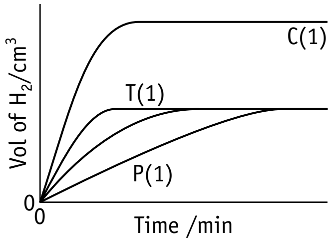
(iii) The $[OH^-]$ is in such excess [1] that it remains effectively constant [1] and therefore does not affect the reaction rate.

30 (a) By comparing the colour of the mixture under investigation with a solution of iodine containing 1×10^{-5} mol dm^{-3}. [1]
or by colorimetry with a solution of iodine containing 1×10^{-5} mol dm^{-3}. [1]

(b) Order with respect to $H_2O_2 = 1$
Order with respect to $I^- = 1$
Order with respect to $H^+ = 1$ (all three correct [2], two correct [1])
Rate $= k[H_2O_2][I^-][H^+]$ [1]
Units of $k = (\text{mol dm}^{-3})^{-2}\ \text{s}^{-1}$ or $\text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$ [1]

31 (a)

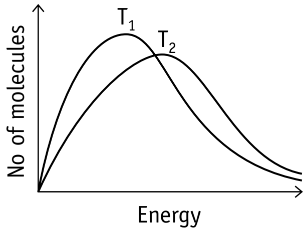


(b) (i) The rate constant for the reaction [1]

(ii) Rate $= k[HI]^2$
$2 \times 10^{-4} = k(0.2)^2$ [1]
$\therefore\ k = 0.5 \times 10^{-2}$ (5×10^{-3}) [1] $(\text{mol dm}^{-3})^{-1}\text{s}^{-1}$ or $\text{mol}^{-1}\,\text{dm}^3\ \text{s}^{-1}$ [1]

(iii) Rate $= k[HI]^2$
$= 5 \times 10^{-3} \times (0.6)^2$
$= 1.8 \times 10^{-3}$ [1] mol dm^{-3} s^{-1} [1]

(c) (i)

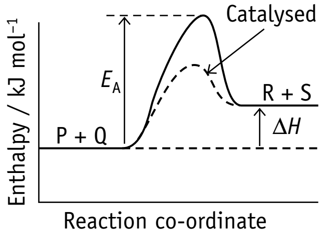


Shapes of curves [1]
T_2 displaced to higher values relative to T_1 [1]
Peak for T_2 lower than T_1 so that area under both curves is the same [1]

(ii) Reactions occur when particles collide with sufficient energy to react, called the activation energy, E_A [1]. With increase in temperature, a greater proportion of molecules possess the E_A [1]. The molecules are also moving faster and therefore collide more frequently [1]. For these 2 reasons (higher proportion with E_A and greater collision frequency) reaction rates increase with increase in temperature.

32 (a) The minimum energy which reactants must possess for a successful reaction [1] when collisions occur.

(b) (i), (ii)



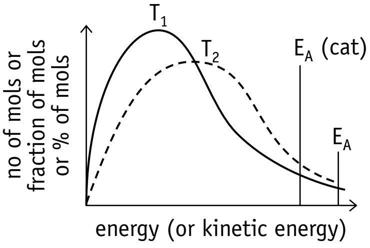
Correct endothermic profile [1]
E_A correctly shown [1]
ΔH correctly shown [1]
Correct catalysed profile (lower) [1]

(iii) Catalyst provides an alternative pathway with a lower E_A. [1] So, a larger fraction of molecules have sufficient energy to react. [1]

(c) (i) nitrogen oxides [1] ⟶ nitrogen [1]
or carbon monoxide [1] ⟶ carbon dioxide [1]
or hydrocarbons, e.g. methane [1] ⟶ carbon dioxide + water [1]

(ii) Some petrol contains lead compounds. [1] If these are used in cars fitted with catalytic converters, the lead coats (poisons) the metal catalyst [1] and reduces its surface area.

(d)



Axes labelled correctly [2]
T_2 peak lower than T_1 peak [1]
T_2 peak to right of T_1 peak [1]
E_A(catalysed) labelled to left of E_A [1]

33 (a) (i) $K_c = \dfrac{[NO_2(g)]^2}{[N_2O_4(g)]}$ [1],
units = mol dm^{-3} [1]

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
concentration at equilibrium

$$\frac{0.5\ [1]}{10\ [1]} \qquad \frac{1.0}{10}\ [1]$$

$$K_c = \frac{(1/10)^2}{(0.5/10)}$$

$= 0.2$ mol dm^{-3} [1]

(iii)

$$\begin{tikzcd} N_2O_4(g) \arrow[rr, "\Delta H_r"] & & 2NO_2(g) \\ & N_2(g) + 2O_2(g) \arrow[ul, "+9.7"] \arrow[ur, "+2 \times 33.9"'] & \end{tikzcd}$$

$\Delta H_r = -9.7 + 67.8$
$= +58.1$ kJ mol^{-1}
(correct numerical result [1], cycle or some working [1])

(iv) At 100 °C, equilibrium will move in endothermic direction by Le Chatelier's principle. [1] Therefore, there would be more NO_2 and less N_2O_4 than at 70 °C. [1]

(b) Reduce pressure [1] so that system will try to nullify the change and produce more molecules by further dissociation forming NO_2. [1]

(c) (i) no effect [1]; (ii) no effect [1]; (iii) increases [1]

(d) The reaction is very slow even at high temperatures [1] because of a very large activation energy due to the high bond energies of both N_2 and O_2. [1]

34 (a) Change in number of moles – decrease. [1] That is because, as pressure increases, there is a higher yield. [1] Therefore, equilibrium has been displaced to products. [1] The system has removed the constraint of increased pressure by forming fewer molecules. [1]

(b) Forward reaction is exothermic [1] because reduction in temperature causes an increased yield [1], i.e. equilibrium has moved to products by lowering the temperature. [1]

(c) (i) $(60 \pm 3)\%$ [1]

(ii) No effect on the position of equilibrium. [1]
Catalysts increase the rate [1] of both the forward and the backward reactions equally. [1]
or catalysts do not change the relative stabilities of the reactants

and products [1] so they do not affect the equilibrium between them. [1]

(d) (i) To increase the reaction rate [1]

(ii) To reduce the cost of expensive pipework/containers and pumps needed at the higher pressure. [1]

35 (a) If a system in equilibrium is subjected to a constraint (change) [1], it will respond (move in a direction) to remove (nullify, oppose) the constraint [1].

(b) (i) Moves to right (more SO_3 produced) [1] as this gives fewer moles of gas (lower pressure) [1].

(ii) Moves to left (more SO_2 and O_2 produced) [1] as this is the endothermic direction (lowers the temperature) [1].

(c) $K_c = \dfrac{[SO_3(g)]^2}{[SO_2(g)]^2[O_2(g)]}$ [1]

(d) (i) No effect. [1] Changing pressure causes changes in amounts and in the volume but overall K_c stays constant.

(ii) Increase in temperature results in less SO_3 at equilibrium [1] so K_c decreases [1].

(e) (i) V_2O_5 or Pt [1]

(ii) High pressure is ideal, but this is very costly on extra-strong pipework/pumps [1] so the pressure used is only slightly above atmospheric.
High temperature is used to ensure a high reaction rate [1] even though high temperature reduces the yield at equilibrium.
A catalyst speeds up the reaction rate. [1]

(f) Economically: cannot afford to waste reactants/costs of recycling are cheaper than buying more SO_2 or O_2. [1]
Environmentally: SO_2 is poisonous/a greenhouse gas/causes acid rain. [1]

36 (a) Moles $Cl_2 = \dfrac{11.1}{71} = 0.156$

Moles PCl_3 = Moles $Cl_2 = 0.156$

Moles $PCl_5 = \dfrac{83.4}{208.5} - 0.156$

$= 0.4 - 0.156$
$= 0.244$ [1]

(b) (i) $K_c = \dfrac{PCl_3(g)][Cl_2(g)]}{[PCl_5(g)]}$ [1]

(ii) $K_c = \dfrac{0.156}{9.23} \times \dfrac{\dfrac{0.156}{9.23}}{\dfrac{0.244}{9.23}}$ [1]

$= 0.0108$ [1] mol dm^{-3} [1]

(c) (i) $K_p = \dfrac{p(PCl_3) \times p(Cl_2)}{p(PCl_5)}$ [1]

(ii) mole fraction of $Cl_2 = \dfrac{0.156}{0.556}$

$= 0.281$ [1]

(iii) partial pressure PCl_5
= mol fraction × total pressure [1]

$= \dfrac{0.244}{0.556} \times 250$

$= 0.439 \times 250$
$= 109.7$ kPa [1]

(iv) partial pressure
$Cl_2 = 0.281 \times 250 = 70.25$ kPa [1]

$K_p = \dfrac{(70.25)^2}{109.7}$

$= 45.0$ [1] kPa [1]

37 (a) $K_w = [H^+][OH^-]$ [1]

(b) (i) $[H^+][OH^-] = 51.3 \times 10^{-14}$
but $[H^+] = [OH^-]$
$\therefore \quad [H^+]^2 = 51.3 \times 10^{-14}$
$[H^+] = 7.16 \times 10^{-7}$ mol dm^{-3} [1]
$pH = -lg[7.16 \times 10^{-7}]$
$= -[0.86 - 7.00] = 6.14$ [1]

(ii) Because $[H^+] = [OH^-]$ [1]

(iii) $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ [1]
Increase in temperature [1] displaces equilibrium towards the right [1].

(c) When 5 cm^3 1.0 M NaOH is added to 995 cm^3 water,

$[OH^-] = 5 \times \dfrac{1}{1000} = 5 \times 10^{-3}$ M [1]

$K_w = [H^+][OH^-]$
$= 1.00 \times 10^{-14}$ at 298 K
$[OH^-] = 5 \times 10^{-3}$
$\therefore \quad [H^+] = 2 \times 10^{-12}$ [1]
$pH = -lg[H^+]$
$= -lg[2 \times 10^{-12}]$
$= -[0.30 - 12]$
$= 11.7$ [1]

38 (a) (i) $K_a = \dfrac{[H^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$

[1]

(ii) $pK_a = -lg[K_a]$
$= -lg(1.7 \times 10^{-5})$ [1]
$= 4.77$ [1]

(iii) $K_a = \dfrac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

Now, $[H^+] = [CH_3COO^-]$ [1]
and $[CH_3COOH] = 0.1 - [H^+]$
$\simeq 0.1$ (as $[H^+]$ is so small) [1]

$\therefore \quad 1.7 \times 10^{-5} = \dfrac{[H^+]^2}{0.1}$

$[H^+] = \sqrt{1.7 \times 10^{-6}}$
$= 1.3 \times 10^{-3}$ [1]

$pH = -lg[H^+]$
$= -lg(1.3 \times 10^{-3})$
$= 2.89$ [1]

(iv) Using a pH meter [1]

(b) (i) CH_3COOH donates an H^+ ion (proton) [1] to OH^- ions [1] in the NaOH(aq) to form water (H_2O).

(ii) phenolphthalein/thymol blue [1]

(c) (i) H^+ ions from the added HCl might affect the pH. [1] The buffer contains a high concentration of ethanoate ions (CH_3COO^-). [1] Most of the H^+ ions react with ethanoate ions (CH_3COO^-) from the aqueous sodium ethanoate [1] to form undissociated ethanoic acid. This removes most of the H^+ ions and the pH changes very little. [1]

(ii) Injections into the body must be buffered.
Buffers control the pH of blood
Buffers in the body ensure the effectiveness of enzymes. (any 1 for [1]).

39 (a) (i) CH_3CH_2COOH [1] $\rightleftharpoons$
$CH_3CH_2COO^- + H$ [1]
($\rightleftharpoons$ may be replaced by $\longrightarrow$)

(ii) $pKa = -lg\ K_a$ [1]
$= -lg(1.22 \times 10^{-5})$
$= 4.91$ [1]

(b) (i) $CH_3CH_2COOH + NaOH \longrightarrow$
$CH_3CH_2COONa + H_2O$ [1]

(ii) phenolphthalein [1]

(c) (i) A solution which resists changes in pH [1] when acid or alkali are added [1].

(ii) $CH_3CH_2COOH \rightleftharpoons$
$CH_3CH_2COO^- + H^+$
(equilibrium) [1]
$CH_3CH_2COONa \longrightarrow$
$CH_3CH_2COO^- + Na^+$ (fully ionised) [1]
The buffer contains a high concentration of undissociated propanoic acid (weak acid) and propanoate ions. [1] When acid is added (i.e. H^+), the extra H^+

ions react with propanoate ions ($CH_3CH_2COO^-$) to form undissociated propanoic acid [1] and the concentration of H^+ ions changes very little [1]. So the pH stays almost constant. When alkali is added (i.e. OH^-), the extra OH^- ions reacts with H^+ ions to form water. [1] More propanoic acid (CH_3CH_2COOH) then dissociates to restore the equilibrium [1] and the pH changes very little.

(5 of the above points well expressed for [5])

(iii) $K_a = \dfrac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$

Half of the propanoic acid has been neutralised by NaOH forming sodium propanoate. [1]

$\therefore$ $[CH_3CH_2COO^-] = [CH_3CH_2COOH]$ [1]

$\therefore$ In the buffer $[H^+] = K_a$ [1]

$\therefore$ pH of buffer $= pK_a = 4.91$

(iv) Blood contains the buffer of carbonic acid (or dissolved carbon dioxide) plus hydrogencarbonate ions. [1] This buffer keeps the pH of blood at a fairly constant value. [1]

40 (a) Mainly H_2CO_3 at low pH [1]
Mainly HCO_3^- at medium pH [1]
Mainly CO_3^{2-} at high pH [1]

(b) H_2CO_3 and/or HCO_3^- [1]

(c) (i) $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
or $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ [1]

(ii) $HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$
or $HCO_3^- + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}$ [1]
(allow arrows in place of equilibrium signs)

(d) (i) Solubility is reduced [1]

(ii) Solubility is increased [1]

(e) (i) $CaCO_3$ reacts to form $Ca(HCO_3)_2$ which is soluble. [1]
$CaCO_3(s) + H_2CO_3(aq) \longrightarrow Ca(HCO_3)_2(aq)$ [1]
($H_2O(l) + CO_2(g)$ might be written in place of $H_2CO_3(aq)$)

(ii) $Ca(HCO_3)_2(aq)$ decomposes to form solid $CaCO_3$ (a precipitate of $CaCO_3$). [1]
$Ca(HCO_3)_2(aq) \longrightarrow CaCO_3(s) + H_2O(l) + CO_2(g)$ [1]

41 (a) Let solubility $= s$ mol dm^{-3}
$AgCl(s) \longrightarrow Ag^+(aq) + Cl^-(aq)$
concentrations at equilibrium
$[Ag^+(aq)] = [Cl^-(aq)] = s$ [1]
$\therefore$ $K_{s.p.}(AgCl) = s^2 = 1.8 \times 10^{-10}$
$s = 1.34 \times 10^{-5}$ mol dm^{-3} [1]
$= 1.34 \times 10^{-5} \times 143.4$ g dm^{-3}
$= 1.92 \times 10^{-3}$ g dm^{-3} [1]
([1] for each correct answer and [1] for evidence of correct working)
Let solubility $= s$ mol dm^{-3}
$CaCO_3(s) \longrightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)$
concentrations at equilibrium
$[Ca^{2+}(aq)] = [CO_3^{2-}(aq)] = s$
solubility $= 0.0300$ g dm^{-3} (from table)

$\therefore$ $s = \dfrac{0.03}{100}$ mol dm^{-3} [1]
$= 0.0003$ mol dm^{-3} [1]
(*or* 3×10^{-4} mol dm^{-3} [1])
$K_{s.p.}(CaCO_3) = s^2$
$= (3 \times 10^{-4})^2$
$= 9 \times 10^{-8}$ mol^2 dm^{-6} [1]

(b) (i) $NaNO_3$ will cause no change. [1] $NaNO_3$ will dissolve to produce $Na^+(aq)$ and $NO_3^-(aq)$ ions. Neither of these will influence the concentration of $Ag^+(aq)$ or $Cl^-(aq)$ [1] and so the solubility of AgCl will remain unchanged.

(ii) NaCl will cause a decrease. [1] NaCl will dissolve to produce $Na^+(aq)$ and $Cl^-(aq)$ ions. The $Cl^-(aq)$ ions will therefore increase the total concentration of $Cl^-(aq)$ ions, but as $[Ag^+(aq)] \times [Cl^-(aq)]$ cannot be exceeded at a particular temperature [1], some AgCl will be precipitated and the overall solubility of AgCl will be less.

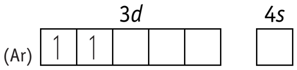
(c) (i) AgCl $= 7.253$ g from 100 cm^3 sea water
$\equiv \dfrac{7.253}{143.4} \times 10$ moles from 1000 cm^3 sea water [1]
$\therefore$ $[Cl^-] = 0.0506$ [1] mol dm^{-3} [1] sea water
or 5.06×10^{-2} mol dm^{-3} sea water.

(ii) Solubility of AgCl $= 1.92 \times 10^{-3}$ g dm^{-3}
$= 1.92 \times 10^{-4}$ g in 100 cm^3 water [1]
So maximum error in 7.253 g of AgCl $= 0.000192$ g

$\therefore$ maximum percentage error
$= \dfrac{0.000192}{7.253} \times 100$ [1]
$= 0.0026\%$ [1]

(d) CO_2 will react with water vapour in the atmosphere or water in rivers, lakes and oceans to form carbonic acid.
$H_2O(l) + CO_2(g) \rightleftharpoons H_2CO_3(aq)$
([1] for statement of reaction or the equation).
Carbonic acid can react with calcium carbonate as chalk, limestone or marble in rocks or with the small quantities of dissolved calcium carbonate to form soluble calcium hydrogencarbonate.
(Knowledge of reaction with $CaCO_3$ in rocks and in the oceans [1])
$H_2CO_3(aq) + CaCO_3(s) \longrightarrow Ca(HCO_3)_2(aq)$ [1]
These reactions will reduce the rising levels of atmospheric CO_2.

42 (a) V^{3+} ion



[1]

(b) Variable oxidation state/formation of complex ions/catalytic properties of metal and its compounds (any 2 for [2])

(c) (i) +5 [1]

(ii) Dioxovanadium(V) [1]

(d) (i) A mixture of VO_2^+ and VO^{2+} [1]

(ii) V^{3+} or VO^+ [1]

(iii) V^{2+} [1]

(e) (i) Reducing agents donate electrons/lose electrons [1]

(ii) $Zn \longrightarrow Zn^{2+} + 2e^-$ [1]

(f) (i) $VO_2^+ + 2H^+ + e^- \longrightarrow VO^{2+} + H_2O$ [1]

(ii) $Zn + 2VO_2^+ + 4H^+ \longrightarrow 2VO^{2+} + 2H_2O + Zn^{2+}$ [1]

43 (a) The e.m.f./potential/voltage produced between the metal/metal ion half-cell [1] and a hydrogen half-cell/electrode under standard conditions [1].

(b) (i) $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$ [1]

(ii) From zinc to copper [1]

(iii) From standard electrode potential data
$Zn^{2+} + 2e^- \longrightarrow Zn$; $E^\ominus = -0.76$ V
$Cu^{2+} + 2e^- \longrightarrow Cu$; $E^\ominus = +0.34$ V

When the cell in the diagram is set up:
$Zn \rightarrow Zn^{2+} + 2e^-$ and
$Cu^{2+} + 2e^- \rightarrow Cu$
or $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$ [1]
$\therefore \quad E^{\ominus} = -(-0.76) + 0.34$
$= 1.10$ V [1]

(c) (i) It reduces the e.m.f. [1]

(ii) Reducing $[Cu^{2+}(aq)]$ makes the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ less likely [1], but does not affect the process $Cu \rightarrow Cu^{2+} + 2e^-$ [1]. This means that $E^{\ominus}$ for $Cu^{2+} + 2e^- \rightarrow Cu$ is reduced (less positive than $+\,0.34$ V) [1] so the overall e.m.f. is reduced.

(iii) Change in any concentration by one power of ten affects e.m.f. by ±0.03, hence 1.01 V. [1]

(iv) Adding $NH_3(aq)$ will cause $[Cu(NH_3)_4]^{2+}(aq)$ to form [1] and reduce the concentration of $Cu^{2+}(aq)$ ions [1]. The reduced concentration of $Cu^{2}(aq)$ will reduce the likelihood of the reaction $Cu^{2+} + 2e^- \rightarrow Cu$ and reduce the overall e.m.f. [1].

(d) (i) Fe goes into solution as $Fe^{2+}(aq)$
$Fe \rightarrow Fe^{2+} + 2e^-$ (statement or equation [1])
Fe^{2+} is then further oxidized to Fe^{3+}
$Fe^{2+} \rightarrow Fe^{3+} + e^-$ (statement or equation [1])
Oxidation is achieved by dissolved oxygen in water
$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^-$ [1]
(max. [2])

(ii) Zn is more reactive than iron [1] so Zn forms Zn^{2+} ions in preference to Fe forming Fe^{2+} ions [1].

44 (a) The standard electrode potential of a half-cell is the potential difference between the half-cell and a standard hydrogen half-cell [1], measured under standard conditions (gases at 1 atm pressure, aqueous solutions 1.0 mol dm^{-3}, temperature 298 K) [1].

(b) (i) +0.34 V [1]

(ii) When $\log[Cu^{2+}]$ is zero, $[Cu^{2+}] = 1$ mol dm^{-3} and the value is the *standard* electrode potential, $E^{\ominus}$. [1]

(iii) There is a linear relationship between the electrode potential and $\log[Cu^{2+}]$. [1]
i.e. $E = \text{constant} \times \log[Cu^{2+}] + E^{\ominus}$

(c) (i) Cr^{2+} [1]

(ii) Yes [1], because the reaction $Cr + 2H^+ \rightarrow Cr^{2+} + H_2$ has $E^{\ominus} = +0.91$ V and is therefore feasible [1].

(iii) orange ($Cr_2O_7^{2-}(aq)$) to yellow ($CrO_4^{2-}(aq)$) [1]

(d) (i) A = CaO
B = $Ca(OH)_2$
C = $Ca(OH_2)_2(aq)$/limewater,
D = $CaCO_3$
E = $Ca(HCO_3)_2(aq)$,
R = CO_2
Names or formulas could be given.
All six correct [3]
4 correct [2]
2 correct [1]
I $CaCO_3 \rightarrow CaO + CO_2$
II $CaO + H_2O \rightarrow Ca(OH)_2$
III $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
IV $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
V $Ca(HCO_3)_2 \rightarrow CaCO_3 + H_2O + CO_2$
4 or 5 equations correct [2]
2 or 3 equations correct [1]

(ii) Na_2CO_3 is soluble or Na_2CO_3 is not decomposed so readily. [1]

45 (a) Potential/e.m.f./voltage of a particular half-cell relative to a standard hydrogen half-cell/hydrogen electrode [1] under standard conditions [1].

(b) (i) $Fe + I_2 \rightarrow Fe^{2+} + 2I^-$ [1]
or $Fe + 2Cu^+ \rightarrow Fe^{2+} + 2Cu$ [1]
as this produces a large positive overall $E^{\ominus}$ [1].

(ii) $2Cu + I_2 \rightarrow 2Cu^+ + 2I^-$ [1]
as this produces a very small positive overall $E^{\ominus}$ [1].

(c) (i) Labels on diagram should show Fe(s) electrode in $Fe^{2+}(aq)$ solution [1]; solution 1 mol dm^{-3} [1]; Pt electrode [1] in solution containing I_2 and I^- [1] both at 1 mol dm^{-3} [1]; salt bridge [1]. (max. [5])

(ii) Arrow from Fe electrode to I_2/I^- cell [1]

(iii) $+0.54 - (-0.44) = +\,0.98$ V [1]

(iv) The cell potential/e.m.f. would increase [1] because there would be a greater tendency for Fe to form Fe^{2+} [1].

46 (a) Aluminium [1]
(b) SiO_2 [1]
(c) Magnesium [1]
(d) $2Na + 2H_2O \rightarrow 2NaOH + H_2$
formulas correct [1], balanced [1]

47 (a) (i) Atomic radius decreases [1], increasing nuclear charge (no. of protons) [1], exerts a greater attractive force [1] on electrons in the same shell [1].

(ii) Atomic radius increases [1], an additional shell of electrons is added [1] (from one element to the next), causing increased shielding [1] and weaker attraction from the nucleus [1].

(b) Boiling point increases from Na to Si [1] then drops to low boiling points for P, S Cl_2 and Ar [1].
Na, Mg and Al have giant metallic structures [1] with strong attractive forces between positive centres and a sea of electrons (outer electrons) [1]. Bonding and hence b.pt. increases from Na to Al as outer (valence) electrons increase in number [1].
Si has a giant covalent structure [1] with strong covalent bonds between atoms [1] and a very high boiling point [1].
P, S, Cl_2 and Ar have simple molecular structures [1] with weak forces (Van der Waals forces) between molecules [1] and hence low b.pts. (max. [9])

(c) (i) Each successive ionisation creates an ion with one extra positive charge [1] which makes it more difficult to remove a negative electron [1].

(ii) $C^{4+}(g) \rightarrow C^{5+}(g) + e^-$ ([1] for correct charges, [1] for balanced equation)

(iii) The I.E.s can indicate electrons with similar or very different energies. [1] This gives evidence for shells of electrons. [1]
e.g. the large increase between the 4th and 5th I.E. [1] suggests a new shell [1] (of more stable electrons). The data suggests C has one shell (close to the nucleus) with 2 electrons and a second with 4 electrons. [1]
(max. [4])

48 (a) (i) Cs and Ba are in the same period. Cs has one outer shell electron and Ba has two. [1] The forces between the Ba^{2+} ions and the sea of electrons is greater in Ba than in Cs. [1] This results in a smaller atomic radius for Ba, causing a greater density [1] and the greater forces between atoms in Ba results in higher m.pt. and greater hardness [1]. (max. [3])

(ii) Electrons falling from high/excited levels to lower/ground level. [1]

(iii) A line spectra for Cs.

(b) (i) Ratio by mass Na : O
$= 58.97 : 41.03$
Ratio by moles Na : O

$$= \frac{58.97}{23} : \frac{41.03}{16}$$

$= 2.56 : 2.56$
$= 1 : 1$ [1]
$\therefore$ empirical formula = NaO [1]

(ii) $M_r(\mathbf{Y}) = 78$, $M_r(\text{NaO}) = 39$
$\therefore$ molecular formula
$= Na_2O_2$ [1]

(iii) Take a known mass of **Y** and add excess ice-cold H_2SO_4 to produce H_2O_2 (**Z**). Calculate the number of moles H_2O_2 from mass of **Y** and its M_r. [1] Titrate the solution of H_2O_2 (**Z**) with a solution of $KMnO_4$ of known concentration [1] until there is a slight excess of $KMnO_4$ and the mixture is faintly pink [1].

49 (a) (i) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ [1]

(ii) $Mg(NO_3)_2(s) \longrightarrow MgO(s) + 2NO_2(g) + \frac{1}{2}O_2(g)$ [1]

(b) (i) $Be(NO_3)_2$ [1]

(ii) The change from nitrate to oxide in the crystal [1] is most favourable when the cation is small [1].

(c) The process of dissolving involves the reverse of the lattice energy. [1]
i.e. $Mg^{2+}SO_4^{2-}(s) \longrightarrow Mg^{2+}(g) + SO_4^{2-}(g)$ (reaction 1)
followed by hydration [1]
$Mg^{2+}(g) + SO_4^{2-}(g) + (aq) \longrightarrow Mg^{2+}(aq) + SO_4^{2-}(aq)$ (reaction 2)
For $MgSO_4$ compared to $BaSO_4$, reaction 1 is more endothermic but reaction 2 is more exothermic because Mg^{2+} is smaller than Ba^{2+}. [1]
However, the overall process is more favourable (and more exothermic) for $MgSO_4$ than $BaSO_4$. [1] (max. [2])

(d) (i) $Ca^{2+} + 2e^- \longrightarrow Ca$ [1]
$2Cl^- \longrightarrow Cl_2 + 2e^-$ [1]

(ii) hydrogen (H_2) [1]
chlorine (Cl_2) or oxygen (O_2) [1]

50 (a) (i) white precipitate [1]
$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s)$ [1]

(ii) Add $AgNO_3$ [1]
White ppte of AgCl forms which turns grey. [1]
$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

(b) (i) For these substances to be soluble in water, the overall process (reverse lattice enthalpy + hydration enthalpy) must be exothermic [1] (i.e. hydration enthalpy must be more exothermic than lattice enthalpy). This is the case for $MgSO_4$, but not for $BaSO_4$. [1]

(ii) High m.pt./b.pt./soluble in water/soluble in polar solvents/insoluble in non-polar solvents/conducts when aqueous or molten. (any 2 for [1])

(c) Mg is required to synthesise chlorophyll which is essential for photosynthesis. [1]

51 (a) Boiling points increase from Cl_2 to Br_2 to I_2. [1]
M_r increases from Cl_2 to Br_2 to I_2 [1]; so the increasing number of electrons increases the likelihood of induced dipoles [1] and therefore stronger induced-dipole attractions (Van der Waals forces). [1] (any 3 for [3])

(b) Electronegativity is the power of an atom in a covalent bond [1] to attract electrons [1]. Electronegativity increases from I to Cl. [1] Cl has the smallest atoms [1] (smallest atomic radius) with the least shielding of outer electrons [1]. It therefore attracts outer electrons in any covalent bond most strongly even though its nuclear charge is smaller. [1] (any 5 for [5])

(c) The reducing power increases from Cl^- to I^-. [1] As ionic radius increases, the outer electrons are further away [1] and more shells give increased shielding [1].
The outer electrons in Hal^- ions are therefore most easily removed in I^-, in spite of its large nuclear charge. [1]
$Cl_2(aq)$ added to $Br^-(aq)$: solution becomes yellow/orange [1] as $Br_2(aq)$ is produced [1].
$Cl_2(aq) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$ [1]
$Cl_2(aq)$ added to $I^-(aq)$: solution becomes red/brown [1] as $I_2(aq)$ or $I_2(s)$ is produced [1].
$Cl_2(aq) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(aq)$ [1] (max. [8])

52 (a) (i) Left-hand side anode, right-hand side cathode. [1]

(ii) Anode (+): $2Cl^- \longrightarrow Cl_2 + 2e^-$ [1]
Cathode (−): $H^+ + e^- \longrightarrow \frac{1}{2}H_2$ *or* $H_2O + e^- \longrightarrow \frac{1}{2}H_2 + OH^-$ [1]
(cathode equation may be double those above)

(iii) Sodium chloride [1]

(iv) They would precipitate $Mg(OH)_2$ and $Ca(OH)_2$ in the cell. [1] They would clog up the diaphragm. [1] They would increase the impurity in the NaOH. [1] (max. [2])

(b) (i) $Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$ [1]
(state symbols not needed)

(ii) $3ClO^- \longrightarrow 2Cl^- + ClO_3^-$ [1]
The oxidation number of Cl in ClO^- is +1
The oxidation number of Cl in Cl^- is −1
The oxidation number of Cl in ClO_3^- is +5 [1]
Disproportionation involves a reaction in which one species (in this case, ClO^-) is both oxidised and reduced. [1]

(c) (i) Suitable use such as drain cleaner, manufacture of bleach, manufacture of soap, purifying cellulose. [1]

(ii) Suitable use such as water sterilisation, manufacture of bleach, manufacture of P.V.C., manufacture of TCP, manufacture of D.D.T. [1]

(iii) Suitable use of H_2 such as manufacture of NH_3, hydrogenation of fats/oil, manufacture of margarine, rocket fuel. [1]

(d) Add NaClO(aq) + acid [1] to KI(aq) or KBr(aq). Then shake with immiscible organic solvent. [1]
Orange colour – bromine [1], purple colour – iodine [1].
Alternatively, add $AgNO_3(aq)$ [1] followed by $NH_3(aq)$ [1] to KI(aq) or KBr(aq). Cream (off-white) precipitate which dissolves slowly in $NH_3(aq)$ – Br^-. [1] Yellow precipitate, insoluble in $NH_3(aq)$ – I^-. [1]

53 (a) (i) $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$ ([1] for $NaHSO_4$, [1] for balanced equation)

(ii) NaCl – white fumes (misty fumes) or colourless liquid [1]
NaBr – orange/red/brown vapour/liquid or pungent/sharp smell of SO_2 [1]
NaI – purple vapour or dark brown/black solid or bad egg smell of H_2S. [1]

(iii) Conc. H_2SO_4 can act as oxidising agent. [1] The ease of oxidation is $I^- > Br^- > Cl^-$. [1] (or $I^- > Br^-$ but Cl^- is not oxidised by conc. H_2SO_4)
I^- is oxidised most readily because it will lose an electron most easily due to its large ionic radius (extra shielding of electron) [1] in spite of the fact that I^- will have a larger nuclear charge [1]. (any 3 key points for [3])

(b) Add $AgNO_3(aq)$ followed by $NH_3(aq)$. NaCl(aq) gives a white precipitate of AgCl [1], soluble in $NH_3(aq)$ [1]. NaBr(aq) gives a cream (off-white) precipitate of AgBr [1], which dissolves in excess $NH_3(aq)$ [1]. NaI(aq) gives a pale yellow precipitate of AgI [1], insoluble in $NH_3(aq)$ [1]. (any 5 for [5])

(c) No precipitate/no reaction [1], AgF is soluble [1].

54 (a) (i) Precipitates fine/suspended/colloidal particles or removes phosphates. [1]

(ii) Kills bacteria (micro-organisms). [1]

(b) (i) Al^{3+} ions are poisonous/toxic/cause Alzheimer's disease. [1]

(ii) Maximum level of Al is 6×10^{-7} mol dm^{-3}

$= \dfrac{6 \times 10^{-7}}{2}$ mol

$Al_2(SO_4)_3$ dm^{-3} [1]

$= \dfrac{6 \times 10^{-7}}{2} \times 342$ g

$Al_2(SO_4)_3$ dm^{-3} [1]

$= \dfrac{6 \times 10^{-7}}{2} \times 342 \times 1000$ g

$Al_2(SO_4)_3$ in 1000 dm^3 (1 tonne)

$= \dfrac{6 \times 10^{-7}}{2} \times 342 \times 1000 \times 1000$ g

$Al_2(SO_4)_3$ in 1000 tonnes [1]
= 102.6 g [1] (max. [3])

(c) $Cl_2 + CH_4 \rightarrow CH_3Cl + HCl$ [1]

55 (a) (i) +2 in CO [1], +4 in CO_2 [1].

(ii) Oxidation [1]

(iii) Allow CO to burn in plenty of air or O_2. [1]

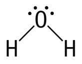
(b) (i) $1s^2 2s^2 2p^2$ [1]

(ii)

$O{=}C{=}O$

(bonds shown linearly) [1]

(iii)



(bonds shown at an angle, lone pairs unnecessary) [1]

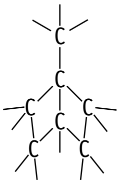
(iv) Shapes of simple molecules are dictated by the number of negative centres around the central atom. [1] CO_2 has two negative centres (two double bonds) around the C atom [1] which repel as far apart as possible to 180°. H_2O has four negative centres (two single bonds and two lone pairs) on the O atom. [1] These repel to approx. tetrahedral positions and the H—O—H bond angle is approx. tetrahedral (actually 105°).

(c) (g) rather than (s) or very much more volatile or very much lower m.pt./b.pt. or more acidic, etc. [1]

(d) PbO_2 can be readily reduced to lead(II) compounds. [1] Specific example: e.g. with conc. HCl [1]

(e) (i) From metals to non-metals [1], C (diamond) and Si are regarded as non-metals, C (graphite) and Ge are regarded as metalloids, Sn and Pb are regarded as metals [1].

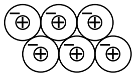
(ii) Carbon (diamond) consists of C atoms joined to four neighbours by strong covalent bonds. [1]



[1]

This strong bonding makes the diamond unreactive. [1]

Lead consists of lead atoms in a close packed structure. Each lead atom is surrounded by six others.



[1]

The structure can be regarded as positive ions in a sea/cloud of mobile outer electrons. [1] The outer electrons are removed fairly easily to form Pb^{2+} ions. [1] (max. [4])

56 (a) Co-ordinate bond [1] is formed from a lone pair of electrons on the ligand to the positive metal ion. [1]

(b) (i) 1, 2-diaminoethane [1]

(ii) bidentate [1]

(iii) +3 [1]

(iv) 6 [1]

(v) octahedral [1]

(c) Dissolve $CoCl_2$ in water [1] Pass $Cl_2(g)$ through this solution [1] (to oxidise $CoCl_2$ to $CoCl_3$). Add correct molar amount of 1, 2-diaminoethane. [1]

57 (a) (i) **A** is $[Cu(H_2O)_4]^{2+}(aq) + SO_4^{2-}(aq)$ (*or* $[Cu(H_2O)_6]^{2+}$) [1]
B is $[CuCl_4]^{2-}(aq)$ [1]
C is $Cu(OH)_2(s)$ (*or* $Cu(OH)_2(H_2O)_2$ *or* $Cu(OH)_2(H_2O)_4$) [1]
D is $[Cu(NH_3)_4]^{2+}(aq)$ (*or* $[Cu(NH_3)_4(H_2O)_2]^{2+}(aq)$) [1]

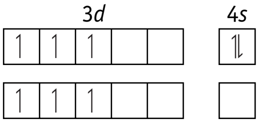
(ii) The solution goes blue. [1] Water ligands replace Cl^- around the Cu^{2+}. [1]
(*or* $[CuCl_4]^{2-}(aq)$ becomes $[Cu(H_2O)_4]^{2+}(aq)$)

(b) (i) $Cu(OH)_2(s)$ (*or* $[Cu(OH)_2(H_2O)_2]$ *or* $[Cu(OH)_2(H_2O)_4]$) [1]

(ii) Hexadentate or polydentate [1]

(iii) EDTA ligands form very strong bonds to Cu^{2+} ions [1] so there are no $[Cu(H_2O)_4]^{2+}(aq)$ ions which might react with $OH^-(aq)$ [1].

58 (a)



[1]

[1]

(b) (i) It has unoccupied orbitals in the 3*d* sub-shell. [1] Electrons can become excited and move from slightly lower 3*d* energy levels to