

CHEMISTRY

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Pre-U

Answers to Exercises

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1. Atomic Structure

Answers 1.1

1. A
2. B
3. C
4. D

Answers 1.2

1. C
2. B
3. D

Answers 1.3

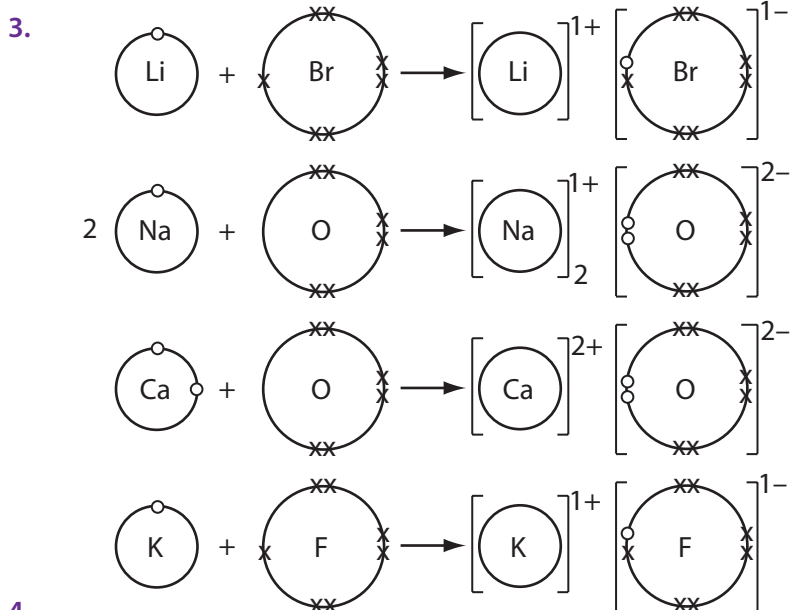
1. C
2. D
3. D
- 4.

Electron shells										
Shell number	1 st	2 nd		3 rd			4 th			
Subshells	s	s	p	s	p	d	s	p	d	f
Orbitals	1	1	3	1	3	5	1	3	5	7
Maximum number of electrons	2	2	6	2	6	10	2	6	10	14
Total	2	8		18			32			

5. A
6. B
7. C
8. D
9. B
10. D
11. B

2. Chemical Forces

Answers 2.1



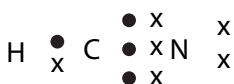
BaS, Ca₃P₂, CsI and GaN

5.

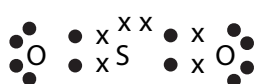
Binary ionic compound	Formula	Electronic configuration of the metal's cation	Electronic configuration of the non-metal's anion
Lithium sulfide	Li ₂ S	1s ² or [He]	[Ar]
Potassium arsenide	K ₃ As	[Ar]	[Kr]
Aluminium nitride	AlN	[Ne]	[Ne]
Sodium selenide	Na ₂ Se	[Ne]	[Kr]
Barium chloride	BaCl ₂	[Xe]	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ or [Ar]

6. A single covalent bond is a shared pair of electrons found between two atoms. Each atom contributes one electron to the shared pair. A dative covalent bond is also a shared pair of electrons found between two atoms, but both electrons are donated by one of the atoms. Dative covalent bonds are also referred to as coordinate bonds.

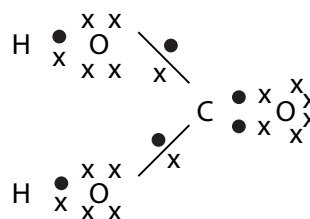
7.



Hydrogen cyanide



Sulfur dioxide



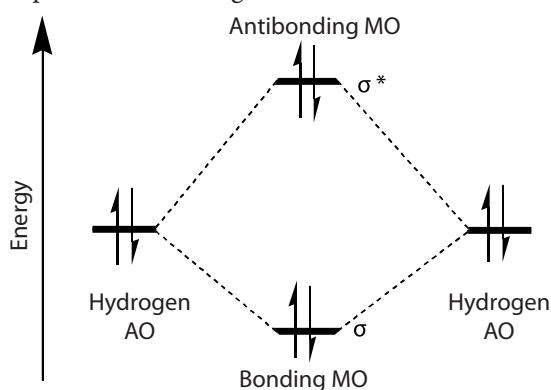
Carbonic acid

Sulfur can expand its octet to accommodate more than eight electrons in its outer shell.

8. C

Answers 2.2

1. Two electrons would have to go into an antibonding molecular orbital. This is energetically unfavourable because the increase in energy of the antibonding orbital is greater than the decrease in energy of the bonding orbital. Helium molecules do not form because they would be at higher energy than the separate helium atoms and the forces of repulsion would be greater than the forces of attraction.



AO: Atomic orbital
MO: Molecular orbital

2. D
3. D

Answers 2.3

1.

	Nitrogen	Oxygen	Fluorine
Bond order	3	2	1
Relative bond strength	strongest	middle	weakest
Relative bond length	shortest	middle	longest

2. D

Answers 2.4

1. B. Ammonia is pyramidal – whilst all the rest are trigonal planar.
2. A. A quick way to decide whether a molecule contains an unpaired electron is by adding up the Group numbers for the atoms present in the molecule. Hydrogen is counted as being a member of Group 1. If the total is odd then the molecule contains an unpaired electron.

Molecule	Sum of Group numbers	Unpaired electrons
N=O	15 + 16 = 31	√
N≡N	15 + 15 = 30	×
H-O-H	1 + 16 + 1 = 18	×
H-C≡N	1 + 14 + 15 = 30	×

3.

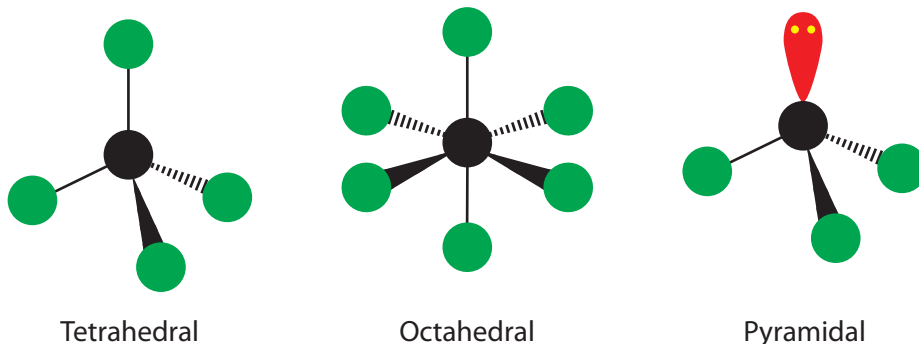
Oxide	Unpaired electrons
NO ₂	√
N ₂ O ₄	×
Cl ₂ O	×
ClO ₂	√

Answers 2.5

1.

Formula	Incorrect shape	Correct shape
BrF ₃	trigonal planar	T-shape
ICl ₄ ⁻	octahedral	square planar
SF ₄	tetrahedral	see-saw (saw-horse)

2.



3. Boron has no lone pairs and its three bonding pairs of electrons repel each other until they are as far apart as possible, which leads to a bond angle of 120°. The nitrogen in ammonia has three bonding pairs and one lone pair of electrons. The repulsion is greatest between the lone pair and the bonding pairs. This leads to a squashing of the tetrahedral angle leading to a pyramidal shape with an HNH bond angle of 107°.
4. Carbon dioxide is a linear molecule with dipoles. It has no dipole moment as the dipoles cancel each other out because they are equal and in opposite directions. Sulfur dioxide has a lone pair on the central sulfur atom, which leads to a V-shaped molecule and so its dipoles do not cancel each other and it has a dipole moment (A3.2a).

Answers 2.6

1. **Equation:** PCl₃ + Cl₂ → PCl₅
- Geometry:** pyramidal trigonal bipyramidal
- Bond angles:** 107° 90° and 120°
2. **Equation:** 2 SO₂ + O₂ ⇌ 2 SO₃
- Geometry:** V-shaped trigonal planar
- Bond angles:** 120° 120°

Answer 2.7

1.

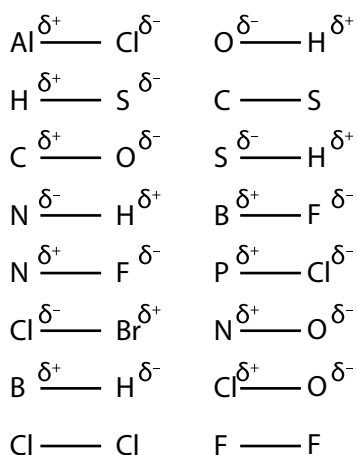
Hydrogen halide	ΔE_{neg}
H-F	1.9
H-Cl	0.9
H-Br	0.7
H-I	0.4

Bond energies decrease as the ΔE_{neg} values decrease.

Answers 2.8

1. They have identical atoms joined by covalent bond(s) that have identical electronegativities. There is an even sharing of the bonding electrons so there will be no dipole.

2.



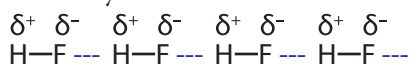
3. C-F > C-O > C-Cl > C-H

4.

Molecule's name	Formula	Polar	Non-polar
Propanone	$(\text{CH}_3)_2\text{C}=\text{O}$	√	
Carbon tetrachloride	CCl_4		√
Hydrogen chloride	HCl	√	
Chloromethane	CH_3Cl	√	
1,1-dichloroethane	CHCl_2CH_3	√	

Answers 2.9

1. The rise in boiling point $\text{HCl} < \text{HBr} < \text{HI}$ is due to an increase in Van der Waals forces as the number of electrons increases. Hydrogen fluoride has an anomalous boiling point because it also has hydrogen bonding between its molecules, as shown by the dashed lines.



2.

- Non-polar molecules are expected to have a symmetrical distribution of electrons.
- Electron cloud wobbles leading to a momentary uneven distribution of electrons.
- An instantaneous and temporary dipole is set up.
- The instantaneous dipole induces another temporary dipole in neighbouring atoms of molecules.
- The adjacent molecules with opposite dipoles in close proximity attract each other.
- Dipoles may be temporary and they are forming and disappearing all the time, but the attraction that is produced is permanent and is called the Van der Waals force.

Answer 2.10

1. Van der Waals forces are thought to be continually changing instantaneous dipole-induced dipole electric charge interactions between molecules. As the number of electrons increases down Group 17, so does the polarisability of the atoms because they have a greater number of electrons. A greater fluctuation in the asymmetry of the electron clouds will lead to larger temporary dipoles and therefore a greater Van der Waals force of attraction.

Answers 2.11

1. It 'dimerises' forming two intermolecular hydrogen bonds.
2. A

3. Energy Changes

Answers 3.1

- $\Delta_f H = -1253.6 \text{ kJ mol}^{-1}$
- $\Delta_f H = -1169.6 \text{ kJ mol}^{-1}$
- The two things that affect the size of hydration energies are ionic radius and the charge on the ion. The higher the charge on the ion the more exothermic $\Delta_{\text{hydr}} H$. The value for Mg^{2+} is nearly five times as large as Na^+ . Al^{3+} is nearly two and a half times as big as Mg^{2+} . By comparing the values for the Group 1 ions, the smaller the ion the more exothermic is $\Delta_{\text{hydr}} H$. So it is the charge density of the ion that relates to the size of $\Delta_{\text{hydr}} H$. The greater the charge density for the ion the greater its ion-dipole (electrostatic) interaction with water molecules.
- C
- All three neutralisations are the same reaction, *i.e.* $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$ or $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$. The spectator ions (Cl^- , Br^- , NO_3^- , Na^+) have no real effect on the enthalpy change as they do not take part in the reaction and remain in aqueous solution throughout it.
- Ethanoic acid, being a weak acid, is only partially ionised so some energy is lost in ionisation.
- D
- A

Answers 3.2

- Same reaction, if you remove spectator ions. $\text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{H}_2\text{O}(\text{l})$
- Sources of error:* Heat loss through the top and side of the calorimeter, draughts (convection currents) around the apparatus leading to cooling and movement of the flame, incomplete combustion, restricted oxygen supply. *Observations:* Soot observed underneath the beaker, smoky or orange flame. *Improvements:* Insulate sides of beaker (mineral wool), lid on beaker, draught screen around the flame.
- $\Delta H = -217 \text{ kJ mol}^{-1} = -217000 \text{ J mol}^{-1}$. Amount of copper(II) sulfate = $0.1 \times \frac{50}{1000} = 0.005 \text{ mol}$
 $q = 217000 \times 0.005 = 1085 \text{ J}$
 $q = m c \Delta T$ [rearrange the equation]
 $\Delta T = \frac{q}{mc} = \frac{1085}{(50 \times 4.2)} = 5.17 \text{ K (5.2K)}$
- As weak acids are not fully ionised, some energy is absorbed in the ionisation of the acid to replace the H^+ ions that react with OH^- ions in the neutralisation reaction.
 $\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \Delta H = + \text{ve}$
 $\text{HCl} + \text{KOH} \rightarrow \text{KCl} + \text{H}_2\text{O}$
 $\text{CH}_3\text{COOH} + \text{KOH} \rightarrow \text{CH}_3\text{COO}^- \text{K}^+ + \text{H}_2\text{O}$
- B
- Heat (q) = $m c \Delta T = 100 \times 4.2 \times 2 = 840 \text{ J}$
- Heat evolved = $m c \Delta T = 500 \times 4.18 \times 19.6 = 40964 \text{ J}$

$$\text{Amount of ethanol} = \frac{1.50}{46} = 0.0326 \text{ mol}$$

$$\text{Enthalpy of combustion} = -40.964/0.0326 = -1257 \text{ (-1260) kJ mol}^{-1}.$$

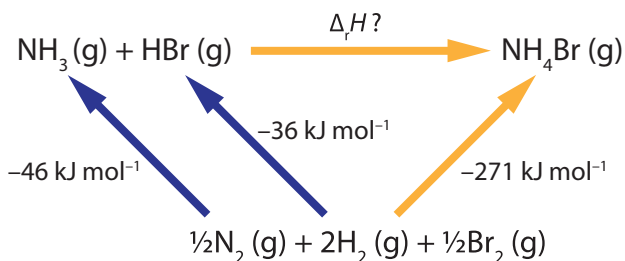
Value calculated experimentally is lower than the listed value because heat is lost to the surroundings.

8. The change is exothermic, there is a rise in temperature, heat is gained by the surroundings and energy is lost by the chemical system.

Answers 3.3

1. -93 kJ mol^{-1}

2.



$$\Delta_r H = +46 + 36 - 271 = -189 \text{ kJ mol}^{-1}.$$

3. $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \Delta_r H$ (methane)

$$\text{C}(\text{s}) \rightarrow \text{C}(\text{g}) \Delta_{\text{atm}} H$$
 (graphite)

$$2 \text{H}_2(\text{g}) \rightarrow 4 \text{H}(\text{g}) \Delta_{\text{atm}} H$$
 (hydrogen) $\times 4$

$$\Delta_r H = +75 + 717 + (218 \times 4) = +1664 \text{ kJ mol}^{-1}$$

$$\frac{\Delta_r H}{4} = \text{bond dissociation energy} = \frac{1664}{4} = +416 \text{ kJ mol}^{-1}$$

4. $\Delta_r H = +110.5 + -108.7 = 1.8 \text{ kJ mol}^{-1}$

5. D

6. B

7. A

8. C

9. C

Answers 3.4

1. $\Delta_r H = -127 \text{ kJ mol}^{-1}$

2. $\Delta_r H = -16 \text{ kJ mol}^{-1}$

3. $\Delta_r H = -485 \text{ kJ mol}^{-1}$ $\Delta_r H = -242.5 \text{ kJ mol}^{-1}$ [$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$]

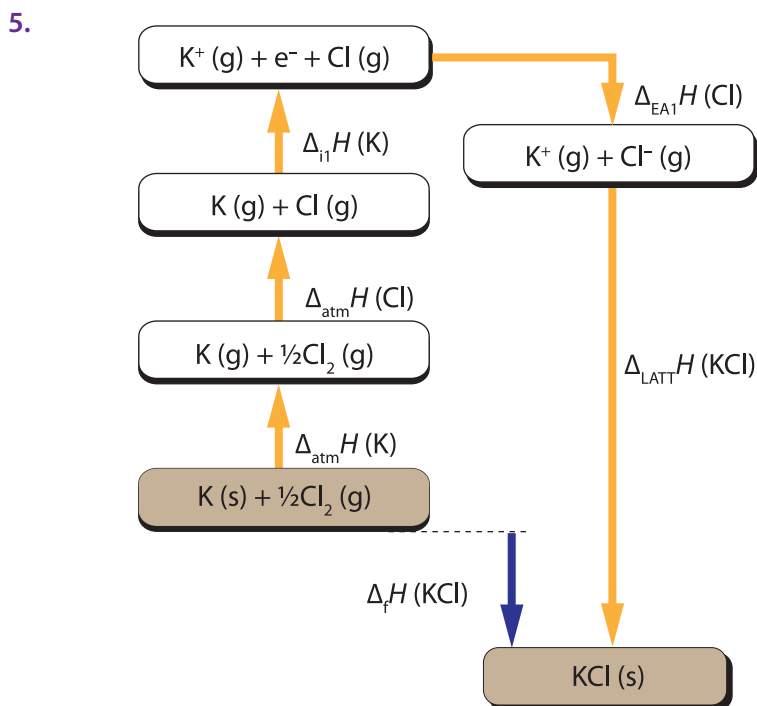
4. $\Delta_r H = -92.5 \text{ kJ mol}^{-1}$

- $\Delta_c H = -778 \text{ kJ mol}^{-1}$
- $\Delta_f H = -982.5 \text{ kJ mol}^{-1}$
- $\Delta_f H = -577 \text{ kJ mol}^{-1}$, which is highly exothermic so gases produced will expand rapidly at the high temperatures. Also, there are $\frac{3}{2}$ more moles of products than reactants.
- Different molecules have different bond strengths for a particular type of bond that depend on its precise environment. For example, the O–H in water (H_2O) is different from the O–H in methanol (CH_3OH). Bond enthalpy data are averages for many molecules rather than the exact value for an individual covalent molecule.
- The enthalpy of reaction is endothermic because, in simple dissociations, only bonds are broken and this is an endothermic process. $\text{N}_2\text{O}_4 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g})$

Answers 3.5

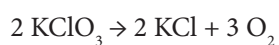
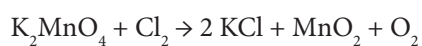
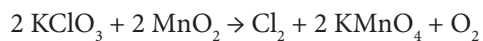
- Magnesium oxide (MgO) has the largest $\Delta_{\text{latt}} H$ because it has the cation with the smallest ionic radius. The smaller the ion, the closer the oppositely charged ions can approach and the stronger the attractive force between them.
- Magnesium oxide will have the largest $\Delta_{\text{latt}} H$ because each ion is doubly charged compared with the singly charged ions in sodium chloride, leading to greater attraction between Mg^{2+} and O^{2-} . The other factor affecting the size of $\Delta_{\text{latt}} H$ is the smaller ionic radius of Mg^{2+} compared with Na^+ , which leads to an even greater charge density on the doubly charged cation and, therefore, greater attraction between Mg^{2+} and O^{2-} .
- I = $\text{Na} (\text{g}) \rightarrow \text{Na}^+ (\text{g}) + \text{e}^-$, II = $\frac{1}{2}\text{F}_2 (\text{g}) \rightarrow \text{F} (\text{g})$, III = $\text{Na}^+ (\text{g}) + \text{F}^- (\text{g}) \rightarrow \text{NaF} (\text{s})$, IV = $\text{Na} (\text{s}) + \frac{1}{2}\text{F}_2 (\text{g}) \rightarrow \text{NaF} (\text{s})$
 $\text{V} = \text{F} (\text{g}) + \text{e}^- \rightarrow \text{F}^- (\text{g})$, VI = $\text{Na} (\text{s}) \rightarrow \text{Na} (\text{g})$ & IV = VI + I + II + V + III

4. $\Delta_{\text{latt}} H = -3401 \text{ kJ mol}^{-1}$



Answers 3.6

1. D
2. B
3. The purple colour is due to KMnO_4 = potassium manganate(VII). The green colour is due to the impurity, chlorine gas (Cl_2) mixed in with the oxygen gas.



The three equations add together to give the overall decomposition equation which is the same as the uncatalysed reaction showing that MnO_2 is indeed acting as a catalyst.

Answer 3.7

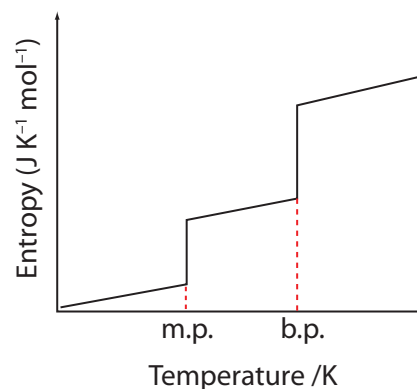
1. D [inhibitors remove reactive intermediates from the normal reaction sequence].

4. Free Energy and Entropy

Answers 4.1

- D
- B
- $2 \text{ Na (s)} + \text{Cl}_2 \text{ (g)} \rightarrow 2 \text{ NaCl (s)}$. There is a decrease in entropy as a highly ordered lattice is the result of the reaction between a solid and a gas.

$2 \text{ H}_2 \text{ (g)} + \text{O}_2 \text{ (g)} \rightarrow 2 \text{ H}_2\text{O (l)}$. There is a decrease in entropy as two gases react to form an ordered hydrogen bonded liquid.
- At absolute zero (0 K), a perfect crystal will have zero entropy. As the temperature increases, the particles will have more thermal energy and will be vibrating more about fixed positions. At the melting point (m.p.), there will be a large increase in entropy as bonds are broken. This will also happen at the boiling point (b.p.) as particles have weak van der Waals forces.



Answers 4.2

- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \Rightarrow \Delta S_{\text{total}} = +336 + -302 \Rightarrow \Delta S_{\text{total}} = +34 \text{ J K}^{-1} \text{ mol}^{-1}$
- $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \Rightarrow +86 = \Delta S_{\text{system}} + -96 \Rightarrow \Delta S_{\text{system}} = 86 + 96 \text{ J K}^{-1} \text{ mol}^{-1} = +182 \text{ J K}^{-1} \text{ mol}^{-1}$
- C

Answers 4.3

- $\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}} = (135.0 + 213.6 + 69.9) - (2 \times 101.7) = +215.1 \text{ J K}^{-1} \text{ mol}^{-1}$.
- $\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}} = (102.5 + 69.9) - (109.6) = +62.8 \text{ J K}^{-1} \text{ mol}^{-1}$
- $$\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$$

$$-198.8 = (2 \times \text{NH}_3) - (191.6 + 3 \times 130.6)$$

$$-198.8 = (2 \times \text{NH}_3) - (583.4)$$

$$2 \text{ NH}_3 = -198.8 + 583.4$$

$$2 \text{ NH}_3 = 384.6 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{NH}_3 = +192.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

4. $\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}}$
 $+160 = (39.7 + 213.6) - (\text{CaCO}_3)$
 $+160 = 253.3 - \text{CaCO}_3$
 $160 - 253.3 = -\text{CaCO}_3$
 $-93.3 = -\text{CaCO}_3$
 $\text{CaCO}_3 = +93.3 \text{ J K}^{-1} \text{ mol}^{-1}$
5. $\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}} = (88.0 + 130.6) - (52.3 + 2 \times 69.9) = (218.6) - (192.1) = +26.5 \text{ J K}^{-1} \text{ mol}^{-1}$
6. $\Delta S_{\text{system}} = S_{\text{products}} - S_{\text{reactants}} = 42.6 - \left(33.2 + \frac{205}{2}\right) = 42.6 - 135.7 = -93.1 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answers 4.4

1. $\Delta S_{\text{surroundings}} = -\frac{\Delta_r H}{T}$ and since $\Delta_r H$ is always negative for an exothermic reaction, $\Delta S_{\text{surroundings}}$ will be positive since multiplying two negatives (a negative \times a negative) gives a positive.
2. $\Delta S_{\text{surroundings}} = -\frac{\Delta_r H}{T} = -\frac{-214000}{333} = +642.6 \text{ J K}^{-1} \text{ mol}^{-1}$.
3. $\Delta S_{\text{surroundings}} = -66 \text{ J K}^{-1} \text{ mol}^{-1}$. As a bunsen burner blue flame can reach 1300K it is practicable to carry out this reaction in a laboratory.
4. $\Delta S_{\text{surroundings}} = -\Delta_r H/T$ & $\Delta_r H = -178000 \text{ J mol}^{-1}$ & $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$

	T / °C	T / K	$\Delta S_{\text{surroundings}} / \text{J K}^{-1} \text{ mol}^{-1}$	$\Delta S_{\text{total}} / \text{J K}^{-1} \text{ mol}^{-1}$
a.	25	298	-597	-437
b.	832	1105	-161	-0.6
c.	1127	1400	-127	33.4

The reaction is not feasible at room temperature as ΔS_{total} is negative. At 832°C, the value of ΔS_{total} approximates zero and it is above this temperature that the reaction becomes feasible as ΔS_{total} becomes positive.

Answers 4.5

1. D
2. $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. Therefore $\Delta S_{\text{system}} = \Delta S_{\text{total}} - \Delta S_{\text{surroundings}}$ $\Delta S_{\text{system}} = 57 - 118 = -61 \text{ J K}^{-1} \text{ mol}^{-1}$
3. $\Delta S_{\text{surroundings}} = -\Delta_r H/T$ and since $\Delta_r H$ is always positive for an endothermic reaction $\Delta S_{\text{surroundings}}$ will be negative. From the equation $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ for the process to be feasible, ΔS_{total} is positive. For an endothermic reaction ΔS_{system} has to be more positive than $\Delta S_{\text{surroundings}}$ is negative.
4. According to the second law of thermodynamics, the entropy of the universe (ΔS_{total}) is increased in a spontaneous process. When water freezes, ΔS_{system} decreases as its molecules become more ordered and as it adopts a low density open structure, similar to diamond, as additional hydrogen bonds form. This means the increase in $\Delta S_{\text{surroundings}}$ more than compensates (outweighs) the decrease in ΔS_{system} .

5. B

Answers 4.6

- $\Delta G = -336.2 \text{ kJ mol}^{-1}$
- $\Delta G = -214.4 \text{ kJ mol}^{-1}$
- $\Delta H = -196 \text{ kJ mol}^{-1}$
- $\text{C}_6\text{H}_{12}\text{O}_6 (\text{s}) + 6 \text{O}_2 (\text{g}) \rightarrow 6 \text{CO}_2 (\text{g}) + 6 \text{H}_2\text{O} (\text{l})$

With such a large and negative ΔG the reaction is thermodynamically feasible but, fortunately, glucose does not spontaneously combust as this reaction is kinetically very slow as it has a large activation energy.

- $2 \text{Pb}(\text{NO}_3)_2 (\text{s}) \rightarrow 2 \text{PbO} (\text{s}) + 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$.

$\Delta H = \Delta G$ at 0 K so $\Delta H = 600 \text{ kJ mol}^{-1}$.

Plotting a graph of ΔG (x -axis) and T (y -axis) gives the slope $\Delta S = 850\text{--}880 \text{ J K}^{-1} \text{ mol}^{-1}$.

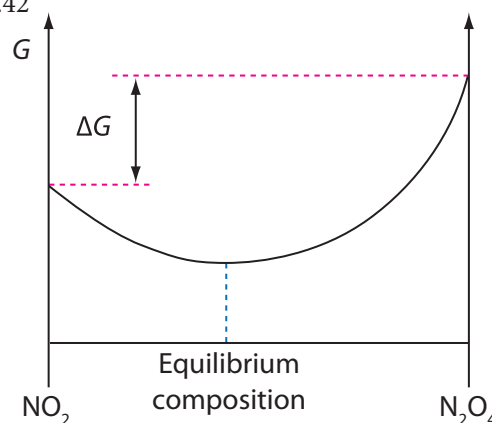
The reaction becomes feasible at temperatures $>680 \text{ K}$ when ΔG becomes negative.

Answers 4.7

- D
- ΔG is zero, because the equilibrium constant $K = 1$ which happens when $[A] = [B]$.
- $\Delta G = -4.6 \text{ kJ mol}^{-1} = \Delta G = -4600 \text{ J mol}^{-1}$ where $\Delta G = -RT \ln K$

Therefore $K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(\frac{4600}{8.3 \times 298}\right) = \exp\left(\frac{4600}{2473.4}\right) = \exp 1.86 = 6.42$

- $K < 1$ as the minimum is towards the reactant (NO_2) and because the Gibbs free energy of the reactant (NO_2) is lower than the Gibbs free energy of the product (N_2O_4).



5. Equilibrium

Answers 5.1

- D
- It is useful for making qualitative predictions about how changes in temperature, pressure and concentration will effect the equilibrium position.
- The equilibrium will shift in the endothermic direction, *i.e.* to the right hand side.
- The equilibrium will shift in the exothermic direction, *i.e.* to the left hand side.
- The equilibrium will shift in the exothermic direction, *i.e.* to the right hand side.
- There is 1 mole on the left hand side and there are 2 moles on the right hand side. If the pressure is increased, the equilibrium will shift towards the side with the fewest moles, *i.e.* it will shift towards the left hand side in an attempt to minimise the applied change.
- There are 9 moles on the left hand side and 6 moles on the right hand side. If the pressure is increased, the equilibrium will shift towards the side with the fewest moles, *i.e.* it will shift towards the right hand side in an attempt to minimise the applied change.
- There are 2 moles on the left hand side and 2 moles on the right hand side. If the pressure is increased the equilibrium will not shift from the established equilibrium position since there are an equal number of moles on both sides of the equilibrium.
- Approaching from the left hand side, dissolve sodium chromate(VI) in water and add acid. Approaching from the right hand side, dissolve sodium dichromate(VI) in water and add alkali.
- Removal of some chlorine will decrease its concentration. The equilibrium will shift towards the side containing chlorine, *i.e.* it will shift towards the left hand side in an attempt to minimise the applied change by replacing the lost chlorine.
- Addition of some hydrogen will increase its concentration. The equilibrium will shift away from the side containing hydrogen, *i.e.* it will shift towards the right hand side in an attempt to minimise the applied change by removing the added hydrogen.

12.

Equilibria	Shift left hand side	No shift	Shift right hand side
$\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$	√		
$2 \text{CO}(\text{g}) + 2 \text{NO}(\text{g}) \rightleftharpoons 2 \text{CO}_2(\text{g}) + \text{N}_2(\text{g})$			√
$\text{CH}_4(\text{g}) + 2 \text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$	√		
$\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$		√	
$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$	√		
$2 \text{N}_2\text{O}(\text{g}) + 3 \text{O}_2(\text{g}) \rightleftharpoons 2 \text{N}_2\text{O}_4(\text{g})$			√

13.

Equilibria	$\Delta_r H / \text{kJ mol}^{-1}$	Shift left hand side	Shift right hand side
$\text{CO (g)} + 2 \text{H}_2 \text{(g)} \rightleftharpoons \text{CH}_3\text{OH (g)}$	- 18	✓	
$\text{N}_2 \text{(g)} + 3 \text{H}_2 \text{(g)} \rightleftharpoons 2 \text{NH}_3 \text{(g)}$	- 92	✓	
$\text{N}_2\text{O (g)} + \text{NO}_2 \text{(g)} \rightleftharpoons 3 \text{NO (g)}$	+ 156		✓
$\text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)} \rightleftharpoons \text{CO (g)} + \text{H}_2\text{O (g)}$	+ 41.2		✓
$4 \text{NH}_3 \text{(g)} + 5 \text{O}_2 \text{(g)} \rightleftharpoons 4 \text{NO (g)} + 6 \text{H}_2\text{O (g)}$	-909	✓	

Answers 5.2

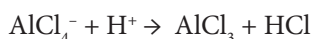
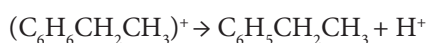
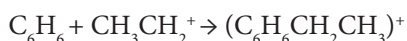
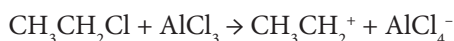
1. Conjugate pairs are identified by the colour of their cells in each row of the table.

	Acid	Base	Conjugate acid	Conjugate base
a.	NH_3	NH_3	NH_4^+	NH_2^-
b.	HCO_3^-	H_2O	H_3O^+	CO_3^{2-}
c.	HCl	NH_3	NH_4^+	Cl^-
d.	H_2O	NH_2^-	NH_3	OH^-
e.	H_2SO_4	HNO_3	H_2NO_3^+	HSO_4^-
f.	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	H_2O	H_3O^+	$[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$
g.	$\text{C}_6\text{H}_5\text{OH}$	H_2O	H_3O^+	$\text{C}_6\text{H}_5\text{O}^-$
h.	$\text{C}_6\text{H}_5\text{CO}_2\text{H}$	H_2O	H_3O^+	$\text{C}_6\text{H}_5\text{CO}_2^-$

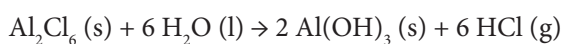
2. C

3. A

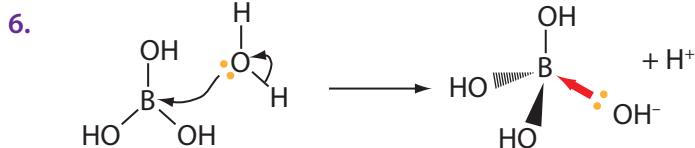
4. Aluminium chloride accepts a pair of electrons from the Cl atom in chloroethane. It is a Lewis acid because it is an electron pair acceptor. Benzene reacts more quickly with chloroethane in the presence of aluminium chloride. In the following scheme, AlCl_3 shows itself to be a catalyst as it takes part in the reaction and is regenerated at the end.



Aluminium chloride is hydrolysed by water to produce aluminium hydroxide and hydrogen chloride gas.



5. D

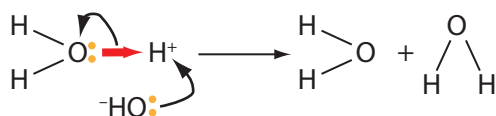


$B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$. $B(OH)_3$ is an electron pair acceptor and water is an electron pair donor.

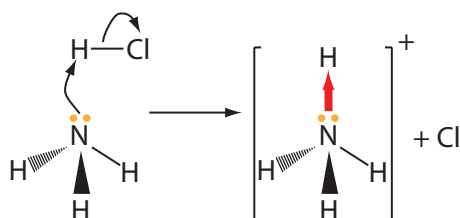
7.

Reaction 1	H_3O^+ (aq)	OH^- (aq)
Lewis acid	√	
Lewis base		√
Reaction 2	NH_3 (aq)	HCl (aq)
Lewis acid		√
Lewis base	√	

Reaction 1 Mechanism



Reaction 2 Mechanism



Answers 5.3

1. A
2. A high value of K_c is due to a high yield of products.
3. K_c is fixed at a particular temperature.

4.

	K_c expression	K_c units
a. $2 SO_2(g) + O_2(g) \rightleftharpoons 2 SO_3(g)$	$K_c = \frac{[SO_3(g)]_{eq}^2}{[SO_2(g)]_{eq}^2 [O_2(g)]_{eq}}$	$mol^{-1} dm^3$
b. $2 NO(g) + O_2(g) \rightleftharpoons 2 NO_2(g)$	$K_c = \frac{[NO_2(g)]_{eq}^2}{[NO(g)]_{eq}^2 [O_2(g)]_{eq}}$	$mol^{-1} dm^3$
c. $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$	$K_c = \frac{[PCl_5(g)]_{eq}}{[PCl_3(g)]_{eq} [Cl_2(g)]_{eq}}$	$mol^{-1} dm^3$
d. $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$	$K_c = \frac{[CO_2(g)]_{eq} [NO(g)]_{eq}}{[CO(g)]_{eq} [NO_2(g)]_{eq}}$	no units
e. $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$	$K_c = \frac{[HI(g)]_{eq}^2}{[H_2(g)]_{eq} [I_2(g)]_{eq}}$	no units

Answers 5.4

1. The ideal gas equation is $pV = nRT$. Rearranging this equation gives $P = \frac{n}{V}RT$ and since $\frac{n}{V}$ = concentration $P = cRT$. At a constant temperature, R and T are fixed, therefore P is proportional to c .

2.

	K_p expression	K_p units
a. $2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{SO}_3(\text{g})$	$K_p = \frac{p(\text{SO}_3(\text{g}))_{\text{eq}}^2}{p(\text{SO}_2(\text{g}))_{\text{eq}}^2 p(\text{O}_2(\text{g}))_{\text{eq}}}$	Pa^{-1}
b. $\text{CO}(\text{g}) + \text{NO}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{NO}(\text{g})$	$K_p = \frac{p(\text{CO}_2(\text{g}))_{\text{eq}} p(\text{NO}(\text{g}))_{\text{eq}}}{p(\text{CO}(\text{g}))_{\text{eq}} p(\text{NO}_2(\text{g}))_{\text{eq}}}$	No units
c. $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$	$K_p = \frac{p(\text{HI}(\text{g}))_{\text{eq}}^2}{p(\text{H}_2(\text{g}))_{\text{eq}} p(\text{I}_2(\text{g}))_{\text{eq}}}$	No units

Answer 5.5

1.

a. $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq})$	$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})]_{\text{eq}} [\text{CO}_3^{2-}(\text{aq})]_{\text{eq}}$	$\text{mol}^2 \text{dm}^{-6}$
b. $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$	$K_{\text{sp}} = [\text{Ba}^{2+}(\text{aq})]_{\text{eq}} [\text{SO}_4^{2-}(\text{aq})]_{\text{eq}}$	$\text{mol}^2 \text{dm}^{-6}$
c. $\text{PbS}(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + \text{S}^{2-}(\text{aq})$	$K_{\text{sp}} = [\text{Pb}^{2+}(\text{aq})]_{\text{eq}} [\text{S}^{2-}(\text{aq})]_{\text{eq}}$	$\text{mol}^2 \text{dm}^{-6}$

Answers 5.6

1. Stronger weak acids will have a greater degree of ionization and will therefore have a greater $[\text{H}^+] = [\text{A}^-]$.
Since $K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$, it will increase as the concentration of both the protons and the conjugate base increase.

2. They are both indicators and weak acids.

3. a. $K_a = \frac{[\text{H}^+(\text{aq})][\text{HCOO}^-(\text{aq})]}{[\text{HCOOH}(\text{aq})]}$ b. $K_a = \frac{[\text{H}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$
- c. $K_a = \frac{[\text{H}^+(\text{aq})][\text{C}_6\text{H}_5\text{O}^-(\text{aq})]}{[\text{C}_6\text{H}_5\text{OH}(\text{aq})]}$ d. $K_a = \frac{[\text{H}^+(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{H}_2\text{CO}_3(\text{aq})]}$

Answers 5.7

1. Only gaseous components are included in the equilibrium expression K_p , so the solid is left out.

$$K_p = \frac{p(\text{H}_2) \times p(\text{CO})}{p(\text{H}_2\text{O})} \text{ and the units} = \text{Pa.}$$

2. $K_p = 1.14 \times 10^{-4} \text{ atm}^{-2}$

Answers 5.8

- K_{sp} for $MgCO_3 = 1.0 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$
 K_{sp} for $AgBr = 5.0 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$
- $\sqrt[3]{\frac{6.3 \times 10^{-50}}{4}} = 2.51 \times 10^{-17} \text{ mol dm}^{-3}$
 - $1.41 \times 10^{-6} \text{ mol dm}^{-3}$
 - $\sqrt[3]{\frac{2.45 \times 10^{-9}}{4}} = 8.49 \times 10^{-4} \text{ mol dm}^{-3}$

Answers 5.9

- K_a for $H_3PO_4 = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$
- K_a for $HCO_2H = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$
- K_a for $HOCl = 3.6 \times 10^{-8} \text{ mol dm}^{-3}$
- $pH = -\log_{10}(\sqrt{1.29 \times 10^{-4} \times 0.01}) = 2.94$
- $pH = 3.29$
- $pH = 2.65$

Answers 5.10

1.

Temperature / K	pH
273	7.47
283	7.27
298	7.00
313	6.77
373	6.14

2. The pH falls as the size of K_w increases.

Answers 5.11

- $pH = 3$
 - $pH = 0.3$
 - $pH = 1.4$
 - $pH = 0.$
- $2.45 \times 10^{-3} \text{ mol dm}^{-3}$
 - $3.8 \times 10^{-6} \text{ mol dm}^{-3}$
 - $1.78 \times 10^{-3} \text{ mol dm}^{-3}$
 - 3.16 mol dm^{-3}
 - $4.37 \times 10^{-5} \text{ mol dm}^{-3}$
 - $1.66 \times 10^{-7} \text{ mol dm}^{-3}$
- $pH = 7.4$
- $pH = 3.44$
 - $pH = 2.40$
 - $pH = 2.66$
 - $pH = 2.58$
 - $pH = 1.64$

5. a. HOCl ($pK_a = 7.43$) b. HCN ($pK_a = 9.31$)
 c. C_2H_5COOH ($pK_a = 4.89$) d. H_3PO_4 ($pK_a = 2.10$).

The order of acidity is $H_3PO_4 > C_2H_5COOH > HOCl > HCN$.

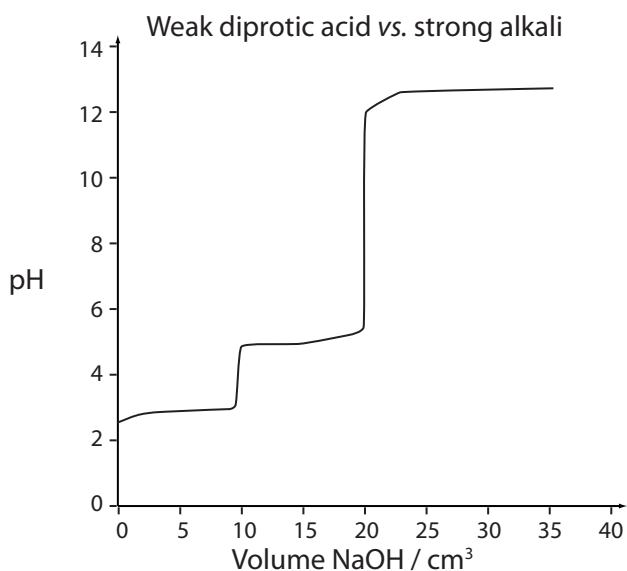
6. K_a for C_6H_5COOH ($K_a = 6.3 \times 10^{-5} \text{ mol dm}^{-3}$) & K_a for C_6H_5OH ($K_a = 1.3 \times 10^{-10} \text{ mol dm}^{-3}$).
7. pH = 2.01

Answers 5.12

1. D
2. A titration curve is a graph that shows how pH varies with the addition of acid to a base or the addition of a base to an acid in a neutralization reaction.
3. Start the curve at the actual pH of the starting acid, if it is known. If its concentration and K_a are known, work the pH out.)

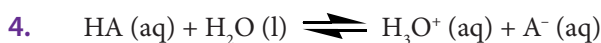
	Start the curve
Strong acid	pH = 1
Weak acid	pH = 3
	Finish the curve
Strong base	pH = 13
Weak base	pH = 9

4. a. red b. colourless c. yellow
5. The two vertical sections correspond to the following equilibria as the two acidic protons are removed selectively from the dicarboxylic acid.



Answers 5.13

1. C & D
2. pH = 4.5, therefore it is an acidic buffer.
3. Acidic buffers consist of weak acids and sodium salts of these weak acids.
Alkaline buffers consist of weak alkalis and chloride salts of these weak alkalis.



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$
 and rearranging this equation gives

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]}$$
 and taking $-\log_{10}$ of both sides gives

$$-\log_{10} [\text{H}_3\text{O}^+] = -\log_{10} K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]}$$

$$\text{pH} = \text{p}K_a - \log_{10} \frac{[\text{HA}]}{[\text{A}^-]}$$
 which can be rewritten as

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$
, which is the Henderson Hasselbach equation.

5. B
6. C
7. Reaction with acid: $\text{H}_3\text{N}^+ - \text{CHR} - \text{COO}^- + \text{H}^+ \rightarrow \text{H}_3\text{N}^+ - \text{CHR} - \text{COOH}$
Reaction with alkali: $\text{H}_3\text{N}^+ - \text{CHR} - \text{COO}^- + \text{OH}^- \rightarrow \text{H}_2\text{N} - \text{CHR} - \text{COO}^- + \text{H}_2\text{O}$
8. **B** corresponds to the buffer zone (nearly horizontal section of the titration curve). In this region, only small changes in pH are observed over quite a large region. In this region, there is a mixture of NH_3 and NH_4Cl , *i.e.* a weak alkali and its conjugate acid.
9. pH = 4.38
10. Mass of $\text{CH}_3\text{CO}_2\text{Na} = 14 \text{ g}$.

Answers 5.14

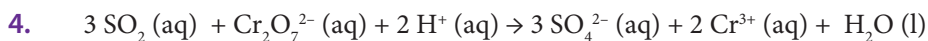
1. Mass of copper = 0.533 g
2. Mass of silver = 0.322 g
3. Time = 760 seconds.

Answers 5.15

1. Ferric chloride = Fe^{3+} (oxidation number +3) & ferrous chloride is Fe^{2+} (oxidation number +2)
2. $\text{Zn (s)} \rightarrow \text{Zn}^{2+} \text{ (aq)} + 2 \text{ e}^-$ *oxidation* $\text{Cu}^{2+} \text{ (aq)} + 2 \text{ e}^- \rightarrow \text{Cu (s)}$ *reduction*

3.

	Oxidised species	Reduced species
a.	Br ⁻	Cl ₂
b.	H ₂	CuO
c.	H ₂	O ₂
d.	I ⁻	Fe ³⁺

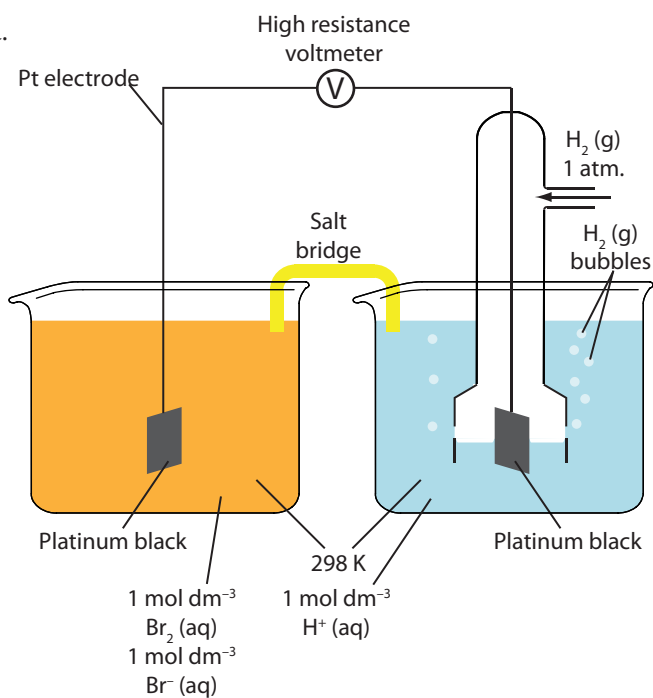


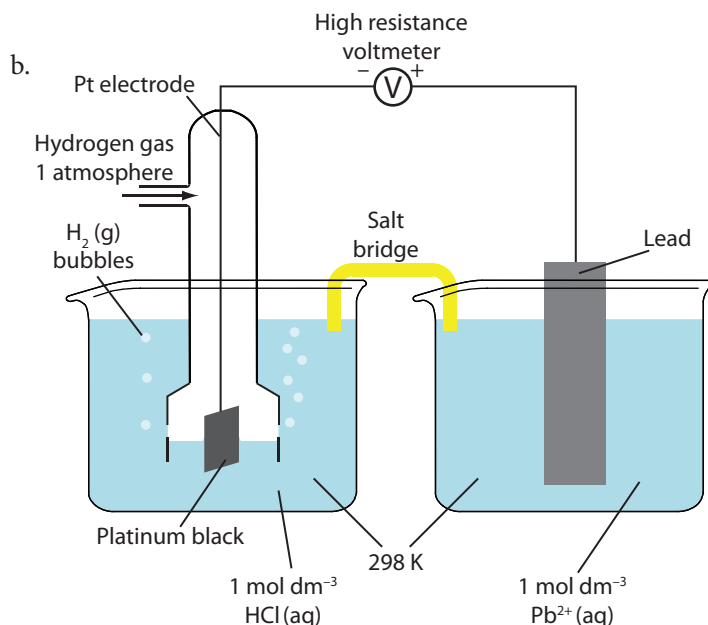
Answers 5.16

1. $\text{Cu}(\text{s}) + (\text{aq}) \rightleftharpoons \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^-$. The copper is oxidised as it loses electrons and its oxidation number increases.
2. 0.00 V.
3. Adsorption
4. $[\text{H}_2\text{SO}_4] = 0.5 \text{ mol dm}^{-3}$, since it is diprotic the $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$.

Answers 5.17

1. Platinum is used as the electrode when the half cells system does not include a metal, *i.e.* for non-metals and a mixture of ions.
2. D
3. B
4. a.





Answer 5.18

1. a. $E^\ominus_{\text{cell}} = + 2.00 \text{ V}$ b. $E^\ominus_{\text{cell}} = + 1.61 \text{ V}$ c. $E^\ominus_{\text{cell}} = + 2.75 \text{ V}$
 d. $E^\ominus_{\text{cell}} = + 1.17 \text{ V}$ e. $E^\ominus_{\text{cell}} = + 2.10 \text{ V}$

Answers 5.19

1. ΔG is the maximum amount of electrical work that the electrochemical cell can supply to a device.
 2. $\Delta G = - n F E^\ominus_{\text{cell}} = - (10 \times 96500 \times 0.97) \div 1000 = - 936 \text{ kJ mol}^{-1}$
 3. $\Delta G = - 147 \text{ kJ mol}^{-1}$
 4. $\Delta G = - n F E^\ominus_{\text{cell}}$ (rearranging)
 $E^\ominus_{\text{cell}} = \frac{\Delta G}{n F}$ (need to convert kJ mol^{-1} to $\text{J mol}^{-1} \times 1000$) $= \frac{122000}{2 \times 96500} = 0.63 \text{ V}$

Answers 5.20

1. a. The direction of electron flow will be from copper to chlorine.
 b. The direction of electron flow will be from zinc to silver(I).
 c. The direction of electron flow will be from copper to iron(III).
 d. The direction of electron flow will be from lithium to lead(II).
 2. a. not feasible $E^\ominus_{\text{cell}} = -0.53 \text{ V}$ b. not feasible $E^\ominus_{\text{cell}} = -0.80 \text{ V}$
 c. feasible $E^\ominus_{\text{cell}} = +0.23 \text{ V}$ d. not feasible $E^\ominus_{\text{cell}} = -0.09 \text{ V}$

Answers 5.21

- $E_{\text{cell}}^{\ominus}$ will decrease because this equilibrium $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$ will shift to the left hand side according to Le Chatelier's Principle. This results in the half cell's potential becoming more negative as more electrons are released from the zinc electrode. The half cell potential of the zinc will become nearer to that for magnesium, therefore $E_{\text{cell}}^{\ominus}$ gets smaller.
- If the $[\text{Cl}^{-}(\text{aq})]$ is increased for the chlorine half cell it will cause the equilibrium shown to shift to the left hand side making this half cell potential less positive. $\frac{1}{2}\text{Cl}_2(\text{g}) + \text{e}^{-} \rightleftharpoons \text{Cl}^{-}(\text{aq})$

As $E_{\text{right hand side}}$ decreases the size of E_{cell} will decrease because: $E_{\text{cell}}^{\ominus} = E_{\text{right hand side}}^{\ominus} - E_{\text{left hand side}}^{\ominus}$

If $\text{Cl}^{-}(\text{aq})$ is added to the silver half cell, it will cause silver chloride to precipitate since $\text{Ag}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq}) \rightarrow \text{AgCl}(\text{s})$. This will result in a decrease in the $[\text{Ag}^{+}(\text{aq})]$ making the silver electrode less positive. The silver electrode's potential will then be further away from the chlorine electrode's potential, so $E_{\text{cell}}^{\ominus}$ will increase.

Answers 5.22

- $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
 - Electrolysis of water (acidified)
- Negative plate: $\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 8\text{H}^{+} + 8\text{e}^{-}$ Positive plate: $2\text{O}_2 + 8\text{H}^{+} + 8\text{e}^{-} \rightarrow 4\text{H}_2\text{O}$
- Three major factors are cost of the cars, their limited top speeds and ranges.

6. Gases and Kinetics

Answers 6.1

- The distance between helium atoms is very much greater than the atomic diameter.
- D
- Gas particles are in continuous and random motion. There are no intermolecular forces between particles. The particles occupy zero volume. When particles collide their collisions are perfectly elastic and the average kinetic energy for the particles is proportional to the temperature (kelvin).

Answers 6.2

- A
- A
- B
- Volume is $V = 4.8 \times 10^{-5} \text{ m}^3$. Temperature is $T = 291 \text{ K}$. $PV = \frac{m}{M_r} \times RT$ and rearranging gives $M_r = \frac{mRT}{PV}$.

$$M_r = \frac{0.14 \times 8.31 \times 291}{98400 \times 4.8 \times 10^{-5} \text{ m}^3} = 71.7 \text{ g mol}^{-1}$$
- Volume is $V = 0.0001 \text{ m}^3$. Temperature is $T = 301 \text{ K}$. Pressure is $P = 101300 \text{ Pa}$.
 M_r for $\text{N}_2\text{O} = 2 \times 14.0 + 16.0 = 44 \text{ g mol}^{-1}$.
 $PV = \frac{m}{M_r} \times RT$ and rearranging gives $m = \frac{PVM_r}{RT}$.

$$m = \frac{101\,300 \times 0.0001 \times 44.0}{8.31 \times 301} = 0.178 \text{ g}$$

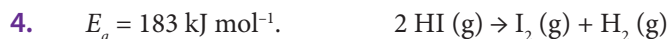
Answers 6.3

- The particles will collide and bounce off each other without reaction.
- At any temperature, there will be a range of molecular speeds. There are few molecules moving very slowly or very quickly, with the majority of molecules at speeds near the average. At high temperatures, there are more molecules with faster speeds than at lower temperatures. At high temperatures there is a greater spread of kinetic energies than at lower temperatures. At higher temperatures the peak (modal kinetic energy) is lower and further to the right compared with the peak at lower temperatures. The area under the curve is proportional to the total number of molecules. The reaction goes faster at higher temperatures because the shaded area beyond E_a increases.
- D

Answers 6.4

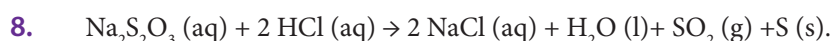
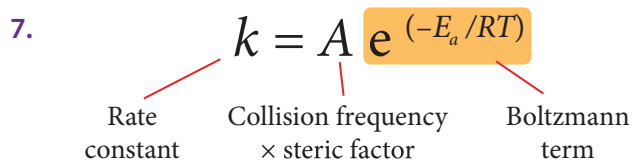
- The rate at which particles collide.
- Arrhenius equation.

3. *Arrhenius equation: $k = A \exp\left(-\frac{E_a}{RT}\right) = A e^{\left(-\frac{E_a}{RT}\right)}$ where k = rate constant, A = pre-exponential factor, E_a = activation energy, R = molar gas constant (8.31 J K⁻¹ mol⁻¹), and T = thermodynamic temperature (K). The negative sign indicates that the higher the activation energy, the slower the reaction. It also indicates that the higher the temperature, the faster the reaction.*

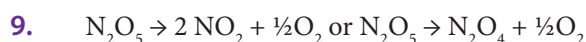


5. C

6. C



The rate of reaction can be taken as the reciprocal of the time it takes for a cross placed beneath the reaction flask to be obscured by the sulfur which turns the mixture from colourless to milky. A plot of $\log_e k$ (y -axis) and $1/T$ in Kelvin (x -axis) gives an activation energy in the range 27 to 32 kJ mol⁻¹.



A plot of $\log_e k$ (y -axis) and $1/T$ in Kelvin (x -axis) gives an activation energy $E_a = 105 \text{ kJ mol}^{-1}$.

10.

Reaction #	A	E_a	k
1	4.3×10^{11}	89.5×10^3	8.66×10^{-5}
2	2.4×10^{11}	81.6×10^3	1.17×10^{-3}
3	7.9×10^8	10.5×10^3	1.14×10^7

The reaction rate is $3 > 2 > 1$. The fastest is 3 and the slowest is 1.

Answers 6.5

- $\text{CH}_3\text{COCH}_3 + \text{I}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$. The catalyst (H^+) is a homogeneous catalyst.
- A
- iron (heterogeneous)
 - vanadium(V) oxide (heterogeneous)
 - manganese(IV) oxide (heterogeneous)
 - proton (homogeneous)
- $\text{H}_2\text{NCONH}_2 + \text{H}_2\text{O} \rightarrow 2 \text{ NH}_3 + \text{CO}_2$. The hydrolysis is catalysed by urease.
- D
- Van der Waals
 - ionic
 - hydrogen bonding
- $2 \text{ NO} + \text{Cl}_2 \rightarrow 2 \text{ NOCl}$

Bromine is acting as a catalyst in the reaction between nitrogen monoxide and chlorine to form nitrosyl chloride.

8. $2 \text{KClO}_3 \rightarrow 2 \text{KCl} + 3 \text{O}_2$. The catalyst is manganese(IV) oxide (MnO_2).

Answers 6.6

- $1 + 1 = 2$
 - $1 + 2 = 3$
 - 1
 - $1 + 2 = 3$
 - $1 + 2 + 1 = 4$
- C
- Units for $k = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
- Units for $k = \text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$
- D
- The molecularity is three and it can be described as trimolecular.
- The overall order is the sum of the powers of the concentration terms in the rate equation, e.g. the overall order is 2 for rate = $k [\text{CH}_3\text{COCH}_3] [\text{H}^+] [\text{I}_2]^0$.
- Step 1 is unimolecular (molecularity 1) and steps 2 & 3 are bimolecular (molecularity 2).

Answers 6.7

- The rds is step 1 as it is the slowest step. The rate equation is rate = $k [\text{N}_2\text{O}_5]$
- The rds is the slow step 1. The rate equation is rate = $k [\text{H}_2\text{O}_2]^1 [\text{I}^-]^1 [\text{H}_3\text{O}^+]^0$
The overall equation is $\text{H}_2\text{O}_2 (\text{aq}) + 2 \text{H}_3\text{O}^+ (\text{aq}) + 2 \text{I}^- (\text{aq}) \rightarrow \text{I}_2 (\text{aq}) + 4 \text{H}_2\text{O} (\text{l})$

Answers 6.8

- Step 1: $\text{CH}_2=\text{CH}_2 + \text{H}^+ \xrightarrow[\text{rds}]{\text{Slow}} \text{CH}_3\text{CH}_2^+$

Step 2: $\text{CH}_3\text{CH}_2^+ + \text{H}_2\text{O} (\text{g}) \xrightarrow{\text{Fast}} \text{CH}_3\text{CH}_2\text{OH} + \text{H}^+$
- Step 1: $\text{NO} + \text{NO} \rightarrow \text{NO}_2 + \text{N}$ (rate determining step)

Step 2: $\text{N} + \text{O}_2 \rightarrow \text{NO}_2$ (fast step)
- The equation for the reaction is $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$

Step 1: $\text{NO}_2 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_3$ (rate determining step)

Step 2: $\text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2$ (fast step)

Answers 6.9

- The rate at the start of the reaction when time $t = 0$ seconds.
- Rate = $k [F]^2 [G]^1$ & $k = 0.448 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$.
- The initial rates method is a series of experiments where the rate is determined for different concentrations of reactants from the gradient of a tangent drawn next to the curve on a concentration *vs.* time graph when time = 0 seconds. The order of each reaction is worked out from how concentration affects the rate and this allows a rate equation and rate constant to be determined. The initial rates method is useful for slow reactions.
- Rate = $k [H^+]^1 [CH_3COCH_3]^1 [I_2]^0$
 $k = 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
 Expt #5 $[H^+] = 0.60 \text{ mol dm}^{-3}$

5.

Experiment #	[R] / mol dm ⁻³	[S] / mol dm ⁻³	Initial rate / mol dm ⁻³ s ⁻¹
1	0.20	0.10	0.142
2	0.20	0.20	0.568
3	0.40	0.10	0.284

The rate constant $k = 71 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

6. A

Answers 6.10

1. C

2.

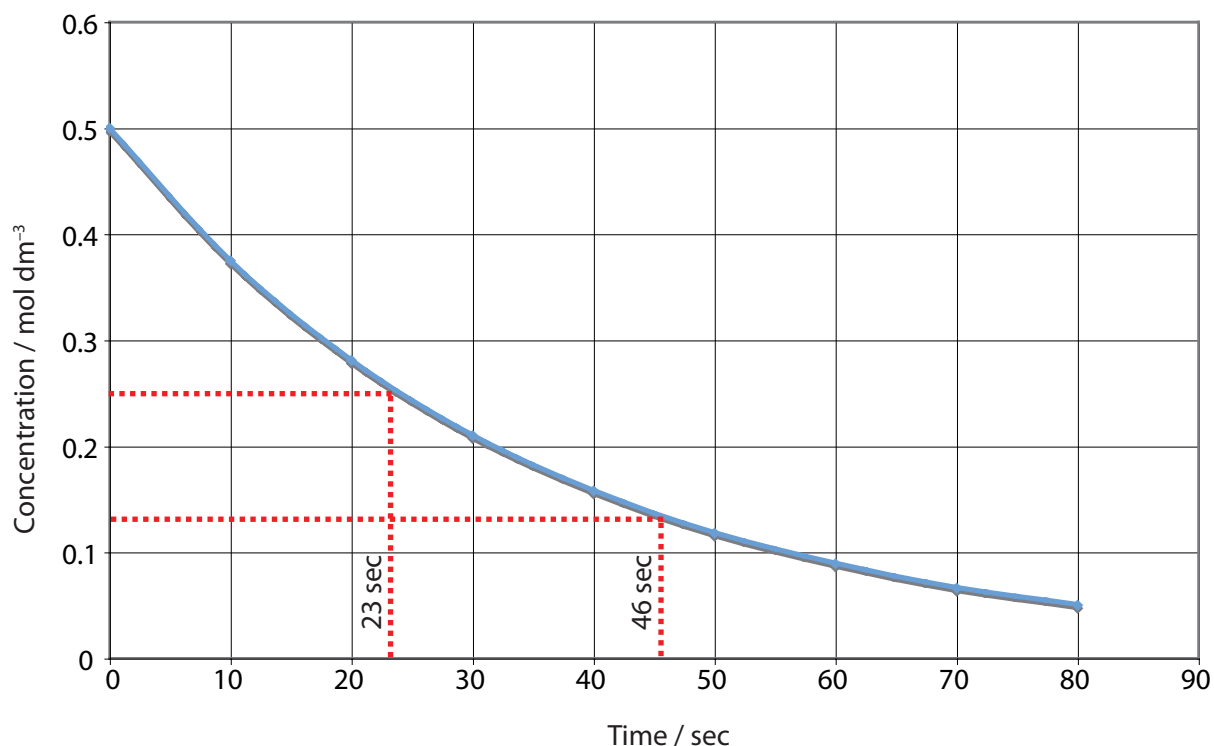
Order	Successive $t_{1/2}$
0	decrease
1	constant
2	increase

3. B

4. a. $0.032 \text{ mol dm}^{-3}$ (2 half-lives). b. $0.008 \text{ mol dm}^{-3}$ c. $0.004 \text{ mol dm}^{-3}$

5. A

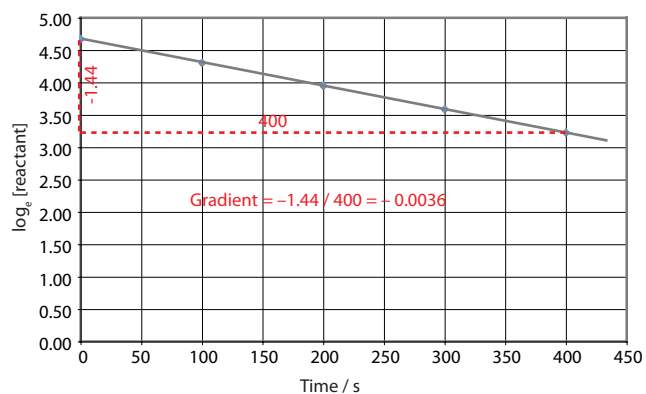
6. A graph of [reactant] vs. time gives a constant $t_{1/2} = 23$ seconds so the reaction is first order.



7. Plotting a graph of \log_e [reactant] vs. time gives a straight line where the gradient is equal to the negative of rate constant $k = 3.6 \times 10^{-3} \text{ s}^{-1}$.

Time / sec	0	100	200	300	400
\log_e [reactant] / mol dm ⁻³	4.68	4.32	3.96	3.60	3.24

Using the equation $t_{1/2} = \frac{0.693}{k}$ gives the half life as 192.5 seconds.



7. Chemical Models and Evidence

Answers 7.1

1. A
2. C

Answers 7.2

1. D
2. Boron oxide B_2O_3 has a small highly charged cation (B^{3+}) which will be highly polarising. This will lead to a significant difference in the lattice enthalpy values as electron density will be distorted for the cation and found between the oppositely charged ions.
3. Experimental lattice enthalpies are calculated using Born-Haber cycles. Lattice enthalpies are always negative (exothermic) and depend on the size of the ions and the size of their charges.
4. When ΔE_{neg} is high.
5. B

8. Periodic Table

Answer 8.1

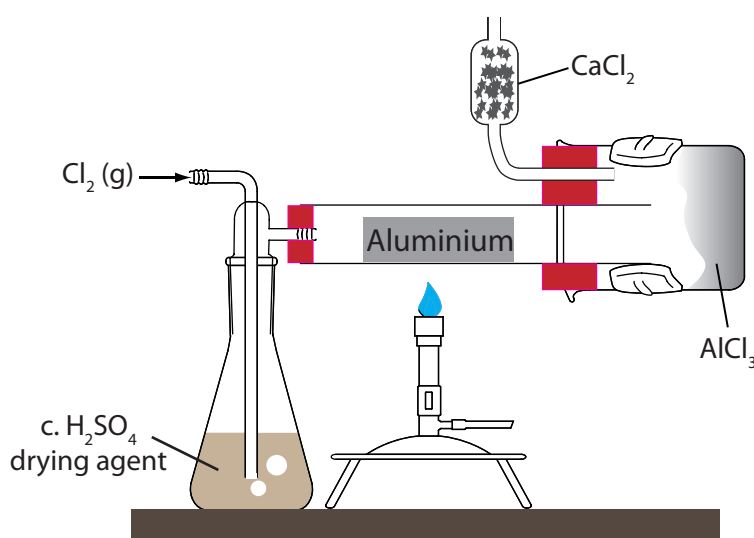
1. C

Answer 8.2

1. Boron, Carbon, Silicon, Germanium, Arsenic and Selenium.

Answer 8.3

1. $2 \text{Al (s)} + 3 \text{Cl}_2 \text{(g)} \rightarrow 2 \text{AlCl}_3 \text{(s)}$. Heating aluminium in a stream of dry chlorine gas. CaCl_2 tube prevents humidity reacting with AlCl_3 . $\text{AlCl}_3 \text{(s)} + 3 \text{H}_2\text{O (g)} \rightarrow \text{Al(OH)}_3 \text{(s)} + 3 \text{HCl (g)}$



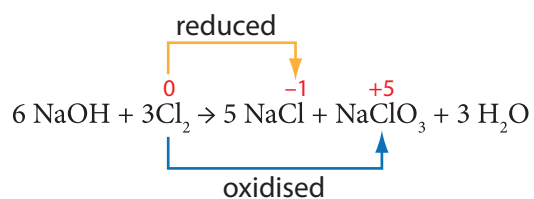
Answer 8.4

1. The green gas passes over a white solid and a colourless liquid PCl_3 would be formed which, after a while, would contain a pale yellow solid precipitate of PCl_5 . One might also expect the white solid to melt due to the heat of the reaction.

Answers 8.5

1. B

2.



Disproportionation reaction as the same species (Cl_2) is simultaneously oxidised and reduced.

3.

Oxoacid	Oxidation Number of chlorine
HOCl	+1
HClO ₂	+3
HClO ₃	+5
HClO ₄	+7

4. A

5.

Oxidation Number	Oxidation Number	Oxidation Number change
+7	+2	-5
KMnO ₄	MnSO ₄	Reduction (+ 5 electrons)
Oxidation Number	Oxidation Number	Oxidation Number change
+2	+3	+1
FeSO ₄	Fe ₂ (SO ₄) ₃	Oxidation (-1 electron)

Answer 8.6

1.

Element	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulfur	Chlorine
Oxide	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₄ O ₁₀	SO ₃	Cl ₂ O ₇
Oxidation Number	+1	+2	+3	+4	+5	+6	+7

As you progress across Period 3 from sodium, each subsequent oxide has an additional half mole increase in oxygen.

Answer 8.7

1. Cold water: $\text{Mg (s)} + 2 \text{H}_2\text{O (l)} \rightarrow \text{Mg(OH)}_2 \text{(aq)} + \text{H}_2 \text{(g)}$

Steam: $\text{Mg (s)} + \text{H}_2\text{O (g)} \rightarrow \text{MgO (s)} + \text{H}_2 \text{(g)}$

Magnesium is much less reactive than sodium which reacts vigorously with cold water.

Answer 8.8

1.

Element Symbol	Oxide formula	Oxide bonding	Nature of oxides solution, e.g. acidity
Na	Na ₂ O	ionic	strongly alkaline
Mg	MgO	ionic	slightly alkaline
Al	Al ₂ O ₃	ionic	
Si	SiO ₂	giant covalent	
P	P ₂ O ₃ (P ₅ O ₁₀)	molecular covalent	acidic
S	SO ₂ , SO ₃	molecular covalent	acidic
Cl	Cl ₂ O (ClO ₂)	molecular covalent	acidic

Answers 8.9

- C
- D
- $\text{AlCl}_3(\text{s}) + 3 \text{H}_2\text{O}(\text{g}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3 \text{HCl}(\text{g})$. HCl turns damp blue litmus paper red.
- One Cl atom in SiCl_4 is replaced by an OH group to make the intermediate $\text{Si}(\text{OH})\text{Cl}_3$. Two molecules of $\text{Si}(\text{OH})\text{Cl}_3$ react with each other with elimination of a water molecule to make $\text{Cl}_3\text{SiOSiCl}_3$ as shown in the two reactions.

$$\text{SiCl}_4(\text{l}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SiCl}_3(\text{OH})(\text{l}) + \text{HCl}(\text{g})$$

$$\text{SiCl}_3(\text{OH})(\text{l}) + \text{SiCl}_3(\text{OH})(\text{l}) \rightarrow \text{Cl}_3\text{SiOSiCl}_3(\text{l}) + \text{H}_2\text{O}(\text{l})$$
- Silicon has vacant d orbitals which can accept a lone pair from the oxygen atom in water. Carbon is not able to expand its octet and, being much smaller than a silicon atom, is sterically hindered from attack by nucleophiles.
- $\text{P}_4(\text{s}) + 10 \text{Cl}_2(\text{g}) \rightarrow 4 \text{PCl}_5(\text{s})$. A green gas (chlorine) passing over a white solid (phosphorus) to make a pale yellow solid (phosphorus pentachloride).
- White fumes given off that turn moist blue litmus paper red. A white solid is formed that eventually dissolves in the water.
- $\text{PCl}_5(\text{s}) + 4 \text{H}_2\text{O}(\text{l}) \rightarrow 5\text{HCl}(\text{aq}) + \text{H}_3\text{PO}_4(\text{aq})$. White fumes, (exothermic), colourless liquid forms.
- B
- D
- A
- C
-

Formula	State (RT)	Bonding	Effect on moist air
NaCl	(s)	Ionic	None
MgCl_2	(s)	Ionic	It is deliquescent
AlCl_3	(s)	Covalent	Fumes
SiCl_4	(l)	Covalent	Fumes
PCl_3 & PCl_5	(l) & (s)	Covalent	Both give fumes
S_2Cl_2	(l)	Covalent	Fumes
Cl_2	(g)	Covalent	None

9. Main Group Chemistry

Answers 9.1

- D
- B
- The much smaller Li^+ ion has a greater charge density than the other Group 1 ions. This leads to greater polarising of the carbonate ion with sufficient weakening of the C-O to allow decomposition to occur.

4.

carbonates	cation size	cation charge
most stable carbonates	large	low
most unstable carbonates	small	high

5. C

Answers 9.2

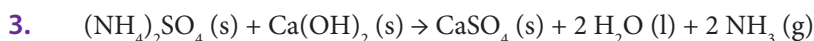
- C
- A

Answers 9.3

- A
- The atoms are held by a strong triple bond, the molecule is non-polar so is not vulnerable to attack by electrophiles or nucleophiles, and the lone pairs of electrons are in low energy orbitals.

Answers 9.4

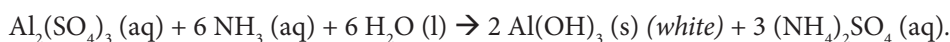
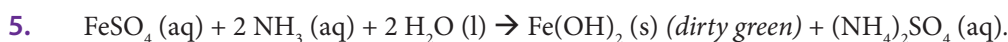
1. B



Ammonium sulfate is an acid. Ammonia turns moist red litmus paper blue.



Ammonia is the base (proton acceptor) and hydrobromic acid is the acid (proton donor) and the product, ammonium bromide, is a salt. The reaction is an acid-base (neutralisation) reaction.



Safety: Wear goggles and gloves as H_2O_2 is corrosive at this concentration.

7. a) $0.417 \text{ mol dm}^{-3}$ b) 1.67 mol dm^{-3} c) 8.33 mol dm^{-3}

Answers 9.7

1. C
2. $\text{NO}_2(\text{g}) + \text{SO}_2(\text{g}) \rightarrow \text{SO}_3(\text{g}) + \text{NO}(\text{g})$
 $\text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$



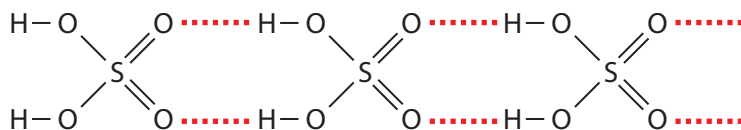
3. $\text{H}_2\text{O}_2(\text{aq}) + \text{SO}_2(\text{g}) \rightarrow \text{H}_2\text{SO}_4(\text{aq})$

The amount of sulfuric acid can be determined by titration (acid-base or conductimetric) or by precipitating BaSO_4 . From the results of the quantitative analysis, the amount of SO_2 can be calculated as using the 1:1 stoichiometric ration ($\text{SO}_2 : \text{H}_2\text{SO}_4$).

4. $\text{Ca}(\text{OH})_2(\text{aq}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$
5. A

Answers 9.8

1. Sulfuric acid is acting as an oxidising agent as the oxidation state of sulfur increases from -2 in H_2S to 0 in S . There is conproportionation of sulfur from -2 and $+6$ to 0 .
2. Concentrated sulfuric acid absorbs water so will dry gases such as nitrogen that bubble through it. Ammonia is a base which reacts with sulfuric acid to make ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$.
3. Since concentrated sulfuric acid is very hygroscopic, it will absorb water vapour out of the air and its concentration will decrease as it becomes more dilute.
4. The presence of hydrogen bonding links sulfuric acid molecules together which raises its boiling point.
5. A
6. $\text{H}_2\text{SO}_4(\text{aq}) + 2 \text{NH}_3(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{aq})$. Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ finds use as a nitrogenous fertilizer.



Answers 9.9

1. The oxidation state of fluorine is always -1 . This makes the oxidation state of chlorine $+1$ in FCl and $+3$ in ClF_3 . The pattern from these two compounds is that the bond enthalpy decreases as the oxidation state increases.
2. Bond enthalpies are weak when both atoms in a bond have lone pairs due to lone pair : lone pair repulsion. This is why the N-N bond in hydrazine (163 kJ mol^{-1}) is much weaker than the C-C bond (346 kJ mol^{-1}) in ethane.

Answers 9.10

- $\text{SiO}_2(\text{s}) + 4\text{HF}(\text{l}) \rightarrow \text{SiF}_4(\text{g}) + 2\text{H}_2\text{O}(\text{l})$. Hydrogen fluoride is used to etch glass.
- $\text{Mg}(\text{s}) + 2\text{HBr}(\text{aq}) \rightarrow \text{MgBr}_2(\text{aq}) + \text{H}_2(\text{g})$. The rate of hydrogen bubble formation would be slower with hydrofluoric acid as it is a weaker acid.
- D
- A

Answers 9.11

- D
- $\text{CaCl}_2(\text{s}) + 2\text{H}_2\text{SO}_4(\text{l}) \rightarrow \text{Ca}(\text{HSO}_4)_2(\text{s}) + 2\text{HCl}(\text{g})$

Answers 9.12

- $2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$
 - $2\text{S}_2\text{O}_3^{2-}(\text{aq}) \rightarrow \text{S}_4\text{O}_6^{2-}(\text{aq}) + 2\text{e}^-$ $\text{I}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{I}^-(\text{aq})$
 - When the brown-yellow solution of iodine becomes pale (straw coloured) a few drops of 1% starch solution is added. Even with only traces of iodine present, starch turns blue-black which changes to colourless at the end point.
- The average titre of 1st and 2nd experiments = 16.5 cm³

$$2\text{S}_2\text{O}_3^{2-}(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow 2\text{I}^-(\text{aq}) + \text{S}_4\text{O}_6^{2-}(\text{aq})$$

$$n(\text{S}_2\text{O}_3^{2-}) = 0.200 \times \frac{16.5}{1000} = 3.3 \times 10^{-3} \text{ mol}$$

$$n(\text{I}_2) = \frac{1}{2} n(\text{S}_2\text{O}_3^{2-}) = \frac{1}{2} \times 3.3 \times 10^{-3} \text{ mol} = 1.65 \times 10^{-3} \text{ mol}$$

$$2\text{Cu}^{2+}(\text{aq}) + 4\text{I}^-(\text{aq}) \rightarrow 2\text{CuI}(\text{s}) + \text{I}_2(\text{aq})$$

$$\text{moles Cu}^{2+} = 2 \times n(\text{I}_2) = 2 \times 1.65 \times 10^{-3} \text{ mol} = 3.3 \times 10^{-3} \text{ mol}$$

$$\text{mass Cu} = \text{moles} \times A_r$$

$$\text{mass Cu} = 3.3 \times 10^{-3} \times 63.5 = 0.21 \text{ g in } 25 \text{ cm}^3$$

$$\text{mass Cu} = 4.2 \text{ g in } 500 \text{ cm}^3$$

$$\% \text{ Cu} = \frac{4.2}{16.8} \times 100\% = 25\% \text{ (experimental value).}$$

$$\% \text{ Cu in } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \text{ (theoretical value)}$$

$$\% \text{ Cu} = \frac{63.5}{249.6} \times 100\% = 25.44\%$$

$$\text{Purity of Copper sulfate is } \frac{25}{25.44} \times 100\% = 98.27\%$$
- Chlorine is the stronger oxidising agent as it oxidises sulfur in thiosulfate from +2 to +6 in the sulfate, whereas iodine oxidises the sulfur in thiosulfate from +2 to +2.5 in tetrathionate.

Answers 9.13

1.

Oxidation state	-1	+1	+5
Product	NaCl	NaOCl	NaClO ₃

2. In the course of the reaction, chlorine, which has an oxidation number of zero, undergoes both an increase in oxidation number (+1 in HOCl) and a decrease in oxidation number (-1 in HCl).

3. Disproportionation. The iodine is both oxidised +5 in NaIO₃ and reduced -1 in NaI from +1 in NaOI.

4. C

5. a. $\text{ClO}^- + 2\text{H}^+ + 2\text{I}^- \rightarrow \text{I}_2 + \text{H}_2\text{O} + \text{Cl}^-$ b. $\text{ClO}^- + 2\text{H}^+ + 2\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{H}_2\text{O} + \text{Cl}^-$

These are correct because of the acidic conditions. In alkaline conditions, both oxidations proceed much further.

6. $\text{Cl}^- + \text{ClO}^- + 2\text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Cl}_2$ Toxic chlorine gas is evolved in this reaction.

Answers 9.14

1. It is a powerful oxidising agent. It has a small bond dissociation energy and it has a very small atomic radius (0.071 nm). This means that more atoms can fit around actinides such as uranium. It forms strong bonds with other elements.

2. All halogens, except fluorine, are obtained by oxidation of the halide ions, *e.g.*

$\text{Br}_2(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{I}_2(\text{aq})$. Fluorine is obtained during electrolysis using a graphite anode and a steel cathode, *i.e.* $2\text{F}^- - 2\text{e}^- \rightarrow \text{F}_2$ (OILRIG springs to mind). This is achieved by electrolysis of KF in liquid HF. Aqueous solutions cannot be used as fluorine reacts with water.

10. Group 14

Answers 10.1

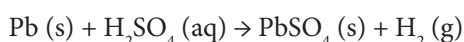
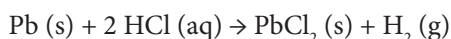
1. Different forms of an element are called allotropes and they are graphite, diamond and buckminsterfullerene.
2. C

Answers 10.2

1. A
2. B
3. C

Answers 10.3

1. B [carbon is more electronegative than hydrogen so it takes the negative O.S.]
2. B
3. A
4. Lead(II) oxide PbO is formed, in which the oxidation state of lead is +2. +2 is the most stable oxidation state for lead. +4 is an unstable oxidation state for lead. +4 oxidation states: CO₂, SiO₂, GeO₂ and SnO₂.
5. PbO₂ : 2 PbO [since they add together to give Pb₃O₄]. A glowing splint will burn more or rekindle (catch fire).
6. $\text{Pb (s)} + 2 \text{HNO}_3 \text{ (aq)} \rightarrow \text{Pb(NO}_3)_2 \text{ (aq)} + \text{H}_2 \text{ (g)}$



Sulfuric acid is diprotic (dibasic) so there will be the same number of moles of H⁺ (aq) in half the concentration and the same volume to keep it a fair test. The reactions with hydrochloric and sulfuric acids will be slower as both reactions lead to insoluble lead(II) salts which will coat the surface of lead, preventing further reaction from proceeding at a rate similar to that with nitric acid.

7.

	Lead salt or solution	Colour
(a)	PbSO ₄ (s)	white
(b)	PbCl ₂ (s)	white
(c)	PbCrO ₄ (s)	yellow
(d)	PbI ₂ (s)	yellow
(e)	PbO ₂ ²⁻ (aq)	colourless
(f)	PbCl ₄ ²⁻ (aq)	colourless
(g)	Pb(OH) ₂ (s)	white

Answers 10.4

1. D
2. Oxygen $E_{\text{neg}} = 3.5$ & silicon $E_{\text{neg}} = 1.8$. $\Delta E_{\text{neg}} = 1.7$ which means there is ~50% ionic bonding in the Si-O bond.
3. $2 \text{GeO} (\text{s}) \rightarrow \text{GeO}_2 (\text{s}) + \text{Ge} (\text{s})$. The oxidation state of germanium in GeO (+2) is simultaneously reduced Ge (0) and oxidised GeO_2 (+4).
4. $\text{SnO} (\text{s}) + \frac{1}{2} \text{O}_2 (\text{g}) \rightarrow \text{SnO}_2 (\text{s})$. The tin(IV) oxide is the more thermodynamically stable oxide.
5. C

Answers 10.5

1. B
2. The standard electrode potentials hint at the differences in stability of tin and lead in the +2 and +4 oxidation states, e.g. Pb^{4+} is less stable than Sn^{4+} . Sn^{2+} is a better reducing agent than Pb^{2+} and Pb^{4+} is a better oxidising agent than Sn^{4+} .
3. Ge ($4s^2$), Sn ($5s^2$) and Pb ($6s^2$).

11. Transition Elements

Answers 11.1

- It has valence electrons in a 3d subshell.
- $[\text{Ar}] 3d^{10} 4s^2$
 - $[\text{Ar}] 3d^{10} 4s^0$
 - $[\text{Ar}] 3d^6 4s^2$
 - $[\text{Ar}] 3d^5 4s^0$
 - $[\text{Ar}] 3d^{10} 4s^1$
 - $[\text{Ar}] 3d^{10} 4s^0$
 - $[\text{Ar}] 3d^9 4s^0$
 - $[\text{Ar}] 3d^5 4s^0$
 - $[\text{Ar}] 3d^5 4s^1$
 - $[\text{Ar}] 3d^3 4s^0$

Answers 11.2

- A = Ti, B = Mn, C = Co and D = Cu.
- False, Sc^{3+} and Zn^{2+} have empty and full 3d sub-shells respectively.
 - True.
 - False, slight falls in ΔH_{II} from Ti to V and Co to Ni.
 - False, Zn^{2+} has colourless solutions and forms white solids.
- Each additional electron enters a 3d sub-shell which helps to shield the 4s electrons from the increasing nuclear charge.
- D
- C

Answers 11.3

- A
- D
-

Formula	Name of complex ion
$[\text{Cu}(\text{NH}_3)_4]^{2+}$	tetraammine copper(II) ion
$[\text{Fe}(\text{SCN})(\text{H}_2\text{O})_5]^{2+}$	pentaaquathiocyanato iron(III) ion
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	hexaaqua cobalt(II) ion
$[\text{CoCl}_4]^{2-}$	tetrachloro cobaltate(II) ion
$[\text{CrCl}_2(\text{NH}_3)_4]^+$	tetraamminedichloro chromium(III) ion
$[\text{Co}(\text{NH}_3)_6]^{3+}$	hexaammine cobalt(III) ion
$[\text{Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}]^{2+}$	tetraamminechloronitro platinum(IV)
$[\text{Ni}(\text{CO})_4]^0$	tetracarbonyl nickel(0)

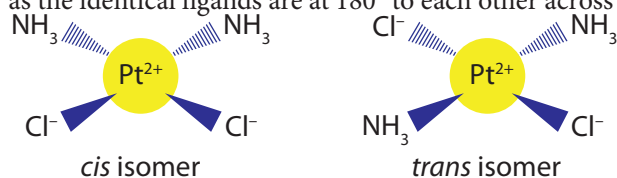
4.

Name of complex ion	Formula
Hexacarbonyl chromium(0)	$[\text{Cr}(\text{CO})_6]^0$
Tetrahydroxo zincate(II) ion	$[\text{Zn}(\text{OH})_4]^{2-}$
Diammine silver(I) ion	$[\text{Ag}(\text{NH}_3)_2]^+$
Hexaammine nickel(II) ion	$[\text{Ni}(\text{NH}_3)_6]^{2+}$
Diamminedichloro platinum(II) ion	$[\text{PtCl}_2(\text{NH}_3)_2]^0$
Hexacyano ferrate(III) ion	$[\text{Fe}(\text{CN})_6]^{3-}$
Hexaaquamanganese (II) ion	$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$
Diaquatetrafluoro ferrate(III) ion	$[\text{FeF}_4(\text{H}_2\text{O})_2]^{1-}$
Dithiosulfato argentate(I) ion	$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$

5. a. A central metal atom/ion surrounded by ligands.
 b. An ion or molecule with a lone pair of electrons capable of forming a coordinate bond.
 c. The number of lone pairs dative covalently bonded to a central metal atom/ion.
6. $\text{Ti}(\text{NO}_3)_4$

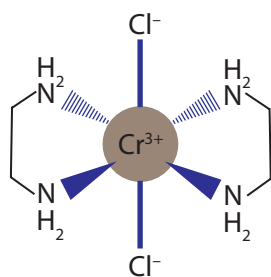
Answers 11.4

1. A, B & E are *cis* isomers as the chloride ligands are adjacent. C & D are *trans* isomers as the chloride ligands are diagonally opposite.
2. A
3. C
4. D
5. The molecule is too small to be able to offer both its nitrogen lone pairs to a metal ion with an angle of 90° .
6. The *trans* isomer will have zero dipole moment and, therefore, negligible electrical conductivity as its dipole will cancel as the identical ligands are at 180° to each other across the molecule.



7. D

8. It can also form a *trans* isomer where the two chloride ligands are diagonally opposite each other.



9. a. diamminedichloro platinum(II) b. +2 (Pt^{2+}) c. square planar
d. four (4) e. ammonia and chloride

Answers 11.5

- Ligands form bonds along the Cartesian axes (x , y & z) and this leads to repulsion and a greater increase in energy of the $3d_{x^2-y^2}$ and $3d_z$ orbitals than of the other three orbitals, which lie between the axes. So it is the ligands that cause the d-orbital splitting.
- Energy is conserved as the potential energy of the separated ions and ligands is converted first into kinetic energy and then dispersed (otherwise the complex falls apart again). Some of the energy released by the formation of ligand to metal bonds goes into raising the energies of all five d orbitals, but most is released through heat (the process is exothermic, naturally).
- This is moving of an electron from a lower energy 3d orbital to a higher energy 3d orbital by the absorption of light energy.

Answers 11.6

- B
- Exact amounts of energy (quanta) must be absorbed for promotion of electrons from lower to higher energy orbitals. Different colours of light will have exact amounts of energy for these electronic transitions.
- $E = hf$ $E = 6.63 \times 10^{-34} \times 6 \times 10^{14} = 3.98 \times 10^{-19} \text{ J}$
- As the energy gap, ΔE , increases, the colour of the metal complexes shifts towards the red end of the spectrum. As the energy gap ΔE decreases, the colour of the metal complexes shifts towards the blue end of the spectrum.

Answers 11.7

- He could make solutions of known concentration of the violet and dark green chromium(III) complexes. Then react them both with excess AgNO_3 (aq). The free chloride ions will react to form silver chloride solid according to the equation Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s). $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} 3\text{Cl}^-$ will react with three molar equivalents of AgNO_3 and $[\text{CrCl}_2(\text{H}_2\text{O})_4]^+ \text{Cl}^-$ will react with one molar equivalent of AgNO_3 . The test tube that has the most precipitate contains the violet complex.
- Cyanide is a stronger ligand than water so it will replace all the water ligands in a ligand exchange reaction. The coordination number for the complex ion remains at six and there is no change in the geometry, which is still octahedral.



8. Mass of Fe = 0.765 g of Fe $\frac{0.765}{0.97} \times 100\% = 78.9\%$

9. 0.474 g of FeSO₄

$$0.006\text{M} \times 0.0104\text{L} = 0.0000624 \text{ mol manganate(VII).}$$

$$0.0000624\text{mol} \times 5 = 0.000312 \text{ mol iron(II) in 10ml.}$$

$$0.000312\text{mol} \times 10 = 0.00312 \text{ mol iron(II) in total.}$$

$$0.00312\text{mol} \times 55.8 \text{ g/mol} = 0.174\text{g iron(II)}$$

$$\frac{0.174\text{g}}{0.96\text{g}} = 18.1\% \text{ Fe}^{2+} \text{ by mass}$$

The question asks for % of iron, not iron(II) sulfate.

$$\frac{(0.174\text{g} \times \frac{151.9}{55.8})}{0.96\text{g}} = 49.4\% \text{ by mass iron(II) sulfate}$$

The colour change at the end point will be from yellow (Fe³⁺) to purple (MnO₄⁻).

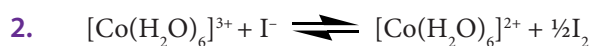
Answers 11.9

1. B
2. When the dissociation curve shifts to the right, haemoglobin becomes more efficient at releasing oxygen. Therefore the tissues can receive more oxygen and can continue aerobic respiration at these partial pressures.
3. Carbon monoxide is a by-product produced during smoking. The neutral ligand carbon monoxide inhaled by smokers binds with a higher affinity to haemoglobin at the site normally occupied by oxygen to give *carboxyhaemoglobin*. This means that smokers carry significantly less oxygen round their bodies compared to non-smokers. This reduction in oxygen leaves smokers struggling with aerobic activities.

Answers 11.10

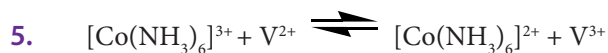
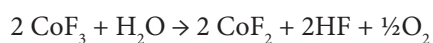
1.

Metal/ion	Electron configuration
cobalt	[Ar] 4s ² 3d ⁷
cobalt(II)	[Ar] 4s ⁰ 3d ⁷
cobalt(III)	[Ar] 4s ⁰ 3d ⁶



3. A

4. Water is oxidised to oxygen which suggests the cobalt will be reduced from +3 to +2.



6. a. [Co(CN)₆]³⁻ is hexacyanocobaltate(III) ion which is stable in the presence of water.

b. [Co(CN)₅]³⁻ is pentacyanocobaltate(II) ion which is unstable in the presence of water.

12. Crystallography

Answers 12.1

1. B
2. A

Answers 12.2

1.

Metal	HCP	CCP
Cadmium	√	
Silver		√
Platinum		√
Magnesium	√	
Cobalt	√	
Nickel		√
Zinc	√	
Gold		√
Copper		√

2. The letter B represents the holes above which atoms sit in the second layer and A & C represent the holes above which atoms sit in the third layer for close packed structures. An ABAB arrangement happens for HCP structures and an ABC arrangement happens for CCP structures.
3. B
4. The coordination number is 12 and it follows it has the the ABAB stacking arrangement as the uppermost (third) layer is directly above the lower (first) layer.

Answers 12.3

1. A unit cell is the simplest repeating unit of the lattice which shows the full symmetry of the crystal.
2. Two pieces of information are the distance between the Na⁺ ions and the Cl⁻ ions and also the formula which is NaCl.
3. In this unit cell there is one atom in the centre and there are eight eighths of atoms at the corners. The unit cell occupancy is therefore $1 + (8 \times \frac{1}{8}) = 2$
4. A

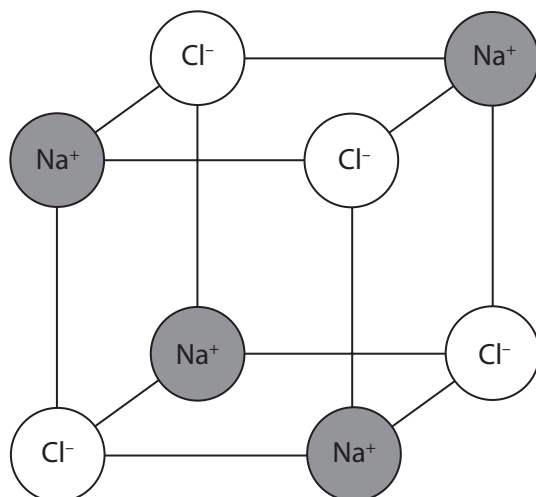
Answers 12.4

1. For NaCl, the ratio of coordination numbers is 6:6 and for CaF₂ the ratio of coordination numbers is 8:4. The ratio of coordination numbers matches the stoichiometric ratio found in the formulae.

2. B

3. C

4.



5. The coordination number for Ca²⁺ is 8. This means that there are eight nearest neighbours of opposite charge, *i.e.* F⁻. The coordination number for F⁻ is 4 which means that there are four nearest neighbours of opposite charge, *i.e.* Ca²⁺.

6. The lattice is for fluorite where the white circles (○) are Ca²⁺ and the black circles (●) are F⁻. The coordination number for calcium is eight, which matches the diagram. A description of the lattice is - "In fluorite, each calcium ion is placed in the centre of a cube with fluoride ions at the corners of the cube. Only every other cube of fluoride ions has a calcium ion at its centre".

7. The radius ratio of the ions and the stoichiometry.

8.

Crystal	C.N. of Cation	C.N. of Anion
NaCl	6	6
CaF ₂	8	4

Answers 12.5

1. A

2. If you have two layers of close-packed spheres, one on top of the other, then there are two ways to stack a third layer of close-packed spheres on top of these two layers. One way is for the third layer of close-packed spheres to sit above the tetrahedral holes in the second layer which are directly above the spheres in the first layer. The other way is for the third layer of close-packed spheres to sit above the octahedral holes in the second layer directly above the hollows in the first layer.

3. The tetrahedral holes will be in the **A and B** positions and the octahedral holes in the C position.

Answers 12.6

1.

Property	Minimised	Maximized
Contact between oppositely charged ions		√
Contact between ions of the same charge	√	
Repulsive forces	√	
Attractive forces		√
Stability in terms of energy		√
Lattice enthalpies		√
Lattice entropies	√	

2.

Mineral	Formula	Crystal type	Position of six consecutive layers	Geometry of occupied holes
Fluorite	CaF ₂	HCP	ABABAB	tetrahedral
Halite	NaCl	CCP	ABCABC	octahedral

3. The tetrahedral holes are smaller than the octahedral holes. It is mainly due to the stoichiometry (and hence the charge ratio) that it must fit into the tetrahedral holes and expand them so that the (smaller) Ca²⁺ ions are no longer close packed.

Answer 12.7

1. The experimental value for lattice energies (ΔH_{latt}) is determined using Born-Haber cycles.

The theoretical value for lattice energies (ΔH_{latt}) is determined using crystal data.

13. Organic Chemistry: Preliminaries

Answer 13.1

Name	Molecular Formula	Molar mass (g mol ⁻¹)
Dopamine	C ₈ H ₁₁ NO ₂	153
Cinnamaldehyde	C ₉ H ₈ O	132
Citric acid	C ₆ H ₈ O ₇	192
Adrenaline	C ₉ H ₁₃ NO ₃	183

Answers 13.2

1.

Isomers	Chemical properties	Physical properties	Effect on ppl
structural	same (approx.)	different	none
geometric	different	different	none
optical	same	same	rotates

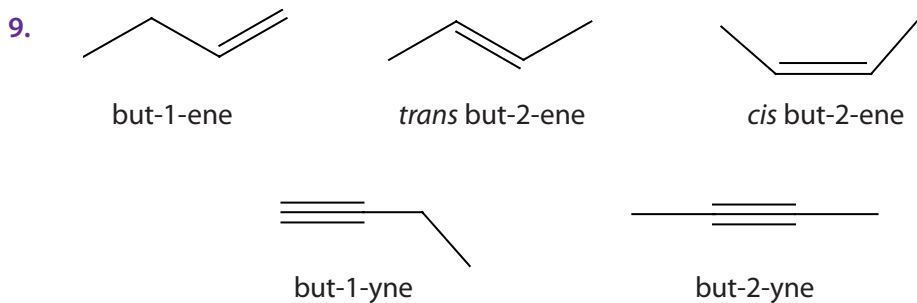
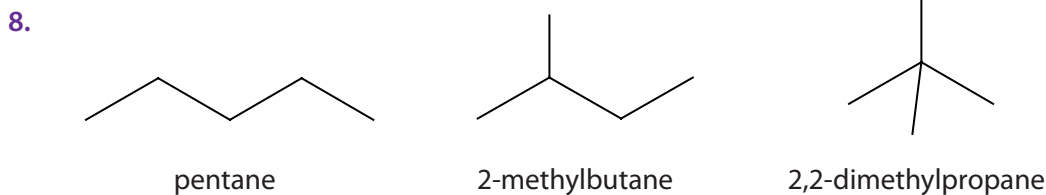
2.

Pair of molecules	Structural isomers	Geometric isomers	Not isomers
but-1-ene & but-2-ene	√		
<i>cis</i> but-2-ene & <i>trans</i> but-2-ene		√	
propan-1-ol & propan-2-ol	√		
propanal & propanone	√		
1,1-dichloroethene & 1,2-dichloroethane			√

Answers 13.3

- A = 2-chloropentane, B = 3-chloropentane, C = 2,3-dichloropentane D = 3-bromo-2-chloropentane
- E = methyl ethanoate, F = methyl methanoate, G = ethyl ethanoate H = ethyl methanoate, I = methyl propanoate, J = ethyl propanoate
- C
- C
- C
- B

7. C_4H_{10} is the simplest alkane to have isomers. Straight chain isomer is butane $CH_3CH_2CH_2CH_3$. Branched isomer is 2-methylpropane $(CH_3)_2CHCH_3$. They both have the same molecular formula but different structural formulae. They are structural (chain) isomers.



and the dienes, the triene, the diyne, and the enyne.

10. C

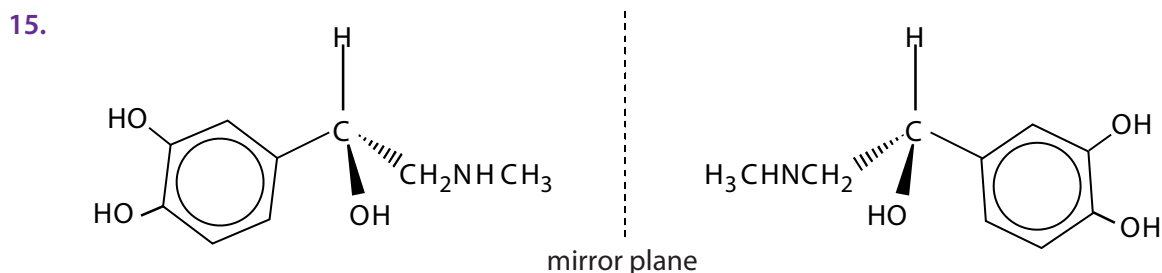
11. (2-)methylpropene.

12. Six structural isomers;

1,1-dichlorobutane	$CH_3CH_2CH_2CHCl_2$
1,2-dichlorobutane	$CH_3CH_2CHClCH_2Cl$
2,2-dichlorobutane	$CH_3CH_2CCl_2CH_3$
1,3-dichlorobutane	$CH_3CHClCH_2CH_2Cl$
2,3-dichlorobutane	$CH_3CHClCHClCH_3$
1,4-dichlorobutane	$ClCH_2CH_2CH_2CH_2Cl$

13. No isomerism. As both carboxylic acid groups are on the same carbon atom of the carbon-carbon double bond (C=C).

14. Mass spectrometry to show all had the same molar mass from the parent ion in the spectrum. Take a known concentration of all and see how they affect plane polarised light. Use a polarimeter to measure the angle $^\circ$. + would have an equal and opposite angle $^\circ$ to the - isomer. The racemic mixture \pm would not rotate ppl. Identical ^{13}C nmr and IR spectra.

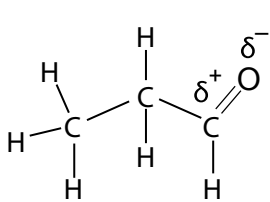


16. A

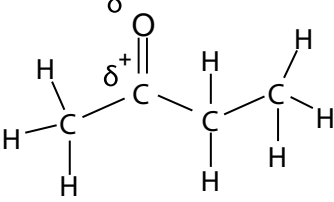
17. [+ , - and \pm racemic mixture]

14. Functional Group Level

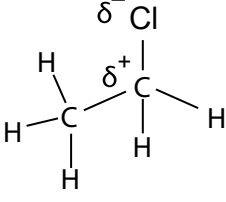
Answers 14.1

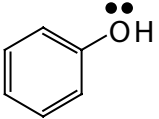
- 1.
- 

propanal




butanone

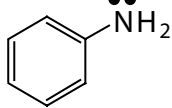


chloroethane
- 2.
- 

phenol

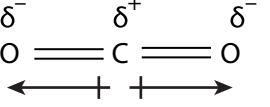


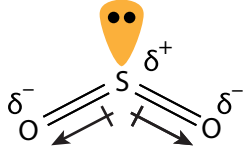
ethane-1,2-diol



phenylamine

Answers 14.2

- 1.
- | Molecule | Deflected | Undeflected |
|--------------------|-----------|-------------|
| trichloromethane | √ | |
| tetrachloromethane | | √ |
| cyclohexane | | √ |
2. Carbon dioxide is a linear molecule so its equal and opposite dipoles cancel. This is easy to imagine if they are vectors being added together. Sulfur dioxide is non-linear (V-shaped) and its dipoles do not cancel.
- 


3. The order of polarity starting with the most polar is $\text{CH}_3\text{CH}_2\text{Cl} > \text{CH}_3\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{I}$. Nucleophiles such as H_2O , OH^- & NH_3 will attack the positive end of the dipole on the carbon atom adjacent to the halogen $\text{C}^{\delta+}-\text{X}^{\delta-}$
4. C

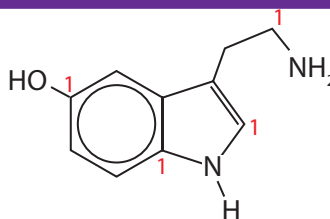
Answers 14.3

- Ester OCOCH_3 & carboxylic acid COOH .
- Ether OCH_3 , phenol ArOH & aldehyde CHO .
- Trans* alkene (olefin) $\text{CH}=\text{CH}$, arene C_6H_5 & aldehyde CHO . Molecular formula $\text{C}_9\text{H}_8\text{O}$
- Alkene (cyclopentene), ester (in the ring) and four alcohol groups OH [allow enol].

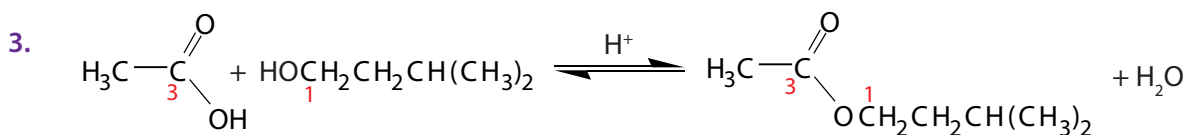
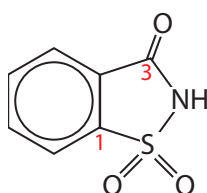
5. Tertiary amine RNMe_2 , two secondary amines R_2NH , ether (5-membered ring), thioether CH_2SCH_2 , three alkenes, e.g. $\text{R}_2 = \text{CHR}$. Bonus mark if student recognises furan ring system.

Answers 14.4

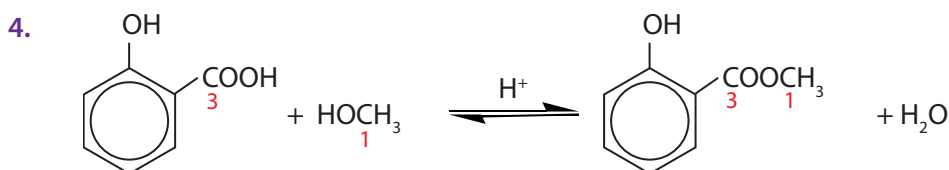
1. Molecular formula is $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}$



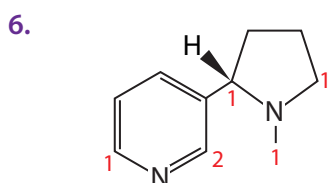
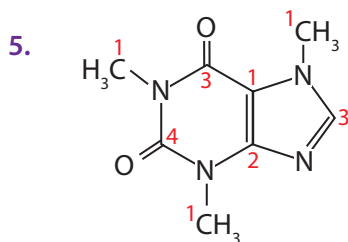
2. Molecular formula is $\text{C}_7\text{H}_5\text{NO}_3\text{S}$



Ethanoic acid reacts with 3-methylbutan-1-ol in the presence of an acid catalyst to form the pheromone ester and water in a reversible reaction. There are no changes in FGL in going from carboxylic acid (FGL 3) to ester (FGL 3).



Methanol reacts with 2-hydroxybenzoic acid in the presence of an acid catalyst to form the oil of wintergreen and water in a reversible reaction. There are no changes in FGL in going from carboxylic acid (FGL 3) to ester (FGL 3).



Answer 14.5

1. There is no FGL change on the aromatic carbon adjacent to the nitrogen atom (FGL 1) or the carbonyl carbon of the aldehyde or the ketone of indigo (FGL 2). The carbonyl carbon of propanone has FGL 2 and the carbon of the carboxyl group has FGL 3.

Answers 14.6

1. D

2.

	Reactant	Reagent	Product
	CH ₃ CH ₂ OH	SOCl ₂	CH ₃ CH ₂ Cl
FGL	1		1

There is no change in FGL and as the OH group swaps for a Cl atom it is a substitution reaction.

3.

	Reactant	Reagent	Product
	CH ₃ COOH	SOCl ₂	CH ₃ COCl
FGL	3		3

There is no change in FGL and, as the OH group of the carboxylic acid swaps for a Cl atom, it is a substitution reaction.

4. B

Answers 14.7

1. The FGL of the carbon adjacent to the nitrogen is FGL 1 for both nitrobenzene and phenylamine. The reaction can be described as a reduction because there is loss of oxygen from C₆H₅NO₂ and gain of hydrogen to form C₆H₅NH₂ and the reducing agent tin changes oxidation state from zero to +4.

2.

Reactant	Reducing agent	Product(s)	Change in FGL
CH ₃ COOH	LiAlH ₄	CH ₃ CH ₂ OH	3 to 1
CH ₃ COOC ₂ H ₅	LiAlH ₄	CH ₃ CH ₂ OH	3 to 1
CH ₃ COOCH ₃	LiAlH ₄	CH ₃ CH ₂ OH & CH ₃ OH	3 to 1
CH ₃ CONH ₂	LiAlH ₄	CH ₃ CH ₂ NH ₂	3 to 1
CH ₃ CH ₂ CN	LiAlH ₄	CH ₃ CH ₂ CH ₂ NH ₂	3 to 1

Answers 14.8

1. Step 1: ethanol FGL 1 oxidised to ethanal FGL 2.

Step 2: ethanal FGL 2 oxidised to ethanoic acid FGL 3.

The reactions are both oxidations as there is an increase in FGL in both steps.

2. The reaction is an oxidation as there is an increase in FGL from toluene (FGL 0) to benzoic acid (FGL 3).

3. The reaction is an oxidation as there is an increase in FGL from but-2-ene (FGL 0) to ethanal (FGL 2).

4. The reaction is an oxidation as there is an increase in FGL from toluene (FGL 0) to benzaldehyde (FGL 2).
5. Step 1: propanoic acid (FGL 3) reduced to propan-1-ol (FGL 1).
- Step 2: propan-1-ol (FGL 1) substitution reaction (halogenation) to 1-bromopropane (FGL 1).
- Step 3: 1-bromopropane (FGL 1) Grignard reaction to pentan-2-ol (FGL 1).
- Step 4: pentan-2-ol (FGL 1) oxidised to pentan-2-one (FGL 2).

Answers 14.9

1.

Carbonyl level (three carbon atoms)	
Aldehydes	propanal
Ketones	propanone

2.

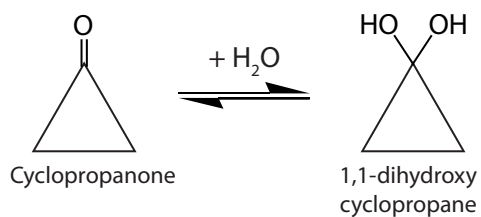
Carboxylic acid level (two carbon atoms)	
Carboxylic acid	Ethanoic acid
Ester	Methyl methanoate
Amide	Ethanamide (acetamide)
Nitrile	Methanenitrile (methyl cyanide)
Acyl Chloride	Ethanoyl chloride

3.

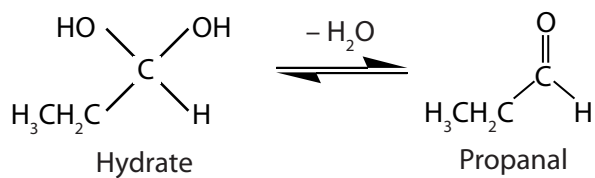
Reactant	Product	FGL → FGL	Reaction type
Ethanol	Ethanal	1 → 2	oxidation
Ethanal	Ethanoic acid	2 → 3	oxidation
Propanal	Propanoic acid	2 → 3	oxidation
Propanal	Propan-1-ol	2 → 1	reduction
Bromoethane	Ethanol	1 → 1	hydrolysis
Ethanol	Bromoethane	1 → 1	substitution
Ethanoyl chloride	Ethanoic acid	3 → 3	hydrolysis
Ethanenitrile	Ethylamine	3 → 1	reduction

Answers 14.10

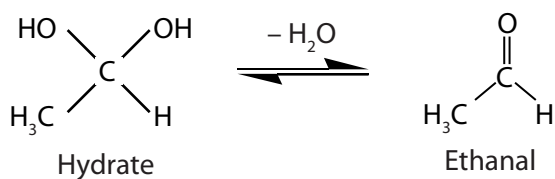
1.



2.



3.



4.

Name	Formula	Hydrolysis product
Phosgene		CO ₂
Urea		CO ₂
Guanidine		CO ₂

15. Alcohol Level

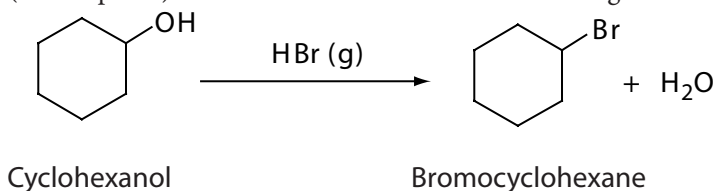
Answers 15.1

- A
- C
- 2°, propan-2-ol 1°, propan-1-ol 1°, 2-methylpropan-1-ol 3°, 2-methylpropan-2-ol
- C
- C

Answer 15.2

- $\text{NaBr (s)} + \text{c.H}_2\text{SO}_4 \text{ (aq)} \rightarrow \text{NaHSO}_4 \text{ (aq)} + \text{HBr (g)}$ $\text{NaHSO}_4 \text{ (aq)} + \text{c.H}_2\text{SO}_4 \text{ (aq)} \rightarrow \text{Na}_2\text{SO}_4 \text{ (aq)} + \text{HBr (aq)}$

(Nucleophilic) substitution. FGL 1 \rightarrow FGL 1 : No change.



Answer 15.3

- $\text{CH}_3\text{CH}_2\text{Br} + \text{NH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4\text{Br}$

Heat the two reactants using ethanol as the solvent in a sealed tube to generate a pressure exceeding atmospheric pressure. Excess ammonia should prevent substitution of ethylamine to give diethylamine or triethylamine. NH_4Br can be neutralised with an organic base such as pyridine ($\text{C}_5\text{H}_5\text{N}$) or sodium hydrogencarbonate (NaHCO_3).

Answer 15.4

- $3 \text{CH}_3\text{CH}_2\text{OH} + \text{PBr}_3 \rightarrow 3 \text{CH}_3\text{CH}_2\text{Br} + \text{H}_3\text{PO}_3$. No change in FGL and the reaction is a substitution reaction.

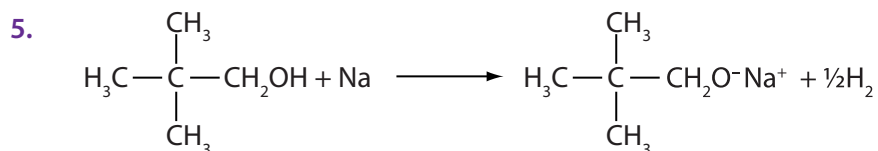
Answers 15.5

- $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{SO}_2 + \text{HCl}$

The advantage is that purification of 1-chloropropane is much more straightforward as both undesired products are gaseous, but the disadvantage is that both gaseous products (sulfur dioxide and hydrogen chloride) are toxic.

- C
- A & B

4. 3-methylpentan-2-ol



Answers 15.6

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I} + \text{KCN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} + \text{KI}$ butyl cyanide (pentanenitrile). Addition of $\text{Pb}^{2+}(\text{aq})$ or $\text{Ag}^+(\text{aq})$ will react with iodide to give a yellow precipitate of PbI_2 and AgI respectively.

2.

	step 1	step 2	step 3
Change in FGL	1 to 1	1 to 0	3 to 1
Type of reaction	substitution	reduction	reduction

Answers 15.7

1.

	CH_3OH	\rightarrow	HCHO	\rightarrow	HCOOH
name	methanol	\rightarrow	methanal	\rightarrow	methanoic acid
FGL	1	\rightarrow	2	\rightarrow	3
type of reaction		oxidation		oxidation	

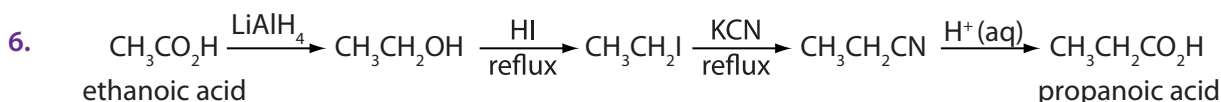
2.

	CH_3CHO	\rightarrow	$\text{CH}_3\text{CH}_2\text{OH}$
name	ethanal	\rightarrow	ethanol
FGL	2	\rightarrow	1
type of reaction		reduction	

3.

#	Reactant	Reagent	Product
1	1-bromopropane	$\text{OH}^-(\text{aq})$	propan-1-ol
2	cyclohexanol	$\text{HBr}(\text{g})$	bromocyclohexane
3	1,1-dichloroethane	x.s. $\text{KOH}(\text{ethanolic})$	ethyne
4	2-chloropropane	H_2O	propan-2-ol
5	butan-1-ol	SOCl_2	1-chlorobutane
6	1-iodopropane	NaCN	butanenitrile
7	ethanol	Na	sodium ethoxide
8	ethanol	$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$	ethanal
9	butan-2-ol	$\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$	butanone
10	propan-1-ol	PCl_5	1-chloropropane
11	pentan-1-ol	PBr_3	1-bromopentane
12	1-iodopropane	NH_3	propylamine

4. Deliberately not given...
5. Ethanal (most volatile) > ethanol > ethane-1,2-diol (least volatile). Ethanal is the most volatile as it does not form hydrogen bonds. The diol is the least volatile as it can form the most hydrogen bonds between molecules.



7. A halogenoalkane is essentially an alkane molecule where one or more hydrogen atoms have been substituted for a halogen atom. The Group 17 element could be F, Cl, Br or I.

Simplest 1° chloroalkane = chloromethane = CH_3Cl

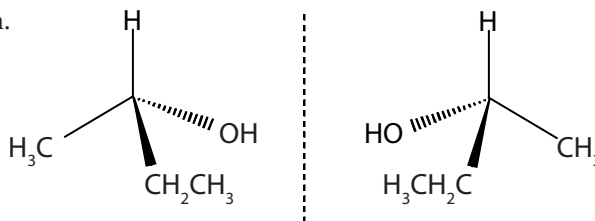
Simplest 2° chloroalkane = 2-chloropropane = $\text{CH}_3\text{CHClCH}_3$

Simplest 3° chloroalkane = 2-chloro-2-methylpropane (CH_3)₃CCl

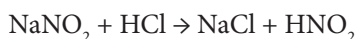
8. 1° halogenoalkanes = 1-chloropentane, 1-chloro-2-methylbutane & 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylpropane. 2° halogenoalkanes = 2-chloropentane, 3-chloropentane, 2-chloro-3-methylbutane. 3° halogenoalkane = 2-chloro-2-methylbutane.

9. Increase in FGL (1 to 2) so the reaction is an oxidation.

10. Butan-2-ol has a chiral centre on the second carbon.



11. Bubbles of a colourless gas would be seen. It is a hydrolysis reaction as the 1° amine (FGL 1) changes into an alcohol (FGL 1) which gives its name to this FGL. Addition of hydrochloric acid to solid sodium nitrite makes nitrous acid:



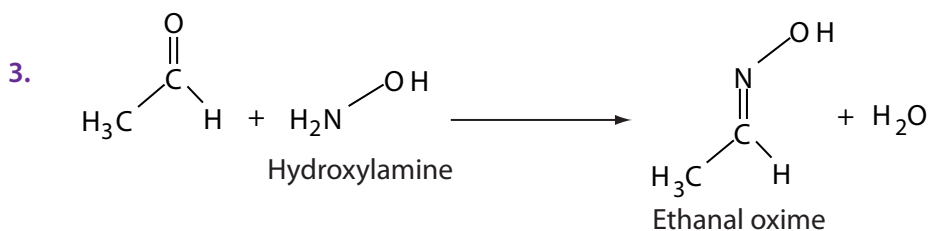
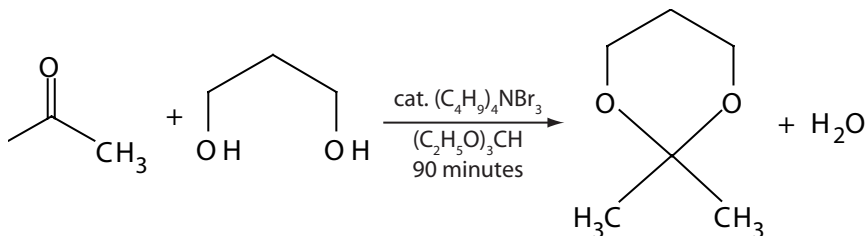
12. Rate of hydrolysis relates to the C-X bond strength. The C-I bond is the weakest and the C-Cl bond is the strongest.

Halogenoalkane	Time / sec	Precipitate (name & colour)
$\text{C}_4\text{H}_9\text{Cl}$	75	silver chloride (white)
$\text{C}_4\text{H}_9\text{Br}$	30	silver bromide (cream)
$\text{C}_4\text{H}_9\text{I}$	15	silver iodide (yellow)

16. Carbonyl Level

Answers 16.1

- B
- The product is a ketal which is at FGL 2 the same as propanone.

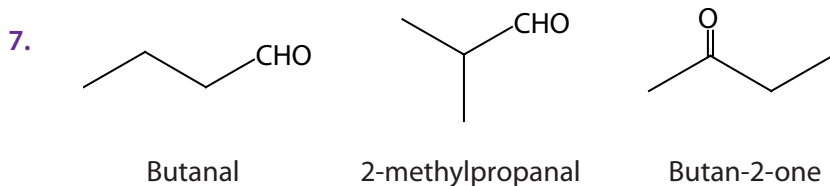


Ethanal has FGL = 2 and the product ethanal oxime has FGL = 2. Because there is no increase or decrease in FGL during the course of the reaction, it is neither an oxidation nor a reduction. The reaction is in fact an addition-elimination which can be thought of as a condensation.

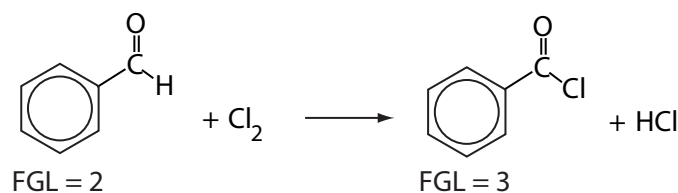
Hydrazone can be prepared by reacting aldehydes and ketones with hydrazine (NH_2NH_2). In these reactions there is no change in the FGL as both reactants and products are FGL = 2. Propanone reacts with hydrazine to make propanone hydrazone which is a stable compound.

The reaction of carbonyls with 2,4-dinitrophenylhydrazine (Brady's reagent) is a characteristic test for these parent functional groups, namely aldehydes and ketones. The resulting phenylhydrazones are characteristically bright yellow or orange precipitates with sharp melting points when recrystallised from hot ethanol.

- B
- A
- (i) propanone, (ii) propanoic acid, (iii) 2-methylpropanoic acid, (iv) 2-methylpropan-2-ol (no reaction)



- To prevent further oxidation you would use a stoichiometric amount of oxidising agent, *i.e.* not an excess, and carry out the reaction using distillation apparatus so that the highly volatile aldehyde is distilled before it can undergo further oxidation.
- The reaction can be classified as an oxidation as there is an increase in FGL from 2 to 3.



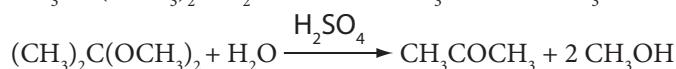
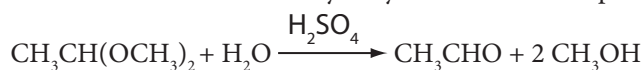
10. Substances ending their names in *one* are ketones. The general formula for a ketone is R_2CO where R = alkyl and or aryl groups. This means that the simplest member of the homologous series has three carbon atoms, whereas *meth* and *eth* are prefixes for compounds with only one and two carbon atoms respectively. The general formula for an aldehyde is $RCHO$ where R = H or an alkyl or aryl group. The simplest member of the homologous series is methanal where R = H and the next one is ethanal where R = methyl (CH_3).
11. Ethene has FGL = 0 and ethanal has FGL = 2. It is an oxidation reaction as there is an increase in FGL. The chlorides of palladium and copper act as catalysts.

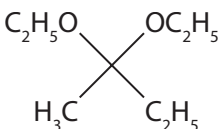
Answers 16.2

1. $CH_2Cl_2 + H_2O \rightarrow HCHO + 2 HCl$ or $CH_2Cl_2 + 2OH^- \rightarrow HCHO + 2Cl^- + H_2O$.

Intermediate = $HOCH_2Cl$ = Chloromethanol

Both acetals and ketals are hydrolysed to their corresponding aldehydes and ketones under acidic conditions, e.g.



2. 

Answers 16.3

1. The acids can be neutralised with $Na_2CO_3(aq)$ and the pure aldehyde collected by distillation. Sodium bisulfite will also work,
2. C
3. A & B

Answers 16.4

1. B
2. C
3. D
4. B
5. A
6. (i) Pentanal, (ii) Pentan-3-one, (iii) Benzaldehyde & (iv) Phenylethanone (Methyl phenyl ketone or acetophenone).
7. (i) $CH_3COCH_2CH_2CH_2CH_3$, (ii) $CH_3CH_2COCH_2CH_2CH_3$ & (iii) $CH_3CH_2CH_2CHO$

Answers 16.5

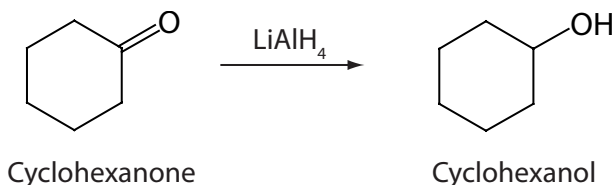
1. Phenylethanone has a FGL = 2 and it moves down to FGL = 0 for ethylbenzene.

2.

	CH_3CHO	\rightarrow	$\text{CH}_3\text{CH}_2\text{OH}$
name	ethanal	\rightarrow	ethanol
FGL	2	\rightarrow	1
type of reaction		reduction	

3. Reducing agents include NaBH_4 or LiAlH_4 or H_2 with a nickel catalyst. Aldehydes are reduced to primary (1°) alcohols.

4.



Answers 16.6

1. (a) propylmagnesium bromide, (b) ethylmagnesium chloride & (c) phenylmagnesium bromide.

2. (a) propan-2-ol, (b) ethanol & (c) 2-methylbutan-2-ol.

In the carbonyls FGL = 2 and in all the products FGL = 1 so the reactions are reductions as an FGL is moved down.

3. The Grignard reagent is pentylmagnesium bromide. The solvent is ethoxyethane.

The organic product is 3-methyl octan-3-ol.

4. Benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$)

5. The solvent needs to be an anhydrous ether such as ethoxyethane ($\text{C}_2\text{H}_5\text{O}$). Ethers can be dried by adding sodium (as a wire) or molecular sieves that have been kept in a drying oven. The Grignard reagent is RMgX where R = ethyl and X = Cl, Br or I made by reacting ethyl halide with magnesium turnings. The reaction is given an acid (H_3O^+) 'work up'.

6.

Reagent	Product from ethanal	Product from propanone	Type of reaction
HCN	$\text{CH}_3\text{CH}(\text{OH})(\text{CN})$	$(\text{CH}_3)_2\text{C}(\text{OH})(\text{CN})$	Addition (Reduction)
NaHSO_3	$\text{CH}_3\text{CH}(\text{OH})(\text{SO}_3\text{Na})$	$(\text{CH}_3)_2\text{C}(\text{OH})(\text{SO}_3\text{Na})$	Addition
LiAlH_4	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{CH}_3\text{CHOHCH}_3$	Addition (Reduction)
Ag^+ (Tollens')	CH_3COOH	no reaction	Oxidation
Cu^{2+} (Benedict's)	CH_3COOH	no reaction	Oxidation
CH_3MgBr (Grignard)	$(\text{CH}_3)_2\text{CHOH}$	$(\text{CH}_3)_3\text{COH}$	Addition (Reduction)
$\text{Cr}_2\text{O}_7^{2-} / \text{H}^+$	CH_3COOH	no reaction	Oxidation

17. Addition and Elimination Reactions

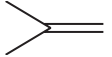
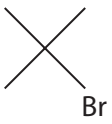
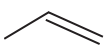
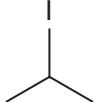
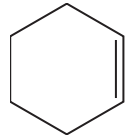
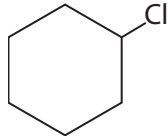
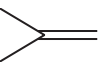

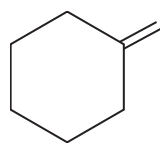
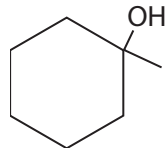
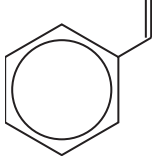
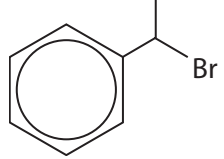
Answer 17.1

- The C=C of alkenes is electron rich and is attacked by electrophiles not nucleophiles. The C=O of carbonyls is polarised due to oxygen being more electronegative (3.5) than carbon (C = 2.5). Nucleophiles attack the δ^+ carbon atom of the C=O. Having a point at which a reagent can attack because a molecule has a dipole moment is more important than the relative bond enthalpies. So, despite their relative strengths, the carbon of the C=O attracts nucleophiles.

Answers 17.2

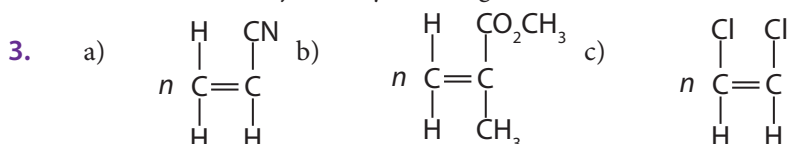
- C
- D
- Ethene is reacted with steam at high temperature (300°C), high pressure (60 atmospheres) and with phosphoric acid (H_3PO_4) as the catalyst.
- C

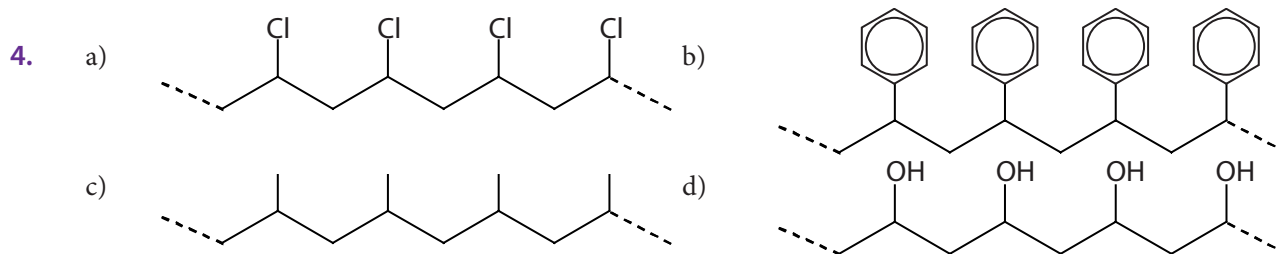
5.

	Reactants		Product		Reactants		Product
i.	 + HBr	→		ii.	 + HI	→	
iii.	 + HCl	→		iv.	 + Br ₂	→	
v.	 + H ₂ O, H ⁺	→		vi.	 + HBr	→	

Answers 17.3

- B
- Addition polymerisation is the process by which addition polymers are made from monomers containing a C=C double bond. The monomers are smaller units (alkenes) which add together to give large molecules called polymers where the carbon atoms are joined by C-C single bonds.





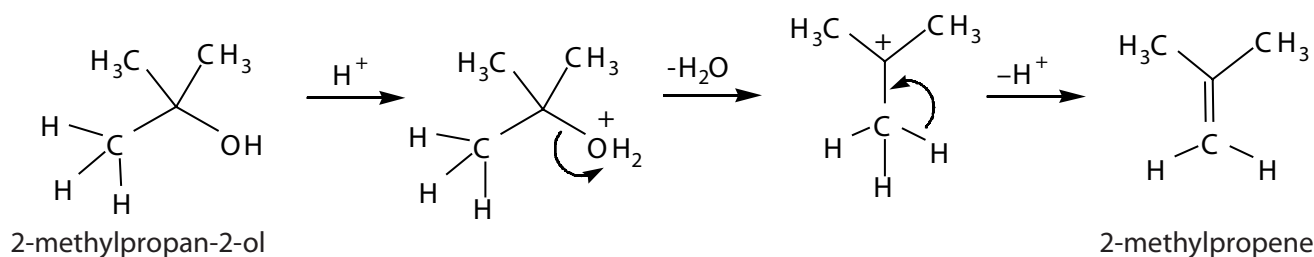
5. **Step 1** = addition polymerisation (radical initiated, e.g. dibenzoyl peroxide). **Step 2** = hydrolysis (NaOH in methanol).

Answers 17.4

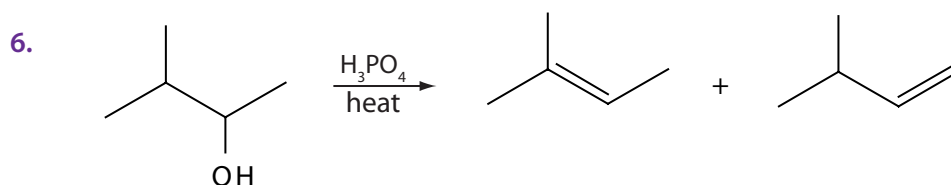
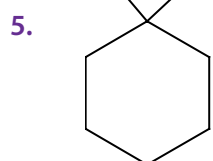
1. a) This is an elimination reaction which can also be described as a dehydration reaction as water is removed from ethanol to make ethene. $C_2H_5OH \rightarrow C_2H_4 + H_2O$.
 b) Excess acid minimises a side reaction in which diethyl ether (C_2H_5)₂O is produced and holds the water released.
 c) A colourless gas is produced which decolourises the orange-red bromine water. The colourless organic product formed is the liquid 1,2-dibromoethane which is immiscible with water.
 d) Heat the flask in an oil bath or a sand bath or an electric heating mantle.

2. **Reaction A:** Excess c.H₂SO₄, low pH, & high temperature. **Reaction B:** low temperature, H₂SO₄ + NaBr to generate HBr *in situ*.

3. The equation for the reaction is $(CH_3)_3COH \xrightarrow{H_2SO_4} CH_2=C(CH_3)_2 + H_2O$. There is a three step mechanism; step 1 is a protonation, step 2 is a dehydration & step 3 is a deprotonation.



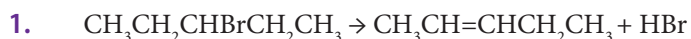
4. a) cyclohexene b) cyclopropene c) *cis*-but-2-ene & *trans*-but-2-ene



An ice-cooled mixture of the products can be separated by fractional distillation under reduced pressure, as 2-methylbut-2-ene has a b.p. = 39°C and the more volatile 3-methylbutene has a b.p. = 20.5°C.

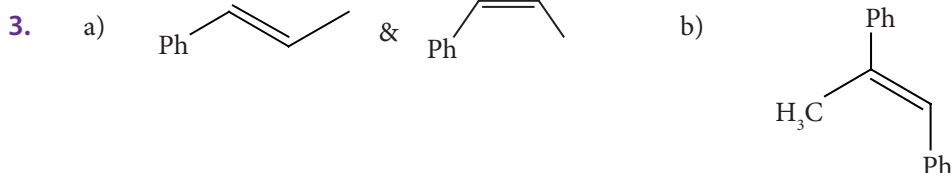
7. B

Answers 17.5



The organic product is a mixture of *cis*-pent-2-ene & *trans*-pent-2-ene. This alkene will decolourise bromine water. The inorganic product is HBr which will turn moist blue litmus red.

2. The two competing reactions are elimination of hydrogen bromide (HBr) to make 2-methylpropene and substitution to form 2-methylpropanol and bromide. Low temperature and dilute solutions of NaOH (aq), *i.e.* low pH will favour substitution, whilst high temperature and concentrated solutions of NaOH (aq), *i.e.* high pH, will favour elimination.



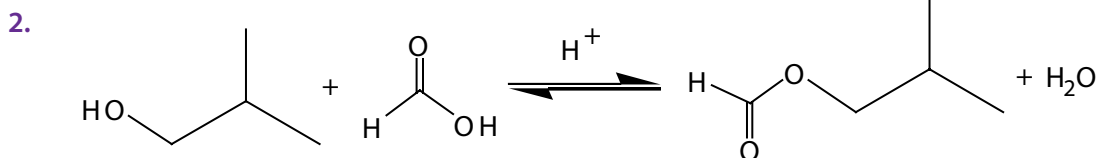
4. Elimination of HX has a greater ΔS as two molecules ($\text{RX} + \text{OH}^-$) become three (alkene, water, halide) compared with substitution where two molecules ($\text{RX} + \text{OH}^-$) become two (alcohol and halide). Therefore the entropy contribution to $-T\Delta S$ is greater in elimination reactions and ΔG will be negative for this mechanism and therefore more feasible at higher temperatures.

18. Green Chemistry

Answers 18.1

1. $C_6H_{10} + Br_2 \rightarrow C_6H_{10}Br_2$; $M_r(C_6H_{10}) = 82.0$; $M_r(Br_2) = 159.8$; $M_r(C_6H_{10}Br_2) = 241.8$:

$$\% \text{ atom economy} = \frac{241.8}{241.8} \times 100\% = 100.0\%$$



$$M_r(\text{alcohol}) = 74.0; M_r(\text{methanoic acid}) = 46.0; M_r(\text{ester}) = 102; M_r(H_2O) = 18.0:$$

$$\% \text{ atom economy} = \frac{102.0}{(74.0 + 46.0)} \times 100\% = 85.0\%$$

3. $M_r(\text{cyclohexanone}) = 98.0$; $M_r(\text{triphenyl phosphonium ylide}) = 276$; $M_r(\text{methylene cyclohexane}) = 96.0$:

$$M_r(\text{triphenylphosphine oxide}) = 278; \% \text{ atom economy} = 96.0 / (98.0 + 276.0) \times 100\% = 25.7\%$$

It is not a very green reaction because it has a low atom economy and it uses stoichiometric quantities and the triphenylphosphine oxide would need disposing of or purifying if it was to be used in other reactions. It is a reduction as the FGL changes from 2 on the carbon of the carbonyl to 0 in the alkene.

Answer 18.2

1. Atom economy allows the waste generated by alternative processes to be compared. The higher the atom economy the less waste is produced.

Answers 18.3

1.

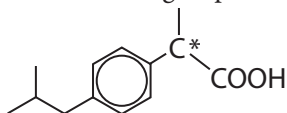
Step	Atom economy
#1	81%
#2	100%

Step 1 is 'green' as the only by-product is water. Step 2 is 'green' because the atom economy is 100% and there is no waste.

2.

Step	Metal catalyst	Atom economy	reactant \rightarrow product	Type of reaction
#1	Pd	100%	Ketone \rightarrow secondary alcohol	Hydrogenation or reduction
#2	$PdCl_2$	100%	Secondary alcohol \rightarrow carboxylic acid	Carbonylation

96% of the product in the second step is one enantiomer (B3.12d). The chiral centre is marked with an asterisk and the four different groups on this carbon atom are H, CH_3 , COOH and the arene part (moiety).



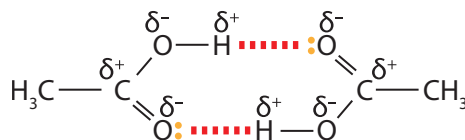
Answer 18.4

1. The solvent is water, carried out at 1 atmosphere and room temperature, stereoselective, very fast, much higher turnover number can be achieved and there is less waste. Usually lower toxicity than metal or metal compounds and any toxic enzymes are easily rendered inert.

19. Carboxylic Acid Level

Answers 19.1

- C
- A
- B
- $\text{CH}_3\text{CH}_2\text{COOH}$ = propanoic acid.
- Ethanoic acid forms 'dimers' *via* intermolecular hydrogen bonding. Additional energy is needed to overcome these hydrogen bonds which cannot form in the ester.



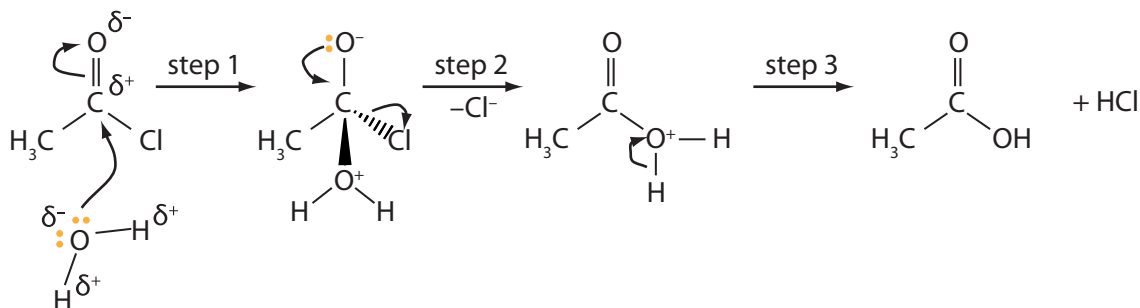
Answers 19.2

- (a) **L** hydrolyses to give $\text{H}_2\text{NCH}_2\text{COOH}$ (glycine) & $\text{H}_2\text{NCH}(\text{CH}_2\text{OH})\text{COOH}$ (serine). **M** hydrolyses to give $\text{H}_2\text{NCH}(\text{CH}_2\text{OH})\text{COOH}$ (serine) & $\text{H}_2\text{NCH}(\text{CH}_3)\text{COOH}$ (alanine)
- (b) Thin layer chromatography can be used to identify the amino acids with authentic samples. The locating agent of choice is ninhydrin. Mixed melting points could also be used once pure samples have been obtained.

2.

Ester	Carboxylic acid	Alcohol
methyl propanoate	propanoic acid	methanol
propyl butanoate	butanoic acid	propan-1-ol
ethyl methanoate	methanoic acid	ethanol
phenyl benzoate	benzoic acid	phenol

- $\text{CH}_3\text{CH}_2\text{CONH}_2 + \text{H}_2\text{O} + \text{HCl} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4\text{Cl}$
 - $\text{C}_6\text{H}_5\text{CN} + 2 \text{H}_2\text{O} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{COOH} + \text{NH}_4\text{Cl}$
 - $\text{CH}_3\text{CH}_2\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HCl}$
 - $\text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3(\text{CH}_2)_3\text{COOH} + \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
- (a) The reaction for this hydrolysis is $\text{CH}_3\text{COCl} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{HCl}$.



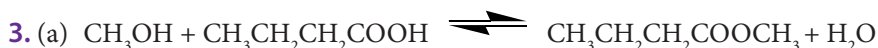
- (b) Addition of silver nitrate will indicate the presence of any chloride ions if a white precipitate is formed. $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$
- B

6. Benzoic acid (C_6H_5COOH)
7. Soap and glycerol (propane-1,2,3-triol).

Answers 19.3

1. (a) D (b) C (c) A (d) B

2. D

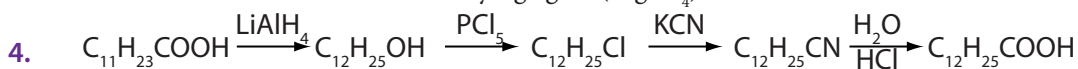


Methyl butanoate

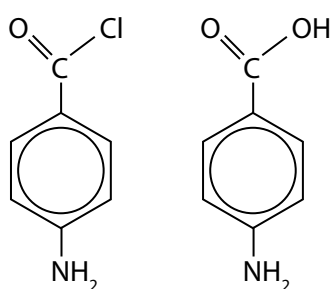
- (b) It is a reversible reaction and an esterification (making ester reaction) - and a substitution and a condensation.

- (c) Add a few drops of $c.H_2SO_4$ as these reactions are catalysed by acids.

- (d) Remove the water as it is formed in the reaction. This can be achieved by use of anhydrous molecular sieves (zeolites) or the addition of a non-reactive drying agent ($MgSO_4$).



5. The acyl chloride will react fastest with the alcohol to form benzocaine.

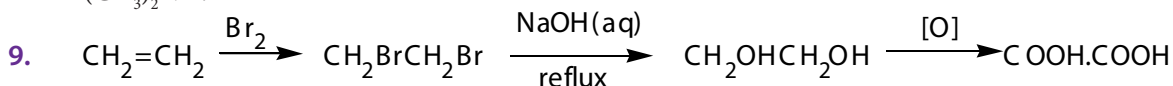


6. (a) C, D and G (b) A and F (c) B and E (d) D, E and F (e) A, C and G (f) D and G

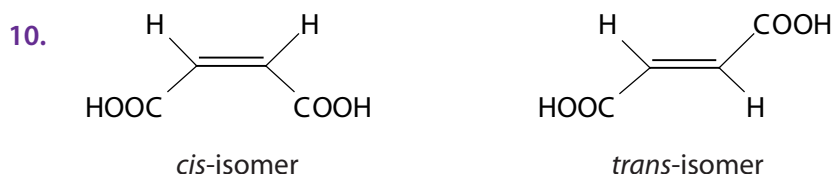
- 7.

M_r of reagent	M_r of CH_3COCl	Sum of all reactants M_r	% atom economy
PCl_5 (208.5)	78.5	268.5	29.2
$SOCl_2$ (119.1)	78.5	179.1	43.8

8. N,N-dimethylethanamide $CH_3CON(CH_3)_2$ can be made by reacting ethanoyl chloride (CH_3COCl) and dimethyl amine ($(CH_3)_2NH$).



A suitable oxidising agent for the final step is acidified dichromate(VI).

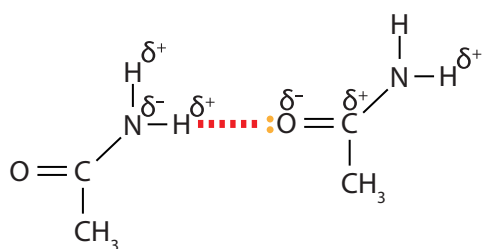


11. Phenylamine ($C_6H_5NH_2$) and propanoyl chloride (CH_3CH_2COCl).

12. B

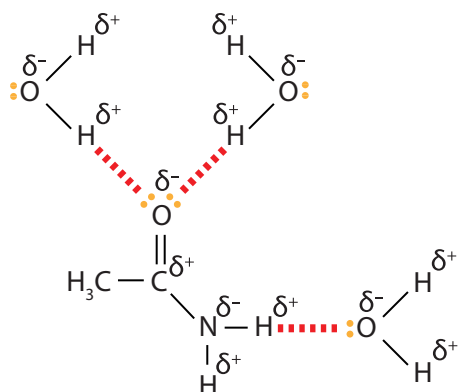
13. The chlorine atom in acyl chlorides is electron withdrawing ($-I$ effect) and this leads to an increased δ^+ charge on the carbon of the carbonyl making it more susceptible to nucleophilic attack. Also, Cl^- is a better leaving group than OH^- .

14. Amides are solids except HCONH_2 because they form hydrogen bonds between molecules as shown for ethanamide.



Amides are water soluble because they form hydrogen

bonds with water as shown for ethanamide.



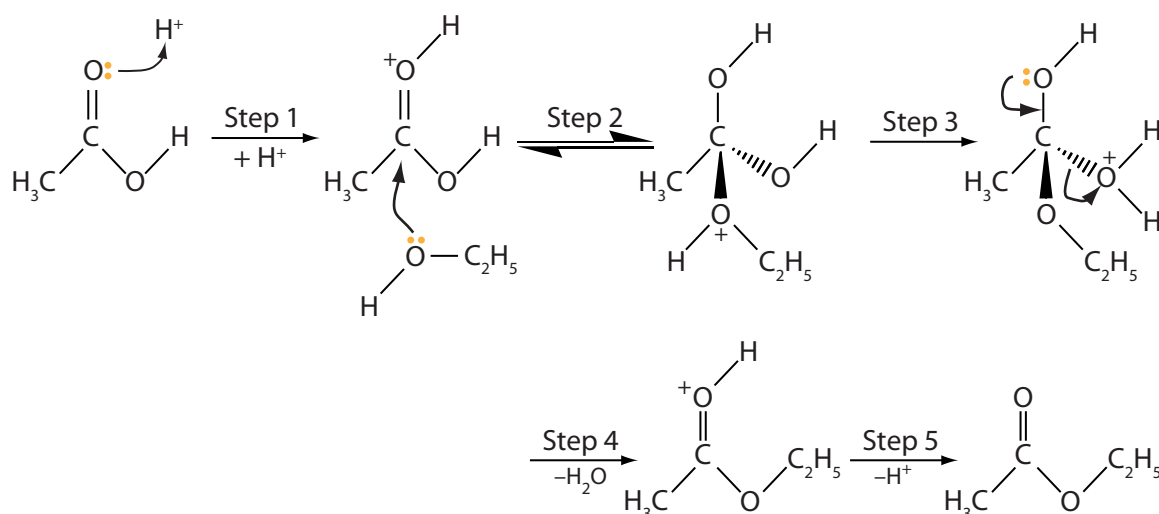
15. Step 1: protonation of the carbonyl of the carboxylic acid to form an intermediate cation.

Step 2: nucleophilic attack by the alcohol on the cation.

Step 3: rearrangement

Step 4: dehydration (loss of water).

Step 5: deprotonation



If an isotopically labelled alcohol is used $\text{CH}_3\text{CH}_2^{18}\text{OH}$, the ^{18}O ends up in the ester $\text{CH}_3\text{CO}^{18}\text{OCH}_2\text{CH}_3$ and **not** in the water. Proton nmr spectroscopy also provides evidence for the protonation of the carbonyl of the carboxylic acid in Step 1.

16. D

Answers 19.4

1. Thin layer chromatography (TLC) using authentic amino acid samples and ninhydrin spray as the locating agent.

2.

Condensation Polymers	Hydrolysis products
polysaccharides	disaccharides and monosaccharides
proteins	Peptides and amino acids

3. D

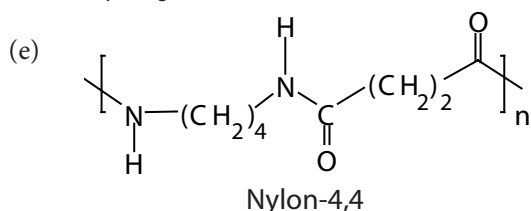
4. C

5. C

6. (a) **1a** = 1,4-diaminobutane and **1b** = butanedioyl chloride. (b) Condensation polymerisation.

(c) Hydrogen chloride - white smoke with NH_3 .

(d) Polyamide.



7. (a) D(+)-glucose and D(-)-fructose (b) Disaccharide (c) $\text{C}_{12}\text{H}_{22}\text{O}_{11}$

(d) $\text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{C}_{12}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O}$ (e) Ether

8.

Condensation polymer	Functional group
Polycarbonate	Carbonate
Poly(lactic acid)	Ester

9. There is a C-O-C ether link connecting carbon atoms 1 & 4 in adjacent glucose units. Carbon atom 1, which is adjacent to the oxygen in the pyranose ring, has two oxygen atoms directly attached making it an acetal since it fits the formula for an acetal $[\text{RCH}(\text{OR})_2]$.

Answers 19.5

1. C

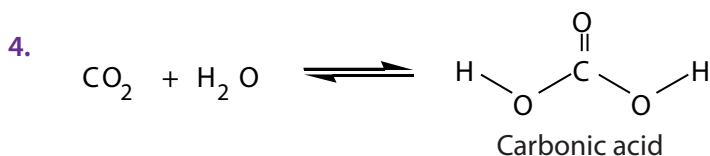
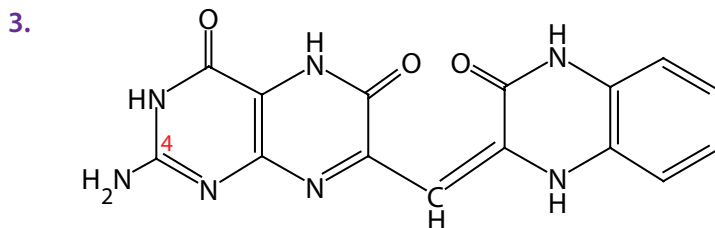
2. There is no decrease in FGL for any of the carbon atoms in the reaction so it cannot be a reduction. The reaction is a substitution reaction and the ester and amide are both in FGL 3.

20. Carbon Dioxide Level

Answers 20.1

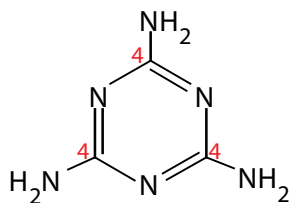
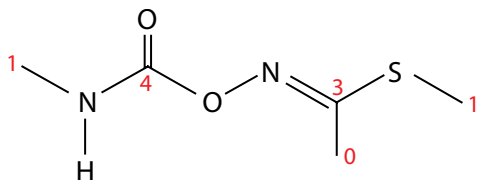
1. B

2. D



There are no changes in FGL as the carbon in CO_2 and the carbon in carbonic acid both have four bonds to heteroatoms, *i.e.* both are in FGL 4.

5. All three carbon atoms are at the Carbon Dioxide level (FGL = 4).

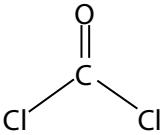
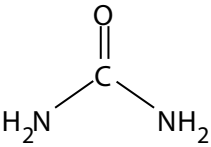
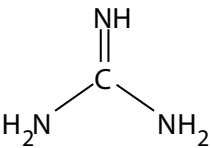
6. The molecular formula of methomyl is $\text{C}_5\text{H}_{10}\text{N}_2\text{O}_2\text{S}$ 

Answers 20.2

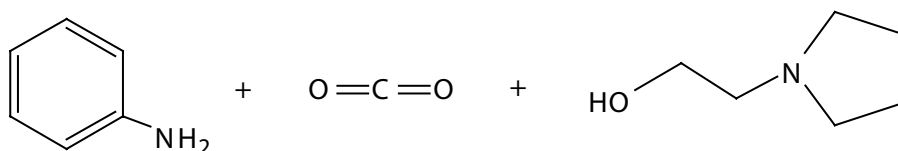
1.

Hydrolysis product	Test	Result
Carbon dioxide	Bubble through limewater	Gives a white precipitate which dissolves with excess carbon dioxide
Ammonia	Damp red litmus paper	Turns the litmus paper blue

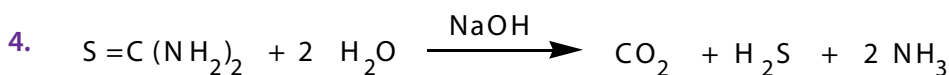
2.

Name	Formula	CO ₂	HCl	NH ₃
Phosgene		✓	✓	
Urea		✓		✓
Guanidine		✓		✓

3. As the carbamate is at FGL = 4 one of the products of hydrolysis will be carbon dioxide.



Some students might hydrolyse the amine as well to get ethane-1,2-diol, butane-1,4-diol and ammonia.



5. A

6. D

7. As the central carbon of diethylcarbonate is at FGL 4 it will react with water (hydrolyse) to form carbon dioxide. The equation for the hydrolysis of diethylcarbonate is: $\text{CO}(\text{OC}_2\text{H}_5)_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{C}_2\text{H}_5\text{OH}$

Answers 20.3

1. A white solid will be formed which is benzoic acid (C₆H₅CO₂H).

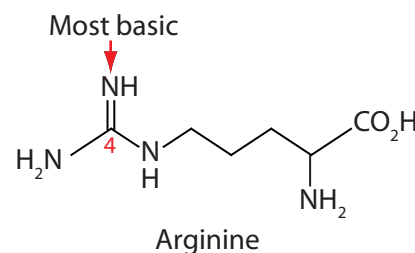
2. (a) iodomethane CH₃I (b) 1-iodopropane CH₃CH₂CH₂I (c) 1-iodohexane CH₃(CH₂)₅I (d) iodobenzene C₆H₅I

3. Three halogenoalkanes are: bromoethane, chloroethane and iodoethane. Each halogenoalkane can form a Grignard reagent when reacted with magnesium turnings in anhydrous diethyl ether. Solid dry ice (CO₂) is then added and the mixture is acidified to yield propanoic acid.

4. Arginine is a guanidine derivative and has a carbon atom at FGL 4 as indicated.

5. The reaction is a dehydration (water is lost) and there is no change in FGL as urea and carbodiimide are both in the Carbon Dioxide level (FGL 4)

6. Hydrolysis as carbon dioxide is formed from urea (FGL 4).



21. Mechanisms

Answers 21.1

1. C
2. D
3. B
4. C
5. A

Answer 21.2

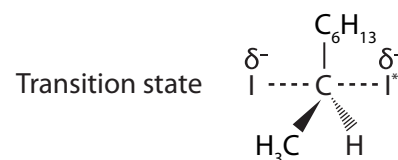
1. C

Answers 21.3

1. A
2. B

Answers 21.4

1. C
2. The reaction can be monitored by looking at the distribution of the radioactive iodine isotope (^{128}I) in the inorganic iodide and the iodoalkane. The reaction can also be monitored using a polarimeter. Optical activity will move towards zero. The inversion and displacement rates will be identical.



Answers 21.5

1. D
2. A racemic is a 50:50 mixture of two optically active molecules (enantiomers). The only difference between the enantiomers is the direction that they rotate plane polarised light. The racemic mixture does not rotate plane polarised light (or rather any rotations are cancelled out statistically).

Answers 21.6

- i. I = $\text{CH}_3\text{CH}_2\text{CN}$ II = NaBr
- ii. III = $(\text{CH}_3\text{CH}_2)_4\text{N}^+\text{Br}^-$
- iii. IV = CH_3Br V = OH^-
- iv. VI = $\text{CH}_3\text{CH}_2\text{NH}_2$ VII = $\text{CH}_3\text{CH}_2\text{Br}$
- v. VIII = $(\text{CH}_3)_3\text{COH}$ IX = Br^-

2. C
3. D
4.

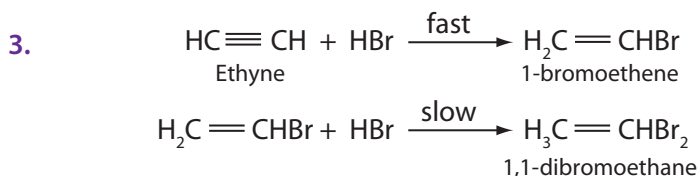
Name of nucleophile	Formula of nucleophile	Products with bromoethane
water	H ₂ O	CH ₃ CH ₂ OH & HBr
hydroxide	OH ⁻	CH ₃ CH ₂ OH & Br ⁻
cyanide	CN ⁻	CH ₃ CH ₂ CN & Br ⁻
ammonia	NH ₃	CH ₃ CH ₂ NH ₂ & CH ₃ CH ₂ NH ₃ ⁺ Br ⁻

5. A

Answers 21.7

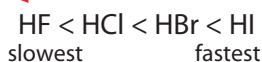
1. The product formed in greater amounts will be 2-bromopentane. The positive inductive effect is greater for a methyl group than an ethyl group. This means the more stabilised intermediate carbocation will be in the 2-position and this is the carbon atom that the electronegative bromine atom joins with. Both isomers form the same products because after they lose their unsaturation, the C-C bonds are freely rotatable.

2. It is an electrophilic addition reaction. 2-iodopropane (Markovnikov product) forms in a higher proportion than 1-iodopropane.



4. The rate of addition increases with increasing acid strength. Acid strength is the readiness to release a proton (H⁺). The weakest bond is between hydrogen-iodine so it is the one that ionises the most easily, hence hydroiodic acid is the strongest acid of the hydrogen halides.

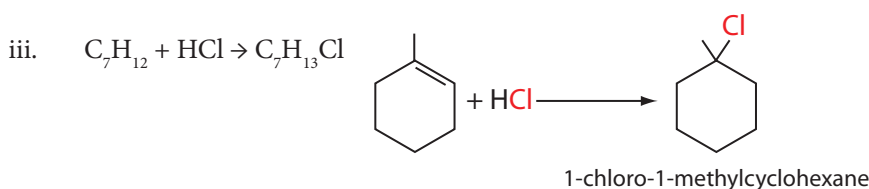
Decreasing acid strength



5. D

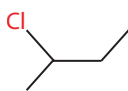
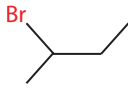

Answers 21.8

1. B
2. i. Visible white fumes of HCl (g) over the surface of the reaction mixture will indicate completion.
ii. Markovnikov product is 1-chloro-1-methylcyclohexane



- iv. Anhydrous sodium sulfate removes traces of water to form a crystalline hydrate.
- v. Dichloromethane is more volatile than the halogenoalkane product.

3.

	Markovnikov products	Skeletal formulae
a.	2-chlorobutane	
b.	2-bromobutane	
c.	2-iodo-2-methylpropane	

Answers 21.9

1. C
2. $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{ONO}_2$
- 3.

Conditions	2-bromopropane	1-bromopropane
Polar and pure reactants	√	
Presence of sunlight		√
Presence of hydrogen peroxide		√

Answers 21.10

1. C
2. D

Answers 21.11

1. Nucleophilic addition of hydrogen cyanide to ethanal followed by hydrolysis (reflux HCl) results in the formation of lactic acid. Front side attack of the nucleophile (CN^-) is shown leading to the formation of (*R*)-lactic acid. There will be a racemic mixture of 50:50 (*R*)-lactic acid and (*S*)-lactic acid as attack of the nucleophile is equally likely from the reverse side.
2. B

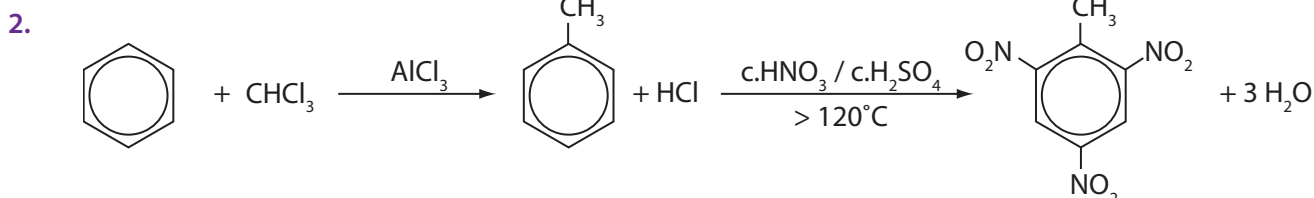
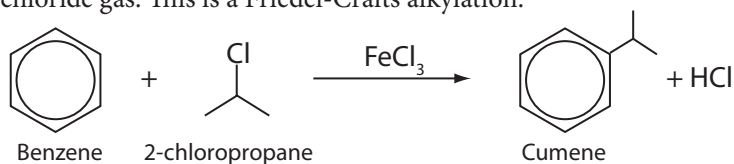
22. Aromatic Chemistry

Answer 22.1

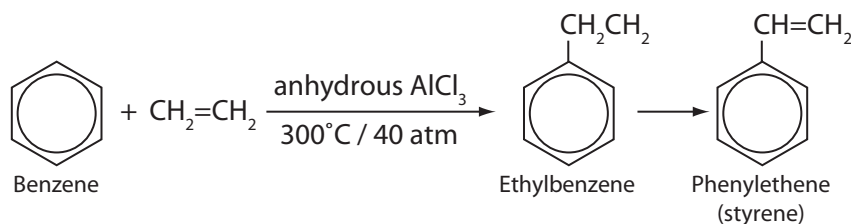
1. A & B are isomers with molecular formula C_7H_8O . A is 2-methylphenol (2-hydroxymethylbenzene). B is Benzyl alcohol (phenylmethanol). A is a phenol because the hydroxyl (OH) group is directly attached to the arene ring.

Answers 22.2

1. Reacting 2-chloropropane with benzene in the presence of anhydrous iron(III) chloride makes cumene and hydrogen chloride gas. This is a Friedel-Crafts alkylation.



3. Styrene can be prepared by reacting benzene with ethene under pressure in the presence of a halogen carrier such as anhydrous aluminium chloride in a Friedel-Crafts alkylation reaction. The product ethylbenzene is then dehydrogenated at high temperature with a catalyst such as ZnO or Fe_3O_4 .

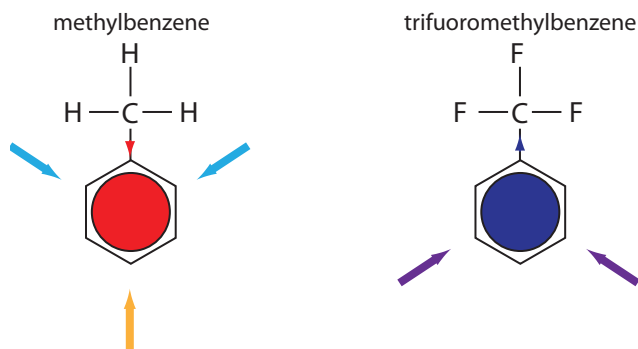


Answer 22.3

1. (a) $AlCl_3$ or $FeCl_3$ or $AlBr_3$ or $FeBr_3$ or $SnCl_2$ or $BF_3 \cdot OEt_2$ are suitable Lewis acid catalysts.
 (b) The reaction is a Friedel-Crafts acylation (c) It is an electrophilic substitution reaction.
 (d) The functional groups present in Fenbufen are: arene, ketone and carboxylic acid. (e) $C_{16}H_{14}O_3$.

Answers 22.4

1. Activating groups increase the rate of reaction with electrophiles because they increase the electron density in the aromatic π -system. Deactivating groups decrease the rate of reaction with electrophiles because they decrease the electron density in the aromatic π -system.
2. The expected ratio is 2:1. As the alkyl group increases it partially blocks the *ortho* position (steric effect).
3. The methyl group activates the benzene ring and the trifluoromethyl group deactivates the benzene ring. Methylbenzene will be more reactive towards electrophilic substitution than trifluoromethylbenzene. The CH_3 group will lead to *ortho* and *para* substitutions and the CF_3 group will lead to *meta* substitutions.

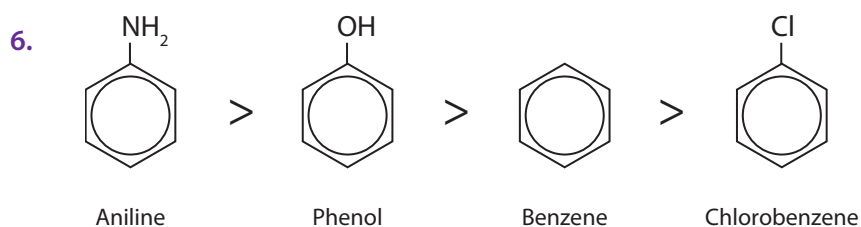


Answer 22.5

- Chlorine (Cl) is an electron withdrawing substituent because it is a highly electronegative group and is $-I$. It is *ortho/para* directing because the chlorine atom's lone pair of electrons in the $3p_z$ orbital overlap weakly with the π -system of the benzene ring. Resonance structures can be drawn which show increased electron density in the *ortho* (2-) and *para* (4-) positions.

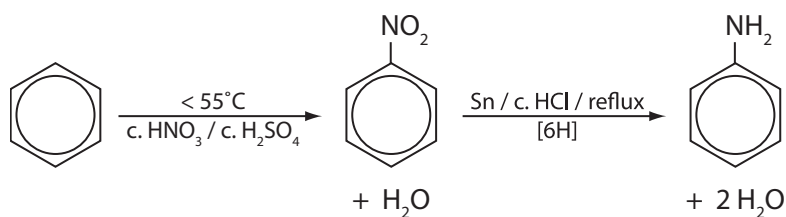
Answers 22.6

- C
- D
- C
- C
- D

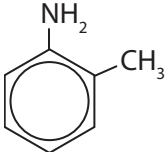
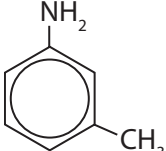
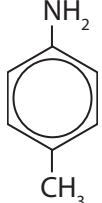
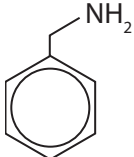
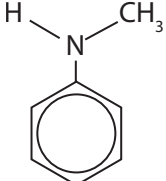


Answers 22.7

- A
- The first step is nitration of benzene at $<55^\circ\text{C}$ followed by reduction of the nitro group with tin and concentrated hydrochloric acid.



3.

Name	Structure	Type of amine
2-methylaniline		1° aromatic amine
3-methylaniline		1° aromatic amine
4-methylaniline		1° aromatic amine
phenylmethanamine		1° amine
N-methylphenylamine		2° aromatic amine

23. Acidity & Basicity

Answers 23.1

- The phenoxide ion ($\text{C}_6\text{H}_5\text{O}^-$) is stabilised by delocalisation.
- $\text{C}_2\text{H}_5\text{OH} < \text{H}_2\text{O} < \text{C}_6\text{H}_5\text{OH}$
least acidic *most acidic*
- A

Answers 23.2

- $\text{CH}_3\text{NH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{NH}_3^+\text{Cl}^-$
 - $\text{C}_6\text{H}_5\text{NH}_2 + \text{HBr} \rightarrow \text{C}_6\text{H}_5\text{NH}_3^+\text{Br}^-$
 - $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2 + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{NH}_3^+\text{Cl}^-$
- The lone pair on the nitrogen of phenylamine is delocalised with the π -system of the arene ring. This results in less electron density on the nitrogen, making it less likely to accept a proton than benzylamine. The positive inductive effect (+I) of the benzyl group results in an increase in electron density on the nitrogen atom of benzylamine, making it a stronger base, as it more easily accepts protons, than phenylamine.

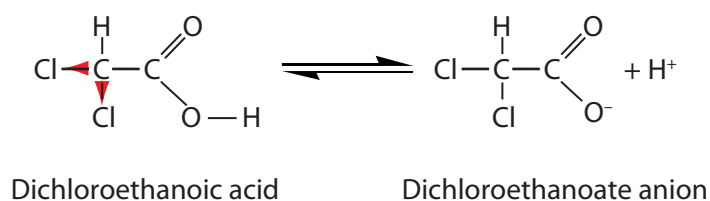
3.

Name of amine	1°	2°	3°	aliphatic	aromatic
Triethylamine			√	√	
Ethylphenylamine		√			√
Phenylamine	√				√
Diethylamine		√		√	
Ethylmethylphenylamine			√		√
Ethylamine	√			√	

- $\text{CH}_3\text{CH}_2\text{NH}_2 + \text{H}_2\text{O} \rightarrow [\text{CH}_3\text{CH}_2\text{NH}_3^+] + \text{OH}^-$ ethylamine ethylammonium ion
- C

Answers 23.3

- C
- B
- Dichloroethanoic acid is a stronger acid than ethanoic acid. This is because the two chlorine atoms withdraw electron density (-I) from the COOH group. This reduces the O-H bond strength which increases the amount of dissociation. This negative inductive effect results in a greater $[\text{H}^+]$ compared with ethanoic acid (for the same concentration). The dichloroethanoate ion is more stable than the ethanoate ion because it has a 'smaller' negative charge on the O^- .



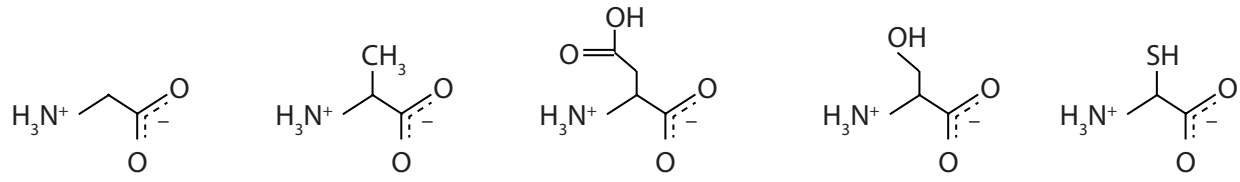
- B

- Benzoic acid is the stronger of the two acids as it has a larger K_a value. This suggests that the phenyl group (C_6H_5) has a smaller +I effect than the methyl (CH_3) group.
- React in separate test tubes equal volumes of methanoic acid and ethanoic acid having the same concentration with a fairly reactive metal such as magnesium. The stronger acid will effervesce the most and the metal will dissolve fastest in this acid.
- The smaller the pK_a the stronger the acid so the order of acidity is $CH_2FCO_2H > CH_2ClCO_2H > CH_2BrCO_2H > CH_2ICO_2H$. Fluoroethanoic acid is the strongest of these acids because the fluorine atom has the highest electronegativity value so it will have the greatest -I effect.
- The further the chlorine atom is away from the carboxylic acid group, the less -I effect it has and the less strong the acid. 2-chloropropanoic acid is a stronger acid than 3-chloropropanoic acid.

Answers 23.4

- 2,6-diaminohexanoic acid
 - $C_6H_{14}N_2O_2$
 - H-Lys-OH
 - $H_3N^+(CH_2)_4CHNH_3^+COOH$
 - $H_3N^+(CH_2)_4CHNH_3^+COO^-$
 - i
 - i
 - i
- These amino acids act as buffers because there is negligible change in the pH of an amino acid solution on the addition of either a small amount of alkali (OH^-) or acid (H^+). In solution, amino acids exist as zwitterions ($RCHNH_3^+COO^-$). To simplify matters we will consider the reaction between oppositely charged ions leaving the rest of the molecule as R.

$$RNH_3^+ + OH^- \rightarrow RNH_2 + H_2O$$

$$RCO_2^- + H^+ \rightarrow RCO_2H$$
- 
- D

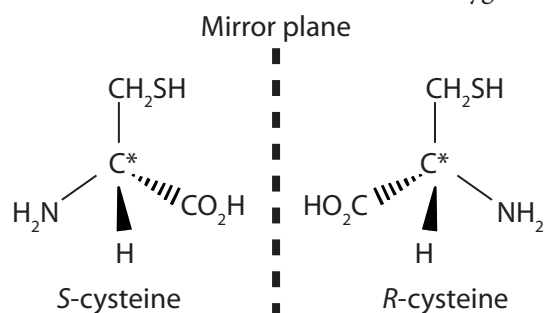
24. Stereochemistry

Answers 24.1

- They are unambiguous set of rules which describe the absolute configuration about a chiral centre.
- Molecules with a carbon attached to four different groups will not have a plane of symmetry. Such a molecule has asymmetry and is often described as chiral. Such a molecule can exist in two forms known as enantiomers. These enantiomers have non-superimposable mirror images which are identified by the letters R or S according to the C-I-P priority rules.
- The molecule shown is the *R*-isomer
-

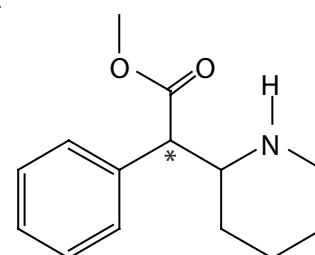
	Name
W	<i>S</i> -butan-2-ol
X	3-hydroxy-2-methylpropanol (achiral)
Y	<i>R</i> -bromochlorofluoromethane

- Cysteine has the opposite configuration to the other amino acids because the presence of the sulfur atom changes the priority order of its R group (CH₂SH). Biologists often use the CORN rule to determine the absolute configuration of α-amino acids, e.g. alanine where CO is CO₂H, R is CH₃ and N is NH₂. In amino acids other than cysteine, the R contains atoms of lower atomic number than oxygen found in the carboxylic acid group.



Answer 24.2

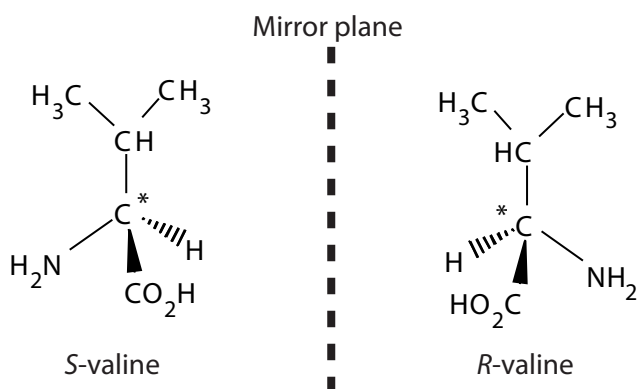
- Methylphenidate has a molecular formula C₁₄H₁₉NO₂ and it contains an arene, an ester and a secondary (2°) amine.



Answers 24.3

- S*-glyceraldehyde would have an optical rotation of -9.4° and a racemic mixture would have no optical rotation (0°).
- The absolute configurations at chiral centres are determined by x-ray crystallography. When a molecule is drawn on paper each chiral centre has an *R* or *S* configuration which is determined using the C-I-P priority rules. The optical rotation can only be empirically determined using a polarimeter. There is no relationship between the *R/S* notation and the direction that plane polarised light is rotated ($+$ or $-$).

3. R-valine will have a specific optical rotation of -27.5° which is equal and opposite to its S-isomer.



Answers 24.4

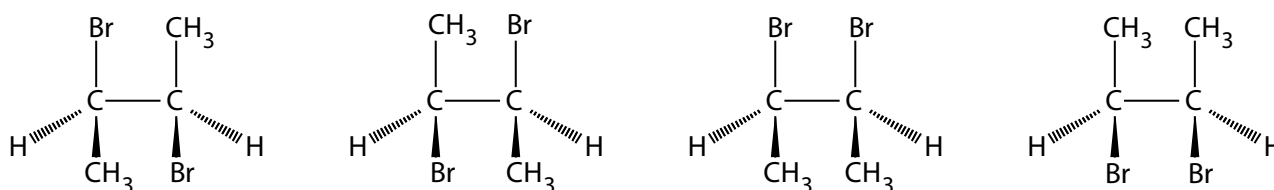
1. The formula is 2^n where n = number of chiral carbons. A molecule with four chiral centres $2^n = 2^4 = 16$ stereoisomers. There will be 2^{n-1} pairs of enantiomers = $2^3 = 8$ pairs of enantiomers.
2. A racemic mixture contains 50% of each enantiomer. $ee = 50\% - 50\% = 0\%$.

3.

	SR	RS	RR	SS
SR		enantiomers	diastereoisomers	diastereoisomers
RS	enantiomers		diastereoisomers	diastereoisomers
RR	diastereoisomers	diastereoisomers		enantiomers
SS	diastereoisomers	diastereoisomers	enantiomers	

4. i. TRUE ii. TRUE iii. FALSE iv. TRUE v. FALSE vi. TRUE vii. FALSE

5.



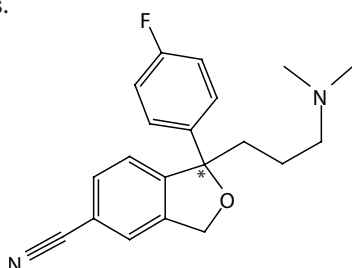
(RR) 2,3-dibromobutane

(SS) 2,3-dibromobutane

meso (RS) 2,3-dibromobutane

meso (SR) 2,3-dibromobutane

6. The configuration at the chiral centres is $1R, 2S$ and $5R$. The number of stereoisomers = 2^n where n = number of chiral centres = 3. So there are eight possible stereoisomers for menthol.
7. The number of possible stereoisomers = $2^{100} = 1.2676 \times 10^{30}$. All amino acids found in proteins are in the L-form (laevorotatory). This phenomenon is believed to be an accident propagated by evolution.
8. The two chiral centres are R,R in their absolute configuration.
9. It is prescribed as a racemic mixture as it is expensive to separate enantiomers. One stereoisomer will be active and the other one will have limited side effects.



25. Qualitative & Quantitative Analysis

Answer 25.1

1. D

Answers 25.2

- C_2H_5O
- (a) FeO (b) Fe_3O_4 (c) Fe_2O_3
- A
- C
- C_3H_8 propane
- CH_2O methanal (formaldehyde)

Answer 25.3

1. Ethanol, with a molecular formula of C_2H_6O

Answers 25.4

- a) 0.2 mol dm^{-3} b) 3.2 mol dm^{-3} c) 2.0 mol dm^{-3} d) 0.1 mol dm^{-3} .
- B
- a) True, b) True, c) False, d) True & e) False
- $0.0532 \text{ mol dm}^{-3}$
- $0.0741 \text{ mol dm}^{-3}$

Answer 25.5

- 1.

Substance	Conc. (mol dm^{-3})	Volume (cm^3)	M_r (g mol^{-1})	Mass (g)
$BaCl_2$	0.1	500	208.0	10.4
$K_2Cr_2O_7$	0.2	250	294.2	14.7
$FeSO_4$	0.3	750	151.9	34.18
$KMnO_4$	0.1	500	158.0	7.9

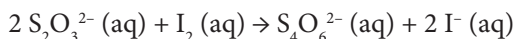
Answers 25.6

$$1. \quad n(\text{I}_2) = \frac{c \times v}{1000} = \frac{0.2 \times 25}{1000} = 0.005 \text{ mol}$$

$$n(\text{S}_2\text{O}_3^{2-}) = 2 \times n(\text{I}_2); n(\text{S}_2\text{O}_3^{2-}) = 2 \times 0.005 \text{ mol} = 0.01 \text{ mol}$$

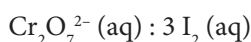
$$\frac{v}{1000}(\text{S}_2\text{O}_3^{2-}) = \frac{n}{c} = \frac{0.01}{0.36} = 0.0278 \text{ dm}^3 = 27.8 \text{ cm}^3$$

2. A 1% starch solution can be added to sharpen the end point. Starch forms a dark blue colour with iodine which turns to colourless once all the iodine has been consumed in the reaction.

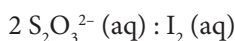


$$M_r \text{ of } \text{K}_2\text{Cr}_2\text{O}_7 = 294 \text{ g mol}^{-1}; \text{ amount } (\text{K}_2\text{Cr}_2\text{O}_7) = \frac{1.185}{294} = 0.004031 \text{ mol in } 250 \text{ cm}^3$$

$$[\text{K}_2\text{Cr}_2\text{O}_7] = 0.004031 \times 4 = 0.0161 \text{ mol dm}^{-3}$$



$$\text{In } 25.0 \text{ cm}^3 \text{ amount of iodine} = \frac{3 \times c \times v}{1000} = \frac{3 \times 0.0161 \times 25}{1000} = 1.208 \times 10^{-3} \text{ mol}$$



$$\text{In } 17.5 \text{ cm}^3 \text{ amount of thiosulfate} = 2 \times 1.208 \times 10^{-3} = 2.416 \times 10^{-3} \text{ mol}; [\text{Na}_2\text{S}_2\text{O}_3] = \frac{n}{\frac{v}{1000}} = \frac{2.416 \times 10^{-3}}{\frac{17.5}{1000}} = 0.138 \text{ mol dm}^{-3}$$

Answers 25.7

1. A
2. B
3. C
4. D

Answers 25.8

1. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ can be analysed in a variety of ways:

- Dehydrate to BaCl_2 and the number of moles of H_2O of crystallisation calculated.
- The cation can be tested for $\text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s})$.
- The anion can be tested for $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$.

Precautions:

- Precipitates need to be filtered, washed and dried to constant mass.
- Precipitates need to be heated until a constant mass is obtained.

- Cooling apparatus can be kept in a dessicator with a suitable drying agent (CaCl_2).
- Barium chloride is toxic, wear gloves and goggles.

Answers 25.9

1. 0.0337 m^3 or 33.7 dm^3
2. D
3. B

Answers 25.10

1.

Gas	Mass (g) of 1 dm^3	M_r of gas	Molar volume / dm^3
Nitrogen	1.152	28	24.31
Carbon monoxide	1.150	28	24.35
Carbon dioxide	1.810	44	24.31

2. C

3. Volume = 0.643 dm^3

4. $n = \frac{m}{A} = \frac{8.6}{55.8} = 0.154$ mol of iron. 1 mol iron : 1 mol hydrogen from the stoichiometric ratio. Therefore 0.154 mol hydrogen gas will be produced. $V = 24 \times n = 3.696 \text{ dm}^3 = 3696 \text{ cm}^3$

5.

Density = $\frac{\text{mass}}{\text{volume}}$. Therefore Volume = $\frac{\text{mass}}{\text{density}}$. Since hydrogen is diatomic (H_2) and $M_r = 2$

Volume = $2/0.089 = 22.47 \text{ dm}^3 = 22 \text{ dm}^3$ to 2 sig. figs.

26. Mass Spectrometry

Answers 26.1

- A
- B

Answer 26.2

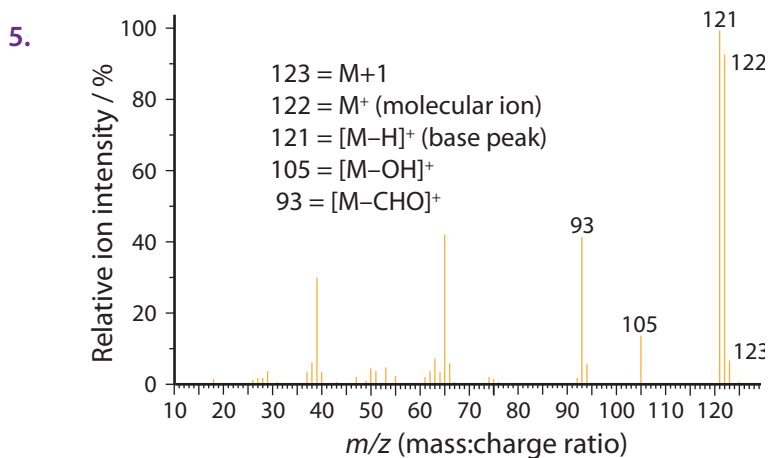
- C

Answers 26.3

- A
- This is the case for labile compounds. These substances fragment so little that no molecular ion reaches the detector. The molecule can be ionised by a method called chemical ionisation.

Answers 26.4

- Impact of high speed electrons with molecules can result in transfer of sufficient energy to break bonds in the molecule. Fragments are positively charged ($1+$) in the same way that the parent ion is (M^+).
- A
- C
- The peak at 68 corresponds to the molecular ion M^+ and the peak at 69 is $M+1$ where one of the carbon atoms is a carbon-13 isotope.



Answers 26.5

1. C
2. The peak at 17 has the highest intensity so it is the base peak and given the relative intensity of 100%. Ammonia is formed when urea decomposes so the peak at 17 might correspond to $[\text{NH}_3]^+$. The peak at 44 corresponds to $[\text{M}-\text{NH}_2]^+$. The peak at 60 is the molecular ion M^+ and the one at 61 is that due to $[\text{M}+1]^+$.
3. The relative atomic mass of lead (A_r) is the mean of the atomic masses for each isotope accounting for their relative abundances.
$$\text{Lead } (A_r) = \frac{(204 \times 1.5) + (206 \times 23.6) + (207 \times 22.6) + (208 \times 52.3)}{100} = 207.2(42)$$
4. The element is bromine and the two peaks are due to the element having two isotopes ^{79}Br and ^{81}Br in a 1:1 ratio.

27. Electronic Spectroscopy

Answers 27.1

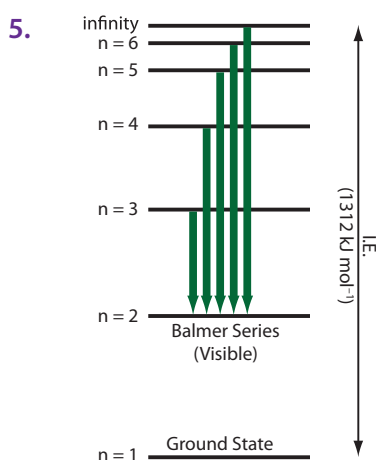
- Equation 9: $E = h \times f$. Therefore $\frac{E}{h} = f = \frac{496}{4 \times 10^{-13}} = 1.24 \times 10^{15}$ Hz
- $v = f\lambda$ (where v = speed of light in a vacuum). Line number 1 rearranging $v = f\lambda$ gives $\lambda = \frac{v}{f}$
 Multiplying $c = v$ by 1×10^9 gives the final answer in nm (10^{-9} m). $\lambda = \frac{3.00 \times 10^8 \times 1 \times 10^9}{4.568 \times 10^{14}} = 656.7$ nm

#	Wavelength (nm)	colour
1	656.7	red
2	486.5	blue-green
3	434.3	blue-violet
4	410.5	violet
5	397.3	(ultra) violet

- Since $v = f\lambda$, rearranging $f = \frac{v}{\lambda}$. Frequency of light = $\frac{3.00 \times 10^8}{700 \times 10^{-9}} = 4.286 \times 10^{14} \text{ s}^{-1}$
 $E = hf = 6.63 \times 10^{-34} \times 4.286 \times 10^{14} = 2.841 \times 10^{-19} \text{ J}$.

Answers 27.2

- Measure the frequency of the lines as they converge in the Lyman series. These are the lines in the most energetic part of the spectrum, *i.e.* highest frequency and lowest wavelength. Substitute the value for the frequency of the convergence limit into Planck's equation, $E = h \times f$ to give the photon energy. Multiply the photon energy in Joules by Avogadro's constant (L) and divide the answer by 1000 to give the answer in kJ mol^{-1} .
- B
- D
- B



The Balmer series arises when electrons fall from high energy levels to $n = 2$. For the $1s^1$ electron of hydrogen its ground state has a value of $n = 1$. Therefore ionisation of hydrogen is measurable from the convergence limit (Lyman series) when the electronic transition is ($n = \text{infinity}$ to $n = 1$).

- B

28. Infra-red Spectroscopy

Answers 28.1

1. D
2. A
3. The odd one out is mass spectrometry because all the others are spectroscopies which make use of electromagnetic radiation interacting with matter.

Answers 28.2

1. As sulfur dioxide is a V-shaped molecule, its dipoles do not cancel in bending and stretching modes of vibration so it will absorb infra-red radiation.
2. C
3. A
4. D
- 5.

Carbon dioxide	Vibration	IR absorbed?
CO ₂	asymmetrical stretching	√
CO ₂	bending	√
CO ₂	symmetrical stretching	

Answers 28.3

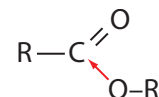
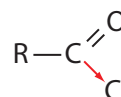
1. D
2. An infra-red spectrum is a graph which shows how the percentage transmittance or absorbance varies with the frequency of the infra-red radiation. Where troughs occur the molecule is absorbing infra-red radiation at this frequency by stretching or bending of polar molecular bonds.
3. Wavenumber is the reciprocal of wavelength ($1/\lambda$) in cm and its units are cm^{-1} and it is found on the x -axis of an infra-red spectrum. Wavenumber tells you how many waves there are in one centimetre.
4. i) 667 cm^{-1} & ii) 385 cm^{-1}
5. i) $\lambda = 9.8 \times 10^{-6} \text{ m} = \text{C-O bond}$, ii) $\lambda = 5.7 \times 10^{-6} \text{ m} = \text{C=O bond}$, iii) $\lambda = 4.3 \times 10^{-6} \text{ m} = \text{C}\equiv\text{N bond}$ & iv) $\lambda = 2.9 \times 10^{-6} \text{ m} = \text{N-H bond}$
6. As bond order decreases so does the frequency of vibration: $\text{BO} = 3 > \text{BO} = 2 > \text{BO} = 1$ (where BO = bond order).

Answer 28.4

1. A

Answers 28.5

1. There is a strong absorption at 1700 cm^{-1} showing it contains a carbonyl $\text{C}=\text{O}$ group. There are two C-H stretches typical of an aldehyde at 2740 cm^{-1} and 2820 cm^{-1} . There are three strong aromatic absorptions at 1311 cm^{-1} , 1456 cm^{-1} , and 1584 cm^{-1} which are likely to be attributed to the aromatic Ar-H absorptions.
2. There is a strong absorption at 1740 cm^{-1} showing it contains a carbonyl $\text{C}=\text{O}$ group. There is a C-O stretch at 1250 cm^{-1} typical of an ester. There is a C-H stretch at 2940 cm^{-1} .
3. There is a medium sized trough at 3070 cm^{-1} corresponding to a C-H stretch. There are three strong absorptions at 1450 , 1480 & 1580 cm^{-1} showing it is aromatic. The C-Cl stretch is most likely to be the absorption at $\sim 740\text{ cm}^{-1}$.
4. There is a sharp trough at 3200 cm^{-1} corresponding to a C-H stretch. The $\text{C}\equiv\text{N}$ stretch is most likely to be the absorption at $\sim 2250\text{ cm}^{-1}$.
5. $c = 3.00 \times 10^8\text{ m s}^{-1}$ therefore $c = 3.00 \times 10^{10}\text{ cm s}^{-1}$. $\nu = f\lambda$ so by rearranging $\lambda = \frac{\nu}{f} = \frac{3.00 \times 10^{10}}{2.3 \times 10^{13}} = 1.3 \times 10^{-3}\text{ cm}$
& since wavenumber $= \frac{1}{\lambda}\text{ (cm)} = \frac{1}{1.3 \times 10^{-3}}\text{ cm} = 767\text{ cm}^{-1}$
6. Stronger bonds need more energy to make them vibrate, so consequently they absorb a higher frequency of infra-red radiation (higher wavenumber). The heaviest halogen (iodine) resonates at a lower frequency than the much lighter halogen (chlorine).
7. The absorption at 3000 cm^{-1} is due to C-H stretching. This occurs at high frequency because the H atom has such small mass. The strong absorption at 1730 cm^{-1} is due to the stretch of the carbonyl $\text{C}=\text{O}$ bond. The bands in the finger print region at energy lower than 1500 cm^{-1} arise from bending motions of C-H bonds and stretching and bending motions of C-C bonds. Note the absence of C-O and O-H troughs.
8. In the acid chloride, the highly electronegative chlorine withdraws electrons (inductive effect), as shown by the arrow, and this serves to shorten and strengthen the $\text{C}=\text{O}$ bond which then resonates at higher frequency than the parent carboxylic acid. The opposite inductive effect is taking place with the electron releasing OR' group of the ester.



The inductive effect is in the same direction as for Cl (and is stronger). The difference is that the electron donation from the O lone pair in the ester is greater than from Cl in the acid chloride. This is a mesomeric (resonance / delocalisation) effect though, and not an inductive effect through sigma bonds.

9. C

10. B

11. D

12. Since $\nu = f\lambda$ rearranging $\lambda = \frac{\nu}{f}$ and $c = 3.00 \times 10^{10}\text{ cm s}^{-1}$, $\lambda = \frac{3.00 \times 10^{10}}{9.3 \times 10^{13}} = 3.226 \times 10^{-4}\text{ cm}$

$$\text{Wavenumber} = \frac{1}{\lambda} = \frac{1}{3.226 \times 10^{-4}} = 3100\text{ cm}^{-1}.$$

29. Carbon-13 NMR Spectroscopy

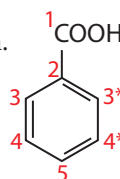
Answer 29.1

1. C

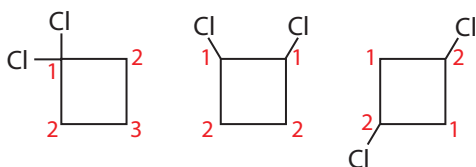
Answers 29.2

1. C
2. B
3. D
4. There are 5 peaks in benzoic acid's carbon-13 NMR spectrum.

There are equivalent carbons in the aromatic ring.



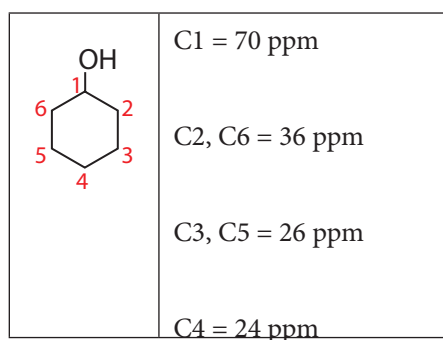
5. 1,1-dichlorobutane will have 3 peaks; 1,2-dichlorocyclobutane will have 2 peaks & 1,3-dichlorobutane will have 2 peaks.



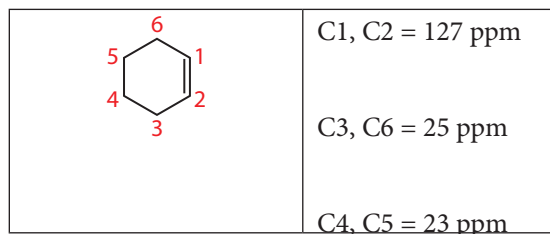
Answers 29.3

1. The peak at 0 ppm is TMS (tetramethylsilane), the internal standard. The peak at 18 ppm corresponds to C2 as C-C (0-50 ppm). The peak at 58 ppm corresponds to C1 of C-O as C-O (50-100 ppm).
2. The peak at 10 ppm corresponds to C-C of the CH₃ (methyl group), *i.e.* C3. The peak at 26 ppm corresponds to C-C of the CH₂ (methylene group), *i.e.* C2. The peak at 64 ppm corresponds to C-O of the alcohol, *i.e.* C1. The symbol for chemical shift is δ and the unit is ppm (parts per million).
3. The peak at 25 ppm corresponds to C-C of the two CH₃ (methyl groups), *i.e.* C1 and C3. The peak at 64 ppm corresponds to C-O of the R₂HCOH (2° alcohol group), *i.e.* C2. Propan-1-ol is its isomer and it would have an additional peak in the carbon-13 NMR spectrum due to the methylene group (CH₂) between 0-50 ppm.

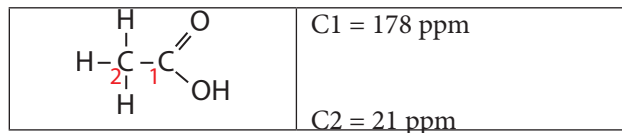
- 4.



5.

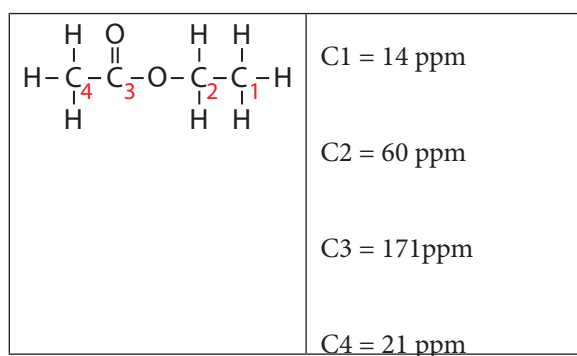


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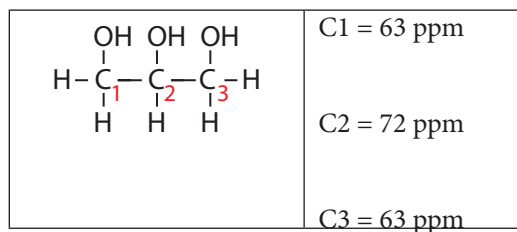


Answers 29.4

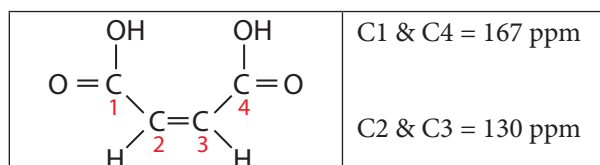
1.



2.



3.



4.

	Substance	# peaks
(a)	Maleic anhydride	2
(b)	Lactic acid (2-hydroxypropanoic acid)	3
(c)	1,4-Dioxane	1
(d)	Ethylene glycol (1,2-dihydroxyethane)	1
(e)	Butane-1,3-diol	4
(f)	Butane-2,3-diol	2

30. NMR of other spin $\frac{1}{2}$ Nuclei

Answers 30.1

1. A
2. B
3. C
4. D
5. (a) electrons, (b) greater, (c) flip

Answers 30.2

1. The methyl CH_3COOH at ~ 2.1 ppm and the acidic proton CH_3COOH at ~ 11.5 ppm
2. D
3. The aliphatic ROH is at ~ 4.5 ppm and the aromatic proton ArOH at ~ 7.0 ppm
4. C

Answers 30.3

1. The peak at 0 ppm is TMS. The peak at 2.05 ppm corresponds to methyl (CH_3COOH) and the smaller but broader peak at 11.7 ppm is the hydroxyl (CH_3COOH).
2. Measurement of the integration traces shows the proton environments at 8.1 ppm and 3.7 ppm are in a 1:3 ratio. The peak at 8.1 ppm is due to the HCOOCH_3 and is in the region for an aldehyde, despite the molecule being an ester. The peak at 3.7 ppm corresponds to the protons of the methyl (HCOOCH_3).
3. Measurement of the integration traces shows the proton environments at 2.0 ppm and 3.7 ppm are in a 1:1 ratio. The peak at 3.7 ppm is due to the methyl protons adjacent to the oxygen ($\text{CH}_3\text{COOCH}_3$). The peak at 2.0 ppm corresponds to the protons of the methyl adjacent to the carbonyl ($\text{CH}_3\text{COOCH}_3$).
4. CH_3 is a triplet as $n = 2$. CH_2 next to the CH_3 is a sextet as $n = 5$. CH_2 next to OH is a triplet as $n = 3$. OH is a singlet as there is no splitting through heteroatoms.
5. C
6. C
7. There will be three peaks in the proton nmr spectrum of propan-2-ol. There will be a doublet with relative intensities of 1:1 which corresponds to the methyl groups ($\text{CH}_3\text{CHOHCH}_3$). There will be a singlet which corresponds to the OH proton ($\text{CH}_3\text{CHOHCH}_3$) which will disappear when D_2O is added. There will be a complex multiplet (heptuplet) which corresponds to the methine proton ($\text{CH}_3\text{CHOHCH}_3$) with relative intensities of 1:6:15:20:15:6:1.
8. A B C D E F G H I J K L M N O P Q R S T U V W X Y Z
9. B
10. D

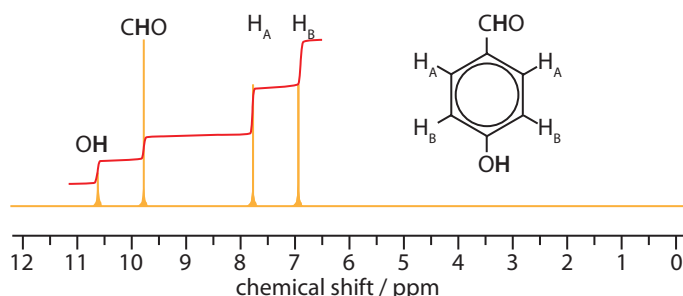
11. Integrated traces are steps by each of the peaks in an nmr spectrum whose heights give the ratio of the different types of protons found in a molecule.
12. B
13. a. $\text{CF}_3\text{CO}_2\text{H}$ singlet b. CHF_2CHFOH (doublet) & CHF_2CHFOH (triplet)
 c. $(\text{CF}_3)_2\text{CO}$ singlet d. CHF_2COF (doublet) & CHF_2COF (triplet)
14. Triphenylphosphine oxide will also give a singlet but its chemical shift will be more downfield, *i.e.* with a more positive value in ppm. The actual value is 28 ppm. This shift is because the highly electronegative oxygen will deshield the phosphorus nucleus so it will resonate at a higher frequency.

Answers 30.4

1.

n	n+1	Name	Abbreviation
0	1	singlet	s
1	2	doublet	d
2	3	triplet	t
3	4	quartet	q

2. The peak at 10.6 ppm is for the phenolic proton (OH) as it is a labile proton which can exchange with deuterium. The peak at 9.8 ppm is the aldehyde (CHO). There are two types of aromatic proton from the integrals and chemical shifts which suggest the structure is 4-hydroxybenzaldehyde. The aromatic protons adjacent to the aldehyde group are most downfield at 7.8 ppm, whilst the aromatic protons adjacent to the OH group are at 7.0 ppm.



3. 1,1,1-trichloroethane will give a singlet for its three equivalent protons (3H) whereas 1,1,2-trichloroethane will give a triplet (1H) and a doublet (2H).

4.

Formula	CH_3	CH_2	CO	CH_3
chemical shift	1.0 ppm	2.5 ppm		2.0 ppm
multiplicity	triplet	quartet		singlet
integral ratio	3	2		3

5. Both ethyl ethanoate and methyl propanoate will give a singlet (3H), quartet (2H) and a triplet (3H). They will have different chemical shifts, *e.g.* the singlet in ethyl ethanoate will be at 2.0 ppm for $\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$ and the singlet for methyl propanoate will be at 3.7 ppm for $\text{CH}_3\text{OCOC}_2\text{H}_5$. Chemical shifts will be more downfield (larger ppm) when adjacent to electronegative atoms such as oxygen.
6. 2-chloropropane $(\text{CH}_3)_2\text{CHCl}$.

