Structure 1.1

Exercises

1. C

Consider each of the options in turn:

A Water and oil are immiscible liquids– heterogeneous.

B Sand is insoluble in water – heterogeneous.

C Salt dissolves in water to give a clear solution – homogeneous.

D Sand and salt can mix but the mixture has a non-uniform composition – heterogeneous.

2. B

Consider each of the options in turn:

I. The components of a mixture can be elements or compounds.

II. All components **do not** need to be in the same state.

III. The components do retain their individual properties in a mixture.

3. C

Bronze and steel are both alloys.

4. **(a)** Fertilizers are soluble.

(b) Large energy requirement and so is expensive.

5. The solvent evaporates. The oil has changed chemically by reacting with oxygen in the air.

6. Calculate the total mass of each coin and then calculate the percentage composition.

	Mass / g				
Coin	**Copper**	**Aluminium**	**Zinc**	**Tin**	**Total mass**
20 cent	5.11	0.287	0.287	0.057	5.741
% composition	89.0	5.00	5.00	0.99	
50 cent	6.94	0.39	0.39	0.08	7.80
% composition	89.0	5.00	5.00	1.03	

Both coins are made from a homogeneous mixture with the same composition:

Cu 89%,Al 5%, Zn 5%, Sn 1%.

7. X has moved more quickly; therefore, the particles of X have smaller mass.

8. The average kinetic energy increases with temperature. The particles will move faster and the rate of diffusion increases.

9. D

Solid: the particles can vibrate (in three dimensions).

Liquid: the particles can move freely but in a limited volume

Gaseous: particles can move freely with no interaction

10. **(a)** Bubbles will be present throughout the volume of the liquid. A brown gas will be visible above the brown liquid.

(b) As the two states are at the same temperature, the particles have the same average kinetic energy and are moving at the same average speeds. The inter-particle distances in the gas are significantly larger than those in the liquid.

11. D

Solid → gas: sublimation.

12. C

Freezing, melting and boiling occur at a fixed temperatures at a given pressure.

Evaporation occurs over a range of temperatures.

13. B

Evaporation occurs when particles have sufficient energy to escape from the surface. The rate of evaporation increases if the temperature or the surface area is increased.

At certain conditions of low temperature and low humidity, snow changes directly to water vapour by sublimation, without going through the liquid state.

14. **(a)** Ice, as it has a melting point of 0 °C.

(b) They are vibrating with increasing frequency.

(c) They are moving freely in a fixed volume as it is the liquid state.

(d) The heat energy is used to separate the particles and not increase their movement.

(e) 52.5 °C

(f) Temperature predicted = 127.5 °C. Water boils at 100 °C, which would be reached after around 980 s, and so the temperature does not follow the predicted pattern. The temperature is likely to be 100 °C.

15. D

0 °C = 273 K

50 °C = 273 + 50 K = 323 K

16. B

The kinetic energy of the particles does not change as the temperature remains constant.

The separation between the particles decreases as the solid is more closely packed.

17. C

As they have the same temperature, the average kinetic energy of the atoms is the same. The object with a larger mass contains more atoms and so has the greater total energy.

18. D

There are only two states present. I could be a liquid and II could be a gas.

19. Steam will condense on the skin, releasing energy as it forms liquid at the same temperature (portion e–d on S1.1 Figure 5). This is additional to the energy released when both the boiling water and the condensed steam cool on the surface of the skin.

Challenge yourself

1. The molecules of ethanol can partly fit between the spaces between the water molecules, and vice versa.

2. A mixture may appear to be homogenous with the naked eye but on closer inspection with a microscope may be heterogenous. The classification depends on the scale on which the components are analysed.

3. In 1827 Robert Brown dropped pollen grains into water and examined them under a microscope. The pollen grains moved around erratically in the water. This so-called ‘Brownian motion’ was explained in 1905 by Albert Einstein. He realized that the pollen was being jostled by something even smaller than the pollen grains: water molecules. Einstein didn’t just base this theory on his observations – he used complex mathematics to show that a particle model could explain Brownian motion.

4. In cold climates, temperature may approach or go below the boiling point of butane so it stays liquid even when released from the pressure it is under when stored in its canister. This makes it ineffective as a fuel.

5. $\Delta E = mc\Delta T$

gradient of graph = $\dfrac{\Delta T}{\Delta E} = \dfrac{1}{mc}$

The gradient is determined by the mass and the specific heat capacity of the substance as solid, liquid and gas.

Practice questions

1. D

These statements are all correct.

2. A

When the temperature of gas is reduced, the average kinetic energy of the molecules decreases. They collide with the walls of the container less frequently.

3. B

When a solid is converted to a liquid at the melting point, the average kinetic energy of the particles remain constant as the temperature is constant but the separation between the particles increases.

4. B

When a liquid is converted to a gas at its boiling point, the kinetic energy of the particles remains constant but the separation between the particles increases.

5. D

As the substance is heated at a contant rate the energy increases most during the largest time inteval.

6. A

The remaining ice is still at 0 °C.

7. C

Consider each of the options in turn:

A Olive oil and vinegar are immiscible liquids– heterogeneous.

B Sand is insoluble in water – heterogeneous.

C Carbon dioxide dissolves in water to give a clear solution, carbonated water – homogeneous.

D Salt and pepper can mix but the mixture has a non-uniform composition, – heterogeneous.

8. B

Sublimation is the change from solid to gas: $I_2(s) \rightarrow I_2(g)$

9. B

Consider each diagram in turn.

Diagram	Description
I	Each molecule is composed of atoms from different elements. A compound in the gaseous elements.
II	The particles have an ordered arrangement in a defined volume: it is in the solid state.
III	It is a mixture. The particles have an irregular arrangement in a defined volume: A heterogeneous mixture in the solid state.

10 B

Fractional distillation can separate liquids with different boiling points.

11 A

Consider each mixture in turn.

	Addition of water	Addition of ethanol
P and S	P is insoluble and so can be separated by filtration	P is insoluble and so can be separated by filtration
Q and S	Q is insoluble and so can be separated by filtration	Both are soluble. Filtration cannot be used.
R and S	Both are soluble. Filtration cannot be used.	R is insoluble and so can be separated by filtration
Q and P	Both are insoluble. Filtration cannot be used.	P is insoluble and so can be separated by filtration

12 **(a)** Smoke: heterogeneous – the solid particles are suspended in the air. (1)

(b) Sugar and water: homogeneous – the sugar dissolves in the water. (If it is a saturated solution with excess sugar that cannot dissolve, the overall mixture is then heterogeneous.) (1)

(c) Steel: homogeneous – it is an alloy of iron and carbon (+ other components) with the same properties throughout. (1)

13. (At certain conditions of low temperature and low humidity), snow changes directly to water vapour by sublimation, without going through the liquid phase.

14 **(a)** Any two from:

forces between gas particles are smaller than between liquid particles

speed of gas particles greater than speed of liquid particles

movement of gas particles is less restricted than that for liquid particles

separation of particles (generally) much greater in a gas than in a liquid (2)

(b) the gas particles do not have the same speed (1)

the speed of individual particles changes with each collision (1)

(c) **(i)** increased kinetic energy of the particles (1)

(ii) heat energy used to separate the particles (1)

no increase in kinetic energy (as indicated by temperature) (1)

15 **(a)** Any value between –15 °C and +10 °C. (The experimental value = –7.2 °C.) (1)

(b) Boiling points increase (1)

(c) gas (1)

(d) **(i)** liquid (1)

the molecules are close together but have an irregular arrangement (1)

(ii) increased movement of molecules (1)

with increased separation between particles (1)

(Note the molecules do not break into individual atoms.)

(iii) The bromine molecule break into atoms or ions, which then combine with atoms or ions of other elements. (1)

(iv) Temperature is a measure of the average kinetic energy: increase in temperature results in increase in movement / rate of diffusion. (1)

Structure 1.2

Exercises

1. Tellurium has a greater proportion of heavier isotopes (those with more neutrons).

2. The number of protons = atomic number

   The number of neutrons = mass number – atomic number

	Species	No. of protons	No. of neutrons	No. of electrons
(a)	^{7}Li	3	4	3
(b)	^{1}H	1	0	1
(c)	^{14}C	6	8	6
(d)	$^{19}\text{F}^{-}$	9	10	10
(e)	$^{56}\text{Fe}^{3+}$	26	30	23

3. atomic number = no. of protons. The chemical symbol can be found from the periodic table

   charge = no. of protons – no. of electrons

   mass number = no. of protons + no. of neutrons

	Species	No. of protons	No. of neutrons	No. of electrons
	$^{40}\text{Ca}^{2+}$	20	20	18
(a)	$^{40}_{18}\text{Ar}$	18	22	18
(b)	$^{39}_{19}\text{K}^{+}$	19	20	18
(c)	$^{35}_{17}\text{Cl}^{-}$	17	18	18

4. D

	${}^{14}_{6}\text{C}$	${}^{14}_{7}\text{N}$
No of protons (p)	6	7
No of electrons (e)	6	7
No of neutrons (n)	14 – 6 = 8	14 – 7 = 7

5. Examples are density (related to mass) and, as chlorine is a gas, rate of diffusion.

6. C

Isotopes different by their number of neutrons.

7. C

Organizing your answer in a table will help with a question like this …

	Species	**No. of protons**	**No. of neutrons**	**No. of electrons**
		taken from the question (but also in the periodic table)	the mass number minus the atomic (proton) number	subtract the charge from the proton number
A	${}^{2}_{1}\text{H}$	1	2 – 1 = 1	1 = 0 = 1
B	${}^{11}_{5}\text{B}$	5	11 – 5 = 6	5 – 0 = 5
C	${}^{16}_{8}\text{O}^{2-}$	8	16 – 8 = 8	8 – (–2) = 10
D	${}^{19}_{9}\text{F}^{-}$	9	19 – 9 = 10	9 – (–1) = 10

Only C has more electrons (10) than neutrons (8).

8. B

${}^{71}\text{Ga}^{+}$ must have 31 protons (information from the periodic table) and 40 neutrons (since these add up to 71, the atomic mass). A neutral gallium atom would have 31 electrons, so therefore Ga^{+} must have 30 electrons.

9. A

Isotopes are atoms of the same element with different mass numbers.

They have the same chemical properties and the same number of protons in their nucleus.

They have different numbers of neutrons.

10. C

Isotopes have the atomic number and different mass numbers.

11. No individual atom with this mass exists. Silicon has a number of isotopes and this is an average value. The claim is true.

12. D

No. of protons = 5, No of neutrons = 11 – 5 = 6

13. B

All atoms of phosphorus have the same number of protons and electrons.

14. RAM = $\frac{(50\times4.31)+(52\times83.76)+(53\times9.55)+(54\times2.38)}{100}$ = 52.0569 ≈ 52.06

15. RAM = $\frac{(20\times x)+(22\times y)}{100}=20.18$ and $x + y = 100$; $y = 100 - x$

$(20\times x)+(22\times100)-(22\times x)=2018$

$2x = 2200 - 2018 = 182$

$x = 91$; abundance ^{20}Ne = 91%

16. Let the abundance of ^{25}Mg be x. Consider 100 atoms.

$24.31 = \frac{(78.90\times24)+(x\times25)+([100-78.90-x]\times26)}{100}$

$2431 = 1893.6 + 25x + 548.6 - 26x$

$2431 = 2442.2 - x$

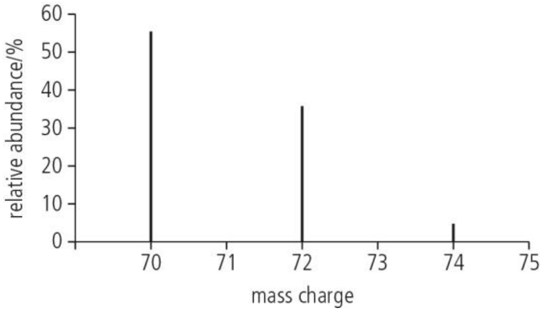
$x = 11.20$

^{25}Mg is 11.20% and ^{26}Mg is 9.90%

17. ^{35}Cl–^{35}Cl is present at an abundance of 75% × 75% = 56.25%

^{35}Cl–^{37}Cl is present at an abundance of 2 × 75% × 25% = 37.5%

^{37}Cl–^{37}Cl is present at an abundance of 25% × 25% = 6.25%



ratio is 9 : 6 : 1

Challenge yourself

1. Potash, soda, magnesia and barytes are compounds of group 1 and 2 elements. These compounds were later broken down into their component elements by electrolysis. (See Reactivity R3.2.)

2. High energy alpha particles can get so close to the nucleus that the strong nuclear force, not included in the Rutherford model, begins to act on them.

3. $${}^{0}_{+1}\mathrm{e} + {}^{0}_{-1}\mathrm{e} \rightarrow 2\,{}^{0}_{0}\gamma$$

Note the left-hand subscripts which represent the charges are balanced.

The negligible masses of the positron and electron are converted into energy in the form of two photons.

4. The nucleons are attracted to each other by the short-range strong nuclear force, which is stronger than the electrostatic repulsive forces.

5. $$V_{\text{nucleus}} = \frac{4\pi}{3} \times R^3 = \frac{4\pi}{3} \times (1.2 \times 10^{-15} \times A^{\frac{1}{3}})^3 = 7.24 \times 10^{-45} \times A\ \text{m}^3$$

the mass of the nucleus is A u, i.e. $A \times 1.67 \times 10^{-27}$ kg

$$\text{density } (\rho) = \frac{\text{mass}}{\text{volume}} = \frac{A \times 1.67 \times 10^{-27}\ \text{kg}}{7.24 \times 10^{-45} \times A\ \text{m}^3} \approx 2.3 \times 10^{17}\ \text{kg m}^{-3}$$

The density is independent of mass number and so all nuclei have the same density.

This is to be expected as all nuclei are composed of protons and neutrons packed closely together and so have similar densities.

The density of the nucleus is extremely high compared to the bulk density of an element. For example, the density of mercury is 1.35×10^4 kg m^{-3} (so the nucleus is denser by 13 orders of magnitude).

6. mass of H atom = mass of proton (H^+) plus mass of electron

$$= 1.672622 \times 10^{-27}\ \text{kg} + 9.109383 \times 10^{-31}\ \text{kg}$$

$$= 1.67353 \times 10^{-27}\ \text{kg}$$

The mass of a hydrogen atom is the same as the mass of a hydrogen ion to 3 significant figures (1.67) and the 4th significant figure only differs by 0.001. The mass of the atom is 1.673 and the ion 1.674.

7. The difference in mass between the molecules is very small. The molecules can only be separated over large distances. A large area of ground is needed.

8. Technetium, Tc, has no stable isotopes. Note that its relative mass is an integer and given in parentheses.

9. Double-charged ions could be formed so some ions could be detected with

$$\frac{m}{z} = \frac{69}{2} = 34.5 \text{ and } \frac{71}{2} = 35.5$$

10. Sample 1

$$\text{RAM} = \frac{(16 \times 99.759) + (18 \times 0.241)}{100} = 16.00482$$

Sample 2

$$\text{RAM} = \frac{(16 \times 99.757) + (18 \times 0.243)}{100} = 16.00486$$

Ice core sample 2 has a higher abundance of the heavier isotopes, which suggests it originated from lower temperatures as heavier water molecules need more energy to evaporate.

11. mass contributed by BrCl = 128 – 14 = 114

${}^{35}_{17}\text{Cl}$ and ${}^{79}_{35}\text{Br}$ present; other isotope combinations give a greater mass

probability 75% × 50% = 37.5%

Practice questions

1. A

Isotopes have the same chemical properties and atomic number.

2. C

The number of protons equals the number of electrons as an atom has no charge.

3. B

All atoms of chlorine have the number of protons and of electrons.

4. D

n. of electrons = atomic number + negative charge = 15 + 3 = 18

5. no. of protons = 25 (1)

no. of electrons = 25 – 2 = 23 (1)

no. of neutrons = 55 – 25 = 30 (1)

6. $$\text{RAM} = \frac{(54 \times 5.95) + (56 \times 91.88) + (57 \times 2.17)}{100} = 55.90$$ (1)

7. **(a)** Cobalt has a greater proportion of heavier isotopes (*OWTTE*) *or* cobalt has greater number of neutrons. (1)

(b) 27 protons and 25 electrons (1)

8. **(a)** different number of neutrons (1)

(b) Same chemical properties because they have the same number of electrons; it is electrons that are responsible for chemical properties. (1)

(c) mass spectrometer (1)

(d) $$\text{RAM} = \frac{(28 \times 92.18) + (29 \times 4.70) + (30 \times 3.12)}{100} = 28.11$$

9. A

$$\text{RAM} = (23 \times 80) + \frac{28 \times 80}{100} = 24$$

10. **(a)** $$\text{RAM} = \frac{(124 \times 2) + (126 \times 4) + (128 \times 6) + (130 \times 5)}{17} = 127.65$$ (1)

The element is likely to be tellurium (Te), assuming it is a typical sample of the element. (1)

(b) Te has an atomic number of 52;

the remaining mass is due to neutrons = 127.68 − 52 = 75.68 (1)

$$\% \text{ mass due to neutrons} = \frac{75.68}{127.68} \times 100 = 59\%$$ (1)

Structure 1.3 Solutions

Exercises

1. C

The lines in the spectra are produced by the transition of electrons between atomic energy levels.

2. A

Visible transitions result in the Balmer series of transitions and are for transitions that end at the $n = 2$ level. There are three possible transitions: $n = 5$ to $n = 2$, $n = 4$ to $n = 2$, and $n = 3$ to $n = 2$. Any other transitions would fall outside of the visible region of the spectrum.

3. **(a)** C

The shortest wavelength corresponds to the largest energy transition.

(b) B

The lines converge at higher frequency as the energy levels converge at higher energies.

4. The transition corresponds to a larger energy change in the atom. The emitted photon has more energy and corresponds to a lower wavelength.

5. The order of increasing energy 4s < 4p < 4d < 4f

6.

Sublevel	4s	4p	4d	4f
No. of orbitals	1	3	5	7

7. $1s^22s^22p^63s^23p^64s^2$

Calcium has an atomic number of 20 and so has 20 electrons. These will fill the 1s, 2s, 2p, 3s, 3p, and 4s energy levels. The electron configuration for calcium is $1s^22s^22p^63s^23p^64s^2$, which totals 20 electrons.

8. $1s^22s^22p_x^22p_y^22p_z^23s^23p_x^13p_y^13p_z^1$

The electrons in the 3p orbitals are all unpaired so three unpaired electrons.

The atomic number of phosphorus is 15. Fill up the sub-orbitals with electrons. When the 3p orbital is reached, there are three electrons, but according to Hund's third rule they have to occupy separate p orbitals.

9. Number of orbitals = $n^2 = 4^2 = 16 = (1 \times s) + (3 \times p) + (5 \times d) + (7 \times f) = 16$

10. C

Energy level 1 has s orbital, energy level 2 has s and p orbitals, energy level 3 is the first level with d orbitals, energy level 4 is the first level with f orbitals. 3f is the non-existent sublevel.

11. C

Consider each of the options in turn;

A is wrong: 3d should be after 4s

B is wrong: 5s should be after 4p

C is correct

D is wrong: 5p should be after 4d

12. **(a)** V is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

(b) K is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(c) Se is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^4$

(d) Sr is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 5s^2$

13. D

Iodine is near the end of period 5, so it has full 3d and 4d orbitals.

This requires 20 d electrons.

14. B

It is unusual to have more than one unfilled set of orbitals. $[Ne]3s^2 3p^3 4s^1$ is the excited state and $[Ne]3s^2 3p^4 4s^0$ would be the ground state.

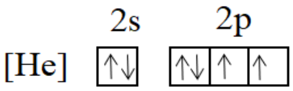
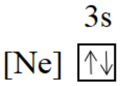
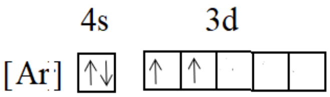
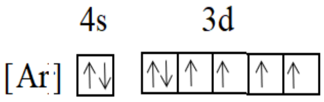
Chromium ($[Ar]3d^5 4s^1$) and similar elements have two unfilled orbitals, but these are exceptional, and show the stability of the half-filled d orbital.

15. B

Titanium is element 22, so its electron configuration is the same as argon (element 18) plus four electrons: $[Ar]4s^2 3d^2$. The 4s electrons are paired (as the orbital is full) but the two electrons in the 3d orbitals will be unpaired in separate orbitals (Hund's rule).

16. D

Consider each option in turn.

A	**O** 8 electrons:$1s^22s^22p^4$ Two unpaired electrons	
B	**Mg** 12 electrons: $1s^22s^22p^6\,3s^2$ No unpaired electrons	
C	**Ti** 22 electrons: $1s^22s^22p^6 3s^23p^64s^23d^2$ Two unpaired electrons	
D	**Fe** 26 electrons: $1s^22s^22p^6 3s^23p^64s^23d^6$ Four unpaired electrons	

17. The first two are relatively easy. From the atomic number and the charge, we can deduce the number of electrons. We then arrange the electrons as usual.

(a) ${}_{8}O^{2-}$ has 10 electrons: $1s^22s^22p^6$

(b) ${}_{17}Cl^{-}$ has 18 electrons: $1s^22s^22p^63s^23p^6$

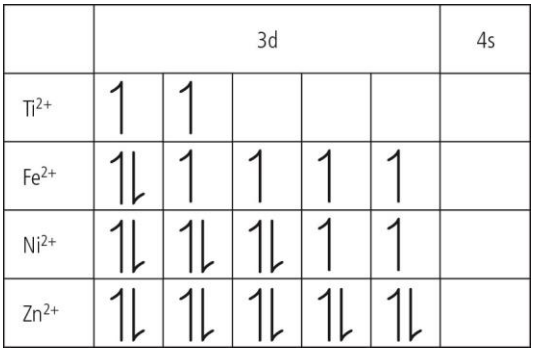
The d-block elements are trickier because the ions form by losing 4s electrons before any 3d electrons. ${}_{22}Ti$ is $1s^22s^22p^63s^23p^63d^24s^2$.

(c) The atom: ${}_{22}Ti$ is $1s^22s^22p^63s^23p^63d^24s^2$.The ion: ${}_{22}Ti^{3+}$ is $1s^22s^22p^63s^23p^63d^14s^0$

(d) With copper it is more complex still, as we need to remember the $4s^1$ configuration for the atom, although this isn't relevant when looking at Cu^{2+}.

The atom: ${}_{29}Cu$ is $1s^22s^22p^63s^23p^63d^{10}4s^1$. The ion: ${}_{29}Cu^{2+}$ is $1s^22s^22p^63s^23p^63d^94s^0$

18. Remember that d electrons will only pair up if all five d orbitals have a single electron in them. When the ions form, it is the 4s electrons which are lost first:



	3d					4s
Ti^{2+}	↑	↑				
Fe^{2+}	↑↓	↑	↑	↑	↑	
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	
Zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	

19. **(a)** Ne is $1s^22s^22p^6$

(b) Negatively charged ions would be $F^–$, $O^{2–}$ or $N^{3–}$; positively charged ions would be Na^+, Mg^{2+} or Al^{3+}.

20. First find the electron configuration of the neutral atom and then remove electrons if the species is a positive ion or add electrons for negative ions.

(a)	Ni atom: $[Ar]3d^84s^2$	Ni^{2+} ion; $[Ar]\ 3d^8$
(b)	Pb atom $[Xe]\ 5d^{10}6s^26p^2$	Pb^{2+} ion $[Xe]\ 5d^{10}6s^2$
(c)	S atom $[Ne]\ 3s^23p^4$	$S^{2–}$ ion $[Ne]\ 3s^23p^6$
(d)	Si atom: $[Ne]\ 3s^23p^2$	Si^{4+} ion : [Ne]

21. Use the periodic table to find out the atomic numbers.

You also need to recall that the orbitals are filled in the order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s

(a) Cl is $1s^22s^22p^63s^23p^5$

(b) Nb is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^35s^2$

(c) Ge is $1s^22s^22p^63s^23p^63d^{10}4s^24p^2$

(d) Sb is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^3$

22. atomic number = no of electrons = electrons in noble gas core + outer electrons

(a) no. of electrons =10 + 4 =14, Si

(b) no. of electrons =18 + 7 =25, Mn

(c) no. of electrons = 36+ 2 = 28, Sr

(d) no. of electrons = 21, Sc

23. 11

Tin (Sn) has an electronic configuration of $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^2$. Each p subshell is made up of three p orbitals. In total, there are 3 for the 2p subshell, 3 for the 3p subshell, 3 for the the 4p subshell and then the 2 5p orbitals.

24. 20

Barium has an electronic configuration of $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{10}5p^{6}6s^{2}$. Therefore, there are 20 electrons in d orbitals.

25. $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}4d^{10}$, which can also be given as $[Kr]4d^{10}$

Neutral cadmium has an electronic configuration of $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}4s^{2}3d^{10}4p^{6}5s^{2}4d^{10}$. When it forms the Cd^{2+} ion, it loses its two 5s electrons.

26. $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{14}5s^{2}5p^{6}5d^{10}6s^{2}6p^{6}5f^{4}$

Use the Periodic Table to find the atomic number = 92.

You also need to recall that the orbitals are filled in the order:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 5p, 5d, 6s, 6p, 7s,5f.

Neutral uranium has a predicted electronic configuration; $1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{14}5s^{2}5p^{6}5d^{10}6s^{2}6p^{6}7s^{2}5f^{4}$. *

When it forms the U^{2+} ion it loses its two 7s electrons.

* As the 6d and 5f are close in energy the actual configuration of the atom is

$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{14}5s^{2}5p^{6}5d^{10}6s^{2}6p^{6,}\ 6d^{1}5f^{3}7s^{2}$), So the ion has the configuration not predicted by our model:

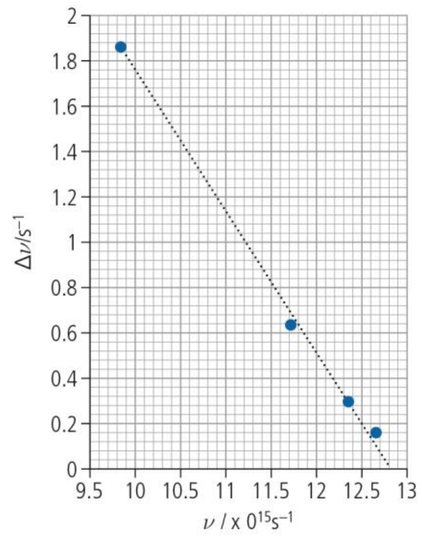
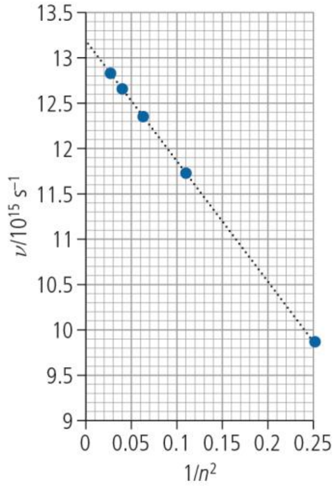
$1s^{2}2s^{2}2p^{6}3s^{2}3p^{6}3d^{10}4s^{2}4p^{6}4d^{10}4f^{14}5s^{2}5p^{6}5d^{10}6s^{2}6p^{6}5f^{3}6d^{1}$

27. $E = hv = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{590\times10^{-9}}$

For one mole

$$E = 6.02 \times 10^{23} \times \frac{6.63\times10^{-34}\times3.0\times10^{8}}{590\times10^{-9}} = 203\ \text{kJ mol}^{-1}$$

28. The convergence can be found graphically.

Method 1	Method 2
	
The equation of the best fit line $\Delta v = -0.613v + 7.884$ When $\Delta v = 0$, $v = 12.86 \times 10^{-15}\ s^{-1}$ Ionization energy = 5132 kJ mol^{-1}	The equation of the best fit line $v = \frac{-13.278}{n^2} + 13.191$ When $n = \infty$, $\frac{1}{n^2} = 0$ $v = 13.19 \times 10^{-15}\ s^{-1}$ Ionization energy = 5264 kJ mol^{-1}

29. Li^{2+}: 11 900 kJ mol^{-1}

For one atom: $E = hv = 6.63 \times 10^{-34} \times 2.97 \times 10^{16}$ J

For one mole: $E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 2.97 \times 10^{16} = 11\ 900$ kJ mol^{-1}

Be^{3+}: 21 000 kJ mol^{-1}

For one atom: $E = hv = 6.63 \times 10^{-34} \times 5.27 \times 10^{16}$ J

For one mole: $E = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times 5.27 \times 10^{16} = 21\ 000\ 00$ kJ mol^{-1}

30. From the graph $\lambda = 233.0$ nm

$$E = hv = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^{8}}{233.0 \times 10^{-9}}$$

For one mole:

$$E = 6.02 \times 10^{23} \times \frac{6.63 \times 10^{-34} \times 3.0 \times 10^{8}}{233.0 \times 10^{-9}} = 514 \text{ kJ mol}^{-1}$$

31. B

There is a sharp increase in ionization energy between the second and third ionization energies, so the first two electrons are easier to remove than the others. Hence the element must be in group 2.

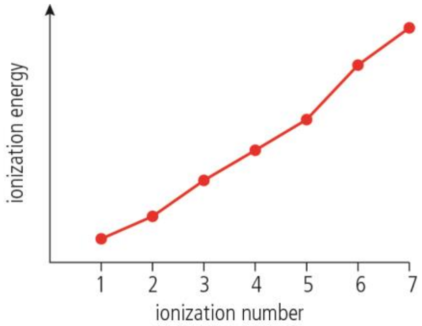
32. B

There is a sharp increase in ionization energy between the second and third ionization energies, so the first two electrons are easier to remove than the others. Hence the element must be in group 2. Of those listed in the question, it must be calcium.

33. **(a)** Carbon has the electronic configuration $1s^2 2s^2 2p^2$. The 4th electron is removed from a 2s orbital, the 5th electron from the 1s orbital. Electrons in 1s orbitals are closer to the nucleus and experience a stronger force of electrostatic force of attraction.

(b) The 2nd electron is removed from a 2p orbital, the 3rd electron from the 2s orbital. Electrons in 2s orbitals are closer to the nucleus and so experience a stronger electrostatic force of attraction.

34.



The first seven electrons all come from the outer energy level, so there will be no sudden increases in ionization energy. There are jumps between the second and third, and the fifth and sixth. The third electron comes from the half-filled 2p orbitals, and the sixth comes from the full 2s orbital. In both cases, removal of an electron from the stable arrangement is found to be difficult.

35, **(a)** There is a general increase from left to right across a period, as the nuclear charge increases. As the electrons are removed from the same main energy level, there is increase in the force of electrostatic attraction between the nucleus and outer electrons.

(b) Mg has the electron configuration [Ne] $3s^2$, Al has the electron configuration [Ne] $3s^2 3p^1$. The 3p electron, removed from Al, has more energy and is further away from the nucleus than the 3s electron removed from Mg.

(c) P has the configuration [Ne] $3s^2 3p^1{}_x 3p^1{}_y 3p^1{}_z$, S has the configuration [Ne] $3s^2 3p^2{}_x 3p^1{}_y 3p^1{}_z$. The electron removed from S comes from a doubly occupied 3p orbital, which is repelled by its partner and is easier to remove than the electron removed from P, which comes from a half-filled orbital.

Challenge yourself

1. D

$$E_{\text{photon}} = \frac{hc}{\lambda} = \frac{6.63 \times 10^{-34} \times 3.0 \times 10^{8}}{588 \times 10^{-9}} = 3.38 \times 10^{-19}\ \text{J}$$

$\Delta E_{\text{atom}} = 3.38 \times 10^{-19}$ J

This corresponds to IV → II: $-2.42 \times 10^{-19} - (-5.80 \times 10^{-19}) = 3.38 \times 10^{-19}$ J

2. The Schrödinger model:

does not have well defined orbits for the electrons

does not treat the electron as a localized particle but gives a probability wave description

predicts the relative intensities of various spectral lines.

3. A

The Bohr model of the hydrogen atom predicts the energy of the lines in the emission spectra of atomic hydrogen. It does not explain the elative intensity of the different spectral lines in the emission spectrum of atomic hydrogen.

4. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6 6d^2 7s^2$

or [Rn] $6d^2 7s^2$

5. **(a)** [Rn] $7s^2 5f^{14} 6d^7$

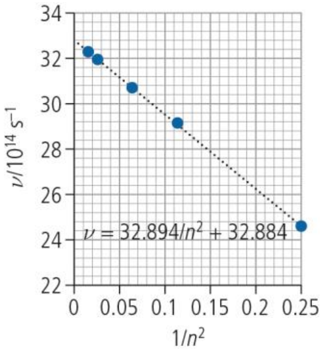
(b) The first g block element would be [Rn] $7s^2 5f^{14} 6d^{10} 7p^6 8s^2 8g^1$

$Z = 86 + 2 + 14 + 10 + 6 + 2 + 1 = 121$

6. **(a)** In 2 dimensions, the *xy* plane, there would be two types of p orbital (p_x and p_y) and two types of d orbitals(d_{xy} and d_{x2-y2})

(b) The change in the number of orbitals changes the number of groups in the p and d blocks. 4 groups in the p and d block.

7.



The frequency corresponding to $n = \infty$ can be read as the intercept on the *y*-axis and equals 32.884×10^{-14} s^{-1}.

We can use the frequency obtained to calculate the ionization energy.

Using the equation $E = h\, v$ we have the ionization energy for one atom:

$E = 32.884 \times 10^{-14}\ s^{-1} \times 6.63 \times 10^{-34}\ J\ s$

So for one mole the ionization energy is given by:

I.E. = $32.884 \times 10^{-14}\ s^{-1} \times 6.63 \times 10^{-34}\ J\ s \times 6.02 \times 10^{23}\ mol^{-1} = 1312\ kJ\ mol^{-1}$

This agrees with the value given in Section 8 of the IB data booklet.

The second method gives a more accurate value as the points better fit a straight line.

Practice questions

1. D

Neutral chromium has an electronic configuration of $1s^22s^22p^63s^23p^64s^13d^5$. When it forms the Cr^{2+} ion it loses its one 4s and one 3d electrons: $1s^22s^22p^63s^23p^63d^4$

2. A

From Section 5 of the data booklet, ultraviolet are high energy and short wavelength and infrared are lower energy and low frequency.

3. B

It is a positive ion with a complete d sublevel. It is an ion of copper: Cu^+.

We see in S3.1 that the distinctive color of Cu^{2+} ions is due to its incomplete d sublevel.

4. B

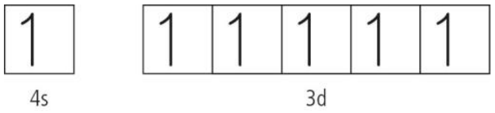
Visible light is emitted when electrons fall to the $n = 2$ level.

5 **(a)** the electron configuration of argon, which is $1s^22s^22p^63s^23p^6$ (1)

(b) $x = 1$ and $y = 5$

(1)

(c)



(1)

Accept all six arrows pointing down rather than up.

6 **(a)** IV < I < II < III *or* ultraviolet radiation < yellow light < red light < infrared radiation (1)

(b) A continuous spectrum has all colors/wavelengths/frequencies whereas a line spectrum has only lines of sharp/discrete/specific colors/wavelengths/frequencies. (1)

7. B

The large jump between the fourth and fifth ionization energies suggest that there are 4 electrons in the outer energy level and at least 4 in the next. It is in group 4 but not carbon. It is silicon.

8. B

The large jump between the second and third ionization energies suggest that there are 2 electrons in the outer energy level. As these electrons are easily lost it forms X^{2+}ions. X is a group 2 element.

9. B

The large jump between the fourth and fifth ionization energies suggest that there are 4 electrons in the outer energy level and at least 3 in the next. It is in group 4 and so has a ns^2np^2 configuration. The electron is removed from a p orbital.

10. $1s^22s^22p^63s^1$ (1)

Do not accept [Ne]3s¹

First electron easy/easiest to remove *or* 1 electron in outermost/n = 3 energy level/furthest from nucleus (1)

large increase between 1st and 2nd I.E. as electron now removed from n = 2 (1)

next 8 electrons slightly more difficult to remove *or* show (relatively) small increase as these electrons are in the same energy level/second energy level/n = 2 (1)

large increase between 9th and 10th I.E. as electron now removed from n = 1 *or* last two electrons very hard/most difficult to remove *or* innermost/lowest/closest to the nucleus/energy level (*OWTTE*) (1)

electron 11 also comes from 1s, so shows a small increase (1)

max (4)

11. **(a)** Evidence for main levels:

highest values for noble gases / lowest values for alkali metals / *OWTTE* (1)

general increase across a period (1)

Evidence for sublevels:

drop in I.E. from Be to B/Mg to Al/group 2 to group 13 (1)

drop in I.E. from N to O/P to S/group 15 to group 16 (1)

(b) $M^+(g) \rightarrow M^{2+}(g) + e^-$ *OWTTE* (1)

Accept e instead of e⁻

12. From the graph λ = 294 nm (1)

$$E = hv = \frac{hc}{\lambda} = \frac{6.63\times10^{-34}\times3.0\times10^{8}}{294\times10^{-9}}$$

For one mole

$$E = 6.02\times10^{23}\times\frac{6.63\times10^{-34}\times3.0\times10^{8}}{294\times10^{-9}} = 410\ \text{kJ mol}^{-1}$$ (1)

Structure 1.4

Exercises

1. Note that slightly different answers might be obtained if $L = 6 \times 10^{23}$ is used.

(a) 1 mole of C_2H_5OH contains 6 moles of hydrogen atoms

1 mole of C_2H_5OH contains $6 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of C_2H_5OH contains 3.61×10^{24} hydrogen atoms

0.020 moles therefore contains $(3.61 \times 10^{24}) \times 0.020 = 7.2 \times 10^{22}$ hydrogen atoms

(b) 1 mole of H_2O contains 2 moles of hydrogen atoms

1 mole of H_2O contains $2 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of H_2O contains 1.20×10^{24} hydrogen atoms

2.50 moles therefore contains $(1.20 \times 10^{24}) \times 2.50 = 3.01 \times 10^{24}$ hydrogen atoms

(c) 1 mole of $Ca(HCO_3)_2$ contains 2 moles of hydrogen atoms

1 mole of $Ca(HCO_3)_2$ contains $2 \times (6.02 \times 10^{23})$ hydrogen atoms

1 mole of $Ca(HCO_3)_2$ contains 1.20×10^{24} hydrogen atoms

0.10 moles therefore contains $(1.20 \times 10^{24}) \times 0.10 = 1.2 \times 10^{23}$ hydrogen atoms

2. Propane contains 3 carbon atoms and 8 hydrogen atoms. If the three carbon atoms are equivalent to 0.20 moles of carbon, then 1 carbon atom = $\frac{0.20}{3}$ moles of carbon. So, 8 atoms of hydrogen would be equivalent to $\frac{0.20}{3} \times 8$ moles of hydrogen = 0.53 moles of H.

3. Sulfuric acid contains four oxygen atoms. If there are 6.02×10^{23} atoms of oxygen in total then there must be $\frac{6.02 \times 10^{23}}{4}$ molecules of sulfuric acid $= 1.51 \times 10^{23}$ molecules of sulfuric acid (= 0.250 mol of sulfuric acid).

4. As the value for Ar is closer to 35 than 37, the 35Cl must be the most abundant isotope.
A 50 : 50 mixture would have Ar of 36.

5. **(a)** Magnesium phosphate, $Mg_3(PO_4)_2$

Element	**Relative atomic mass**	**Number of atoms of each element**	**Relative mass**
Mg	24.31	3	72.93
P	30.97	2	61.94
O	16.00	8	128.00
M_r			262.87

(b) Ascorbic acid, $C_6H_8O_6$

Element	**Relative atomic mass**	**Number of atoms of each element**	**Relative mass**
C	12.01	6	72.06
H	1.01	8	8.08
O	16.00	6	96.00
M_r			176.14

(c) Calcium nitrate, $Ca(NO_3)_2$

Element	**Relative atomic mass**	**Number of atoms of each element**	**Relative mass**
Ca	40.08	1	40.08
N	14.01	2	28.02
O	16.00	6	96.00
M_r			164.10

(d) Hydrated sodium thiosulfate, $Na_2S_2O_3.5H_2O$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Na	22.99	2	45.98
S	32.07	2	64.14
O	16.00	8	128.00
H	1.01	10	10.10
M_r			248.22

6. Calculate the M_r of calcium arsenate, $Ca_3(AsO_4)_2$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
Ca	40.08	3	120.24
As	74.92	2	149.84
O	16.00	8	128.00
M_r			398.08

The M_r is the mass of 1 mole of calcium arsenate.

0.475 moles therefore has a mass of 398.08 × 0.475 = 189.1 g

7. (If not using calculator, then use rounded values for A_r)

M_r of $CO_2 = 12 + (16 \times 2) = 44$

$$\text{moles} = \frac{\text{mass}}{M_r} = \frac{66}{44} = 1.5$$

8. Copper(II) chloride has a M_r of $63.55 + (35.45 \times 2) = 134.45$

0.5 g is equivalent to $\frac{0.5}{134.45}$ mol of copper chloride, i.e. 3.72×10^{-3} mol

There are 2 chloride ions in each copper chloride molecule.

There must be $2 \times (3.72 \times 10^{-3})$ mol of chloride ions present,

i.e. 7.44×10^{-3} mol (= 0.0074 mol)

9. 36.55 g of carbon = $\frac{36.55}{12.01}$ = 3.04 mol of carbon

1 mole of carbon contains 6.02×10^{23} atoms of carbon

Therefore 3.04 moles of carbon contain

$3.04 \times (6.02 \times 10^{23})$ atoms of carbon = 1.83×10^{24} atoms

10. (If not using calculator, then use rounded values for A_r)

Calculate the M_r of sucrose, $C_{12}H_{22}O_{11}$

Element	Relative atomic mass	Number of atoms of each element	Relative mass
carbon	12	12	144
hydrogen	1	22	22
oxygen	16	11	176
M_r			342

This is the mass of 1 mole of sucrose, therefore the mass of 0.500 mol of sucrose is 171 g

11. (If not using calculator, then use rounded values for A_r)

Water: the M_r of H_2O = 18 (= 16 + 2 × 1)

Therefore 10 g of water is equivalent to $\frac{10}{18}$ mol of water (= 0.55 mol)

Mercury: the relative atomic mass of mercury is 201

Therefore 10 g is equivalent to $\frac{10}{201}$ mol of mercury (≈ 0.05 mol)

10 g of water contains more particles than 10 g of mercury because it has more moles.

12. (If not using calculator, then use rounded values for A_r)

M_r of N_2H_4 is (2 × 14) + (4 × 1) = 32. 1 mol therefore has a mass of 32 g

M_r of N_2 is (2 × 14) = 28. 2 mol therefore has a mass of 56 g

M_r of NH_3 is 14 + (3 × 1) = 17. 3 mol therefore has a mass of 51 g

M_r of H_2 is (2 × 1) = 2. 25 mol therefore has a mass of 50 g

So in order of decreasing order of mass:

nitrogen > ammonia > hydrogen > hydrazine

13. **(a)** C_2H_2: the ratio of carbon to hydrogen atoms can be simplified to CH

(b) $C_6H_{12}O_6$: the ratio of atoms can be simplified to CH_2O

(c) $C_{12}H_{22}O_{11}$: the ratio of atoms cannot be simplified – the empirical and molecular formula are the same.

(d) C_8H_{18}: the ratio of atoms can be simplified to C_4H_9

(e) C_8H_{14}: the ratio of atoms can be simplified to C_4H_7

(f) CH_3COOH, i.e. $C_2H_4O_2$: the ratio of atoms can be simplified to CH_2O

14.

	Sodium	**Sulfur**	**Oxygen**
mass / g	0.979	1.365	1.021
moles	$\frac{0.979}{22.99}=0.043$	$\frac{1.365}{32.07}=0.043$	$\frac{1.021}{16.00}=0.064$
divide by smallest	1.00	1.00	1.49
nearest whole number ratio	2	2	3

The empirical formula is $Na_2S_2O_3$

15.

	Cobalt	**Sulfur**	**Oxygen**	**Water (H_2O)**
mass / g	2.10	1.14	2.28	4.50
moles	$\frac{2.10}{58.93}=0.036$	$\frac{1.14}{32.07}=0.036$	$\frac{2.28}{16.00}=0.143$	$\frac{4.50}{18.02}=0.250$
divide by smallest	1.00	1.00	3.97	6.94
nearest whole number ratio	1	1	4	7

The empirical formula is $CoSO_4.7H_2O$

16.

	Carbon	**Hydrogen**	**Nitrogen**
% by mass	83.89	10.35	5.76
moles	$\frac{83.89}{12.01}=6.985$	$\frac{10.35}{1.01}=10.248$	$\frac{5.76}{14.01}=0.411$
divide by smallest	16.995	24.934	1.00
nearest whole number ratio	17	25	1

The empirical formula is $C_{17}H_{25}N$

17. M_r of NH_3 = 14.01 + (3 × 1.01) = 17.04

% by mass of N is $\frac{14.01}{17.04}\times 100 = 82.22\%$

M_r of $CO(NH_2)_2$ = 12.01 + 16.00 + 2 × [14.01 + (2 × 1.01)] = 62.07

% by mass of N is $\frac{28.02}{62.07}\times 100 = 45.14\%$

(Note: 28.02 since there are two nitrogen atoms in the molecule)

M_r of $(NH_4)_2SO_4$ = (2 × 14.01) + (8 × 1.01) + 32.07 + (4 × 16.00) = 132.17

% by mass of N is $\frac{28.02}{132.17}\times 100 = 21.20\%$

(Note: 28.02 since there are two nitrogen atoms in the molecule)

So overall, ammonia, NH_3, has the highest % by mass of nitrogen.

18. moles of nitrogen = $\frac{0.673}{14.01}$ = 0.048

In the formula there are 3 moles of metal associated with each mole of metal.

Therefore, moles of metal in the compound = 3 × 0.048 = 0.144

relative atomic mass $= \frac{\text{mass}}{\text{moles}} = \frac{1.00}{0.144} = 6.94$

From the periodic table, it can be seen that the element is lithium.

19. $$\text{percentage by mass} = \frac{\text{relative atomic mass of cadmium}}{M_r} \times 100\%$$

- for CdS, percentage by mass = $\frac{112.41}{112.41 + 32.07} \times 100 = 77.80\%$
- for CdSe, percentage by mass = $\frac{112.41}{112.41 + 78.96} \times 100 = 58.74\%$
- for CdTe, percentage by mass = $\frac{112.41}{112.41 + 127.60} \times 100 = 46.84\%$

Overall, CdS has the highest percentage by mass of cadmium.

You could also approach this question by considering the A_r of the other element in the compound. Sulfur has the lowest A_r and so CdS will have the highest percentage by mass of cadmium.

20.

	Carbon	**Hydrogen**
% by mass	100 – 7.74 = 92.26	7.74
moles	$\frac{92.26}{12.01} = 7.68$	$\frac{7.74}{1.01} = 7.66$
divide by smallest	1.00	1.00
nearest whole number ratio	1	1

Empirical formula is therefore CH. This has a mass of 13.02 g mol^{-1}. This number divides into the molar mass of the whole compound 6 times (i.e. $\frac{78.10}{13.02} = 6$).

The molecular formula is therefore 6 times the empirical formula = C_6H_6

21.

	Hydrogen	**Phosphorus**	**Oxygen**
mass / g	0.0220	0.3374	0.8821 – (0.0220 + 3374)= 0.5227
moles	$\frac{0.0220}{1.01} = 0.02178$	$\frac{0.3374}{30.97} = 0.01089$	$\frac{0.5227}{16.00} = 0.03266$
divide by smallest	2.00	1.00	2.99
nearest whole number ratio	2	1	3

Empirical formula is therefore H_2PO_3. This has a mass of 80.99 g mol^{-1}. This number divides into the molar mass of the whole compound 2 times (i.e. $\frac{162}{80.99} = 2$).

The molecular formula is therefore 2 times the empirical formula = $H_4P_2O_6$

22.

	Carbon	**Hydrogen**	**Nitrogen**	**Phosphorus**	**Oxygen**
mass / g	0.1927	0.02590	0.1124	0.1491	0.3337
moles	$\frac{0.1927}{12.01} = 0.0160$	$\frac{0.02590}{1.01} = 0.0256$	$\frac{0.1124}{14.01} = 0.0080$	$\frac{0.1491}{30.97} = 0.0048$	$\frac{0.3337}{16.00} = 0.0208$
divide by smallest	3.33	5.33	1.66	1.00	4.33
nearest whole number ratio	10	16	5	3	13

Note:

- the mass for oxygen is obtained by subtracting all the masses of the other elements from 0.8138 g
- the nearest whole number ratio is obtained by multiplying by 3 to round everything up (numbers ending in '.33' and '.66' are the clue here).

The empirical formula is $C_{10}H_{16}N_5O_{13}P_3$. The formula mass of this is 507 g mol^{-1} so the empirical and molecular formulae are the same.

23. moles of CO_2 = $\frac{0.66}{12.01+(16.00\times 2)}=0.015$

- this is the same as the number of moles of carbon atoms present
- moles of water = $\frac{0.36}{(1.01\times 2)+16.00}=0.020$
- twice this number is the number of moles of hydrogen atoms present, i.e. 0.040

Convert these into masses in order to find the mass of oxygen in the original sample:

mass of carbon = 0.015 × 12.01 = 0.18 g

mass of hydrogen = 0.04 × 1.01 = 0.04 g

therefore mass of oxygen = 0.30 – 0.18 – 0.04 = 0.08 g

Now the calculation can proceed as usual.

	Carbon	**Hydrogen**	**Oxygen**
mass / g	0.18	0.04	0.08
moles	$\frac{0.18}{12.01}=0.015$	$\frac{0.04}{1.01}=0.040$	$\frac{0.08}{16.00}=0.005$
divide by smallest	3.00	8.00	1
nearest whole number ratio	3	8	1

Empirical formula is C_3H_8O

24.
- Weigh the chalk before and after the name has been written.
- Subtract the values to obtain the mass of chalk used.
- Calculate the number of moles of chalk used.

$$\text{moles}=\frac{\text{mass}}{M_r\,\text{CaCO}_3}=\frac{\text{mass}}{40.08+12.01+(3\times 16.00)}=\frac{\text{mass}}{100.09}$$

This is the same as the number of moles of carbon atoms used.

Therefore, the number of carbon atoms used = moles of chalk × (6.02 × 10^{23})

25. number of moles required = concentration × volume

$= 0.200\ \text{mol dm}^{-3} \times 0.250\ \text{dm}^3$ ($1\ \text{dm}^3 = 1000\ \text{cm}^3$)

$= 0.0500\ \text{mol}$

Formula of potassium hydroxide is KOH. (You should know that the ions are K^+ and OH^-.)

mass of 1 mol of KOH = 39.10 + 16.00 + 1.01 = 56.11 g

mass of 0.050 mol of KOH = 0.0500 × 56.11 = 2.81 g

26. $MgSO_4.7H_2O$ has a molar mass of $24.31 + 32.07 + 11 \times 16.00 + 14 \times 1.01 = 246.52\ \text{g mol}^{-1}$

$0.100\ \text{dm}^3$ of a $0.200\ \text{mol dm}^{-3}$ solution contains $0.100 \times 0.200 = 0.0200$ mol of solute

0.0200 mol of $MgSO_4.7H_2O$ has a mass of $0.0200 \times 246.52\ \text{g mol}^{-1} = 4.93$ g

27. In $0.250\ \text{dm}^3$ of $0.0200\ \text{mol dm}^{-3}$ of solution, there are

0.250 × 0.0200 = 0.00500 mol of solute

For every mole of $ZnCl_2$, two moles of chloride ions are released in solutions:

$ZnCl_2(s) \rightarrow Zn^{2+}(aq) + 2Cl^-(aq)$

so, 0.00500 mol of $ZnCl_2$ will give 0.0100 mol of chloride in solution.

28. $250\ \text{cm}^3$ of solution contain 5.85 g of sodium chloride

$1\ \text{dm}^3$ of solution contains $5.85 \times \frac{1000}{250}$ = 23.40 g of sodium chloride

23.40 g of NaCl is equivalent to $\frac{23.40}{22.99 + 35.45}$ = 0.40 mol

So concentration is $0.40\ \text{mol dm}^{-3}$

29. $100\ \text{cm}^3$ of $0.5\ \text{mol dm}^{-3}$ nitric acid contains 0.05 moles of acid

volume of $16.0\ \text{mol dm}^{-3}$ acid to contain this number of moles = $\frac{0.05}{16.0} \times 1000 = 3.1\ \text{cm}^3$

30. M_r lead sulfate, $PbSO_4 = 207 + 32 + (16 \times 4) = 303$

mol $PbSO_4(s)$ precipitated = $\frac{1.13\ \text{g}}{303}$ = 0.003729 mol

reaction is 1: 1 : 1 ratio of reactants and $PbSO_4$

so mol $PbSO_4$ = mol Na_2SO_4 = mol $Pb(NO_3)_2$ = 0.003729 mol in the reacting volumes

Therefore conc $Na_2SO_4 = \frac{1000}{35.30\ \text{cm}^3} \times 0.003729\ \text{mol} = 0.106\ \text{mol dm}^{-3}$

And conc $Pb(NO_3)_2 = \frac{1000}{32.50} \times 0.003729\ \text{mol} = 0.115\ \text{mol dm}^{-3}$

31. Equal numbers of moles in all balloons, so equal number of particles.

Therefore, mass determined by molar mass:

Ar = 40, CH_4 = 16, N_2 = 28, H_2 = 2

Ar is the heaviest.

32. A_r argon = 40, A_r neon = 20

same mass of neon therefore has more particles, so occupies greater volume than same mass as argon

33. 3 moles hydrogen → 2 moles ammonia

So 3 volumes H_2 → 2 volumes NH_3

So 30 dm^3 NH_3 produced from $\frac{30}{2} \times 3 = 45\ dm^3$

34. One mole of H_2 occupies 10 dm^3

So one mole of H atoms occupies 10 dm^3 under the same conditions

(assuming they don't react together to form H_2)

Practice Questions

Questions 1–11 are multiple choice questions similar to those in Paper 1 of IB examinations. As we are only looking for the best answer here, it is generally appropriate to round the values for relative atomic mass to whole numbers to make the calculations easier.

1. D

Note that the value of the Avogadro constant will be given in the examination.

One mole of $CuSO_4.5H_2O$ will contain 9 moles of oxygen atoms.

0.100 moles of $CuSO_4.5H_2O$ will contain 0.900 moles of oxygen atoms.

0.900 moles = $0.900 \times N_A$ atoms = $0.900 \times 6.02 \times 10^{23}$ atoms = 5.42×10^{23} atoms.

2. B

We can assume that the gases are all ideal gases. This means that under the same

conditions of pressure, volume and temperature, they all contain the same amount of gas molecules.

The heaviest container will therefore contain the gas with the largest molar mass.

Nitrogen: $M(N_2) = 2 \times 14\ \text{g mol}^{-1} = 28\ \text{g mol}^{-1}$

Oxygen: $M(O_2) = 2 \times 16\ \text{g mol}^{-1} = 32\ \text{g mol}^{-1}$

Ethane: $M(C_2H_6) = (2 \times 12) + (6 \times 1)\ \text{g mol}^{-1} = 30\ \text{g mol}^{-1}$

Neon: $M(\text{Ne}) = 20\ \text{g mol}^{-1}$

Oxygen has the largest molar mass so the heaviest container will be B.

3. A

$$n(FeSO_4) = cV = 0.020\ \text{mol dm}^{-3} \times \frac{100}{1000}\ \text{dm}^3$$

$$= 0.0020\ \text{mol} = 2.0 \times 10^{-3}\ \text{mol}$$

$n(SO_4^{2-}) = n(FeSO_4) = 2.0 \times 10^{-3}$ mol

4. B

To calculate a concentration, we first need to convert the mass of $NaNO_3$ to moles using the M_r of 85 provided for $NaNO_3$:

$n(NaNO_3)$ = 1.7 g

85 g mol^{-1} = 0.020 mol

$[NaNO_3]$ = $$[NaNO_3] = \frac{n}{V} = \frac{0.020\ \text{mol}}{0.20\ \text{dm}^3} = 0.1\ \text{mol dm}^{-3}$$

5. D

Based on the empirical formula of the gas, CH_2, the relative formula mass can be calculated:

relative formula mass (CH_2) = 12 + (2 × 1) = 14

Dividing the relative molar mass by the relative formula mass gives us the multiplier, *x*, that must

be applied to the empirical formula to give the molecular formula:

$$x = \frac{\text{relative molecular mass}}{\text{relative formula mass}} = \frac{56}{14} = 4$$

Molecular formula = ‘4 × CH_2’ = C_4H_8

6. D

1 mole of benzamide, $C_6H_5CONH_2$, will contain 7 moles of hydrogen atoms.

1.0 moles of $C_6H_5CONH_2$ will contain 7.0 moles of hydrogen atoms.

7.0 moles = 7.0 × (6.02 × 10^{23}) atoms = 4.2 × 10^{24} atoms

7. C

We first calculate the total number of moles of NaCl present in the two solutions:

n(total) = n(solution 1) + n(solution 2) = $c_1V_1 + c_2V_2$

$$\left(0.200\ \text{mol dm}^{-3} \times \frac{10.0}{1000}\text{dm}^{-3}\right) + \left(0.600\ \text{mol dm}^{-3} \times \frac{30.0}{1000}\text{dm}^{-3}\right)\left(0.200\ \text{mol dm}^{-3} \times \frac{10.0}{1000}\text{dm}^{-3}\right) + \left(0.600\ \text{mol dm}^{-3} \times \frac{30.0}{1000}\text{dm}^{-3}\right)$$

= 0.00200 mol + 0.0180 mol

= 0.0200 mol

$$[\text{NaCl}] = \frac{n}{(V_1 + V_2)}$$

$$= \frac{0.0200\ \text{mol}}{\frac{(10.0 + 30.0)}{1000}}\ \text{dm}^{-3}$$

$$= \frac{0.0200\ \text{mol}}{0.0400\ \text{dm}^{-3}} = 0.500\ \text{mol dm}^{-3}$$

8. D

Determine the empirical formula of the compound.

	C	H	O
Mass (g)	12	2	16
Moles	$\frac{12g}{12\text{g mol}^{-1}}$	$\frac{2g}{1\text{g mol}^{-1}}$	$\frac{16g}{16\text{g mol}^{-1}}$
	=1.0	=2.0	=1.0

Empirical formula = CH_2O

Formula mass (CH_2O) = (12 + (2 × 1) + 16) g mol^{-1} = 30 g mol^{-1}

Dividing the molar mass by the formula mass gives us the multiplier, *x*, that must be applied to the empirical formula to give the molecular formula:

$$x = \frac{\text{relative molecular mass}}{\text{relative formula mass}} = \frac{60\text{ g mol}^{-1}}{30\text{ g mol}^{-1}} = 2$$

Molecular formula = ‘2 × CH_2O’ = $C_2H_4O_2$

9. C

We can calculate the final concentration, c_2,

using the dilution formula $c_1V_1 = c_2V_2$.

$$\begin{aligned} c_2 &= \frac{c_1V_1}{V_2} \\ &= \frac{0.5\text{ mol dm}^{-3} \times 200\text{ cm}^{-3}}{(200+300)\text{ cm}^{-3}} \\ &= \frac{0.5\text{ mol dm}^{-3} \times 200\text{ cm}^{-3}}{500\text{ cm}^{-3}} \\ &= 0.2\text{ mol dm}^{-3} \end{aligned}$$

10. D

The question asks for an approximate value

so we can use whole numbers for the atomic

masses of the constituent elements of

$MgSO_4.7H_2O$:

$M(MgSO_4.7H_2O)$ = (24 + 32 + (4 × 16) + (14 × 1) + (7 × 16)) g mol^{-1}

= 246 g mol^{-1}

11. A

For a molecular formula to also be an empirical formula it cannot be converted to a simpler ratio.

With the exception of C_5H_{12} all of the formulas provided can be simplified.

$C_5H_{10} \rightarrow CH_2$ $C_4H_8 \rightarrow CH_2$ $C_4H_{10} \rightarrow C_2H_5$

Correct answer is **A**.

12 **(a)** We first find the mass of water that was removed in drying the potassium carbonate:

$m(H_2O) = m(\text{hydrated } K_2CO_3) - m(\text{dry } K_2CO_3)$

$= 10.00 \text{ g} - 7.93 \text{ g}$

$= 2.07 \text{ g}$

$$n(H_2O) = \frac{m}{M(H_2O)} = \frac{2.07g}{18.02g \text{ mol}^{-1}} = 0.115 \text{ mol} \qquad (1)$$

(b) $$n(K_2CO_3) = \frac{m}{M(K_2CO_3)} = \frac{7.93g}{138.21g \text{ mol}^{-1}} = 0.0574 \text{ mol} \qquad (1)$$

(c) We can determine the value of *x* in the hydrated potassium carbonate:

$$x = \frac{n(H_2O \text{ removed})}{n(\text{dry } K_2CO_3)} = \frac{0.115\text{mol}}{0.0574\text{mol}} = 2.00$$

Therefore, the formula of the hydrate is $K_2CO_3.2H_2O$ (1)

(d) By repeating the process of heating and weighing until a constant mass is obtained. (To ensure accurate results it will be necessary to cool the sample to room temperature before each weighing.) (1)

13. We can work out the % O by subtracting the total of the other elements from 100

% O = 100 – (62.02 + 10.43) = 27.55 % (1)

We can then convert the % to relative number of atoms by dividing each percentage by the relative atomic mass. (Note we work to 4 SF here as that was the precision of the data in the question.)

This can be expressed as a simpler ratio by dividing by the smallest number, in this case 1.73.

% by mass	**C**	**H**	**O**
Divide % by mass by A_r	$\frac{62.02}{12.01} = 5.164$	$\frac{10.43}{1.01} = 10.43$	$\frac{27.55}{16.01} = 1.73$
divide by smallest	2.99	6.06	1

(1)

Rounding these numbers gives us the ratio which we can express as an empirical formula.

Empirical formula = C_3H_6O (1)

14. **(a)** Similar to **Q13**, we first need to determine the % oxygen by subtraction.

% O = 100 – 43.6 = 56.4 % (1)

We can then convert the % to relative number of atoms by dividing each percentage by the relative atomic mass.

This can be expressed as a simpler ratio by dividing by the smallest number, in this case 1.41.

% by mass	**P**	**O**
Divide % by mass by A_r	$\frac{43.6}{30.97} = 1.41$	$\frac{56.4}{16.01} = 3.52$
divide by smallest	1	2.49

(1)

As we want to express the formula as whole numbers of atoms, we double this ratio 1 : 2.49 ⟶ 2 : 4.98 and then round this ratio slightly.

Empirical formula = P_2O_5 (1)

(b) Molecular formula = (empirical formula)n

From the empirical formula calculated above, we can calculate its relative formula mass, and substitute these values into the equation above.

$$285 \text{ g mol}^{-1} = [(30.97 \times 2) + (16.01 \times 5)]\ n$$

$$= 141.99 \times n$$

$$n = \frac{285}{142} = 2$$

Once we know the value of *n*, we multiply the empirical formula by this value to give the molecular formula.

Molecular formula = P_4O_{10} (1)

15 **(a)** Calculate the amount in moles required for the solution:

n ($NaHCO_3$) = conc × volume

$$= 0.500 \text{ mol dm}^{-3} \times \frac{250.00}{1000.00} \text{ dm}^3$$

$$= 0.125 \text{ mol}$$

Calculate the relative formula mass of sodium hydrogencarbonate:

$M(NaHCO_3) = 22.99 + 1.01 + 12.01 + (16.00 \times 3) = 84.00 \text{ g mol}^{-1.}$ (1)

And from this determine the mass of $NaHCO_3(s)$ required for the solution:

mass ($NaHCO_3$) = 0.125 mol × 84.00 g mol^{-1} = 10.50 g [1]

Make sure that you name the apparatus involved in preparing the solution and dilution.

Measure the mass of 10.50 g $NaHCO_3$ using a **balance** and transfer to a **250.00 cm^3 volumetric flask** (2)

Add **distilled water** to the flask, with frequent shaking, up to the mark. (1)

(b) To prepare dilutions of stock solution:

Using a 10.00 cm^3 pipette transfer 10.00 cm^3 of the stock solution (from **a**) into a 100.00 cm^3 volumetric flask.

Make up to the mark with distilled water → 0.0500 mol dm^{-3} solution and shake thoroughly. (2)

Using a clean 10.00 cm^3 pipette transfer 10.00 cm^3 of the 0.0500 mol dm^{-3} solution into a 100.00 cm^3 volumetric flask.

Make up to the mark with distilled water → 0.00500 mol dm^{-3} solution. (2)

Structure 1.5

Exercises

1. A

The volume of ideal gas particles is assumed to be negligible and so is unaffected by any changes. The average kinetic energy and speed is constant as the temperature is constant. Although the speed of the particles stays the same, the frequency of collisions increases as the volume of the container increases. There are no intermolecular forces in an ideal gas.

2. C

The ideal gas model assumes that collisions between molecules and the container are elastic.

3. A

The average kinetic speed and speed increases with temperature. As the speed increases there will be a greater frequency of collisions as the volume of the container is constant. This results in increased pressure.

4. D

All the statements are assumptions of the kinetic model of ideal gases.

5. D

The pressure of an ideal gas increases when the temperature is increased as the particles collide with the walls of the container more frequently. The particles also collide with each other more frequently but it is the collisions with the walls of the container that produce the pressure.

6. 3 and 4

Noble gas atoms:

- have a range of atomic speeds and move randomly. The average kinetic energy of the atoms is particles is proportional to the temperature.
- collide **elastically with the walls of a container.**
- have weak dispersion intermolecular forces between the atoms
- have some volume.

7. B

Gases deviate from ideal gas behaviour because their particles have intermolecular forces of attraction.

8. **(a)** Particles are in constant random motion and collide with each other and with the walls of the container in perfectly elastic collisions. The kinetic energy of the particles increases with temperature. There are no intermolecular forces and the volume of the particles is negligible relative to the volume of the gas.

(b) At low temperature, the particles have lower kinetic energy, which favours the formation of intermolecular forces and reduces gas pressure. $PV = nRT$

9. The assumptions are most valid when the gas particles are widely separated and the intermolecular forces weakest. These occur at conditions of high temperature and low pressure.

10. D

$T(\text{K}) - 273 = T(^{\circ}\text{C})$

$323\ \text{K} - 273 = 50\ ^{\circ}\text{C}$

11. C

As the volume is constant: $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{2.0}{273+27} = \frac{P_2}{273+27+300}$$

$$P_2 = (273+27+300) \times \frac{2.0}{273+27} = 600 \times \frac{2}{300} = 4\ \text{atm}$$

12. D

$PV = k$ where k is a constant that depends on the amount and temperature of the gas.

13. B

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$P_2 = \frac{P_1 T_2}{T_1} = 1.0 \times 10^5 \times \frac{273+160}{273+15} = 1.50 \times 10^5\ \text{Pa}$$

14. D

The pressure of a fixed mass of gas at constant temperature is inversely proportional to its volume.

$P = \frac{k}{V}$ where k is a constant that depends on the amount and temperature of the gas

$V = \frac{k}{P}$ .A graph of $\frac{1}{P}$ against V is a straight line that goes through the origin if it is extrapolated from the experimental data (the origin corresponds to infinite pressure

Note the temperature is given in °C in the question. The pressure and volume are both proportional to the absolute temperature measure in K.

15, **(a)** It is is a linear relationship.

It is not a proportional relationship as the line does not pass through the origin.

(b) The equation of the best fit line is: $P = 0.3338T + 95.625$

When $P = 0$, $0.3338T + 95.625 = 0$

$$T = \frac{-95.625}{0.3338} = -286.5\ °\text{C}$$

(c) The temperature is lower than expected.
The literature value is aboslute zero = –273 °C

(d) Proportional; a straight line which passes through/close to the origin.

(e) In the ideal gas model, as the temperature decreases, the particles decrease their movement until at 0 K there is no movement and the particles are attracted together in a minimal volume. With the experimental results, the volume of the gas will not be precisely zero as the molecules have some volume.

16. For a given volume, Curve 1 has the higher pressure. It therefore has the higher temperature.

At higher temperature, the molecules collide more frequently with the walls of the container.

17. **(a)** $P_1V_1 = P_2V_2$

$$V_2 = \frac{P_1V_1}{P_2} = \frac{2.02 \times 10^6 \times 0.0400}{1.01 \times 10^5} = 0.800\ \text{m}^3$$

volume of balloon is $0.800 - 0.0400 = 0.760\ \text{m}^3$

(b) The atoms will decrease their speed.

18. B

$$R = \frac{PV}{T}$$

Unit of $R = \dfrac{\text{N m}^{-2} \times \text{m}^3}{\text{K}} = \dfrac{\text{N m}}{\text{K}} = \text{J K}^{-1}$

19. C

$PV = nRT$

$$n = \frac{PV}{RT}$$

$$= \frac{1.00 \times 10^5 \times 41 \times 10^{-6}}{8.31 \times 298}$$

$= 0.001656$ mol

$$M = \frac{m}{n} = \frac{0.067}{0.001656} = 40$$

20. 90 kPa

Using the gas laws: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{8.5\text{ k Pa} \times 2.50\text{ dm}^3}{273 + 25} = \frac{P_2 \times 2.75\text{ dm}^3}{273 + 75}$$

$$\frac{8.5\text{ kPa} \times 2.50\text{ dm}^3}{298} = \frac{P_2 \times 2.75\text{ dm}^3}{328}$$

$$P_2 = \frac{328 \times 8.5\text{ kPa} \times 2.50\text{ dm}^3}{298 \times 2.75\text{ dm}^3} = 90\text{ kPa}$$

21. 16 °C

Using the combined gas law for a fixed mass: $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{1 \times 10^5 \times 675}{T_1} = \frac{2 \times 10^5 \times 350}{273 + 27}$$

$$T_1 = \frac{1 \times 10^5 \times 675 \times 300}{2 \times 10^5 \times 350} = 289\text{ K} = 16\text{ °C}$$

22. 3.0 dm^3

Using $\frac{P_1 \times V_1}{T_1} = \frac{P_2 \times V_2}{T_2}$

$$\frac{P_1 \times 4.0}{T_1} = \frac{4P_1 \times V_2}{3T_1}$$

Rearranging and solving for V_2 gives

$$V_2 = \frac{3 \times T_1 \times P_1 \times 4}{4 \times P_1 \times T_1} = 3\text{ dm}^3$$

23. 2.8 dm^3

Using $M = \frac{mRT}{PV}$

Rearranging for V gives

$$V = \frac{mRT}{PM}$$

$$V = \frac{4.40 \times 8.31 \times 300}{90 \times 10^3 \times 44.01}$$

$V = 2.8 \times 10^{-3}\text{ m}^3$ (= 2.8 dm^3)

24. $M = 131\ \text{g mol}^{-1}$ so gas is Xe

At STP, 1 mole of the gas would occupy $22.7\ \text{dm}^3$

1 mole would have a molar mass of $5.84\ \text{g dm}^{-3} \times 22.7\ \text{dm}^3\ \text{mol}^{-1} = 132.6\ \text{g mol}^{-1}$

From Section 7 of the data booklet, xenon (a noble gas) has a molar mass of $131.29\ \text{g mol}^{-1}$

25. $90.4\ \text{g mol}^{-1}$

Using $M = \dfrac{mRT}{PV}$

$$M = \frac{0.0121 \times 8.31 \times 298}{1300 \times 255 \times 10^{-6}} = 90.4$$

26. helium (a greater mass in the same volume; density is $\dfrac{\text{mass}}{\text{volume}}$)

As $\text{density} = \dfrac{\text{mass}}{\text{volume}}$ for a fixed volume of gas, the density will depend on the formula mass of the element. Hydrogen has a formula mass of 2.02 and helium of 4.00. Hence helium has the greater density.

27. At higher altitude the external air pressure is less. As the air in the tyre expands on heating (due to friction with the road surface), the internal pressure increases.

28. NH_3 is a polar molecule CH_4 is nonpolar. NH_3 shows greater deviation than CH_4 due to stronger intermolecular attractions, especially at low temperature.

29. III as $\dfrac{PV}{RT} < 1$ at low pressure

(a) Attractive forces from other particles reduce the speed of the colliding particles and lead to a less energetic collision with the wall. The pressure is lower than for an ideal gas as it is reduced by intermolecular forces.

(b) III as $\dfrac{PV}{RT} >>> 1$ as the pressure increases

The pressure is greater than an ideal gas due to the space occupied by the molecules.

The volume of the molecules becomes more significant as the pressure increases.

Challenge yourself

1. If the molecular collisions are not perfectly elastic, then the kinetic energy of the molecules would be gradually lost. The molecules would slow down and the pressure would gradually reduce to zero.

2. **(a)** At constant temperature: PV = constant : $P_1V_1 = P_0V_2$

(b) At constant volume: $\frac{P}{T}$ = constant : $\frac{P_0}{T_1} = \frac{P_2}{T_2}$

(c) From **(b)**, $P_0 = \frac{P_2T_1}{T_2}$

Substitution in **(a)**, $\frac{P_1V_1}{V_2} = \frac{P_2T_1}{T_2}$, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

3. The atmospheric pressure decreases with altitude. When the pressure inside the balloon is larger than the external pressure the volume of the balloon increases.

4. **(a)** $PV = nRT$; 18.0 g = 1 mol; $n = 1$

$V = \frac{RT}{P}$

$= \frac{8.31 \times 500}{1.00 \times 10^5}$

$= 0.04155\ \text{m}^3$

$= 41\,550\ \text{cm}^3$

An approximate value for the volume of the particles can be obtained by consider 18.0 g of water, which has a volume of 18 cm^3

% volume occupied by particles = $\frac{18}{41550} \times 100$ = 0.04%

(b) $V = \frac{RT}{P}$

$= \frac{8.31 \times 400}{5.00 \times 10^7}$

$= 6.65 \times 10^{-5}\ \text{m}^3$

$= 66.5\ \text{cm}^3$

% volume occupied by particles = 27%

In Challenge yourself **5** and **6**, we are considering 1 mol of gas, so $n = 1$.

5. $\left(P+\frac{a}{V^2}\right)(V-b)=RT$

At high pressure, $\frac{a}{V^2}$ can be neglected.

$PV - Pb = RT$

$\frac{PV}{RT}=1+\frac{Pb}{RT}$

Note the deviation, which depends on *b*, increases as the pressure is increased and the temperature is decreased, in agreement with S1.5 Figure 12.

6. $\left(P+\frac{a}{V^2}\right)(V-b)=RT$

At low pressure, the parameter *b* can be neglected.

$\left(P+\frac{a}{V^2}\right)V=RT$

$PV+\frac{a}{V}=RT$

$\frac{PV}{RT}=1-\frac{a}{VRT}$

Note the deviation, which depends on *a*, increases as the temperature is decreased, in agreement with **S1.5 Figure 12**.

Practice questions

1. C

As the temperature is constant, there will be no change in speed of the particles.

They will however collide less frequently as they are moving in a larger volume.

2. C

At constant pressure $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ so, $V_2 = \frac{V_1}{T_1} \times T_2$

The temperatures must be in K. $= \frac{1.0}{273 + 25} \times (273 + 50) = 1.08 = 1.1$

3. D

At constant temperature: $P_1V_1 = P_2V_2$

$$V_2 = \frac{300\text{ kPa} \times 80\text{ cm}^3}{150\text{ kPa}} = 160\text{ cm}^3$$

Note non-SI units can be used as the units of pressure cancel.

4. A

At constant pressure $\frac{V_1}{T_1} = \frac{V_2}{T_2}$ so, $T_2 = \frac{T_1}{V_1} \times iu_2$

The temperatures must be in K. $= \frac{(273 + 27) \times 4.0}{5.0} = 1.08 = 240\text{ K} = -33\ ^{o}\text{C}$

5. B

Pressure is inversely proportional to volume. As the pressure is doubled the volume is halved.

6. C

Deviations from ideal gas behaviour occur at pressure occur if the volume of the gas particles is not negligible.

7. C

The molecular kinetic model can be used to derive the ideal gases equation.

8. A

Gases show ideal gas behaviour at low pressure, and high temperature. The density is low under these conditions.

(Gases can be turned into liquids under opposite conditions: high pressure and low temperature)

9. C

From the ideal gas equation: $pV = nRT$.

At constant volume we have $\frac{R}{V} = \frac{P_1}{n_1T_1} = \frac{P_2}{n_2T_2}$

$$P_2 = \frac{P}{n_1T_1} \times_1 n_2T_2 = \frac{P_1}{4(273+25)} \times n_2T_2$$

The pressure will be highest when n_2T_2 is a maximum.

Consider each of the options in turn:

A $n_2T_2 = 4 \times (273 + 300)$ (= 2292)

B $n_2T_2 = (4 + 2) \times (273)$ (= 1638)

C $n_2T_2 = (4 + 1) \times (273 + 200)$ (= 2365)

D $n_2T_2 = (4 - 1) \times (273 + 350)$ (= 1869)

As it is a multiple-choice question, you may be able to see by inspection that **C** is answer without the need to calculate the values.

10. D

Noble gases are monatomic atoms and so are non-polar. They have the weakest intermolecular forces.

11. **(a)** two from:

weak intermolecular/dispersion forces

small atomic volume

smaller number of electrons (2)

(b) $n = \frac{pV}{RT}$ (1)

$$= \frac{2.0 \times 10^6 \times 3.0 \times 10^{-2}}{8.31 \times 300}$$

= 24.1 (mol) (1)

(c) $N = 24.1 \times 6.02 \times 10^{23} = 1.45 \times 10^{25}$ (1)

volume of 1 atom = $\frac{3.00 \times 10^{-2}\ \text{m}^3}{1.45 \times 10^{25}} = 2.07 \times 10^{-27}\ \text{m}^3$ (1)

Accept value from 1×10^{-27} *to* 6×10^{-27} *m*

(d) assuming the atoms each occupy a cube; distance = $\sqrt[3]{2.07\times10^{-27}}$ 1.27×10^{-9} m

assuming the atoms each occupy a sphere; distance = 7.9×10^{-10} m

12. **(a)** temperature: 4

mass: 3

pressure: 3 (1)

(b) 0.0650 kg = 65.0 g

$$n = \frac{65.0}{65.02} = 1.00 \text{ (mol)} \qquad (1)$$

No penalty for using whole number atomic masses.

(c) $n(N_2) = \frac{3}{2} \times 1.00 = 1.50$ (mol)

$T = 25.00 + 273.15 = 298.15$ K *or* $25.00 + 273 = 298$ K

$P = 1.08 \times 1.01 \times 10^5$ Pa *or* $1.08 \times 1.01 \times 10^2$ kPa *or* 1.09×10^5 Pa *or* 1.09×10^2 kPa

$R = 8.31$ J K^{-1} mol^{-1} (from data booklet)

Use $PV = nRT$ (from data booklet)

$$V = \frac{nRT}{P} = \frac{1.50\times8.31\times298.15}{1.08\times1.01\times10^5} = 0.034.1 \text{ m}^3 = 34.1 \text{ dm}^3 \qquad (4)$$

Award (4) for correct final answer.

*Award (**3 max**) for 0.0341 dm^3 or 22.7 dm^3.*

*Award (**3 max**) for 34.4 dm^3.*

*Award (**2 max**) for 22.9 dm^3.*

*Award (**2 max**) for 0.0227 dm^3.*

*Award (**2 max**) for 0.034 dm^3.*

13. **(a)** Gas behaves ideally; as $p \propto T$ (in K) «at constant V» (1)

$P = 0$ gives $0.400T = -109.2$

$$T = \frac{-109.2}{0.400} = -273 \text{ °C} \qquad (1)$$

(b) From a point on the graph, find the temperature in K and the pressure,

e.g., $T = 0$ °C = 273 K, $P = 109.2$ kPa

$PV = nRT$

$$n = \frac{PV}{RT} = \frac{109.2\times10^3\times1.0\times10^{-3}}{8.31\times273} = 0.048135 \text{ mol} \qquad (1)$$

$$M = \frac{m}{n} = \frac{0.193}{0.048135} = 4.01 \text{ g mol}^{-1}$$

The gas is helium. (1)

14. molar volume at STP = 22.4 $dm^3\ mol^{-1}$

density = 1.94 $g\ dm^{-3}$

molar mass = molar volume × density

= 22.4 × 1.94 = 43.456 $g\ mol^{-1}$ (1)

OR

$PV = nRT$; $n = \frac{PV}{RT} = \frac{1\times10^5\times1\times10^{-3}}{8.31\times273}$ = 0.044 mol, which have mass of 1.94 g

1 mol has mass of 44.01 g (1)

the alkane is C_3H_8 (1)

15 **(a)** The reaction stops after 25 cm^3 of O_2 is added. (1)

(b) $n(\text{NO}) = \frac{PV}{RT} = \frac{1\times10^5\times50\times10^{-6}}{8.31\times273}$ = 0.0022 mol (1)

$n(\text{O}_2) = \frac{PV}{RT} = \frac{1\times10^5\times25\times10^{-6}}{8.31\times273}$ = 0.0011 mol (1)

(c) volume = 75 cm^3 – 25 cm^3 = 50 cm^3 (1)

$n(\text{X})$ = 0.0022

(d) $2NO(g) + O_2(g) \rightarrow 2X(g)$ therefore X = NO_2 (1)

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ (1)

Structure 2.1

Exercises

1. D

Ionic bonding arises due to the electrostatic attraction between oppositely charged ions.

2. D

Aluminium is in group 3 so has a charge Al^{3+}

Sulfur is in group 6 so has a charge S^{2-}

The charges of the positive and negative ions must balance:

2 Al^{3+} have a charge of +6

3 S^{2-} have a charge of –6

Formula is Al_2S_3

3. C

In an ionic compound: metals form positive ions and non-metals form negative ions.

An electron is transferred from lithium to fluorine.

4. A

NH_4Cl and NH_4NO_3 are ionic. NH_4^+ is unusual in that it is a positive ion formed from non-metal elements.

HCl is covalent molecule although it does form ions when added to water.

5. **(a)** KBr

potassium bromide; ions present: K^+ Br^-, so forms KBr

(b) ZnO

zinc oxide; ions present: Zn^{2+} O^{2-}, so forms ZnO

(c) Na_2SO_4

sodium sulfate; ions present: Na^+ SO_4^{2-}, 2 × 1+ with 1 × 2–, so forms Na_2SO_4

Note: Na does not need to be put in brackets because it contains a single atom

(d) $CuBr_2$

copper(II) bromide; ions present: Cu^{2+} Br^-, 1 × 2+ with 2 × 1–, so forms $CuBr_2$

(e) $Cr_2(SO_4)_3$

chromium(III) sulfate; ions present: Cr^{3+} SO_4^{2-}, 2 × 3+ with 3 × 2–, so forms $Cr_2(SO_4)_3$

(f) AlH_3

aluminium hydride; ions present: Al^{3+} H^-, 1 × 3+ with 3 × 1–, so forms AlH_3

6. The names are deduced directly from the formulae, referring to the table of ions in the book if needed. Note that where a Roman numeral is given in brackets after the name of the cation, it refers to the oxidation number. This is used where an element may form different ions with different oxidation states.

(a) tin(II) phosphate

(b) titanium(IV) sulfate

(c) manganese(II) hydrogencarbonate

(d) barium sulfate

(e) mercury(I) sulfide

(f) vanadium(III) oxide

(g) chromium(III) oxide

(h) lead(IV) oxide

7. X_3Y_2

X will have a charge of 2+ (group 2) and Y will have a charge of 3– (group 15).

Three X^{2+} have a charge of 6+ and two Y^{3-} have a charge of 6–. The formula is X_3Y_2.

8. Mg: $Z = 12$: electron configuration [Ne] $3s^2$

Br: $Z = 35$: electron configuration [Ar] $3d^{10}4s^24p^5$

The magnesium atom loses its two electrons from the 3s orbital to form Mg^{2+}, with electron configuration [Ne].

Two bromine atoms each gain one electron into their 4p subshell to form Br^-, with electron configuration [Kr].

The ions attract each other by electrostatic forces and form a lattice with the formula $MgBr_2$.

9. Ionic bonding between NH_4^+ ions and NO_3^- ions. Covalent bonding within NH_4^+ ions and NO_3^- ions.

Note the compound does not contain any metal ions.

10. B

Metals on the bottom left of the periodic table lose electrons most easily, while non-metals on the top right gain electrons most easily. The ionic character of a compound MX increases with an increase in electronegativity difference between the elements M and X

Cs F is the most ionic as Cs is the least electronegative metal.

11. Test the melting point: ionic solids have high melting points.

Test the solubility: ionic compounds usually dissolve in water but not in hexane.

Test the conductivity: ionic compounds in aqueous solution are good conductors.

12. **(a)** D

E will have a charge of 1+ (group 1) and G will have a charge of 2– (group 16).

Two X^+ ions have a charge of 2+ and balance the 2– charge on G^{2-}. The formula is E_2G.

(b) A

Group 1 elements form ionic compound with non-metals.

(c) C

As the compound is ionic it conducts electricity in the liquid and aqueous state when the ions are free to move, but not in the solid state when the ions are fixed in position.

13. B

The magnitude of the lattice enthalpy increases with the product of the ionic charges of the ions and decreases with a sum of the ionic radii. The magnitude of the lattice enthalpy is greater for ions with a larger charge density as they have a small radius and are highly charged. Mg^{2+} and O^{2-} are the ions with the greatest charge density.

Challenge yourself

1. Our calculation does not include the shielding effect of electrons in a lower sublevel. The two 3s electrons in aluminium, for example, partially shield the 3p electron so it (the 3p electron) experiences a smaller effective nuclear charge than the +3 calculated using the simple model. The reduced effective nuclear charge makes it is easier to remove the 3p electron from aluminium than to remove one of the 3s electrons in magnesium.

2. For example, the production of chlorine during the electrolysis of sodium chloride provides indirect evidence for the existence of ions. The negative chloride ion is attracted to the positive electrode and is discharged with the production of gaseous chlorine.

3.

Identity of ion	Location of atoms	Number of locations	Contribution	Total atoms
Cl^-	centre of face	6	$6 \times \frac{1}{2}$	3
Cl^-	corner	8	$8 \times \frac{1}{8}$	1
Na^+	centre of edge	12	$12 \times \frac{1}{4}$	3
Na^+	centre of cube	1	1×1	1

4NaCl. This confirms the formula unit as NaCl.

4. The ionic radius of Mg^{2+} is smaller than Na^+. The smaller radius would also lead to increased attraction between the ions.

   Our analysis has also assumed that the compounds have similar structures. This may not be so, in which case the structures may also affect the melting point.

5. Aluminium fluoride (1564 K) has a higher melting point than magnesium fluoride (1534 K), due to the increased charge of the aluminium cation.

   The melting point of aluminium oxide (2345 K) is less than magnesium oxide (3125 K), which is not expected from the ionic model. This suggests that aluminium oxide has some covalent character.

6. Some things to consider:

   - Model shows cubic structure very clearly.
   - Model shows ionic bonds with grey connections as directional. Ionic bonds are due to electrostatic attraction of ions. They are not physical connections.
   - Model shows ions as separated. Ions in real structures fill most of the volume, as illustrated in other models shown earlier in the chapter.

Practice questions

1. C

The first three elements in group 14: carbon, silicon and germanium do not generally form ions in chemical reactions.

2. B

Ionic compounds generally contain metal and non-metal elements and have high melting and boiling points.

3. B

Aluminium is in group 3 and oxygen in group 16. In the reaction between aluminium and oxygen each aluminium loses 3 electrons to form Al^{3+} ions and each oxygen gains two electrons to form $O^{2–}$ ions.

4. D

X and Z have high melting and boiling points and conduct electricity in the liquid state. They are ionic. Z is not SiO_2.

Y has very high melting and boiling points but does not conduct electricity in the liquid state. It is not ionic and has a covalent network structure. (See S2.2.7). Y is SiO_2.

5. B

Barium phosphate; ions present: Ba^{2+} $PO_4^{3–}$, 3 × 2+ with 2 × 3– so forms $Ba_3(PO_4)_2$.

Note "ate" in a name indicates the presence of oxygen.

6. C

Ionic compounds have high electrical conductivity in aqueous solution, are insoluble in non-polar solvents and have low volatility.

7. D

The oxidation number of the copper needs to be given in the name.

CuBr: As the bromide ion, $Br^–$ is present. The copper ion is Cu^+. It is a copper(I) compound.

CuO: As the oxide ion $O^{2–}$ is present. The copper ion is $Cu^{2+.}$ It is a copper(II) compound.

8. A

Compounds of metal with non-metals are generally ionic. Magnesium chloride and iron(II) chloride are ionic.

9. Electrostatic attraction increases with charge and decreases with distance. (1)

Mg^{2+} has a smaller radius than Ba^{2+}, $O^{2–}$ has a smaller radius than $S^{2–}$ (1)

so the ionic radius of MgO is smaller than BaS. (1)

10. **(a)** electrostatic attraction (1)

between Fe^{3+} and O^{2-} ions (1)

(b) Fe^{3+}: $1s^22s^22p^63s^23p^63d^54s^2$ (1)

O^{2-}: $1s^22s^22p^6$ (1)

(c) iron(III) oxide (1)

(d) Applied force moves layers so ions of the same charge are forced to be closer. (1)

Repulsion between layers makes the compound brittle. (1)

(e) $Fe_3O_4 - Fe_2O_3 = FeO$, so the additional ion of iron is Fe^{2+} (1)

11. **(a)** Structure: lattice of ions (1)

Bonding: electrostatic attraction between K^+ ions and S^{2-} ions (1)

(b) K^+: $1s^22s^22p^63s^23p^6$ (1)

S^{2-}: $1s^22s^22p^63s^23p^6$ (1)

(c) S^{2-} is larger than K^+ (1)

Both have same electron configuration but K has larger nuclear charge so attracts electrons more strongly. (1)

(d) Solid: doesn't conduct because no mobile ions (1)

Molten: conducts because of free moving/mobile ions in molten state (1)

12. **(a)** +5 (1)

Ionization energies increase in a linear pattern and then there is a large jump when 6th electron removed/removal of 6th electron is unfavourable. (1)

(b) X_2O_5 (1)

Ion would have large charge density and so would polarize the anion; compound would show covalent character (1)

(c) X^{2+} and X^{3+} (1)

13. Ionic bonding/electrostatic attraction between Na^+ and NO_3^- ions. (1)

Covalent bonding between nitrogen and oxygen atoms within the nitrate ion. (1)

Structure 2.2

Exercises

1. C

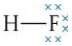
As a covalent bond involves two atoms sharing pairs of electrons, it is the electrostatic attraction between the nuclei of the atoms (positively charged) and the pairs of electrons (negatively charged) that holds the atoms in place. Note that answers B and D would experience electrostatic repulsion as the particles involved have the same charge.

2. A

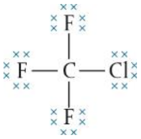
The octet rule predicts that atoms will gain a total of 8 electrons when forming bonds with other atoms. The octet rule is generally accurate in its predictions but does have some exceptions where atoms have less than 8 valence electrons known as an *incomplete* octet and more than 8 electrons known as an *expanded* octet.

3. The steps to follow: (1) Calculate the total number of valence electrons in the molecule; (2) Draw a skeletal structure of the molecule and add one pair of electrons between each outer atom and the central atom; (3) Complete the Lewis formula by adding non-bonding pairs of electrons to the outer atoms and then the central atom so that each achieves 8 valence electrons (except H which only requires 2 valence electrons); (4) Check the total number of electrons matches the number calculated in step 1. Remember that you can use a dots (••), crosses (××), a line (–) or a mixture of these to represent a pair of electrons.

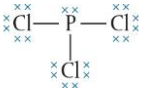
(a)



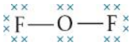
(b)



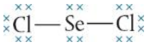
(c)



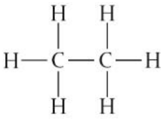
(d)



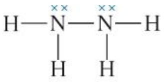
(e)



(f)



(g)



4. Calculate the total number of valence electrons in the molecule by multiplying the number of valence electrons of each element by the number of atoms of the element in the formula and totaling these. The number of valence electrons can be identified using the following:

Group no.	1	2	13	14	15	16	17
No. valence electrons	1	2	3	4	5	6	7

(a) $2 + (7 \times 2) = 16$

(b) $3 + (7 \times 3) = 24$

(c) $4 + (7 \times 4) = 32$

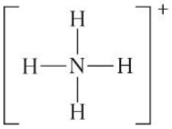
(d) $5 + (1 \times 3) = 8$

(e) $6 + (7 \times 2) = 20$

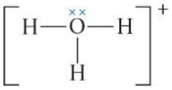
(f) $5 + (7 \times 3) = 26$

5. Follow the same steps as described in question **3** but remember that for calculating the total number of valence electrons in ions we must remove 1 electron for each positive charge and add 1 electron for each negative charge. For example, the total number of valence electrons in $NH_4^+ = (5 \times 1) + (1 \times 4) - \mathbf{1} = 8$. Note that the Lewis formulas of ions must show their charge outside square brackets.

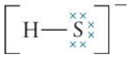
(a)



(b)

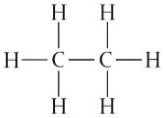


(c)

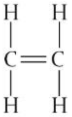


6. Follow the same steps as described in question **3** but after adding all electron pairs, in part **(b)** and **(c)** you will need to move non-bonding pairs from the carbon atoms to form a double and triple bond respectively so that each is able to gain a complete octet.

(a)



(b)



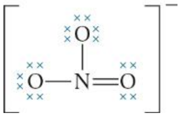
(c)

7. **C**

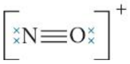
For each additional pair of electrons shared between two atoms, the bond will become shorter due to increased electrostatic attraction between the nuclei and these electrons. For this reason, bond length decreases in the following order: single > double > triple. So C_2H_2, with a triple bond, will have the shortest carbon-carbon bond.

8. In each of the structures below, you will see that in the process of drawing the Lewis structure, at least one non-bonding pair has been placed between the N and an O to form a multiple bond in order for all atoms to complete their octet. We must also show the charge outside of square brackets.

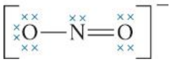
(a)



(b)

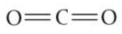


(c)

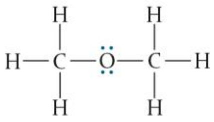


9. C

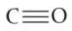
A



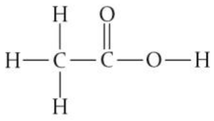
B



C



D



Substances A and D contain carbon-oxygen double bonds and compound B contains carbon-oxygen single bonds. Compounds C (carbon monoxide) contains a triple bond. Triple bonds are shorter than both single and double bonds.

10. A

More pairs of electrons shared between two atoms will lead to stronger electrostatic attraction between the nuclei of the atoms and the shared electrons. So a triple bond, with 3 shared pairs of electrons will be a shorter, stronger bond than a double bond (with 2 shared pairs of electrons) and a double bond will be shorter, stronger bond than a single bond (with only 1 shared pair of electrons).

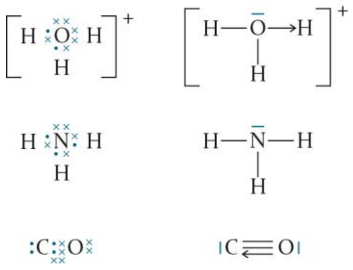
11. D

A coordination bond is identical to a normal covalent bond except that both of the shared electrons come from the same atom. Answer A is true of a coordination bond but is not the 'best' description.

12. A

Once formed, a coordination bond is identical to a normal covalent bond with a pair of electrons shared between two atoms.

13. B

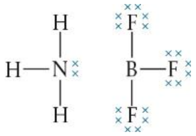


Using dots and crosses to identify the electrons from individual atoms shows that both I and III contain coordination bonds.

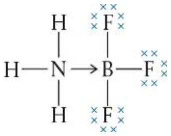
14. D

Complex ions are formed when molecules (known as ligands) donate pairs of electrons to form coordination bonds with a transition element ion. The six arrows indicate that 6 coordination bonds are formed between the H_2O molecules and Fe^{3+} ion producing the $[Fe(H_2O)_6]^{3+}$ complex ion.

15. Drawing Lewis formulas for the individual molecules shows that the N in ammonia has a non-bonding pair of electrons which can be used to form a coordination bond with the B of boron trifluoride as it has an incomplete octet.

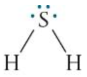


The resulting Lewis formula shows the coordination bond using an arrow.



16. Steps to follow: (1) Work out the Lewis formula; (2) Count the number of electron domains around the central atom which determines the electron geometry; (3) Determine the position of bonded atoms within this geometric arrangement to give the shape of the molecule; (4) Adjust bond angles in the case of the presence of non-bonding pairs of electrons or multiple bonds.

(a) H_2S: Lewis formula is



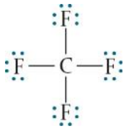
Four domains of electrons around the sulfur atom, electron domain geometry is tetrahedral.

Two lone pairs and two bonded pairs so shape is bent (as drawn in Lewis structure).

As lone pairs repel more than bonded pairs the bond angles are less than 109.5°.

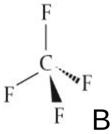
Observed bond angle is 105°.

(b) CF_4: Lewis formula is



Four domains of electrons around the carbon atom, electron domain geometry is tetrahedral.

All electron pairs are bonded so shape is tetrahedral.



Bond angles are 109.5°.

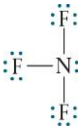
(c) HCN: Lewis formula is

H—C≡N:

Two domains of electrons around the carbon atom, electron domain geometry is linear.

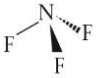
All electron pairs are bonded so shape is linear (as drawn in Lewis structure). Bond angle is 180°.

(d) $NF_{3:}$ Lewis formula is



Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

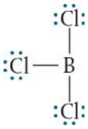
One lone pair and three bonded pairs so shape is trigonal pyramidal.



As lone pairs repel more than bonded pairs the bond angles are less than 109.5°.

Observed bond angle is 107°.

(e) $BCl_{3:}$ Lewis formula is

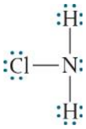


Three domains of electrons around the boron atom, electron domain geometry is trigonal planar.

All electron pairs are bonded so shape is trigonal planar. Bond angles are 120°.

120° bond angle, triangular planar, three domains of electrons around the boron atom.

(f) NH_2Cl: Lewis formula is



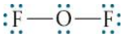
Four domains of electrons around the nitrogen atom, electron domain geometry is tetrahedral.

One lone pair and three bonded electron pairs so shape is trigonal pyramidal.

As lone pairs repel more than bonded pairs the bond angles are less than 109.5°.

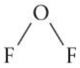
Observed bond angle is 107°.

(g) OF_2: Lewis formula is



Four domains of electrons around the oxygen atom, electron domain geometry is tetrahedral.

Two lone pairs and two bonded pairs so shape is bent.

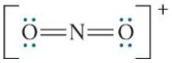


As lone pairs repel more than bonded pairs the bond angles are less than 109.5°.

Observed bond angle is 105°.

17. First, draw a Lewis formula and identify the number of bonding and non-bonding domains around the central atom.

(a) NO_2^+: Lewis structure is

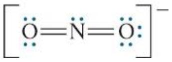


Two electron domains around the nitrogen atom so electron domain geometry is linear.

Both electron domains are bonding domains so shape is linear.

Bond angle is 180°.

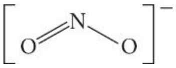
(b) NO_2^-: Lewis structure is



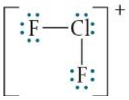
Three electron domains around the nitrogen atom so electron domain geometry is triangular planar.

One non-bonding domain and two bonding domains so shape is bent/V-shaped.

Bond angle is less than 120° (in range 100–119°) due to additional repulsion from lone pair.



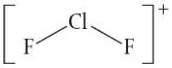
(c) ClF_2^+: Lewis structure is



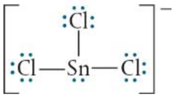
Four electron domains around the Cl atom so electron domain geometry is tetrahedral.

Two non-bonding domains and two bonding domains so shape is bent/V-shaped.

Bond angle is less than 109.5° (in range 100–108°) due to additional repulsion from two lone pairs.



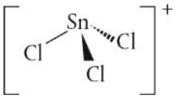
(d) $SnCl_3^-$: Lewis structure is



Four electron domains around the Sn atom so electron domain geometry is tetrahedral.

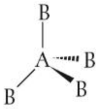
One non-bonding domain and three bonding domains so shape is trigonal pyramidal.

Bond angles are less than 109.5° (in range 100–108°) due to additional repulsion from the lone pair.



18. Drawing the shapes will help you to visualize them.

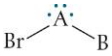
(a)



A tetrahedral shape can only be obtained from a tetrahedral electron domain geometry

with four electron domains and with all domains bonded.

(b)



A bent shape can be formed from a tetrahedral electron domain geometry with

four electron domains if two domains are bonded and there are two lone pairs.

(c)

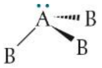
A linear shape can be obtained from a linear electron domain geometry with two electron

domains if both domains are bonded.

A linear shape can also be obtained from a trigonal bipyramidal electron domain geometry with five electron domains if two domains are bonded and there are three lone pairs.

(Note that geometries with five and six electron domains around the central atom (an ‘expanded octet’) are visited later in the chapter in Structure 2.2.13)

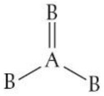
(d)



A trigonal pyramidal shape can be obtained from a tetrahedral electron domain geometry

with four electron domains if three domains are bonded and there is one lone pair.

(e)



A trigonal planar shape can only be obtained from a trigonal planar electron domain geometry with three electron domains and with all domains bonded.

19. D

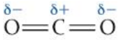
Answers A and C are both ionic compounds but contain polyatomic ions (NO_3^- and NH_4^+ respectively) which contain covalent bonds between atoms of non-metallic elements. Answer B is phosphoric acid which is a covalent molecule and contains only non-metallic elements (although acids do have significant ionic character as demonstrated by their ability to dissociate into ions when dissolved in water). The correct answer is $CaCl_2$ which contains only Ca^{2+} and Cl^- ions.

20. Any bonds between two different atoms will be polar to some extent: the element which is further to the left and/or lower will be $\delta+$ and the element that is further to the right and/or higher will be $\delta-$. These can be predicted from the periodic table without the need to check electronegativity values.

(a)

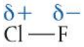
$\overset{\delta+}{H}-\overset{\delta-}{Br}$

(b)



$\overset{\delta-}{O}=\overset{\delta+}{C}=\overset{\delta-}{O}$

(c)

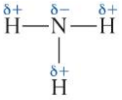


$\overset{\delta+}{Cl}-\overset{\delta-}{F}$

(d)

$O=O$

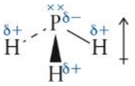
(e)



21.	**(a)**	C 2.6	H 2.2	difference = 0.4
		C 2.6	Cl 3.2	difference = 0.6, more polar
	(b)	Si 1.9	Li 1.0	difference = 0.9
		Si 1.9	Cl 3.2	difference = 1.3, more polar
	(c)	N 3.0	Cl 3.2	difference = 0.2
		N 3.0	Mg 1.3	difference = 1.7, more polar

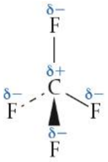
22. The polarity of a molecule depends on the presence of polar bonds and whether or not those bonds are symmetrically arranged. The steps to follow are: (1) Work out the shape of the molecule; (2) From the relative position of the polar bonds, determine whether or not there is a net dipole.

(a) PH_3



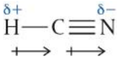
This is a pyramidal molecule, it is polar.

(b) CF_4



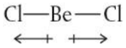
This is a tetrahedral molecule, all bond dipoles cancel, so it is non-polar.

(c) HCN



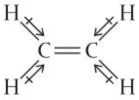
This is a linear molecule, the two dipoles (from the H–C bond and the C–N bond) do not cancel (in fact, they add together), so it is polar.

(d) $BeCl_2$



This is a linear molecule, the two dipoles cancel, so it is non-polar.

(e) C_2H_4



Each C is trigonal planar, each C–H bond is slightly polar, the C=C is non-polar, the structure is symmetrical, so non-polar.

(f) ClF

Polar, due to uneven distribution of electrons as fluorine is more electronegative than chlorine.

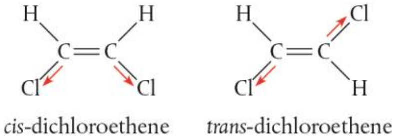
(g) F_2

Non-polar; F_2 is a symmetrical molecule so the bonding electrons are shared equally between atoms.

(h) BF_3

Non-polar; although F is more electronegative than B, the shape of the molecule is trigonal planar, and so all the dipoles cancel out.

23.



The *cis* isomer has a net dipole moment as both the electronegative atoms are on the same side of the molecule and so there is an overall dipole moment for the molecule. In the *trans* isomer the dipoles cancel out.

24. Similarities: composed of carbon atoms only, both are covalent network structures.

Differences: each carbon is bonded to 4 other carbon atoms in diamond and 3 other carbon atoms in graphite; geometry around carbons is tetrahedral in diamond and trigonal planar in graphite; diamond is continuous C–C structure whereas graphite is distinct layers of carbon atoms (layers are held together by weak intermolecular forces); graphite has delocalized electrons but diamond does not.

25. Similarities: strong, high melting points, insoluble in water, non-conductors of electricity, good thermal conductors.

Differences: diamond is stronger and more lustrous; silicon can be doped to be an electrical conductor.

26. Graphite and graphene have delocalized electrons that are mobile and so conduct electrical charge. In diamond all electrons are held in covalent bonds and are not mobile.

27. **A** Metal; it conducts electricity when solid.

B Covalent network; it doesn't dissolve in water (so isn't an ionic compound), it doesn't conduct electricity when solid (so isn't a metal) and it has the highest melting point.

C Polar molecular; it is soluble in water but doesn't conduct electricity (so isn't an ionic compound) and its melting point is low (but not the lowest) so it isn't the non-polar molecular solid.

D Non-polar molecular solid; it isn't soluble in water (so isn't an ionic compound), it doesn't conduct electricity when solid (so isn't a metal) and it has the lowest melting point.

E Ionic compound; it is soluble in water, the aqueous solution conducts electricity while the solid doesn't and it has the second highest melting point.

28. A

Both methanol and ethanol **(**D**)** are soluble in water due to hydrogen bonding between the alcohol and water; however, methanol will be the more soluble as it has the smaller nonpolar part of the molecule. Neither methane **(**B**)** nor ethane **(**C**)** will dissolve in water as neither have any polar bonds.

29. **(a)** London dispersion forces; as it is a non-polar molecule.

(b) London dispersion, dipole-dipole, hydrogen bonding; as it is a polar molecule due to its asymmetrical trigonal pyramidal molecular geometry. Nitrogen has a lone pair and is sufficiently electronegative to allow hydrogen bonding to occur.

(c) London dispersion forces; as it is a non-polar molecule.

(d) London dispersion, dipole-dipole; as it is a polar molecule given the bent molecular geometry about the O atom which also has two lone pairs.

(e) London dispersion, dipole-dipole, dipole-induced dipole; CH_3COCH_3 is polar so will have intermolecular dipole-dipole forces with other CH_3COCH_3 molecules and can induced a dipole in non-polar C_6H_{14} molecules.

30. **(a)** C_2H_6; both molecules will have only London dispersion forces as they are non-polar; C_2H_6 is a smaller molecule with fewer electrons so will have weaker temporary dipoles therefore weaker London dispersion forces.

(b) H_2S; both molecules are polar but H_2S is unable to form intermolecular hydrogen bonds so will have a lower boiling point. (H_2O can form hydrogen bonds due to the additional electronegativity of the O atom.)

(c) Cl_2; both molecules will have only London dispersion forces; Cl_2 is a smaller molecule with fewer electrons so will have weaker temporary dipoles therefore weaker London dispersion forces.

(d) HCl; both molecules are polar but HCl is unable to form intermolecular hydrogen bonds so will have a lower boiling point. (HF can form hydrogen bonds due to the additional electronegativity of the F atom.)

31. C

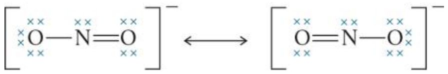
The retardation factor value is calculated using $R_\text{f} = \dfrac{\text{distance moved by component}}{\text{distance moved by solvent}}$.

32. Using the formula in the previous question, R_f spot 1 = $\dfrac{9}{12}$ = 0.75; R_f spot 2 = $\dfrac{6}{12}$ = 0.50

33. **(a)** R_f spot X = $\dfrac{24}{80}$ = 0.30; R_f spot Y = $\dfrac{72}{80}$ = 0.90

(b) Compound Y has travelled further that compound X so must be more soluble in the non-polar solvent (mobile phase). This suggests that compound Y is less polar than compound X.

34. First draw a Lewis formula and identify the alternative position for the N=O double bond. Then draw the second Lewis formula.



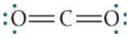
35. The C–O bond order for each species can be determined from their Lewis structures.

CO: Lewis structure is

$$:C\equiv O:$$

It contains a $C\equiv O$ triple bond, bond order = 3.

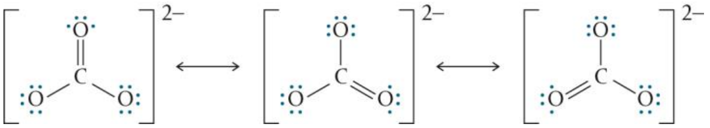
CO_2: Lewis structure is



$$:\ddot{O}=C=\ddot{O}:$$

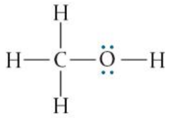
It contains two C=O double bonds, bond order = 2.

CO_3^{2-}Three resonance structures:



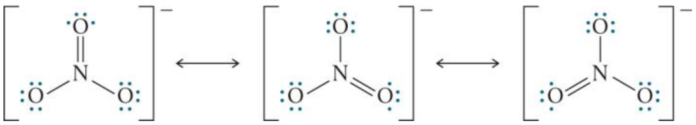
The C–O bonds are delocalized and have a bond order of 1.33.

CH_3OH: Lewis structure is



It contains a C–O single bond, bond order = 1. To rank in order of increasing CO bond length we need to put the species with the shortest bond (highest CO bond order) first: $CO < CO_2 < CO_3^{2-} < CH_3OH$.

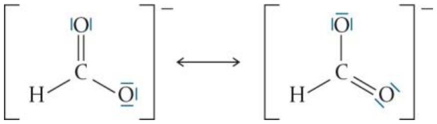
36. NO_3^- has three resonance structures and the N–O bond order is 1.33:



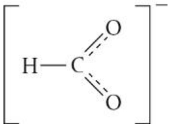
HNO_3 has two resonance structures and there are two distinct N–O bonds. The N–O(H) bond is always a single bond and has a bond order of 1. The N–O bond that resonates has a bond order of 1.5.

Bond lengths decrease as bond order (and bond strength) increases, therefore the N–O bonds in the nitrate(V) ion that all have a bond order of 1.33 will be longer than the two bonds in nitric(V) acid with a bond order of 1.5 and shorter than the N–O bond with a bond order of 1.

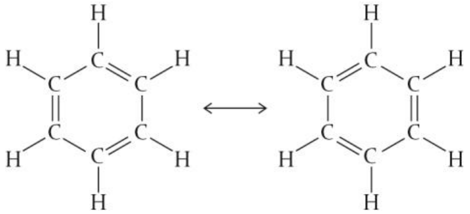
37. First draw the resonance structures of $HCOO^-$ by identifying alternative positions for the C=O double bond in a Lewis formula.



Then use dotted lines to show the positions where the double bond can be found.



38.



39 As the delocalized pi electrons in benzene are shared across all bonding positions in the carbon ring, we find the bond lengths are identical and of an intermediate value instead of alternating single and double bond lengths. (See structure 2.2.16 for more detail on ‘pi’ bonds.)

40 Benzene contains six carbon atoms arranged in a hexagonal ring, each also with a single bond to a hydrogen atom. The bonds between the carbon atoms are identical and have a length and strength that lies in between that of a single and double bond. This is due to the delocalization of pi electrons which are shared equally across the carbon ring, increasing its energetic stability. (See structure 2.2.16 for more detail on ‘pi’ bonds.)

41. D

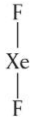
Answer I: The bond enthalpy values for all carbon–carbon bonds in benzene are identical with an intermediate value lying between that of a single bond and a double bond. This is evidence for delocalization. Answer II: The additional stability of the ring of delocalized electrons in benzene limits its ability to undergo addition reactions which would require breaking permanent breaking of the ring.

42. Following the same steps as question 17:

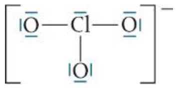
(a) XeF_2: Lewis structure is

Five electron domains around the xenon atom so electron domain geometry is trigonal bipyramidal.

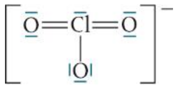
Three non-bonding domains and two bonding domains so molecular geometry is linear with bond angle of 180°.



(b) ClO_3^-: Lewis structure is

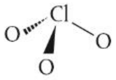


Once you have covered 'formal charge' in Structure 2.2.14 you will recognise that the following Lewis formula where the Cl atom has an 'expanded octet' is valid and is in fact the preferred structure. Both formulas will lead to the correct answer.

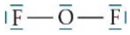


In both cases, there are four electron domains around the central Cl atom so the electron domain geometry will be tetrahedral.

One non-bonding domain and three bonding domains so shape is trigonal pyramidal with bond angles of less than 109.5° (in the range 100-108°) due to additional repulsion from the lone pair.



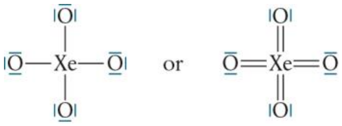
(c) OF_2: Lewis structure is



Four electron domains around the oxygen atom so electron domain geometry will be tetrahedral.

Two non-bonding domains and two bonding domains so molecular geometry is bent/V-shaped with a bond angle of less than 109.5° (in the range 100-107°) due to additional repulsion from two lone pairs.

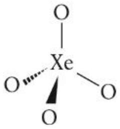
(d) XeO_4: Lewis structure is



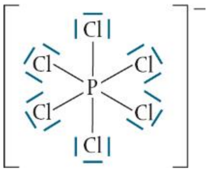
Both are valid, however applying formal charge (seen in Structure 2.2.14) to both structures indicates that the Lewis formula on the right, where Xe has an expanded octet, is the preferred structure. Both will lead to the correct answer.

Four electron domains around the Xe atom so electron domain geometry is tetrahedral.

All electron domains are bonding domains so molecular geometry will also be tetrahedral with bond angles of 109.5°.

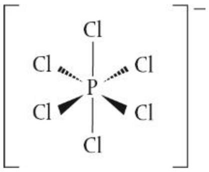


(e) PCl_6: Lewis structure is

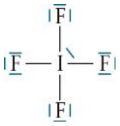


Six electron domains around P atom so electron domain geometry is octahedral.

All electron domains are bonding domains so molecular geometry is also octahedral with bond angles of 90°.



(f) IF_4^+: Lewis structure is



Five electron domains around I atom so electron domain geometry is trigonal bipyramidal.

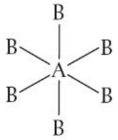
One non-bonding domain and four bonding domains so molecular geometry is be seesaw (or unsymmetrical tetrahedron) with bond angles of less than 90° **and** less than 120° due to the additional repulsion from the lone pair.

43. The table on page 189 confirms the relationships between the number of charge centers and the shape of the molecule.

(a)

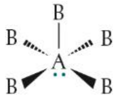
A square planar shape can be obtained from an octahedral electron domain geometry with six electron domains if four domains are bonded and there are two lone pairs.

(b)



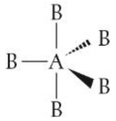
An octahedral shape can be obtained from an octahedral electron domain geometry with six electron domains if all six domains are bonded.

(c)



A square pyramidal shape can be obtained from an octahedral electron domain geometry with six electron domains if five domains are bonded and there is one lone pair.

(d)



A trigonal bipyramidal shape can be obtained from an octahedral electron domain geometry with five electron domains if all five domains are bonded.

(e)

B—A—B

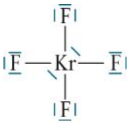
A linear shape can be obtained from a linear electron domain geometry with two electron domains if both domains are bonded.

A linear shape can also be obtained from a trigonal bipyramidial electron domain geometry with five electron domains if two domains are bonded and there are three lone pairs.

Note that in part **(e)**, linear geometry can arise from two charge centers with no lone pairs (e.g. $BeCl_2$, C_2H_2) or from five charge centers with three lone pairs (e.g. I_3^-)

44. Again, it is helpful to draw Lewis formulas for each molecule before deducing the molecular geometry and then bond angles.

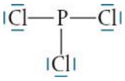
(a)



Six electron domains around Kr atom so electron domain geometry is octahedral.

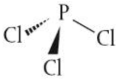
Two non-bonding and four bonding domains so molecular geometry is square planar with bond angles of 90°.

(b)

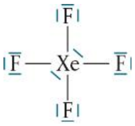


Four electron domains around the P atom so electron domain geometry is tetrahedral.

One non-bonding domain and three bonding domains so molecular geometry will be trigonal pyramidal with bond angles of less than 109.5° (in range 100-108°).

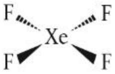


(c)

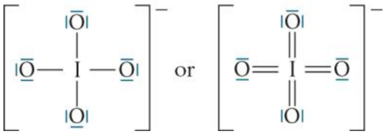


Six electron domains around Xe atom so electron domain geometry is octahedral.

Two non-bonding and four bonding domains so molecular geometry is square planar with bond angles of 90°.



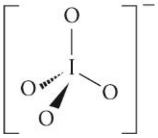
45. (a)



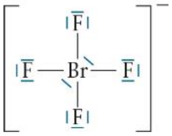
Both are valid, however applying formal charge (seen in Structure 2.2.14) to both structures indicates that the Lewis formula on the right, where I has an expanded octet, is the preferred structure. Both will lead to the correct answer.

Four electron domains around the I atom so electron domain geometry is tetrahedral.

All electron domains are bonding domains so molecular geometry will also be tetrahedral with bond angles of 109.5°.

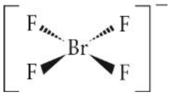


(b)

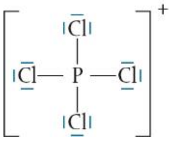


Six electron domains around Br atom so electron domain geometry is octahedral.

Two non-bonding and four bonding domains so molecular geometry is square planar with bond angles of 90°.

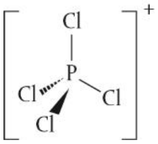


(c)



Four electron domains around the P atom so electron domain geometry is tetrahedral.

All electron domains are bonding domains so molecular geometry will also be tetrahedral with bond angles of 109.5°.



(d)

Four electron domains around F atom so electron domain geometry is tetrahedral.

Two non-bonding domains and two bonding domains so molecular geometry is bent/V-shaped with bond a bond angle of less than 109.5° (in range 100-107°) due to additional repulsion from two lone pairs.

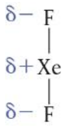
46. **(a)** XeF2: Lewis formula is

Five electron domains around the xenon atom, electron domain geometry is trigonal bipyramidal.

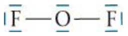
Three non-bonding domains and two bonding domains so shape is linear (as indicated by Lewis structure).

Bond angle is 180°.

The Xe-F bond dipoles cancel out due to the symmetrical linear shape so molecule is non-polar.



(b) OF_2: Lewis formula is

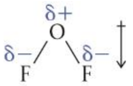


Four electron domains around the oxygen atom, electron domain geometry is tetrahedral.

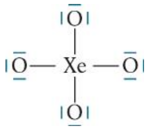
Two non-bonding domains and two bonding domains so shape is bent.

Bond angle is less than 109.5° due to additional repulsion from two lone pairs.

The O–F bond dipoles do not cancel out in this structure so molecule is polar.



(c) XeO_4: Lewis formula is

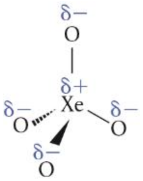


Four electron domains around the xenon atom, electron domain geometry is tetrahedral.

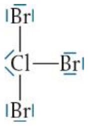
All electron domain are bonding domains so the shape is tetrahedral.

Bond angles are 109.5°.

The Xe–O bond dipoles cancel out due to the symmetrical tetrahedral shape so molecule is non-polar.



(d) $ClBr_3$: Lewis formula is

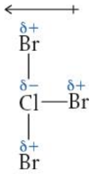


Five electron domains around the chlorine atom, electron domain geometry is trigonal bipyramidal.

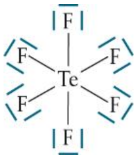
Two non-bonding domains and three bonding domains so the shape is T-shaped.

Bond angles are less than 90° due to additional repulsion from lone pairs.

The Cl-Br bond dipoles do not cancel out in this structure so the molecule is polar.



(e) Lewis formula is

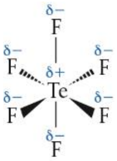


Six electron domains around the tellurium atom, electron domain geometry is octahedral.

All electron domains are bonding domains so the shape is octahedral.

Bond angles are 90°.

The Te–F bond dipoles cancel out due to the symmetrical octahedral shape so molecule is non-polar.



47. Apply the following equation to each atom in the Lewis formula: Formal charge = number of valence electrons in unbonded atom – number of electrons assigned to atom in Lewis formula. Remember that the 'number of electrons assigned' can be calculated by the sum of ½ the number of electrons in bonded pairs and the number of electrons in lone pairs.

So for the central Xe = 8 – (4+4) = 0 and for each F = 7 – (1 + 6) = 0.

48. The steps to follow: (1) Assign formal charges to each atom in both Lewis formulas using the equation in the previous question; (2) Determine the preferred structured by identify which set of formal charges have values closer to 0.

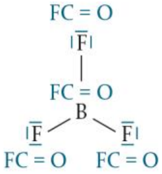
Left-hand structure: P = 5 – 4 = +1; each O = 6 – (1 + 6) = −1

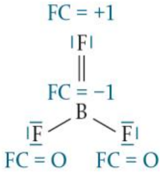
Right-hand structure: P = 5 – 5 = 0; top O = 6 – (2 + 4) = 0;

left/right/bottom O = 6 – (1 + 6) = −1

Right-hand structure has formal charges closest to 0 so is the preferred structure.

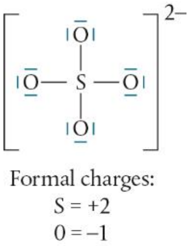
49. Assigning formal charges to Lewis formulas of BF_3 with and without a complete octet:



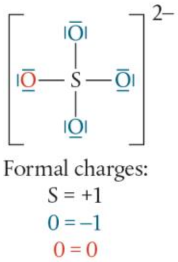


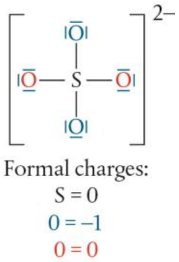
BF_3 with an incomplete octet is the preferred structure as all the atoms have formal charge of 0.

50. First draw a Lewis formula with a complete octet.



To draw a Lewis formula with an expanded octet, take one or more non-bonding pairs from oxygen atoms to form double bonds with the sulfur atom. Here are two possibilities for an expanded octet where the sulfur has 10 valence electrons (left-hand structure) and 12 valence electrons (right-hand side).





The expanded octet is the preferred structure in either case as it has formal charges closest to zero.

51. A sigma bond is formed by the head-on combination of atomic orbitals where the electron density is concentrated along the bond axis. A pi bond is formed by the lateral combination of p-orbitals where the electron density is concentrated on opposite sides of the bond axis.

52. B

Here we must consider which combinations will produce an area of electron density concentrated along the bond axis. Answer I and III can both achieve this as the orbitals can combine 'head-on'. Answer II will not achieve this as the lateral (sideways) overlap of p orbitals will form a pi bond with electron density concentrated above and below the bond axis.

53. A carbon-carbon sigma bond is stronger than a pi bond as there is greater overlap of the atomic orbitals so the shared electron density is located closer to the two nuclei.

54. Remember for this question that a sigma bond occurs through the head-on combination of orbitals where the electron density is concentrated along the bond axis.

(a) H–H in H_2

(b) H–F in HF

(c) Cl–Cl in Cl_2

(d) C–H in CH_4

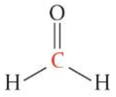
(e) C–H in C_2H_4

(f) C–H in C_2H_2

(g) C–Cl in CH_2CHCl

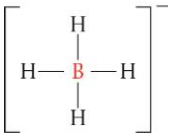
To deduce the type of hybridization found for a particular atom we can first draw a Lewis formula of the molecule and then identify how many electron domains it possesses. Two electron domains will require sp hybridization, three electron domains will require sp^2 hybridization and four electron domains will require sp^3 hybridization.

55 **(a)** Lewis formula of H_2CO:



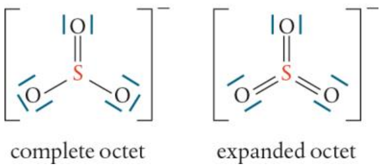
There are 3 electron domains around the carbon atom so it will be sp^2 hybridized.

(b) Lewis formula of BH_4^-:



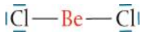
There are 4 electron domains around the boron atom so it will be sp^3 hybridized.

(c) Two possible Lewis formula of SO_3:



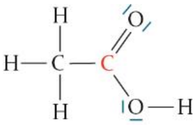
Whether you choose the structure with a complete octet or an expanded octet (both acceptable although the expanded octet is preferred), there are 3 electron domains around the sulfur atom so it will be sp^2 hybridized.

(d) Lewis formula of $BeCl_2$:



There are 2 electron domains around the boron atom so it will be sp hybridized.

(e) Lewis formula of CH_3COOH:



There are 3 electron domains around the carbon atom so it will be sp^2 hybridized.

56. In C_6H_{12} (cyclohexane) the carbon atoms are sp^3 hybridized, each forming a tetrahedral arrangement with two neighboring carbon atoms and two hydrogen atoms. The bond angles of 109.5° give the puckered shape. In C_6H_6 (benzene) the carbon atoms are all sp^2 hybridized, forming a planar triangular arrangement with bond angles of 120°.

Challenge yourself

1. F_2 has lower bond enthalpy (158 kJ mol^{-1}) than expected from its atomic radius due to repulsion between the non-bonding lone pairs on the two F atoms. The F–F bond length is so short (142 pm) that the lone pairs on the two atoms are close enough to repel each other and weaken the bond.

2. The definition of electronegativity relates to the attraction of an atom to electrons in a covalent bond. As group 18 elements tend not to bond with other atoms, we do not assign them an electronegativity value (Pauling value).

3. Oxygen will have a partial positive charge when it is covalently bonded to a more electronegative atom. As fluorine is the only element with a greater electronegativity value on the Pauling scale the compound must involve an O–F bond e.g. OF_2.

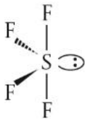
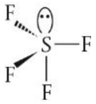
4. The high thermal conductivity of diamond is because of its strong covalent bonds. When heated, the bonds becoming vibrationally excited, and, as they are all connected, thermal energy could be readily transferred through the network from one bond to the next. Silicon is similarly a good thermal conductor, which is why computer chips need to be cooled to prevent overheating.

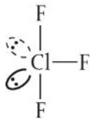
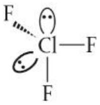
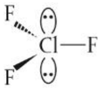
5. Diamonds are kinetically stable with respect to graphite, as the conversion has a very high activation energy (see Reactivity 2.2.4). So the reaction generally occurs too slowly to be observed.

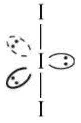
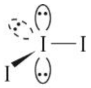
6. Run each solution out from separate burettes, and see whether the stream of liquid is deflected in the presence of a charged rod. Only the polar solution will show deflection.

Test solubility with ionic and covalent solutes in the two solutions. The polar solution will be a better solvent (more solute will dissolve) for polar and ionic solutes; the non-polar solution for non-polar covalent solutes.

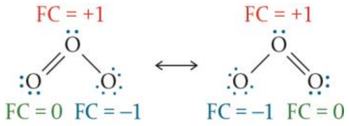
7. For each molecule, we first need to draw a Lewis formula and then consider the possible positions of the bonding and non-bonding electron domains. Then we can count the number of lone pair-lone pair 90° angles followed by lone pair-bonding pair 90° angles.

Possible arrangements	 seesaw − preferred	
LP-LP 90° angles	none	none
LP-BP 90° angles	2	3

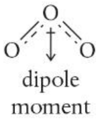
Possible arrangements	 T-shaped − preferred		
LP–LP 90° angles	0	1	0
LP–BP 90° angles	4	3	6

Possible arrangements	 linear − preferred		
LP–LP 90° angles	0	2	2
LP–BP 90° angles	6	3	4

8 Central oxygen has 2 bonding domains and 1 non-bonding domain so geometry is bent or V-shaped. The resonance structures and formal charges on each atom are follows:



The central oxygen (at the top of the Lewis formula) has a formal charge of +1 and an outer oxygen (pointing down) has a formal charge of –1 in both structures. So, the actual structure, the resonance hybrid, has a permanent dipole moment:



9 One problem is that it is difficult to know exactly how many valence electrons to assign in a transition metal when it forms a complex ion. The calculation of formal charges also involves treating the metal-ligand bonds as being purely covalent, but in reality these bonds often have some ionic character. Formal charge values obtained for the central metal in complex ions can be negative, which implies this model may not be appropriate for complex ions.

10 Molecules with an expanded octet require a central atom to have more than four electron domains around the central atom. The combination of s and p orbitals can form a maximum of four sp^3 hybrid orbitals so for each additional hybrid orbital required, atoms can use one or more d-orbitals in the hybridization process as well. Phosphorous in PCl_5 requires five hybrid orbitals so will undergo sp^3d hybridization and sulfur in SF_6 requires six hybrid orbitals so will undergo sp^3d^2 hybridization.

Practice questions

1. C

The larger electronegativity difference between the two atoms involved in a covalent bond, the more polar it will be.

Electronegativity difference	0.4	0.7	0.9	1.9

2. A

Carbon (including allotropes such as diamond, graphite and graphene) forms a covalent network structure where the atoms are all linked to each other by strong covalent bonds. Carbon has a high melting point as melting it involves breaking these strong bonds (buckminsterfullerene, C_{60}, is not a network covalent structure but is a large covalent molecule with a relatively high melting point of around 600 °C). Carbon dioxide, CO_2, is a non-polar covalent molecule so will have weak intermolecular forces (only London dispersion) which are easily overcome, giving CO_2 a very low melting point.

3. A

As these are non-polar or weakly polar compounds, the boiling points will depend on the strength of the London dispersion forces between the molecules. These increase with the size of the atoms in the molecules so the order is:
$CH_3CH_3 < CH_3CH_2Cl < CH_3CH_2Br < CH_3CH_2I$.

4. A

Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently

bonded to a highly electronegative atom, N,

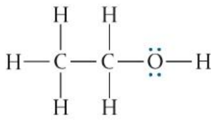
O or F

(ii) they have a lone pair on a highly electronegative atom, N, O or F.

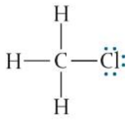
The structures of the compounds are (see Structure 3.2 for structures of organic

compounds):

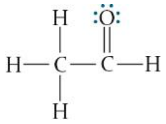
A



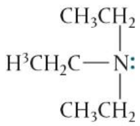
B



C



D

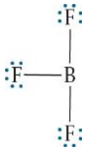


Only C_2H_5OH meets both requirements.

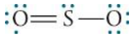
5. B

Lewis structures of molecules:

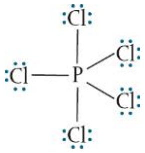
A



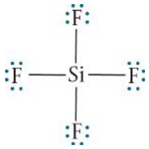
B



C



D

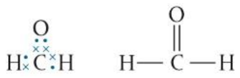


Only SO_2 has a lone pair of electrons on the central atom.

6. C

A coordination bond is formed when one atom donates both of the shared electrons in a covalent bond. Lewis formulas using dots and crosses can be useful to identify structures containing a coordination bond.

Lewis formula for HCHO:

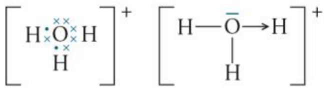


All covalent bonds are formed using one electron from each bonding atom. No coordination bonds are present.

Lewis formula for CO:

The O atom donates both electrons in one of the bonds to the C atom. A coordination bond is present.

Lewis formula for H_3O^+:

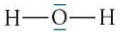


The O atom donates both electrons in the bond to the hydrogen on the right. A coordination bond is present.

Note that where a coordination bond is present in Species II and III, the oxygen atom is forming three covalent bonds instead of the two covalent bonds that we would expect for it to complete its octet. This means the oxygen atom must use a lone pair to form the additional bond.

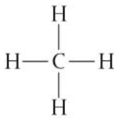
7. D

Lewis formula of H_2O is



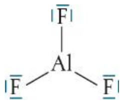
Two non-bonding domains and two bonding domains around the O atom so the shape will be bent/v-shaped.

Lewis formula of CH_4 is



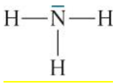
Four bonding domains around the C atom so the shape will be tetrahedral.

Lewis formula of AlF_3 is



Three bonding domains around the Al atom so the shape will be triangular planar.

Lewis formula of NH_3 is



One non-bonding domain and three bonding domains around the N atom so the shape will be triangular pyramidal.

8 B

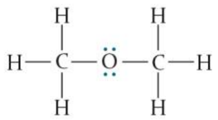
Compounds can form hydrogen bonds when:

(i) they contain a hydrogen atom covalently bonded to a highly electronegative atom, N, O or F

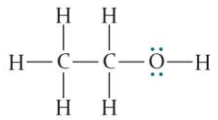
(ii) they have a lone pair on a highly electronegative atom, N, O or F.

Consider the structures of the compounds (see Structure 3.2 for structures of organic compounds):

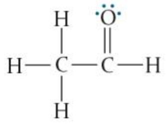
A



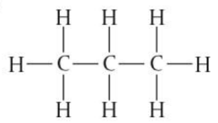
B



C



D

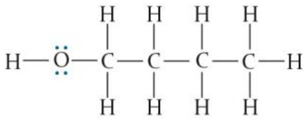


Only CH_3CH_2OH meets both requirements.

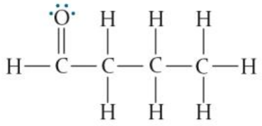
9. B

The retardation factor value is calculated using $R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}} = \frac{y}{x}$.

10. Consider the structures of butan-1-ol and butanal (see Structure 3.2 for structures of organic compounds):



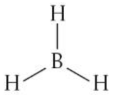
butan-1-ol



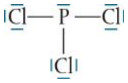
butanal

The intermolecular forces present in butan-1-ol are hydrogen bonding as it contains a hydrogen atom bonded to a highly electronegative oxygen as well as a lone pair on the highly electronegative oxygen. The intermolecular forces present in butanal are dipole–dipole interactions due to the polar C=O bond. Because hydrogen bonding is a stronger intermolecular force than dipole–dipole interactions butan-1-ol will have a higher boiling point than butanal.

11. (a) (i) BH_3 will contain 3 + 3(1) = 6 valence electrons. As boron can have an incomplete octet, the Lewis formula will be



PCl_3 will contain 5 + 3(7) = 26 valence electrons. The Lewis formula will be

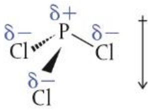


(ii) In BH_3 there are three bonding domains around the B atom so the geometry will be triangular planar with bond angles of 120°.

In PCl_3 there is one non-bonding electron domain and three bonding domains around the P atom so the shape will be triangular pyramidal. Bond angles will be less than 109.5° due to the additional repulsion from the lone pair.

(iii) The [very small] B–H bond dipoles in BH_3 will cancel out due to the symmetrical shape of the molecule. The molecule will be non-polar.

The P-Cl bond dipoles will not cancel out in PCl_3 as the shape of the molecule is asymmetrical. The molecule will be polar.



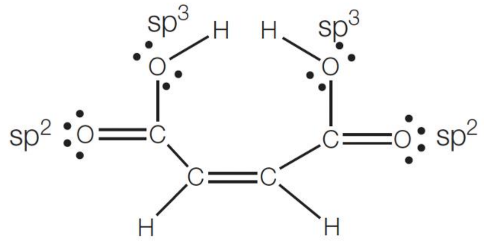
(b) (i) In ethyne, a sigma bond is formed by the head-on combination of sp hybrid orbitals from each carbon. In a sigma bond, the electron density is concentrated along the bond axis. Two pi bonds are formed by the lateral combination of p-orbitals on the carbon atoms. In a pi bond, the electron density is concentrated on opposite sides of the bond axis.

(ii) Each single bond is a sigma bond. A double bond contains one sigma bond and one pi bond. In total, there are 11 sigma bonds and 3 pi bonds.

(iii) This question relies on an understanding of the role of -OH groups (found in the carboxyl functional group) in hydrogen bonding. In the *trans*-but-2-ene-1,4-dioic acid, the -OH groups are found on opposite sides of the molecule so can be used to form hydrogen bonds with -OH groups on other molecules. In the *cis*-but-2-ene-1,4-dioic acid, the -OH groups are on the same side of the molecule and so will form *intra*molecular hydrogen bonds (within the molecule). This limits their interaction with -OH groups on other molecules and leads to a relatively lower melting point than the *trans* isomer.

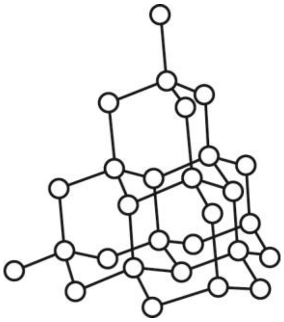
(iv) In the *cis*-but-2-ene-1,4-dioic acid isomer, the carboxyl functional groups are on the same side of the molecule. Given their proximity, the two groups can react upon heating to produce a molecule of water and the cyclic anhydride. This is known as a condensation reaction (see Structure 2.4.6). In the *trans* isomer, the carboxyl functional groups are on opposite sides of the molecule and so cannot carry out this same reaction.

(c) Knowing that oxygen cannot have an incomplete or expanded octet, we can add non-bonding pairs of electrons to each oxygen as follows:

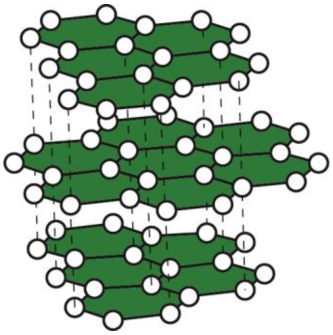


Each oxygen atom with four electron domains is sp^3 hybridized and each oxygen with three electron domains is sp^2 hybridized.

12. **(a)**

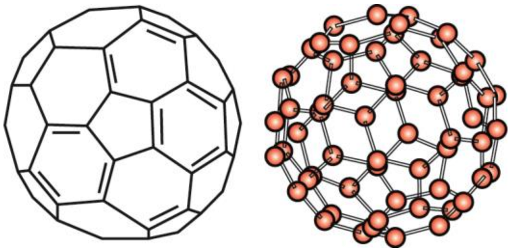


Diamond is a covalent network structure where the carbon atoms are sp^3 hybridized and every carbon atom is covalently bonded to four others, forming a repeating tetrahedral arrangement with 109.5° bond angles. Diamond does not have delocalized electrons so it is not able to conduct electricity.



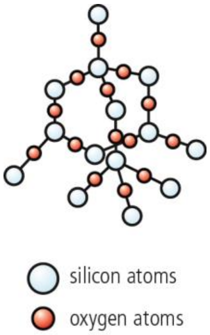
Graphite is a covalent network structure where the carbon atoms are sp^2 hybridized and each atom is covalently bonded to three other atoms, with bond angles of 120°, forming sheets of interlinked hexagons.

London dispersion forces exist between the sheets. Electrons are delocalized over each sheet so graphite is able to conduct electricity.



C_{60} fullerene contains carbon atoms that are sp^2 hybridized and each atom is covalently bonded to three other atoms to form interlinked hexagons and pentagons with bond angles between 109.5° and 120°, resulting in a cage-like structure. London dispersion forces exist between the C_{60} fullerenes. Electrons are delocalized on each fullerene but limited contact between the individual fullerenes makes fullerene a semiconductor at room temperature.

(b) **(i)** SiO_2 is a covalent network solid with each silicon bonded to four oxygen atoms and each oxygen atom bonded to two silicon atoms, giving the empirical formula SiO_2.



(ii) Because SiO_2 is a covalent network solid it is necessary to break strong covalent bonds for it to melt. This requires a large amount of energy and SiO_2 has a high melting point so it is a solid at room temperature.

CO_2 is a discrete molecule with weak London dispersion forces between the molecules. These intermolecular forces are weak and easy to overcome so CO_2 has a low boiling point and is a gas at room temperature.

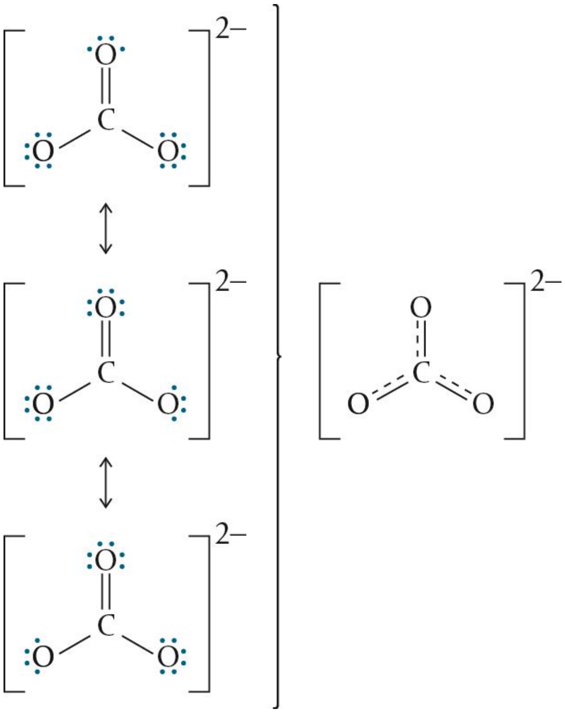
(c) The Lewis formula of carbon monoxide is:

$$:C\equiv O:$$

The carbon and oxygen atoms are both sp hybridized and they form a covalent triple bond. One of these bonds is a coordination bond where the oxygen atom has donated both electrons.

(d) The delocalization of pi electrons occurs when a multiple bond can occur in more than one position within a molecule. When this situation occurs two or more equally valid Lewis structures (resonance structures) can be drawn for the molecule. The reality is that the pi bond is shared over all the positions and is represented as a partial bond occurring in all positions.

In the carbonate ion the central carbon atom is sp^2 hybridized, giving a trigonal pyramidal shape and there are three resonance structures:

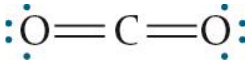


Because the pi electrons are delocalized over the three positions this reduces electron–electron repulsions and increases the stability of the carbonate ion.

(e) Hybridization is the mixing of atomic orbitals to form new hybrid orbitals. The number of hybrid orbitals that are formed is equal to the number of atomic orbitals that mix to form the hybrids.

In carbon dioxide the carbon atom has two electron domains so it is sp hybridized.

One p orbital has mixed with the s orbital to form two sp hybrid orbitals, leaving two unhybridized p orbitals able to form the pi bonds.

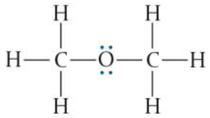


In diamond (see picture in Q19(a)) the carbon atoms have four electron domains so they are sp^3 hybridized. The three p orbitals have mixed with the s orbital to form four sp^3 hybrid orbitals.

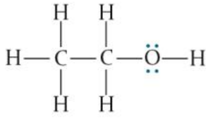
In graphite (see picture in Q19(a)) the carbon atoms have three electron domains so they are sp^2 hybridized. Two p orbitals have mixed with the s orbital to form three sp^2 hybrid orbitals, leaving one unhybridized p orbital able to form a pi bond.

In the carbonate ion (see picture Q19(d)) the carbon atom has three electron domains so it is sp^2 hybridized. Two p orbitals have mixed with the s orbital to form three sp^2 hybrid orbitals, leaving one unhybridized p orbital able to form a pi bond.

13. Consider the Lewis formulas (see Structure 3.2 for structures of organic compounds):



2-methoxymethane

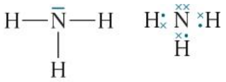


ethanol

In methoxymethane the intermolecular forces present are London dispersion forces and dipole–dipole interactions due to the polar C–O bond. These are relatively weak intermolecular forces so methoxymethane will have a low boiling point (–24 °C).

In ethanol hydrogen-bonding intermolecular forces can occur as there is a hydrogen atom bonded to a highly electronegative oxygen atom and a lone pair of electrons on a highly electronegative oxygen atom. As hydrogen bonding is significantly stronger than London dispersion forces and dipole–dipole interactions, ethanol will have a much higher boiling point (78 °C) than methoxymethane.

14. **(a)** **(i)** NH_3 will contain 5 + 3(1) = 8 valence electrons and so the Lewis formula will be

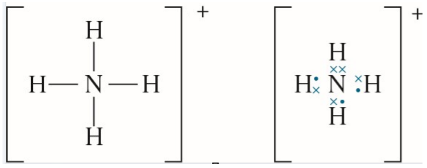


There is one non-bonding domain and three bonding domains around the N atom so the molecular geometry will be triangular pyramidal. The bond angles will be less than 109.5° due to the additional repulsion from the lone pair.

(ii) NH_2^- will contain 5 + 2(1) + 1 = 8 valence electrons and so the Lewis formula will be

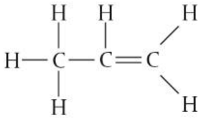
There are two non-bonding domains and two bonding domains around the N atom so the molecular geometry will be bent/v-shaped. The bond angles will be less than 109.5° due to the additional repulsion from the two lone pairs.

(iii) NH_4^+ will contain 5 + 4(1) –1 = 8 valence electrons and so the Lewis formula will be



There are four bonding domains around the N atom so the molecular geometry will be tetrahedral. The bond angles will be 109.5°.

(b) **(i)** A sigma bond is formed by the head-on combination of sp hybrid orbitals from each carbon. In a sigma bond, the electron density is concentrated along the bond axis. Pi bonds are formed by the lateral combination of p-orbitals on the carbon atoms. In a pi bond, the electron density is concentrated on opposite sides of the bond axis.



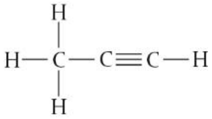
(ii) The structure of propene is

Each single bond is a sigma bond and the double bond contains one sigma bond and one pi bond. In total, there are eight sigma bonds and one pi bond.

(iii) There are four electron domains around the left-hand carbon and all of them are bonding pairs. The molecular geometry will be tetrahedral with bond angles of 109.5°.

The central and right-hand carbon have three electron domains and they are all bonding pairs of electrons so the molecular geometry will be triangular planar with bond angles of approximately 120°.

Note that for both the central and right-hand carbon, the additional repulsion of the double bond will distort these angles slightly. The bond angles between the double bond and adjacent single bond will be slightly larger than 120° and so the bond angles between the single bonds will be slightly less than 120°.



(iv) The structure of propyne, C_3H_4, is

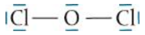
Both carbon atoms involved in the triple bond are sp hybridized. This means they will each contain two singly occupied sp hybrid orbitals.

One sp hybrid orbital from each carbon will combine head-on to form a sigma bond between them. The electron density in this bond is concentrated along the bond axis. (Note that the second sp hybrid orbital on each carbon is used to form a sigma bond with the atoms either side of the triple bond.)

Each carbon also has two single occupied p orbitals which can combine laterally with the p orbitals on the adjacent carbon to form two pi bonds. In a pi bond, the electron density is concentrated on opposite sides of the bond axis.

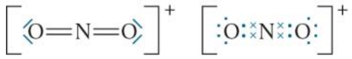
Note that the second sp hybrid orbital on each carbon is used to form a sigma bond with the atoms either side of the triple bond.

15. **(a)** **(i)** Cl_2O will contain 2(7) + 6 = 20 valence electrons and so the Lewis formula will be



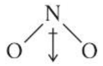
There are two non-bonding domains and two bonding domains around the O atom so the molecular geometry will be bent/v-shaped. The bond angles will be less than 109.5° due to additional repulsion from the two lone pairs.

(ii) NO_2^+ will contain 5 + 2(6) – 1 = 16 valence electrons and so the Lewis formula will be

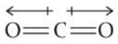


There are two bonding domains around the N atom so the molecular geometry will be linear. The bond angles will be 180°.

(b) Knowing that in a polar molecule, the bond dipoles do not cancel out, we can assume that NO_2 must be asymmetrical. Given that there are only three atoms in this molecule, it must have a bent/v-shaped geometry. As the oxygens have a greater electronegativity than nitrogen, they will be the partially negative side of the molecule.



In a non-polar molecule, the bond dipoles do cancel out, we can assume that CO_2 must be symmetrical. Given that there are only three atoms in this molecule, it must have a linear geometry.

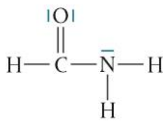


Note that single bonds could be shown in CO_2 as the question requires a 'diagram' to explain its non-polar nature and not a Lewis formula.

(c) Silicon dioxide is a covalent network solid with each silicon covalently bonded to four oxygen atoms and each oxygen atom bonded to two silicon atoms, giving the empirical formula SiO_2. The geometry around each silicon atom is tetrahedral and the geometry around each oxygen atom is bent/v-shaped.

(d) **(i)** The formula of methanamide provided in the question, $HCONH_2$, is a condensed structural formula which provides information about the order in which these atoms are bonded (see Structure 3.2.1 for more details). To draw the Lewis formula we must find the total number of valence electrons in the molecule. This will be 1+4+6+5+2(1) = 18.

Using the condensed structural formula, we can draw the Lewis formula:



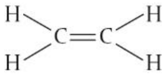
(ii) A sigma bond is formed by the head-on combination of sp hybrid orbitals from each carbon. In a sigma bond, the electron density is concentrated along the bond axis. Pi bonds are formed by the lateral combination of p-orbitals on the carbon atoms. In a pi bond, the electron density is concentrated on opposite sides of the bond axis.

(iii) In the Lewis formula, we can see that there are three electron domains around the carbon atom (all bonding pairs) so it requires sp^2 hybridization. There are four electron domains around the nitrogen atom (three bonding pairs and one lone pair) so it requires sp^3 hybridization.

16. **(a)** C_2H_2 will contain 2(6) + 2(1) = 14 valence electrons. A triple covalent bond is required to complete the octet of both carbon atoms. The Lewis formula will be

$$H-C\equiv C-H$$

C_2H_4 will contain 2(6) + 4(1) = 16 valence electrons. A double covalent bond is required to complete the octet of both carbon atoms. The Lewis formula will be



(b) A covalent bond is the electrostatic attraction between the nuclei of two atoms and the shared electrons. With a greater number of shared pairs of electrons, there will be stronger electrostatic forces of attraction and so a shorter, stronger bond. Therefore, the triple covalent bond in ethyne (containing three pairs of shared electrons) will be shorter and stronger than the double bond in ethene (with only two pairs of shared electrons).

(c) As C_2H_2 is a symmetrical molecule and the electronegativity of carbon and hydrogen are very similar, ethyne is a non-polar molecule and will experience only London dispersion forces between molecules.

17. **(a)** The retardation factor value is calculated using $R_f = \frac{\text{distance moved by component}}{\text{distance moved by solvent}}$ so is a measure of how far a component spot has travelled in comparison to the solvent front (mobile phase). This value indicates the relative solubility of the component in both the stationary and mobile phases.

(b) Using the formula in 28(a), $R_f = \frac{32}{96} = 0.33$

(c) To identify the components present on a chromatogram, we can compare experimental R_f values with known literature values. However, we must make sure that the literature values for comparison used the same solvent mixture (mobile phase) as we did in our experiment.

(d) The distance that a component travels on a chromatogram is dependent on its solubility in both the stationary phase and mobile phase (solvent). If the component is more soluble in the solvent, then it will travel further and vice versa.

(e) Thin layer chromatography is similar to paper chromatography but the stationary phase is composed of a layer of silicon dioxide or aluminium oxide coated onto a thin piece of glass, metal or plastic.

18. A

See diagrams on page 200.

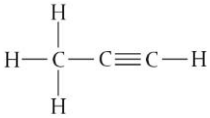
In diamond, carbon atoms are all linked to four other atoms in a tetrahedral arrangement and the carbon atoms are sp^3 hybridized.

In graphite, the carbon atoms are linked to three other atoms, forming sheets of interlocked hexagons and the carbon atoms are sp^2 hybridized.

In fullerenes, the carbon atoms are linked to three other atoms, forming interlocked hexagons and pentagons that create a closed spherical cage and the carbon atoms are sp^2 hybridized.

19. B

The Lewis formula for propyne is:

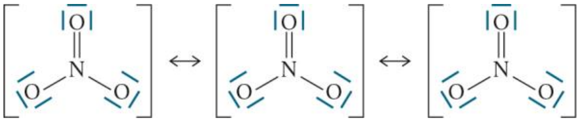


Each single bond is a σ bond. The triple bond contains one σ and two π bonds so there are a total of six σ and two π bonds.

20. D

Delocalized electrons found in species have resonance structures. Draw Lewis formulas for each species and identify which does **not** allow for more than one position for a double bond.

Lewis formula for NO_3^-



The N=O double bond can be placed in three different bonding positions so there will be delocalized electrons.

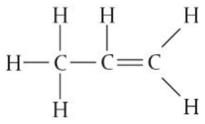
Lewis formula for NO_2^-:

The N=O double bond can be placed in two different bonding positions so there will be delocalized electrons.

Lewis formula for O_3:

The O=O double bond can be placed in two different bonding positions so there will be delocalized electrons.

Lewis formula for C_3H_6:



The C=C double bond cannot be placed in a different bonding position (without also moving hydrogen atoms) so there will be no delocalized electrons.

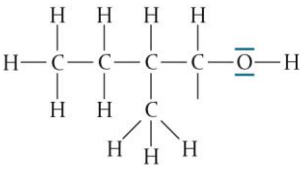
21. B

Statement **I** and **III** are correct. Statement **II** is incorrect as a σ bond can also be formed by the axial (head-on) combination of p orbitals or hybrid orbitals. (Or a mixture of any two s/p/hybrid orbitals that overlap along the bond axis).

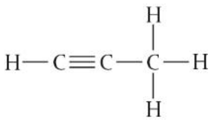
22. C

Atoms that have a trigonal planar of electron domains around them are sp^2 hybridized. Consider the structures of the compounds (see Structure 3.2 for structures of organic compounds):

A

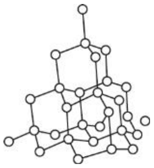


B



C

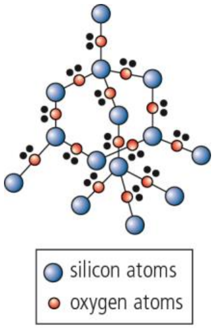
D



23. D

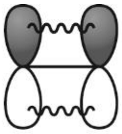
When a central atom has two bonding and three non-bonding pairs there is a trigonal bipyramidal arrangement of the electron domains around the central atom but the shape is linear due to the two bonded atoms.

24. A



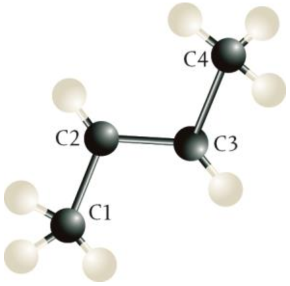
The silicon atoms in SiO_2 are surrounded by four bonding pairs so they are sp^3 hybridized. The oxygen atoms in SiO_2 are surrounded by two bonding and two non-bonding pairs so they are sp^3 hybridized.

25. **(a)** The pi bond is formed by the lateral combination of p-orbitals on C2 and C3 leading to electron density concentrated on opposite sides of the bond axis.



π-bonding overlap

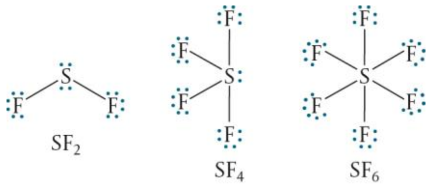
(b)



C1 has four electron domains so it is sp^3 hybridized.

C2 has three electron domains so it is sp^2 hybridized.

26.



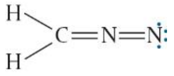
In SF_2 there are four electron domains around the central atom and two of these are bonded so the molecule has a bent shape.

In SF_4 there are five electron domains around the central atom and four of these are bonded so the molecule has a see-saw shape.

In SF_6 there are six electron domains around the central atom and all six are bonded so the molecule has an octahedral shape.

27. Formal charge (FC) on atom = $\text{valence atoms} - \left(\frac{1}{2}\ \text{bonding electrons} + \text{lone pair electrons}\right)$

(a) (i)



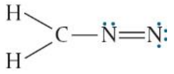
$$\text{FC (H)} = 1 - \left(\frac{1}{2} \times 2\right) = 0$$

$$\text{FC (C)} = 4 - \left(\frac{1}{2} \times 6\right) = +1$$

$$\text{FC (N1)} = 5 - \left(\frac{1}{2} \times 6 + 2\right) = 0$$

$$\text{FC (N2)} = 5 - \left(\frac{1}{2} \times 4 + 4\right) = -1$$

(ii)



$$\text{FC (H)} = 1 - \left(\frac{1}{2} \times 2\right) = 0$$

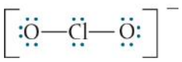
$$\text{FC (C)} = 4 - \left(\frac{1}{2} \times 6\right) = +1$$

$$\text{FC (N1)} = 5 - \left(\frac{1}{2} \times 6 + 2\right) = 0$$

$$\text{FC (N2)} = 5 - \left(\frac{1}{2} \times 4 + 4\right) = -1$$

Although both structures only contain two atoms with small formal charges the first structure will be preferred as the carbon in the second structure only has six electrons and an incomplete valence shell.

(b) **(i)**

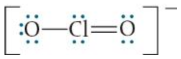


FC (O1) = $6-\left(\frac{1}{2}\times 2+6\right) = -1$

FC (Cl) = $7-\left(\frac{1}{2}\times 4+4\right) = +1$

FC (O2) = $6-\left(\frac{1}{2}\times 2+6\right) = -1$

(ii)



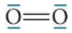
FC (O1) = $6-\left(\frac{1}{2}\times 2+6\right) = -1$

FC (Cl) = $7-\left(\frac{1}{2}\times 6+4\right) = 0$

FC (O2) = $6-\left(\frac{1}{2}\times 4+4\right) = 0$

The second structure will be preferred as it has formal charges closest to zero.

28. **(a)** O_2 will contain 2(6) = 12 valence electrons. A double bond is required to complete the octet on both oxygens. The Lewis formula will be:



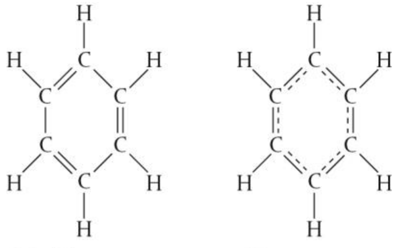
O_3 will contain 3(6) = 18 valence electrons. The two possible Lewis formulas (resonance structures) will require a single and double bond.

(b) There are two possible Lewis formulas for ozone. The two resonance structures indicate that the pi electrons will be delocalized across the two bonding positions in the true structure of ozone so will we can predict a bond length (and strength) that is an intermediate value between a single and double bond.

The observed value is 128 pm.

(c) There are 3 electron domains around the central oxygen atom so the electron domain geometry will be triangular planar. Only 2 of these electron domains are bonding domains so the molecular geometry will be bent or V-shaped with a bond angle of less than 120° due to additional repulsion from the non-bonding pair of electrons (observed angle is 117°).

29 It is helpful to compare the Kekulé structure with the true structure of benzene which takes into account the ring of delocalized electrons shared equally between all carbons:



Kekulé structure True structure

Physical evidence:

As the Kekulé structure contains alternating single and double carbon–carbon bonds, we would expect to see longer and shorter bonds respectively and so a distorted hexagonal shape. However, experimental data shows a regular hexagonal shape with identical carbon–carbon bond lengths and strengths (of an intermediate value between that of a single and double bond).

Chemical evidence:

Benzene more readily undergoes substitution reactions (replacing a hydrogen with another atom or group of atoms) than addition reactions so that it maintains the energetically stable ring of delocalized electrons. An addition reaction would involve disrupting the ring of delocalized electrons to form an additional bond on one or more carbons, making it an energetically unfavorable process. For this reason, benzene does not react with Br_2(aq) as would be expected from a compound with alkenyl functional groups. The stability of the delocalized ring of electrons also leads to less exothermic enthalpy changes than expected for reactions such as hydrogenation and combustion of the Kekulé structure (cyclohexa-1,3,5-triene).

Structure 2.3

Exercises

1. B

The formation of a metallic bond occurs when atoms of a metallic element delocalize valence electrons to form positively charged ions (cations). The electrostatic attraction between the sea of delocalized electrons and the lattice of cations is the metallic bond.

2. **(a)** Delocalized electrons are able to move freely so can move across a metallic structure in response to an applied voltage.

(b) Delocalized electrons and closely packed cations enable efficient transfer of thermal energy. In order for a substance to be a good thermal conductor, the kinetic energy of particles must be easily transferred across its structure. In a metallic structure, the delocalized electrons can already move freely and the vibration of one cation can easily cause vibration in adjacent cations as they are closely packed together.

(c) The metallic bond is non-directional due to the random movement of delocalized electrons. This allows the metallic bond to remain intact when the lattice of cations undergoes conformation changes under pressure.

3. **(a)** malleability, thermal conductivity, high melting point

(b) light, strong, forms alloys (alloys are discussed in Structure 2.4.3)

(c) thermal conductivity, high melting point, non-corrosive (aluminium is actually a very reactive metal but quickly reacts with oxygen in air to form a protective outer layer of aluminium oxide which prevents further reaction)

(d) light, strong, non-corrosive

4. Beryllium has stronger electrostatic attraction in its metallic bond as it forms a structure of smaller cations with greater magnitudes of charge (Be^{2+}) and delocalizes two electrons for each cation formed. Lithium has larger cations with only one positive charge (Li^{+}) and delocalizes only one electron for each cation formed. A metallic bond will always be stronger when formed by cations with a smaller radius, greater magnitudes of change and a larger number of delocalized electrons.

5. C

Na, K and Rb are all group 1 elements. For metals in the same group, we expect decreasing melting and boiling points down the group because the cations, which have the same magnitude of charge (1+ for group 1 elements), are increasing in size. This means that the delocalized electrons will be further from the nuclei of the cations so experience less electrostatic attraction and form a weaker metallic bond.

6. The strength of metallic bonding decreases down a group as the size of the cation increases, reducing the attraction between the delocalized electrons and the positively charged nuclei. In this question, we do not need to consider the magnitude of charge on the cations as they are identical for elements in the same group (2+ for group 2 elements).

7. A

   The transition elements are found in the d-block of the periodic table with the exception of zinc (see Structure 3.1.8 for more detail on the definition). Therefore, Zr and Pd are transition elements whereas Pb, in group 14, is not. Note that there is debate over whether some other d-block elements, including scandium and cadmium, are considered transition elements.

8. Transition elements are able to delocalize d-electrons in addition to their valence s−electrons to form ions with higher magnitudes of charge than s and p block metals. This leads to stronger electrostatic attraction in the metallic bond and so higher melting points.

9. Transition elements form a metallic structure with a large number of delocalized electrons leading to high electrical conductivity.

Challenge Yourself

1 Silver is used in small amounts due to its high cost. It is mostly used on the interior of electronic devices as it can tarnish when exposed to sulfur-containing gases in the air. This tarnish can occur even with low concentrations of gases such as sulfur dioxide and hydrogen sulfide.

Practice questions

1. C

   Smaller cations with larger magnitudes of charge have a higher charge density so will experience stronger electrostatic attraction to delocalized electrons in the metallic structure. This leads to a stronger metallic bond.

2. D

   It is helpful to use data from the periodic table to highlight the key factors at play in this question.

	Ionic radius (10^{12} m)	**Charge on cations**	**No. delocalized electrons per cation**
Na	102	1+ (Group 1 element)	1
K	138	1+ (Group 1 element)	1
Mg	72	2+ (Group 2 element)	2
Al	54	3+ (Group 3 element)	3

The metallic structure of aluminium contains more delocalized electrons and has a lattice of cations with smaller ionic radii and higher magnitudes of charge. This leads to greater electrostatic attraction and so a stronger metallic bond.

3. A

Metals are able to conduct electricity in the molten (liquid) state as well as the solid state because the metallic bond remains intact (although the cations now have enough kinetic energy to move somewhat freely). This means that the sea of delocalized electrons can still move through the structure in response to an applied voltage.

4. B

Li, Na, K and Rb are all group 1 elements. For metals in the same group, we expect decreasing melting and boiling points down a group because the cations, which have the same magnitude of charge (1+ for group 1 elements), are increasing in size. This means that the delocalized electrons will be further from the nuclei of the cations so experience less electrostatic attraction and form a weaker metallic bond.

5. **(a)** the electrostatic attraction; (1)

between lattice of cations AND delocalized electrons; (1)

mobile electrons are able to carry charge across a metallic structure. (1)

(b) calcium has smaller ionic radius; (1)

greater attraction between delocalized electrons and «nuclei of» cations; (1)

OR

strontium has a larger ionic radius; (1)

weaker attraction between delocalized electrons and «nuclei of» cations. (1)

6. metallic bond/electrostatic attraction/movement of delocalized electrons is non-directional; (1)

metallic bond remains intact when structure undergoes conformation changes; (1)

closely packed cations AND delocalized electrons; (1)

allow for efficient transfer of thermal energy «across metallic structure». (1)

7. able to delocalise d-electrons «in addition to valence s and/or p-electrons»; (1)

larger number of delocalised electrons «leading to better electrical conductivity». (1)

Structure 2.4

Exercises

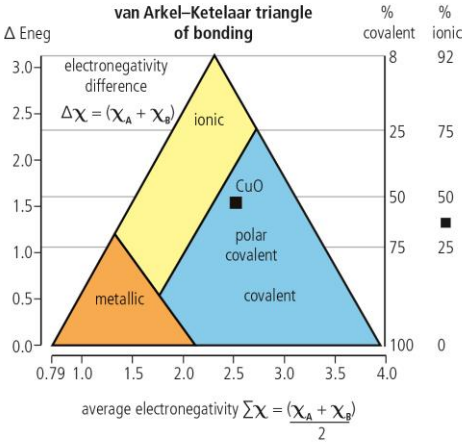
1. Use the data booklet for the electronegativity values of each element in these binary compounds. The 2nd column is the average of the two values, and the 3rd column is the difference between them. These data are then applied to the bonding triangle in the data booklet, to deduce the type of bonding. (Note the % ionic character is not asked for in the question but is given for reference.)

	Substance	χ_{average}	Δ_{χ}	% ionic character	Bonding
(a)	Cl_2O	3.3	0.2	6	(polar) covalent
(b)	$PbCl_2$	2.5	1.4	44	polar covalent
(c)	Al_2O_3	2.5	1.8	56	Ionic
(d)	HBr	2.6	0.8	25	polar covalent
(e)	NaBr	1.95	2.1	66	ionic

Hint: with questions like this, use your knowledge to double-check that your answers make sense – for example, you know that bonding between two non-metals is likely to be covalent, not ionic.

2. The electronegativity values are: Cu 1.9 O 3.4

Substance	χ_{average}	Δ_{χ}	% ionic character	Bonding
CuO	2.65	1.5	47	polar covalent



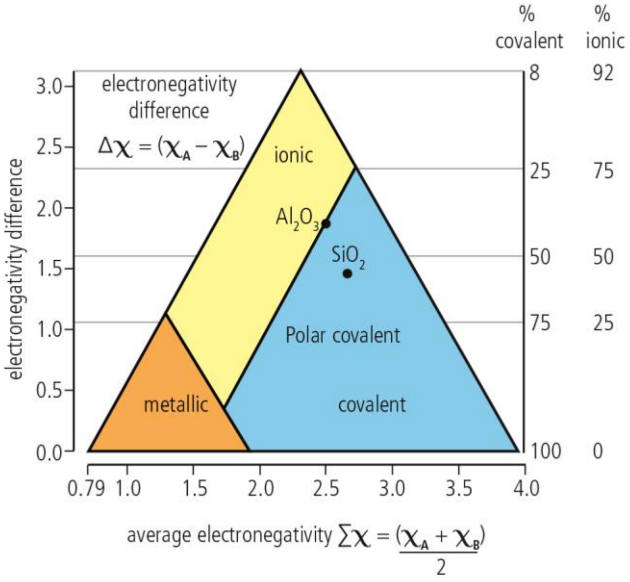
Although the classification puts CuO in the polar covalent section of the bonding triangle, we can see that it also has significant ionic character - as we would expect from a compound of a metal with a non-metal.

3. Electronegativity values from the data booklet:

Si. 1.9 Al 1.6 O 3.4

	SiO_2	Al_2O_3
Electronegativity difference (Δ_χ)	$\Delta_\chi = 3.4 - 1.9 = 1.5$	$\Delta_\chi = 3.4 - 1.6 = 1.8$
Average electronegativity (χ_{average})	$\chi_{\text{average}} = \dfrac{3.4 + 1.9}{2} = 2.65$	$\chi_{\text{average}} = \dfrac{3.4 + 1.6}{2} = 2.5$

Applying these data, we can position these compounds in the bonding triangle. SiO_2 is positioned lower and to the right of Al_2O_3 and therefore has the greater covalent character.



4. A

Alloys always contain a metal, and either another metal or a non-metal.

5. B

If you do not know that silver is element, you could find out by consulting Table 6 of the data booklet where the elements are listed in alphabetical order. Silver is therefore not an alloy, and the correct answer is B**.**

The other answers are all alloys:

solder = tin, lead and other metals, bronze = copper + tin, brass = copper + lead

6. To explain the modification of the properties, it is important to refer to the lattice of cations in the model of metal structure and bonding.

Alloying element(s) disrupts regular/repeating (metal) lattice.

Difficult for one layer to slide over another/atoms smaller than the metal cations can fit into the (holes of) metal lattice disrupting bonding

Can make metal harder/stronger/more corrosion resistant/brittle

7. To show the difference between these two terms, it is important to make matching comparisons.

An alloy is a mixture of one or more metals with other elements. Composites may not contain a metal. Alloys are generally homogeneous mixtures whereas a composite is always a heterogeneous mixture with the components present as separate phases.

8. B

As polyethene is an addition polymer of ethene, they must have the same ratio of atoms, that is the same empirical formula.

9. C

The monomer used to make this polymer is unsaturated and must have the substituent ethyl -C_2H_5 groups and chloro -Cl groups on adjacent C atoms.

(Note here the repeating unit actually shows 2 monomers joined).

10. A

First deduce the molecular structure of the monomer. It must be unsaturated and contain a substituent methyl -CH_3 group. Therefore, it is CH_3-CH-CH_2. This has the molecular formula C_3H_6 so the correct answer is A.

11. In descriptive questions like this, it is important to give specific information about the chemistry of the structures discussed, and avoid terms such as 'environmentally friendly'.

Recyclable means a substance can be processed by chemical means into new products.

Biodegradable means a substance will be broken down in the natural environment into harmless end products.

Reusable means a substance can be reused without being changed physically or chemically.

Reusable plastics potentially have a low impact on the environment, as they can remain in circulation rather than accumulating in land-fill or oceans, and there are no side products of processing. This depends though on individual responsibility for reusing rather than disposing.

Biodegradable plastics also reduce the environmental impact of plastics as they break down into harmless products. This depends though on time and on the conditions during the breakdown process. In some cases, biodegradable plastics may not break down fully.

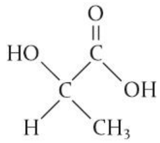
Recyclable plastics enable parts or all of substances to be reused rather than discarded, which reduces their environmental impact. But the sorting, processing and manufacturing stages in the recycling process have side-products, energy costs and waste products which may themselves have an environmental impact.

The best way to reduce the amount of plastic waste is to reduce consumption. For example, limiting the use of single-use plastics and packaging, and encouraging more reusable plastics. Individuals also must be mindful of responsible disposal of plastics according to their chemical nature and ability to be recycled, biodegraded or composted.

12. We recognize from the question that this a condensation polymer involving an amine and a carboxylic acid. The IUPAC names tell us that the amine has two -NH_2 groups and six C atoms; the carboxylic acid has two carboxylic groups and ten C atoms, including the two that are in the terminal -COOH groups.

$$-\left[\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-(\text{CH}_2)_8-\text{CO}-\right]_n-$$

13. From the structure we see that PLA is a polyester. The monomer must contain an acid functional group and an alcohol functional group.



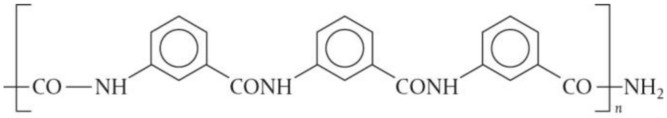
14 **(a)** $\left[\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}\right]_n + \text{H}_2\text{O}$

(b) $\left[\text{HN}-\text{CH}_2-(\text{CH}_2)_4-\text{CH}_2-\text{NH}-\text{CO}-\text{CH}_2-\text{CH}_2-\text{CO}\right]_n + \text{HCl}$

15. **(a)** The primary amine and carboxylic acid groups

(b) H_2O

(c)



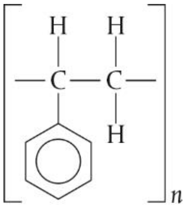
(d) The polymer formed has straight chains as the functional groups are on opposite sides of thr benzene ring. Hydrogen bonds can form between the closley packed chains.

(e) The elements in Kelar – C.H. N and O – have a lower relative atomoic mass than Fe. He aoms in Kevlar are not close-packed, unlike in a metal, so Kevlar will have less mass per unit volume and so a lower density.

Challenge yourself

1. Alloys are a mixture of metals in which the components are held together by metallic bonding. These bonds are able to form between atoms of the same and of different metals due to their non-directional nature. In order to separate a metal from an alloy, the bonds between the different metals have to be broken. This can be done by heating until the metal with the lower melting point forms liquid and can be separated by filtration from the remaining solid. This is not an economically efficient process. Alloys can also be separated into their component metals by chemical means, such as selectively dissolving with acids.

2.



Practice questions

1. A

The term ‘binary’ is familiar from discussion of binary compounds in the bonding triangle, meaning 2 components. Alloys are mixtures not compounds.

2. A

The position of a substance in the bonding triangle gives information about its bonding and therefore leads to predictions about physical properties, and whether it is an element or a compound. It does not help deduce the chemical formula.

3. A

Addition polymers form from alkenes, which have names ending in -ene. So, even if you are not familiar with all these names, it can be deduced that polyester is not an addition polymer.

4 First apply the information given in the question to the bonding triangle. Substance X top right is ionic/ polar covalent, substance Y bottom left is metallic and Z bottom right is covalent.

(a) Y: bottom left position is metallic bonding (2)

(b) X and Y, ionic compounds and metals, respectively, generally have high melting points. It is also true that they both conduct electricity when molten. (2)

(c) X: ionic compounds are brittle, as when the regular structure of the lattice is displaced, the ionic bonds can no longer hold the oppositely charged ions in position. (2)

(d) Z: covalent substances have low boiling points due to relatively weak intermolecular forces. (2)

5 Section 9 in the data booklet gives the electronegativity values for the determination of data for the 2nd and 3rd columns. These data applied to the bonding triangle enable us to deduce the position for each substance and so its main type of bonding. From knowledge of bonding, we can predict some physical properties.

Substance	χ_{average}	$\Delta\chi$	Type of bonding (deduced from position in triangle)	Predicted properties	
Sn	2.0	0.0	metallic	high mp and bp. electrical and thermal conductor	(2)
P_4O_{10}	2.8	1.4	polar covalent	soluble in water, high mp	(2)
Cd_3Mg	1.5	0.5	metallic	high mp and bp. electrical and thermal conductor	(2)
MgO	2.4	2.3	ionic	high mp and bp, conductor of electricity when molten or in solution	(2)
NCl_3	3.0	0.0	covalent	low mp / bp, non-conductor of electricity, not soluble in water	(2)

6. The wording “could be considered” suggests there are different aspects to the question, and it is good to try and present these in the answer.

Polymerization reactions of polypropylene are addition reactions with only one product, the polymer. So, all the atoms of reactant are found in the product and the atom economy is 100%. In this sense, the reactions are “green chemistry”, as there is no waste or by-product.

However, factors such as energy usage, catalysts and yield less than 100%, may all have environmental impact. (2)

7. Here it is important to refer to the model of metallic bonding, and how the regular cation lattice is disrupted by the introduction of atoms of a different metal. (1)

The alloy is stronger than the pure metal. Adding atoms of different size disrupts the (1)

regular metal lattice so that it is difficult for one layer to slide over another. Alloying can make the metal harder, stronger, and more resistant to corrosion. (1)

8. The question directs you to use electronegativity values of La and Sb from the data booklet, and use these to determine the position of the compound in the bonding triangle and so deduce its main types of bonding.

(a) Polar covalent

Average electronegativity = $\chi_{\text{average}} = \frac{3.0 + 2.0}{2} = 2.5$

AND electronegativity difference = 3.0 – 2.0 = 1.0

(b) Here we deduce that lanthanum, like group 2 metals, will form an ionic compound with bromine. From this we can explain its brittleness.

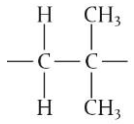
Ionic bonding OR electrostatic forces between ions

<slight> movement brings ions of same charge adjacent to each other <causing the crystal to break>

OR

<slight> movement results in repulsion between layers <causing the crystal to break>

9 **(a)** Work from the IUPAC name to deduce the structure of the monomer. Then consider how this undergoes addition reaction to form the polymer, by breaking its double bond, and leaving open bonds (continuation bonds) at each end.



or

$-CH_2C(CH_3)_2-$

Continuation bonds needed for mark. (1)

No penalty if brackets present or ‘n’ appears after the bracket/formula.

(b) We know that addition reactions have no by-product and so have 100% atom economy.

Same mass of product as reactant, thus 100% (1)

Accept ‘less than 100%’ only if a reason is given (eg the catalyst is not converted into the product, or other reasonable answer)

(c) Questions like this with “suggest” are generally open to several possible answers as shown.

Due to stability of plastics/strong covalent bonds

OR

Low volatility preventing good mixing with oxygen <gas>

OR

Lack of/insufficient oxygen

OR

Plastics are often parts of devices with non-combustible components <which mechanically prevent the combustion of plastic components>

OR

PVC already partly oxidized <because some C-H bonds are replaced with C-Cl bonds>, so it cannot produce enough heat for complete combustion

OR

Many industrial/household materials contain additives that reduce their flammability/act as flame retardants (1)

10 **(a)** Use the bonding triangle to confirm the position of AB - lower left.

Therefore, metallic bonding.

(b) The question requires the use of electronegativity values to calculate the data to assign position in the bonding triangle. This shows the intermediate position of this compound which makes it difficult to classify.

$\Delta EN = 0.6$ AND average $EN = 1.7$ Bonding between metallic and ionic

OR

Not just one type of bonding (1)

$\Delta EN = 0.6$ ***AND*** average $EN = 1.7$

11. B

Amide links form by condensation reactions between amines and carboxylic acid groups. So when a polyamide is hydrolysed it forms these components.

12. D

From the name we know that *amino acids* contain an amine group and a carboxylic acid group, which can react together to form amide links. They do not react by addition reactions, so no C–C double bonds are broken. Condensation reactions always release a small by-product so do not have an atom economy of 100%.

Structure 3.1

Exercises

1. D

The number of electrons increases with atomic number from 11 to 20.

2. C

The diagonal band of metalloids divides the metals from the non-metals.

It is related to the similar electronegativities of these elements.

B 2	C 2.6	N 3	O 3.4	F 4
Al 1.6	Si 1.9	P 2.2	S 2.6	Cl 3.2
Ga 1.8	Ge 2	As 2.2	Se 2.6	Br 3
In 1.8	Sn 2	Sb 2	Te 2.1	I 2.7
Tl 1.8	Pb 1.8	Bi 1.9	Po 2	At 2.2

3. B

Graphite is only non-metal element conductor of electricity.

Silicon is a semiconductor.

4.

	Element	**Period**	**Group**
(a)	helium	1	18
(b)	chlorine	3	17
(c)	barium	6	2
(d)	francium	7	1

This question is just checking that you know what 'group' and 'period' mean – the answers can then be taken from the periodic table (Section 7 of the data booklet).

5. **(a)** Periods are rows and groups are columns.

The 'period' of an element is the number of its atoms' energy levels (shells) that have electrons. Periods are the horizontal rows in the periodic table.

The 'group' of an element is the number of electrons in the outer energy level – although this is complicated for transition elements. Groups are the vertical columns in the periodic table.

(b) $1s^22s^22p^63s^23p^3$

The valence or outer energy level is the third principal energy level, so the element is in period 3. It has the $3p^3$ configuration, so it is in the third group of the p block, which is group 15.

6. Element 51 is antimony (Sb), which is in group 15. Its valence electrons are $5s^25p^3$, and so it has 5 valence electrons.

You can use Section 6 of the data booklet to locate elements.

7. C

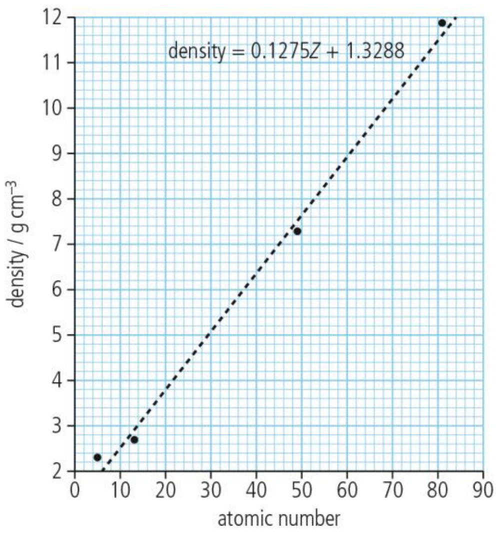
Elements are arranged in the periodic table in order of increasing atomic number.

8. A

${}^{294}_{118}\text{Og}$ has an atomic number and so its nucleus has a relative charge of +118.

It is a noble gas with an outer electron configuration $7p^6$

9.



Drawing a best fit line, we can read the density for an element with atomic number 31.

Predicted density 5.3 g cm^{-3}. This agrees with the measured value of 5.1 g cm^{-3}.

10. C

Across the period from sodium to argon, the number of protons increases (so the nuclear charge increases). Electronegativity also increases as the period is traversed from left to right.

Atomic radius decreases across a period.

11. A

Ionization energy and electron affinity are both properties of gaseous atoms.

Ionization energy: $M(g) \rightarrow M+(g) + e^-$ and electron affinity: $X(g) + e^- \rightarrow X^-(g)$

electronegativity is a property of an atom in a molecule.

12. B

Separating particles is generally endothermic and bring them together (provided there is no mutual repulsion) is exothermic.

Removing electrons from the Ca atom and adding an electron to a negatively charged O^- ion requires energy and is endothermic.

Adding an electron to an iodine atom is an exothermic process.

(See Section 9 in the data booklet for the values).

13. B

Electronegativity decreases down the periodic table and increases from left to right across the periodic table. Elements that are diagonally next to each other (on a top left to bottom right diagonal) tend to have similar electronegativities. (See Section 9 in the data booklet for the values.)

14. D

Ionization energy decreases down the group as the outer electron becomes further from the nucleus and so becomes easier to remove.

Ionic radius (A) and atomic radius (B) increase down a group as more electron shells are added. Neutron/proton ratio (C) also increases down a group; it is 1 : 1 for Mg and Ca but 1.4 : 1 for Ba.

15. D

Electron affinity, electronegativity and ionization energies follow the same trends. They decrease down groups and increase across a period.

Atomic radius increases down a group but decreases across a period. Down a group, further electron energy levels are added, increasing the atomic radius. Across a period, further electrons are added into the same electron energy level, and the attraction between the nucleus and the outer electrons increases as the nuclear charge increases.

16. B

All the species have the same electron configuration and have the same number of electrons. The chloride ion (Cl^-) has the largest radius as has the smallest nuclei charge. Ca^{2+} has the smaller ionic radius as it has the highest nuclear charge.

17. **(a)** Half the distance between the nuclei of neighboring atoms of the same element bonded together by a covalent bond.

(b) **(i)** The noble gases do not form bonds so the distance between neighboring atoms is not defined.

(ii) The atomic radii decrease across a period. The nuclear charge increases as the number of protons increases. Electrons are added to the same main energy level. The electrostatic attraction between the outer electrons and the nucleus increases.

18. Si^{4+} has two occupied energy levels (isoelectronic with Ne) and Si^{4-} has three (isoelectronic with Ar) and so Si^{4-} is larger.

19. **(a)** The electron in the outer electron energy level (level 4) is removed to form K^+. The net attractive force increases as the electrons in the third energy level experience a greater effective nuclear charge.

(b) P^{3-} has one more principal energy level than Si^{4+}. Positive ions are smaller than their parent ions while negative ions are larger than their parent ions.

(c) The ions have the same electron configuration: both have two complete energy levels, Na has a higher nuclear charge due to its extra two protons and so attracts the electrons more strongly.

20. $Cl^- > Cl > Cl^+$

Electron–electron repulsion in the outer energy level increases with number of electrons.

The chloride ion has the most electrons and so is the largest ion.

The Cl^+ ion has the smallest number of electrons and so is the smallest ion.

21. D

The most reactive element in group 1 (i.e. the lowest in the group) must react with the most reactive in group 17 (i.e. the highest in the group).

22. D

As the group is descended the number of electrons in the molecule increases. The intermolecular dispersion forces increase with number of electrons for non-polar molecules.

23. B

Melting points decrease down the group 1 and reactivity increases. Cs has a low melting point and reacts vigorously with water.

24. Sodium floats on the surface; it melts into a sphere; there is fizzing/effervescence/bubbles; sound is produced; solution gets hot; white smoke is produced.

$2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Gas is produced. The gas may ignite with an orange/yellow flame.

The heat of the reaction melts the sodium metal: $Na(s) \rightarrow Na(l)$

And could ignite the gas: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$. The orange color is due to the presence of sodium.

25. Down the group, the reactivities of the alkali metals increase but those of the halogens decrease.

26. They all have valence electron configuration ns^1. They react by losing this electron. The electron is easier to remove as the atomic radii increase due to decreased attraction between the electron and the nucleus: the first ionization energies down the group.

27. They all have valence electron configuration ns^2np^5. They react by gaining an electron. An electron is easier to add as the atomic radii decrease due to increased attraction between the electron and the nucleus. The most reactive element, fluorine, has the smallest atomic radii.

28. A

Only Mg forms a basic oxide.

Al_2O_3 is amphoteric, P_4O_6, P_4O_{10}, SO_2, and SO_3 are acidic. The oxides of sulfur are gases or liquids, but the other oxides are solids, so this information is not helpful in answering the question.

29. D

SO_3 is the only small covalent molecular oxide, therefore this one forms an acidic aqueous solution.

Na_2O and MgO are ionic, but the oxide ion reacts with water to form alkaline hydroxide ions. SiO_2 has a network covalent structure and does not dissolve or react with water.

30. C

SO_2 and N_2Os are both covalent molecular oxides and form an acidic aqueous solution.

31. STP conditions: 273.15 K and 100 kPa and SATP conditions: 298.15 K and 100 kPa. (See Section 4 of data booklet.)

(a) $MgO(s)$, $SiO_2(s)$, $P_4O_{10}(s)$, $SO_2(g)$

(b) MgO: giant structure with ionic bonding; strong attraction between oppositely charged ions.

SiO_2 (quartz): network covalent bonding; strong covalent bonds throughout structure.

$P_4O_{10}(s)$molecular, covalent bonding; weak van der Waals' forces between molecules; P_4O_{10} is larger molecule and so has stronger intermolecular bonding.

SO_2: molecular, covalent bonding; weak van der Waals' forces between molecules; SO_2 is smaller molecule and so has weaker intermolecular bonding.

(c) MgO: alkaline solution

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$

SiO_2 (quartz): oxide is insoluble

P_4O_{10}: acidic solution

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

SO_2: acidic solution

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

(d) **(i)** $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

This is essentially a reaction between the acidic H^+ ions and the basic O^{2-} ions:

(ii) $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq)$

Aluminium shows its amphoteric nature by reacting with bases as well as acids.

32. The oxides of Na and Mg are basic; the oxide of Al is amphoteric; the oxides of Si to Cl are acidic. Ar forms no oxide.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

33. **(a)** Natural rain contains dissolved carbon dioxide, which reacts with water to form carbonic acid:

$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$

(b) sulfuric(VI) acid

Produced by the combustion of coal containing sulfur impurities:

$S(s) + O_2(g) \rightarrow SO_2(g)$ and $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

The oxides form acid solution when the dissolve in water: $H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$

Sulfur dioxide dissolves in water to produce sulfuric(IV) acid: $H_2O(l) + SO_2(g) \rightarrow H_2SO_3(aq)$

(c) nitric acid

production reduced by use of lean burn engines, catalytic converters, recirculation of exhaust gases

34. C

Consider each of the compound in turn.

Compound	Option		Oxidation state
Cr_2O_3	A	$2Cr + 3(-2) = 0\ Cr = +\frac{6}{2} = +3$	+3
CrO_3	A/B	$Cr + 3(-2) = 0\ Cr = +6$	+6
$CrCl_3$	B	$Cr + 3(-1) = 0\ Cr = +3$	+3
K_2CrO_4	C	CrO_4^{2-} $Cr + 4(-2) = -2\ Cr = +6$	+6
$K_2Cr_2O_7$	C	$Cr_2O_7^{2-}$ $2Cr + 7(-2) = -2\ Cr = +6$	+6
CrO_2	D	$Cr + 2(-2) = 0\ Cr = +4$	+2

Chromium is in the same oxidation state +6 in K_2CrO_4 and $K_2Cr_2O_7$.

35. C

$Na_2S_4O_6$. As Na has the oxidation state of + 1 in its compounds.

$4S + 6(2) = -2$

$4S = +10$

$S = +2.5$

36. The states are assigned following the strategy on page (HL 316/ SL 256. In most of these it is best to assign the values for O [–2] and H [+1] first, and then assign values to the remaining elements so that the net charge = the charge on the species (or is zero in the case of neutral species). This is the order of the oxidation states given in the answers below. Remember that the elements P, S, and N, as well as the transition metals, can take different oxidation states, in different compounds.

(a) NH_4^+ = H +1 and N −3,

(b) $SnCl_2$ = Cl −1 and Sn +2,

(c) H_2O = H +1, and O −2

(d) NO_3^- = O −2 and N +5

(e) PbO_2 = O −2 and Pb +4,

(f) PO_4^{3-} = O −2 and P +5,

(g) ClO_4^- = O −2 and Cl +7,

(h) HOCl = H +1, O −2 and Cl +1

37. Three of the elements show their common oxidation states: O = –2, H = +1, and Cl = –1.

The oxidation state of S(+6) can be determined from the formula of the sulfate ion SO_4^{2-}

The oxidation states of the other elements help to name the compound. Remember that the sum of the oxidation states is zero.

(a) nitric(V) acid

(b) nitric(III) acid

(c) phosphoric(V) acid

(d) lead(IV) oxide

(e) lead(II) sulfate(VI)

38. In all the first three cases the oxidation state can be consider as the charge on the metal

(a) Cu_2O

copper(I) contains Cu^+ 2 Cu^+ balances with O^{2-}

(b) Fe_2O_3

Iron(III) contains Fe^{3+} 2 Fe^{3+} balances with 3 O^{2-}

(c) SnO_2

Tin(IV) can be considered as Sn^{4+} 1 Sn^{4+} balances with 2 O^{2-}

This is a simplification as tin(IV) compounds show covalent character, but this does not affect the answer.

(d) $NaBrO_3$

The bromate ion contains bromine and oxygen and has a charge of 1– as it is balanced by the positive charge from Na^+.

Let the formula be $Br0_x^-$. The oxidation state of Br is +5 so: $+5 + -2(x) = -1$

$x = 3$

39. Write the oxidation state below each element in the equation. Elements which have an increase in oxidation state are oxidised. Elements with a decrease are reduced.

(a) I is oxidized (–1 to 0), Cl is reduced (0 to –1)

$Cl_2(aq) + 2NaI(aq) \rightarrow I_2(aq) + 2NaCl(aq)$

0 +1 −1 0 +1 −1

(b) O is oxidized (–2 to 0), F is reduced (0 to –1)

$2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$

+1 −2 0 +1−1 0

(c) P is oxidized (0 to +5), F is reduced (0 to –1)

$P_4(s) + 10F_2(g) \rightarrow 4PF_5(g)$

0 0 +5 −1

(d) Na is oxidized (0 to +1), H is reduced (0 to –1)

$2Na(s) + H_2(g) \rightarrow 2NaH(s)$

0 0 +1 −1

40. C

The ionization energies increase when the electrons are removed from the same sublevel.

Electrons are all removed from the 3p sublevel in the case of Al, Si and P.

A graph of ionization energies is shown on page 300/HL 240/SL. The values are given in Section 9 of the data booklet.

41. A

Ca^{2+} and Ti^{4+} both have the same electron configuration as: [Ar]

Cu^{2+} has an incomplete d sublevel which accounts for the color of the ion in solution.

42. A

Vanadium is element 23, so its electron configuration is the same as argon (element 18) plus five electrons: $[Ar]4s^23d^3$ or $[Ar]\ 3d^3\ 4s^2$. The 4s electrons are the first to be removed. V^{2+} $[Ar]\ 3d^3$

43. **(a)** $M(g) \rightarrow M^+(g) + e^-$

The electron is removed from a gaseous atom.

(b) repeating pattern

(c) In B: an electron is removed from a 2p sublevel. In Be, the electron is removed from 2s sublevel

2p higher energy (as more shielded from nucleus).

(d) Electron removed from nitrogen is from a doubly occupied p orbital, electron repulsion makes it easier to remove.

44. D

Elements in the d block are metals; conducting heat and electricity well is a key property of metals.

A is not correct – some complexes are uncharged, e.g. hydroxides such as $Cu(H_2O)_4(OH)_2$. B is not the correct answer because some d block elements are not transition metals. For example, zinc doesn't have any colored compounds. C is not correct – the elements all have strong metallic bonds.

45. D

In order to show paramagnetic properties, the metal must have unpaired electrons. Mn has an electronic arrangement of $1s^22s^22p^63s^23p^64s^23d^5$. As a consequence of Hund's third law each of the 5d electrons are in a separate d orbital, and so are unpaired.

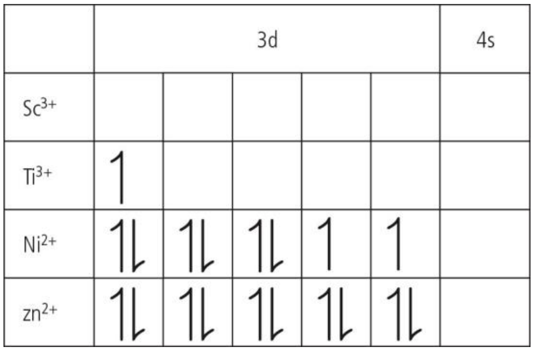
Looking at the electronic arrangements of the other elements in the question, you can see that all their electrons are paired.

46. **(a)** $1s^22s^22p^63s^23p^63d^{10}4s^2$

(b) $1s^22s^22p63s^23p^63d^{10}$

(c) The element does not form ions with partially filled d orbitals.

47.



	3d					4s
Sc^{3+}						
Ti^{3+}	↑					
Ni^{2+}	↑↓	↑↓	↑↓	↑	↑	
zn^{2+}	↑↓	↑↓	↑↓	↑↓	↑↓	

48. Chromium has the electron configuration [Ar] $3d^54s^1$; it has six unpaired electrons, which is the maximum number for the series. Zn has the [Ar] $3d^{10}$ configuration, with no unpaired electrons.

49. The sample near the electromagnet would go down and so appear to have more mass. It is pulled into magnetic field as it has lone pairs of electrons.

50. B

+2 is the only oxidation state shown by every transition element.

51. D

Counting the electrons (the superscript figures) we find that this is element 23, vanadium. The $3d^34s^2$ configuration should also have told you that this is vanadium. Vanadium shows oxidation states of +2, +3, +4 and +5 – as the outer electrons are removed.

52. Al only shows the +3 state, which corresponds to the loss of the two outer 3s electrons and one 3p electron. The other electrons are in lower energy levels and so are not available for bonding. Cr shows oxidation states ranging from +2 to +6. The 3d and 4s orbitals are of similar energy and so are available for bonding.

53. Fe^{2+} has configuration [Ar] $3d^6$ and Zn^{2+} is [Ar] $3d^{10}$. Color is due to splitting of partially filled d orbitals at different energy levels; color absorbed as electrons are excited from lower sublevel to higher sublevel and the complementary color transmitted. Fe^{2+} has partially filled d orbitals and Zn^{2+} does not so Zn^{2+} is not colored.

54. any value or range between 400 and 424 nm

Using the color wheel, the complex appears yellow as it absorbs the complementary color violet.

55. The color of a transition metal complex depends on the energy separation between the orbitals. This depends on the interaction between the ligands and the central ion.

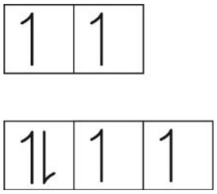
(a) difference in nuclear charge of metal (ion)

(b) difference in oxidation number or the number of d electrons present

(c) difference in ligand

56. λ_{max} = 525 nm. This is in the range for green given in the color wheel in Section 15 of the data booklet; the color transmitted is red/violet. (Note: $[Ti(H_2O)_6]^{3+}$ is violet; answers depend on the color wheel used.)

57. For an ion $[Ar]3d^6$ in the field of the complex the d sublevel splits, to give



(This is called a high spin complex. Other configurations are possible depending on the ligand and the size of the energy splitting. If ΔE is large all six electron can pair up in the lower d orbitals.)

Challenge yourself

1. ytterbium, yttrium, terbium, erbium

2. $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^76s^{2,}$ or

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^7\ 5s^2\ 5p^6\ 6s^2$/ $[Xe]4f^76s^2$

3 Eleven gases: H_2, He, N_2, O_2 F_2, Ne, Cl_2 , Ar, Kr, Xe, Rn

4. ‘Metalloid’ refers to the properties of certain elements in relation to the periodic table. ‘Semiconductor’ refers to the physical properties of materials (including alloys and compounds). There is a partial overlap between the two sets.

5. Coal and oil are fossilized decayed plants or animals; the plants and animals would have contained amino acids. The amino acids methionine and *cysteine* contain sulfur. Coal and oil with a higher percentage of sulfur are considered ‘dirty’ because of the sulfur dioxide pollution that is produced on combustion. Sulfur dioxide results in acid rain.

6. Carbonates react with dilute acids to produce a salt, water and carbon dioxide.

$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l) + CO_2(g)$; $CaSO_4(s)$ has low solubility

$CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + H_2O(l) + CO_2(g) \rightarrow Ca(NO_3)$ has high solubility

7. The d sublevel splits due to the presence of the ligand's lone pair of electrons. Electron transitions between d orbitals is the result of the absorption of energy from the visible region of the EM spectrum. The energy difference between the two sets of d orbitals depends on the coordination number, which changes from six to four, and the ligand, which changes from H_2O to Cl^-.

8. The broad absorption spectrum of the complex ions should be contrasted with the sharp lines of atomic spectra (discussed in Structure 1.3). Both phenomena are due to electronic transitions, but the spectrum of a complex ion is affected by surrounding ligands which can possess both vibrational and rotational energy. This allows the central ion to accept a wider range of frequencies, as any excess energy can be taken up by the ligands in the form of increased vibrational and rotational energy. The isolated gaseous ions which are excited in atomic absorption spectra do not have this option so will only absorb energy of the exact wavelength required to move an electron from a lower energy to a higher energy atomic orbital.

Practice questions

1. C

Atomic radii decrease across period 3 due to the increased (effective) nuclear charge.

2. A

The electronegativity of the elements increases across period 3 and the atomic radii of the elements decreases across period 3.

3. B

The electronegativity decreases down all groups in the periodic table.

4. B

Non-metals oxides produce acidic solution when added to water.

Phosphorus and sulfur are both non-metals.

5. B

Electronegativity is the attraction of an atom for a bonding pair of electrons.

6. D

When sodium is added to water:

- hydrogen gas is evolved.
- the temperature of the water increases as the reaction is exothermic.
- a clear, colorless solution is formed as the product sodium hydroxide is soluble in water.

7. A

The oxidation state of S in is $Na_2S_2O_3 = +2$

The oxidation state in the reactant must be less than this.

Considering each of the options in turn. The oxidation state of S in:

- $S = 0$
- $SO_2 = +4$
- $H_2SO_3 = +4$
- $H_2SO_4 = +4$

8. D

Consider each of the options in turn:

Ox(Cu) + 4(–1) = −2: Ox(Cu)= +2.

The coordination number of the copper ion is 4; there are 4 chloride ions bonded to the central Cu.

Chloride ions are behaving as ligands as the are forming a coordinate bond with the lone pair of electrons.

9. D

Consider each of the compound in turn.

	Complex		Oxidation state
I	$[Fe(H_2O)_6]^{3+}$	H_2O has no charge. Fe + 6(0) = +3	+3
II	$[Fe(H_2O)_5(CN)]^{2+}$	H_2O has no charge CN^- Fe + (–1) = +2 Fe = +3	+3
III	$[Fe(CN)_6]^{3-}$	CN^- Fe +6(–1) = –3 Fe = +3	+3

10. A

Acid rain is produced by the formation of nitrogen and sulfur oxides.

Sulfur oxides are produced when fossil fuels containing sulfur impurities are burnt.

Nitrogen oxides can be produced when nitrogen and oxygen from the air combine during the high temperatures of other combustions reactions.

11. C

The absorption of light when electrons move between different d orbitals of different energies, due to the presence of ligands in a complex ion is responsible for the color of a transition metal complex.

12. D

Complex		Oxidation state
$[Fe(OH)_2(H_2O)_4]^+$	H_2O has no charge OH^- Fe +2(–1) = +1 Fe = +3	+3
$[FeCl_4]^-$	Cl^- Fe +4(–1) = –1 Fe = +3	+3

13. (a) the amount of energy required to remove one (mole of) electron(s) (1)

from (one mole of) an atom(s) in the gaseous state (1)

(b) greater positive charge on nucleus / greater number of protons / greater core charge (1)

greater attraction by Mg nucleus for electrons (in the same shell) / smaller atomic radius (1)

14. $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ (1)

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ (1)

State symbols are not needed.

Na_2O is basic and SO_3 is acidic (1)

15. (a) solution becomes yellow/orange/brown/darker (1)

chlorine is more reactive than iodine (and displaces it from solution) / *OWTTE* (1)

Allow correct equation $Cl_2(g) + 2KI(aq) \rightarrow 2KCl(aq) + I_2(s)$ *for second mark or stating that iodine/*I_2 *is formed.*

(b) no color change / nothing happens as fluorine is more reactive than chlorine / *OWTTE* (1)

16. (a) atomic number / Z (1)

Accept nuclear charge / number of protons.

(b) Across period 3: increasing number of protons / atomic number / Z / nuclear charge (1)

(atomic) radius/size decreases / same shell/energy level / similar shielding/screening (from inner electrons) (1)

No mark for shielding/screening or shielding/screening increases.

Noble gases: do not form bonds (easily) / have a full/stable octet/shell/energy level / cannot attract more electrons (1)

Do not accept 'inert' or 'unreactive' without reference to limited ability/inability to form bonds or attract electrons.

17. (a) Na: 11 p, 11/2.8.1 e^- and Na^+: 11 p, 10/2.8 e^-

OR

Na^+ has two electron shells/energy levels, Na has three / *OWTTE* (1)

Na^+ has greater net positive charge/same number of protons pulling smaller number of electrons (1)

(b) Si^{4+}: 10 e^- in two (filled) energy levels / electron arrangement 2.8 / *OWTTE* (1)

P^{3-}: 18 e^- in three (filled) energy levels / electron arrangement 2.8.8, thus larger / *OWTTE* (1)

OR

Si^{4+} has two energy levels whereas P^{3-} has three /

P^{3-} has one more (filled) energy level (1)

Si^{4+} has 10 e^- whereas P^{3-} has 18 e^- / Si^{4+} has fewer electrons / P^{3+} has more electrons (1)

18. **(a)** ions are in fixed positions in the solid state / there are no moveable ions / *OWTTE* (1)

Do not accept answer that refers to atoms or molecules.

(b) $2O^{2-} \rightarrow O_2 + 4e^-$ / $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$ (1)

Accept e instead of e^-*.*

(c) **(i)** basic (1)

allow alkaline

(ii) $Na_2O + H_2O \rightarrow 2NaOH$ / $Na_2O + H_2O \rightarrow 2Na^+ + 2OH^-$ (1)

do not accept $\rightleftharpoons$

19. **(a)** repeating pattern of (physical and chemical) properties (1)

(b) 2.8.8 (1)

Two of: the outer energy level/shell is full; the increased charge on the nucleus; great(est) attraction for electrons (2)

(c) 17 p in Cl nucleus attract the outer shell electrons more than 11 p in Na nucleus / greater nuclear charge attracts outer shell electrons more (1)

Allow converse for Na. Do not accept 'has larger nucleus'.

(d) S^{2-} has one proton less/smaller nuclear charge so outer level held less strongly / *OWTTE* (1)

Allow converse for chloride. Do not accept 'has larger nucleus'.

(e) The radii of the metal atoms increase (from Li → Cs) (so the forces of attraction are less between them) / *OWTTE* (1)

The forces of attraction between halogen molecules are van der Waals forces (1)

these forces increase with increasing mass/number of electrons. (1)

20. **(a)** complex (ion) / the charge is delocalized over all that is contained in the brackets (1)

(b) color is due to energy being absorbed when electrons are promoted within the split d orbitals

OR

the color observed is the complementary color to the energy absorbed / *OWTTE* (1)

Accept either answer for the first mark.

changing the ligand / coordination number / geometry changes the amount the d orbitals are split/energy difference between the d orbitals / *OWTTE* (1)

21. (a) Fe^{2+}(aq) absorbs any value or range between 647 and 700 nm (1)

Fe^{3+}(aq) absorbs any value or range between 400 and 491 nm (1)

(b) Both are attracted into magnetic field as both have unpaired electrons (1)

Fe^{3+} is more magnetic as it contains more unpaired electrons (1)

Structure 3.2

Exercise 1

1. **(a)** $CH_3CH(OH)CH_3$

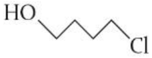
(b) $CH_3CH(CH_3)CH_2CH_3$

(c) $CH_3CHCHCH_3$

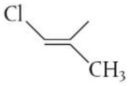
(d) $CH_3C(CH_3)_2CH_2CH_3$

2. **(a)**

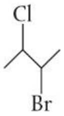
(b)



(c)



(d)



3. **(a)** $CH_3CHClCHBrCH_3$

(b) $CH_3CH_2C(CH_3)CHCH_3$

(c) $CH_3CHCClCHClCH_3$

4. Functional groups are atoms, or groups of atoms, that are present in organic Compounds. Compounds that contain the same functional group belong to the same class.

(a) Class: carboxylic acid Functional Group: carboxy

(b) Class: alkene Functional Group: alkenyl

(c) Class: alcohol Functional Group: hydroxyl

(d) Class: ester Functional Group: ester

(e) Class: aldehyde Functional Group: aldehyde (carbonyl)

(f) Class: amine Functional Group: amine

5. B

Amides contain $–CONH_2$ group

6. D

Esters contain –COO– group

7. D

Members of a homologous series belong to same class of compounds and CH_3COOH is the only carboxylic acid.

8. A

Members of homologous series belong to same class of compounds.

I has two chloroalkanes so belong to the same homologous series

II has a chloroalkane and a bromoalkane so not in the same homologous series

III has a bromoalkane and a dibromoalkane so not in the same homologous series

9. B

A is incorrect as CH_3CH_2COOH is a carboxylic acid and will have the strongest intermolecular forces and highest boiling point.

B is correct as CH_3CH_3 is an alkane so has weakest intermolecular forces. The other two are carboxylic acids with high boiling points. The larger acid will have the highest boiling point.

C is incorrect CH_3COOH is a carboxylic acid and will have the strongest intermolecular forces and highest boiling point.

D is incorrect. All three are alkanes but $CH_3CH(CH_3)CH_3$ has the most branching and will have the lowest boiling point.

10. Order: $CH_3CH_2CH_3 < CH_3CH_2CH_2Br < CH_3CH_2COOH$

Reasoning: strength of intermolecular forces goes in order: alkane (London dispersion forces) < halogenoalkane (dipole-dipole) < carboxylic acid (H-bonding); volatility is reverse to this order.

11. The solubility of the alcohols will decrease as the chain length increases. The alcohols contain a highly polar –OH group and a non-polar carbon chain. As the carbon chain increases in length the alcohol will become less polar overall and therefore less soluble in water which is a polar solvent.

12

(a)	Class:	alkane	Name:	2-methylbutane
(b)	Class:	carboxylic acid	Name:	2-methylpropanoic acid
(c)	Class:	ketone	Name:	butanone
(d)	Class:	ester	Name:	propyl ethanoate
(e)	Class:	alcohol	Name:	propan-2-ol
(f)	Class:	aldehyde	Name:	pentanal

13. **(a)** HCOOH

(b) $CH_3CH_2CCCH_2CH_3$

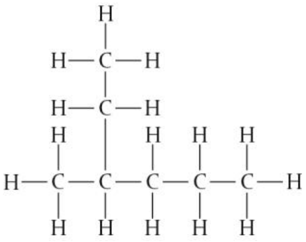
(c) $CH_3CH_2CH_2CH_2CHO$

(d) $CH_3COCH_2CH_3$

(e) $CH_3COOCH_2CH_2CH_3$

(f) $CH_3CHBrCH_2OH$

14.



The longest chain contains six carbons. The correct name is 3-methylhexane.

15. D

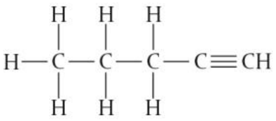
Structural isomers have the same molecular formula

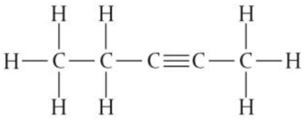
I – both compounds have the same molecular formula; C_4H_{10}

II – compounds have different molecular formula; C_4H_{10} and C_3H_7

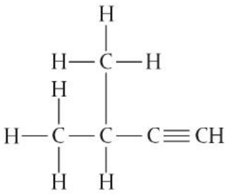
III – both compounds have the same molecular formula; $C_4H_{11}O$

16 **(a)**





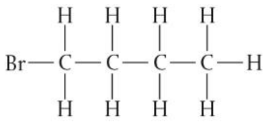
(b)



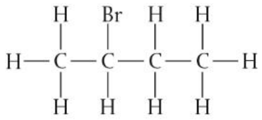
17. D

A secondary carbon is attached to two other carbons and the functional group or substituent.

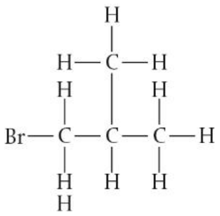
18.



1-bromobutane, primary

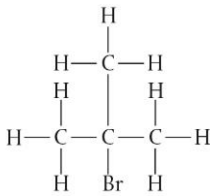


2-bromobutane, secondary



1-bromo-2-methylpropane

primary



2-bromo-2-methylpropane

tertiary

19 **(a)** $CH_3OCH_2CH_3$ and $CH_3CH_2CH_2OH$

Methoxyethane propanol

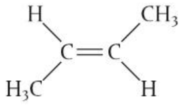
(b) CH_3COCH_3 and CH_3CH_2CHO

propanone propanal

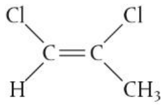
(c) $CH_3CH_2CH_2COOH$ and $CH_3CH_2COOCH_3$ or $CH_3COOCH_2CH_3$

butanoic acid methyl propanoate ethyl ethanoate

20. **(a)**



(b)



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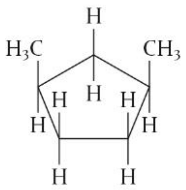

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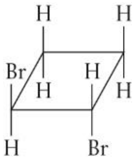


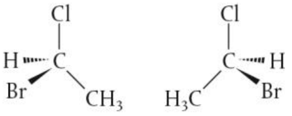
21. **(a)** *cis*-1,3-dibromocyclobutane

(b) *trans*-butan-2,3-diol

(c) *cis*-1,2-dimethylhex-3-ene

(d) *trans*-1,3-dichlorocyclopentane

22. There is one chiral carbon, the optical isomers are mirror images.



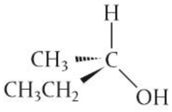
23. D

All three structures have a chiral carbon and so can exist as optical isomers.

24. **(a)** $CH_3CH_2\underset{\uparrow}{C}H(CH_3)CH_2CH_2CH_3$

Chiral carbon

(b)



butan-2-ol

25. C

$C_2H_3O = 43$, not detected

$C_3H_5O = 57$, is detected

$C_4H_8O = 72$, is detected

26. C

Molecular ion peak is at 88, so it could be B**,** C or D. The peak at 73 suggests the loss of CH_3, the peak at 31 suggests an OCH_3 fragment, both of which are unique to compound C**.**

27. Spectrum A corresponds to propanal (CH_3CH_2CHO)

Spectrum B corresponds to propanone (CH_3COCH_3)

Similarities: Both spectra have a molecular ion with $m/z = 58$

Differences: A has peaks at $m/z = 29$ ($CH_3CH_2^+$) and $m/z = 57$ ($CH_3CH_2CO^+$)

B has a peak at $m/z = 43$ (CH_3CO^+)

28. **(a)**

Mass / charge	Mass / charge
15	CH_3^+
29	$C_2H_5^+$
43	$C_3H_7^+$
58	$C_4H_{10}^+$

(b) The molecular formula is C_4H_{10} as this has a molar mass with the mass of the parent ion which is 58 and is a multiple of the empirical formula, C_2H_5. The masses of the fragments show a pattern consistent with a straight chain alkane so the molecular structure is $CH_3CH_2CH_2CH_3$

29. B

Radiation of longest wavelength corresponds to the lowest frequency. Single bonds with heavy atoms will vibrate at the lowest frequency

30. IR radiation of the shortest wavelength corresponds to the highest frequency

(a) C=O is a stronger bond than C–O so will vibrate at the higher frequency and absorb radiation of a shorter wavelength.

(b) Cl is lighter than Br so C–Cl will vibrate at a higher frequency and absorb radiation of a shorter wavelength.

31. The molecular formula of the two compounds is consistent with the general formula for carboxylic acid and esters.

(a) The bonds corresponding to the absorption frequencies are O–H (2900 cm^{-1}), C=O (1730 cm^{-1}) and C–O (1230 cm^{-1}). This indicates the compound is a carboxylic acid.

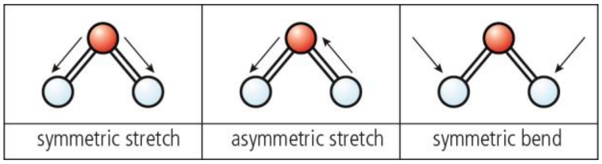
Compound A is propanoic acid

(b) Compound B does not have an O–H bond present as there is no absorption in the 2500–3000 cm^{-1} region. The bonds that are present are C=O (1730 cm^{-1}) and C–O (1230 cm^{-1}). This indicates the compound is an ester.

There are two possible esters: CH_3COOCH_3 (methyl ethanoate) and $HCOOCH_2CH_3$ (ethyl methanoate)

32. Molecules can only absorb IR radiation if it results in a change in the overall dipole. For diatomic molecules this can only happen if they are polar molecules. N_2 and O_2 are both non-polar diatomic molecules so they cannot absorb IR radiation and contribute to the greenhouse effect.

33. SO_2 is V-shaped (bent) so it has three modes of vibration.



All three modes are IR active as each results in a change in the overall dipole.

34. Because it contains a C=C double bond hex-1-ene will have an IR absorption in the range 1610–1680 cm^{-1}. Hexane only contains C–C single bonds so will not have an absorption in this range.

35. Ethanol contains C–H, C–C, C–O and O–H bonds. Of these the only bonds that absorb at 2900 cm^{-1} are C–H bonds. (The O–H bond in alcohols absorbs in the 3200–3600cm^{-1} range.)

36. **(a)** Two signals. The two $–CH_3$ groups are in different chemical environments.

(b) One signal. The molecule is symmetrical so the two $–CH_3$ groups have the same chemical environment.

(c) One signal. All four $–CH_3$ groups are equivalent so the protons have the same chemical environment.

(d) Two signals. The two $–CH_3$ groups are equivalent so their protons have the same chemical environment. The H on the central carbon will have a different chemical environment

37.

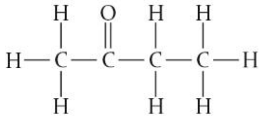
Signal	**Generated by**	**Chemical shift (ppm)**
1	$\mathbf{CH_3}CH_2COOH$	0.9–1.0
2	$CH_3C\mathbf{H_2}COOH$	2.0–2.5
3	$CH_3CH_2COO\mathbf{H}$	9.0–13.0

38. C

A is an alkane so would have no signals above 1.5ppm. B is an aldehyde so would have a signal in the 9.4–10.0 ppm range. D is an alkane so would have no signals above 1.5ppm. C is a ketone so would have two signals in the 2.2–2.7ppm range due to the protons on the two carbons adjacent to the carbonyl group.

39. **(a)**

$CH_3COCH_2CH_3$



(b)

Hydrogen atom	**Chemical shift (ppm)**	**No. of H atoms**	**Splitting pattern**
$C\mathbf{H_3}COCH_2CH_3$	2.2–2.7	3	singlet
$CH_3COC\mathbf{H_2}CH_3$	2.2–2.7	2	quartet 1:3:3:1
$CH_3COCH_2C\mathbf{H_3}$	0.9–1.0	3	triplet 1:2:1

40.

Compound	**Hydrogen atom**	**Chemical shift (ppm)**	**No. of H atoms**	**Splitting pattern**
ethanal CH_3CHO	$C\mathbf{H_3}CHO$	2.2–2.7	3	doublet 1:1
	$CH_3C\mathbf{H}O$	9.4–10.0	1	quartet 1:3:3:1
propanone CH_3COCH_3	$C\mathbf{H_3}COC\mathbf{H_3}$	2.2–2.7	6	singlet

41. The formula $C_3H_6O_2$ is consistent with a carboxylic acid or an ester. However, the singlet at 10.0 ppm is only consistent with the $–COO\mathbf{H}$ of a carboxylic acid.

The compound is propanoic acid: CH_3CH_2COOH

Chemical shift / ppm	**Number of H atoms**	**Splitting pattern**	**Hydrogen atom**
1.3	3	3	$C\mathbf{H_3}CH_2COOH$
4.3	2	4	$CH_3C\mathbf{H_2}COOH$
10.0	1	1	$CH_3CH_2COO\mathbf{H}$

Challenge yourself

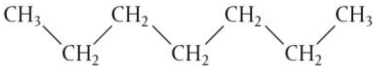
1. Using the experimental data, the ratio of the carbon−carbon bond length to the radius of a carbon nucleus can be calculated;

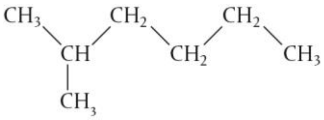
$$\text{Ratio} = \frac{154\times10^{-12}\ \text{m}}{2.7\times10^{-15}\ \text{m}} = 57\,000$$

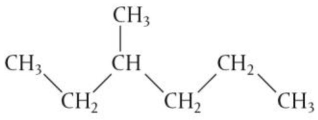
Therefore, the plastic stick used in a model would need to be 57 000 times longer than the radius of the plastic ball used to represent a carbon nucleus.

57 000 × 0.5 cm = 28 500 cm = 285 m

2.


heptane


2-methylhexane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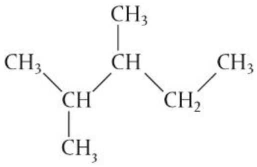
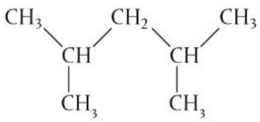

2,3-dimethylpentane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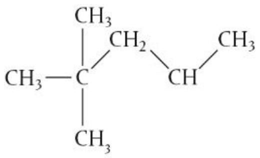
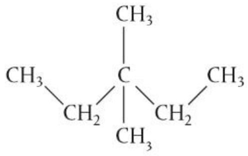
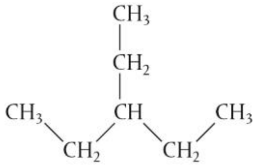
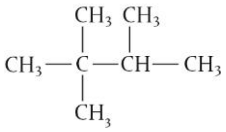

2,2-dimethylpentane


3,3-dimethylpentane


3-ethylpentane


2,2,3-trimethylbutane

Practice Questions

1. B

Structural isomers have the same molecular formula. I, II and III all have the molecular formula; C_4H_8O

2. D

Secondary alcohols have the –OH group attached to a carbon bonded to two other carbons. A and B are primary alcohols. C is a tertiary alcohol.

3. A

Secondary nitrogens are bonded to two carbon atoms and one hydrogen atom B and C contain are primary nitrogens. D has a tertiary nitrogen.

4. D

Decreasing volatility occurs with increasing intermolecular forces. Alcohols have stronger intermolecular forces than ketones or aldehydes. Branched alcohols will have weaker intermolecular forces than straight chain alcohols.

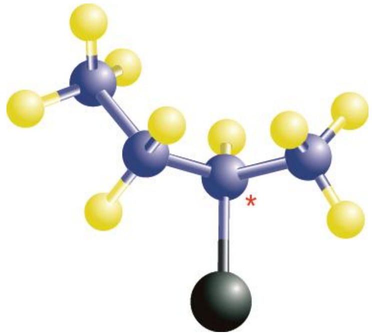
5 **(a)** **A** 1-bromobutane (1)

B 2-bromobutane (1)

C 2-bromo-2-methylbutane (1)

D 1-bromo-2-methylpropane (1)

(b) Optical isomers (enantiomers) are a type of stereoisomer that exist in compounds that contain chiral carbons with four different groups attached. Isomer **B**, 2-bromobutane has a chiral carbon, shown in the diagram below with a *, and can exist as two optical isomers.



(1)

A polarimeter measures the angle that plane-polarized light is rotated through due to its interactions with an optical isomer. One optical isomer will rotate the plane in a clockwise direction whereas the other optical isomer will rotate the plane by the same amount in the anti-clockwise direction. (1)

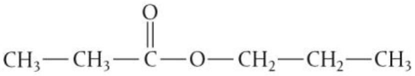
The physical properties of optical isomers are identical except for their rotation of plane-polarized light. (1)

The chemical properties of optical isomers are also identical except for their reactions with other chiral compounds. (1)

6 **(a)** The compound contains the –COO– group so it is an ester. (1)

(b) ethyl butanoate (1)

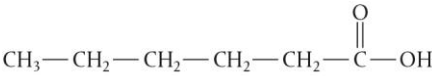
(c) Belonging to same class: propyl propanoate (other ester isomers are possible)



$$CH_3—CH_3—\overset{O}{\overset{\|}{C}}—O—CH_2—CH_2—CH_3$$

(1)

Belonging to different class: hexanoic acid (other branched carboxylic acid isomers are possible)



$$CH_3—CH_2—CH_2—CH_2—CH_2—\overset{O}{\overset{\|}{C}}—OH$$

(1)

7. **(a)** **A**: 1-chlorobutane. It is a primary compound

B: 2-chloro-2-methylpropane. It is a tertiary compound

1 mark for correct name for **A**.

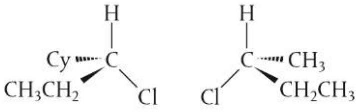
1 mark for correct name for **B**.

1 mark for primary for **A and** tertiary for **B**. (3)

(b) 1-chlorobutane will have four signals as there are four different proton chemical environments

2-chloro-2-methylpropane will only have one signal as the –CH_3 protons all have the same chemical environment. (1)

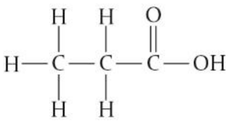
(c) (2)



8 **(a)** **(i)** ethyl methanoate and methyl ethanoate are both esters (1)

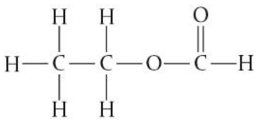
(ii) the three compounds are structural isomers (1)

(iii) (1) (1) (1)



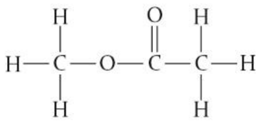
$$H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—\overset{O}{\overset{\|}{C}}—OH$$

propanoic acid



$$H—\underset{H}{\overset{H}{C}}—\underset{H}{\overset{H}{C}}—O—\overset{O}{\overset{\|}{C}}—H$$

ethyl methanoate



$$H—\underset{H}{\overset{H}{C}}—O—\overset{O}{\overset{\|}{C}}—\underset{H}{\overset{H}{C}}—H$$

methyl ethanoate

(b)

Compound	Number of signals	Chemical shift range / ppm	Integrated area	Splitting pattern
ethyl methanoate	3	0.9–1.0	3	triplet
		3.7–4.8	2	quartet
		9.4–10.0	1	singlet
propanoic acid	3	0.9–1.0	3	triplet
		2.0–2.5	2	quartet
		9.0–13.0	1	singlet
methyl ethanoate	2	3.3–3.7	3	singlet
		2.0–2.5	3	singlet

(5)

9. D

I is a di-substituted cycloalkanes that can exhibit *cis-trans* isomerism. **II** is a di-substituted alkanes that cannot exhibit *cis-trans* isomerism. **III** is an alkene that can exhibit *cis-trans* isomerism.

10. D

Optical isomers have the same molecular formula so C is true.

They rotate plane-polarized light in opposite directions so B is true.

They have the same physical properties (except for the rotation of polarized light) so **A** is true and D is not true.

11. D

Chiral carbons have four different groups attached. $CH_3\mathbf{C}HCl\mathbf{C}H(CH_3)\mathbf{C}HBrCH_3$ has three chiral carbons shown in bold.

12. A

Diatomic gases can only be IR active if they have a molecular dipole. N_2 is a non-polar diatomic molecule so it will be IR inactive.

13. C

Different bonds absorb IR radiation of different frequencies.

14. B

Splitting patterns result from spin-spin coupling with hydrogen atoms on neighbouring carbon atoms. The pattern observed depends on the number of hydrogen atoms on the neighbouring carbon atoms.

15. D

The number of signals gives the number of different chemical environments. If there is only one signal there is only one chemical environment so D is correct. The number of signals does not tell us how many hydrogen atoms are generating these signals so A cannot be confirmed as correct.

16. **A**

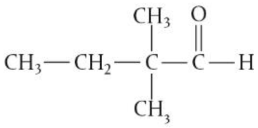
B is incorrect as $CH_3CH_2CH_2CHO$ would give four signals in its spectrum

C is incorrect as CH_3CH_2COOH would give a quartet, triplet and singlet but the singlet due to the acid proton would only have an integrated intensity of 1

D is incorrect as CH_3COOCH_3 would give two signals in its spectrum

17. D

The structure of 2,2-dimethylbutanal is



$CH_3-CH_2-C(CH_3)_2-C(=O)-H$

There will be four signals as the two $-CH_3$ groups of the 2nd carbon (numbered from right) are equivalent. From left to right the intensities for the signals will be 3 (CH_3-) ; 2 (-CH_2-) : 6 (2 × $-CH_3$) : 1 (-C**H**O)

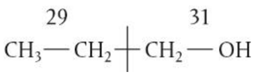
18. C

Benzene is a ring structure with all C-C bonds having the bond order and same bond length. As a result, it only has one isomer and its ^{1}H NMR spectrum shows one signal.

19 **(a)** $m/z = 60$ corresponds to the molecular ion, $C_3H_8O^+$. (1)

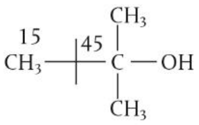
(b) $m/z = 31$ corresponds to the fragment ion, CH_3O^+ (CH_2OH^+) (1)

(c) **A** has fragment peaks corresponding to $CH_3CH_2^+$ at $m/z = 29$ and CH_2OH^+ $m/z = 31$ (loss of CH_2CH_3). The structure that can give these fragments is



$\overset{29}{CH_3-CH_2}\,|\,\overset{31}{CH_2-OH}$

B has fragment peaks corresponding to at $m/z = 45$ that corresponds to loss of $-CH_3$. There are no peaks at $m/z = 29$ corresponding to a $CH_3CH_2^+$ or at $m/z = 31$ corresponding to a loss of CH_3CH_2. The structure that can give these fragments is



$\overset{15}{CH_3}\,|\,\overset{45}{C(CH_3)_2-OH}$

20. When IR radiation is absorbed by CO_2 this excites molecular vibrations and results in a change in the molecular dipole. (1)

The C=O bond lengths change (symmetric stretch). (1)

The OCO bond angle changes (symmetric bend). (1)

21. **(a)** B

A is a symmetrical compound and would only have one signal in its spectrum. C has four different chemical environments and would have four signals in its spectrum.

B has three different chemical environments so would have three signals in its spectrum and the integrated areas of these signals would have the 1:2:3 ratio observed. (1)

(b) The signal at 2.5ppm is due to hydrogen atoms adjacent to a carbonyl group (–C=O). This would also occur for compound A where the CH_3 hydrogens are adjacent to a C=O group. (1)

(c) **(i)** CH_3–CH_2–CHO would have an absorption at 1700–1750cm^{-1} due to the C=O bond.

(ii) The infrared spectrum of compound C would have absorptions at 1620–1680cm^{-1} due to the C=C bond and at 3200–3600cm^{-1} due to the O–H bond.

(d) The mass spectrum of compound X will show peaks at *m*/*z* values of:

- 58 due to the molecular ion $CH_3CH_2CHO^+$
- 29 which could be due to the fragments CHO^+ or $CH_3CH_2^+$
- 15 due to the fragment CH_3^+ (2)

22 **(a)** To be IR active, the absorption of IR energy by the bond must involve a change in the bond dipole. As H–Br is a polar bond, the absorption of IR radiation by the bond stretch will result in a longer bond and a change in the bond dipole so it is IR active. As Br–Br is non-polar there will be no dipole change if it absorbs IR radiation and stretches the bond so it is IR inactive. (1)

(b) **(i)** I is a strong, very broad absorption at 3000cm^{-1}. The bond responsible is O–H (2500–3000cm^{-1} for acids). (1)

II is a strong absorption at 2750 cm^{-1}. The bond responsible is C–H (2850–3090 cm^{-1}). Although this absorption is outside the range in the data booklet it is most likely to be responsible. (1)

III is a strong absorption at 1700 cm^{-1}. The bond responsible is C=O (1700-1750 cm^{-1}.) (1)

(ii) The peak at *m*/*z* = 102 is due to the molecular ion $C_5H_{10}O_2^+$. (1)

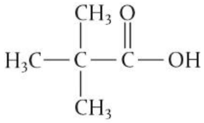
The peak at *m*/*z* = 57 is due to the fragment ion $C_4H_9^+$. (1)

The peak at *m*/*z* = 45 is due to the fragment ions $COOH^+$ (1)

(iii) The signal in the ^{1}H NMR spectrum at 11.5 ppm is due to the proton in the acid group –COO<u>H</u>. (Acid protons occur in the range 9.0–13.0 ppm). (1)

(iv) The signal at 1.2 ppm has an integrated area of 9. This tell us that none protons share the same chemical environment. This is consistent with a –$C(CH_3)_3$ group. (1)

(v) From **(ii)** and **(iii)** we have deduced that X contains a –$C(CH_3)_3$ group and an acid functional group –COOH. The structure must be:



$H_3C-C(CH_3)_2-C(=O)-OH$

(vi) $CH_3COOCH_2CH_2CH_3$ has four different proton chemical environments so it will have four signals with integration 3:2:2:3. (1)

Because it is an ester it will not have a signal due to an acid proton in the 9.0–13.0 ppm region. (1)

23 **(a)** A is a strong, very broad absorption at 2900 cm^{-1}. The bond responsible is O–H (2500–3000cm^{-1} for acids).

B is a strong absorption at 1700 cm^{-1}. The bond responsible is C=O (1700–1750 cm^{-1})

C is a strong absorption at 1200 cm^{-1}. The bond responsible is C–O (1050–1410 cm^{-1})

All three correctly assigned = 2 marks

Any two correctly assigned = 1 mark (2)

(b) The peak at *m*/*z* = 74 is due to the molecular ion $C_3H_6O_2^+$. (1)

The peak at *m*/*z* = 45 is due to the fragment ions $COOH^+$. (1)

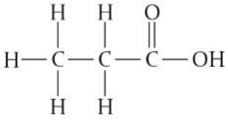
The peak at *m*/*z* = 29 is due to the fragment ion $C_2H_5^+$. (1)

(c) The signal in the ^{1}H NMR spectrum at 11.73 ppm is due to the proton in the acid group – $COO\underline{H}$. (Acid protons occur in the range 9.0–13.0 ppm). (1)

(d) IR peaks at 2900 cm^{-1}, 1700 cm^{-1} and 1200 cm^{-1} along with a mass spectrometer peak at *m*/*z* = 45 and a ^{1}H NMR signal at 11.73 ppm are all consistent with an acid group (–COOH) being present.

A mass spectrometer peak at *m*/*z* = 29 along with ^{1}H NMR signals at 1.2 ppm (3H triplet) and 2.4 ppm (2H quartet) are consistent with CH_3-CH_2 – being present.

The structure is:



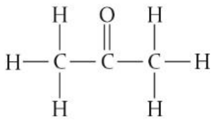
$H-C(H)_2-C(H)_2-C(=O)-OH$

24. **(a)** The structure provided contains an O–H bond. The spectrum is not of this structure as a strong, very broad peak would be observed in the 3200–3600cm^{-1} region if an O–H bond of an alcohol was present.

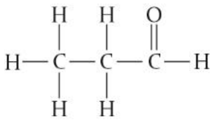
The structure provided is an alkene and contains a C=C bond. The spectrum is not of this structure as a strong peak would be observed in the 1620–1680^{-1} region if a C=C bond was present.

The IR spectrum of X shows a strong absorption at 1750 cm^{-1} which indicates that a C=O bond is present. The structure provided does not contain a C=O bond so it is not consistent with the IR spectrum. (2)

(b) The molecular formula of C_3H_6O is consistent with either a ketone or an aldehyde. Possible structures are:



I



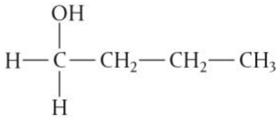
II

Structure I is not the correct structure as it is a symmetrical molecule and only has one proton chemical environment. The ^1H NMR spectrum of I would only contain one signal.

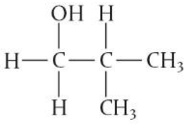
Structure II is the correct structure. (1)

This would give a ^1H NMR spectrum with three signals as it has three different proton chemical environments. $\mathrm{C}\mathbf{H}_3$- , -$\mathrm{C}\mathbf{H}_2$- and -C**H**O. The integrated areas of these signals would be 3:2:1. (1)

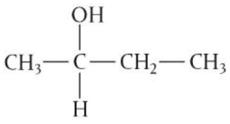
25. **(a)** The structures of the four alcohols are given below:



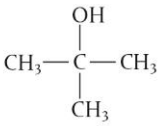
butan-1-ol



2-methylpropan-1-ol



butan-2-ol



2-methylpropan-1-ol

(i) Spectrum 1 has two signals in the ^1H NMR spectrum so the alcohol responsible must contain two different proton chemical environments. From the structures above, we can see that the only alcohol with two chemical environments is 2-methylpropan-2-ol.

(Butan-1-ol and butan-2-ol have five different proton chemical environments and 2-methylpropan-1-ol has four chemical environments.) (1)

The signal at 1.3 ppm with an integration trace of nine units is due to the nine protons on the three chemically equivalent –$\mathrm{C}\mathbf{H}_3$ groups. (1)

The signal at 2.0ppm with an integration trace of one unit is due to the alcohol proton, -O**H**. (1)

(ii) Spectrum 2 has four signals in the 1H NMR spectrum so the alcohol responsible must contain four different proton chemical environments. From the structures above, we can see that the only alcohol with two chemical environments is 2-methylpropan-1-ol. (1)

The signal at 0.9 ppm with an integration trace of six units is due to the six protons on the two chemically equivalent –C**H**$_3$ groups. (1)

The signal at 3.4 ppm with an integration trace of two units is due to the two protons on the carbon attached to the hydroxyl group –C**H**$_2$OH. (1)

(b) **(ii)** The peak at *m*/*z* = 74 is due to the molecular ion $C_4H_{10}O^+$. (1)

The peak at *m*/*z* = 59 is due to the fragment ion $C_3H_7O^+$ (loss of CH_3) (1)

The peak at *m*/*z* = 45 is due to the fragment ion $C_2H_5O^+$ (loss of CH_2CH_3) (1)

From the structures we can see that the loss of CH_3 and CH_2CH_3 to give $C_3H_7O^+$ and $C_2H_5O^+$ can occur for two of the alcohols; butan-1-ol and butan-2-ol. (1)

(ii) The peak at *m*/*z* = 31 is due to the fragment ion CH_3O^+ (loss of $CH_2CH_2CH_3$). (1)

From the structures, we can see that the loss of $CH_2CH_2CH_3$ can only occur for butan-1-ol. (1)

(c) The IR spectra for the four alcohols will be similar as they contain the same bonds; C–H, C–C, C–O and O–H (1)

and will absorb IR energy of the same frequencies. (1)

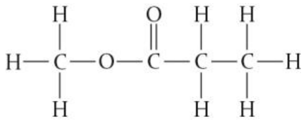
26. With the molecular formula $C_4H_8O_2$ the compound could be a carboxylic acid or an ester. The ^{1}H NMR spectrum does not have a signal in the region expected for an acid proton, 9.0–13.0 ppm so the compound is more likely to be an ester. (1)

The signal at 3.7 ppm is a singlet with an integrated area of three units, which indicates a methyl group –C**H**$_3$. Because it is a singlet, the *n* + 1 rule tells us there are no protons on the neighbouring atoms. Because it is at a high chemical shift, this indicates it is adjacent to the oxygen atom of the carboxy group, C**H**$_3$–O–CO–.
(From the data booklet R–CO–OC**H**$_2$– occurs at 3.7–4.8 ppm). (1)

The signal at 2.3 ppm is a quartet with an integrated area of two units, which indicates a methylene group –C**H**$_2$–. Because it is a quartet, the *n* + 1 rule tells us there are three protons on the neighbouring atoms: CH_3–C**H**$_2$– . Because it is at a moderately high chemical shift, this indicates it is adjacent to the carbon atom of the carboxy group, –C**H**$_2$–CO–O–. (From the data booklet RO–CO–C**H**$_2$– occurs at 2.0–2.5 ppm). (1)

The signal at 1.0 ppm is a triplet with an integrated area of three units, which indicates a methyl group –C**H**$_3$. Because it is a triplet, the *n* + 1 rule tells us there are two protons on the neighbouring atoms: C**H**$_3$–CH_2–. Because it is at a low chemical shift, this indicates it is reasonably distant from the carboxy group, C**H**$_3$–CH_2–CO–O–.
(From the data booklet –C**H**$_3$ occurs at 0.9–1.0 ppm).

The structure is:



(1)

27 **(a)** **(i)** The peak with the highest *m*/*z* occurs at 88. This is likely to be caused by the molecular ion so the relative molecular mass is 88. (1)

The empirical formula provided is C_2H_4O which has a relative formula mass of 44. As the molecular mass obtained from the mass spectrum is twice that of the formula mass, the molecular formula is $2 \times C_2H_4O = C_4H_8O_2$. The molecular ion is therefore $C_4H_8O_2^+$. (1)

(ii) The peak at *m*/*z* = 29 could be due to fragment ions $C_2H_5^+$ or CHO^+ (only one needed). (1)

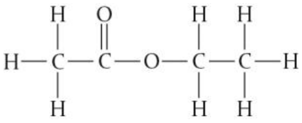
(iii) A peak at *m*/*z* = 59 could result from the loss of CH_2CH_3 to give the fragment ion $C_3H_7O^+$. As $CH_2CH_3^+$ is observed at *m*/*z* = 29, this indicates that any C_3H_7O fragment formed from the loss of CH_2CH_3 is not charged. (If a fragment is not charged it cannot be deflected and observed in a mass spectrum.) (1)

(b) **(i)** A is a strong absorption at 1750 cm^{-1}. The bond responsible is C=O (1700–1750 cm^{-1}).

B is a strong absorption at 1250 cm^{-1}. The bond responsible is C–O (1050–1410 cm^{-1})

(ii) The IR spectrum shows that both C=O and C–O bonds are present, which is consistent with either an ester or an carboxylic acid. The strong broad peak observed for acid –OH bonds at 2500–3000cm^{-1} is not observed, so X must contain an ester functional group. (1)

(c) **(i)** a possible structure is



Reasoning:

From the IR spectrum, it was determined that the compound was an ester.

From the ^1H NMR spectrum:

the signal at 2.0 ppm is a singlet with an integrated area of three units which indicates a methyl group $–C\mathbf{H}_3$. Because it is a singlet, the *n* + 1 rule tells us there are no protons on adjacent atoms. The moderately high chemical shift indicates it is adjacent to the carbon of the carboxy group, $C\mathbf{H}_3$–CO–O–. (From the data booklet, RO–CO–$C\mathbf{H}_2$– occurs at 2.0–2.5 ppm)

the signal at 4.1 ppm is a quartet with an integrated area of two units which indicates a methylene group $–C\mathbf{H}_2–$. Because it is a quartet, the *n* + 1 rule tells us there are three protons on adjacent atoms; -$C\mathbf{H}_2$ –CH_3. The high chemical shift indicates it is adjacent to the oxygen of the carboxy group, CH_3–$C\mathbf{H}_2$–O–CO–. (From the data booklet, R–CO–$C\mathbf{H}_2$– occurs at 3.7–4.8 ppm)

because the signal at 4.1 ppm is a quartet, we can conclude that third signal must be generated by three protons in the same environment. The $–CH_2–$ generating the quartet must be adjacent to a methyl group, $–CH_3$.

(ii)

Signal	**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

The third signal is due to the methyl group at the end of the carbon chain, CH_3–CO–O–CH_2–C**H**$_3$. The relative area will be 3. (1)

The *n* + 1 rule tells us this signal will be a triplet due to the two protons on the neighbouring carbon. (1) From the data booklet, we see that –C**H**$_3$ occurs at 0.9–1.0 ppm. (1)

(iii) The signal at 4.1 ppm is due to the methylene protons in the carbon chain, CH_3–CO–O–C**H**$_2$–CH_3. (1)

It is a quartet as there are three protons on the neighbouring atoms. (1)

Reactivity 1.1

Exercises

1. Heat is transferred from the object with a high temperature T_H to the object at temperature T_C.

The two objects will have the same final temperature. The final temperature is closer to T_H than T_C.

2. $\Delta T = 310 - 300 = 10$ K

$\Delta T = (310 - 273) - (300 - 273) = 10$ °C

3. B

If the temperature drops, the process must be endothermic. ΔH for endothermic reactions is always positive.

4. B

Exothermic reactions give out heat.

5. B

The most energetic molecules leave the surface of the liquid when it evaporates, so the average kinetic energy of the molecules and the temperature decrease.

6. C

The two objects have the same temperature, so the atoms have same average kinetic energy.

The object with the greater mass has the largest number of atoms, and therefore the largest total energy.

7. A

Heat is produced during the reaction. The products are more stable than the reactants as they have less potential energy.

8. B

In an endothermic reaction, heat is transferred from the surroundings to the system.

The enthalpy of the system increases and $H_{products} > H_{reactants}$

9. A

The enthalpy and potential energy of the system increases as heat is added to the system.

It is an endothermic reaction, and the reactants are more stable as they have lower potential energy.

10. A

The equation you need is $\Delta H = mc\Delta T$. Rearranging gives $\frac{\Delta H}{mc} = \Delta T$. The largest temperature increase will be in the metal with the smallest specific heat capacity.

11. D

Again use $\Delta H = mc\Delta T$

(energy = mass × specific heat capacity of copper × temperature rise).

$\Delta H = 5.0 \times 0.385 \times 2 = 3.85$ J

12. C

Since the mass of each are the same and the heat change is the same, the temperature change is inversely proportional to the heat capacity. The substance with the lowest heat capacity must therefore have the highest temperature change. Assuming that they all started at the same temperature, cadmium must have the highest final temperature as it has the lowest heat capacity.

13. A

The mass of the burner will decrease as its contents are burned. The temperature recorded by the thermometer will increase as the heat from combustion warms the water.

14. A

An accurate result requires that all the heat produced by loss of alcohol is used to heat the water in the calorimeter. It should be clear that heat loss reduces the rise in temperature of the water (I). Loss of fuel by evaporation suggests that more fuel had been burned (II). If the thermometer touched the bottom of the container, then the calculated enthalpy of combustion would be higher than predicted (III).

15. C

Incomplete combustion and heat loss would result in a lower enthalpy of combustion value than expected.

16. C

Consider each of the statements in turn:

The thermochemical equations states that if 1.00 mol (44.11 g) of propane is burnt completely, 2219 kJ of energy are produced. If 1.00 is burnt $\frac{2219}{44.11} = 50$ kJ are produced.

I is false.

The reaction is exothermic, so the reactants have more potential energy than the products. **II** is true.

The reaction is exothermic, the enthalpy change is negative.

III is true.

17. **(a)** B

Heat added to water = $m_{water} \times 4.18 \times \Delta T$

No. of moles of methanol = $\frac{m_{methanol}}{M_{methanol}} = \frac{m_{initial} - m_{final}}{32.05}$

Heat per mol = $\frac{m_{water} \times 4.18 \times \Delta T \times 32.05}{m_{initial} - m_{final}}$

(b) C

The calculations assume that all the heat energy goes to the water and the specific heat capacity of the beaker is 0.

18. B

In the second reaction there are $\frac{1}{4}$ of the number of the reactions, so $\frac{1}{4}$ the amount of heat is produced.

The mass of water is also reduced by the same factor, so the temperature change will be the same.

In detail:

Reaction 1

$n_{HNO_3} = 20 \times \frac{2.0}{1000} = 0.040 \qquad n_{KOH} = 40.0 \times \frac{1.0}{1000} = 0.040$

Heat produced = $0.040 \times \Delta H^{\ominus}_{\mathbf{neut}} = 75 \times 4.18\ \Delta T_1$

$\Delta T_1 = \frac{0.040}{60} \times \Delta H^{o}_{neut} \times 4.18 = \frac{0.020}{30} \times \Delta H^{\ominus}_{\mathbf{neut}} \times 4.18$

Reaction 2

$n_{HNO_3} = 5.0 \times \frac{2.0}{1000} = 0.010 \qquad n_{KOH} = 10.0 \times \frac{1.0}{1000} = 0.010$

Heat produced = $0.010 \times \Delta H^{\ominus}_{\mathbf{neut}} = 15 \times 4.18\ \Delta T_2$

$\Delta T_2 = \frac{0.010}{15} \times \Delta H^{\ominus}_{\mathbf{neut}} \times 4.18$

$\Delta T_1 = \Delta T_2$

19. $q = mc\Delta T$, so $\Delta T = \frac{q}{mc}$

$\frac{q}{mc} = \frac{100}{100 \times 0.138} = 7.2\ °\mathrm{C}$

$T = 25.0 + 7.2 = 32.2\ °\mathrm{C}$

20. **(a)** $\Delta T = 36.50 - 25.85 = 10.65\ °\mathrm{C}$ (or K)

$$\begin{aligned} q &= mc\Delta T \\ &= [m(H_2O) \times c(H_2O) \times \Delta T(H_2O)] + [m(Cu) \times c(Cu) \times \Delta T(Cu)] \\ &= (200.00\ \text{g} \times 4.18\ \text{g}^{-1}\ \text{K}^{-1} \times 10.65\ \text{K}) + (120.00\ \text{g} \times 0.385\ \text{g}^{-1}\ \text{K}^{-1} \times 10.65\ \text{K}) \\ &= 8903.4 + 492.0\ \text{J} \\ &= 9395.4\ \text{J} \end{aligned}$$

$$n(C_6H_{12}O_6) = \frac{1.10\ \text{g}}{180.18\ \text{g mol}^{-1}}$$

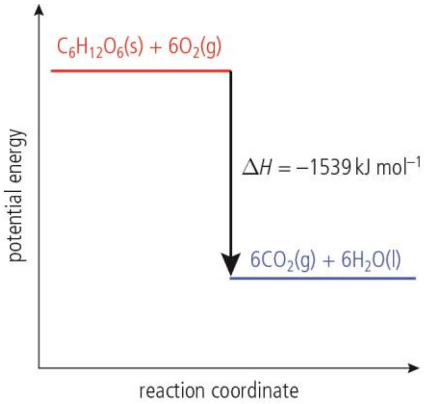
$$= 6.11 \times 10^{-3}\ \text{mol}$$

$$\Delta H_c = \frac{9395.4\ \text{J}}{6.11 \times 10^{-3}\ \text{mol}}$$

$$= -1539 \times 10^3\ \text{J mol}^{-1}$$

$$= -1539\ \text{kJ mol}^{-1}$$

(b)



21. $q = mc\Delta T$

$$= 150.00\ \text{g} \times 4.18\ \text{J g}^{-1}\ \text{K}^{-1} \times (31.5 - 25.0)\ \text{K}$$

$$= 4075.5\ \text{J}$$

$$n(P) = \frac{0.0500\ \text{g}}{30.97\ \text{mol}^{-1}}$$

$$= 1.614 \times 10^{-3}\ \text{mol}$$

$$\Delta H_c = \frac{4075.5\ \text{J}}{1.614 \times 10^{-3}\ \text{mol}}$$

$$= 2525 \times 10^3\ \text{J mol}^{-1}$$

$$\approx 2500\ \text{kJ mol}^{-1}$$

The precision of the answer is limited by the precision of measurement of the temperature difference. The value is lower than the literature value owing to heat losses and incomplete combustion.

22. **(a)** m(propan-1-ol) = 45.65 – 45.05 = 0.60 (g)

$$n(\text{propan-1-ol}) = \frac{0.60}{60.11} = 0.00998\ \text{mol}$$

(b) $\Delta T = 41.5 - 23.7 = 17.8$ (K)

$$\begin{aligned} q &= mc\Delta T \\ &= 210 \times 4.18 \times 17.8 \\ &= 15.62\ \text{kJ} \end{aligned}$$

(c) $$\text{enthalpy change (kJ mol}^{-1}) = \frac{15.62\ \text{kJ}}{0.00998\ \text{mol}} = -1565\ \text{kJ mol}^{-1}$$

(d) Not all heat produced transferred to water as heat is lost to surroundings. Incomplete combustion, with carbon and carbon monoxide being formed instead of carbon dioxide also leads to a less exothermic reaction.

Challenge yourself

1. When heat energy is added to water some of the energy is needed to break hydrogen bonds and so less energy is available to increase the kinetic energy. The presence of hydrogen bonds reduces the temperature increase and so increases the specific heat capacity.

2. $Q = m \times c \times \Delta T$

temperature change (water and aluminium) = 77.5 − 24.5 = 53.0 ± 0.2 K

energy lost by brass = energy gained by water and calorimeter

energy gained by water and calorimeter = (200.00 × 4.18 × 53.0) + (80.00 × 0.900 × 53.0) J

= 44 308 + 3 816 = 48 124 J

energy lost by brass = 48 124 J

$212.10 \times 0.400 \times (T_{\text{Bunsen}} - 77.5) = 48\,124$ J

$$T_{\text{Bunsen}} - 77.5 = \frac{48\,124}{212.10 \times 0.400} = 567.2\ ^\circ\text{C}$$

temperature of brass in Bunsen flame = 567.2 + 77.5 °C

= $644.7 \approx 645$ °C

Practice questions

1. A

$Q = mc \times \Delta T_{X =} mc_Y \Delta T_Y$

$c_X 5 = c_Y 10$

$c_X = 2c_Y$

2. D

$\Delta T = 50 - 20 = 30\ °C$

$$Q = mc\Delta T = 10 \times 8.99 \times 10^{-1} \times 30\ J = 10 \times 8.99 \times 10^{-1} \times \frac{30}{1000}\ KJ$$

3. B

$Q = mc\Delta T = 200 \times 4.18 \times y\ J$

$$n_{HCl} = n_{NaOH} = 100 \times \frac{0.01}{1000} = 0.010\ mol$$

$$\Delta H = 200 \times 4.18 \times \frac{y}{0.010}\ J\ mol^{-1}$$

$$\Delta H = 200 \times 4.18 \times \frac{y}{1000 \times 0.010}\ kJ\ mol^{-1}$$

4. C

$\Delta T = 30 - 20 = 10\ °C$ (or K)

$q = mc\Delta T$

$q = m(H_2O) \times c(H_2O) \times \Delta T(H_2O) = 100.0\ g \times 4.18\ J\ g^{-1}\ K^{-1} \times 10\ K = 100.0 \times 4.18 \times 10\ J$

$$n(C_2H_5OH) = \frac{2.30\ g}{46.08\ g\ mol^{-1}}$$

$$\Delta H_c = \frac{100.0 \times 4.18 \times 10.0}{\frac{0.230}{46.08}}\ J = \frac{100.0 \times 4.18 \times 10.0}{\frac{0.230}{46.08} \times 1000}\ kJ$$

5. D

The temperature change is reduced due to heat loss to the surroundings. This is the most significant systematic error in measuring enthalpy changes.

6. **(a)** **(i)** m(methanol) = 80.557 – 80.034 = 0.523 (g) (1)

$$n(\text{methanol}) = \frac{0.523\ g}{32.05\ g\ mol^{-1}} = 0.0163\ (mol)$$ (1)

*Award **(2)** for correct final answer.*

(ii) $\Delta T = 26.4 - 21.5 = 4.9$ (K) (1)

$q = mc\Delta T = 20.000 \times 4.18 \times 4.9$ (J) *or* $20.000 \times 4.18 \times 4.9 \times 10^{-3}$ (kJ) (1)

= 410 J *or* 0.41 kJ (1)

*Award **(3)** for correct final answer.*

(iii) $\Delta H^{\ominus}_{c} = -\dfrac{410\text{ (J)}}{0.0163\text{ (mol)}}$ *or* $-\dfrac{0.41\text{ (kJ)}}{0.0163\text{ (mol)}}$ (1)

$= -25\,103\text{ J mol}^{-1}$ *or* -25 kJ mol^{-1} (1)

*Award **(2)** for correct final answer. Award **(1)** for (+)25 (kJ mol^{-1}).*

(b) not all heat produced transferred to water / heat lost to surroundings/environment / *OWTTE* / incomplete combustion (of methanol) / water forms as $H_2O(l)$ instead of $H_2O(g)$ *[Do not allow just 'heat is lost']* (2)

7. **(a)** all heat is transferred to water/copper sulfate solution / no heat loss;

specific heat capacity of zinc is zero/negligible / no heat is absorbed by the zinc;

density of water/solution = 1.0 / density of solution = density of water;

heat capacity of cup is zero / no heat is absorbed by the cup;

specific heat capacity of solution = specific heat capacity of water;

temperature uniform throughout solution;

*Award **(1)** each for any two. Accept 'energy' instead of 'heat'.* (2)

(b) **(i)** $T_{\text{final}} = 73.0$ (°C) (1)

Allow in the range 72 to 74 (°C).

$\Delta T = 73.0 - 24.8 = 48.2$ (°C) (1)

*Allow in the range 47 to 49 (°C). Award **(2)** for correct final answer. Allow ECF if T_{final} or $T_{initial}$ correct.*

(ii) temperature decreases at uniform rate (when above room temperature) / *OWTTE* (1)

(iii) 10.1 (kJ) (1)

Allow in the range 9.9 to 10.2 (kJ).

(c) Complete colour change shows all the copper has reacted

so $n(\text{Zn}) = n(\text{CuSO}_4) = \dfrac{1.00 \times 50.0}{1000} = 0.0500$ (mol) (1)

(d) -201 kJ mol^{-1} (1)

Allow in the range –197 to –206 (kJ mol^{-1}). Value must be negative to award mark.

8. **(a)** $\Delta T = 30.3 - 24.5 = 5.8$ K

$q = m(H_2O) \times c(H_2O) \times \Delta T(H_2O)$

$= 100.0\text{ g} \times 4.18\text{ J g}^{-1}\text{ K}^{-1} \times 5.8\text{ K}$

= 2424.4 J

KOH is the limiting reagent.

$$n(\text{KOH}) = \frac{50 \times 0.950}{1000} = 0.0475 \text{ mol}$$

$$\Delta H = -\frac{2424.4}{0.0475} = -68.64 \times 10^3 \text{ J mol}^{-1}$$

$= -51.04 \text{ kJ mol}^{-1}$

(b) Assumptions: no heat loss, c(solution) = c(water), m(solution) = $m(H_2O)$, density(H_2O) = 1.00

9. $\Delta H_{\text{reaction}} = -\Delta H_{\text{water}}$

$q = mc\Delta T$

$\Delta H_{\text{water}} = 100.00 \text{ g} \times 4.18 \text{ J g}^{-1}\text{K}^{-1} \times (21.79 - 25.55) \text{ K} = -1571.68 \text{ J}$

$$n(NH_4Cl) = \frac{5.35 \text{ g}}{53.50 \text{ g mol}^{-1}} = 0.100 \text{ mol}$$

$$\Delta H = \frac{-\Delta H_{\text{water}}}{n(NH_4Cl)} = \frac{-(-1571.68 \text{ J})}{0.100 \text{ mol}} = +15\,716.8 \text{ J mol}^{-1} = +15.7 \text{ kJ mol}^{-1}$$

Reactivity 1.2

Exercises

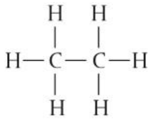
1. B

   Reaction I involves *breaking bonds* (intermolecular hydrogen bonds), so it is endothermic. **Reaction II** involves *forming bonds* (intermolecular van der Waals' bonds), so it is exothermic. **Reaction III** involves *breaking bonds* (intramolecular covalent bonds), so it is endothermic.

2. A

   B is wrong because it also involves formation of H–H and Cl–Cl bonds; C is wrong because ions form (the bond has been broken heterolytically with both electrons going to the chlorine atom). All the products and reactants must be in the gas phase, so D is wrong.

3. This question needs you to know the structure of C_2H_6 (ethane):



   Six C–H bonds and one C–C bond are broken.

   1 × C–C + 6 × C–H

4. B

   The bond enthalpy is the energy required to break 1 mole of the bonds in molecules and atoms, all in the gaseous state. A and C involve carbon as a solid. D involves forming O=O bonds in O_2.

5. B

   The reaction for the hydrogenation of a double bond is

   $–CH=CH– + H_2 \rightarrow –CH_2–CH_2–$

   Bonds broken: 1 × C=C and 1 × H–H, i.e: +614 + (+436) = +10 450 kJ mol^{-1}

   Bonds made: 1 × C–C and 2 × C–H, i.e.: –346 + 2(–414) = –1174 kJ mol^{-1}

   Overall enthalpy change = +10 450 + (–1176) kJ mol^{-1} = –124 kJ mol^{-1}

6. D

   Bonds broken: 1 × C=C and 1 × F–F, i.e.: +614 + (+159) = +773 kJ mol^{-1}

   Bonds formed: 1 × C–C and 2 × C–F, i.e.: –346 + 2(–492) = –1330 kJ mol^{-1}

   Overall energy change = +773 + (–1330) kJ mol^{-1} = –557 kJ mol^{-1}

7. –482 kJ mol^{-1}

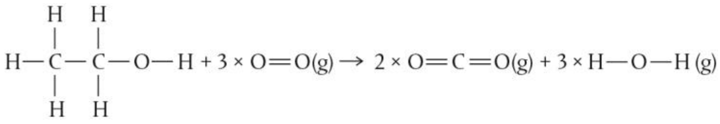
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

2 H – H   O= 0   2 H – O – H

Bonds broken	**$\Delta H^{\ominus}$ / kJ mol^{-1}**	**Bonds formed**	**$\Delta H^{\ominus}$ / kJ mol^{-1}**
2 H–H	2 × (+436)	4 × O–H	4 × (–+463)
O=O	3 (+498)		
Total	+1370		–1852

$\Delta H^{\ominus}$ =+1370 – 1852 kJ mol^{-1} =–482 kJ mol^{-1}

8. $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$



Bonds broken	**$\Delta H^{\ominus}$ / kJ mol^{-1}**	**Bonds formed**	**$\Delta H^{\ominus}$ / kJ mol^{-1}**
C–C	+346	4 C=O	4 × (–804)
3 × O=O	3 × (+498)	6 H–O	6 × (–463)
O–H	+463		
C–O	+358		
5 × C–H	5 × (+414)		
Total	+4731		–5994

$\Delta H^{\ominus}$ =+4731 – 5994 kJ mol^{-1} =–1263 kJ mol^{-1}

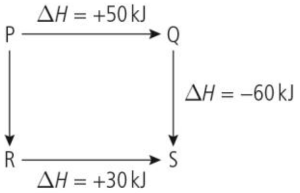
The calculated value is less exothermic that the enthalpy of combustion in Table 14

(–1367 kJ mol^{-1}) because the bond enthalpy calculation assumes all species are in the gaseous state: water and ethanol are liquids.

10. B

The enthalpy changes correspond to reaction in the directions of the arrows.

The enthalpy changes for reverse reactions should also be reversed.



Consider of the options in turn:

I P → S $\Delta H = +50 - 60 = -10$ kJ

II R → Q $\Delta H = -30 - 60 = -90$ kJ

III P → R $\Delta H = = +50 - 60 + 30 = +20$ kJ

I and **III** are correct.

11. B

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta H_1 = -283 \text{ kJ mol}^{-1}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H_2 = -572 \text{ kJ mol}^{-1}$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l) \qquad \Delta H_3 = ?$$

We can think of the reaction as a journey from $CO_2(g)$ and $H_2(g)$ to $CO(g)$ and $H_2O(l)$). We must go by an alternative route suggested by the equations given.

Reaction 1 includes $CO_2(g)$ as a product, so we reverse it and the enthalpy change:

$$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H = +283 \text{ kJ mol}^{-1}$$

Reaction 2 leads to the formation of 2 mol of $H_2O(l)$ so need to reduce the amounts by a factor of 2:

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \ \Delta H_2 = \frac{1}{2} -572 \text{ kJ mol}^{-1}$$

We can now combine these equations:

$$CO_2(g) + H_2(g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) + H_2O(l) \qquad \Delta H = +283 + \frac{1}{2} -572 \text{ kJ mol}^{-1}$$

Simplifying:

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(l) \qquad \Delta H = +283 + \frac{1}{2} -572 \text{ kJ mol}^{-1} = -3 \text{ kJ mol}^{-1}$$

12. $\Delta H^{\ominus} = -394 - (-283)\text{ kJ} = -111\text{ kJ mol}^{-1}$

Adding the first reaction to the reverse of the second:

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta H^{\ominus} = -394\text{ kJ}$

$CO_2(g) \rightarrow CO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^{\ominus} = +283\text{ kJ}$

$C(\text{graphite}) + O_2(g) + CO(g) \rightarrow \frac{1}{2}O_2(g)\ \ CO_2(g) + CO_2(g) \qquad \Delta H^{\ominus} = -394 + 283\text{ kJ}$

$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta H^{\ominus} = -111\text{ kJ}$

13. $\Delta H^{\ominus} = -180.5 + (+66.4) = -114.1\text{ kJ mol}^{-1}$

Adding the reverse of the first reaction to the second

$2NO(g) \rightarrow N_2(g) + O_2(g) \qquad \Delta H^{\ominus}\ -180.5\text{ kJ}$

$N_2(g) + 2O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H^{\ominus} = +66.4\text{ kJ}$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H^{\ominus} = -180.5 + 66.4\text{ kJ}$

14. $\Delta H^{\ominus} = 2 \times (-33.2) + (+9.16) = -57.24\text{ kJ mol}^{-1}$

The first equation needs to be reversed and then multiplied by 2 and then added to the second equation.

15. C

Bromine is not in its standard state, which is a liquid under standard conditions.

16. B

$C_{60}(s)$ doesn't have a standard heat of formation value of zero as graphite is the most stable of carbon under standard conditions.

17. D

The enthalpy of formation is defined as the formation of 1 mole of substance from its elements in their standard states. **A** doesn't start with elements, equation **B** doesn't balance (where does the 'aq' come from), **C** doesn't start with elements.

18.

	$H_2(g)$	$CH_4(g)$
$\Delta H_c^{\ominus}$ / kJ mol^{-1}	–286	– 891
M / g mol^{-1}	2.02	16.05
Heat/ kJ g^{-1}	142	55.5

19. **(a)** $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

$C_4H_{10}(g) + 6\frac{1}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

(b) 1 mol of $C_3H_8(g)$ releases 2219 kJ mol^{-1} $\frac{\text{heat}}{\text{mass}} = \frac{2219}{44.11} = 50.3$ kJ g^{-1}

1 mol of $C_4H_{10}(g)$ releases 2878 kJ mol^{-1} $\frac{\text{heat}}{\text{mass}} = \frac{2878}{58.14} = 49.5$ kJ g^{-1}

$C_3H_8(g)$ releases the most energy per gram.

20. **(a)** $3C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3COCH_3(l)$ $\Delta H_f^{\ominus} = -248$ kJ mol^{-1}

(b) Under standard conditions of 298 K (25 °C) and 1.00×10^5 Pa

21. C

Write down the equation with the enthalpy of combustion data below each compound

$C_{10}H_{22}(l) \rightarrow C_8H_{18}(l) + C_2H_4(g)$

-6778 -5470 -1411 $\Delta H_c^{\ominus}$ /kJ mol^{-1}

$\Delta H^{\ominus} = \Sigma\Delta H_c^{\ominus}(\text{reactants}) - \Sigma\Delta H_c^{\ominus}(\text{products})$

$= -6778 - (-5470 + -1411) = +103$ kJ mol^{-1}

22. B

Write down the equation with the corresponding enthalpies of formation underneath with the amounts:

$C_6H_{14}(l) + \mathbf{9.5}O_2(g) \rightarrow 6CO_2(g) + 7H_2O(g)$

X $\mathbf{9.5}(0)$ $6y$ $7z$ $\boldsymbol{\Delta H_f^{\ominus}}$ /kJ mol^{-1}

$\Delta H^{\ominus} = \boldsymbol{\Delta H_f^{\ominus}}(\text{products}) - \boldsymbol{\Delta H_f^{\ominus}}(\text{reactants}) = 6y + 7z - x$

23. D

Write down the equation with the corresponding enthalpies of formation underneath with the amounts:

$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$

$2(-188)$ $2(-286)$ 0 $\Delta H_f^{\ominus}$ /kJ mol^{-1}

$\boldsymbol{\Delta H^{\ominus}} = \boldsymbol{\Delta H_f^{\ominus}}(\text{products}) - \boldsymbol{\Delta H_f^{\ominus}}(\text{reactants}) = 2(-286) - 2(-188) = -196$ kJ mol^{-1}

24. The value for the enthalpy of combustion of benzene is -3268 kJ mol^{-1}.

(a) $6C(\text{graphite}) + 3H_2(g) \rightarrow C_6H_6(l)$

(b) $\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

$= [6 \times (-394) + 3 \times (-286)] - (-3268)$

$= +46$ kJ mol^{-1}

(c) $\Delta H_f^{\ominus}(C_6H_6(l))$ in Section 12 of the data booklet is $+49$ kJ mol^{-1}. The values are in approximate agreement. Experimental error accounts for the disparity between the values.

25. –136 kJ mol^{-1}

$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$

$\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants}) = [-1411 + -286] - (-1561)$

$= -136 \text{ kJ mol}^{-1}$

26. +330 kJ mol^{-1}

$Fe_3O_4(s) + 2C(\text{graphite}) \rightarrow 3Fe(s) + 2CO_2(g)$

–1118 2(0) 3(0) 2(–394) $\Delta H_f^{\ominus}$ /kJ mol^{-1}

$\Delta H^{\ominus} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants}) = 2(-394) - -1118 = +330 \text{ kJ mol}^{-1}$

27. $2MgO(s) + C(s) \rightarrow CO_2(g) + 2Mg(s)$

$\Delta H_{\text{reaction}}^{\ominus} = (-394) - 2(-602) = +810 \text{ kJ mol}^{-1}$

Such an endothermic reaction is unlikely to be spontaneous over a wide range of temperatures. Carbon is not a suitable reducing agent.

(As discussed in Reactivity 1.4, there is an increase in entropy of the system as $CO_2(g)$ is produced so the reaction could become feasible at very high temperatures.)

28. A

As the electron is attracted to the positively charged nucleus of the Cl atom, the process is exothermic. All the other processes are endothermic (i.e. require energy to take place).

29. C

Electron affinity is the adding of an electron to an element in its gaseous state.

30. D

Enthalpy of atomization is the formation of 1 mole of gaseous atoms from the element in its standard state.

31. C

The magnitude of the lattice enthalpy increases with an increase with the product of the ionic charges of the ions and decreases with a sum of the ionic radii. The magnitude of the lattice enthalpy is greatest for magnesium bromide.

32. B

The magnitude of the lattice enthalpy increases with an increase with the product of the ionic charges of the ions and decreases with a sum of the ionic radii.

Ca^{2+} is the positive ion with the greater charge density, O^{2-} is the negative ion with the greater charge density. CaO has the greatest lattice enthalpy.

33. A

Theoretical lattice enthalpies are based on the ionic model. The theoretical values are closest to experimental values when the compound shows the most ionic character, which depends on the difference in electronegativity between the elements.

Ca is the metal with the lowest electronegativity. O is the non-metal with highest electronegativity. CaO has the most ionic character and so its theoretical lattice enthalpies are likely to be closer to the experimental values.

34. **(a)** $K_2O(s) \rightarrow 2K^+(g) + O^{2-}(g)$

(b) $W = \frac{1}{2}E(O{=}O)$

$X = 2\Delta H_i^\ominus(K)$

$Y = \Delta H_{e1}^\ominus(O) + \Delta H_{e2}^\ominus(O)$; the sum of the first and second electron affinities

$Z = \Delta H_f^\ominus(K_2O)$

(c) $\Delta H_{latt}^\ominus(K_2O) = +361 + 2(89.2) + \frac{1}{2}(498) + 2(419) + (-141) + 753 = +2238.4 \text{ kJ mol}^{-1}$

35. **(a)** They decrease down group 17 as the ionic radius of the halide ion increases.

(b)

Halide	**$\Delta H_{latt}^\ominus$/ kJ mol^{-1}**		**Difference between ionic model and experimental values/ kJ mol^{-1}**	**% Difference between ionic model and experimental values**
	Ionic model	**Experimental**		
NaF	+912	+930	–18	–1.94
NaCl	+770	+790	–20	–2.53
NaBr	+735	+754	–19	–2.52
NaI	+687	+705	–18	–2.55

The agreement between the model generally decreases down group 17. Halides with larger ionic radius have more covalent character as they are more easily polarized.

36. Consider first the effect of increased ionic charge (Na^+/Mg^{2+} and Cl^-/O^{2-}). The charge of both the positive and negative ions is doubled. This leads to a quadrupled increase in the lattice energy. This effect is further enhanced by the decrease in ionic radius of the Mg^{2+} compared to Na^+ due to the increased nuclear charge of the metal and the smaller ionic radius of the oxide ion as it has only two energy levels occupied compared to chlorine with three.

37. **(a)** M_C^+

(b) Theoretical values are based on an ionic model. It does not take into account any additional covalent contributions to the bonding.

(c)

	% Agreement between ionic model and experimental values
M_ABr	0.94
M_BBr	0.46
M_CBr	0.50

(d) The largest difference in values occurs for M_ABr, indicating this has the most covalent character. M_A has the lowest electronegativity.

Challenge yourself

1 **(a)** The bond enthalpies generally decrease down the halogen group but the bond enthalpy in F_2 is weaker than Cl_2 and Br_2. This is due to repulsion between the non-bonding pairs in the two fluorine atoms.

(b)

Average of E(H–H) and E(F–F) / kJ mol^{-1}	E(H–F) / kJ mol^{-1}	$E(\text{H–F}) - \left(\frac{E(\text{H}-\text{H})+E(\text{F}-\text{F})}{2}\right)$ / kJ mol^{-1}
$\frac{436+159}{2} = +297.5$	+567	+269.5

The difference shows that the H–F bond is very polar and F is very electronegative.

2. The difference in the values is largely due to the assumption that H_2O is gaseous in the bond enthalpy calculation.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H^\ominus = -891$ kJ mol^{-1}

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H^\ominus = -808$ kJ mol^{-1}

The difference is due to formation of H_2O in different states:

$2H_2O(l) \rightarrow 2H_2O(g)$ $\Delta H^\ominus = 891 - 808 = +83$ kJ mol^{-1}

$H_2O(l) \rightarrow H_2O(g)$ $\Delta H^\ominus = +41.5$ kJ mol^{-1}

There are (on average) 2 hydrogen bonds between each water molecule so the strength of a hydrogen bond is approximately 20 kJ mol^{-1}.

This assumes that all other molecular interactions, such as dipole–dipole and London forces, are negligible, which is an additional approximation.

3. **(a)** E(O–O) = +144 kJ mol^{-1}, E(O=O) = +498 kJ mol^{-1}. The average value = 321 kJ mol^{-1}.

This suggests that the oxygen–oxygen bond in ozone is intermediate between a single bond and double bond, as discussed in Structure 2.2.

(b) The O=O bond in O_2 is stronger than the bond in O_3. Less energy / longer wavelength radiation is required to dissociate O_3 than O_2.

4. The compounds must be heated for reaction to occur. It is difficult to distinguish any energy changes due to the reaction from the heat input.

5. Within the sheets of graphite, the bond order is 1.5, the coordination number is 3, and there are weak intermolecular forces between the layers. In diamond, each carbon is bonded to four other atoms by single covalent bonds. The total bonding is slightly stronger in graphite.

Practice questions

1. C

Adding the reverse of the second reaction to the first.

$Cu(s) + CuO(s) \rightarrow Cu_2O(s) \quad \Delta H^\ominus = -11\ \text{kJ}$

$Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow 2CuO(s)\ \Delta H^\ominus = -144\ \text{kJ}$

$Cu(s) + CuO(s) + Cu_2O(s) + \frac{1}{2}O_2(g) \rightarrow Cu_2O(s) + 2CuO(s)\ \ \Delta H^\ominus = -11 + -144\ \text{kJ}$

Simplifying: $Cu(s) + \frac{1}{2}O_2(g) \rightarrow CuO(s) \qquad \Delta H^\ominus = -11 + -144\ \text{kJ} = -155\ \text{kJ}$

2. B

The bond enthalpy is the energy required to break 1 mole of the bonds in molecules and atoms, all in the gaseous state.

3. C

Multiplying the first two reactions by 2 and adding to the third.

$2CH_4(g) + 2O_2(g) \rightarrow 2HCHO(l) + 2H_2O(l)\ \ \Delta H^\ominus = 2x$

$2HCHO(l) + O_2(g) \rightarrow 2HCOOH(l) \qquad \Delta H^\ominus = 2y$

$2HCOOH(l) + \frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + H_2O(l)\ \Delta H^\ominus = z$

$2CH_4(g) + 2O_2(g) + 2HCHO(l) + O_2(g) + 2HCOOH(l) + \frac{1}{2}O_2(g)$

$\rightarrow 2HCHO(l) + 2H_2O(l) + 2HCOOH(l) + (COOH)_2(s) + H_2O(l) \qquad \Delta H^\ominus = 2x + 2y + z$

Simplifying:

$2CH_4(g) + 3\frac{1}{2}O_2(g) \rightarrow (COOH)_2(s) + 3H_2O(l) \qquad \Delta H^\ominus = 2x + 2y + z$

4. D

Two O–H bonds are broken when a gaseous water molecule is separated into individual gaseous atoms: H–O–H(g) → O(g) + 2H(g)

The bond enthalpy of the O–H bond corresponds to: $\frac{1}{2}H_2O(g) \rightarrow H(g) + \frac{1}{2}O(g)$

5. B

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$: 564 kJ are released by the combustion of 2 mol so $\frac{1}{2}$ 564 kJ are released by the combustion of 1 mol. = $\frac{1}{2} \times 564$ kJ = 282 kJ

6. A

Bond enthalpy data can only be accurately applied when the reactants and products are both in the gaseous state.

7. bonds broken: 4 × N–H, 1 × N–N, 1 × O=O = +2220 (kJ mol^{-1}) (1)

bonds formed: 1 × N≡N, 4 × O–H = –2797 (kJ mol^{-1}) (1)

enthalpy change = –2797 + 2220 = –577 kJ mol^{-1} (1)

*Award **(3)** for correct final answer.*

8. A

The magnitude of the lattice enthalpy increases with an increase with the product of the ionic charges of the ions and decreases with a sum of the ionic radii.

Mg^{2+} is the positive ion with the greater charge density, O^{2-} is the negative ion with the greater charge density. MgO has the greatest lattice enthalpy.

9. A

Endothermic processes generally involve the separation of mutually attracted particles.

Considering each change in turn:

A $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Li(s) \rightarrow Li(g)$

Both changes are endothermic. Two chlorine atoms are separated in the first process by breaking a covalent bond and the lithium atoms are separated as the solid is turned into a gas.

B $Cl(g) + e^- \rightarrow Cl^-(g)$ and $Li(g) \rightarrow Li^+(g) + e^-$

The electron affinity is exothermic as the added electron is attracted by the positively charged nucleus. Ionization energy is an endothermic process as the electron is pulled away from the nucleus.

C $Li^+(g) + Cl^-(g) \rightarrow LiCl(s)$

This is exothermic as the oppositely charged ions are brought together in a lattice by their mutual attraction.

D $\frac{1}{2}Cl_2(g) \rightarrow Cl(g)$ and $Cl(g) + e^- \rightarrow Cl^-(g)$

The first process is endothermic as two chlorine atoms are separated by breaking a covalent bond. The electron affinity is exothermic as the added electron is attracted by the positively charged nucleus.

10. **(a)** bonds broken are C=C and H–H

energy required = 614 + 436 = 1050

bonds formed are C–C and 2(C–H)

energy released = 346 + 2(414) = 1174 (1)

overall: $\Delta H = 1050 - 1174 = -124\ \text{kJ mol}^{-1}$ (1)

Or allow full consideration of breaking all bonds and forming all the new bonds, which gives values of 2706 and 2830.

bonds broken are C=C + H–H + 4(C–H)

energy required = 614 + 436 + 4(414) = 2706

bonds formed are C–C + 6(C–H)

energy released = 346 + 6(414) = 2830 (1)

overall: $\Delta H = 2706 - 2830 = -124\ \text{kJ mol}^{-1}$ (1)

(b) $\Delta H = -1411 + (-286) - (-1561) = -136\ \text{kJ mol}^{-1}$ (1)

(c) The actual values for bond enthalpies for the specific bonds may be different to the average values / the combustion values referred to the specific compounds / *OWTTE* (1)

(d) **(i)** $-124\ \text{kJ mol}^{-1}$ (1)

(ii) average bond enthalpies do not apply to the liquid state / *OWTTE*; (1)

the enthalpy of vaporization/condensation of cyclohexene and cyclohexane / *OWTTE* (1)

11. **(a)** I is atomization/sublimation (of Mg) / $\Delta H_{\text{atomization}}{}^{\ominus}(Mg)$ / $\Delta H_{\text{sublimation}}{}^{\ominus}(Mg)$ (1)

V is enthalpy change of formation of ($MgCl_2$) / $\Delta H_{\text{formation}}{}^{\ominus}(MgCl_2)$ (1)

(b) energy value for II is +242 (1)

energy value for III: is +738 + 1451 = +2189 (1)

energy value for IV is 2 × (–349) = –698 (1)

$\Delta H_{\text{lat}}{}^{\ominus}(MgCl_2) = 642 + 148 + 242 + 2189 + -698 = (+)2523\ \text{kJ}$ (1)

(c) theoretical value assumes ionic model (1)

experimental value greater due to (additional) covalent character (1)

(d) oxide has greater charge (1)

oxide has smaller radius (1)

Accept opposite arguments.

12. (a) $\frac{1}{2}O_2(g) \rightarrow O^{2-}(g)$

«$\Delta H_{\text{atomisation}}$(O) + 1st EA + 2nd EA = 249 kJ mol^{-1} − 141 kJ mol^{-1} + 753 kJ mol^{-1} =» «+»861 «kJ mol^{-1}» (1)

$Na(s) \rightarrow Na^{+}(g)$

«$\Delta H_{\text{atomisation}}$(Na) + 1st IE = 107 kJ mol^{-1} + 496 kJ mol^{-1} =» «+»603 «kJ mol^{-1}» (1)

(b) lattice enthalpy = 861 «kJ mol^{-1}» + 2 × 603 «kJ mol^{-1}» −(−414 «kJ mol^{-1}») (1)

«= +» 2481 «kJ mol^{-1}» (1)

*Note: Award **(2)** for correct final answer.*

If given values are used:

M1: lattice enthalpy = 850 «kJ mol^{-1}» +2 × 600 «kJ mol^{-1}» −(−414 «kJ mol^{-1}»)

M2: «= +» 2464 «kJ mol^{-1}»

(c) K^{+} ion is larger than Na^{+}

OR

smaller attractive force because of greater distance between ion «centres» (1)

(d) $\sum\Delta H_f$(products) = 2 × (−1130.7) = −2261.4 «kJ» (1)

$\sum\Delta H_f$(reactants) = 2 × (−510.9) + 2 × (−394) = −1809.8 «kJ» (1)

ΔH = «$\sum\Delta H_f$(products) − $\sum\Delta H_f$(reactants) = −2261.4 − (−1809.8) =» −451.6 «kJ» (1)

***Note**: Award **(3)** for correct final answer.*

*Award **(2 max)** for “+ 451.6 «kJn*

(e) only valid for covalent bonds

OR

only valid in gaseous state (1)

Reactivity 1.3

Exercises

1. C

Write a balanced equation for the combustion of 1 mol of each element.

$$Al(s) + \frac{3}{4}O_2(g) \rightarrow \frac{1}{2}Al_2O_3(s)$$

$$Mg(s) + \frac{1}{2}O_2(g) \rightarrow MgO(s)$$

$$Na(s) + \frac{1}{4}O_2(g) \rightarrow \frac{1}{2}Na_2O(s)$$

$S(s) + O_2(g) \rightarrow SO_2(g)$

1 mol of Na reacts with $\frac{1}{4}$ mol of $O_2(g)$.

2. A

Carbon dioxide and water are products of complete combustion.

$X + 2.5O_2(g) \rightarrow yCO_2(s) + zH_2O(l)$

Consider each of the options in turn:

$C_2H_2 + 2.5O_2(g) \rightarrow 2CO_2(s) + H_2O(l)$ X could be C_2H_2

$CH_3CHO + 2.5O_2(g) \rightarrow 2CO_2(s) + 2H_2O(l)$ X could be CH_3CHO

$CH_3CH_2OH + 3O_2(g) \rightarrow 2CO_2(s) + 3H_2O(l)$

3. C

As the reaction is exothermic (and with an increase in entropy as seen in Reactivity 1.4), it would be predicted to occur on energetic grounds.

The only constraint must be the high activation energy.

4. 8.78 g

Start with the equation: $C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

1 mol 4 mol

$$\frac{n(C_4H_{10}(g))}{n(CO_2(g))} = \frac{1}{4}$$

$$n(C_4H_{10}(g)) = \frac{2.9}{M(C_4H_{10}(g))} = \frac{2.9}{412.01+101.01} = \frac{2.9}{58.14} = 0.050 \text{ mol}$$

$n(CO_2(g)) = 4 \times 0.050 = 0.20$ mol

$m(CO_2(g)) = 0.20 \text{ mol} \times (12.01 + 2 \times 16.00) \text{ g mol}^{-1} = 8.80$ g

5. CH_2O

The compound contains C and H and possibly O

$n(CO_2) = \frac{0.88}{44.01} = 0.0200 = n(C)$

0.60 g contains 0.0200 × 12.01 = 0.24 g of C

$n(H_2O) = \frac{0.36}{18.02} = 0.0200$; $n(H) = 0.0400$

0.60 g contains 0.0200 × 2 × 1.01 = 0.0404 g of H

Mass of O = 0.60 – (0.24 + 0.04) = 0.32 g; $n(O) = \frac{0.32}{16.00} = 0.02$

Empirical formula = CH_2O

6. $C_xH_y + (x + \frac{y}{4})O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}H_2O(l)$

7. $C_xH_y + (\frac{x}{2} + \frac{y}{4})O_2(g) \rightarrow xCO(g) + \frac{y}{2}H_2O(l)$

8. $C_6H_{14} + 8O_2(g) \rightarrow 3CO(g) + 3CO_2(g) + 7H_2O(l)$

9. **(a)** $2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

(b) 1 mol of C_8H_{18} reacts with $12\frac{1}{2}$ mol of O_2

114.26 g of C_8H_{18} reacts with 400 g of O_2

1.00 g of C_8H_{18} reacts with 3.50 g of O_2

(c) mass of air = $\frac{100}{20} \times 3.50$ g =17.5 g

(d) CO affects oxygen uptake in the blood. It is absorbed by the lungs and binds to haemoglobin in red blood cells more effectively than oxygen and is bound permanently. This prevents oxygen from being transported around the body.

(e) catalytic converters

10. **(a)** Carbon has a higher enthalpy of combustion than hydrogen (per mol) but the atomic mass of hydrogen is much less than the atomic mass of carbon. As the percentage carbon content decreases and the percentage hydrogen content increases, the specific energy increases.

(b) Carbon dioxide is a greenhouse gas and causes global warming.

(c)

Fuel	Specific energy / kJ g^{-1}	Carbon content by mass / %	Carbon dioxide produced / g
Coal	32	94	108
Oil	42	83	72
Natural gas	55	75	50
Wood	15	70	171
Hydrogen	142	0	0

Hydrogen is the best fuel and wood is the worst fuel on this basis. But, the carbon dioxide in the wood was taken out of the atmosphere when the wood was growing and more wood can be grown. Taking this into account, coal is the worst fuel.

11. (a) Empirical formula: $C_{135}H_{96}O_9NS$ or $C_{136}H_{97}O_9NS$. (It typically also contains trace amounts of silicon, sodium, calcium, aluminium, nickel, copper, zinc, arsenic, lead and mercury.)

(b) Some elements burn to give acidic oxides that dissolve/react with water to give acid rain.

$S(s) + O_2(g) \rightarrow SO_2(g)$; $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$H_2O(aq) + SO_2(g) \rightarrow H_2SO_3(aq)$; $H_2O(l) + SO_3(g) \rightarrow H_2SO_4(aq)$

$2N(g) + O_2(g) \rightarrow 2NO(g)$; $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$; $2NO_2(g) + H_2O(l)$

$\rightarrow HNO_3(aq) + HNO_2(aq)$

12. (a) $$\frac{\text{useful output energy}}{\text{total input energy}} = \frac{\text{useful electrical energy}}{\text{total input heat energy}} = 0.38$$

$$\text{heat energy produced by combustion per second} = \frac{5.00 \times 10^5 \text{ kJ s}^{-1}}{0.38}$$

$$\text{mass per second} = \frac{5.00 \times 10^5 \text{ kJ s}^{-1}}{0.38 \times 33.0 \text{ kJ g}^{-1}}$$

$= 39\,872 \text{ g s}^{-1} \approx 39.9 \text{ kg s}^{-1}$

(b) We have the balanced equation: $4CH(s) + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O(g)$

no. of moles of CO_2 = no. of moles of CH

$$\text{no. of moles of CH burnt per second} = \frac{39872}{12.01+1.01} = 3062 \text{ mol}$$

mass of CO_2 per second = $3062 \times 44.01 = 134\,775 \text{ g} \approx 135 \text{ kg}$

13. Carbon-containing fuels are non-renewable.

They are needed as chemical feedstocks.

Their combustion adds carbon dioxide to the atmosphere which contributes to global warming.

14. **(a)** High specific energy / energy density. As a liquid it is convenient to handle and deliver. Easy to vaporize, which assists combustion.

(b) It was formed by the partial decomposition of marine plants millions of years ago.

15. It is more efficient.

It produces more thermal energy per unit of mass / has a higher specific energy / energy density.

It produces less CO_2 per unit of output energy.

16. **(a)** Fossil fuels and biomass are derived from the sun through photosynthesis.

(b) Advantages: renewable and has little environmental impact.

Disadvantages: photosynthesis is not very efficient, so relatively little of the available solar energy is trapped. Land used to grow plants for biomass could be used to grow plants for food.

17. **(a)** $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

(b) chlorophyll

(c) Process: fermentation

Equation: $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Conditions: acidity / absence of oxygen / below 40 °C. Yeast provides enzyme.

18. **(a)** methane

(b) particulates (soot), hydrocarbons, carbon monoxide

(c) Fossil fuels are being phased out due to carbon dioxide production and limited resources. Biomass is a renewable source.

19. **(a)** $H_2(g)$ is oxidized at the anode: $2H_2(g) \rightarrow 4H^+(aq) + 4e^-$

$O_2(g)$ is reduced at the cathode: $4H^+(aq) + O_2(g) + 4e^- \rightarrow 2H_2O(l)$

(b) Less waste heat produced and more chemical energy converted to useful energy. They can use a renewable energy source to form the hydrogen, which is more efficient.

Challenge yourself

1. The compound contains C, H and N.

$$n(CO_2) = \frac{0.456}{44.01} = 0.010361 = n(C)$$

0.20 g contains 0.010361 × 12.01 g of C = 0.124439 g of C

$$n(H_2O) = \frac{0.248}{18.02} = 0.013762$$

$n(H) = 2 \times 0.013762 = 0.027525$

0.20 g contains 0.027525 × 1.01 g of H = 0.0278 g of H

mass of N = 0.20 – 0.124439 – 0.0278 = 0.047761 g

$$n(N) = \frac{0.047761}{14.01} = 0.003409$$

	C	H	N
Mol	0.010361	0.027525	0.003409
Ratio	3	8	1

Empirical formula = C_3H_8N

2. combination of nitrogen and oxygen at high temperatures: $N_2(g) + O_2(g) \rightarrow 2NO(g)$

acid rain and (photochemical) smog

3. **(a)** % mass of C in coal:

$$\frac{12.01}{13.02} \times 100 = 92.24\%$$

% mass of C in wood:

$$\frac{5 \times 12.01}{5 \times 12.01 + 9 \times 1.01 + 4 \times 16.00} \times 100 = 45.10\%$$

(b) Carbon footprint of coal:

mass of coal needed:

$$\frac{1.33 \times 10^6\,\text{kJ}}{31\,\text{kJ g}^{-1}} \times \frac{100}{65} = 66\,005\text{ g} = 66.0\text{ kg}$$

mass of carbon dioxide produced:

$$66.0\text{ kg} \times \frac{92.24\%}{100} \times \frac{44.01}{12.01} = 223.1\text{ kg}$$

Carbon footprint of wood:

mass of wood needed:

$$\frac{1.33\times10^{6}\,\text{kJ}}{22\ \text{kJ g}^{-1}}\times\frac{100}{70} = 86\ 364\ \text{g} = 86.4\ \text{kg}$$

mass of carbon dioxide produced:

$$86.4\ \text{kg} \times \frac{45.10\%}{100}\times\frac{44.01}{12.01} = 142.7\ \text{kg}$$

(c) Carbon footprint for wood doesn't account for the carbon dioxide taken in while the wood was growing or that more wood can be grown relatively quickly, taking carbon dioxide out of the atmosphere.

4 **(a)** Distant from localized areas of pollution; data present an accurate measure of global levels of CO_2.

(b) The annual variation is due to CO_2 uptake by growing plants. Over a year, the uptake is highest in the northern hemisphere springtime. Considerably more of the northern hemisphere is land (for plants) compared with the southern hemisphere.

(c) Photosynthesis: $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$

CO_2 dissolves in water: $CO_2 + H_2O \rightleftharpoons H_2CO_3(aq)$

(d) Decreased level of photosynthesis: less CO_2 taken in by plants.

5 **(a)** 1%

(b) Wavelength of radiation not absorbed by chlorophyll. Some radiation is reflected or heats the surface of the Earth. Plants do not cover all the Earth's surface.

6 **(a)** $2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow xH_2 + yCO + zCO_2$

–1/16				+2	+4	C
+1	+1		0			H
−2	−2	0		−2	−2	O

(b) C is oxidized

O and H are reduced

(c) Balancing the H atoms:

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + yCO + zCO_2$

$x = 42$

(d) Total change of oxidation number of H = −84

Total change of oxidation number of O = −4

Total increase in oxidation number of C = +88

Balancing the change in oxidation numbers for C: $+88 - 2 = 2y + 4z$

Balancing the C atoms: $y + z = 32$

Solving the equations: $2z = 86 - 64 = 22$

$z = 11$ and $y = 21$

$2C_{16}H_{23}O_{11} + 19H_2O + O_2 \rightarrow 42H_2 + 21CO + 11CO_2$

(e) $2H_2 + CO \rightarrow CH_3OH$

$42H_2 + 21CO \rightarrow 21CH_3OH$

2 molecules of wood produce 21 molecules of methanol

1 molecule of wood produces 10.5 molecules of methanol

7 The entropy decrease is smaller for the reaction which produces one mole of gaseous water, which leads to a larger efficiency. This is discussed in more detail in Reactivity 1.4.

Practice questions

1 **(a)** long wavelength / infrared / IR radiation from Earth's surface

(some of this radiation) is absorbed (by gas) (1)

Do not accept 'trapped' or 'blocked'.

Do not award mark for 'IR from Sun'.

causes (increased) vibration in bonds

re-radiates heat back to the Earth (1)

Accept 're-transmits'

Do not accept 'reflects/bounces'

(b) no change in polarity/dipole (moment) when molecule vibrates; (1)

(c) two from:

CO: prevents haemoglobin from transporting oxygen

Particulate/soot: respiratory problems, lung diseases, carcinogenic

Nitrogen oxides: photochemical smog / acid deposition/rain (2)

2 **(a)** two from:

wide availability

produce energy at appropriate rate

ease of transportation

current technology is based on fossil fuels

high energy density / specific energy (2)

(b) hydrogen (1)

3 **(a)** coal 92.2%, petrol 84.1% and natural gas 74.8% (3)

(b) two from:

they have higher specific energy

liquid or gaseous state make them more convenient to use / easier to transport

produce less pollution / smaller carbon foot print (2)

(c) two from:

hydrogen has a very high specific energy / energy density

it is clean burning, producing only H_2O when it is burned

can be generated by electrolysis, electricity can come from renewable sources (2)

4. **(a)**

Formula	***M*** **/g mol^{-1}**	**ΔH_c / kJ mol^{-1}**	**Specific enthalpy / kJ g^{-1}**
C_3H_8	44.11	−2219	$\frac{2219}{44.11} = 50.31$
C_4H_{10}	58.14	−2878	$\frac{2878}{58.14} = 49.50$

(2)

(b) $pV = nRT$

$$\rho = \frac{m}{V};\ M = \frac{m}{n}$$

$$\rho = \frac{PM}{RT}$$

C_3H_8

$$\rho = \frac{1.00 \times 10^5 \times 44.11}{8.13 \times 273} = 1987 \text{ g m}^{-3} = 1.987 \times 10^{-3} \text{ g cm}^{-3}$$

heat produced per cm^3 $= 50.31 \text{ kJ g}^{-1} \times 1.987 \times 10^{-3} \text{ g cm}^{-3}$

$= 0.09999 \text{ kJ g}^{-1}$

$\approx 0.10 \text{ kJ g}^{-1}$

C_4H_{10}

$$\rho = \frac{1.00 \times 10^5 \times 58.14}{8.13 \times 273} = 2620 \text{ g m}^{-3} = 2.620 \times 10^{-3} \text{ g cm}^{-3}$$

heat produced per cm^3 $= 49.50 \text{ kJ g}^{-1} \times 2.620 \times 10^{-3} \text{ g cm}^{-3}$

$= 0.1297 \text{ kJ g}^{-1}$

$\approx 0.13 \text{ kJ g}^{-1}$ (3)

5. **(a)** photosynthesis (1)

(b) $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$ (1)

(c) fermentation

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$ (2)

6. (a)

Fuel	**Formula**	**Standard enthalpy of combustion ΔH / kJ mol^{-1}**	**Relative molecular mass**	**Specific energy / kJ g^{-1}**
methane	CH_4	−891	16.05	55.5
methanol	CH_3OH	−726	32.05	22.7

(2)

(b) CH_4:

4 × H is +4, so ox. no. (C) = −4

CH_3OH:

4 × H is +4 and O is –2, so ox. no. (C) = −2 (1)

(c) the more oxidized the C the lower the specific energy (1)

(d) for $C_6H_{12}O_6$, specific energy = $\frac{2803}{180.18}$ = 15.56 kJ g^{-1}

for $C_6H_{12}O_6$: 12 × H is +12, 6 × O is –12, so ox. no. C = 0

the result supports the hypothesis (3)

7. (a) Cathode: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

Anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

award ***(1)*** *if both equations given but at wrong electrodes* (2)

8. (a) $M_r(C_8H_{18})$ = 114.26 and $\Delta H_c^{\ominus}$ = –5470 «kJ mol^{-1}»;

«specific energy = $\frac{5470\text{ kJ}}{0.11426\text{ kg}}$ =» 4.79×10^4 / 47873 / 47900 «kJ kg^{-1}»;

Award ***(2)*** *for correct final answer.*

Accept "48 x 10^3 «kJ kg^{-1}»" ***OR*** *"47.9 x 10^3 «kJ kg^{-1}»".*

(b) Wood is less useful because it requires «about three times» more mass for same energy (1)

Accept "octane is more useful because it has higher specific energy".

9. (a) specific energy = $\frac{\text{energy released}}{\text{molecular mass}} = \frac{5470\text{ kJ mol}^{-1}}{114.26\text{ g mol}^{-1}}$ = 47.9 «kJ g^{-1}»

energy density = specific energy × density = 47.9 kJ g^{-1} × 0.703 g cm^{-3}» = 33.7 «kJ cm^{-3} »

Do ***not*** *accept "–47.9 «kJ g^{-1}»".*

Do ***not*** *accept "–33.7 «kJ cm^{-3}»" unless "–47.9 «kJ g^{-1}»" already penalized.* (2)

(b) energy is lost «to the surroundings» as heat/sound/friction

OR

energy is lost to the surroundings «as heat/sound/friction»

OR

incomplete combustion

*Do **not** accept just "energy is lost".* (1)

10. (a) Methane is the major component of natural gas. It has the formula CH_4. (1)

$CH_4(g) + 2O_2 (g) \rightarrow CO_2(g) + 2H_2O(g)$ (1)

(b) Natural gas is the cleanest of the fossil fuels to burn as it has a high H:C ratio. (1)

The combustion of natural gas produces minimal amounts of carbon monoxide, hydrocarbons and particulates. (1)

It does contribute to global warming but does not contribute to acid rain, unlike coal and oil. (1)

(c) Natural gas is the fossil fuel in the shortest supply and it is unevenly distributed around the world. Oil is expected to last a little longer. Coal, which is distributed more evenly around the world, is expected to last longer still. (1)

Reactivity 1.4

Exercises

1. B

   $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

   is the only reaction that does not change the number of gas molecules.

2. C

   Reaction **I** decreases entropy because liquids are more ordered than gases, reaction **II** increases entropy because two moles of gas have more entropy than one mole, and reaction **III** increases entropy because aqueous ions have more entropy than ions in a lattice.

3. A

   A solid is turning into a gas; there is an increase in disorder and an increase in entropy. ΔS is positive. Intermolecular bonds are broken as the solid turns into a gas, so ΔH is positive and the change is endothermic.

4. D

   In this reaction, solid and solution react to give products, one of which is a gas. The increase in entropy is larger than for any of the other reactions given. A shows an overall decrease in entropy as a solid is formed as one of the products. In B and C both the reactants and products are gases so any entropy change won't be as large as for D, especially for C where there is a decrease in the number of moles of gas.

5. **(a)** ΔS is negative. The number of moles of gas decreases from reactants to products.

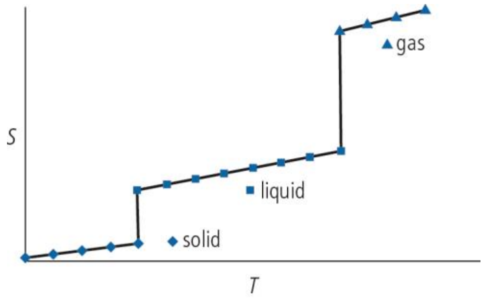
   (b) ΔS is negative. Three moles of solid and four moles of gas changes into one mole of solid and four moles of gas. There is a small decrease in disorder.

   (c) ΔS is positive. The number of moles of aqueous ions increases from reactants to products.

6. The entropy increases gradually with temperature in the solid, liquid, or gaseous states.

   The entropy increases dramatically during a phase change.

   For example:



More detailed response

For a solid/liquid or gas

$$\Delta S = \frac{Q}{T} = \frac{mc\Delta T}{T}$$

Assuming c doesn't change with temp

$S = m \times c \times lnT$

S increases with the natural log of temp; it is not strictly a linear relationship.

7. The textbook gives these entropy values:

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

191 3 × 131 2 × 193 $S^{\ominus}$/J K^{-1} mol^{-1}

$\Delta S^{\ominus} = (2 \times 193) - (191 + 3 \times 131)$

$= -198$ J K^{-1} mol^{-1}

The value is negative, as expected, since the two moles of gas produced have less entropy than the four moles of reactant gas.

8. $C(graphite) + 2H_2(g) \rightarrow CH_4(g)$

5.7 2 × 131 186 $S^{\ominus}$/J K^{-1} mol^{-1}

$\Delta S^{\ominus} = (186) - (5.7 + 2 \times 131) = -81.7$ J K^{-1} mol^{-1}= -82 J K^{-1} mol^{-1}

When adding figures, the figure with the smallest number of decimal places determines the precision.

9. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

131 $\frac{1}{2} \times 205$ +70 $S^{\ominus}$/J K^{-1} mol^{-1}

$\Delta S^{\ominus} = (70) - (131 + \frac{1}{2} \times 205) = -163.5$ J K^{-1} mol^{-1} = -164 J K^{-1} mol^{-1}

When adding figures, the figure with the smallest number of decimal places determines the precision.

10. D

$\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ values for the combustion of methane are both negative.

Combustion is an exothermic reaction so $\Delta H^{\ominus}$ is negative.

There is a decrease in the number of moles of gas in the combustion reaction. There will be a decrease in entropy.

11. C

$NH_4Cl(aq)$ has a larger entropy than $NH_4Cl(s)$. A is false – exothermic processes are energetically favourable. B is not true – the bonds in $NH_4Cl(s)$ are stronger than the bonds between the hydrated ions and water, which is why the process is endothermic. D is wrong because the decrease in temperature represents heat loss from the surroundings, which is a decrease in entropy.

12. D

$\Delta G = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$

$= +100 - T(100 \times 10^{-3})\ \text{kJ mol}^{-1}$

At low temperatures

$\Delta G \approx 100\ \text{kJ mol}^{-1}$ and the reaction is non-spontaneous.

At 1000 K

$\Delta G = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$

$= +100 - (1000 \times 100 \times 10^{-3}) = 0\ \text{kJ mol}^{-1}$

So the reaction will be spontaneous at temperature above this.

13. $\Delta G = (-604 + -394) - (-1129) = +131\ \text{kJ mol}^{-1}$

As ΔG is very positive, the reaction is not spontaneous under standard conditions. This accounts for the stability of calcium carbonate in the form of limestone, chalk and marble.

14. **(a)** $\Delta G = \Delta H - T\Delta S$

$$\Delta S = \frac{\Delta H_{\text{reaction}} - \Delta G_{\text{reaction}}}{T}$$

$$= \frac{(-217 - -212) \times 10^3}{298}$$

$$= -16.8\ \text{J K}^{-1}\ \text{mol}^{-1}$$

It is a small entropy change as there no changes in the number of moles of solid, liquid or gas during the reaction.

(b) 212 kJ mol^{-1} of free energy is available to produce electrical energy.

15. B

It is not possible to give absolute enthalpy values, H; so we cannot say that the values are zero. The definitions of enthalpy change of formation and free energy change of formation both refer to the formation of a substance from its elements in their standard states. In both cases, elements in their standard states need no reaction to be formed, so the values for ΔH_f and ΔG_f are zero.

16. A

$\Delta G = \Delta H^{\ominus} - T\,\Delta S^{\ominus}$

At low temperatures

$\Delta G \approx \Delta H^{\ominus}$

Exothermic reactions are spontaneous at low temperatures.

At high temperatures

$\Delta G \approx -T\,\Delta S^{\ominus}$

So the reaction will be non-spontaneous if $\Delta S^{\ominus}$ is negative.

17. D

As before:

At low temperatures: $\Delta G \approx \Delta H^{\ominus}$

Endothermic reactions are not spontaneous at low temperatures.

At high temperatures: $\Delta G \approx -T\,\Delta S^{\ominus}$

So the reaction will be spontaneous if $\Delta S^{\ominus}$ is positive.

18. B

As before:

At low temperatures: $\Delta G \approx \Delta H^{\ominus}$ It is spontaneous

At high temperatures: $\Delta G \approx -T\,\Delta S^{\ominus}$ It is non spontaneous at higher temperatures.

19. C

ΔS is positive. The number of moles of gas increases from reactants to products.

ΔG is negative at the temperature of the reaction.

As the reaction is not spontaneous at low temperatures. ΔH is positive.

20. $\Delta G = \Delta H - T\Delta S$

$\Delta H = +178$ kJ mol^{-1}; $\Delta S = +161$ J K^{-1} mol^{-1}; $T = 2000$ K

$\Delta G = +178 - (2000 \times +161 \times 10^{-3})$

$= -144$ kJ mol^{-1}

21. **(a)** $2C(\text{graphite}) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(l)$

(b) $\Delta S^{\ominus}_{\text{reaction}} = +161 - (2 \times 5.7) - (3 \times 130.6) - (\frac{1}{2} \times 205)$

$= -344.7$ J K^{-1} mol^{-1}

(c) $\Delta G_{\text{reaction}} = -278 - (500 \times -344.7 \times 10^{-3})$

$= -105.65$ kJ mol^{-1}

(d) The reaction is spontaneous as ΔG is negative.

(e) At high temperature: $\Delta G = -T\Delta S$ and so is positive. The reaction will stop being spontaneous at higher temperature.

22. **(a)** $H_2O(s) \rightarrow H_2O(l)$

$\Delta H^\ominus = -286 - (-292)$

$= +6.0 \text{ kJ mol}^{-1}$

(b) If ice is melting, then $\Delta G = 0$

$\Delta G = \Delta H - T\Delta S$; $\Delta H = T\Delta S$

$$T = \frac{\Delta H^\ominus(\text{reaction})}{\Delta S^\ominus(\text{reaction})} = \frac{6000}{22.0} = 273 \text{ K}$$

23. C

The total entropy is a maximum and the Gibbs energy is a minimum.

24. C

For a reaction to be spontaneous, ΔG has to be negative.

At low temperature $\Delta G(\text{system}) \approx \Delta H(\text{system})$, as $T\Delta S \approx 0$ – hence exothermic reactions can occur at low temperatures.

At high temperatures $\Delta G(\text{system}) \approx -T\Delta S(\text{system})$ as the temperature is sufficiently high as to make the term $\Delta H(\text{system})$ negligible.

Hence if $\Delta S(\text{system})$ is positive then $-T\Delta S(\text{system})$ will be a negative value –i.e. the reaction is spontaneous.

It is considered to be a complete reaction if $\Delta G(\text{reaction}) < -30 \text{ kJ mol}^{-1}$.

25. A

At equilibrium the free energy is a minimum, and the entropy at a maximum.

If $\Delta G(\text{reaction}) = 0 \text{ kJ mol}^{-1}$ then an equilibrium constant is 1.

This is the difference in the Gibb's energy between the reactant and products.

26. B

For a reaction to be reversible ΔG generally has to be between –30 and +30 kJ mol^{-1}.
In the equation $\Delta G = \Delta H - T\Delta S$, in order for the reaction to be spontaneous the right-hand side of the equation has to be negative. If ΔH and ΔS are either both negative or both positive, this condition is achieved.

27. D

Equilibrium occurs at the minimum of the Gibb's energy: Z

$\Delta G = G(\text{products}) - G\ (\text{reactants}) = -X$

28. **(a)** 0

if $K = 1$ then $\Delta G = 0$, because $\ln 1 = 0$

(b) negative

If $K > 1$ then ΔG = negative, because ln (positive number) = a positive number, so the right-hand side of the equation is negative overall (R is a constant with a positive value and T (absolute temperature is, by definition, greater than 0).

(c) positive

If $K < 1$ then ΔG = positive, because ln (negative number) = a negative number, so the right-hand side of the equation is positive overall.

29. $\Delta G = \Delta G^{\ominus} + RT\ln Q = 0$

$\Delta G^{\ominus} = -RT\ln K$

$\Delta G = RT\ln Q - RT\ln K = RT\ln\frac{Q}{K}$

At equilibrium $\Delta G = 0$

$\ln\frac{Q}{K} = 0$

$Q = K$

30. When $\Delta G = -30\text{ kJ mol}^{-1}$

$-30\text{ kJ mol}^{-1} = -123 - (T_1 \times -128 \times 10^{-3})\text{ kJ mol}^{-1}$

$93 = (T_1 \times 128 \times 10^{-3})$

$T_1 = 727\text{ K}$

When $\Delta G = +30\text{ kJ mol}^{-1}$

$+30\text{ kJ mol}^{-1} = -123 - (T_2 \times -128 \times 10^{-3})\text{ kJ mol}^{-1}$

$153 = (T_2 \times 128 \times 10^{-3})$

$T_2 = 1195\text{ K}$

31. $\Delta G^{\ominus} = -RT\ln K_c$

$= -(8.31\text{ J K}^{-1}\text{ mol}^{-1}) \times (500\text{ K}) \times \ln 160$

$= -21\text{ kJ mol}^{-1}$

32. (a) $\Delta G^{\ominus} = 0$

(b) $\Delta G^{\ominus} = -RT\ln K_c$

$= -8.31 \times 298 \times \ln(1.7 \times 10^{12})$

$= -70\text{ kJ mol}^{-1}$

Challenge yourself

1 The outcome is identical. Neither reaction is favored so an equilibrium mixture with equal amounts of reactant and product is likely to be produced.

2 The entropy is due to mixing. The entropy of both pure states will be the same.

Consider the simple case of 6 Reactants → 6 Products

S (5 Reactants, 1 Product) = S (1 Reactant, 5 Products)

The entropy increases to a maximum at S (3 Reactants, 3 Products)

3 When $K_c = 1$, $\Delta G^\ominus = 0$

When $K_c > 1$, $\Delta G^\ominus < 0$

When $K_c < 1$, $\Delta G^\ominus < 0$

Possible function: $\Delta G^\ominus_{\text{reaction}} = -A \ln K_c$ where A is constant with units kJ mol^{-1}.

Practice questions

1. C

$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$ is the only reaction that increases the number of gas molecules as it goes from reactants to products.

2. D

A reaction that increases then decreases the number of gas molecules as it goes from reactants to products will lead to a decrease in entropy.

3. B

First, write the chemical equation with the values below:

$C_2H_5OH(l)\ (s) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

$-175 \qquad 3 \times 0 \qquad 2 \times -394 \qquad 3 \times -229 \qquad \Delta G^{\ominus}_{\text{formation}}$ / kJ mol^{-1}

$\Delta G = \Sigma\Delta G^{\ominus}_{\text{formation}}(\text{products}) - \Sigma\Delta G^{\ominus}_{\text{formation}}(\text{reactants})$

$= -175 - (2\times -394\ + 3\times -229)$ kJ mol^{-1}

$= -1300$ kJ mol^{-1}

4. B

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$2(198) \qquad 205 \qquad 2(214) \qquad S^{\ominus}$/ J K^{-1} mol^{-1}

$\Delta S^{\ominus} = 2(214) - (2\times 198 + 205) = -173$ J K^{-1} mol^{-1}

5. B

$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\Delta S^{\ominus}_{\text{reaction}}$

$= +10.00 - (298 \times 10.00 \times 10^{-3})$ kJ mol^{-1} = $+7.02$ kJ mol^{-1}

6. A

$\Delta S^{\ominus}_{\text{surroundings}} = -\Delta H^{\ominus}_{\text{system}} / T$

Condensation is an exothermic process so $\Delta H^{\ominus}_{\text{system}}$ is negative and $\Delta S^{\ominus}_{\text{surroundings}}$ is positive.

$\Delta S^{\ominus}_{\text{system}}$ is negative as there is a decrease in the number of gaseous molecules.

7. B

The free energy is a minimum at equilibrium.

8. B

$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}} - T\,\Delta S^{\ominus}_{\text{reaction}}$

The gradient of the line = $-\Delta S^{\ominus}_{\text{reaction}}$

The gradient is negative so the standard entropy change of the reaction is positive.

$\Delta G_{\text{reaction}} = \Delta H^{\ominus}_{\text{reaction}}$ when $T = 0$ K so the standard enthalpy change of the reaction is positive.

9. **(a)** «$-398.9\ \text{kJ mol}^{-1} - (-306.4\ \text{kJ mol}^{-1}) = -92.5\ \text{kJ mol}^{-1}$» (1)

(b) «$\Delta S = 364.5\ \text{J K}^{-1}\,\text{mol}^{-1} - (311.7\ \text{J K}^{-1}\,\text{mol}^{-1} + 223.0\ \text{J K}^{-1}\,\text{mol}^{-1})$

$= -170.2\ \text{J K}^{-1}\,\text{mol}^{-1}$» (1)

(c) «$\Delta G = -92.5\ \text{kJ mol}^{-1} - (298\ \text{K} \times -0.1702\ \text{kJ mol}^{-1}\,\text{K}^{-1})$

$= -41.8\ \text{kJ mol}^{-1}$» (2)

If –87.6 and –150.5 are used then –42.8

(d) «$\Delta G = -41.8\ \text{kJ mol}^{-1} = -\dfrac{8.31\,\text{J mol}^{-1}\,\text{K}^{-1}}{1000} \times 298\ \text{K} \times \ln K$»

OR

«$\Delta G = -41800\ \text{J mol}^{-1} = -8.31\ \text{J mol}^{-1}\,\text{K}^{-1} \times 298\ \text{K} \times \ln K$»

«$\ln K =$ » 16.9 (1)

«$K = e^{16.9}$ =» 2.14×10^{7} (1)

*Award **(2)** for correct final answer.*

Accept range of 1.80×10^{6}–2.60×10^{7}.

If –43.5 is used then 4.25×10^{7}

10. **(a)** «ΔH =» (−635 «kJ» + –393.5 «kJ») – (−1207 «kJ»)

«ΔH = + » +179 «kJ» (2)

*Award **(1 max)** for −179 kJ.*

(b) «$\Delta S = (40\ \text{J K}^{-1} + 214\ \text{J K}^{-1}) - (93\ \text{J K}^{-1})$ =» +161 «J K^{-1}» (1)

(c) «spontaneous» if $\Delta G = \Delta H - T\Delta S < 0$

OR

$\Delta H < T\Delta S$ (1)

«$T > \dfrac{179\ \text{kJ}}{0.161\ \text{kJ K}^{-1}}$ » 1112 «K» (2)

Accept 1056 K if both of the incorrect values are used to solve the problem.

*Do **not** award M2 for any negative T value.* (1)

Reactivity 2.1

Exercises

1. For each of these questions **(a)** to **(e)**:

- write the information from the question in the form of an equation
- check the number of atoms on each side of the equation
- introduce coefficients in front of the formulae in order to ensure that there are equal numbers of atoms on each side of the equation.

(a) $CuCO_3 \rightarrow CuO + CO_2$

(b) $2Mg + O_2 \rightarrow 2MgO$

(c) $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

(d) $N_2 + 3H_2 \rightarrow 2NH_3$

(e) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

2. For each of these questions **(a)** to **(e)**:

- introduce coefficients in front of each formula to ensure that there are equal numbers of atoms on each side of the equation.

(a) $2K + 2H_2O \rightarrow 2KOH + H_2$

(b) $C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

(c) $Cl_2 + 2KI \rightarrow 2KCl + I_2$

(d) $4CrO_3 \rightarrow 2Cr_2O_3 + 3O_2$

(e) $Fe_2O_3 + 3C \rightarrow 3CO + 2Fe$

3. For each of these questions **(a)** to **(e)**:

- introduce coefficients in front of each formula to ensure that there are equal numbers of atoms on each side of the equation.

(a) $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

(b) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

(c) $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

(d) $6H_2O_2 + 2N_2H_4 \rightarrow 2N_2 + 10H_2O + O_2$

(e) $4C_2H_7N + 15O_2 \rightarrow 8CO_2 + 14H_2O + 2N_2$

4. **(a)** From the stoichiometric equation 2 moles of iron can be made from 1 mole of iron oxide. Hence 2 × 1.25 mol = 2.50 mol of iron can be made from 1.25 mol of iron oxide.

   (b) From the stoichiometric equation 2 moles of iron need 3 moles of hydrogen.

   Hence 3.75 mol of iron need $\frac{3}{2}$ × 3.75 mol = 5.63 mol of hydrogen.

   (c) From the stoichiometric equation 3 moles of water are produced from 1 mole of iron oxide.

   Hence 12.50 moles of water are produced from:

   $\frac{1}{3}$ × 12.50 mol = 4.167 moles of iron oxide.

   4.167 moles of iron oxide have a mass of:

   $4.167 \times M_r(\text{Fe}_2\text{O}_3) = 4.167\text{ mol} \times 159.70\text{ g mol}^{-1} = 665.46\text{ g } (= 666\text{ g})$

5. **(a)** Write the chemical equation:

   $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

   Then balance the equation by deducing the appropriate numbers in front of the formulae:

   $2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O$

   (b) From the equation 2 moles of butane produce 10 moles of water.

   $\frac{2.46\text{g}}{18.02\text{g mol}^{-1}} = 0.137$ moles of water were produced.

   0.137 moles of water must have been made from:

   $\frac{2}{10}$ × 0.137 = 0.0274 moles of butane.

   0.0274 moles of butane has a mass of:

   $0.0274 \times M_r(C_4H_{10}) = 0.0274\text{ mol} \times 58.14\text{ g mol}^{-1} = 1.59\text{ g}$

6. From the equation, 1 mole of Al reacts with 1 mole of NH_4ClO_4

   26.98 g of Al react with 14.01 + (4 × 1.01) + 35.45 + (4 × 16.00) = 117.50 g of NH_4ClO_4

   Therefore 1000 g of Al react with $\frac{117.50}{26.98}$ × 1000 = 4355 g = 4.355 kg of NH_4ClO_4

7. **(a)** $CaCO_3 \rightarrow CaO + CO_2$

   (b) 0.657 g of $CO_2 = \frac{n}{M} = \frac{0.657\text{g}}{44.01\text{g mol}^{-1}} = 0.0149$ moles of CO_2

   This was produced from 0.0149 moles of $CaCO_3$.

   0.0149 moles of $CaCO_3$ has a mass of:

   $0.0149 \times M_r(CaCO_3) = 0.0149\text{ mol} \times 100.09\text{ g mol}^{-1} = 1.49\text{ g}$

   Therefore % of $CaCO_3$ in the impure limestone = $\frac{1.49\text{g}}{1.605\text{g}}$ × 100 = 92.8%

(c) Assumptions are:

- $CaCO_3$ is the only source of carbon dioxide
- all the $CaCO_3$ undergoes complete decomposition
- all CO_2 released is captured
- heating does not cause any change in mass of any of the other minerals present.

8. (a) 1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 54.5 dm^3 is equivalent to $\frac{54.5}{22.7}$ mol = 2.40 mol

(b) 1 mole of gas has a volume of 22.7 dm^3 at STP.

This is equivalent to 22.7 × 1000 cm^3 = 227 000 cm^3

Therefore 250.0 cm^3 of gas contains $\frac{250.0}{227000}$ mol = 1.101×10^{-3} mol (= 0.01101 mol)

(c) 1 mole of gas has a volume of 22.7 dm^3 at STP.

This is equivalent to 0.0227 m^3

1.0 m^3 of gas therefore contains $\frac{1}{0.0227}$ mol = 44 mol

9. (a) 44.00 g of N_2 is equivalent to $\frac{44.00\text{g}}{(2\times 14.01)\text{g mol}^{-1}}$ of N_2 gas = 1.57 mol

1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 1.57 mol has a volume of 35.6 dm^3

(b) 1 mole of gas has a volume of 22.7 dm^3 at STP.

Therefore 0.25 mol of ammonia has a volume of 5.7 dm^3

10. moles HgO = $\frac{12.45\text{g}}{(200.59+16.00)\text{g mol}^{-1}}$ = 0.05748 mol

On decomposition this would produce 0.02874 mol of oxygen (since 2 mol of HgO produces 1 mol of O_2). 1 mol of gas has a volume of 22.7 dm^3 at STP.

Therefore 0.02874 mol has a volume of –0.6524 dm^3

11. Assume all measurements are made at STP.

3.14 dm^3 of bromine is equivalent to $\frac{3.14\text{dm}^3}{22.7\text{ dm}^3\text{mol}^{-1}}$ = 0.138 mol Br_2

11.07 g of chlorine is equivalent to $\frac{11.07\text{g}}{(2\times 35.45)\text{g mol}^{-1}}$ = 0.1561 mol Cl_2

Therefore, the sample of chlorine contains more molecules.

12. 0.200 g calcium is $\frac{0.200\text{g}}{40.08\text{g mol}^{-1}}$ = 4.99×10^{-3} mol

4.99×10^{-3} mol of Ca will make 4.99×10^{-3} mol of hydrogen

4.99×10^{-3} mol of hydrogen will occupy 4.99×10^{-3} mol × 22.7 $\text{dm}^3\ \text{mol}^{-1}$ = 0.113 dm^3 (or 113 cm^3) at STP.

13. The first step, as usual, is to calculate how many moles of reactant we have.

1.0 g of ammonium nitrate is $\frac{1.0\text{g}}{80.06\text{g mol}^{-1}}$ = 0.012 mol

According to the balanced chemical equation,

0.012 mol of ammonium nitrate will produce 0.012 mol of dinitrogen oxide.

At STP, 1 mole of gas occupies 22.7 dm^3,

so 0.012 mol will occupy 22.7 $\text{dm}^3\ \text{mol}^{-1}$ × 0.012 mol = 0.28 dm^3

14. $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$ moles of NaOH = cV

$$= 0.147\ \text{mol dm}^{-3} \times \frac{36.42}{1000}\ \text{dm}^3 = 5.35 \times 10^{-3}\ \text{mol}$$

As this reacts with the sulfuric acid in a 2 : 1 ratio,

the number of moles of sulfuric acid present = 2.68×10^{-3} mol

Hence concentration of sulfuric acid = $\frac{n}{V} = \frac{2.68 \times 10^{3}\text{mol}}{\left(\frac{15.00}{1000}\right)\text{dm}^3}$ = 0.178 mol dm^{-3}

15. moles of KOH used in titration = cV = 0.0100

mol dm^{-3} × $\frac{11.00}{1000}$ dm^3 = 1.10×10^{-4} mol

Since KOH reacts with HCl in a 1:1 ratio, moles of HCl = 1.10×10^{-4} mol

Concentration of HCl = $\frac{n}{V} = \frac{1.10 \times 10^{-4}\text{mol}}{\left(\frac{5.00}{1000}\right)\text{dm}^3}$ = 0.0220 mol dm^{-3}

Molar mass of HCl = (1.01 + 35.45) g mol^{-1} = 36.46 g mol^{-1}

Quantity of HCl is equivalent to 36.46 × 0.0220 = 0.802 g dissolved in 1 dm^3

Concentration of HCl in g dm^{-3} = 0.0220 mol dm^{-3} × 36.46 g mol^{-1} = 0.802 g dm^{-3}

Therefore in 1.00 cm^3 there would be 0.000802 g of HCl

Assuming a density of 1.00 g cm^{-3} a 1.00 cm^3 sample of solution has a mass of 1.00 g

$$\%HCl = \frac{\text{mass HCl}}{\text{mass solution}} \times 100$$

$$= \frac{0.000802\text{g}}{1.00\text{g}} \times 100$$

$$= 0.0802\%$$

16. $Na_2SO_4(aq) + Pb(NO_3)_2(aq) \rightarrow PbSO_4(s) + 2NaNO_3(aq)$

First determine the moles of $PbSO_4$ formed in the reaction:

$$n(PbSO_4) = m/M(PbSO_4) = \frac{1.13g}{303.25\text{g mol}^{-1}} = 3.73 \times 10^{-3}\text{ mol}$$

From the balanced equation: $n(PbSO_4)$ formed = $n(Pb(NO_3)_2)$ reacted

= $n(Na_2SO_4)$ reacted

= 3.73×10^{-3} mol

$$[Pb(NO_3)_2] = \frac{n}{V} = \frac{3.73 \times 10^{-2}\text{mol}}{\frac{32.50}{1000}\text{dm}^3} = 0.115\text{mol dm}^{-3}$$

$$[Na_2SO_4] = \frac{n}{V} = \frac{3.73 \times 10^{-3}\text{mol}}{\frac{35.30}{1000}\text{dm}^3} = 0.106\text{mol dm}^{-3}$$

Two assumptions are:

(a) No side reactions occur that generate other products.

(b) All of the $PbSO_4$ formed precipitates out as a solid and can be weighed.

17. C

In the balanced equation, the reacting mole ratio of Mg to HCl = $\frac{1}{2}$ = 0.5.

The reactant mole ratio given = $\frac{0.40}{0.20}$ = 2.0. As the reactant mole ratio given is larger than the ratio in the balanced equation, we must have too much (excess) Mg and so HCl will be the limiting reactant.

Using the 2HCl : $1H_2$ ratio in the balanced equation and the moles of the limiting reactant (HCl), the theoretical yield of hydrogen will be: $n(H_2) = \frac{1}{2}n(HCl) = \frac{1}{2} \times 0.20\,mol$ = 0.10 mol.

18. B

In the balanced equation, the reacting mole ratio of HCl to $CaCO_3 = \frac{2}{1} = 2$

The reacting mole ratio given = HCl to $CaCO_3 = \frac{0.30}{0.30} = 1.0$.

As the reactant mole ratio given is smaller than the ratio in the balanced equation, we must have too much (excess) $CaCO_3$ and so HCl will be the limiting reactant.

Using the 2HCl : $1CO_2$ ratio in the balanced equation and the moles of the limiting reactant (HCl), the theoretical yield of carbon dioxide will be:

$n(CO_2) = \frac{1}{2} \times n(HCl) = \frac{1}{2} \times 0.30\,\text{mol} = 0.15\,\text{mol}$.

19. In questions involving the volume of gases under the same conditions, remember that the volume is proportional to the number of moles.

(a) When amounts of both reactants are given, first work out the limiting reactant. In the balanced equation, the reacting mole ratio of N_2 to $H_2 = \frac{1}{3} = 0.33$

The reactant mole ratio given (the same as the volumes of the gases)

$$= N_2 \text{ to } H_2 = \frac{5}{20} = 0.25.$$

As the reactant mole ratio given is smaller than the ratio in the balanced equation, we must have too much (excess) H_2 and so N_2 will be the limiting reactant.

Using the $1N_2 : 2NH_3$ ratio in the balanced equation and the moles of the limiting reactant (N_2), the expected yield of ammonia will be:

$V(NH_3) = 2V(N_2) = 2 \times 5 = 10\text{ cm}^3$.

(b) N_2 reacts with H_2 in a 1 : 3 ratio so 5 cm^3 of N_2 (the limiting reactant) will react with 15 cm^3 H_2. The volume of H_2 remaining = 20 cm^3 – 15 cm^3 = 5 cm^3

20. **(a)** moles of $H_2 = \frac{12.0\text{g}}{2.02\text{g mol}^{-1}} = 5.94$ mol

moles of CO = $\frac{74.5\text{g}}{28.01\text{g mol}^{-1}} = 2.66$ mol

As the CO reacts with H_2 in a 1 : 2 ratio, this means that the H_2 is in excess

(2 × 2.66 mol = 5.32 mol).

2.66 mol of CO therefore produce 2.66 mol of CH_3OH.

This has a mass of 2.66 × *Mr*(CH3OH) = 2.66 mol × 32.05 g mol^{-1} = 85.3 g

(b) moles of H_2 in excess = 5.94 mol – (2 × 2.66) mol = 0.62 mol

This is equivalent to a mass of 0.62 mol × mol^{-1} = 1.3 g

21. moles of C_2H_4 = $\dfrac{15.4\text{g}}{(2\times 12.01)+(4\times 1.01)\text{g mol}^{-1}}$ = 0.5488 mol

moles of Cl_2 = $\dfrac{3.74\text{g}}{(2\times 35.45)\text{g mol}^{-1}}$ = 0.0528 mol

As the reactants react in the ratio of 1 : 1, C_2H_4 is in excess.

moles of product formed = 0.0528 mol

mass of product formed = 0.0528 × $M_r(C_2H_4Cl_2)$

= 0.0528 mol × 98.96 g mol^{-1} = 5.23 g

22. moles of $CaCO_3$ = $\dfrac{255\text{g}}{(40.08+12.01+(4\times 16.00))\text{g mol}^{-1}}$ = 2.55 mol

moles of SO_2 = $\dfrac{135\text{g}}{(32.07+(2\times 16.00))\text{g mol}^{-1}}$ = 2.11 mol

Therefore as they react in a 1 : 1 ratio, the

number of moles of $CaSO_3$ produced = 2.11 mol

mass of $CaSO_3$ = 2.11 mol × (40.08 + 32.07 +(3 × 16.00)) g mol^{-1} = 254 g

Therefore percentage yield = $\dfrac{198\text{g}}{254\text{g mol}^{-1}}$ × 100 = 78%

23. moles of CH_3COOH used = $\dfrac{3.58\text{g}}{((2\times 12.01)+(4\times 1.01)+(2\times 16.00))\text{g mol}^{-1}}$ = 0.0596 mol

moles of $C_5H_{11}OH$ = $\dfrac{4.75\text{g}}{((5\times 12.01)+(12\times 1.01)+16.00)\text{g mol}^{-1}}$ = 0.0539 mol

Therefore $C_5H_{11}OH$ is the limiting reagent, so 0.0539 mol of $CH_3COOC_5H_{11}$ is the maximum that can form.

This will have a mass of 0.0539 × [(7 × 12.01) +(14 × 1.01) + (2 × 16.00)] g mol^{-1} = 7.01 g

This is the 100% yield, therefore 45% yield has a mass of 0.45 × 7.01 g = 3.16 g

24. 100 g of C_6H_5Cl is equivalent to

$\dfrac{100\text{ g}}{((6\times 12.01)\ +\ (5\times 1.01)\ +\ 35.45)\text{g mol}^{-1}}$ = 0.888 mol

If this is 65% yield then 100% yield would be

0.888 mol × $\dfrac{100}{65}$ = 1.37 mol

1.37 moles of benzene has a mass of

1.37 mol × [(6 × 12.01) + (6 × 1.01)] g mol^{-1} =107 g

25. For questions involving atom economy, we can use this formula found in section 1 of the data booklet: % atom economy= $\frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$

M(desired product) = 63.55 + 32.07 + 4(16.00) = 159.62 g mol^{-1}

M(all reactants) = 63.55 + 12.01 + 3(16.00) + 2(1.01) + 32.07 + 4(16.00) = 221.65 g mol^{-1}

Using the formula, atom economy $= \frac{159.62 \text{ g mol}^{-1}}{221.65 \text{ g mol}^{-1}} \times 100 = 72.0\ \%$

26. M(desired product) = 2(12.01) + 3(1.01) + 35.45 = 62.50 g mol^{-1}

M(all reactants) = 2(12.01) + 4(1.01) + 2(35.45) = 98.96 g mol^{-1}

Using the formula from exercise 25, atom economy $= \frac{62.50 \text{g mol}^{-1}}{98.96 \text{g mol}^{-1}} \times 100 = 63.2\ \%$

27. In method 2, the desired product (HCl) is the *only* product so it will have an atom economy of 100 % which will be greater than method 1 (which has an undesired product so must have a % atom economy of less than 100 %). Note that if the two different methods both contained undesirable products, then we would need to calculate the atom economy in order to compare them.

Challenge yourself

1 Write balanced equations for the combustion reactions of ammonia and hydrazine:

$$2NH_3(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + 3H_2O(g)$$

$$N_2H_4(g) + O_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

As we do not know the relative moles of ammonia and hydrazine:

let x = moles of ammonia, NH_3, in the reaction mixture

let y = moles of hydrazine, N_2H_4, in the reaction mixture

Determine equations for the total moles of $N_2(g)$ and $H_2O(g)$ formed in the two reactions using x and y:

$n(N_2) = 0.5x + y$

$n(H_2O) = 1.5x + 2y$

The question tells us that $n(N_2) = 0.40 \text{ x } n(H_2O)$:

$0.5x + y = 0.40(1.5x + 2y)$

$0.5x + y = 0.60x + 0.80y$

$0.2y = 0.1x$

$y = 0.5x$

If $y = 0.5x$ this means that the mixture contains half as much hydrazine, N_2H_4, as it does ammonia, NH_3.

Consider a mixture with exactly 1 mol of NH_3 and 0.5 mol of N_2H_4:

$m(NH_3) = nM(NH_3) = 1 \text{ mol} \times 17.04 \text{ g mol}^{-1} = 17.04 \text{ g}$

$m(N_2H_4) = nM(N_2H_4) = 0.5 \text{ mol} \times 32.06 \text{ g mol}^{-1} = 16.03 \text{ g}$

$$\%NH_3 = \frac{\text{mass } NH_3}{\text{total mass of mixture}} \times 100\%$$

$$= \frac{17.04\text{g}}{17.04\text{g} + 16.03\text{g}} \times 100\% = 52\% \text{ to 2 d.p.}$$

Two assumptions are:

(a) No side reactions occur that generate other products.

(b) The gases behave as ideal gases therefore volumetric ratios are identical to molar ratios.

2 Many reactions with 'useless' by-products could have a high stoichiometric yield under optimum conditions, but low atom economy, for example the production of methanoic acid from the reaction of sodium methanoate and sulfuric acid:

$2NaCOOH + H_2SO_4 \rightarrow 2HCOOH + Na_2SO_4$

For 100% conversion with stoichiometric reactants, the yield = 100%.

$$\%\ \text{atom economy} = \frac{\text{mass of desired product}}{\text{total mass of reactants}} \times 100\%$$

$$= \frac{2 \times M(\text{HCOOH})}{2 \times M(\text{NaHCOO}) + M(H_2\text{SO}_4)} \times 100\%$$

$$= \frac{2 \times 46.03}{(2 \times 68.01) + 98.08} \times 100\%$$

$$= 39.33\%$$

3 First write the balanced equations for the two steps of the process, recognizing that in the first step it is the $Ca_3(PO_4)_2$ in the phosphate rock that reacts with H_2SO_4.

1 $Ca_3(PO_4)_2(s) + 3H_2SO_4(aq) \rightarrow 3CaSO_4(s) + 2H_3PO_4(aq)$

2 $H_3PO_4(aq) + 3NH_3(l) \rightarrow (NH_4)_3PO_4(s)$

Determine theoretical mass of $(NH_4)_3PO_4$ (s) given that 1000 tonnes represents a 95% yield:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

$$\text{theoretical yield} = \frac{\text{experimental yield}}{\text{percentage yield}} \times 100\%$$

$$= \frac{1000\ \text{tonnes}}{95\%} \times 100\%$$

$$= 1053\ \text{tonnes}$$

Determine the number of moles in 1053 tonnes of $(NH_4)_3PO_4(s)$ recognizing that the mass that is given in tonnes must first be converted to grams: $n((NH_4)_3PO_4) = \frac{m}{M((NH_4)_3PO_4)}$

$$= \frac{1053 \times 10^6 g}{149.12\text{g mol}^{-1}} = 7.061 \times 10^6\ \text{mol}$$

From equation 2, $n((NH_4)_3PO_4) = n(H_3PO_4) = 7.061 \times 10^6$ mol

From equation 1, $n(Ca_3(PO_4)_2) = \frac{n(H_3PO_4)}{2} = \frac{7.061 \times 10^6\text{mol}}{2} = 3.531 \times 10^6$ mol

Calculate the mass of $Ca_3(PO_4)_2(s)$:

$$m(Ca_3(P\ O_4)_2) = nM(Ca_3(PO_4)_2) = (3.531 \times 10^6\ mol) \times 310.18\ g\ mol^{-1}$$

$$= 1.095 \times 10^9\ g$$

$$= 1095\ tonnes$$

Determine the total mass of phosphate rock based on 90% of phosphate rock being $Ca_3(PO_4)_2$:

$$\%Ca_3(PO_4)_2 = \frac{mass\ Ca_3(PO_4)_2}{mass\ phosphate\ rock} \times 100\% = 90\%$$

$$\text{Mass of phosphate rock} = \frac{mass\ Ca_3(PO_4)_2}{\%\ Ca_3(PO_4)_2} \times 100\% = \frac{1095\ tonnes}{90\%} \times 100\% = 1217\ tonnes$$

4 First we need to determine the moles of H_2SO_4 present in 980 tonnes of $H_2SO_4(l)$:

$$n(H_2SO_4) = \frac{m}{M(H_2SO_4)} = \frac{980 \times 10^6 g}{98.08 g\ mol^{-1}}\ n(H2SO4) = 9.99 \times 10^6\ mol$$

From equation 3, $n(SO3) = n(H2SO4) = 9.99 \times 10^6$ mol

From equation 2, $n(SO2) = n(SO3) = 9.99 \times 10^6$ mol

From equation 1, $n(S) = n(SO2) = 9.99 \times 10^6$ mol

We can now calculate the mass of sulfur required:

$$m(S) = nM = 9.99 \times 10^6\ mol \times 32.06\ g\ mol^{-1}$$

$$= 3.20 \times 10^8\ g = 3.20 \times 10^5\ kg$$

5 $n(KMnO_4) = cV = 0.0500\ mol\ dm^{-3} \times \frac{18.00}{1000}\ dm^3 = 9.00 \times 10^{-4}\ mol$

From the balanced equation, $n(H_2O_2) = \frac{5}{2} n(KMnO_4) = \frac{5}{2} \times 9.00 \times 10^{-4}\ mol = 2.25 \times 10^{-3}\ mol$

Determine the concentration of the H_2O_2 solution:

$$[H_2O_2] = \frac{n}{V} = \frac{2.25 \times 10^{-3} mol}{\frac{10.00}{1000}}\ dm^3 = 0.225\ mol\ dm^{-3}$$

6 For the reaction with Na_2CO_3:

From Step 1 we can determine an equation for the moles of HCl(aq) reacting with the Na_2CO_3 initially present in the solution:

$$n(HCl) = c(HCl) \times V(HCl) = Y\ mol\ dm^{-3} \times \frac{P}{1000}\ dm_3 = \frac{YP}{1000}\ mol$$

Balanced equation 1 tells us that $n(Na_2CO_3) = n(HCl) = \frac{YP}{1000}$ mol.

We can then determine an equation for the concentration of the Na_2CO_3 initially present:

$$[Na_2CO_3] = \frac{n}{V} = \frac{\frac{YP}{1000}\text{mol}}{\frac{X}{1000}\text{dm}^{-3}} = \frac{YP}{X}\text{mol dm}^{-3} = \left(\frac{PY}{X}\text{mol dm}^{-3}\right)$$

For the reaction with $NaHCO_3$: In Step 2 the HCl being added reacts with the $NaHCO_3$ initially present *and* the $NaHCO_3$ formed in Step 1.

The amount of $NaHCO_3$ formed in Step 1 will be equal to the amount of Na_2CO_3 initially present and it will also react with P cm_3 of HCl. Therefore, the $NaHCO_3$ that was initially present reacts with (Q – P) cm_3 of HCl.

$$n(\text{HCl}) = c(\text{HCl}) \times V(\text{HCl}) = \text{Y mol dm}^{-3} \times \frac{(Q-P)}{1000}\text{dm}^3 = \frac{Y(Q-P)}{1000}\text{mol}$$

Balanced equation 2 tells us that $n(NaHCO_3) = n(\text{HCl}) = \frac{Y(Q-P)}{1000}\text{mol}$

We can then determine an equation for the concentration of the $NaHCO_3$ initially present:

$$[NaHCO_3] = \frac{n}{V} = \frac{\frac{Y(Q-P)}{1000}\text{mol}}{\frac{X}{1000}\text{dm}^{-3}} = \frac{Y(Q-P)}{X}\text{mol dm}^{-3}$$

In the initial solution $[Na_2CO_3] = \frac{YP}{X}\text{mol dm}^{-3}$

and $[NaHCO_3] = \frac{Y(Q-P)}{X}\text{mol dm}^{-3} = \left(\frac{(Q-P)Y}{X}\text{mol dm}^{-3}\right)$

7 The balanced equation for the combustion of pentane under the reaction conditions stated is:

$C_5H_{12}(l) + 8O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$

Moles of pentane combusted: $n = \frac{m}{M(C_5H_{12})} = \frac{720\text{g}}{72.17\text{g mol}^{-1}} = 9.98\text{ mol}$

From the balanced equation:

$n(CO_2) = 5 \times n(C_5H_{12}) = 5 \times 9.98\text{ mol} = 49.9\text{ mol}$

$n(H_2O) = 6 \times n(C_5H_{12}) = 6 \times 9.98\text{ mol} = 59.9\text{ mol}$

Moles of gas formed in the reaction = (49.9 +59.9) mol = 109.8 mol

Calculate the total moles of gas present after reaction using the ideal gas equation

$PV = nRT$.

$$n(\text{gas}) = \frac{PV}{RT} = \frac{400 \times 10^3\text{Pa} \times 2.00\text{ m}^3}{8.31\text{ J K}^{-1}\text{mol}^{-1} \times 740\text{ K}} = 130\text{ mol}$$

Determine the amount of unreacted O_2 present after combustion:

n(unreacted O_2) = total moles of gas − moles of unreacted O_2

= 130 mol − 109.8 mol = 20 mol

Determine the amount of O_2 that reacted with the pentane using the balanced equation:

n(reacted O_2) = 8 × n(C_5H_{12}) = 8 × 9.98 mol = 79.8 mol

The amount of O_2 initially present is the sum of the amount that reacted and the unreacted excess:

n(initial O_2) = 20 mol + 79.8 mol = 100 mol

Calculate the mass of O_2 that was initially present:

m(initial O_2) = nM(O_2) = 100 mol × 32.00 g mol^{-1} = 3200 g = 3.20 kg

Practice questions

1. D

There are 4 oxygen atoms in the $\mathrm{CuS}\mathbf{O_4}$ component of this formula and 5 oxygen atoms in the **5** $\mathrm{H_2}\mathbf{O}$ molecules. Total = 4 + 5 = 9 oxygen atoms.

2. D

The balanced equation is $\underline{\mathbf{1}}\mathrm{Fe_2O_3} + \underline{\mathbf{3}}\mathrm{CO} \rightarrow \underline{\mathbf{2}}\mathrm{Fe} + \underline{\mathbf{3}}\mathrm{CO_2}$. Sum of coefficients = 1 + 3 + 2 +3 = 9. It is important to note that although a coefficient of 1 is usually not written in a balanced equation, it is technically still there are should be included when summing.

3. B

First, we will need to write a balanced equation for this reaction (see Reactivity 3.1.7 for neutralization reactions): $\mathrm{2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O}$.

The reacting mole ratio in the balanced equation of $\mathrm{NaOH/H_2SO_4} = \frac{2}{1} = 2$. So a mixture in which NaOH is the limiting reactant must have a reactant mole ratio of less than 2.

Answer **A**: $\frac{0.10}{0.05} = 2$

Answer **B**: $\frac{0.05}{0.05} = 1$

Answer **C**: $\frac{0.20}{0.05} = 4$

Answer **D**: $\frac{0.20}{0.10} = 2$

4. C

The ratio of $\mathrm{H_2S}$: NaOH in the equation is 1 : 2

so: $n(\mathrm{NaOH}) = 2n(\mathrm{H_2S}) = 2 \times 0.050 = 0.100$ mol.

To find the volume of NaOH(aq), rearrange the formula

$$n = c\,V \text{ to give } V = \frac{n}{c} = \frac{0.100\,\mathrm{mol}}{0.40\,\mathrm{mol\ dm^{3}}} = 0.25\,\mathrm{dm^3} = 250\,\mathrm{cm^3}$$

5. C

First, we will need to calculate the moles of each reactant from the data provided:

$$n(\mathrm{CaCO_3}) = \frac{m}{M} = \frac{1.00\,\mathrm{g}}{100.00\,\mathrm{g\ mol^{-1}}} = 0.0100\,\mathrm{mol}$$

$$n(\mathrm{HCl}) = cV = 2.00\,\mathrm{mol\,dm^{-3}} \times 0.0200\,\mathrm{dm^3} = 0.0400\,\mathrm{mol}$$

The reacting mole ratio in the balanced equation of $CaCO_3$ to HCl = $\frac{1}{2}$ = 0.5 and the reactant mole ratio given = $\frac{0.01}{0.04}$ = 0.25 so the $CaCO_3$ is the limiting reactant.

$CaCO_3$ and CO_2 are in a 1 : 1 ratio in the balanced equation so reacting $\frac{1.00}{100.00}$ mol $CaCO_3$, we will produce $\frac{1.00}{100.00}$ mol CO_2.

Multiplying this by 22.7 $dm^3\ mol^{-1}$ will give the volume (assuming STP)

so $V(CO_2) = \frac{1.00}{100.00} \times 22.7$

6. D

O_2 is the limiting reactant as 40 cm^3 H_2 would require 20 cm^3 O_2.

Using the $1O_2 : 2H_2O$ ratio of in the balanced equation and the moles of the limiting reactant (O_2), the volume of water produced will be:

$V(H_2O) = 2V(O_2) = 2 \times 10 = 20\ cm^3$.

7. D

From the balanced equation provided in the question:

$n(H_2)$ produced $= \frac{3}{2} n(Al)$ reacted

If 3 mol of Al reacts, the amount of H_2 produced $= \frac{3}{2} \times 3$ mol = 4.5 mol.

$m(H_2) = nM(H_2) = 4.5\ mol \times 2\ g\ mol^{-1} = 9.0\ g$

8. D

To calculate the percentage yield we use the formula

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

From the data provided, the experimental yield of ethanol = $\frac{m}{M} = \frac{6\,g}{46\,g\ mol^{-1}}$ mol.

As C_2H_4 and C_2H_5OH are in a 1 : 1 ratio in the balanced equation, the theoretical yield of ethanol, $n(C_2H_5OH) = n(C_2H_4) = \frac{m}{M} = \frac{7\,g}{28\,g\ mol^{-1}}$ mol.

Placing these in the formula: Percentage yield $= \frac{\frac{6}{46}}{\frac{7}{28}} \times 100 = \frac{6 \times 28 \times 100}{46 \times 7}$ %

9. D

The balanced equation is $2C_2H_2 + 5O_2(g) \rightarrow 4CO_2(g) + 2H_2O$.

Sum of coefficients = 2 + 5 + 4 + 2 = 13

10. A

O_2 is the limiting reactant as 10.0 mol of C_2H_3Cl would require 25.0 mol of O_2.

From the balanced equation, $n(H_2O) = \frac{2}{5} n(O_2)$.

If 10.0 mol of O_2 reacts the amount of H_2O produced = $\frac{2}{5} \times 10.0$ mol = 4.00 mol.

11. **(a)** First use the data provided and the molar volume at STP (22.7 $dm^3\ mol^{-1}$) to find the moles of nitrogen: $n(N_2) = \frac{80.0\,dm^3}{22.7\,dm^3\,mol^{-1}} = 3.52$ mol. (1)

Then use the molar ratio in the equation to find the moles of sodium azide:

$n(NaN_3) = \frac{2}{3} n(N_2) = \frac{2}{3} \times 3.52\text{ mol} = 2.35\text{ mol}$. (1)

Then convert from moles to mass:

$m(NaN_3) = nM = 2.35\text{ mol} \times (22.99\text{ g mol}^{-1} + 3(14.01\text{ g mol}^{-1})) = 153\text{ g}$ (1)

(b) As Na and NaN_3 are in a 1 : 1 ratio: $n(Na) = n(NaN_3) = 2.35$ mol. (1)

Converting from moles to mass: $m(Na) = nM = 2.35\text{ mol} \times 22.99\text{ g mol}^{-1} = 54.0\text{ g}$ (1)

12 The reacting mole ratio in the balanced equation of NH_3 to NO = $\frac{4}{6} = 0.66$

Using the volumes of each gas we can determine the reactant mole ratio given = $\frac{30.0}{30.0} = 1$

so NH_3 is in excess and NO is the limiting reactant.

Using the $4NH_3 : 6NO$ ratio in the equation:

$V(NH_3\text{ reacted}) = \frac{4}{6} V(NO) = \frac{4}{6} \times 30.0\,dm^3 = 20.0\,dm^3$.

So $V(NH_3\text{ in excess}) = 30.0\,dm^3 - 20.0\,dm^3 = 10.0\,dm^3$ (1)

Using the ratio of $6NO : 5N_2$ in the balanced equation,

$V(N_2) = \frac{5}{6} V(NO) = \frac{5}{6} \times 30.0\,dm^3 = 25.0\,dm^3$ (1)

13. **(a)** $n(\text{HCl}) = c \times V = 0.200 \text{ mol dm}^{-3} \times \frac{27.20}{1000} \text{ dm}^3 = 0.00544 \text{ mol}$ (1)

(b) We need to write the balanced equation for the neutralization of HCl(aq) with NaOH(aq):

$\text{HCl(aq)} + \text{NaOH(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O(l)}$

From the balanced equation, $n(\text{HCl}) = n(\text{NaOH})$:

$n(\text{NaOH}) = cV = 0.100 \text{ mol dm}^{-3} \times \frac{23.80}{1000} \text{ dm}^3 = 0.00238 \text{ mol}$

$n(\text{HCl})$ in excess = 0.00238 mol (1)

(c) The amount of HCl that reacted with the calcium carbonate in the eggshell is found from the difference between the original HCl added and the excess HCl that then reacted with the NaOH:

$n(\text{HCl reacted}) = 0.00544 \text{ mol} - 0.00238 \text{ mol} = 0.00306 \text{ mol}$ (1)

(d) $2\text{HCl(aq)} + \text{CaCO}_3\text{(s)} \rightarrow \text{CaCl}_2\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$

An acceptable alternative that omits spectator ions is:

$2\text{H}^+\text{(aq)} + \text{CaCO}_3\text{(s)} \rightarrow \text{Ca}^{2+}\text{(aq)} + \text{H}_2\text{O(l)} + \text{CO}_2\text{(g)}$ (2)

(e) From the balanced equation in **j** the amount of CaCO_3 can be determined based on the amount of HCl that reacts:

$n(\text{CaCO}_3) = \frac{1}{2} n(\text{HCl reacted}) = \frac{1}{2} \times 0.00306 \text{ mol} = 0.00153 \text{ mol}$ (2)

(f) $m(\text{CaCO}_3) = nM(\text{CaCO}_3) = 0.00153 \text{ mol} \times 100.09 \text{ g mol}^{-1} = 0.153 \text{ g}$

$\% \text{ CaCO3 in eggshell} = \frac{\text{mass of CaCO}_3}{\text{mass of eggshell}} \times 100\% = \frac{0.153\text{g}}{0.188\text{g}} \times 100\% = 81.4\%$ (3)

(g) The main assumption is that CaCO_3 is the only component of the eggshell that reacts with HCl, i.e. there are no basic impurities present in the eggshell that would also react with HCl.

14 **(a)** For questions involving atom economy, we can use this formula found in section 1 of the data booklet: $\% \text{ atom economy} = \frac{\text{molar mass of desired product}}{\text{molar mass of all reactants}} \times 100$

$M(\text{desired product}) = 3(12.01 \text{ g mol}^{-1}) + 6(1.01 \text{ g mol}^{-1}) + 6(14.01 \text{ g mol}^{-1})$
$= 126.15 \text{ g mol}^{-1}$.

$M(\text{all reactants}) = 24(1.01 \text{ g mol}^{-1}) + 12(14.01 \text{ g mol}^{-1}) + 6(12.01 \text{ g mol}^{-1}) + 6(16.00 \text{ g mol}^{-1})$
$= 360.42 \text{ g mol}^{-1}$. (1)

Using the formula: atom economy = $\frac{126.15 \text{g mol}^{-1}}{360.42 \text{g mol}^{-1}} \times 100\ \% = 35.0\ \%$. (1)

(b) First, calculate the moles of urea broken down:

$n((NH_2)_2CO) = \frac{m}{M} = \frac{14.0\,g}{60.07\,g\,mol^{-1}} = 0.233\text{ mol.}$ (1)

Then, using the $6(NH_2)_2CO : 1C_3H_6N_6$ ratio in the balanced equation, calculate the theoretical amount of melamine produced: $n(C_3H_6N_6) = \frac{1}{6} \times 0.233 = 0.0388\text{ mol.}$

Finally, convert from moles to mass:

$m(C_3H_6N_6) = n \times M = 0.0388\text{ mol} \times 126.15\text{ g mol}^{-1} = 4.89\text{ g.}$ (1)

(c) Using the formula:

$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100 = \frac{4.12}{4.89} \times 100 = 84.3\ \%.$ (1)

(If you used the alternative theoretical yield provided in the question:

$\text{percentage yield} = \frac{4.12}{5.00} \times 100 = 82.4\ \%$)

Reactivity 2.2

Exercises

1. Suitable methods follow from an analysis of the equation given, including a consideration of state symbols and ions.

Reaction gives off CO_2 gas: change in volume of CO_2 gas released could be measured using a gas syringe. (It cannot be measured using the water displacement method as CO_2 gas dissolves in water.)

Reaction gives off CO_2 gas: loss of mass could be measured by conducting the reaction in an open flask on a digital balance.

Reaction involves purple MnO_4^- ions being reduced to colourless Mn^{2+} ions: colorimetry could be used to measure the change in solution absorbance.

Reaction involves a change in the concentration of ions (23 on the reactants side and 2 on the products side): a conductivity meter could be used to measure the change in solution conductivity.

Reaction involves a change in pH as H^+ ions are used up: a pH meter could be used to measure the change in solution pH.

2. C

Here it is best to answer the question yourself without looking at the answers (remember they are designed to trick you). Rate is expressed as the change in concentration with time.

$$\text{Rate} = \frac{\Delta[A]}{\Delta t}$$

$$\text{Units of rate} = \frac{\text{units of concentration}}{\text{units of time}} = \frac{\text{mol dm}^{-3}}{\text{time}} = \text{mol dm}^{-3}\,\text{time}^{-1}$$

(time^{-1} could represent any unit of time, e.g. s^{-1}, min^{-1}, h^{-1} etc.

3. **(a)** As CO_2 gas is produced in the reaction we could measure the decrease in the mass of flask + contents.

As H^+ (HCl) is consumed in the reaction we could measure the increase in pH of the reaction mixture.

As CO_2 gas is produced in the reaction, we could measure the increase in volume of gas collected using a gas syringe. (It cannot be measured using the water displacement method as CO_2 gas dissolves in water.)

(b) The rate of the reaction decreases with time because the concentration of the acid decreases (rate $\propto$ [HCl]).

4. Note that 'time' here is the independent variable so it goes on the x-axis. 'Concentration' is the dependent variable and goes on the y-axis. A graph is plotted using all the data given and a smooth curve is drawn through the points. The rate of the reaction at a particular interval of time = gradient of the tangent to the curve at that time. Tangents to the curve are drawn at time = 60 s and at time = 120 s.

Gradients are calculated from $\frac{\Delta y}{\Delta x}$

At 60 s, a tangent line passes through the points (0, 0.155) and (185, 0).

$$\text{gradient} = \frac{(0 - 0.155)\ \text{mol dm}^{3}}{(185 - 0)\ \text{s}} = -8.4 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

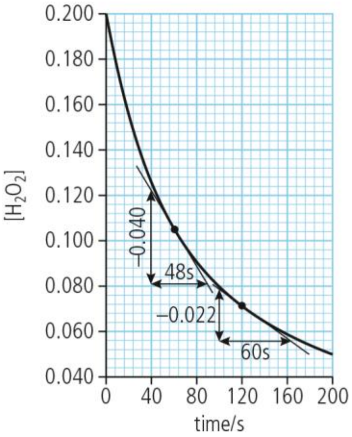
rate of reaction = 8.4×10^{-4} mol dm^{-3} s^{-1}

At 120 s, a tangent line passes through the points (0, 0.114) and (250, 0.023).

$$\text{gradient} = \frac{(0.023 - 0.114)\ \text{mol dm}^{3}}{(250 - 0)\ \text{s}} = -3.6 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Note that the gradient to the tangent can be derived from any values of $\frac{\Delta y}{\Delta x}$ so long as they are measured from a right-angled triangle.

Negative values are obtained for the gradients at t = 60 s and t = 120 s as the experiment is measuring the decrease in concentration of the H_2O_2 reactant. However, rates of reaction are expressed as positive values.



Given the difficulty of drawing an accurate tangent by hand, your answer may not be exactly the same as the ones calculated here but they should be similar.

5. D

Colliding particles must have a kinetic energy that is greater than the activation energy in order that the reaction might take place (they must also have the correct geometry).

6. A

Both the orientation and energy of the molecules are factors in determining whether a reaction will occur.

Note that the volume of the container may impact the *frequency* of collisions when dealing with gaseous reactants but does not affect the nature of the collisions themselves.

7. The reaction requiring the simultaneous collision of two particles is likely to be faster.

The simultaneous collision of three particles is statistically less likely (i.e. the probability of three particles simultaneously colliding is much lower than the probability of two particles colliding).

8. B

Catalysts increase the rate of both the forward and the backward reactions by lowering the activation energy of the reaction in both directions. The use of a catalyst does not necessarily increase the yield of products.

9. B

Catalysts work by decreasing the activation energy for a reaction, which increases the proportion of particles with the required energy for a successful collision. Increasing the temperature of a reaction vessel will increase the average kinetic energy of particles, leading to more frequent collisions (in addition to a greater proportion of particles now having the required activation energy).

10. B

A higher rate of a reaction involving a solid will occur if it is present as a powder as it has a larger surface area. For two concentrations of acid the rate will be faster for the higher concentration as there are more acid (H^+) particles available to collide with the $CaCO_3(s)$.

11. The ashes must contain a catalyst that speeds up the reaction between sugar and oxygen.

(Deduced from the fact that all other factors that affect reaction rate can be ruled out.)

12. **(a)** $2CO(g) + 2NO(g) \rightarrow 2CO_2(g) + N_2(g)$

(b) CO is a toxic gas: it combines with haemoglobin in the blood and prevents it from carrying oxygen. NO is a primary air pollutant: it is oxidized in the air to form acidic oxides, $NO(g) + \frac{1}{2}O_2(g) \rightarrow NO_2(g)$, leading to acid rain:

$NO_2(g) + H_2O(l) \rightarrow HNO_3(aq)$

It also reacts with other pollutants in the atmosphere forming smog.

(c) Coating beads with the catalyst increases the surface area of the catalyst in contact with exhaust gases and increases the efficiency of the catalytic converter.

(d) Catalytic activity involves the catalyst interacting with the gases, and the reaction occurring on its surface. As temperature increases, the increased kinetic energy of the gases increases the frequency with which they bind to the catalyst as well as the rate at which the reaction occurs on the surface and the rate at which the products desorb from the surface.

(e) Catalytic converters reduce pollution from cars but do not remove it completely. As in **(d)**, they are not effective when the engine first starts from cold, when an estimated 80% of pollution occurs. Other pollutants in car exhausts are not removed by the catalyst, e.g. ozone, sulfur oxides, and particulates. Also the catalytic converter increases the output of CO_2, a serious pollutant because of its greenhouse gas properties.

Note: This is a good example of a question which bridges several topics including Reactivity 1.3 and Structure 3.1. Also note that in part **(e)**, where the command term is 'Discuss', you are expected to consider arguments on both sides of the question.

13. B

Statements **I** and **II** are correct. Statement **III** is incorrect as only multi-step reactions contain one or more intermediates.

14. C

The first peak (I) is a transition state between the reactants and intermediate (II). The end of the line on the energy profile (III) indicates the products of the reaction.

15. An intermediate can be identified as a species that is produced in a step and then consumed in a subsequent step. In this example, F is an intermediate as it is produced in step 1 and then used up in step 2.

To deduce the overall reaction equation, we add the two steps together and then cancel out any identical species on both sides of the equation:

$$\begin{array}{c} NO_2 + F_2 \longrightarrow NO_2F + F \\ NO_2 + F \longrightarrow NO_2F \\ \hline 2NO_2 + F_2 + \cancel{F} \longrightarrow 2NO_2F + \cancel{F} \end{array}$$

The overall reaction equation is $2NO_2 + F_2 \rightarrow 2NO_2F$. Note that the intermediate, F, is cancelled out on both sides of the equation.

16. The rate expressions are written by multiplying *k*, the rate constant, by the concentration of each reactant raised to the power of its order, which is given in the table.

Experiment 1: rate = $k[H_2][I_2]$

Experiment 2: rate = $k[H_2O_2]$

Experiment 3: rate = $k[S_2O_8^{2-}][I^-]$

Experiment 4: rate = $k[N_2O_5]$

Beware the mistake of using the values for the coefficients in the balanced equation – they are not directly related to the order.

17. As both NO and O_3 are in the rate equation with their concentration raised to the power 1, the reaction is first order with respect to each of them. The overall order is the sum of the individual orders, therefore second.

18. Here the sum of the orders with respect to the reactants must be 2. This would be the case if the reaction was second order with respect to one reactant and zero order with respect to the other, or if it was first order with respect to each reactant.

The three options are:

rate = $k[CH_3Cl]_2$

rate = $k[CH_3Cl][OH^-]$

rate = $k[OH^-]^2$

19. Because we are told this is a one-step mechanism, the rate expression can be deduced directly from the stoichiometry of that step.

rate = $k[NO_2][CO]$

20. The rate-determining step is $NO_2 + NO_2 \rightarrow NO_3 + NO$.

The rate expression for this step is rate = $k[NO_2]_2$. Because the rate-determining step is the first step this will also be the overall rate expression for the reaction. This mechanism is second order with respect to NO_2 so it is consistent with the experimental observation that the reaction is second order with respect to NO_2.

The mechanism is also consistent with the overall reaction as the two steps of the mechanism combine to give the overall reaction stoichiometry:

$NO_2 + NO_2 \rightarrow NO_3 + NO$

$NO_3 + NO \rightarrow 2NO + O_2$

$2NO_2 \rightarrow 2NO + O_2$

21. C

Statement **I** is only true if the reaction can only happen via a one-step reaction involving two molecules of SO_2 and one O_2 colliding simultaneously. This has a very low probability compared to collisions between two molecules. It is more likely that the reaction could occur through two or more steps so it is not correct to say it must be between two SO_2 and one O_2 molecule.

Statement **II** is not correct as not every collision produces products: only those with sufficient kinetic energy to overcome the activation energy will produce products.

Statement **III** is correct as the slowest step of a mechanism is always the rate-determining step.

22. **(a)** The overall equation is deduced by adding together the steps in the reaction mechanism.

$AB_2 + AB_2 \rightarrow A_2B_4$ slow

$A_2B_4 \rightarrow A_2 + 2B_2$ fast

$2AB_2 \rightarrow A_2 + 2B_2$

Here the A_2B_4 molecules cancel, so the net equation is $AB_2 + AB_2 \rightarrow A_2 + 2B_2$

(or $2AB_2 \rightarrow A_2 + 2B_2$).

(b) The slowest step is the rate-determining step.

The rate expression for the rate-determining step is:

rate = $k[AB_2]^2$

Because the rate-determining step is the first step this is also the overall rate expression for the reaction.

(c) The units for k are derived from the fact that it is a second-order reaction.

rate = $k[AB_2]^2$

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol}^2\ \text{dm}^{-6}} = \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$$

23. C

Here it is best to work out the order with respect to each reactant first, before looking at the answers given.

The order for NO_2 can be deduced by comparing the first two rows where $[F_2]$ stays the same while $[NO_2]$ doubles from 0.1 to 0.2; the rate increases × 4 (from 0.1 to 0.4).

So it is second order with respect to NO_2. The order for F_2 can be deduced by comparing the first and third rows where $[NO_2]$ stays the same while F_2 doubles from 0.2 to 0.4; the rate doubles from 0.1 to 0.2.

So it is first order with respect to F_2.

24. This is similar to question **23**, but slightly harder as there is no data to compare two reactions where $[O_2]$ stays the same. So the order for NO will have to be worked out indirectly as follows.

From experiments 1 and 2, [NO] stays the same while doubling $[O_2]$ leads to a doubling of the rate. So the reaction is first order with respect to O_2.

Knowing this, we can see in experiments 2 and 3 $[O_2]$ doubles, which accounts for a doubling of the rate. But overall, the rate has increased here ×8 from 4.0×10^{-3} to

3.2×10^{-2}. So the rate has increased × 4 due to the doubling of [NO].

Therefore, it must be second order with respect to NO.

The rate expression follows from this: rate = $k[NO]_2[O_2]$

25. From the given rate expression we can deduce that the reaction is second order with respect to A and zero order with respect to B. So changes in [B] will not affect the rate of the reaction.

Comparing experiments 1 and 2, [A] doubles so the rate will increase ×4.

The rate in experiment 2 will be four times the rate in experiment 1

$(3.8 \times 10^{-3}\text{ mol dm}^{-3}\text{ s}^{-1}) \times 4 = 1.5 \times 10^{-2}\text{ mol dm}^{-3}\text{ s}^{-1}$.

Comparing experiments 2 and 3, [A] stays the same so the rate does not change as the change in [B] will not affect the rate.

Rate in experiment 3 = rate in experiment 2 = 1.5×10^{-2} mol dm^{-3} s^{-1}.

26. You can work out the units for *k* for any reaction of known order using the approach given. This is generally better than trying to memorize the units.

(a) Rate = $k[NO_2]^2$: reaction is second order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol}^2\ \text{dm}^{-6}} = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

(b) Rate = $k[CH_3CH_2Br]$: reaction is first order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{(\text{mol dm}^{-3})} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}} = \text{s}^{-1}$$

(c) Rate = $k[NH_3]_0$: reaction is zero order:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^0} = \frac{\text{mol dm}^{-3}s^{-1}}{1} = \text{mol dm}^{-3}\ \text{s}^{-1}$$

(d) Rate = $k[NO]_2[Br]$: reaction is third order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^3} = \frac{\text{mol dm}^{-3}s^{-1}}{(\text{mol dm}^{-3})^3} = \frac{\text{mol dm}^{-3}s^{-1}}{\text{mol}^3\ \text{dm}^{-9}} = \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

(e) Rate = $k[H_2][I_2]$: reaction is second order overall:

$$\text{units of } k = \frac{\text{units of rate}}{(\text{units of concentration})^2} = \frac{\text{mol dm}^{-3}s^{-1}}{(\text{mol dm}^{-3})^2} = \frac{\text{mol dm}^{-3}s^{-1}}{\text{mol}^2\ \text{dm}^{-6}} = \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

27. As the units of *k* are s^{-1}, the reaction must be first order – where the mol dm^{-3} terms have cancelled out (see the answer to question 26 above). As there is only one reactant, the rate expression can only be rate = $k[N_2O_5]$.

Note: this is a good example of a reaction where the rate equation does not match the overall reaction equation.

28. From the information given in the question, we can deduce that:

rate = $k[A]_0[B]_2$ or rate = $k[B]_2$.

Substituting the initial concentration of B and the initial rate into this equation, we get:

$$\text{rate} = k[B]_2$$

4.5×10^{-4} mol dm^{-3} min^{-1} = $k(2.0 \times 10^{-3}\ \text{mol dm}^{-3})^2$

which gives $k = \dfrac{4.5\times10^{-4}\text{mol dm}^{-3}s^{-1}}{4.0\times10^{-6}\text{mol}^2\ \text{dm}^{-6}} = 1.1 \times 10^2\ \text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$

Note: make sure answers for *k* always include units

29. C

Statement **I** is true. Statement **II** is not true: activation energy is not temperature dependent. Statement III is true as it relates to the frequency of collisions with proper orientations.

30. D

As outlined in the previous exercise, the Arrhenius factor takes into account the frequency of collisions with proper orientations.

31. B

Statement **I** is correct, the rate of collisions increases with temperature. Statement **II** is false, the activation energy is not temperature dependent. Statement **III** is correct, *k* (the rate constant) increases with temperature.

32. Using the equation $\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

$$\ln\left(\frac{1.30\ \text{mol dm}^3\text{s}^{-1}}{23.0\ \text{mol dm}^3\text{s}^{-1}}\right) = \frac{E_a}{8.31\ \text{JK}^{-1}\ \text{mol}^{-1}}\left(\frac{1}{800K} - \frac{1}{700K}\right)$$

$-2.87 = -2.15 \times 10^{-5}\ \text{J}^{-1}\ \text{mol} \times E_\text{a}$

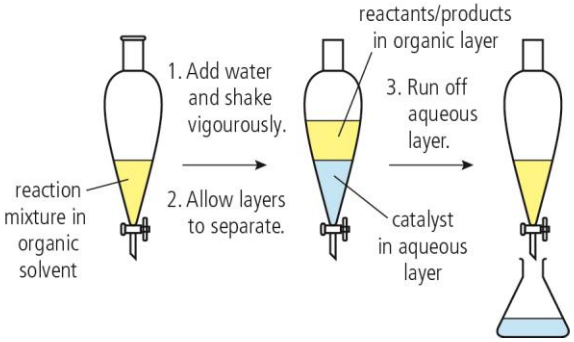
$E_\text{a} = 1.34 \times 10^5\ \text{J mol}^{-1} = 134\ \text{kJ mol}^{-1}$

Challenge

1. As described by Charles' Law, the volume of a gas is proportional to its temperature. By collecting a gas over warm water, the temperature of a gas will increase and, therefore, so will its volume.

2. A homogeneous catalyst is likely to be more difficult to recover as it is in the same phase as the reactants and products.

One option for catalyst recovery is a solvent extraction method which will be appropriate if the catalyst and reactants/products have different solubilities in aqueous and organic solvents. By adding a suitable solvent to a reaction mixture and shaking in a separating funnel, either the catalyst or reactants/products will preferentially transfer to the added solvent. After allowing the immiscible solvent layers to separate for a few minutes, we can then separate the bottom layer by running it out of the separating funnel. These steps are repeated multiple times to maximise the recovery. The process is summarised below:



Another possible technique would be to use distillation. This is appropriate when the reactants/products are volatile organic compounds and so have lower boiling points that the catalyst.

3 After each period of 8 days, the amount of ^{131}I will half. So in a period of 24 days, this will happen three times. Therefore, the mass of ^{131}I remaining will be $0.680\,\text{g} \times 0.5^3 = 0.0850\,\text{g}$.

Practice questions

1. B

Curve Y shows a greater volume of O_2 being produced after it reaches completion than in the initial reaction therefore the change being made must involve a greater amount of reactants than in the initial reaction. The only possible change that will do this is B, where additional hydrogen peroxide solution is added.

2. A

Any change that increases the frequency of collisions between reactants will increase the rate of a reaction.

Increasing pressure of gaseous reactants increases the number of molecules per unit volume so will increase the frequency of collisions.

Increasing temperature results in molecules moving faster and will increase the frequency of collisions (as well as the proportion of successful collisions).

Removing the product will not affect the frequency of collisions between the reactants.

3. A

No gases are produced in the reaction so there would be no change in mass of the reaction mixture and no change in the volume of gas produced. There is also no precipitate produced in the reaction as no solids are found on the product side. There is a change in the number of ions (12 in the reactants and 0 in the products) so we would expect to see a decrease in electrical conductivity as the reaction proceeds.

4. C

The information provided indicates that powdered MnO_2 is a heterogenous catalyst for the decomposition of H_2O_2. Catalysts speed up reactions by providing an alternative reaction pathway with a lower activation energy and are not used up in the reaction so statements **II** and **III** are correct. Statement I is incorrect as increasing the surface area of a solid catalyst speeds up the rate of reaction.

5. **(a)** The general reaction for an acid and metal carbonate is:

acid + metal carbonate → salt + water + carbon dioxide.

For this specific example the equation will be:

$2HCl(aq) + ZnCO_3(s) \rightarrow ZnCl_2(aq) + H_2O(l) + CO_2(g)$

(b) Gaseous carbon dioxide is produced and will escape in an open system.

(c) The rate is greatest at the start of the reaction when the concentration of hydrochloric acid is greatest.

As the concentration of hydrochloric acid decreases over time, collisions between reactants become less frequent and the rate decreases.

The rate approaches zero as the limiting reactant is used up.

(d) The rate of reaction at a specific time can be determined by calculating the gradient of a tangent to the curve at that point. The gradient is proportional to the rate.

To compare the *initial* rates of reaction of curves A and B, we need to draw a tangent at $t = 0$ on both curves and compare the gradients. As curve A is steeper, it will have a higher gradient reflecting a faster initial rate.

(e) Other factors that can impact rate of reaction are temperature, the surface area of solid reactants and the use of a catalyst. As experiment A has a higher rate of reaction, it could have:

- been carried out at a higher temperature
- used smaller pieces of $ZnCO_3$
- used a catalyst that was not used in experiment B.

(f) Higher temperature increases the kinetic energy of particles and so increases the frequency of collisions. Additionally, and more importantly, it increases the proportion of particles with KE > E_a . Both factors increase the frequency of successful collisions.

A smaller particle size of solid reactants leads to a greater surface area and so a higher frequency of collisions between particles. This will increase the frequency of successful collisions.

A catalyst provides an alternative reaction pathway with a lower activation energy. This increases the proportion of particles with KE > E_a which, again, increases the frequency of successful collisions.

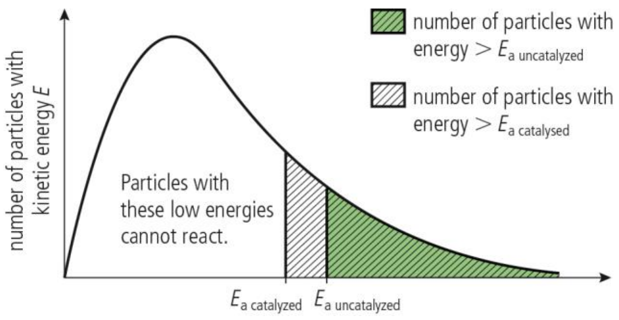
(g) H_2 has a significantly lower molar mass than CO_2 so the change in mass over time will be extremely small in comparison.

This is unlikely to be a satisfactory method for following the rate as it is difficult to measure small changes accurately without very precise measurement equipment. The experimental uncertainty in these measurements will also be large which impacts the validity of the data collected.

6. **(a)/(b)**

Increasing the temperature of a gas increases the average kinetic energy of the particles and so shifts the Maxwell-Boltzmann distribution curve to the right. The height of the peak of the curve will also decrease as the total area under the curve must remain the same (as there are the same number of particles in the sample). Therefore, T2 represents the gas at a higher temperature than T1.

(c) To illustrate the effect of using a catalyst, we will need to draw a Maxwell-Boltzmann distribution curve that labels the activation energy without a catalyst and the activation energy with a catalyst as vertical lines on the x-axis. As the area under the curve represents the number of particles, we must also shade and label the area to the right of both activation energies to show the proportion of particles that have the required activation energy.



As well as drawing the distribution curve, we must also indicate that the proportion of particles with the required activation energy is *greater* when using a catalyst, hence the increase in rate of reaction.

(d) **(i)** The enthalpy change, ΛH , is dependent on the difference in potential energy between the reactants and products. As a catalyst does not affect the potential energy of the reactants and products, the enthalpy change remains the same.

(ii) Although a catalyst speeds up the rate of a reaction, the stoichiometric yield is determined by the amount of the limiting reactant used in a reaction (as well as experimental error). In reversible reactions (discussed in Reactivity 2.3), the position of equilibrium can also affect the yield of product. As a catalyst increases the rate of both the forward and backward reaction equally, it does not affect the position of equilibrium so will not impact the yield.

7. For a reaction that is first order with respect to reactant A, rate = k[A] so the rate will increase proportionally as [A] increases.

8. C

Consider conditions 1 and 2: [Br_2] has been doubled and [NO] is constant.

As rate has increased by a factor of four the reaction is second order with respect to Br_2 and rate α [Br_2]^2.

Consider conditions 2 and 3: [Br_2] is constant and [NO] has been quadrupled. As the rate has not changed the reaction is zero order with respect to NO. Rate = $k[Br_2]^2[NO]^0 = k[Br_2]^2$

9. C

Rate-determining steps are the slowest steps in a reaction mechanism and correspond to the steps with the highest activation energy.

10. A

A rate expression can be derived for the slowest step: rate = $k[N_2O_2][H_2]$.

Because N_2O_2 is an intermediate it is necessary to substitute for [N_2O_2] based on its formation in the first step: $[N_2O_2] = k'[NO]^2$.

The rate expression is therefore rate = $k[H_2][NO]^2$.

11. B

Increasing temperature does not affect the activation energy, order of reaction or enthalpy change of the reaction. Increasing temperature does increase the frequency of collisions as well as the proportion of collisions with sufficient energy to overcome the activation energy.

Increasing temperature will therefore result in a faster reaction with a larger rate constant.

12. D

Consider the rate expressions obtained for the slow step of each mechanism:

A rate = $k[N_2O_4][CO]^2$; substituting for $[N_2O_4]$, rate = $k[NO_2]^2[CO]^2$

B rate = $k[NO_2][CO]$

C rate = $k[NO_2]$

D rate = $k[NO_2]^2$

13. **(a)** As increasing the temperature increases the rate of reaction, we know that the rate constant, k, must also increase with temperature. This is why ln k decreases with $\frac{1}{T}$ $\frac{1}{T}$

(b) The Arrhenius equation can be presented in the form of the equation for a straight line ($y = mx + c$) by taking the natural logarithm of both sides: $\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$.

Therefore, plotting ln k against $\frac{1}{T}$ will give a straight line where the slope $= -\frac{E_a}{R}$.

Using points (1.00×10^{-3}, –2.0) and (1.108×10^{-3}, –5.2):

$$\text{slope} = \frac{-5.2-(-2.0)}{(1.108-1.00)\times 10^{-3} K^{-1}} = \frac{-3.2}{1.08\times 10^{-4} K^{-1}} = -3.0 \times 10^4\ \text{K}$$

$E_a = -\text{slope} \times R = 3.0 \times 10^4\ \text{K} \times 8.31\ \text{J K}^{-1}$

$\text{mol}^{-1} = 2.5 \times 10^5\ \text{J mol}^{-1} = 250\ \text{kJ mol}^{-1}$

Given the errors associated with determining the exact values of points on the line, values between 240 and 260 kJ mol^{-1} are acceptable.

(c) Using the linear equation form of the Arrhenius equation in part **(b)**, we find that the y-intercept = ln A.

Rearranging this gives $A = e^{y-intecept}$ = $e^{-0.9}$ = 0.4 mol $\text{dm}^{-3}\ \text{s}^{-1}$.

Note that the units, although not required for the mark in this question, reflect the units of the rate constant for a second order reaction which is stated in the question.

(d) When 10% of N2O has reacted, [N2O] $= \frac{90}{100} \times 0.200\ \text{mol dm}^{-3} = 0.180\ \text{mol dm}^{-3}$

rate = $k[N_2O]^2 = 0.244\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1} \times \text{l dm}^{-3})_2 = 7.91 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

14. **(a)** Water was added so that the same total volume was used for all of the trials. (Then the concentration of the reactant in the different trials is directly proportional to the volume used.)

(b) **(i)** CH_3COCH_3: In Experiments 1 and 3 [CH_3COCH_3] has halved, [H^+] and [I_2] are constant. The initial rate has halved within experimental error so the reaction is first order with respect to H_3COCH_3.

H^+: In Experiments 1 and 4 [H^+] has halved, [CH_3COCH_3] and [I_2] are constant.

The initial rate has halved so the reaction is first order with respect to H^+.

I_2: In Experiments 1 and 2 [I_2] has increased by 1.5 times, [CH_3COCH_3] and [H^+] are constant. The initial rate is constant within experimental error so the reaction is zero order with respect to KI.

The rate expression for the reaction is rate = $k[CH_3COCH_3][H^+]$.

(ii) Andy and Suhailah's hypotheses were both incorrect as they proposed that the rate of reaction would be dependent on [I_2].

(c) For Experiment 1:

$$[\mathrm{CH3COCH3}] = \frac{c_1V_1}{V_f} = \frac{1.00\ \mathrm{mol\ dm^{-3}} \times 10.0\ \mathrm{cm^{-3}}}{100.0\ \mathrm{cm^{-3}}} = 0.100\ \mathrm{mol\ dm^{-3}}$$

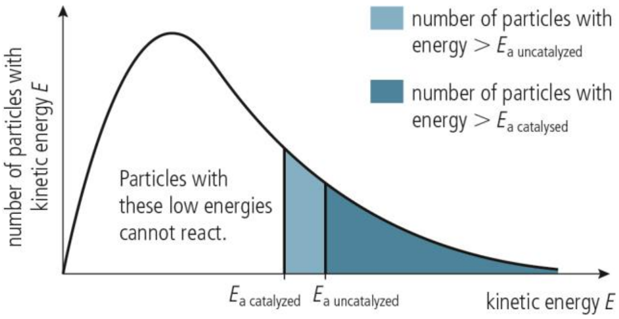
$$[\mathrm{H+}] = \frac{c_1V_1}{V_f} = \frac{1.00\ \mathrm{mol\ dm^{-3}} \times 10.0\ \mathrm{cm^{-3}}}{100.0\ \mathrm{cm^{-3}}} = 0.100\ \mathrm{mol\ dm^{-3}}$$

Initial rate = $k[\mathrm{CH3COCH3}][H^+]$

$$k = \frac{\text{initial rate}}{[\mathrm{CH_3COCH_3}][H^+]} = \frac{4.96 \times 10^{-6}\ \mathrm{mol^{-1}\ dm^{-3}}\ s^{-1}}{0.1.00\ \mathrm{mol^{-1}\ dm^{-3}} \times 0.100\ \mathrm{mol^{-1}\ dm^{-3}}}$$

$$= 4.96 \times 10^{-4}\ \mathrm{mol\ dm^{3}\ s^{-1}}$$

(d) **(i)**



(ii) A catalyst provides an alternative reaction pathway with a lower activation energy.

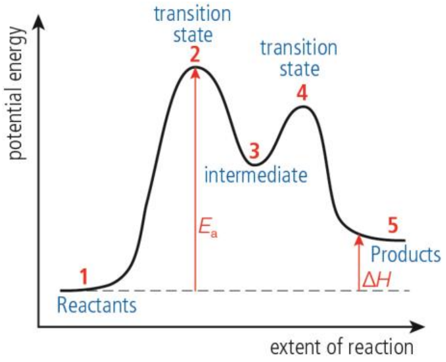
15. **(a)** W + XY → ~~WY~~ + X

~~WY~~ + Z → ~~W~~ + YZ

XY + Z → X + YZ

Overall equation is XY + Z → X + YZ.

(b)



Stage 1 represents the reactants.

Stage 2 represents the transition state for step 1 of the reaction mechanism.

Stage 3 represents an intermediate.

Stage 4 represents a transition state for step 2 of the reaction mechanism.

Stage 5 represents the products.

(c) Species present at stage 1 are reactants XY, Z and the catalyst W.

Species present at stage 2 is transition state formed by W and XY: W ---- X ----Y

Species present at stage 3 is intermediate WY, reactant Z and product X.

Species present at stage 4 is transition state formed by WY and Z: W ---- Y ----Z

Species present at stage 5 are products X, YZ and the catalyst W.

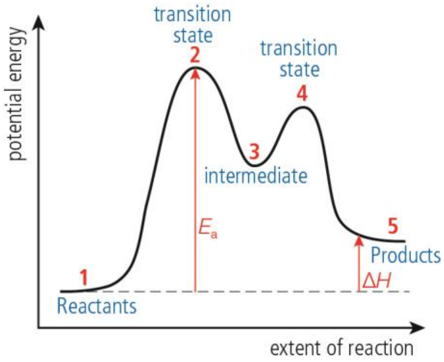
(d) For the two steps provided in the reaction mechanism the rate-determining step will be the one with the highest activation energy. From the diagram provided in the answer for part (b) we can see that the first step in the mechanism ($W + XY \rightarrow WY + X$) has the highest activation energy so it will be the slowest step.

rate = $k[W][XY]$

(e) The reaction is catalysed. W is a catalyst as it is consumed in the first step and regenerated in the second step. (This means that even though it participated in the reaction, there is no overall change in the amount of W present after the reaction has reached completion.)

(f) The enthalpy change, ΔH, refers to the enthalpy change that occurs between the reactants and products. Because this reaction proceeds through an intermediate, and has two steps in the reaction mechanism, there are two activation energies. E_a (step 1) is the energy difference between the reactants and the transition state for the first step, $W + XY \rightarrow WY + X$. E_a (step 2) is the energy difference between the intermediate and the transition state for the second step, $WY + Z \rightarrow W + YZ$.

As E_a (step 1) is larger than E_a (step 2), this is the important one to label on the energy profile as it dictates the rate-determining step.


transition state
2
transition state
4
3
intermediate
potential energy
E_a
1
Reactants
5
Products
ΔH
extent of reaction

Reactivity 2.3

Exercises

1. A

Statement **I** is correct: equilibrium is dynamic, meaning that both the forward and reverse reactions continue. Statement **II** is correct, as this is what defines the equilibrium state. Statement **III** is not correct: equilibrium can be established with a mixture containing mostly reactant, mostly products, or anything in between.

2. C

A is not always true; equilibrium is often established with a product yield of <50%.

B is emphatically not true: at equilibrium the rates of forward and reverse reactions must be equal. C true: because the rates of forward and reverse reactions are equal, the amounts of reactants and products do not change (no change in macroscopic properties). D is not true: both reactions continue as equilibrium is dynamic.

3. B

If the system is in equilibrium, the rate at which ice melts to water and the rate at which water freezes to ice will be equal so A is true. The amounts of ice and water need not be the same at equilibrium, the amounts present will depend on the position of equilibrium so B is *not true* and B is the correct answer. (Note the word ‘not’ in the question!) Equilibrium can be achieved from either the forward or reverse direction so statement C is true. While equilibrium is dynamic at the sub-microscopic level at the macroscopic level no observable changes will occur so D is also true.

4. In each case, the equilibrium constant is equal to the concentrations of the products, each raised to the power of the coefficient of each product in the original equation, divided by the concentrations of the reactants, each raised to the power of the coefficient of each product in the original equation.

(a) $$K = \frac{[NO_2]^2}{[NO]^2[O_2]}$$

(b) $$K = \frac{[NO_2]^4[H_2O]^6}{[NH_3]^4[O_2]^7}$$

(c) $$K = \frac{[CH_3OH][Cl^-]}{[CH_3Cl]\ [OH^-]}$$

5. Note the following points, which sometimes get missed in this work:

- The products of the reaction are found in the numerator (top line of the fraction) of the equilibrium expression, *K*, and the reactants of the reaction are found in the denominator (bottom line of the fraction).

- The stoichiometric coefficient for each reactant or product is equal to the power it is raised to in the equilibrium expression.

(a) $K = \frac{[NO_2]^2}{[N_2O_4]}$

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(b) $K = \frac{[CO]\ [H_2]^2}{[CH_4]\ [H_2O]}$

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

6. In this question it is essential that you first write the chemical equation from the information given. You need to check that it is correctly balanced with respect to each element. Then apply the equilibrium law, using the coefficients from the equation as the powers to which the concentration of each species is raised.

(a) $3F_2(g) + Cl_2(g) \rightleftharpoons 2ClF_3(g)$

$K = \frac{[ClF_3]^2}{[F]^3[Cl_2]}$

(b) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

$K = \frac{[N_2][O_2]}{[NO]^2}$

(c) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$

$K = \frac{[CO]\ [H_2]^3}{[CH_4]\ [H_2O]}$

7. **(a)** $K = 7.4 \times 10^{-26}$. As $K << 1$ this means the denominator in the equilibrium expression must be much larger than the numerator, which occurs when the concentration of reactants is much larger than the concentration of products. The equilibrium mixture must therefore contain mostly reactants.

(b) $K = 2.7 \times 10^{-18}$. As $K << 1$ this means the denominator in the equilibrium expression must be much larger than the numerator, which occurs when the concentration of reactants is much larger than the concentration of products. The equilibrium mixture must therefore contain mostly reactants.

(c) $K = 6.0 \times 10^{13}$. As $K >> 1$ this means the numerator in the equilibrium expression must be much larger than the denominator, which occurs when the concentration of products is much larger than the concentration of reactants. The equilibrium mixture must, therefore, contain mostly products.

8. Here we must first must determine the equilibrium constant expression and then substitute the concentration data into the expression:

$$K = \frac{[NO_2]^2}{[N_2O_2]} = \frac{1.80^2}{1.62} = 2.00.$$

Note that the number of significant figures in the answer should reflect the number of significant figures provided in the data which is three.

9. The equilibrium constant expression for the reverse reaction, $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$, will be $K' = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$.

As this expression is the inverse of the forward reaction, the value of K' will be the inverse of K.

$$K' = \frac{1}{K} = \frac{1}{278} = 3.60 \times 10^{-3} .$$

The answer has been given to three significant figures to reflect the three significant figures in the data provided in the question.

10. B

Stop and think carefully about what a catalyst does before looking at the answers.

A catalyst lowers the activation energy of a reaction and so increases the rate of both forward and reverse reactions. A is incorrect − the rate of both reactions increases. C is incorrect − the enthalpy change is not altered by the catalyst. D is incorrect − a catalyst has no effect on the yield, only on the rate of production.

11. D

Here it is best to consider each column separately and then see which answer has two correct responses. Note that the reaction is endothermic. Position of equilibrium: C and D are correct − increasing temperature favors the forward endothermic reaction. Value of equilibrium constant: B and D are correct − equilibrium shifting to the right increases the value of K here.

12. C

Statement **I**: no − adding a catalyst does not shift the equilibrium in either direction as it has an equal effect on both forward and reverse reactions. Statement **II**: yes − decreasing the oxygen (product) concentration shifts the equilibrium to the right, by Le Chatelier's principle. Statement **III**: yes − increasing the volume will reduce the pressure and so favor the side with the larger number of gas molecules. Here there are 2 moles of gas on the left and 3 on the right, so it will shift to the right.

13. By Le Châtelier's principle to reactions involving gases, an increase in pressure will favor the side of the reaction with the smaller number of molecules. Applying this enables us to predict the directional change in each of the given reactions.

(a) 2 molecules on the left, 3 on the right so equilibrium will shift left.

(b) 3 molecules on the left, 1 on the right so equilibrium will shift right.

(c) 2 molecules on each side, so there will be no shift in the equilibrium position.

14. By studying the given equation, we can deduce:

- 3 molecules of gas on the left, 5 molecules of gas on the right
- forward reaction is endothermic

(a) H_2(g) is a product of the reaction: when its concentration is increased, the equilibrium will shift to the left.

(b) CH_4(g) is a reactant: when its concentration is increased, the equilibrium will shift to the right.

(c) A decrease in volume is equivalent to an increase in pressure. So the equilibrium shifts in the direction of the smaller number of molecules, which is to the left.

(d) CS_2(g) is a product of the reaction. As its concentration is decreased the equilibrium will shift to the right.

(e) An increase in temperature will favor the endothermic (forward) reaction. The equilibrium will shift to the right.

15. From the information given we note:

- there are 3 molecules of gas on the left and 2 on the right the forward reaction is exothermic
- CO is a reactant.

(a) Higher pressure will favor the side with the smaller number of molecules − the products. So the equilibrium will shift to the right and [CO] will decrease.

(b) Increasing [O_2] − a reactant − will shift the equilibrium to the right and so [CO] will decrease.

(c) Increasing the temperature will favor the endothermic − backward − reaction. So [CO] will increase.

(d) Adding a catalyst has no effect on the equilibrium position and so [CO] will be unchanged.

16. C

The question is asking you to distinguish between the effect of a catalyst on the rate of a reaction and on the yield. Deal with each column in the answer options separately.

Remember that a catalyst increases the rate, but has no effect on the yield. When considering the rate of formation of NH_3, answers A, B, and C are correct. When considering the amount of NH_3 formed, only C is correct.

17. B

Analyze the information given in the equation to determine the effects of temperature and pressure on the equilibrium reaction. Temperature: the reaction is exothermic, so, product yield is favored by a low temperature. Pressure: the reaction has 3 moles of gas on the left and 2 moles of gas on the right, so product yield is favored by a high pressure.

18. In order to answer this question, you need to know that the Haber process reaction is exothermic in the forward reaction.

An increase in temperature will favor the endothermic − backward − reaction − so the equilibrium will shift to the left. This will cause:

- the value of *K* to be decreased
- the yield of the reaction to be decreased.

19. **(a)** Calculate *Q* (the reaction quotient) $\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{1.00^2}{0.100 \times 0.100} = 100$

Not at equilibrium. As $Q > K$ the reaction proceeds to the left.

(b) Calculate *Q* (reaction quotient) $\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{0.042^2}{0.49 \times 0.04} = 0.090$

At equilibrium since $Q = K$

(c) Calculate *Q* (reaction quotient) $\frac{[HOCl]^2}{[H_2O][Cl_2O]} = \frac{0.19^2}{0.00033 \times 0.083} = 1.3 \times 10^2$

Not at equilibrium. As $Q > K$ the reaction proceeds to the left.

20. Here we must first deduce the equilibrium constant expression from the reaction equation:

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Then substitute the non-equilibrium concentration values into the expression to determine the reaction quotient, *Q*:

$$Q = \frac{(4.00)(4.00)}{(2.00)(2.00)} = \frac{16.0}{4.00} = 4.00$$

As $Q > K$, the reaction will proceed to the left (decreasing [products] and increasing [reactants]) to reach equilibrium.

21. **(a)** The volume specified is 1.00 dm^3 so the number of moles given is the same as the concentration in mol dm^{-3}.

1.00 mol of HI has decreased to 0.78 mol at equilibrium, so 0.22 mol of HI have reacted.

This is therefore the value for the ‘change’ row. From this value, and the stoichiometry

of the reaction, we can deduce the changes in the concentration of the other components. These enable us to calculate the equilibrium concentration of each component. Application of the equilibrium law leads to calculation of *K*.

	2HI(g) ⇌	H2(g) +	I2(g)
Initial	1.00	0.00	0.00
Change:	–0.22	+0.11	+0.11
Equilibrium	0.78	0.11	0.11

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{(0.11)^2}{(0.78)^2} = 2.0 \times 10^{-2} \text{ (at 440 °C)}$$

(b) A comparison of the values of *K* at the two temperatures indicates that for this reaction an increase in temperature has led to an increase in the value of *K*. A larger value of *K* signifies the equilibrium has shifted to the product side and so the forward reaction must be endothermic.

22. Because *K* is very small, we can deduce that the concentration of reactants at equilibrium is approximately equal to their initial concentrations.

As we do not know the amount of reactant to have reacted to reach equilibrium, we use $-x$ to denote the change in reactant concentration.

This enables us to deduce the change in concentration in terms of *x* of the other components.

The values of equilibrium concentration are then expressed in terms of *x*.

Substituting the equilibrium concentrations into the equilibrium expression leads to evaluation of *x* and hence of the equilibrium values.

	N2(g) +	O2(g) +	⇌ 2NO(g)
Initial	1.6	1.6	0.0
Change:	$-x$	$-x$	$2x$
Equilibrium	$1.6 - x$	$1.6 - x$	$2x$

As *K* is very small, $1.6 - x \approx 1.6$

$$K = \frac{[NO]^2}{[N_2][O_2]} = 1.7 \times 10^{-3}$$

$$\frac{[2x]^2}{1.6 \times 1.6} = 1.7 \times 10^{-3}$$

$4x^2 = 4.4 \times 10^{-3}$

$x = 0.033$

$[NO]_{eqm} = 2x = 0.066 \text{ mol dm}^{-3}$

23. (a) From the initial concentrations of all components and the equilibrium concentrations of H_2 and CO_2, the equilibrium concentrations of the reactants can be calculated. By substituting the values for all the equilibrium concentrations into the equilibrium expression, the value of *K* can be calculated.

	CO(g) +	H2O(g) ⇌	H2(g) +	CO2(g)
Initial	4.0	6.4	0.0	0.0
Change:	–3.2	–3.2	+3.2	+3.2
Equilibrium	0.8	3.2	3.2	3.2

$$K = \frac{[H_2][CO_2]}{[CO][H_2O]} = \frac{(3.2)^2}{(0.8)(3.2)} = 4.0$$

(b) Use the values given to obtain the reaction quotient, *Q*:

$$Q = \frac{[H_2][CO_2]}{[CO][H_2O]} = \frac{(3.0)^2}{(4.0)^2} = 0.56$$

As *Q* is not equal to the value of *K* the reaction is not at equilibrium. As the *Q* value of this mixture is lower than *K*, the reaction will move to the right before equilibrium is established.

24. C

Entropy is at a maximum and Gibbs energy is at a minimum at equilibrium.

25. Using the relationship $\Delta G^{\ominus} = -RT \ln K$:

(a) If $K = 1$ then $\Delta G^{\ominus} = 0$, because ln 1 = 0.

(b) If $K > 1$ then $\Delta G^{\ominus}$ = negative, because ln (positive number) = a positive number, so the right-hand side of the equation is negative overall (*R* is a constant with a positive value and *T* (absolute temperature) is, by definition, greater than 0).

(c) If $K < 1$ then $\Delta G^{\ominus}$ = positive, because ln (negative number) = a negative number, so the right-hand side of the equation is positive overall.

26. **(a)** $\Delta G^{\ominus} = -RT \ln K$

$\Delta G^{\ominus} = -8.31\ \text{K}^{-1}\,\text{mol}^{-1} \times 298\ \text{K} \times \ln(1.00 \times 10^{-14}) = 79.8\ \text{kJ mol}^{-1}$

(b) An increase in temperature has led to an increase in the value of *K*. A larger value of *K* signifies the equilibrium has shifted to the product side and so the forward reaction must be endothermic.

Challenge yourself

1 Earth receives energy from the Sun and disperses energy, largely as heat. Exchange of matter is minimal − the only exceptions to Earth being a closed system are matter received from space such as asteroids and space dust, and matter lost to space such as spacecraft.

2 The different values of K indicate the different stabilities of the hydrogen halides. The bonding is strongest in HCl and weakest in HI.

This is largely because of the size of the atoms. As I has a larger atomic radius than Cl, in HI the bonding pair is further from the nucleus than the bonding pair in HCl, and so experiences a weaker pull.

The HI bond breaks more easily and the reverse dissociation reaction is favored, giving a small K value. As the HCl bond is strong the reverse dissociation reaction is much less favored, giving this reaction a large K_c value.

3 **(a)** Doubling the reaction coefficients squares the equilibrium expression so

$K' = K^2 = 77300$.

(b) This is the inverse reaction in which the reaction coefficients have been halved so

$$K' = \frac{1}{\sqrt{K}} = 0.0600$$

(c) This is the inverse reaction in which the reaction coefficients have been tripled so

$$K' = \frac{1}{K^3} = 4.91 \times 10^{-8}$$

4. The value for K_c at 298 K for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is extremely low, so the equilibrium mixture lies to the left, with almost no production of NO. At higher temperatures, such as in vehicle exhaust fumes, the reaction shifts to the right (as it is an endothermic reaction) and a higher concentration of NO is produced. This gas is easily oxidized in the air, producing the brown gas NO_2 that is responsible for the brownish haze:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.

5 The atom economy of the Haber process is 100% as there is only one product. In other words, there is no waste. But, due to the reversible nature of this reaction, this does not mean that all reactants are converted into product, so the stoichiometric yield is less than 100%.

It is the goal of these industries to maximize yield and efficiency by choosing the optimum conditions, taking equilibrium and kinetic considerations into account.

Practice questions

1. C

When a reaction is at equilibrium, the concentrations of the reactants and products do not change and the equilibrium position remains constant. The reactants and products do continue to react, but as the forward and backward reactions are occurring at the same rate, no observable changes in concentration occur.

2. A

As some of the CO_2(g) has escaped, the concentration of CO_2(g) inside the bottle will have decreased. In response to this change, the equilibrium will shift to the left until the ratio of [CO_2(aq)/[CO_2(g)] returns to the initial value.

3. D

Because the reaction is exothermic ($\Delta H^{\ominus}$ is negative), increasing temperature will shift the equilibrium to the left, decreasing the yield of products and decreasing the equilibrium constant.

4. A

The equilibrium being considered involves the vaporization of methanol, which is an endothermic process, therefore decreasing temperature will move the equilibrium to the left, decreasing the amount of products and decreasing the value of K.

5. C

Increasing temperature will increase the rate of both the forward and reverse reactions. For the amount of chlorine product to increase the rate of the forward reaction must have increased more than the rate of the reverse reaction.

6. D

As H^+ is a product, adding more H^+ will shift the position of the equilibrium to the left. However, the value of K will remain unchanged as the temperature remains constant. (The value of K only changes when the temperature is changed.)

7. A

The equilibrium being considered involves the condensation of water, which is an exothermic process, therefore increasing temperature will move the equilibrium to the left and increase the amount of gas present. As the system will establish a new equilibrium at the new temperature the rate of condensation will be equal to the rate of vaporization at this equilibrium.

8. D

Because the system is at equilibrium the rates of the forward and reverse reactions are equal and the amount of $H_2O(g)$ will not change. The pressure exerted by $H_2O(g)$ will therefore remain constant.

9. **(a)** **(i)** $K = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$ (1)

(II) There are 3 moles of gaseous reactants and 2 moles of gaseous products, therefore, increasing pressure will move the equilibrium position to the right and increase the yield of $SO_3(g)$. (2)

(III) Because the reaction is exothermic ($\Delta H^{\ominus}$ is negative) increasing temperature will move the equilibrium position to the left and decrease the yield of $SO_3(g)$. (2)

(iv) A catalyst will increase the rate of both the forward and reverse reactions. (3)

However, the forward and reverse rates of reaction increase equally so a catalyst has no effect on the position of equilibrium or the value of K.

(b) Using the initial concentrations for NO(g), $H_2(g)$ and $H_2O(g)$ along with the equilibrium concentration of NO(g) provided (shown in bold below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	2NOg) +	$2H_2(g) \rightleftharpoons$	N(g)+	$2H_2O$
Initial	**0.100**	**0.051**	**0**	**0.100**
Change:	*–0.038*	*0.038*	*+0.019*	*+0.038*
Equilibrium	**0.062**	0.013	0.019	0.138

$$K = \frac{[N_2][H_2O]^2}{[NO]^2[H_2]^2} = \frac{0.019 \times 0.138^2}{0.062^2 \times 0.013^2} = 5.6 \times 10^2$$ (4)

10 **(a)** The graph shows that the yield of ammonia decreases as the temperature increases.

A decrease in equilibrium product yield as temperature increases occurs for exothermic reactions therefore the forward reaction is exothermic. (2)

(b) There are 4 moles of gaseous reactants and 2 moles of gaseous products so increasing the pressure will shift the equilibrium to the right and increase the yield of $NH_3(g)$. (2)

(c) $K = \frac{[NH_3]^2}{[N_2][H_2]^3}$

(d) Using the initial concentrations for N_2(g) and H_2(g) along with the equilibrium concentration of NH_3(g) provided (shown in bold below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	N_2(g) +	$3H_2$(g) ⇌	$2NH_3$(g)
Initial	1.00	3.00	0
Change:	*–0.031*	*–0.093*	*+0.062*
Equilibrium	0.969	2.91	0.062

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{0.062^2}{0.969 \times 2.91^3} = 1.6 \times 10^{-4}$$ (1)

(e) A catalyst will increase the rate of both the forward and reverse reactions equally so it has no effect on the position of equilibrium or the value of K. (1)

11 **(a)** If the system is homogeneous all of the reactants and products are in the same phase. If it is in equilibrium the concentrations of the reactants and products remain constant as the rates of the forward and reverse reactions are the same. (2)

(b) $K = \frac{[HI]^2}{[H_2][I_2]}$ (1)

(c) There are 2 moles of gaseous reactants and 2 moles of gaseous products so increasing the pressure will have no effect on the position of equilibrium. (1)

(d) If K decreases as temperature increases then less product is formed at the higher temperature. A decreased yield of product at higher temperature occurs when the forward reaction is exothermic. (1)

(e) $K' = \frac{1}{K} = \frac{1}{160} = 6.25 \times 10^{-3}$ (1)

(f) Using the initial concentrations for H_2(g) and I_2(g) along with the equilibrium concentration of HI(g) provided (shown in bold below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products. *Note that the flask volume is 4.00 dm^3 so the gas concentrations need to be calculated based on this volume.*

Initial $[H_2] = \frac{1.60 \text{ mol}}{4.00 \text{ dm}^2} = 0.400 \text{ mol dm}^{-3}$

initial $[I_2] = \frac{1.00 \text{ mol}}{4.00 \text{ dm}^2} = 0.250 \text{ mol dm}^{-3}$

Equilibrium $[HI] = \frac{1.80 \text{ mol}}{4.00 \text{ dm}^2} = 0.450 \text{ mol dm}^{-3}$

	$H_2(g)$ +	$I_2(g)$ ⇌	2HI(g)
Initial	0.400	0.250	**0**
Change:	*–0.225*	*–0.225*	*+0.450*
Equilibrium	0.175	0.025	0.450

$$K = \frac{[HI]^2}{[H_2][I_2]} = \frac{0.450^2}{0.175 \times 0.025} = 46.3$$ (4)

(g) A catalyst will increase the rate of both the forward and reverse reactions equally so the platinum has no effect on the position of equilibrium or the value of *K*. (2)

12. D

Using the initial concentrations for I_2 and Br_2 along with the equilibrium concentration of IBr provided (shown in bold below) we can calculate the changes occurring (shown in *italics* below) and the equilibrium concentrations of I_2 and Br_2:

	$I_2(g)$ +	$Br_2(g)$ ⇌	2IBr(g)
Initial	**0.50**	**0.50**	**0**
Change:	*–0.40*	*–0.40*	*+0.80*
Equilibrium	0.10	0.10	**0.80**

$$K = \frac{[IBr_2]^2}{[I_2][Br_2]} = \frac{0.80^2}{0.1 \times 0.1} = 64$$

13 **(a)** $K = \frac{[SO_2Cl_2]}{[Cl_2]\ [SO_2]}$ (1)

(b) Using the initial concentrations for $SO_2(g)$ and $Cl_2(g)$ along with the equilibrium concentration of $SO_2Cl_2(g)$ provided (shown in bold below) we can calculate the changes occurring (shown in *italics* below) as well as the equilibrium concentrations of the reactants and products:

	$Cl_2(g)$ +	$SO_2(g)$ ⇌	$SO_2Cl_2(g)$
Initial	8.60×10^{-3}	8.60×10^{-3}	**0**
Change:	*-7.65×10^{-4}*	*-7.65×10^{-4}*	*$+7.65 \times 10^{-4}$*
Equilibrium	7.835×10^{-3}	7.835×10^{-4}	7.65×10^{-4}

(3)

$$K = \frac{[SO_2Cl_2]}{[Cl_2]\ [SO_2]} = \frac{7.65 \times 10^{-4}}{7.835 \times 10^{-3} \times 7.835 \times 10^{-3}}$$

(c) The temperature has decreased from 370 °C to 300 °C. Because the reaction is exothermic ($\Delta H^\ominus$ is negative), decreasing the temperature will move the equilibrium position to the right and increase the equilibrium concentration of $SO_2Cl_2(g)$. This will also result in an increase in the value of K. (3)

(d) There are 2 moles of gaseous reactants and 1 mole of gaseous products so increasing the volume to 1.50 dm^3 (therefore decreasing the pressure) will shift the equilibrium to the left and decrease the equilibrium concentration of $SO_2Cl_2(g)$.

As the temperature has not changed, the value of K will remain constant. (3)

(e) A catalyst will increase the rate of both the forward and reverse reactions equally so it has no effect on the position of equilibrium or the value of K_c and will not affect the equilibrium concentration of $SO_2Cl_2(g)$. (2)

14. ln(1) = 0 so using the formula $\Delta G^\ominus = -RT\ln K$ will give $\Delta G^\ominus = 0$.

(a) Using the data provided and the gas constant, R, from section 2 of the data booklet we can calculate, $\Delta G^\ominus$ in J mol^{-1}: (1)

$$\Delta G^\ominus = -RT\ln K = -8.31\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \ln(1.7 \times 10^{12}) = -7.0 \times 10^4\ \text{J mol}^{-1}.$$

To convert to kJ mol^{-1}, we must then divide by 1000:

$$\Delta G^\ominus = (-7.0 \times 10^4\ \text{J}) \times \frac{1\text{kJ}}{1000\,\text{J}} = -70\ \text{kJ mol}^{-1}$$

At this temperature, the reaction has a very high value of K and large negative value for $\Delta G^\ominus$ so the equilibrium position lies far to the product side and we can say that the reaction essentially goes to completion. (3)

15. First we must deduce the equilibrium constant expression for this reaction:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

We can then calculate the reaction quotient, Q, by substituting the non-equilibrium concentrations into the equilibrium constant expression:

$$Q = \frac{(3.00)^2}{(0.500)(0.400)^3} = 281;$$

As Q is greater than K it must decrease to reach equilibrium and so the position of equilibrium will shift to the left leading to a lower concentration of products and higher concentration of reactants. (3)

Reactivity 3.1

Significant figures and logarithms

Many of the calculations for this chapter involve the use of logarithms. Determining the correct significant figures for logarithm calculations does not involve the same rules as calculations involving addition, subtraction, multiplication or division. When taking a log, the answer will have the same number of decimal places as the number of significant figures in the value that the log is being applied to. For example:

$$\log(5) = 0.7 \quad \log(2.3 \times 10^{4}) = 4.36 \quad \log(1.00 \times 10^{-7}) = 7.000$$

1 s.f. 1 d.p. 2 s.f. 2 d.p. s.f. 3 d.p.

Doing the inverse function (the anti-log) involves the opposite reasoning. Here, the number of significant figures in the answer will be the same as the number of decimal places in the value the anti-log is being applied to. For example:

$$10^{5.2} = 2 \times 10^{5} \quad 10^{-4.20} = 6.3 \times 10^{-5} \quad 10^{0.100} = 1.26$$

1 d.p. 1 s.f. 2 d.p. 2 s.f. 3 d.p. 3 s.f.

Exercises

1. The conjugate acids of the given bases are deduced by adding H^+ to each species.

Remember to adjust the charge by +1 in each case.

- **(a)** HSO_3^-
- **(b)** $CH_{3N}H_3^+$
- **(c)** C_2H_5COOH
- **(d)** HNO_3
- **(e)** HF
- **(f)** H_2SO_4

2. The conjugate bases of the given acids are deduced by removing H^+ from each species.

Remember to subtract 1+ from the net charge in each case.

- **(a)** $H_2PO_4^-$
- **(b)** CH_3COO^-
- **(c)** HSO_3^-
- **(d)** SO_4^{2-}
- **(e)** O^{2-}
- **(f)** Br^-

3. Note that conjugate acid–base pairs follow from Brønsted–Lowry theory. They differ by just one proton – the acid has the extra H^+ and the base has lost it. There are two such pairs in each of the equations in this question; there is an acid and a base on both sides of each equation.

(a) CH_3COOH (acid) / CH_3COO^- (base)

NH_3 (base) / NH_4^+ (acid)

(b) CO_3^{2-} (base) / HCO_3^- (acid)

H_3O^+ (acid) / H_2O (base)

(c) NH_4^+ (acid) / NH_3 (base)

NO_2^- (base) / HNO_2 (acid)

4. To be amphiprotic, the substance must be able to both accept and release protons:

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons PO_4^{3-}(aq) + H_3O^+(aq)$ (acid behaviour as protons are released)

$HPO_4^{2-}(aq) + H_2O(l) \rightleftharpoons H_2PO_4^-(aq) + OH^-(aq)$ (base behaviour as protons are accepted)

5 **(a)** Dissolved carbon dioxide forms the weak acid carbonic acid, which ionizes partially in solution to release H^+ ions. The H^+ ions in solution are responsible for the acidity and the lowering of the pH. Remember to use the equilibrium sign in all equations involving ionization of weak acids and weak bases.

$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$

$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

(b) You should be able to deduce these equations and balance them from the information given in the question. You are not expected to learn these.

$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

(c) As lime, CaO, is a non-metal oxide, you can deduce it is basic. It will therefore react in a neutralization reaction with acid helping to reduce the acidity / raise the pH.

$CaO(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l)$

6. Use of coal as a fuel has become increasingly controversial as concerns about climate change and air pollution intensify. There are political and economic aspects to this, but your answer should focus on the chemistry of the combustion.

Burning coal releases non-metal oxides, such as SO_2 and nitrogen oxides, $NO_{x,}$ which contribute to acid rain. This also contributes to climate change from the release of greenhouse gases, and respiratory diseases from release of particulates and some heavy metals. Coal mining also has large impacts on the environment and health.

7. The pH increases by 1 unit, as the concentration of H^+ ions has been decreased tenfold, and pH is a logarithmic scale, $pH = –\log[H^+]$.

8. $[H^+] = 1.9 \times 10^{-5}$

pH = –log $(1.9 \times 10^{-5}) = 4.72$

9. pH = –log $[H^+]$ = –log [0.01] = 2.0

10. pH = –log$[H^+]$ = –log(3.2×10^{-5}) = 4.49

At 298 K, less than pH 7 means acidic solution.

11. $[H^+] = 10^{-pH} = 10^{-8.3}$

$[H^+] = 5.0 \times 10^{-9}$ mol dm^{-3}

12. In questions like this you must show understanding and be specific about *why* the pH scale is more convenient.

pH scale converts $[H^+]$ values with a wide range of concentrations, and most often with negative exponents, into a simpler numeric scale. pH numbers are usually positive and have no exponents. pH scale is a smaller range of numbers than $[H^+]$ values in mol dm^{-3}.

13. The ionization of water and so the concentration of H^+ ions increases with temperature, causing the pH to decrease. When the temperature is above 298 K, the pH is < 7. The given sample has a pH > 7, and so the temperature must be below 298 K. Note this water is still neutral.

14. $[H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K

$$[H^+] = \frac{1.0\times10^{-14}}{7.8\times10^{-6}} = 1.3 \times 10^{-9} \text{ mol dm}^{-3}$$

15. $[H^+][OH^-] = 2.4 \times 10^{-14}$

In pure water $[H^+] = [OH^-]$ so $[H^+] = \sqrt{2.4\times10^{-14}} = 1.6 \times 10^{-7}$

pH = –log $(1.6 \times 10^{-7}) = 6.8$

16. At pH 9, $[H^+] = 10^{-pH} = 10^{-9}$ mol dm^{-3}

At 25 °C, $K_w = [H^+][OH^-] = 1.00 \times 10^{-14}$

$$\therefore \left[OH^-\right] = \frac{K_w}{\left[H^+\right]} = \frac{1.00\times10^{-14}}{10^{-9}} = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

17. $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

At 298 K: solutions are acidic if $[H^+] > 1 \times 10^{-7}$ mol dm^{-3}, $[OH–] < 1 \times 10^{-7}$ mol dm^{-3}

solutions are basic if $[H^+] < 1 \times 10^{-7}$ mol dm$^{-3,}$ $[OH–] > 1 \times 10^{-7}$ mol dm^{-3}

(a) $1.00 \times 10^{-14} = [3.4 \times 10^{-9}][OH^-]$, hence $[OH^-] = 2.9 \times 10^{-6}$ mol dm^{-3}; solution is basic as $[OH^-] > 1 \times 10^{-7}$ mol dm^{-3}

(b) $1.00 \times 10^{-14} = [H^+][0.010]$, hence $[H^+] = 1.0 \times 10^{-12}$ mol dm^{-3}; solution is basic as $[H^+] < 1 \times 10^{-7}$ mol dm^{-3}

(c) $1.00 \times 10^{-14} = [H^+][1.0 \times 10^{-10}]$, hence $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}; solution is acidic as $[H^+] > 1 \times 10^{-7}$ mol dm^{-3}

(d) $1.00 \times 10^{-14} = [8.6 \times 10^{-5}][OH^-]$, hence $[OH^-] = 1.2 \times 10^{-10}$ mol dm^{-3}; solution is acidic as $[OH^-] < 1 \times 10^{-7}$ mol dm^{-3}

18. A sample of blood has $[H^+] = 4.6 \times 10^{-8}$ mol dm^{-3} at 298 K. Determine its concentration of OH^- ions, and state whether the sample is acidic, basic or neutral.

$[H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K

So $[OH^-] = \dfrac{1.0 \times 10^{-14}}{4.6 \times 10^{-8}} = 2.2 \times 10^{-7}$ mol dm^{-3}

$[OH^-] > [H^+]$ so solution is basic

19 **(a)** $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $\left[H^+\right] = \dfrac{K_w}{\left[OH^-\right]} = \dfrac{1 \times 10^{-14}}{8 \times 10^{-8}}$ $[H^+] = 1.25 \times 10^{-7}$,

so pH = –log[1.25] = 6.9

(b) pH = –log $[H^+]$ = –log $[10^{-2}]$ = 2

(c) $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $\left[H^+\right] = \dfrac{K_w}{\left[OH^-\right]} = \dfrac{1.00 \times 10^{-14}}{6 \times 10^{-10}} = 1.7 \times 10^{-5}$, so pH = 4.8

20. The equation here must show the equilibrium sign.

NH_3 acts as a weak Brønsted–Lowry base because it ionizes only partially in solution to accept a proton.

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

The equilibrium position of this reaction lies to the left, in favor of reactants.

21. B

The solution with the lowest conductivity will be the one with the fewest dissociated ions.

The solution of ethanoic acid (CH_3COOH) will be the poorest conductor of electricity as ethanoic acid is a weak acid and only partially dissociates into its ions in solution. All the other examples are strong acids (HCl), strong bases (NaOH) or salts (NaCl) and so will dissociate into ions completely in solution. As the solutions are all 1 mol dm^{-3}, the total number of ions in the HCl, NaOH and NaCl solutions will be much higher than the number of ions in the CH_3COOH solution.

22. A

Magnesium will react with the acid and not the base (statement I). Sodium hydroxide will react with the acid (liberating heat); there will be no change when added to the base (statement II). As both are equimolar and either a strong acid or a strong alkali that dissociates completely into its ions to create an electrically conductive solution, the bulb will light brightly in both solutions (statement III).

23. **(a)** H_2CO_3 is a weak acid and H_2SO_4 is a strong acid. H_2CO_3 has the stronger conjugate base, as the conjugate base is formed from the weaker of the two acids.

(b) HCOOH is a weak acid and HCl is a strong acid. HCOOH has the stronger conjugate base, as the conjugate base is formed from the weaker of the two acids.

24. acid + metal → salt + hydrogen

acid + base → salt + water

acid + carbonate → salt + water + carbon dioxide

Then check that each equation is balanced and has the correct state symbols.

(a) $H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

(b) $HNO_3(aq) + NaHCO_3(s) \rightarrow NaNO_3(aq) + H_2O(l) + CO_2(g)$

(c) $H_3PO_4(aq) + 3KOH(aq) \rightarrow K_3PO_4(aq) + 3H_2O(l)$

(d) acid + amine → salt of amine $HCl(aq) + CH_3NH_2(l) \rightarrow CH_3NH_3^+Cl^-$

25. B

Metal oxide is a base; base reacts with acid → salt + water

26. **(a)** nitric acid + sodium carbonate (or sodium hydrogencarbonate or sodium hydroxide) e.g. $2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + H_2O(l) + CO_2(g)$

(b) hydrochloric acid + ammonia solution

$HCl(aq) + NH_4OH(aq) \rightarrow NH_4Cl(aq) + H_2O(l)$

(c) copper(II) oxide + sulfuric acid

$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$

(d) methanoic acid + potassium hydroxide

$HCOOH(aq) + KOH(aq) \rightarrow KCOOH(aq) + H_2O(l)$

27. Strong acid and strong base form salt solution of two weak conjugates in which neither ion hydrolyzes and so pH is 7.0.

The point of exact neutralization is the equivalence point.

28. $HNO_3(aq) + KOH(aq) \rightarrow KNO_3(aq) + H_2O(l)$

Start of titration, only acid is in the flask.

$[HNO_3] = [H^+] = 0.01\ mol\ dm^{-3}$

$pH = -\log(0.01) = 2.0$

29. Calculate the mol amount in the solution for which you have volume and conc.

$n(\text{NaOH}) = \frac{10.00}{1000}\ \text{dm}^3 \times 0.01\ \text{mol dm}^{-3} = 1 \times 10^{-4}\ \text{mol}$

Reacting ratio is 1:1 so n(HCl) at equivalence = 1×10^{-4} mol

Vol. at equivalence = $\frac{12.00}{1000} = 0.012\ \text{dm}^3$

So conc HCl = $\frac{1\times10^{-4}}{0.012} = 0.0083\ \text{mol dm}^{-3}$

30. Formula mass of NaOH = $40.00\ \text{g mol}^{-1}$

$n(\text{NaOH}) = \frac{6.0\ \text{g}}{40.0\ \text{g mol}^{-1}} = 0.15\ \text{mol}$

One mole of dissolved NaOH gives one mole of OH^- ions.

$\left[OH^-\right] = \frac{n}{V} = \frac{0.15\ \text{mol}}{1\ \text{dm}^3}$ [OH–] = 0.15 mol

$1.0\ \text{dm}^3 = 0.15\ \text{mol dm}^{-3}$

$K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

Hence $\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.00\times10^{-14}}{0.15} = 6.7 \times 10^{-14}$

so pH = 13.17

31. If $K_w = 2.4 \times 10^{-14} = [H^+]\,[OH^-]$

For water, $[H^+] = [OH^-] = \sqrt{2.4\times10^{-14}} = 1.5 \times 10^{-7}\ \text{mol dm}^{-3}$

$\text{pH} = -\log[H^+] = -\log(1.5 \times 10^{-7}) = 6.81$

As $[OH^-] = [H^+]$, pOH = pH = 6.81

$\text{p}K_w = \text{pH} + \text{pOH} = 6.81 + 6.81 = 13.62$

However, water is still neutral, as $[H^+] = [OH^-]$.

32. $\text{pH} + \text{pOH} = \text{p}K_w = 14.00$ (at 298 K)

pH = 6.77, therefore, pOH = 14.00 – 6.77 = 7.23

$\text{pH} = -\log\,[H^+]$ then $[H^+] = 10^{-\text{pH}} = 10^{-6.77} = 1.7 \times 10^{-7}\ \text{mol dm}^{-3}$

Similarly, if $\text{pOH} = -\log\,[OH^-]$ then $[OH^-] = 10^{-\text{pOH}} = 10^{-7.23} = 5.9 \times 10^{-8}\ \text{mol dm}^{-3}$

$[H^+] > [OH^-]$ so the sample of milk is acidic

33. **(a)** pH = –log [H^+], pH = –log [0.40] = 0.40

(b) [OH^-] = 3.7 × 10^{-4} mol dm^{-3};

$$\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.00\times10^{-14}}{3.7\times10^{-4}} = 2.7 \times 10^{-11} \text{ mol dm}^{-3}$$

pH = –log[H^+] = –log(2.7 × 10^{-11}) = 10.57

(c) As one mole of $Ba(OH)_2$ dissociates to give two moles of OH^- ions a 5.0 × 10^{-5} mol dm^{-3} solution of $Ba(OH)_2$ will have an OH^- concentration of 1.0 × 10^{-4} mol dm^{-3}.

[OH^-] = 1.0 × 10^{-4} mol dm^{-3};

$$\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.00\times10^{-14}}{1.0\times10^{-4}} = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

pH = –log[H^+] = –log(1.0 × 10^{-10}) = 10.00

34. $K_b = \frac{\left[BH^+\right]\left[OH^-\right]}{[B]}$

This is a modified equilibrium constant based on the balanced equation of ionization.

Here, the first step is, therefore, to write the equations. Then identify the base (B) and conjugate acid (BH^+) for each reaction.

(a) $C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_3^+ + OH^-$

B = $C_2H_5NH_2$; BH^+ = $C_2H_5NH_3^+$

$$K_b = \frac{\left[C_2H_5NH_3^+\right]\left[OH^-\right]}{[C_2H_5NH_2]}$$

(b) $HSO_4^- + H_2O \rightleftharpoons H_2SO_4 + OH^-$

B = HSO_4^-; BH^+ = H_2SO_4

$$K_b = \frac{[H_2SO_4]\left[OH^-\right]}{\left[HSO_4^-\right]}$$

(c) $CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$

B = CO_3^{2-}; BH^+ = HCO_3^-

$$K_b = \frac{\left[HCO_3^-\right]\left[OH^-\right]}{\left[CO_3^{2-}\right]}$$

35. The higher the value of K_a, the stronger the acid. So HNO_2 is the weakest and H_2SO_3 is the strongest.

$HNO_2 < H_3PO_4 < H_2SO_3$

36. Dissociation constants are used to give a quantitative measure of the extent of ionization of an acid or base reaction that is in equilibrium. With strong acids and bases, we assume full dissociation, so there is no equilibrium and the concept of an acid or base dissociation constant is not applicable. The H^+ concentration and pH of their solutions can be derived directly from their concentration.

37. B

Because this is a weak acid, we cannot determine the $[H^+]$ at equilibrium from the initial concentration, as this would be assuming complete dissociation. Instead, we have to deduce it from the value of K_a.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.1		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium	$0.1 - x$		x		x

Because K_a is very small, we can assume that $0.1 - x \approx 0.1$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{0.1} = 1.0 \times 10^{-5} \qquad x^2 = 1 \times 10^{-6}$$

$$\therefore x = \sqrt{1 \times 10^{-6}} = 1 \times 10^{-3} \qquad [H^+] = 1 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[H^+] = -\log(1 \times 10^{-3}) = 3.0$$

38. pH + pOH = 14.00

pH = 11.86 so pOH = 14.00 – 11.86 = 2.14

(Temperature at 298 K)

$\therefore [OH^-]$ at equilibrium $= 10^{-pH} = 10^{-2.14}$

$= 7.2 \times 10^{-3}$ mol dm^{-3}

	$C_2H_5NH_2$	+	H_2O	$\rightleftharpoons$	$C_2H_5NH_3^+$ +	+	OH^-
Initial:	0.1				0		0
Change:	–0.0072				+0.0072		+0.0072
Equilibrium	0.0928				0.0072		0.0072

$$K_a = \frac{[C_2H_5NH_3^+][OH^-]}{[C_2H_5NH_2]} = \frac{0.0072^2}{0.928} = 5.6 \times 10^{-4}$$

39. When you are working with an acid and K_a value, you will calculate the $[H^+]$ first and deduce the $[OH^-]$ from this. Again, we are assuming that this is at 298 K – which should have been specified in the question.

This is very similar to the Worked examples.

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.10		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium	$0.10-x$		x		x

Because Ka is very small, we can assume that $[HA]_{\text{equilibrium}} \approx [HA]_{\text{initial}}$,

i.e. $0.10 - x \approx 0.10$

$$\therefore K_a = \frac{x^2}{0.1} = 1.0 \times 10^{-7}$$

$x^2 = 1 \times 10^{-8}$

$\therefore x = [H^+] = \sqrt{1 \times 10^{-6}} = 1.0 \times 10^{-4}$ mol dm^{-3}

because $K_w = [H^+][OH^-] = 1.00 \times 10^{-8}$ we get

$$\left[OH^-\right] = \frac{K_w}{\left[H^+\right]} = \frac{1.00 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

40. The pK_a value must first be converted into K_a.

$pK_a = 4.92$ so $K_a = 10^{-4.92} = 1.2 \times 10^{-5}$

	HA	$\rightleftharpoons$	H^+	+	A^-
Initial:	0.030		0		0
Change:	$-x$		$+x$		$+x$
Equilibrium	$0.030 - x$		x		x

Because the value of K_a is very small, we can assume that $[HA]_{\text{equilibrium}} \approx [HA]_{\text{initial}}$, i.e. $0.030 - x \approx 0.030$

$$\therefore K_a = \frac{x^2}{0.030} = 1.2 \times 10^{-5}$$

$x^2 = 3.6 \times 10^{-7}$

$\therefore x = [H^+] = \sqrt{3.6 \times 10^{-7}} = 6.0 \times 10^{-4}$ mol dm^{-3}

$\therefore pH = -\log[H^+] = -\log(6.0 \times 10^{-4}) = 3.22$

41. A

By definition $pK_a = -\log K_a$

42. The stronger acid has the lower pK_a value. Therefore, HF is a stronger acid than HCN.

43. Once more we assume we are working at 298 K. $pK_a + pK_b = 14.00$

For HCN and CN^- it follows that $9.21 + pK_b = 14.00$

$\therefore pK_b[CN^-] = 4.79$

For HF and F^- it follows that $3.17 + pK_b = 14.00$

$\therefore pK_b[F^-] = 10.83$

The stronger base has the lower pK_b value. Therefore CN^- is a stronger base than F^-.

This confirms our answer to **Q42** that HCN is the weaker acid, so it will have the stronger conjugate base.

44. **(a)** The conjugate base of ethanoic acid, CH_3COOH, is CH_3COO^- (the ethanoate ion).

At 298 K, $pK_a + pK_b = 14.00$

$\therefore pK_b(CH_3COO^-) = 14.00 - pK_a(CH_3COOH)$

$= 14.00 - 4.76 = 9.24$

(b) The conjugate base of methanoic acid, HCOOH, is $HCOO^-$ (the methanoate ion).

At 298 K, $pK_a + pK_b = 14.00$

$pK_b(HCOO^-) = 14.00 - pK_a(HCOOH) = 14.00 - 3.75 = 10.25$

The pK_b value of $HCOO^-$ is higher than the pK_b value of CH_3COO^- so $HCOO^-$ is a weaker base. (In turn, this implies that methanoic acid is a stronger acid than ethanoic acid, which is confirmed by the pK_a values given here.)

45. **(a)** NaCl is a salt of a strong acid (HCl) and a strong base (NaOH).

Neither ion hydrolyzes appreciably. pH = 7

(b) $FeCl_3$ is a salt of strong acid (HCl) and a weak base. Cation hydrolyzes, anion does not. $pH < 7$

(The Fe^{3+} cation exists as $Fe(OH_2)_6^{3+}$ in aqueous solution. $Fe(OH_2)_6^{3+}$ can act as an acid and will give a solution of $pH < 7$;

$Fe(OH_2)_6^{3+}(aq)\ Fe(OH_2)_5(OH)^{2+}(aq) + H^+(aq)$.)

(c) NH_4NO_3 is a salt of a weak base (NH_3) and a strong acid (HNO_3). Cation hydrolyzes, anion does not. $pH < 7$

(d) Na_2CO_3 is a salt of a strong base (NaOH) and a weak acid (HCO_3^-). Anion hydrolyzes, cation does not. $pH > 7$

46. B

A salt solution with $pH > 7$ is characteristic of a salt formed from a strong base and a weak acid.

A: sodium chloride = salt of strong acid (HCl) and strong base (NaOH), pH = 7.

B: potassium carbonate = salt of strong base (KOH) and weak acid (HCO_3^-), $pH > 7$.

C: ammonium nitrate = salt of weak base (NH_3) and strong acid (HNO_3), $pH < 7$.

D: lithium sulfate = salt of strong base (LiOH) and strong acid (H_2SO_4), pH = 7

47. The key to answering this question is to identify the strengths of the acid and base as 'strong' or 'weak'.

(a) Strong acid (H_2SO_4) and weak base (NH_3), salt solution has pH < 7

(b) Weak acid (H_3PO_4) and strong base (KOH), salt solution has pH > 7

(c) Strong acid (HNO_3) and strong base ($Ba(OH)_2$), salt solution has pH = 7

48. Sodium salts are all soluble and so dissociate completely.

$NaHCO_3(aq) \rightarrow Na^+(aq) + HCO_3^-(aq)$

The anion is the conjugate of the weak acid H_2CO_3 and so hydrolyzes.

You must use the equilibrium sign here.

$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

The release of hydroxide ions raises the pH.

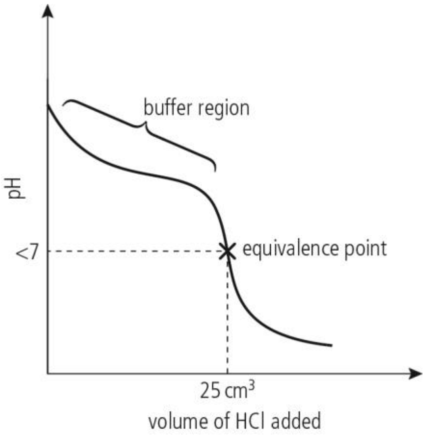
49. D

Statement I: the initial pH will not be the same – the strong acid, which dissociates completely, will have a lower initial pH than the weak acid of the same concentration, which does not dissociate completely.

Statement II: the pH at equivalence point will not be the same – that for the strong acid will be about 7 and that for the weak acid will be > 7.

Statement III: volume of NaOH needed is the same – both acids react in a 1:1 ratio with the base.

50.



The graph makes the following points:

- the pH decreases during the titration as acid is added to base
- initial pH is the pH of NH_3, a weak base
- the buffer region is when some of the base has been neutralized by the acid
- equivalence occurs when 25 cm^3 of acid has been added because they react in a 1:1 ratio and are supplied in equal concentrations
- the pH at equivalence is < 7 because the salt forms from a strong acid and a weak base.

51. Note that no data are given in this question, so no calculations are expected.

(a) If the concentration of the acid is known, its K_a and therefore its pK_a can be calculated from the initial pH of the acid.

$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

$K_a = \frac{[CH_2COO^-][H^+]}{[CH_2COOH]}$ $[H^+] = 10^{-pH}$

As $[CH_3COO^-]$ = $[H^+]$ and assuming that the dissociation is small so $[CH_3COOH]_{eq}$ = $[CH_3COOH]_{initial}$,

$$K_a \approx \frac{[H^+]^2}{[CH_2COOH]}$$

(b) $[CH_3COO^-]$

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

Halfway to the equivalence point half of the CH_3COOH has been converted to CH_3COO^-

Therefore, at half-equivalence $[CH_3COOH] = [CH_3COO^-]$.

At half-equivalence $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = [H^+]$ ($[CH_3COOH]$ and $[CH_3COO^-]$ cancel)

If $K_a = [H^+]$ then pK_a = pH

The pH value that can be obtained from the titration curve at the half-equivalence point is therefore equivalent to the pK_a of the weak acid (CH_3COOH in this example).

52. D

Different indicators have different pH values at which they change color (so **A** is wrong).

The size of the pH range over which the color change occurs and the pK_a of an indicator are not related (so **B** is wrong).

The color observed in acidic solution will depend on the specific indicator (so **C** is wrong).

The pH range of the color change always includes the pK_a of the indicator.

53. **(a)** Its pH range for color change occurs at between pH 3.8 and pH 5.4. This lies within the pH range at equivalence for titrations of (i) strong acid and strong base (pH 3–11) and (ii) strong acid and weak base (pH 3–7).

(b) An estimate for the pK_a of an indicator corresponds to about halfway through its color-change range. As the pH range for the color change for bromocresol green is pH 3.8–5.4 its p$K_a \approx 4.6$.

(c) Bromocresol green changes from yellow to blue as pH increases, therefore its color will be yellow at pH 3.6 (and at all pH values < 3.8).

54. B

A buffer solution must contain approximately equal amounts of a weak acid or weak base with its conjugate base or acid. In the examples given here, you must consider how the given components will react together and the proportions of products and unused reactants that will result.

A: equimolar quantities of weak acid and strong base which react in 1 : 1 ratio, with the resulting mixture containing salt and water only: not a buffer.

B: weak acid and strong base in 2 : 1 ratio by moles. These react in 1 : 1 ratio, so the resulting mixture contains (unreacted) weak acid and salt in equimolar amounts: this is a buffer.

C: weak acid and strong base in 1 : 2 ratio by moles. These react in 1 : 1 ratio, so the resulting mixture contains salt and (unreacted) strong base: not a buffer.

D: weak acid and strong base in 2 : 1 ratio by moles, but here the reacting ratio will be 2 : 1 as $Ba[OH]_2$ will neutralize 2 moles of CH_3COOH. The resulting mixture contains salt and water only: not a buffer.

55. B

The concept here is similar to **Q54**. You must work out the products of each reaction.

I: The components do not react together. The mixture will contain equal moles of the weak acid CH_3COOH and its salt CH_3COONa. This is a buffer.

II: There is a 2 : 1 ratio of weak acid to strong base, so after reaction the mixture will contain equal quantities of weak acid and its salt. This is a buffer.

III: There is a 1 : 1 ratio of weak acid and strong base, so after reaction the mixture contains salt and water only. This is not a buffer.

56 **(a)** Because it has a higher concentration of the acid and its conjugate base, and so has the capability of buffering to a greater extent than the mixture with the lower concentrations of solution.

57. Use $\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

Assume that all the NaOH is used up reacting with the acid to form salt.

Moles of salt formed = $0.05 \times \frac{v}{1000}$ and

Moles of acid remaining = $\frac{100}{1000} \times 0.05 - \text{moles of salt formed}$

The data we have is pH = 4.23

$K_a = 1.77 \times 10^{-4}$, so $\text{p}K_a = -\log(1.77 \times 10^{-4}) = 3.75$

Inserting all the numbers into the formulae:

$$4.23 = 3.75 + \log \frac{5 \times 10^{-5} \times v}{5 \times 10^{-3} - \left(5 \times 10^{-5} \times v\right)}$$

$$0.48 = \log \frac{5 \times 10^{-5} \times v}{5 \times 10^{-3} - \left(5 \times 10^{-5} \times v\right)}$$

Anti-logging and solving for *v* gives the volume of NaOH needed = 75 cm^3 of 0.05 mol dm^{-3} NaOH

Challenge yourself

1. The product NH_4Cl forms smoke which is a solid, from gaseous reactants and so can be classified as sublimation or deposition.

2. $2OH^- \rightarrow O^{2-} + H_2O$

This shows the transfer of a proton from one hydroxide ion to another. So OH^- is both accepting H^+ to form H_2O (basic behaviour) and losing H^+ to form O^{2-} (acidic behaviour). The two equations showing amphiprotic behaviour are:

$OH^- + H^+ \rightarrow H_2O$ and $OH^- \rightarrow O^{2-} + H^+$

3. $Al_2(SO_4)_3(s) + 6H_2O(l) \rightarrow 2Al(OH)_3(s) + 3H_2SO_4(aq)$

Aluminium sulfate dissolves to form aluminium hydroxide, which is insoluble and so is responsible for the cloudy appearance, and a dilute solution of sulfuric acid, which causes the low pH.

A more detailed explanation is that $Al_2(SO_4)_3(s)$ ionizes in water to form Al^{3+} and SO_4^{2-} ions. As Al^{3+} is small with a high charge density, it hydrolyzes water that is bound to it in the hydrated complex, releasing H^+ and lowering the pH.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5OH]^{2+}(aq) + H^+(aq)$

Aluminium sulfate is the salt of a strong acid and a weak base, and forms an acidic solution.

4. Vinegar is ethanoic acid, CH_3COOH. When added to soil this will lower the pH and cause hydrangea flowers to turn blue, as explained in the text.

5. In weak acids and weak bases, the majority of the acid or base is not ionized at the start of the reaction, so energy is used to break bonds in ionizing the reactants. This endothermic process reduces the net energy released when water forms. For example, the neutralization reaction between NaOH and CH_3COOH is less exothermic than the neutralization reaction between NaOH and HCl.

6. Increasing the length of the carbon chain increases the donation/push of electrons towards the carbonyl C atom, known as a positive inductive effect. This causes less electron withdrawal from the O–H bond, so weakening acid strength.

The basic strength of amines depends largely on the availability of the lone pair electrons on nitrogen. C_2H_5 pushes electrons towards N more than CH_3 does, so it is a stronger base.

7. $HNO_3(aq) + NH_4OH(aq) \rightarrow NH_4NO_3(aq) + H_2O(l)$

Ammonium nitrate is formed from a strong acid and a weak base. The solution will be acidic.

Solid ammonium nitrate decomposes on heating.

$2NH_4NO_3(s) \rightarrow 2N_2(g) + O_2(g) + 4H_2O(g)$

Every 2 moles of solid release 7 moles of gas, which causes a rapid expansion and increase in pressure leading to explosion. Also, O_2 ignites easily.

8. Conductivity decreases during the neutralization as the concentration of the most mobile ions, H^+ and OH^-, falls. After equivalence, the conductivity increases again with the increasing concentration of free ions from the excess acid or base. The minimum level of conductivity therefore can be used to determine the equivalence point.

9. Indicators contain conjugated delocalized electrons, as a result of alternating double bonds. The structure of the indicator changes with the addition/removal of H^+ and the change to the delocalized system changes the energy of light absorbed by the indicator molecule.

10. **(a)** pH increases on dilution of a strong acid as $[H^+]$ decreases.

(b) pH increases on dilution of a weak acid as $[H^+]$ decreases, but the change is less than for a strong acid, as acid dissociation increases with dilution.

(c) pH of a buffer stays the same with dilution, as K_a or K_b and [acid] / [salt] ratio stay constant.

Practice Questions

1. C

Brønsted–Lowry acid–base pairs differ by just one proton. The only pair with this criterion is H_2O / H_3O^+. In this case the acid is H_3O^+ and its conjugate base is H_2O.

2. A

To be amphiprotic, a species must be able both to accept and to donate a proton. That rules out **C** and **D** as they have no proton to donate. OH^- can donate a proton to form O^{2-} and accept a proton to form H_2O. NH_4^+ can donate a proton but has no lone pair to accept a proton.

3. C

As a weak Brønsted–Lowry acid, CH_3OH ionizes only partially to form its conjugate base CH_3O^-. The acid is not a good proton donor so **A** is wrong. The conjugate base will not be present in high concentration so **B** is wrong. The equilibrium between the base and acid lies in favor of the acid, so CH_3O^- is a stronger base. CH_3O^- is not a stronger acid than CH_3OH.

4. A

At the same concentration, differences in pH must be due to differences in extent of ionization. X has the lower pH so must be the stronger acid. It is always wise to double check the other answers to check you haven't missed anything.

5. **D**

It's good to answer questions like this before looking at the answers, as they are designed to trick you. A Brønsted–Lowry base is a proton acceptor.

6. **(a)** **(i)** pH meter/probe and suitable indicator paper/solution (2)

(ii) The key here is to recognize these as strong or weak acids or bases. Note KCl is the salt of a strong acid and strong base.

HCOOH(aq)	5	weak acid
KCl(aq)	7	neutral salt
HNO_3(aq)	1	strong acid
$Ba(OH)_2$(aq)	13	strong base
NH_3(aq)	10	weak base

(3)

(b) **(i)** $2NaHCO_3(s) + 2HCl(aq) \rightarrow Na_2CO_3(aq) + CO_2(g) + H_2O(l)$

Effervescence

Solid being used up

Increase in temperature/exothermic reaction (5)

(ii) HCO_3^- can act as a Brønsted–Lowry acid and base by giving and accepting protons:

As acid: $HCO_3^- \rightarrow H^+ + CO_3^{2-}$

As base: $HCO_3^- + H^+ \rightarrow H_2CO_3$ (4)

(c) Conductivity generates quantitative data which leads to clearer interpretation than qualitative data generated from indicators. (Note that pH meters also generate quantitative data.)

7. **(a)** According to the Bronsted–Lowry theory, an acid is a proton (H^+) donor and a base is a proton (H^+) acceptor.

A weak base is a base that will only be partially protonated in aqueous solution:

$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

A strong base is a base that will be completely protonated in aqueous solution:

$B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$

Ammonia (NH_3) is an example of a weak base.

$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ (3)

(b) Many weak acids can cause damage in the environment. Three common ones are sulfurous acid (H_2SO_3), nitrous acid (HNO_3) and carbonic acid (H_2CO_3).

All of these weak acids can corrode marble and limestone buildings, and cause leaching in soils. Sulfurous and nitrous acid are harmful to plant life as leaching removes minerals from the soil that are essential for plant growth.

Because of increased concentrations of CO_2 in the atmosphere, its absorption by oceans and lakes generates carbonic acid and the increased acidity of the lakes and oceans can impact on aquatic

life. Many aquatic species cannot survive at pH < 5, e.g. the calcium carbonate shells of shellfish dissolve in acidic conditions. (3)

8. The IB mark scheme given here shows how the marks are awarded. Note the importance of specific details such as square brackets.

(a) $(K_w) = [H^+][OH^-]/(K_w) = [H_3O^+][OH^-]$

Do not award mark if [] omitted or other brackets are used. (1)

(b) $[H^+]$ increases, $[OH^-]$ decreases but still some present (K_w constant)/$[OH^-]$ cannot go to zero as equilibrium present / $\left[OH^-\right] = \frac{K_w}{\left[H^+\right]}$, thus $[OH^-]$ cannot be zero/OWTTE (1)

(c) (changing T disturbs equilibrium) endothermic reaction/forward reaction favored/equilibrium shifts to the right; to use up (some of the) heat supplied; K_w increases (as both $[H^+]$ and $[OH^-]$ increase) (3)

(d) (as $[H^+]$ increases) pH decreases/pH < 7

No mark for more acidic.

Inverse relationship between pH and $[H^+]$/pH = $-\log[H^+]$/pH = $\log_{10}\frac{1}{\left[H^+\right]}$

Accept $[H_3O^+]$ in place of $[H^+]$

9. D

For a conjugate acid-base pair, $K_w = K_bK_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{5.0\times10^{-2}} = 2.0\times10^{-13}$$

10. C

Hydrochloric acid is a strong acid and ethanoic acid is a weak acid. Because ethanoic acid does not dissociate fully, it will have a different initial pH to the hydrochloric acid solution, where complete dissociation occurs. Weak acids pass through a buffering zone as they react with added sodium hydroxide and the pH changes observed will not be the same as those with hydrochloric acid, where no buffering occurs, and the equivalence points will not occur at the same pH. Because they are both monoprotic acids the same volume of sodium hydroxide solution will be required to reach the equivalence point, where all of the acid has reacted.

11. C

The equilibrium for the bromophenol blue indicator is $HIn \rightleftharpoons H^+ + In^-$. As pH increases from 3.0 to 4.6 and $[H^+]$ decreases, the equilibrium will shift to the right. At pH 3.0 there will be an excess of HIn and at pH 4.6 an excess of In^-. As the color changes from yellow to blue over this pH range, this means that HIn is yellow and In^- is blue. The equivalence point for the titration of ethanoic acid (weak base) with potassium hydroxide (strong base) will occur at pH >7 so bromophenol blue would not be a suitable indicator.

12. B

The base dissociation constant for ethylamine is:

CH3CH2NH2(aq) + H2O(l) $\rightleftharpoons$ CH3CH2NH3$^+$(aq) + OH$^-$(aq)

$$K_b = \frac{\left[CH_3CH_2NH_3^{\ +}\right]\left[OH^-\right]}{\left[CH_3CH_2NH_2\right]}$$

13. C

For a conjugate acid-base pair, $K_w = K_bK_a$.

$$K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{6.8\times10^{-4}} = 1.5\times10^{-11}$$

14. A

$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

color A color B

Under acidic conditions, the equilibrium will lie to the left and color A will be observed. Under basic conditions the equilibrium will lie to the right and color B will be observed.

At the equivalence point $[HIn] = [In^-]$.

15. A

A salt will only dissolve in water to create an acidic solution if one of the ions is acidic.

Nitrate (NO_3^-), chloride (Cl^-) and sodium (Na^+) ions are all spectator ions and have no effect on pH.

Ethanoate (CH_3COO^-) and hydrogencarbonate (HCO_3^-) ions are basic and will form basic solutions. Ammonium (NH_4^+) is a weak acid so a solution of ammonium nitrate will be acidic.

16. C

A buffer solution contains a mixture of both components of a conjugate acid–base pair.

A contains an excess of base so it will form a basic buffer.

B contains two acids so will not form a buffer solution.

C will contain equal concentrations of CH_3COOH and CH_3COO^- and as it is made from a weak acid it will be an acidic buffer with $pH < 7$.

D is a mixture of a weak acid with a weak base that is not its conjugate and will react to form a salt.

17. **(a)** $K_w = [H^+][OH^-]$ (1)

(b) **(i)** $pK_a(HOCl) = 7.52$

OCl^- is the conjugate base of HOCl.

$$pK_b(OCl^-) = pK_w - pK_a(HOCl)$$

$$= 14.00 - 7.52$$

$$= 6.48$$

$$K_b(OCl^-) = 10^{-pK_b}$$

$$= 10^{-6.48}$$

$$= 3.3 \times 10^{-7}$$ (1)

(ii) Base dissociation reaction for hypochlorite, OCl^-, is:

$OCl^-(aq) + H_2O(l) \rightleftharpoons HOCl(aq) + OH^-(aq)$

$$K_b = \frac{[HOCl]\left[OH^-\right]}{\left[OCl^-\right]}$$

Let $[OH^-] = [HOCl] = x$:

$$K_b = \frac{x^2}{\left[OCl^-\right]}$$

$x_2 = K_b[OCl^-] = 3.3 \times 10^{-7} \times 0.705\ mol\ dm^{-3} = 2.3 \times 10^{-7}$

$x = \sqrt{2.3 \times 10^{-7}} = 4.8 \times 10^{-4}$

$[OH^-] = 4.8 \times 10^{-7}\ mol\ dm^{-3}$

The assumption is that the amount of protonation of OCl^- that occurs is negligible so that the initial $[OCl^-]$ is equal to the $[OCl^-]$ after the acid–base equilibrium is reached, i.e. $[OCl^-]_{eq} = [OCl^-]_{initial} - x \approx [OCl^-]_{initial}$. (3)

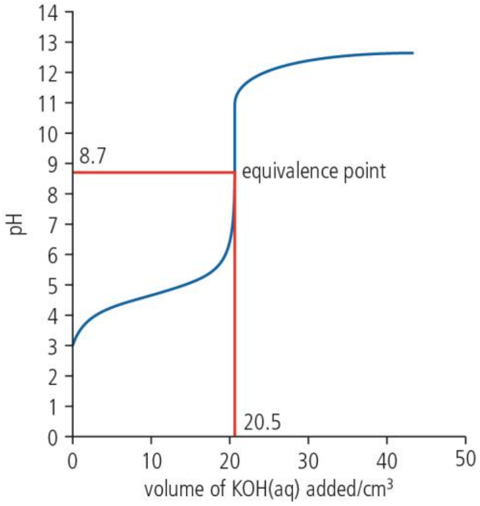
(iii) $K_w = [H^+][OH^-]$

$$\left[H^+\right] = \frac{K_w}{\left[OH^-\right]} = \frac{1.00 \times 10^{-14}}{4.8 \times 10^{-4}} = 2.1 \times 10^{-11}\ mol\ dm^{-3}$$

$pH = -\log[H^+] = -\log(2.1 \times 10^{-11}) = 10.68$ (2)

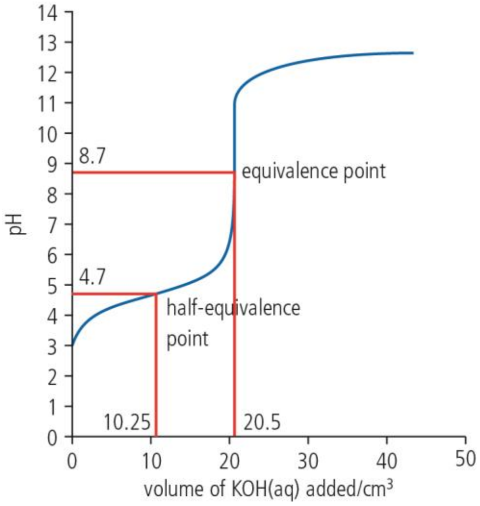
18. (a) (i) Note the question does not require a calculation but a recognition of how to interpret the data in the graph.

The equivalence point occurs at a volume of 20.5 cm_3 of KOH(aq) and a pH of 8.7. (2)



(ii) The pK_a can be found using the half-equivalence point, where half of the KOH(aq) required to reach the equivalence point has been added. At the half-equivalence point pH = pK_a(CH_3COOH).

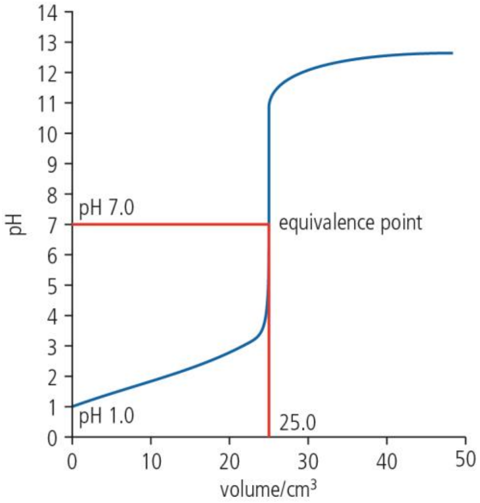
The half-equivalence point occurs at $\frac{20.5\ \text{cm}^3}{2} = 10.25\ \text{cm}^3$.



From the graph we see that the pH was 4.7 when 10.25 cm^3 had been added.

pK_a(CH_3COOH) = 4.7 (2)

(iii)



HNO_3 is a strong acid that dissociates completely. The starting concentration was 0.100 mol dm^{-3} so starting pH = –log(0.100) = 1.0.

Because the concentrations of HNO_3 and OH^- are the same, the equivalence point will occur after 25.0 cm^3 of OH^- has been added.

The equivalence point for the titration of a strong acid with a strong base occurs at pH = 7.0.

At the end of the titration, all of the acid has been neutralized and there is a large excess of the base solution. The pH of the titrated solution will start approaching the pH of the OH^- solution being added.

The concentration of the OH^- solution was 0.100 mol dm^{-3} so pOH = –log(0.100) = 1 and the pH of the OH^- solution is therefore 14 – 1 = 13. The final pH of the titrated solution will be in the pH range 12–13. (4)

(b) **(i)** An indicator (HIn) is a weak acid and the conjugate base (In^-) of the indicator has a different color to the acid.

The acid–base equilibrium of the indicator can be represented as:

$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$

color 1 color 2

In acidic solution the equilibrium lies to the left and the color of the solution will be that of the acid, HIn. As base is added and the equilibrium shifts to the right, the solution will change color to that of the conjugate base, In^-. (3)

(ii) The best indicator for the titration is one whose color change occurs within the steep portion of the titration curve.

From the graph provided, we can see that the best indicator for the titration of ethanoic acid with KOH(aq) will be phenolphthalein as its color change occurs within the pH range 8.2–10.0, which lies within the steep portion of the titration curve. (2)

19. **(a)** A strong acid dissociates completely in solution: $HA(aq) \rightarrow H^+(aq) + A^-(aq)$

From the examples provided HNO_3 is a strong acid: $HNO_3(aq) \rightarrow H^+(aq) + NO_3^-(aq)$

A weak acid dissociates partially in solution:

$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

From the examples provided HCN is a weak acid: $HCN(aq) \rightleftharpoons H^+(aq) + CN^-(aq)$ (3)

(b) $pK_a(HCN) = 9.21$

$K_a(HCN) = 10^{-pK_a} = 10^{-9.21} = 6.2 \times 10^{-10}$ (2)

From the acid dissociation reaction for HCN determined in **(a)**:

$$K_a(\text{HCN}) = \frac{[H^+][\text{CN}^-]}{[\text{HCN}]}$$

(c) The assumption necessary to determine [H^+] (and pH) is that the dissociation of HCN is negligible and $[HCN]_{eq} = [HCN]_{initial}$ at equilibrium, $[H^+] = [CN^-]$.

Let $[H^+] = x$, at equilibrium $[H^+] = [CN^-]$.

$$K_a(\text{HCN}) = \frac{x^2}{[\text{HCN}]}$$

$$6.2\times10^{-10} = \frac{x^2}{0.108}$$

$x_2 = 6.2 \times 10^{-11}$

$x = 8.2 \times 10^{-6}$

$[H^+] = 8.2 \times 10^{-6}$ mol dm^{-3}

pH = $-\log[H^+] = -\log(8.2 \times 10^{-6}) = 5.09$ (4)

20. (a) (i) Note here the importance of the equilibrium sign in the equation.

Acid: $H_2PO_4^-$;

(Conjugate) base: HPO_4^{2-};

No mark for NaH_2Po_4 or Na_2HPO_4

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}\ (aq)$

Acid: $H_2PO_4^-$

(conjugate) base: HPO_4^{2-}

No mark for NaH_2PO_4 or Na_2HPO_4

$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ (3)

(ii) Here the equation must show how the added OH^- reacts with the acid in the buffer and so is removed from the solution.

Strong base/OH^- replaced by weak base (HPO_4^{2-}, and effect minimized)/strong base reacts with acid of buffer/equilibrium in **(i)** shifts in forward direction (2)

(iii) This is a parallel question to **(ii)** above, but now must show how added H^+ reacts with the base in solution.

Strong acid/H^+ replaced by weak acid (H_2PO^{2-}, and effect minimized)/strong acid reacts with base of buffer/equilibrium in **(i)** shifts in reverse direction. (2)

(b) The IB mark scheme shows how the marks are gained here and the steps in the calculations.

(i) NH_3 weak(er) base/partial dissociation (2)

$[OH^-] < 0.1(0)$/pOH > 1 (thus pH < 13/ pH + pOH = 14)

(ii) around pH = 5

Accept a value between 4 and 6.

Strong acid–weak base titration, (thus acidic)/at equivalence point, NH_4^+ present is acidic/$NH_4^+ \rightleftharpoons NH_3 + H^+$ (2)

(iii) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Ignore state symbols, but equilibrium sign required.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \qquad (2)$$

(iv) $[NH_3] = [NH_4^+]$

(v) pOH = 14 – 9.25 = 4.75

pK_b (= pOH) = 4.75

$K_b = 1.76 \times 10^{-5}$

*Ignore units. Award (**3**) for correct answer.*

(vi) optimum/most effective/highest buffer capacity/50%-50% buffer/equally effective as an acidic buffer and as a basic buffer/OWTTE (1)

21. (a) $K_b = 10^{-5.77}/1.698 \times 10^{-6}$

OR

$$K_b = \frac{[N_2H_5^+] \times [OH-]}{[N_2H_4]}$$

$[OH^-]^2 = 1.698 \times 10^{-6} \times 0.0100 = 1.698 \times 10^{-8}$

OR

$[OH^-] = \sqrt{1.698 \times 10^{-8}} \geq 1.303 \times 10^{-4}$ mol dm^{-3}

$$pH = -\log_{10} \frac{1 \times 10^{-14}}{1.3 \times 10^{-4}} \geq 10.1 \qquad (3)$$

(b) This is a titration of a strong acid with a weak base so the pH at equivalence will be less than 7. Any indicator with a pK_a in this range will be suitable.

Methyl red ***OR*** Bromocresol green ***OR*** Bromophenol blue ***OR*** Methyl orange (1)

22. (a) weak acid – only partially / slightly ionized

strong acid – fully ionized (1)

(b) pH scale simpler numbers / avoids use of negative exponents (1)

(c) (i) This titration is weak acid with strong base, so equivalence point will be greater than 7. Phenolphthalein or phenol red have pK_a values in this range. (1)

(ii) n(NaOH) = 0.100 mol dm^{-3} solution of NaOH × 14.0/ 1000 dm^3 = 0.00140 mol NaOH (1)

(iii) reacting ratio $(COOH)_2$: NaOH = 1 : 2

Therefore $n(COOH)_2$ = 0.00140 / 2 = 0.00070 mol (1)

(iv) $M((COOH)_2.2H_2O)$ = 126.06 g mol^{-1}

Therefore $m((COOH)_2.2H_2O)$ in each 25.0 cm^3 sample = 0.00070 mol × 126.06 g mol^{-1} = 0.0882 g

m(impure solid) in each 25.0 cm^3 sample = 5.00 g × 25/1000 = 0.125 g

Therefore percentage purity = 0.0882 g/0.125 g × 100% = 70.56% (3)

23. **(a)** $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b(NH_3) = 1.78 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$[OH^-] = \sqrt{1.50 \times 1.78 \times 10^{-5}} = 5.17 \times 10^{-3}\left(\text{mol dm}^{-3}\right)$$

pH= (14 – pOH = 14 – 2.29 =) 11.71 (2)

(b) **(i)** solution which resists change in pH on the addition of small amounts of acid or base (2)

(ii) Two possible methods are shown in the IB mark scheme. In the first the equilibrium concentrations of the components of the buffer are calculated, after the HCl and NH_3 have reacted together. The calculation is then similar to that in part **(a)**. The second method uses the equation based on pK_b.

$$[NH_3] = \left(\frac{(1.50 \times 0.0200) - (0.500 \times 0.250)}{0.0450} = \right) 0.389\left(\text{mol dm}^{-3}\right)$$

$$[NH_4^+] = \left(\frac{(0.500 \times 0.250)}{0.0450} = \right) 0.278\left(\text{mol dm}^{-3}\right)$$

$$[OH^-] = \left(\frac{K_b[NH_3]}{[NH_4^+]} = \right) \frac{1.78 \times 10^{-5} \times 0.389}{0.278} = 2.49 \times 10^{-5}\left(\text{mol dm}^{-3}\right)$$

pH= (14 – pOH = 14 – 4.60 =) 9.40

OR

$$\text{pOH} = pK_b + \log\frac{[NH_4^+]}{[NH_3]} = pK_b + \log\frac{\left[\frac{12.5}{1000}\right]}{\left[\frac{17.5}{1000}\right]}$$

$$\text{pOH} = 4.75 + \log\frac{[12.5]}{[17.5]} = 4.75 - 0.146 = 4.604$$

pH = (14.0 –4.604 =) 9.40 (4)

(c) **(i)** The reacting ratio is 1:1 so the volume of NH_3 can be calculated from its concentration and molar amount.

$$(V(NH_3)= \frac{25.0 \times 0.500}{1.50} = 8.33 cm^3)$$

$V = V(NH_3) + V(HCl) = 8.33 + 25.0 = 33.3\ cm^3/0.0333\ dm^3$ (1)

(c) **(ii)** The IB mark scheme breaks down the marks awarded for the steps in the calculation. The relationship between pK_a and pK_b of a conjugate acid–base pair is used to calculate the pK_a of NH_4^+. Always check your answer makes sense - titration of weak base with strong acid will have pH < 7 at equivalence.

(NH_4 ions are present at equivalence point $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$ at equivalence $n(NH_4^+ \text{ produced}) = n(NH_3 \text{ added}) = n(HCl)$

$$\left[NH_4^+\right] = \frac{0.500 \times 0.0250}{0.0333} = 0.375\left(\text{mol dm}^{-3}\right)$$

$NH_4^+(aq) \rightleftharpoons NH_3(aq) + H^+(aq)$ or $NH_4^+(aq) + H_2O((l) \rightleftharpoons NH_3(aq) + H_3O^+ (aq)$

$pK_a(NH_4^+) = 14 - pK_b(NH_3) = 14.00 - 4.75 = 9.25)$

$$K_a = \frac{\left[NH_3\,(aq)\right]\left[H^+\,(aq)\right]}{\left[NH_4^+\,(aq)\right]} = 5.62 \times 10^{-10}$$

$$[H^+(aq)] = \sqrt{5.62 \times 10^{-10} \times 0.375} = 1.45 \times 10^{-5}\left(\text{mol dm}^{-3}\right)$$

pH = 4.84

(iii) Bromocresol green and methyl red have pK_a in range of 4.84. (1)

Reactivity 3.2

Exercises

1. B

This is the only equation where the reactants change oxidation state during the reaction.

$Zn(s) + 2HCl(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

0 +1 +2 0 Oxidation states

Zinc is oxidized from 0 → +2

Hydrogen is reduced from +1 → 0

2. C

The oxidation state of iron in $FeCl_3$, Fe_2O_3 and $Fe_2(SO_4)_3$ is +3

The oxidation state of iron $FeCO_3$ is +2.

3. C

Assigning oxidation states:

$MnO_2(s) + 2Cl^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + Cl_2(g) + 2H_2O(l)$

+4 –1 +2 0

MnO_2 undergoes reduction as the oxidation state of Mn decreases.

$Cl^-(aq)$ is the reducing agent as the oxidation state of Cl increases.

4. The oxidation states numbers are assigned following the strategy in the text. In most of these, it is best to assign the values for O [–2] and H [+1] first, and then assign values to the remaining elements so that the net charge = the charge on the species (or is zero in the case of neutral species).

(a) CH_4: C = −4, H = +1

(b) $CuSO_4$: Cu = +2, S = +6, O = −2

(c) C_2H_4: H = +1, O = −2

(d) CO: C = +2, O = −2

(e) $K_2Cr_2O_7$: K = +1, Cr = +6, O = −2

(f) K_2CrO_4: K = +1, Cr = +6, O = −2

(g) H_2O_2: H = +1, O = −1

(h) C_4H_{10}: C = −2.5, H = +1

5. **(a)** $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

oxidation: Sn +2 → +4, so $Sn^{2+}(aq)$ is oxidized reduction: Fe +3 → +2, so $Fe^{3+}(aq)$ is reduced

(b) $2FeCl_2(aq) + Cl_2(aq) \rightarrow 2FeCl_3(aq)$

+2 −1 0 +3 −1

oxidation: Fe +2 → +3, so $2FeCl_2(aq)$ is oxidized

reduction: Cl 0 → –1, so $Cl_2(aq)$ is reduced

(c) $2H^+(aq) + S_2O_3^{2-}(aq) \rightarrow S(s) + SO_2(g) + H_2O(l)$

+1 +2 −2 0 +4 −2 +1 −2

oxidation: S +2 → +4, so $S_2O_3^{2-}(aq)$ is oxidized

reduction: S +2 → 0, so $S_2O_3^{2-}(aq)$ is also reduced

(d) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$

+1 −1 +1 −2 0

oxidation: O −1 → 0, so $H_2O_2(aq)$ is oxidized

reduction: O −1 → −2, so $H_2O_2(aq)$ is also reduced

(e) $I_2(aq) + SO_3^{2-}(aq) + H_2O(l) \rightarrow 2I^-(aq) + SO_4^{2-}(aq) + 2H^+(aq)$

0 +4 −2 +1 −2 −1 +6 −2 +1

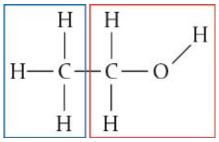
oxidation: S +4 → +6, so $SO_3^{2-}(aq)$ is oxidized

reduction: I 0 → −1, so $I_2(aq)$ is reduced

6. **(a)** assign H = +1, O = −2

Therefore, in ethanol, $(6 \times +1) + -2 + (2 \times C) = 0$, so C = −2

This is an average value as the two carbon atoms are not equivalent.



We can divide the molecule into two regions, each with a zero charge.

For the carbon atom in the red region (CH_2OH), $C + (3 \times +1) + -2 = 0$, so C = −1

For the carbon atom in the blue region (CH_3), $C + (3 \times +1) = 0$, so C = −3

The average oxidation state = $\frac{-3 + -1}{2} = -2$ as expected.

(b) In CO_2, the oxidation state of C is +4

Ethanol is oxidized:

- the elements have combined with oxygen
- hydrogen has been removed
- the oxidation state of carbon has increased from –2 to +4

- the electron density of the carbon atom has reduced but no electron loss has led to production of positive ions.

7. **(a)** reducing agent = $H_2(g)$; oxidizing agent = $Cl_2(g)$

(b) reducing agent = $Al(s)$; oxidizing agent = $PbCl_2(s)$

(c) reducing agent = $KI(aq)$; oxidizing agent = $Cl_2(aq)$

(d) reducing agent = $CH_4(g)$; oxidizing agent = $O_2(g)$

8. A

To balance the equations:

Step		$MnO_4^-(aq) + SO_3^{2-}(aq) + H^+(aq) \rightarrow$ $Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2O(l)$
1	Deduce the oxidation states for the elements in each species	+7 +4 +1 +2 +6 +1 −2 −2 −2 −2
2	Deduce which element is oxidized and which species is reduced.	*Oxidation*: $SO_3^{2-} \rightarrow SO_4^{2-}$ S changes oxidation state from +4 to +6 *Reduction:* $MnO_4^- \rightarrow Mn^{2+}$ Mn changes oxidation state from +7 to +2
3	Deduce half-equations for the oxidation and reduction half reactions.	*Oxidation:* $SO_3^{2-} \rightarrow SO_4^{2-} + 2e^-$ *Reduction:* $MnO_4^- + 5e^- \rightarrow Mn^{2+}$
4	Balance the electrons in both processes:	$5SO_3^{2-} \rightarrow 5SO_4^{2-} + 10e^-$ $2MnO_4^- + 10e^- \rightarrow 2Mn^{2+}$
5	Add the half-equations	$5SO_3^{2-} + 2MnO_4^- \rightarrow 5SO_4^{2-} + 2Mn2^+$
6	The Os are balanced by adding H_2O to the product side.	$5SO_3^{2-} + 2MnO_4^- \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 3H_2O$
7	As the reaction is in acidic conditions the Hs are balanced by adding H^+ to the reactant side.	$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq)$ $\rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$ Note that the charges are balanced (6–)

$5SO_3^{2-}(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 5SO_4^{2-}(aq) + 2Mn^{2+}(aq) + 3H_2O(l)$

5 mol 2 mol

1 mol 0.4 mol

9. C

$MnO_4^-(aq) + H_2O_2(aq) + H^+(aq) \rightarrow Mn^{2+}(aq) + H_2O(l) + O_2(g)$

+7 –1 +1 +2 +1 0

–2 +1 –2

Oxidation: $H_2O_2(aq) \rightarrow O_2(g) + 2e^-$

O changes oxidation state from –1 to 0 so 1 electron released for each oxygen

Reduction: $MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq)$

Mn changes oxidation state from +7 to +2 sp 5 electrons needed

$5H_2O_2(aq) \rightarrow 5O_2(g) + 10e^- \rightarrow \quad 2MnO_4^-(aq) + 10e^- \rightarrow 2Mn^{2+}(aq)$

Adding the equations and balancing the Os by adding H_2O to the product side.

$5H_2O_2(aq) + 2MnO_4^-(aq) \rightarrow 2Mn^{2+}(aq) \rightarrow 5\,O_2(g) + 8H_2O(l)$

Adding the equations and balancing the Hs by adding H^+ to the reactant side.

$5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$

5 mol 2 mol

2.5 mol 1 mol

10 Assign oxidation states to the elements on both sides of the equation and use these to deduce what is being oxidized and what is reduced. Then separate these into half-equations. Remember to balance the charge of each half-equation by adding electrons – to the reactants side in reduction half-reactions, and to the products side in oxidation half-reactions.

(a) $Ca(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + H_2(g)$

0 +1 +2 0

oxidation: $Ca(s) \rightarrow Ca^{2+}(aq) + 2e^-$

reduction: $2H^+(aq) + 2e^- \rightarrow H_2(g)$

(b) $2Fe^{2+}(aq) + Cl_2(aq) \rightarrow 2Fe^{3+}(aq) + 2Cl^-(aq)$

+2 0 +3 −1

oxidation: $2Fe^{2+}(aq) \rightarrow 2Fe^{3+}(aq) + 2e^-$

reduction: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

(c) $Sn^{2+}(aq) + 2Fe^{3+}(aq) \rightarrow Sn^{4+}(aq) + 2Fe^{2+}(aq)$

+2 +3 +4 +2

oxidation: $Sn^{2+}(aq) \rightarrow Sn^{4+}(aq) + 2e^-$

reduction: $2Fe^{3+}(aq) + 2e^- \rightarrow 2Fe^{2+}(aq)$

(d) $Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$

0 −1 −1 0

oxidation: $2Br^-(aq) \rightarrow Br_2(aq) + 2e^-$

reduction: $Cl_2(aq) + 2e^- \rightarrow 2Cl^-(aq)$

11. **(a)** $2I^-(aq) + HSO_4^-(aq) + 3H^+(aq) \rightarrow I_2(aq) + SO_2(g) + 2H_2O(l)$

(b) $I_2(aq) + 5OCl^-(aq) + H_2O(l) \rightarrow 2IO_3^-(aq) + 5Cl^-(aq) + 2H^+(aq)$

(c) $2MnO_4^-(aq) + 5H_2SO_3(aq) \rightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 3H_2O(l) + 4H^+(aq)$

12. **(a)** solution changes from purple to colorless

($KMnO_4$ is purple and Mn^{2+} ions are very pale pink).

(b) $C_2O_4^{2-}(aq) \rightarrow 2CO_2(g) + 2e^-$

(c) $MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$

(d) $2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 10CO_2(g)$

Multiply equation **(b)** by 5 and equation **(c)** by 2 so that when added together the electrons cancel out.

(e) 6.16×10^{-3}

moles of $KMnO_4$ ions $= 0.100 \times \frac{24.65}{1000} = 2.465 \times 10^{-3}$

hence moles of oxalate ions $= 2.465 \times 10^{-3} \times \frac{5}{2} = 6.16 \times 10^{-3}$

(since oxalate reacts with permanganate in the ratio of 5 to 2)

(f) 6.16×10^{-3}

Moles of Ca^{2+} in original sample $= 6.16 \times 10^{-3}$
(since the ratio of calcium ions to carboxylate ions is 1 to 1)

(g) 24.6%

mass of calcium chloride $= (6.16 \times 10^{-3}) \times 110.98 = 0.68$ g

hence percentage of calcium chloride in original mixture $= \frac{0.68}{2.765} \times 100\% = 24.6\%$

13. **(a)** 0.117%

moles of $K_2Cr_2O_7 = 0.0550 \times \frac{9.25}{1000} = 5.09 \times 10^{-4}$

This reacts with 2.54×10^{-4} moles of C_2H_5OH
(as $K_2Cr_2O_7$ and C_2H_5OH react in the ratio 2 : 1).

mass of $C_2H_5OH = (2.54 \times 10^{-4}) \times 46.08 = 0.0117$ g

Therefore, percentage by mass $= \frac{0.0117}{10.000} \times 100 = 0.117\%$

(b) solution changes from orange to green

the chromium is reduced from an oxidation state of +6(orange) to +3(green).

14. D

From the activity series Na is more reactive than Zn. There is no reaction.

15. B

From reaction 1 we can deduce that Q is more reactive than P.

From reaction 2 we can deduce that Q is more reactive than R.

Q is the most reactive.

From reaction 3 we can deduce that R is more reactive than P.

P is the least reactive.

16. **(a)** $CuCl_2(aq) + Ag(s)$; no reaction

Cu is a more reactive metal than Ag

(b) $3Fe(NO_3)_2(aq) + 2Al(s) \rightarrow 2Al(NO_3)_3(aq) + 3Fe(s)$

Al is a more reactive metal than Fe, so is able to reduce Fe^{2+}

(c) $2NaI(aq) + Br_2(aq) \rightarrow 2NaBr(aq) + I_2(aq)$

Br is a more reactive non-metal than I, so is able to oxidize I^-

(d) $KCl(aq) + I_2(aq)$; no reaction

Cl is a more reactive non-metal than I

17. **(a)** W > X > Y > Z

Reaction	**Deduction**	**Reaction**	**Deduction**
$W + X^+ \rightarrow W^+ + X$	W>X	$Y^+ + Z \rightarrow$ no reaction	Y > Z
$X + Z^+ \rightarrow X^+ + Z$	X>Z	$X + Y^+ \rightarrow X^+ + Y$	X > Y

(b) **(i)** no reaction

Y is less reactive than W

(ii) no reaction

Z is less reactive than W

18. C

Ag is less reactive than H. It does not produce hydrogen when added to dilute acids.

Fe and Zn are more reactive than H. They do produce hydrogen when added to dilute acids.

19. B

Acids react with reactive metals to produce hydrogen gas and a salt.

20. **(a)** $2Al(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2(g)$

$2Al(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2(g)$

(b) $Mg(s) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + H_2(g)$

$Mg(s) + 2H^+(aq) \rightarrow Mg^{2+}(aq) + H_2(g)$

(c) $Zn(s) + 2CH_3CO_2H(aq) \rightarrow Zn(CH_3CO_2)_2 + H_2(g)$

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

21. The steps for writing the redox equations are given in the text.

The interim steps for each of these examples are given below:

(a) $Zn(s) + SO_4^{2-}(conc.) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

Assign oxidation states and determine what is being oxidized and reduced:

$Zn(s) + SO_4^{2-}(aq) \rightarrow Zn^{2+}(aq) + SO_2(g)$

0 +6 +2 + 4 oxygen is –2 in reactants and products.

Zn is being oxidized and S is being reduced.

Half-equations:

oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$ reduction: $SO_4^{2-} + 4H^+ + 2e^- \rightarrow SO_2 + 2H_2O$

Electrons are equal (2) in the two half-equations so add half-equations together:

$Zn(s) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow Zn^{2+}(aq) + SO_2(g) + 2H_2O(l)$

(b) $NO_3^-(conc.) + 4Zn(s) + 10H^+(aq) \rightarrow NH_4^+(aq) + 4Zn^{2+}(aq) + 3H_2O(l)$

Assign oxidation states:

$NO_3^-(aq) + Zn(s) \rightarrow NH_4^+(aq) + Zn^{2+}(aq)$

+5 0 –3+2 oxygen is –2 and hydrogen +1 in reactants and products

N is being reduced and Zn is being oxidized.

Half-equations:

reduction: $NO_3^- + 10H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$ oxidation: $Zn \rightarrow Zn^{2+} + 2e^-$

Multiply oxidation half-equation by 4 to equalize electrons in the two half-equations and add half-equations together:

$4Zn(s) + NO_3^-(aq) + 10H^+(aq) \rightarrow 4Zn^{2+}(aq) + NH_4^+(aq) + 3H_2O(l)$

(c) $2NO_3^-(aq) + 3Cu(s) + 8H^+(aq) \rightarrow 2NO(aq) + 3Cu^{2+}(aq) + 4H_2O(l)$

Assign oxidation states:

$NO_3^-(aq) + Cu(s) \rightarrow NO(g) + Cu^{2+}(aq)$

+5 0 +2 +2 oxygen is –2 in reactants and products

N is reduced and Cu is oxidized.

Half-equations:

reduction: $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$ oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$

Multiply reduction half-equation by 2 and oxidation half-equation by 3 to equalize electrons in the two half-equations and add half-equations together:

$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O(l)$

(d) $2NO_3^-(conc.) + Cu(s) + 4H^+(aq) \rightarrow 2NO_2(g) + Cu^{2+}(aq) + 2H_2O(l)$

Assign oxidation states:

$NO_3^-(aq) + Cu(s) \rightarrow NO_2(g) + Cu^{2+}(aq)$

+5 0 +4 +2 oxygen is –2 in reactants and products

N is reduced and Cu is oxidized.

Half-equations:

reduction: $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$

Multiply reduction half-equation by 2 and add half-equations together:

$2NO_3^- + Cu + 4H^+ \rightarrow 2NO_2 + Cu^{2+} + 2H_2O$

22. A

Positive electrode in electrolytic cell	Negative ions are attracted to the electrode. The negative ions are discharged. They lose electrons and are oxidized.
Positive electrode in voltaic cell	Electrons are attracted from the external circuit. Positive ions gain electrons gain electrons and reduced.

23. D

The reaction in an electrolytic cell is not spontaneous. It needs electrical energy to drive the change.

In a voltaic cell electron are produced at the negative electrode by an oxidation reaction. For example: $Zn(s) \rightarrow Zn^{2+}(s) + 2e^-$

24. **(a)** Zn is a more reactive metal than Fe, so is oxidized

Zn / Zn^{2+} is anode; $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

Fe / Fe^{2+} is cathode; $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(b) Mg is a more reactive metal than Fe, so is oxidized

Mg / Mg^{2+} is the anode; $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

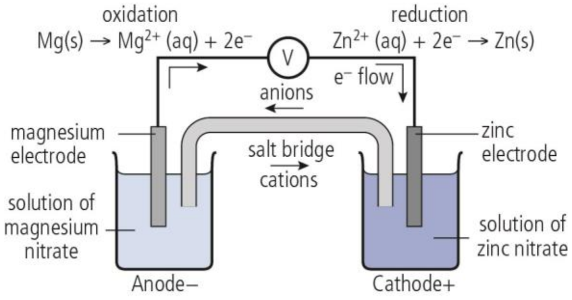
Fe / Fe^{2+} is the cathode; $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$

(c) Mg is a more reactive metal than Cu, so is oxidized

Mg / Mg^{2+} is the anode; $Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

Cu / Cu^{2+} is the cathode; $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

25. **(a)** Mg is a more reactive metal than Zn so will be oxidized in the voltaic cell.



(b) $Mg(s)\ |\ Mg^{2+}(aq)\ ||\ Zn^{2+}(aq)\ |\ Zn(s)$

26. Fe is more reactive than Cu and so will reduce Cu^{2+} ions in solution.

The iron spatula would slowly dissolve as it is oxidized to Fe^{2+} ions. Copper metal (red/brown) would precipitate as Cu^{2+} ions are reduced. The blue color of the solution would fade, as Cu^{2+} ions are removed.

27. **(a)** Oxidation number increases from 0 to +2. Pb(s) is oxidized.

(b) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

(c) $PbSO_4$ is insoluble: the Pb^{2+} ions do not disperse into solution.

(d) Advantage: delivers large amounts of energy over short periods; rechargeable.

Disadvantage: heavy mass; lead and sulfuric acid could cause pollution.

28. **(a)** $CH_3OH(aq) + H_2O(l) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$

(b) $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$

(c) Advantage: does not need to be recharged, less hazardous if broken/exposed to the environment, weighs less for same energy output

Disadvantage: more expensive, needs constant supply of fuel, methanol fuel cells produce carbon dioxide, does not produce high current

29. **(a)** $H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

(b) Fuel cells (and an electric motor) are more efficient as less waste heat produced and more chemical energy converted to useful electrical energy. They may also use a renewable energy source, which is more efficient.

(c) All convert chemical energy **directly** into electrical energy

30. D

Potassium ions are attracted to the cathode which has a negative charge.

31. B

1 is the positive electrode. Electrons are lost and oxidation occurs.

2 is the molten ionic compound where ions migrate.

3 is the external circuit where electron move from the negative terminal to the positive terminal(clockwise).

32. D

Chloride ions are oxidized at the anode.

33. The question is best tackled by:

- writing out the formula for the ions present in each compound
- stating that negative ions are oxidized at the anode
- stating that positive ions are reduced at the cathode
- writing the equations by adding (reduction) or losing (oxidation) the appropriate number of electrons to form the neutral element.

(a) at anode: $2Br^-(l) \rightarrow Br_2(l) + 2e^-$

at cathode: $2K^+(l) + 2e^- \rightarrow 2K(l)$

(b) at anode: $2F^-(l) \rightarrow F_2(g) + 2e^-$

at cathode: $Mg^{2+}(l) + 2e^- \rightarrow Mg(l)$

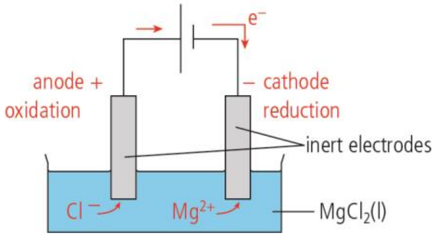
(c) at anode: $S^{2-}(l) \rightarrow S(l) + 2e^-$

at cathode: $Zn^{2+}(l) + 2e^- \rightarrow Zn(l)$

(d) at anode: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

at cathode: $Ca^{2+}(l) + 2e^- \rightarrow Ca(l)$

34. **(a)**



(b) anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$

cathode: $Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$

overall: $Mg^{2+}(aq) + 2Cl^-(aq) \rightarrow Mg(s) + Cl_2(g)$

35. C

$CH_3CH_2CH(OH)CH_3$ is a secondary alcohol. It is oxidized to the ketone: $CH_3CH_2COCH_3$

36. C

Primary alcohols, such as propanol, are oxidized by acidified potassium dichromate first producing an aldehyde and then a carboxylic acid:

$$CH_3CH_2CH_2OH(aq) \xrightarrow{[O]} CH_3CH_2CHO(aq) \xrightarrow{[O]} CH_3CH_2COOH(aq)$$

Both $CH_3CH_2CH_2OH$ and CH_3 CH_2COOH can form intermolecular hydrogen bonds and are less volatile than CH_3 CH_2CHO which can be distilled off as it is formed. If the ethanal is to be oxidized further the mixture is refluxed with excess oxidizing agent.

37. B

The molecules have a similar molecular formula with the same number of electrons.

The difference in boiling points is due to significant differences like hydrogen bonding:

The only molecule with intermolecular hydrogen bonding is $CH_3CH_2CH_2OH$.

38. Balance the carbons and hydrogen from left to right.

And then balance the oxygens from right to left.

$C_4H_9OH(l) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$

$C_5H_{11}OH(l) + 7.5O_2(g) \rightarrow 5CO_2(g) + 6H_2O(g)$

39. When the organic compound is oxidized the dichromate(VI) solution is reduced to Cr^{3+} and the color changes from orange to green.

(a) butanone; orange → green

(b) methanal; orange → green

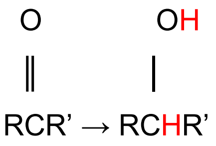
(c) no reaction; no color change

40. B

Carboxylic acids can be reduced to aldehydes.

41. C

Draw the condensed formula with carbonyl group and add H atoms to the carbonyl group:



$$R\overset{\overset{O}{\|}}{C}R' \rightarrow R\overset{\overset{OH}{|}}{C}HR'$$

Ketones are reduced to secondar alcohols.

42. **(a)** Use $LiAlH_4$ in dry ether and heat. The acid is reduced first to the aldehyde and then to the alcohol.

$$CH_3CH_2COOH \xrightarrow{+H} CH_3CH_2CH_2OH$$

(b) Ethanal is heated with $NaBH_4(aq)$.

$CH_3CHO \xrightarrow{+H} CH_3CH_2OH$

43. $CH_3CHO \rightarrow CH_3CH_2OH$

Average oxidation state of C in ethanal = $\frac{(-4+2)}{2} = -\frac{2}{2}$ = −1

Average oxidation state of C in ethanol = $\frac{(-6+2)}{2} = -\frac{4}{2}$ = −2

The carbon atoms decrease their average oxidation state by 1, so 2 electrons are needed:

$CH_3CHO + 2e^- \rightarrow CH_3CH_2OH$

Add $2H^+$ to balance the charges:

$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_3OH$

44. Hydrogenation (of vegetable oils) with nickel catalyst.

Oils are liquid as they contain unsaturated fatty acid chains with C=C.

Margarines are solids as they contain saturated fatty acid chains with C–C.

Double bond has restricted rotation which gives molecule kinks, which restricts packing of molecules and reduces intermolecular forces.

Saturated compounds can pack more effectively and have stronger intermolecular forces.

45. **(a)** $CH_3COCH_3 \rightarrow CH_3CH(OH)CH_3$

Ketones are reduced to secondar alcohols.

(b) $CH_3CO_2H \rightarrow CH_3CH_2OH$

Carboxylic acids are reduced to primary alcohols.

(c) $CH_2CHCl \rightarrow CH_3CH_2Cl$

The carbon–carbon double bond is hydrogenated.

$CH_2{=}CHCl + H_2 \rightarrow CH_3CH_2Cl$

(d) $C_3H_4 \rightarrow C_3H_8$

The 2 pi bonds are hydrogenated.

$CH_2{=}C{=}CH_2 + 2H_2 \rightarrow CH_3CH_2\,CH_3$ or $CH{\equiv}CCH_3 + 2\,H_2 \rightarrow CH_3CH_2\,CH_3$

46. B

The standard hydrogen electrode operating conditions are 1 mol dm^{-3} $H^+(aq)$ in solution and 100 kPa for $H_2(g)$, temperature = 298 K).

1.0 mol dm^{-3} $H_2SO_4(aq)$ does not correspond to 1.0 mol dm^{-3} $H^+(aq)$ as $H_2SO_4(aq)$ is a dibasic acid: an acid which produces two H^+ ions in solution for each molecule.

47. A

Dividing the reaction, $Mg(s) + ZnSO_4(aq) \rightarrow MgSO_4(aq) + Zn(s)$, into half reactions:

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$	$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$
The magnesium atoms lose electrons.	The mass of the zinc electrode increases.
The number of positive ions is increasing.	The number of positive ions is decreasing.

Sulfate ions migrate from the zinc electrode to the magnesium electrode to balance the movement of positive ions.

48. B

From the cell diagram which is consistent with the relative reactivity of Q and R.

$Q(s) \rightarrow Q^{2+}(aq) + 2e^-$	$R^{2+}(aq) + 2e^- \rightarrow R(s)$
The number of positive ions is increasing.	The number of positive ions is decreasing.

Electrons flow in the external circuit from Q to R.

Positive ions flow through the salt bridge from Q to R.

Ions not electrons flow through the salt bridge.

49. C

From the cell diagram which is consistent with the relative reactivity of Q and R

$W(s) \rightarrow W^{2+}(aq) + 2e^-$	$X^{2+}(aq) + 2e^- \rightarrow X(s)$

Electrons flow in the external circuit from W to X.

W is oxidized $E^\ominus$

50. $E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell}}$ where Cd^{2+} reduced − $E^\ominus_{\text{half-cell}}$ where Cr oxidized

From the given standard electrode potential values, first deduce in which half-cell reduction will occur.

Due to its higher (less negative) *E* value, it will be the Cd cell. So now the *E* values can be substituted.

$E(Cd^{2+}) - E(Cr^{3+}) = -0.40 - (-0.75) = +0.35$ V

51. A

The strongest oxidizing agent is the species which most readily accepts electrons.

It is the oxidized species in the half reaction with the most positive electrode potential: Sn^{2+}

52. BrO_3^- will be reduced (higher $E^\ominus$ value); I^- will be oxidized.

Cell reaction:

$BrO_3^-(aq) + 6H^+(aq) + 6I^-(aq) \rightarrow Br^-(aq) + 3H_2O(l) + 3I_2(s)$

$E^\ominus_{\text{cell}} = E^\ominus_{BrO3-} - E^\ominus_{I2} = +1.44 - (+0.54) = +0.90\ \text{V}$

53. strongest oxidizing agent Cu^{2+}; strongest agent Mg

The strongest oxidizing agent is the species which most readily accepts electrons.

It is the oxidized species in the half reaction with the most positive electrode potential: Cu^{2+}

The strongest reducing agent is the species which most readily donates electrons.

It is the reduced species in the half reaction with the most negative electrode potential: Mg

54. **(a)** no reaction

I_2 has a greater tendency to be reduced but Cu^{2+} cannot be oxidized.

(b) reaction occurs: $BrO_3^-(aq) + 6H^+(aq) + 3Cd(s) \rightarrow Br^-(aq) + 3H_2O(l) + 3Cd^{2+}(aq)$

$E^\ominus_{\text{cell}} = E^\ominus_{\text{half-cell}}$ where BrO_3 − reduced $- E^\ominus_{\text{half-cell}}$ where Cd oxidized $= 1.44 - (-0.40)$

$= 1.84\ \text{V}$

BrO_3^- will be reduced while Cd will be oxidized, The E_{cell} will be > 0, therefore spontaneous.

(c) no reaction

As given in the question, Cr would be oxidized and Mg^{2+} would be reduced so

$E_{\text{cell}} = -2.37 - (-0.75) < 0$ therefore non-spontaneous.

55. B

If $E^\ominus$ is positive, $\Delta G^\ominus = -nFE^\ominus$, $\Delta G^\ominus$ is negative

If $\Delta G^\ominus$ is negative, $\Delta G^\ominus = -RT \ln K$, $K >> 1$

56. −270 kJ

$\Delta G = -nFE^\ominus$

$n = 3$ (as 3 moles of electrons are transferred)

$F = 96\,500\ (\text{C mol}^{-1})$

$E^\ominus = 0.92\ \text{V}$

Therefore $\Delta G = -3 \times 96\,500 \times 0.92 = -270\,000\ \text{J} = -270\ \text{kJ}$

57. C

Species present at negative electrode (Cathode)		**Species present at positive electrode (Anode)**	
$Cu^{2+}(aq)$	$H_2O(l)$	$Cl^-(aq)$	$H_2O(l)$
Reaction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$		*Reaction:* $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	

58. B

Negative electrode (Cathode)		**Positive electrode (Anode)**	
$MgI_2(l)$	**$MgI_2(aq)$**	**$MgI_2(l)$**	**$MgI_2(aq)$**
Mg^{2+} discharged $Mg(s)$ produced	$H_2O(l)$ reduced $H_2(g)$ produced	I^- oxidized $I_2(g)$ produced	

59.

	Cathode	**Anode**
Ions present	$K^+(aq)$,	$F^-(aq)$,
Relevant half reactions	H^+ has a higher $E^\ominus$ than K^+ H_2O gains electrons most readily as has higher $E^\ominus$ and so is preferentially reduced: $H_2(g)$ is produced	$H_2O(l)$ has a lower $E^\ominus$ than F^- $H_2O(l)$ loses electrons most readily as it has lower $E^\ominus$ and so is preferentially oxidized: $O_2(g)$ is produced.
Reaction at electrode	$H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$
Products	$H_2(g)$	$O_2(g)$

The overall balanced equation is: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

60 **(a)** At the anode, bubbles of gas emitted; at the cathode, pinky brown layer of copper metal deposited. The blue color of the solution fades.

Equations at anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ **or** $4OH^- \rightarrow 2H_2O(l) + O_2(g) + 4e^-$

Depending on the concentration of the solution.

Equations at cathode: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Blue color fades as the concentration of Cu^{2+} ions in solution decreases.

(b) Reaction at the cathode would be the same with copper deposited on the copper electrode. Reaction at the anode would be different: the copper electrode disintegrates as it is oxidized releasing Cu^{2+} ions into the solution. The blue color of the solution would not change as Cu^{2+} ions are produced and discharged at an equal rate.

61. During electrolysis of NaCl(aq) at the cathode. $H_2O(l)$ is reduced:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

62. D

The object to be plated must be a conductor and placed at the negative electrode.

The metal used to plate the object should be at the anode.

63. The mass of the silver anode will decrease as Ag is oxidized to Ag^+ ions that are released into the solution. The mass of the cathode will increase as a layer of Ag is deposited. Impurities may be visible collecting as a sludge at the bottom of the electrolyte as they fall from the decomposing anode.

Challenge yourself

1. assign H = +1 and O = −2, with C variable

For $C_6H_{12}O_6$, $6 \times C + (12 \times +1) + (6 \times -2) = 0$, so C = 0

$6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6O_2(g)$

+4 −2   +1 −2   0 +1 −2   0

oxidation: O −2 → 0, so $6H_2O(l)$ is oxidized

reduction: C +4 → 0, so $CO_2(g)$ is reduced

2. H_2O_2: H = +1, O = −1

The oxidation state for oxygen is −1, which is halfway between 0 (element) and −2 (usual oxidation state in compounds). The oxygen can be oxidized (to 0) or reduced (to −2). It will more easily be reduced from −1 to −2 as it is a very electronegative element, and so acts mainly as an oxidizing agent.

3. $3I_2(aq) + 6KOH(aq) \rightarrow 5KI(aq) + KIO_3(aq) + 3H_2O(l)$

I changes from 0 (in I_2) to −1 (in KI), which is reduction.

I changes from 0 (in I_2) to +5 (in KIO_3), which is oxidation.

These changes occur simultaneously.

4.

Most active								Least active
Mg	Al	C	Zn	Fe	Pb	H_2	Cu	Ag

Carbon is more reactive than Zn and Fe as it can remove oxygen from their oxides.

Carbon is less reactive than aluminium as electricity is needed for the extraction of aluminium.

Hydrogen is more reactive than copper, as copper metal does not react with dilute acids, but less reactive than lead.

5. At the negative electrode (anode); $H_2(g)$ is oxidized:

$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$

At the positive electrode (cathode) $O_2(g)$ is reduced:

$2H_2O(l) + O_2(g) + 4e^- \rightarrow 4OH^-$

6 **(a)** efficiency = $\frac{237}{286} \times 100\% = 82.9\%$

(b) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$

$\Delta H_f^\ominus$ (kJ mol^{-1}) = −242 kJ mol^{-1}

$\Delta G_f^\ominus$ (kJ mol^{-1}) = −229 kJ mol^{-1}

efficiency $\frac{229}{242} \times 100\% = 94.6\%$

(c) Efficiency = $\frac{-\Delta G_{sys}}{-\Delta H_{sys}} \times 100\% = \frac{-\Delta H_{sys} + T\Delta S_{sys}}{-\Delta H_{sys}} \times 100 = 1 + \frac{T\Delta S_{sys}}{-\Delta H_{sys}}$

The entropy decrease is smaller for the reaction which produces one mole of gaseous water, which leads to a larger efficiency.

7. At the anode, oxide ions are oxidized:

$2O^{2-}(l) \rightarrow O_2(g) + 4e^-$

The oxygen is produced at the carbon anode at the operating temperature of around 800°C, so the carbon reacts: $C(s) + O_2(g) \rightarrow CO_2(g)$

8. Aluminium oxide has some covalent character, as aluminium has quite a high electronegativity (1.6).

9. Oxidation state of hydrogen in both compounds = +1

In propane (8 hydrogens) the average oxidation state of C = $-\frac{8}{3}$

In propene (6 hydrogens) the average oxidation state of C = $-\frac{6}{3} = -2$

Combustion of propane involves a bigger change of oxidation state and more oxygen is needed.

10 Consider first the oxidation reaction: ethanol → ethanal

The average oxidation state of C in ethanol (C_2H_6O) = $\frac{(-6+2)}{2}$ −2

The average oxidation state of C in ethanal (C_2H_4O) = $\frac{(-4+2)}{2} = -1$

As both carbon atoms increase their oxidation state by +1 (from −2 to −1), two electrons are released:

$C_2H_5OH \rightarrow CH_3CHO + 2e^-$

Add $2H^+$ to balance the charges:

$C_2H_5OH \rightarrow CH_3CHO + 2e^- + 2H^+$

Reduction: $Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

To deduce the overall reaction, balance the number of electrons in the half reactions, so need 3 × the ethanol/ethanal equation:

$Cr_2O_7^{2-} + 6e^- + 14H^+ \rightarrow 2Cr^{3+} + 7H_2O$

$3C_2H_5OH \rightarrow 3CH_3CHO + 6e^- + 6H^+$

add and simplify:

$Cr_2O_7^{2-} + \cancel{6e^-} + 14H^+ + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO + \cancel{6e^-} + 6H^+$

$Cr_2O_7^{2-} + 8H^+ + 3C_2H_5OH \rightarrow 2Cr^{3+} + 7H_2O + 3CH_3CHO$

11. $HCHO \rightarrow \rightarrow CH_3OH$

The oxidation state of C in methanal = −2 + 2= 0

The oxidation state of C in methanol = −4 + 2 = −2

The carbon atom decreases its oxidation state by 2, so 2 electrons are needed:

$HCHO + 2e^- \rightarrow CH_3OH$

Add $2H^+$ to balance the charges:

$HCHO + 2H^+ + 2e^- \rightarrow CH_3OH$

12. $n_{H2} = \frac{1}{2} \times [2n + 2 - p - s + t]$

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

For C_nH_p:

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

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

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:

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

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 H_2 molecules needed by 1:

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

For $C_nH_pO_qN_rX_s$:

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

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

13 Charge per e^- = 1.602177×10^{-19} C

Electrons per mole = 6.02×10^{23} mol^{-1}

Therefore, charge per mole = $1.602177 \times 10^{-19}\ \text{C} \times 6.02 \times 10^{23}\ \text{mol}^{-1} = 96451.06\ \text{C mol}^{-1}$

14 $\Delta G = -RT \ln K_c$ and $\Delta G = -nFE_{cell}$

$$\text{Therefore } E_{cell} = \frac{RT \ln Kc}{nF}$$

15 Lithium has the lowest (most negative) electrode potential but is not observed to be the most reactive metal in the list. The lower reactivity is possibly due the slower rate of reaction. This may be linked to the relatively high melting point. As it remains as a solid when it reacts, only lithium atoms on the surface are available for reaction. The other group 1 metals melt, which increases the surface area available for reaction.

(The low reactivity of aluminium in some circumstances could also be linked to its relatively high melting point).

Practice questions

1. A

The oxidizing agent is acidified potassium dichromate so an acid that cannot be oxidized is used. $H_2SO_4(aq)$.

To produce a carboxylic acid instead of the aldehyde, the alcohol needs to react with the oxidizing agent for a prolonged period of time. The reaction mixture is heated under **reflux** which means the aldehyde condenses back into the reaction mixture when it evaporates and is oxidized further.

2. B

The nitrogen in NO_2 has an oxidation state of +4.

To be reduced to NO_2 the nitrogen needs to be in a state of +5: NO_3^-

3. C

Assigning oxidation states for the transition metals:

$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O(l)$

+7 +2 +2 +3

MnO_4^- is reduced and gains electrons to form Mn^{2+} and so is the oxidizing agent.

4. A

Assigning oxidation states for the Mn and Br:

$2MnO_4^-(aq) + Br^-(aq) + H_2O(l) \rightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$

+7 −1 +4 +5

$Br^-(aq)$ is oxidized and loses electrons to form BrO_3^- and so is the reducing agent.

5. A

Reduction occurs at the cathode.

6. A

Negative electrode in voltaic cell	Electrons are produced and sent round the external circuit. Species lose electrons and oxidized.
Negative electrode in electrolytic cell	Positive ions are attracted to the electrode. The positive ions are discharged. They gain electrons and are reduced.

7. **(a)** An electrolytic cell converts electrical energy to chemical energy and a voltaic cell converts chemical energy to electrical energy / an electrolytic cell uses electricity to carry out a (redox) chemical reaction and a voltaic cell uses a (redox) chemical reaction to produce electricity / an electrolytic cell requires a power supply and a voltaic cell does not.

An electrolytic cell involves a non-spontaneous (redox) reaction and a voltaic cell involves a spontaneous (redox) reaction.

In an electrolytic cell, the cathode is negative and the anode is positive and vice versa for a voltaic cell.

A voltaic cell has two separate solutions and an electrolytic cell has one solution / a voltaic cell has salt bridge and an electrolytic cell has no salt bridge.

In an electrolytic cell, oxidation occurs at the positive electrode/anode and in a voltaic cell, oxidation occurs at the negative electrode/anode and vice versa.

(2 max)

(b) (solid) ions in a lattice / ions cannot move;

(molten) ions mobile / ions free to move (2)

(c) Reduction occurs at the cathode / negative electrode and oxidation occurs at the anode / positive electrode

Cathode / negative electrode: $Na^+ + e^- \rightarrow Na$

Anode / positive electrode*:* $2Cl \rightarrow Cl_2 + 2e^-$/$Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$

Award (1 max.) if the two electrodes are not labelled/labelled incorrectly for the two half-equations.

Overall cell reaction: $Na^+(l) + Cl^-(l) \rightarrow Na(l) + \frac{1}{2}Cl_2(g)$ (5)

*Award **(1)** for correct equation and **(1)** for correct state symbols.*

Allow NaCl(l) instead of Na^+(l) and Cl^-(l).

(d) Al does not corrode / rust; Al is less dense / better conductor / more malleable (1)

Accept Al is lighter (metal compared to Fe).

Accept converse argument.

(e) Cathode / negative electrode: object to be plated

Allow a specific example here, e.g. spoon.

Accept inert metal / graphite.

Do not accept silver halides or their formulae.

Anode / positive electrode: silver / Ag

Electrolyte: $[Ag(CN)_2]^-$ (3)

Allow silver nitrate / $AgNO_3$ / silver cyanide / any other suitable silver salt/solution.

Do not accept AgCl.

8. **(a)** cathode: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

anode: $2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

*If both equations given but at wrong electrodes award **(1)**.* (2)

(b) cathode: nickel hydroxide / $Ni(OH)_2$

anode: cadmium hydroxide / $Cd(OH)_2$

cell equation: $Cd + 2H_2O + 2NiO(OH) \rightarrow Cd(OH)_2 + 2Ni(OH)_2$ (3)

9. **(a)** contains no lithium / metal / uses lithium salt in an organic solvent (as electrolyte)

involves movement of lithium ions (between electrodes) (2)

(b) Anode:

$LiC_6 \rightarrow Li^+ + 6C + e^-$ / Li^+ ions dissociate from anode (and migrate to cathode)

Cathode:

$Li^+ + e^- + MnO_2 \rightarrow LiMnO_2$ / $Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$ / $Li^+ + e^- + FePO_4 \rightarrow LiFePO_4$ / $Li^+ + e^- + NiO_2 \rightarrow LiNiO_2$ / Li^+ ions are inserted into metal oxide / phosphate (structure)

*Award **(1)** if electrodes are reversed.* (2)

(c) Similarity:

both convert chemical energy directly into electrical energy / both use spontaneous redox reactions (to produce energy) / both are electrochemical cells / voltaic cells / galvanic cells

Difference:

fuel cells are energy conversion devices and rechargeable batteries are energy storage devices / fuel cells require constant supply of reactants and batteries have stored chemical energy / provide power until stored chemicals are used up / batteries can be recharged and fuel cells do not need recharging (have a continuous supply of fuel) / fuel cells are more expensive than rechargeable batteries / the reactions in a rechargeable battery are reversible and in a fuel cell are not (2)

10 **(a)** **(i)** melting point of the cryolite solution is much lower than the melting point of alumina/Al_2O_3 / it lowers the melting point of the mixture / cell operates at lower temperature (1)

Allow lowers melting point or lowers melting point of aluminium oxide.

Do not allow lowers melting point of aluminium.

(ii) positive electrode: $2O^{2-} \rightarrow O_2 + 4e^-$ / $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^-$

negative electrode: $Al^{3+} + 3e^- \rightarrow Al$ (2)

Award ***(1)*** *for correct equations but wrong electrodes.*

Allow e instead of e^-.

(b) use of fossil fuels (to provide energy)

oxidation of the (graphite) positive electrode / anode (2)

11 **(a)** Al is more reactive than Fe / Al is higher than Fe in the reactivity series / it is harder to reduce aluminium ores compared to iron ores / Fe^{3+} is a better oxidizing agent than Al^{3+} / *OWTTE* (2)

(b) **(i)** $Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$

(ii) $Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$ (2)

12 **(a)** Positive electrode: graphite/carbon

negative electrode: graphite / carbon (on a steel liner) (2)

(b) much less energy required to recycle than to produce Al from ore / *OWTTE*

less production of CO_2/greenhouse gases (graphite used in the electrolysis is converted into CO_2) / the more that is recycled the less there will be in landfill sites / *OWTTE* (2)

13 **(a)** **(i)** copper: 0 to +2 / increases by 2 / +2 / 2+

Allow zero/nought for 0.

nitrogen: +5 to +4 / decreases by 1 / −1 / 1− (2)

Penalize missing + sign or incorrect notation such as 2+, 2^+ *or II, once only.*

(ii) nitric acid / HNO_3 / NO_3^- / nitrate (1)

(b) **(i)** 0.100 × 0.0285

2.85×10^{-3} (mol) (2)

*Award **(2)** for correct final answer.*

(ii) 2.85×10^{-3} (mol) (1)

(iii) $(63.55 \times 2.85 \times 10^{-3}) = 0.181$ g (1)

Allow use of 63.5.

(iv) $\left(\frac{0.181}{0.456} \times 100 =\right)$ 39.7% (1)

(v) $\left(\frac{44.2 - 39.7}{44.2} \times 100 =\right)$ 10% / 10.1% (1)

Allow 11.3%, i.e. percentage obtained in (iv) is used to divide instead of 44.2%.

14. Best Answer = **D** (Note there is an error in the question in the original print run of the book. The emf for D should be +1.43 V).

The relative electrode potentials are as follows:

$Al^{3+}(aq) + 3e^- \rightarrow Al(s) \qquad E^{\ominus} = -1.66$ V

$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s) \qquad E^{\ominus} = -0.23$ V

From electrode potentials we see that electrons will move from the half-cell with the more negative electrode potential to the half-cell with the more positive/less negative value. Al(s) is oxidized and the $Ni^{2+}(aq)$ is reduced. The two half-equations:

$3Ni^{2+}(aq) + 6e^- \rightarrow 3Ni(s) \qquad 2Al(s) \rightarrow 2\,Al^{3+}(aq) + 6e^-$

Adding the half-equations: $3Ni^{2+}(aq) + 2Al(s) \rightarrow 3Ni(s) + 2Mn^{3+}(aq)$

$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{half-cell where reduction occurs}} - E^{\ominus}_{\text{half-cell where oxidation occurs}} = -0.23 \;-\; -1.66 \text{ V} = +1.43 \text{ V}$

15 **(a)** $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ (2)

*Correct reactants and products, award **(1)**.*

*Balancing award **(1)**.*

Ignore state symbols and equilibrium sign.

(b) (+) 1.40 (V) (1)

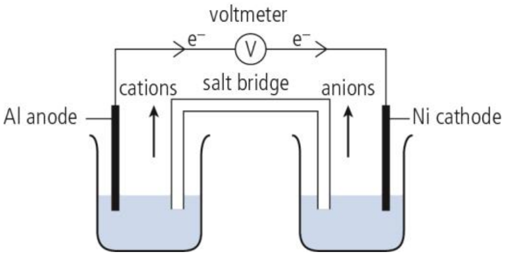
(c) aluminium anode / negative electrode

nickel cathode / positive electrode

electron movement from Al to Ni

correct movement of cations and anions through salt bridge (4)

If electron movement shown correctly but not labelled, award the mark.



16. C

Reaction at cathode: $Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

Reaction at anode: $2H_2O(l) \rightarrow 4H^{+}(aq) + O_2(g) + 4e^{-}$

Balancing number of electrons: $2Cu^{2+}(aq) + 4e^{-} \rightarrow 2Cu(s)$ $2H_2O(l) \rightarrow 4H^{+}(aq) + O_2(g) + 4e^{-}$

2 mol of $Cu(s)$ with 1 mol of $O_2(g)$

17. C

The spoon to be plated must be a conductor and placed at the negative electrode.

The silver used to plate the object should be at the positive electrode (anode).

18. B

Positive electrode (Anode)		**Negative electrode (Cathode)**	
$MgBr_2(aq)$	**$MgBr_2(l)$**	**$MgI_2(aq)$**	**$MgI_2(l)$**
Br^{-} oxidized $Br_2(g)$ produced		$H_2O(l)$ reduced $H_2(g)$ produced	Mg^{2+} discharged $Mg(g)$ produced

19. C

$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{half-cell where Cr2O72-reduced}} - E^{\ominus}_{\text{half-cell where Fe oxidized}} = +1.33 - -0.44\ V = 1.77\ V$

20 **(a)** **(i)** The voltage obtained when the half-cell is connected to the standard hydrogen electrode; under standard conditions of 298 K and 1 mol dm^{-3} solutions; electrons flow (in the external circuit) from the half-cell to the hydrogen electrode / the metal in the half-cell is above hydrogen in the ECS / Fe is a better reducing agent than H_2 / Fe is oxidized more readily than H_2 (3)

(ii) −0.28 V (1)

(iii) Co^{2+} / cobalt(II) ion (1)

(iv) $2Al + 3Fe^{2+} \rightarrow 3Fe + 2Al^{3+}$ (2)

*Award **(1)** for correct reactants and products and **(1)** for correctly balanced; ignore states. Do not accept* $\rightleftharpoons$

(v) to complete the electrical circuit / *OWTTE*; by allowing the movement of ions (2)

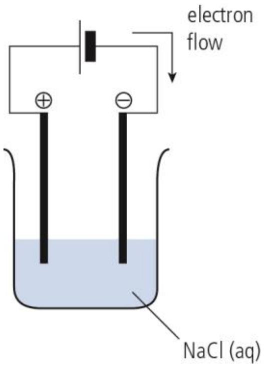
(b) **(i)** +2

(ii) +3

(iii) +2 (3)

Only penalize once if roman numerals are used or if written as 2+ or 3+.

(c) **(i)** diagram to show



battery / source of electricity connected to two electrodes in the solution with positive and negative electrodes correctly labelled;

electrons / current flowing from the cell to the negative electrode;

labelled solution of sodium chloride (3)

*If the connecting wires to electrodes are immersed in the solution **(1 max.)**.*

(ii) Na^+, H^+/H_3O^+, Cl^-, OH^- (2 max.)

*All four correct **(2)**, any 3 correct **(1)**.*

(iii) hydrogen at (−)/cathode and oxygen at (+)/anode

$2H^+ + 2e^- \rightarrow H_2$ / $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ / $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ (3)

*Accept e instead of e^-; if electrodes omitted or wrong way round **(2 max.)**.*

(iv) ratio of $H_2 : O_2$ is 2 : 1 (1)

(d) **(i)** (−)/(cathode) $2H^+ + 2e^- \rightarrow H_2$ / $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

(+)/(anode) $2Cl^- \rightarrow Cl_2 + 2e^-$ (2)

*Accept e instead of e^-; if electrodes omitted or wrong way round **(1 max.)**.*

(ii) (−)/(cathode) $Na^+ + e^- \rightarrow Na$

(+)/(anode) $2Br^- \rightarrow Br_2 + 2e^-$ (2)

*Accept e instead of e^-; if electrodes omitted or wrong way round **(1 max.)**.*

Reactivity 3.3 Solutions

Exercise

1–3. Any species that has an odd number of valence electrons must contain at least one that is unpaired and is therefore a radical.

1. A

F (7 valence electrons) is the only species with an odd number of electrons and is therefore a radical

2. B

NO_2 (17 valence electrons) is the only species with an odd number of electrons and is therefore a radical

3. D

CH_4^+ (7 valence electrons) is the only species with an odd number of electrons and is therefore a radical

4. There is an error in the first print run that will be corrected on reprint. D is the most obvious answer but A occurs by the radical mechanism which involves hemolytic fission in the initiation step. C is a combustion reaction which also occurs via radicals (and therefore must involve homolytic fission) so there are three correct answers.

5. There is an error in the first print run that will be corrected on reprint. There is more than one correct answer. The correct answer is D as breaking bonds is always endothermic – but C also implies an endothermic reaction!

6. Homolytic fission involves both a covalent bon breaking and each atom accepting one electron from the bond. The movement of a single electron is illustrated using a single headed arrow (fish hook).

7. Thermolytic fission is when a bond breaks due to the absorption of heat energy:

$$A—B \xrightarrow{\text{heat}} A\bullet + B\bullet$$

Photolytic fission is when a bond breaks due to the absorption of light energy:

$$A—B \xrightarrow{\text{light}} A\bullet + B\bullet$$

8. The three stages of a radical reaction are initiation, propagation and termination.

Initiation: $Br–Br \xrightarrow{UV} Br^\bullet + Br^\bullet$

Propagation: $CH_4 + Br^\bullet \longrightarrow CH_3^\bullet + HBr$

Termination: $CH_3^\bullet + Br^\bullet \longrightarrow CH_3Br$

9. **(a)** The reaction proceeds through a radical mechanism.

Initiation: $Br–Br \xrightarrow{UV} Br^{\bullet} + Br^{\bullet}$

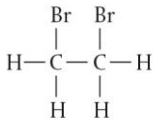
Propagation: $C_2H_6 + Br^{\bullet} \longrightarrow C_2H_5^{\bullet} + HBr$

Termination: $C_2H_5^{\bullet} + Br^{\bullet} \longrightarrow C_2H_5Br$

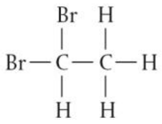
(b) Butane can be formed if two ethyl radicals formed in the propagation steps combine:

$C_2H_5^{\bullet} + C_2H_5^{\bullet} \dashrightarrow C_4H_{10}$

(c)



1,2-dibromoethane

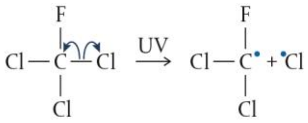


1,1-dibromoethane

10. **(a)** The bromine water would be decolorized as radical substitution reactions require UV light to initiate the reaction.

(b) The bromine water would not be decolorized as there is no UV light radical to initiate the reaction.

11. **(a)** The absorption of UV light causes homolytic fission of a C–Cl bond and the release of a $Cl^{\bullet}$ radical.



(b) $Cl^{\bullet}(g) + O_3(g) \rightarrow O_2(g) + ClO^{\bullet}(g)$

$ClO^{\bullet}(g) + O_3(g) \rightarrow O_2(g) + Cl^{\bullet}(g)$

A chlorine radical reacts in the first step but another is formed in the second step which makes the chlorine radical a catalyst.

Challenge yourself

For the C−F bond:

$$\text{bond energy per molecule} = \frac{492 \times 10^{3}\ \text{J mol}^{-1}}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 8.1728 \times 10^{-19}\,\text{J}$$

Need to use the equation

$$\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{8.1728 \times 10^{-19}\,\text{J}} = 2.43 \times 10^{-7}\ \text{m} = 243\ \text{nm}$$

For the C−Cl bond:

$$\text{bond energy per molecule} = \frac{324 \times 10^{3}\,\text{J mol}^{-1}}{6.02 \times 10^{23}\ \text{mol}^{-1}} = 5.38206 \times 10^{-19}\,\text{J}$$

$$\lambda = \frac{hc}{E} = \frac{6.63 \times 10^{-34} \times 3.00 \times 10^{8}\ \text{m s}^{-1}}{5.3821 \times 10^{-19}\,\text{J}} = 3.70 \times 10^{-7}\ \text{m} = 370\ \text{nm}$$

Practice questions

1. A

Free radical substitution reactions occur between alkanes and halogens.

2. D

The termination stage involves two radicals combining

3 **(a)** Y is HBr (1)

(b) The reaction requires UV light to break the Br–Br bond and initiate the reaction. (1)

(c) Initiation: $Br–Br \xrightarrow{UV} Br^{\bullet} + Br^{\bullet}$ (1)

Propagation: $C_5H_{12} + Br^{\bullet} \longrightarrow C_5H_{11}^{\bullet} + HBr$

Termination: $C_5H_{11}^{\bullet} + Br^{\bullet} \longrightarrow C_5H_{11}Br$ (1)

(d) **(i)** The three products are structural isomers.

(ii)

$CH_2BrCH_2CH_2CH_2CH_3$	$CH_3CHBrCH_2CH_2CH_3$	$CH_3CH_2CHBrCH_2CH_3$	
1-bromopentane	2-bromopentane	3-bromopentane	(3)

4 **(a)** Radical substitution (1)

(b) A radical substitution mechanism has three stages:

Initiation: $Cl–Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet}$ > (1)

Propagation: $C_3H_8 + Cl^{\bullet} \longrightarrow C_3H_7^{\bullet} + HCl$ (1)

Termination: $C_3H_7^{\bullet} + Cl^{\bullet} \longrightarrow C_3H_7Cl$ (1)

(c) $CH_2ClCH_2CH_3 \longrightarrow CH_3CHClCH_3$ (1)

1-chloropropane 2-chloropropane (1)

(d) Propane is regarded as kinetically stable as most of its reactions have high activation energies and it won't react at regular temperatures. The products of these reactions have a lower enthalpy than propane so it is thermodynamically unstable compared to these products. (2)

5 **(a)** The reaction occurs through a radical mechanism which has three stages;

Initiation: $Cl\text{-}Cl \xrightarrow{UV} Cl^{\bullet} + Cl^{\bullet}$

Propagation: $C_2H_6 + Cl^{\bullet} \longrightarrow C_2H_5^{\bullet} + HCl$

Termination: $C_2H_5^{\bullet} + Cl^{\bullet} \longrightarrow C_2H_5Cl$ (4)

(b) Small amounts of butane could be formed in the reaction if two ethyl radicals formed in the propagation steps combine:

$C_2H_5^{\bullet} + C_2H_5^{\bullet} \longrightarrow C_4H_{10}$ (2)

Reactivity 3.4

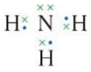
Exercises

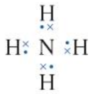
1. A

Nucleophiles are electron-rich species that are attracted to positive charges. They contain a lone pair of electrons that they can donate to electrophiles to form a coordination bond.

2. C

Drawing the Lewis structures shows that NH_3 and H_2O have lone pairs on the central atom and can act as nucleophiles. All electron pairs are bonded in CH_4.





3. D

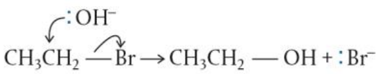
The reaction is a nucleophilic substitution reaction where OH^- substitutes X^-. OH^- is the nucleophile and X^- is the leaving group.

4. Nucleophilic substitution reactions occur when a nucleophile replaces a substituent, such as a halogen, in an organic compound.

In the reaction between NaOH and chloroethane, OH^- acts as the nucleophile and it substitutes the chlorine atom in chlorethane. ($:Cl^-$ is the leaving group)

$CH_3CH_2Cl + OH^- \rightarrow CH_3CH_2OH + Cl^-$

5.



Note: the curly arrows must clearly start at a lone pair or bonded pair of electrons and clearly finish at the atom they are moving to.

6. Section 12 in the data booklet lists the strengths of covalent bonds. From this table the bond strengths for the carbon halogen bonds can be compared:

Bond	C–F	C–Cl	C–Br	C–I
Bond enthalpy / kJ mol^{-1}	492	324	285	228

The bond that is the easiest to break will generate the best leaving group. The weakest bond is C–I so I^- will be the best leaving group.

7. B

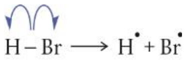
Heterolytic fission involves the breaking of a covalent bond with both bonding electrons going to one atom, forming a cation and an anion.

A and C involve the forming of bonds so both are incorrect

D involves the breaking of a bond with each atom getting one electron (homolytic fission) so is incorrect.

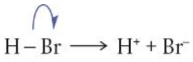
B is the correct answer

8. Homolytic Fission:



The one-headed arrows (fish hooks) show that the bond breaks with one electron going to each atom to form two radicals.

Heterolytic fission:



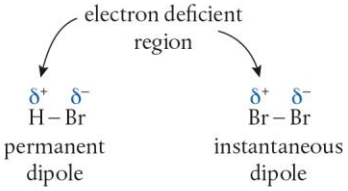
The two-headed arrow shows that the bond breaks with the pair of electrons going to the more electronegative atom to from a positive ion and a negative ion.

9. B

Electrophiles are electron-deficient species that can accept an electron pair from a nucleophile. (Some electrophiles are positively charged but they can also be neutral molecules so **D** is not the best answer)

10. D

H–Br and Br–Br contain permanent or instantaneous dipoles which create electron-deficient regions in the molecules so they can act as electrophiles.



NH_3 is an electron rich species with a lone pair of electrons on the nitrogen atom. It will act as a nucleophile, not as an electrophile.

11. D

The reaction proceeds with H and Cl being added to the carbon atoms on either side of the double bond.

$$CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$$

12. **(a)** This is an addition reaction with HBr: an alkene is converted to a haloalkane.

$CH_3CH_2CHBrCH_3$, 2-bromobutane

(b) With conc. H_2SO_4, –H and –OH add across the alkene double bond, forming an alcohol.

CH_3CH_2OH, ethan-ol

(c) This is an addition reaction with bromine: an alkene is converted to a dibromoalkane.

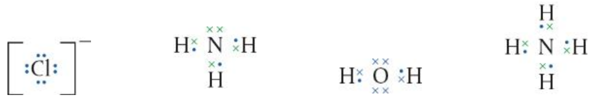
$CH_3CHBrCH_2Br$, 1,2-dibromopropane

13. Bromine water readily reacts with alkenes but will only react with alkanes in the presence of UV light. If no UV light sources are present then:

- adding bromine water to an alkene results in an instantaneous color change (orange/brown to colorless)
- adding bromine water to an alkane results in no color change

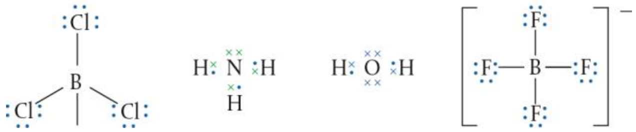
14. D

Lewis bases are electron-pair donors and must contain a lone pair of electrons. Drawing the Lewis structures of these species shows that CH_4 is the only one that does not have a lone pair.



15. A

Lewis acids are electron-pair acceptors and must have a central atom with an incomplete octet . Drawing the Lewis structures of these species shows that BCl_3 has the only structure where the central atom has an incomplete octet.



16. C

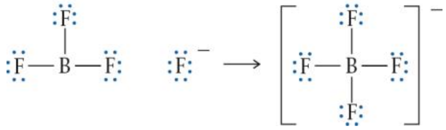
Lewis acid–base reactions involve the donation of an electron pair from a Lewis acid to a Lewis base. Brønsted–Lowry reactions involve the transfer of a proton (H^+). All Brønsted–Lowry reactions are Lewis acid–base reactions.

Reactions **A** and **B** both involve a proton transfer. ($NH_3 \dashrightarrow NH_4^+$ and $H_2O \dashrightarrow H_3O^+$)

Reaction D also involves a proton transfer to NH_3. ($NH_3 \dashrightarrow NH_4^+$)

C does not involve a proton transfer but is a Lewis acid-base reaction as F^- donates a lone pair to BH_3

17. (a) (i)



In Lewis acid–base reactions, the Lewis base donates an electron pair and the Lewis acid accepts the electron pair.

The boron atom in trifluoroborate does not have a complete octet and can accept an electron pair from the fluoride ion.

The bond formed is a coordination bond which is represented as an arrow in the Lewis structure of BF_4^- above. (Unless asked, it is not necessary to show coordination bonds as arrows and they can be drawn as a regular bond in your answer.)

(ii) Because the fluoride ion donates both electrons in forming the covalent bond to boron ithis is a coordination bond.

(b) Brønsted–Lowry acid–base reactions involve the transfer of a proton (H^+). The reaction of BF_3 with F^- does not include any protons so this is not a Brønsted–Lowry reaction.

18. C

Coordination bonds are formed when one species accepts an electron-pair donated by another species.

- Nucleophiles donate electron pairs to electrophiles to form covalent bonds
- Ligands donate electron pairs to transition metal ions to form complex ions
- Lewis bases donate electron pairs to Lewis acids

19. B

The overall charge on the complex ions is equal to sum of the charge on the transition metal ion and the charge on the ligands.

A: Transition metal ion is Fe^{2+} $(2^+ + 6 \times 0 = 2^+)$

B: Transition metal ion is Cr^{3+} $(3^+ + 6 \times 0 = 3^+)$

C: Transition metal ion is Ni^{2+} $(2^+ + 4 \times 1^- = 2^-)$

D: Transition metal ion is Cu^{2+} $(2^+ + 6 \times 0 = 2^+)$

20. The overall charge on a complex ion is equal to sum of the charge on the transition metal ion and the charge on the ligands.

(a) Cyanide ligands, CN^-, have a 1^- charge. Charge on complex ion = $+3 + (6 \times -1) = -3$

Formula of complex ion: $[Fe(CN)_6]^{3-}$

(b) Bromide ligands, Br^-, have a 1^- charge. Charge on complex ion = $+2 + (6 \times -1) = -4$

Formula of complex ion: $[Cu(Br)_6]^{4-}$

(c) Chloride ligands, Cl^-, have a 1– charge and water ligands are neutral. Charge on complex ion = +3 + (4 × 0) + (2 × –1) = +1

Formula of complex ion: $[Cr(H_2O)_4Cl_2]^+$

21. A

There is an error in the first print run which will be corrected on reprint.

C

Tertiary halogenoalkanes react most readily by S_N1 mechanisms**.** A and C are tertiary halogenoalkanes, B and D are primary halogenoalkanes that react via S_N2. I^- is a better leaving group than Cl^- so C reacts more readily than A

22. D

The weakest carbon–halogen bond gives the best leaving group and will react the most quickly in a nucleophilic substitution reaction.

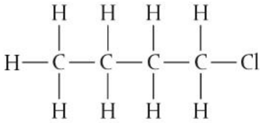
The order of bond strengths are C–I < C–Br < C–Cl < C–F. As C–I is the weakest bond, $CH_3CH_2CH_2CH_2I$ will react the most quickly.

23. B

S_N2 reactions are nucleophilic substitution with a single step mechanism. A refers to S_N1 reactions with a two-step mechanism through a carbocation intermediate. C and D both refer to electrophilic addition reactions.

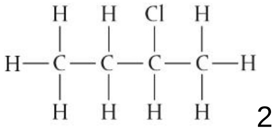
24. The iodo- and bromo- compounds are more useful because they are more reactive than the chloro- compounds. (Br^- and I^- are better leaving groups because C–Br and C–I bonds are easier to break than C–Cl). This means that they can react with a wider range of compounds and give rise to a range of intermediates and products.

25. **(a)** **(i)**



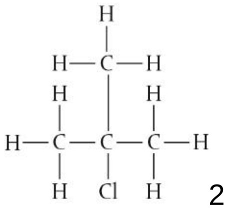
1-chlorobutane (1-chloro-2-methylpropane is also possible)

(ii)



2-chlorobutane

(iii)

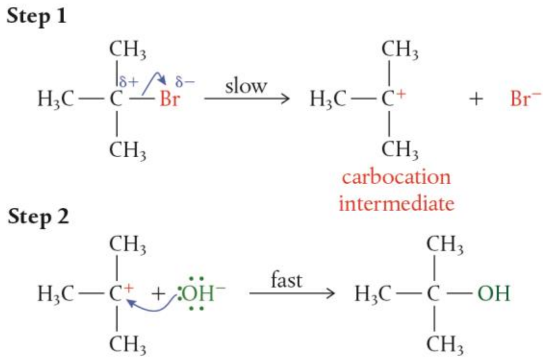


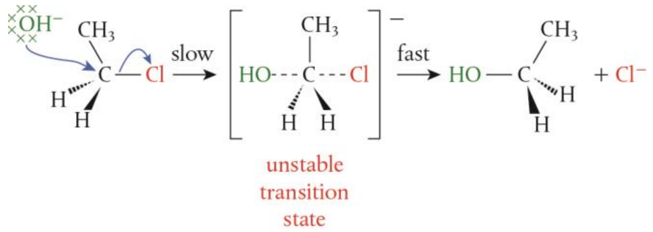
2-chloro-2-methylpropane

(b) **(i)** S_N1 is characteristic of tertiary halogenoalkanes so 2-chloro-2-methylpropane will react almost exclusively by S_N1.

S_N1 stands for substitution, nucleophilic, 1st order (unimolecular).

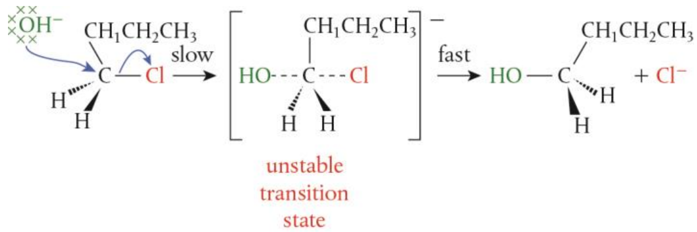
(ii)



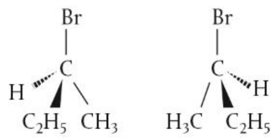


(c) **(i)** S_N2 is characteristic of primary halogenoalkanes so 1-chlorobutane will react almost exclusively by S_N2. (1-chloro-2-methylpropane is also correct)

(ii)

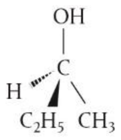


26. **(a)**



(b) For the S_N1 mechanism, an optically pure reactant will give a product mixture that contains equal amounts of the two optical isomers (a racemic mixture).

The –Br is substituted by –OH to give



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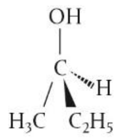
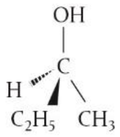
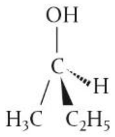


(c) The S_N2 mechanism is stereo retentive, an optically pure reactant will give a product mixture that is also optically pure and only contains one optical isomers.

The –Br is substituted by –OH to give



and



(d) A polarimeter measures the angle that plane-polarized light is rotated through due to its interactions with optical isomers. One isomer will of 2-bromobutane will rotate the plane clockwise and the other rotates the plane an equal amount in the anti-clockwise direction.

If the optical isomer of 2-bromobutane reacts via a S_N1 mechanism, the products are a racemic mixture. Racemic mixtures do not rotate polarized light so no rotation would be observed for the product mixture using a polarimeter.

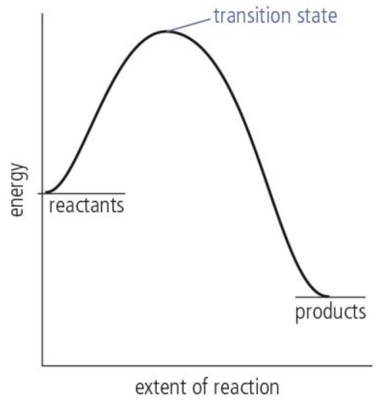
If the optical isomer of 2-bromobutane reacts via a S_N2 mechanism, then only one optically pure product will be formed. This product will rotate polarized light and this would be observed using a polarimeter.

27. **(a)** **(i)** S_N1 reactions are first order so the reaction rate only depends on the concentration of the halogenoalkane: rate = k[R–X]

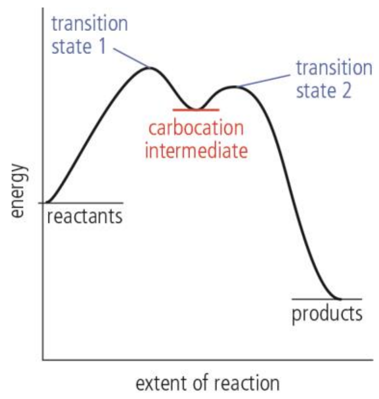
(ii) S_N2 reactions are second order so the reaction rate depends on the concentration of both the halogenoalkane and hydroxide ion: rate = $k[R–X][OH^-]$

(b)

S_N2



S_N1



28. C

Addition reactions involve the breaking of a pi bond in an alkene and the formation of two sigma bonds.

29. A

The addition of HCl to but-2-ene will add a –H to the carbon on one side of the double bond and a –Cl to the carbon on the other side.

Butane would be formed from the addition of H_2 to 2 –bromobutane and 2,3-dichlorobutane would be formed from the addition of Cl_2. 2,2-dichlorobutane cannot be formed from an addition reaction of but-2-ene.

30. C

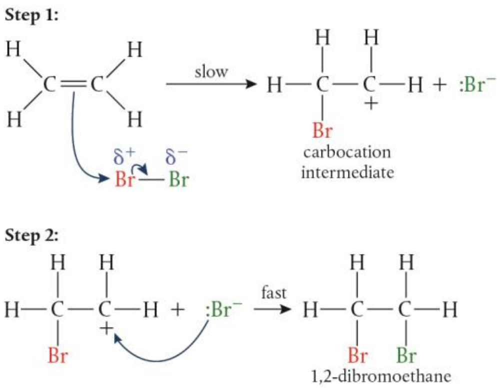
Pent-1-yne is an alkyne which contains two pi bonds and can do the same addition reactions as alkenes. Adding bromine water to pent-2-yne will result in the orange/brown bromine water being decolourized.

31. D

The addition of Br_2 to an alkene will form a dibromoalkane. Br_2 adds to propene to give 1,2-dibromopropane

32. Alkenes have a double bond which is an electron-dense region and so is susceptible to attack by electrophiles which are themselves electron deficient. Alkenes undergo addition reactions because they are unsaturated; one of the bonds in the double bond breaks and incoming groups can add to the two carbon atoms.

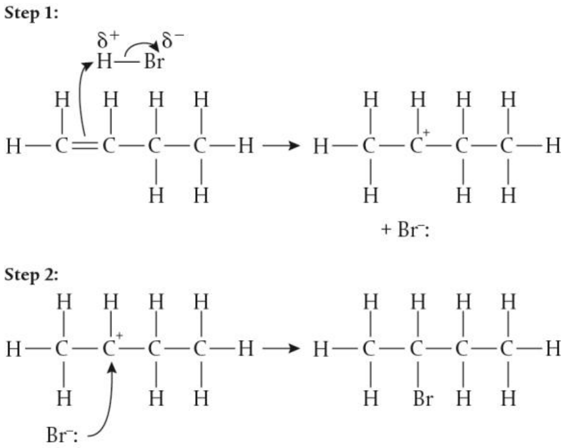
When bromine approaches but-2-ene, the bromine is polarized by the electron density in the double bond. Electrons in the bromine–bromine bond are repelled away from the double bond, leading to the heterolytic fission of the bromine molecule. The Br^+ product now attaches itself to one of the carbon atoms as the carbon–carbon double bond opens. This produces an unstable carbocation which then rapidly reacts with the Br^- ion. The product is 2,3-dibromobutane.



33. Product is butan-2-ol. The reaction conditions require the use of an acid catalyst. (Industrial conditions use solid silicon dioxide coated with phosphoric (V) acid, at a temperature of 300°C and a high pressure (60 atmospheres).

34. but-1-ene + HBr → 2-bromobutane

Application of Markovnikov's rule enables us to predict that the electrophile H^+ will add to the terminal carbon forming a secondary carbocation, as this is stabilized by the positive inductive effect of the alkyl groups. Br^- will then add to carbocation intermediate forming 2-bromobutane.



35. ICl is polarized as $I^{\delta+}$ $Cl^{\delta-}$ owing to the greater electronegativity of Cl than I. So when it undergoes heterolytic fission it will form I^+ and Cl^-. By application of Markovnikov's rule, the I^+ will attach to the terminal carbon, while Cl^- will add to carbon 2. (See worked example on 859–60). The product is therefore 1-iodo-2-chloropropane, $CH_3CHClCH_2I$.

36. B

A mixture of nitric and sulfuric acid produces the NO_2^+ cation which is an electrophile. Electrophiles react with benzene in electrophilic substitution reactions.

37. D

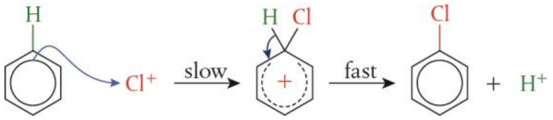
Although the benzene ring contains pi bonds, they are highly stabilized due to resonance and benzene does not undergo addition reactions like regular alkenes. Therefore no reaction occurs, and no colour change is observed when bromine water is added to benzene.

38. Reactants are concentrated H_2SO_4 and concentrated HNO_3.

The stronger acid H_2SO_4 protonates the HNO_3, leading to production of the nitronium ion NO_2^+. This is a strong electrophile which reacts with the π electrons of the benzene ring and NO_2^+ substitutes an H^+ to form nitrobenzene.

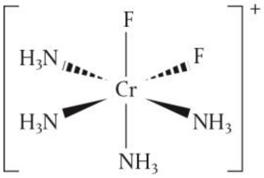
39. **(a)** Electrophilic substitution (the overall reaction has a chlorine substituting a hydrogen on the benzene ring)

(b)

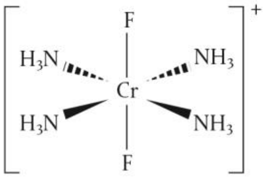


Challenge yourself

1.

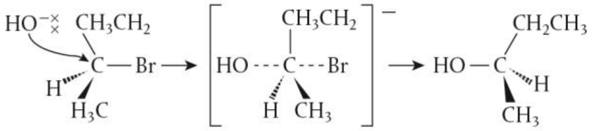


cis-form

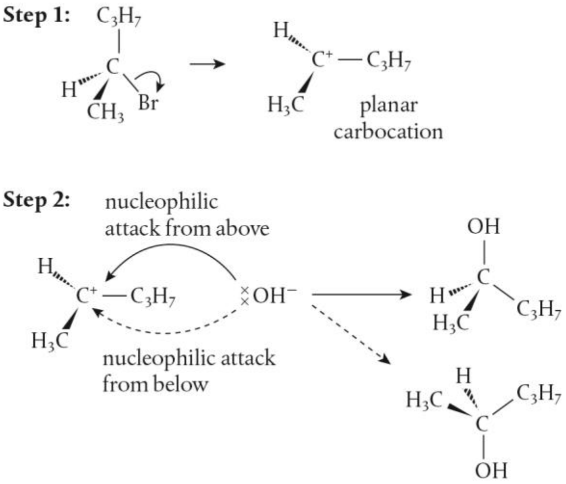


trans-form

2.



3.

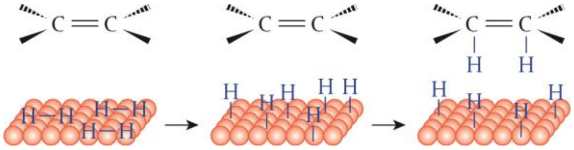


4. The S_N1 reaction is not stereospecific, so will produce 15% of each optical isomer. The S_N2 reaction is stereospecific, so will produce 70% of one optical isomer. Overall, the reactions will produce 15% of one optical isomer and 85% of the other.

5. Due to their small size, the hydrogen atoms in H_2 are not polarizable and this means that the H2 will not readily form instantaneous dipoles. It is therefore a very weak electrophile.

When metal catalysts such as Pt are used, the alkene and H2 are both absorbed onto the surface of the metal.

This breaks the H−H bond and weakens the pi bond of the alkene. The H atoms now present on the metal surface can add to the alkene forming the hydrogenated product.



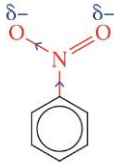
A typical electrophilic substitution mechanism does not require a catalyst and the pi bond in the alkene breaks due to electrophilic attack. (The pi electrons are strongly attracted to the electrophile and form a sigma bond with the electrophilic atom.)

6 Vegetable oils contain long carbon chains with one or more C=C double bonds.

Hydrogenation of vegetable oils results in the formation of saturated products due to the C=C pi bonds breaking and the addition of C–H sigma bonds.

The flexible alkyl chains of the saturated products are able to stack together more readily than the chains in the oils which are more rigid due to the C=C double bonds. This results in the saturated products having stronger intermolecular forces and higher melting points so the saturated products are typically solids (or soft semi-solids) rather than liquids at room temperature.

7 The $-NH_2$ group in phenylamine is electron donating due to conjugation of the lone pair of electrons on N with the ring electrons. As a result, the electron density of the ring is increased, making it more susceptible to electrophilic attack. In contrast, the $-NO_2$ group in nitrobenzene is electron withdrawing due to the electronegativity of the nitrogen and oxygen atoms.



Also, the electrons in its double bond conjugate with the π electrons in the ring, causing the electron density of the ring to be decreased, making it less susceptible to electrophilic attack.

Practice Questions

1. C

Pent-1-ene is an alkene so reacts readily with bromine water via an addition reaction

Pentane, cyclopentane and methane are all alkanes which only react with bromine water in the presence of UV light.

2. B

Br_2 reacts with alkenes to form dibromoalkanes with one bromine atom adding to each of the carbons in the pi bond.

Ethene reacts with Br_2 to form 1,2-dibromoethane. (Although 1,1-dibromoethane is also a dibromoalkane it is not a product as both Br atoms are on the same carbon.)

3. C

The addition of HI to an alkene gives an iodoalkane as a hydrogen atom adds to one of the carbon atoms in the double bond and an iodine atom adds to the other carbon. Therefore ethene reacts with HI to give iodoethane.

Please note that in the first print run of the book, option C is incorrectly given as

1-iodoethane. It should be iodoethane.

4. D

C_4H_9Cl is a halogenoalkane which can be converted into C_4H_9OH by reacting with OH^- via a nucleophilic substitution reaction.

5. A

Lewis acids are electron pair acceptors which means they have vacant orbitals. Brønsted–Lowry acids are proton donors.

The Lewis structures of CH_3OH and NH_3 show that they have complete octets so they cannot accept electron pairs and act as Lewis acids.

Transition metal ions have empty orbitals which make them better Lewis acids than the metals.

6. B

Lewis bases are electron pair donors which means they must contain an electron pair on the central atom.

The Lewis structures of the four compounds shows that NH_4^+ is the only species without a lone pair of electrons.

7. D

Coordination bonds are formed when one species accepts an electron-pair donated by another species.

A-C all form coordination bonds:

- Nucleophiles donate electron pairs to electrophiles to form covalent bonds
- Ligands donate electron pairs to transition metal ions to form complex ions

Lewis bases donate electron pairs to Lewis acidsRadicals combine in termination reactions by each donating a single electron to form a regular covalent bond

8. B

The overall charge on the complex ions is equal to sum of the charge on the transition metal ion and the charge on the ligands.

A: Transition metal ion is Fe^{2+} $(+2 + 6 \times 0 = +2)$

B: Transition metal ion is Cr^{3+} $(+3 + 6 \times 0 = +3)$

C: Transition metal ion is Cu^{+} $(+1 + 4 \times -1 = -3)$

D: Transition metal ion is Co^{2+} $(+2 + 6 \times 0 = +2)$

9 The overall charge on the complex ions is equal to the sum of the charge on the transition metal ion and the charge on the ligands.

(a) Thiocyanate ligands, SCN^{-}, have a 1– charge.

Charge on complex ion = $+3 + (6 \times -1) = -3$

Formula of complex ion: $[Fe(SCN)_6]^{3-}$ (1)

(b) Chloride ligands, Cl^{-}, have a 1– charge and water ligands are neutral.

Charge on complex ion = $+2 + (5 \times 0) + -1 = +1$

Formula of complex ion: $[Co(H_2O)_5Cl]^{+}$ (1)

(c) Fluoride ligands, F^{-}, have a –1 charge and ammonia ligands are neutral.

Charge on complex ion = $+3 + (4 \times 0) + (2 \times -1) = +1$

Formula of complex ion: $[Cr(NH_3)_4F_2]^{-}$ (1)

10. C

Halogenoalkanes react with nucleophiles in nucleophilic substitution reactions.

Electrophilic substitution reactions occur for arene compounds such as benzene.

Nucleophilic addition reactions occur for carbonyl compounds such as ketones (which are not covered in this course).

11. A

Primary halogenoalkanes react via an one-step S_N2 mechanism.
(Tertiary halogenoalkanes react via a S_N1)

The C–Br bond in bromoalkanes is stronger than the C–I bond in iodoalkanes so bromoalkanes react more slowly.

Electrophiles are electron-deficient species that accept electron pairs from nucleophiles OH^- is electron rich and can donate an electron pair therefore it acts as a nucleophile.

The reaction of halogenoalkanes with hydroxide gives alcohol products.

12. A

Electrophilic substitutions occur when arene compounds, such as benzene, react with electrophiles. Although it is already a substituted compound, **A** (nitrobenzene) contains a benzene ring and is able to undergo further electrophilic substitution reactions.

The other compounds do not contain a benzene ring and cannot undergo electrophilic substitution.

13. A

The nitration of benzene requires NO_2^+ as an electrophile. (It is formed from the combination of concentrated H_2SO_4 and HNO_3.)

14. **(a)** Lewis bases are electron pair donors. Brønsted–Lowry bases are proton (H^+) acceptors.

In reaction **(i)**, the OH^- donates a lone pair to CO_2 to form HCO_3^- so it is acting as a Lewis base. (1)

In reaction **(ii)**, the OH^- accepts a proton from H_2CO_3 to form H_2O so it is acting as a Brønsted–Lowry base. (1)

(b) In the $[Fe(OH_2)_6]^{3+}$ complex ion, each water ligand has donated a lone pair of electrons to form a coordination bond with the central Fe^{3+} ion. (1)

Because they have donated electron pairs, the water ligands have behaved as Lewis bases. Because it has accepted electron pairs, the Fe^{3+} ion has behaved as a Lewis acid. (1)

15. **(a)** A: 1-bromobutane (1)

B: 2-bromobutane (1)

C: 2-bromo-2-methylpropane (1)

D: 1-bromo-2-methylpropane (1)

(b) **(i)** S_N1 reactions are favoured by tertiary halogenoalkanes. C is a tertiary bromoalkane so it will react almost exclusively via a S_N1 mechanism. (1)

S_N1 means substitution, nucleophilic, 1st order (unimolecular); i.e. a 1st order nucleophilic substitution reaction. (1)

(A and D are primary bromoalkanes which react via S_N2 and B is a secondary bromoalkane that reacts via both S_N1 and S_N2.)

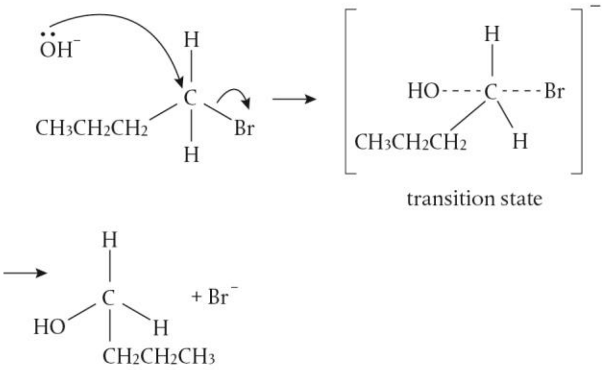
(ii) S_N1 reactions occur via a two-step mechanism. The first step, which involves the breaking of a C–Br bond in the bromoalkane to form a carbocation, is rate determining.

$RBr \rightarrow R^+ + Br^-$ (1)

(iii) S_N2 reactions are favoured by primary halogenoalkanes.

A and D are both primary bromoalkanes so will react almost exclusively via a S_N2 mechanism. (1 mark for A or D)

Drawing a mechanism for either of these two isomers is acceptable. Here it is drawn for isomer A, 1-bromobutane.



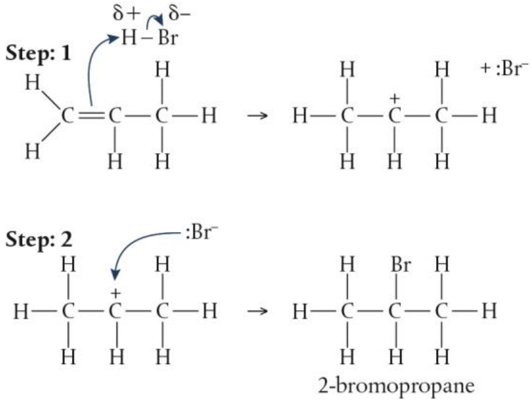
(c) Part **(b)(i)** refers to a S_N1 mechanism which has the rate expression, rate = k[RBr]. The reaction is zero order with respect to OH^-; changing the concentration of OH^- will have no effect on the rate. (1)

Part **(b)(iii)** refers to a S_N2 mechanism which has the rate expression rate = k[RBr][OH^-]. The reaction is first order with respect to OH^-; increasing the concentration of OH^- will proportionally increase the rate. (1)

(d) The C–Br bond is weaker than the C–Cl bond so it breaks easier and Br^- is a better leaving group than Cl^-. 1-bromobutane will react faster than 1-chorobutane. (1)

16. (a) C_3H_6 is an alkene and it reacts with HBr via an **electrophilic addition reaction.** (1)

(b) (4)



(c) The reaction involves an asymmetrical alkene so it follows Markovnikov's rule: the hydrogen atom in HBr bonds to the less substituted carbon atom in the alkene. (1)

The electrophilic attack by HBr causes the pi bond to selectively open so that the more stabilized secondary carbocation is formed. Nucleophilic addition of Br^- to the secondary carbocation gives **2-bromopropane** as the product. (1)

17 **(a)** Comparing trials 1 and 2: $[C_4H_9Br]$ is constant and $[OH^-]$ has been doubled. The initial rate does not change so the reaction is zero order with respect to OH^-.

Comparing trials 1 and 3: $[OH^-]$ is constant and $[C_4H_9Br]$ has been doubled. The initial rate also doubles so the reaction is first order with respect to C_4H_9Br. (1)

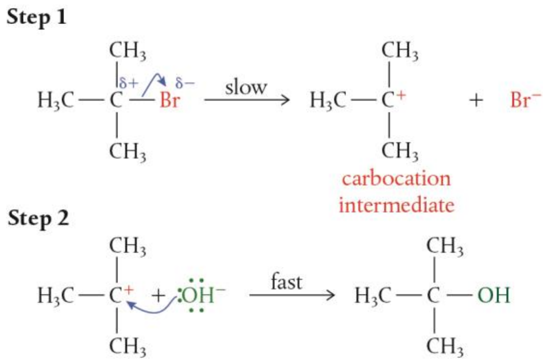
The rate expression is: rate = $k[C_4H_9Br]$ (1)

(b) From **(i)** we see that the reaction is 1st order overall so it must occur via an S_N1 mechanism.

Tertiary halogenoalkanes react almost exclusively by the S_N1 mechanism. There is one isomer of C_4H_9Br that is a tertiary halogenoalkane: **2-bromo-2-methylpropane.**

(1)

(c)



1 mark for double headed arrow going from C-Br bond to Br in first step

1 mark for correct products in first step

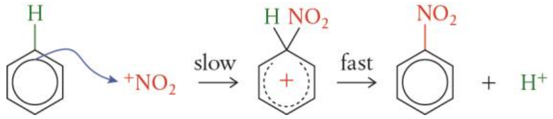
1 mark for double headed arrow from electron pair on OH- to central C in carbocation intermediate in second step

1 mark for correct product in second step

18 **(a)** The other two reactants required are concentrated sulfuric acid, H_2SO_4 and concentrated nitric acid, HNO_3. (1)

The electrophile is the nitronium ion, NO_2^+. (1)

(b)



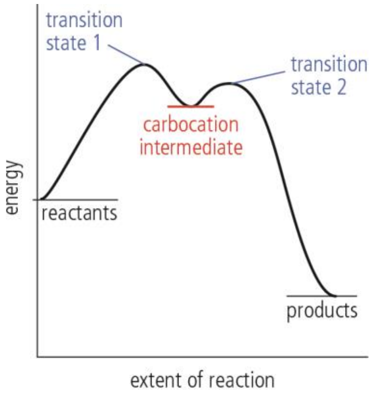
1 mark for double headed arrow from benzene ring (pi electrons) to NO_2^+

1 mark for intermediate structure with H and NO_2 on same carbon

1 mark for (delocalized) positive charge on intermediate

1 mark for correct products

(c)



1 mark for the reaction profile being correct with two steps (two local maxima) and an intermediate (local minimum)

1 mark for carbocation correctly labelled

1 mark for both transition states correctly labelled