}$$

The energy of one mole of photons =  $6.02 \times 10^{23} \text{ mol}^{-1} \times 2.0 \times 10^{-19} \text{ J}$

$$= 120 \text{ kJ mol}^{-1}$$

- 6  $1/\lambda = 2100 \text{ cm}^{-1} = 210000 \text{ m}^{-1}$

$$\lambda = 1/210000 \text{ m} = 4.76 \times 10^{-6} \text{ m}$$

$$v = \frac{3.00 \times 10^8 \text{ m s}^{-1}}{4.762 \times 10^{-6} \text{ m}} = 6.30 \times 10^{13} \text{ s}^{-1}$$

- 7 The answer to this question involves the derivation of the Bragg Equation,  $n\lambda = 2d\sin\theta$ , which is discussed in Chapter 12. A simple derivation is provided in the worked solutions.

## Challenge yourself

1  $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2 \times (-2)) + (-1 \times (-1)) + 0 + (1 \times 1) + (2 \times 2)}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2}$$

$$= 1$$

2  $Y_1^{ave} = Y_2^{ave} = 3$

$$R = \frac{(-2 \times 2) + (-1 \times 1) + 0 + (1 \times (-1)) + (2 \times (-2))}{(-2)^2 + (-1)^2 + 0^2 + 1^2 + 2^2}$$

$$= -1$$