Worked Solutions to Problems
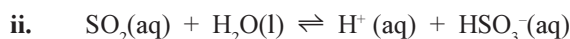
1 Acid Rain

a.

i. $pV = nRT$

$$n = \frac{pV}{RT} = \frac{1.00 \text{ bar} \times 33.9 \text{ L}}{0.08314 \frac{\text{L bar}}{\text{mol K}} \times 298.15 \text{ K}}$$

$n = 1.368$ mol

$c(SO_2) = 1.368$ M

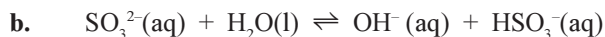**ii.** $SO_2(aq) + H_2O(l) \rightleftharpoons H^+(aq) + HSO_3^-(aq)$

$[H^+] = [HSO_3^-] = x$

$$\frac{x^2}{1.368 \text{ M} - x} = 10^{-1.99} \text{ M}$$

$[H^+] = [HSO_3^-] = 0.1224$ M

$$\frac{0.1224 \text{ M}}{1.386 \text{ M}} \times 100\% = 8.95\% \quad \text{as } HSO_3^-$$

iii.   pH = 0.91

b. $SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)$

$[OH^-] = [HSO_3^-] = x$

$$\frac{x^2}{0.01 \text{ M} - x} = \frac{10^{-14} \text{ M}^2}{10^{-7.18} \text{ M}} = 10^{-6.82} \text{ M}$$

$x = [OH^-] = 3.89 \times 10^{-5}$ M

$[H^+][OH^-] = 10^{-14} \text{ M}^2$ $\qquad\qquad$ $[H^+] = 2.57 \times 10^{-10}$ M

c.

i. $K = \dfrac{[SO_2][SO_3^{2-}]}{[HSO_3^-]^2} = \dfrac{[SO_2][SO_3^{2-}]}{[HSO_3^-]^2} \times \dfrac{[H^+]}{[H^+]} = \dfrac{K_{a2}}{K_{a1}} = 10^{-5.26}$
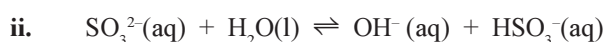
ii. $[SO_2] + [HSO_3^-] + [SO_3^{2-}] = 0.01$ M $\quad$ and $\quad$ $[SO_2] = [SO_3^{2-}]$

$$\frac{[SO_2]^2}{(0.01 \text{ M} - 2[SO_2])^2} = 10^{-5.26}$$

$[SO_2] = 2.33 \times 10^{-5}$ M

d. $M(BaSO_3) = 217.39$ g mol^{-1}

i. $[Ba^{2+}] = 7.36 \times 10^{-4}$ M

ii. $SO_3^{2-}(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HSO_3^-(aq)$

$[OH^-] = [HSO_3^-] = x$

$$[HSO_3^-] + [SO_3^{2-}] = [Ba^{2+}]$$

$$\frac{x^2}{7.36 \times 10^{-4}\ M - x} = 10^{-6.82}\ M$$

$$x = 1.0479 \times 10^{-5}\ M$$

$$[SO_3^{2-}] = 7.26 \times 10^{-4}\ M$$

iii. $K_{sp} = [Ba^{2+}]\,[SO_3^{2-}] = 7.36 \times 10^{-4}\ M \times 7.26 \times 10^{-4}\ M = 5.34 \times 10^{-7}\ M^2$

e. $[Ag^+]^2\,[SO_3^{2-}] = 10^{-13.82}\ M^3$

$$[Ag^+] = 2\,[SO_3^{2-}]$$

$$[Ag^+] = 3.927 \times 10^{-5}\ M$$

f. $K = \dfrac{[Ag^+]^2}{[Ca^{2+}]} = \dfrac{[Ag^+]^2}{[Ca^{2+}]} \times \dfrac{[SO_3^{2-}]^2}{[SO_3^{2-}]} = \dfrac{K_{sp}(Ag_2SO^3)}{K_{sp}(CaSO^3)} = \dfrac{10^{-13.82}\ M^3}{10^{-7.17}\ M^2}$

$K = 10^{-6.65}\ M$

g. Reaction: $2\ H_2O(l) + SO_2(aq) + Br_2(aq) \rightarrow SO_4^{2-}(aq) + 2\ Br^-(aq) + 4\ H^+(aq)$

Equilibrium: $HSO_4^-(aq) \rightleftharpoons SO_4^{2-}(aq) + H^+(aq)$ $K_a = 10^{-1.99}\ M$
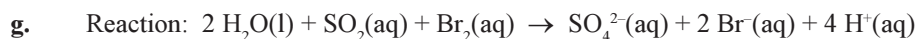
$[SO_4^{2-}] + [HSO_4^-] = 0.01\ M$ and $[H^+] + [HSO_4^-] = 0.04\ M$

$[HSO_4^-] = 0.04\ M - [H^+]$ and $[SO_4^{2-}] = [H^+] - 0.03\ M$

$[H^+] = 0.0324\ M$

h. $[H^+] = 10^{-3.2}\ M$

$K_a = 10^{-1.99}\ M$ $[HSO_4^-] = 10^{-1.28}\ [SO_4^{2-}]$

$[H^+] = 10^{-3.2}\ M = [HSO_4^-] + 2\,[SO_4^{2-}] + [OH^-]$

$10^{-3.2}\ M = 10^{-1.28}\,[SO_4^{2-}] + 2\,[SO_4^{2-}] + 10^{-10.8}\ M$

$[SO_4^{2-}] = 3.074 \times 10^{-4}\ M$ and $[HSO_4^-] = 1.613 \times 10^{-5}\ M$

$c(H_2SO_4) = [HSO_4^-] + [SO_4^{2-}]$

$c(H_2SO_4) = 3.24 \times 10^{-4}\ M$

2   Potassium Chlorate

a. Cathode: $2\ H_2O(l) + 2\ e^- \rightarrow 2\ OH^-(aq) + H_2(g)$

Anode: $2\ Cl^-(aq) \rightarrow Cl_2(g) + 2\ e^-$

b. Reaction: $3\ Cl_2(g) + 6\ OH^-(aq) \rightarrow ClO_3^-(aq) + 5\ Cl^- + 3\ H_2O(l)$
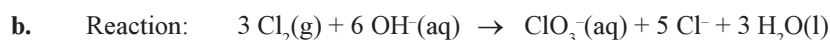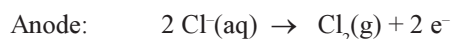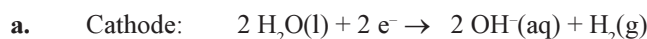
c. Formation of 1 mol $KClO_3$ requires 1 mol KCl and 6 mol electrons.

$m(KClO_3) = 100\ g,\ n(KClO_3) = 0.816\ mol$

formation of 0.816 mol KCl gives: $m(KClO_3) = 60.83$ g

and requires 6×0.816 mol electrons

$Q = I\,t$ and $Q/F =$ amount of e^- in moles

$Q = 6 \times 0.816$ mol $\times$ 96485 C mol^{-1} = 472390.56 C = 472390.56 A s = 131 A h

3   Sugar Inversion

a.
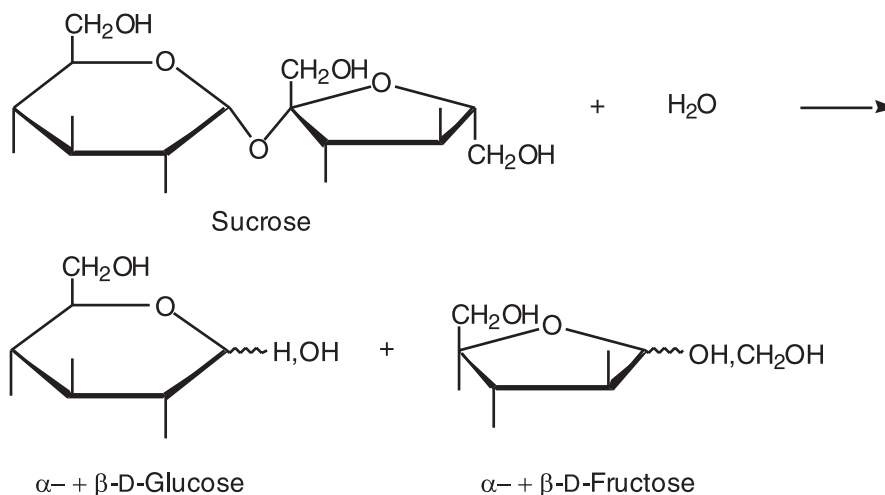
b. $\ln(\alpha_t - \alpha_\infty)$ as a function of time is a straight line, i.e. first order reaction

The slope is -0.0053 min^{-1}

$k = 0.0053$ min^{-1} = 8.83×10^{-5} s^{-1}

c. $k = A\,\exp(-E_a/(R \times 298\ \text{K}))$ and $2\,k = A\,\exp(-E_a/(R\ 303\ \text{K}))$

$\ln 2 = (1/298\ \text{K}^{-1} - 1/303\ \text{K}^{-1})E_a/R$

$E_a = 104$ kJ mol^{-1}.

4   Humus

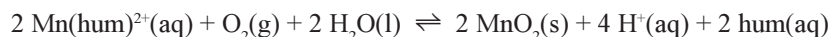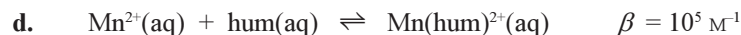**a.** $2\ Mn^{2+}(aq) + O_2(g) + 2\ H_2O(l) \rightarrow 2\ MnO_2(s) + 4\ H^+(aq)$

b. $\Delta G_2^{\ominus} = -2\ F\ E_2^{\ominus} = -233.5$ kJ mol^{-1}

$\Delta G_3^{\ominus} = -2\ F\ E_3^{\ominus} = -474.7$ kJ mol^{-1}

$\Delta G_1^{\ominus} = -2\ \Delta G_2^{\ominus} + \Delta G_3^{\ominus} = -7.7$ kJ mol^{-1}

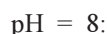**c.** $\Delta G_1^{\ominus} = -RT \ln K_1$

$K_1 = 22.4$ M^2 bar^{-1}

d. $Mn^{2+}(aq) + hum(aq) \rightleftharpoons Mn(hum)^{2+}(aq)$ $\qquad \beta = 10^5 \ M^{-1}$

$2\ Mn(hum)^{2+}(aq) + O_2(g) + 2\ H_2O(l) \rightleftharpoons 2\ MnO_2(s) + 4\ H^+(aq) + 2\ hum(aq)$

$$K = \frac{[hum]^2\ [H^+]^4}{[Mn(hum)^{2+}]^2\ p(O_2)} = \frac{K_{\downarrow}}{\beta^2} = 2.24 \times 10^{-9}\ M^4\ bar^{-1}$$

e. pH = 5:

$$2.24 \times 10^{-9}\ M^4\ bar^{-1} = \frac{(10^{-4}M)^2 \times (10^{-5}M)^4}{[Mn(hum)^{2+}]^2 \times 0.2\ bar}$$

$[Mn(hum)^{2+}] = 4.7 \times 10^{-10}\ M$

pH = 8:

$$2.24 \times 10^{-9}\ M^4\ bar^{-1} = \frac{(10^{-4}M)^2 \times (10^{-8}M)^4}{[Mn(hum)^{2+}]^2 \times 0.2\ bar}$$

$[Mn(hum)^{2+}] = 4.7 \times 10^{-16}\ M$

f. Alkaline soil.

5 Brønsted Acids and Bases

a. $NH_4^+(aq) + OH^-(aq) \rightarrow NH_3(aq) + H_2O(l)$
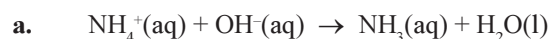
18.7 mmol NH_4Cl and 3.17 mmol $Ba(OH)_2 \cdot 8H_2O$ (6.34 mmol OH^-) produce 6.34 mmol NH_3, and 12.4 mmol NH_4^+ is left unchanged.

$$[H^+] = K_a \frac{[NH_4^+]}{[NH_3]} = 10^{-9.24}\ M \times \frac{12.4}{6.34} = 1.13 \times 10^{-9}\ M$$

$pH = -\log(1.13 \times 10^{-9}) = 8.95$

b. $[NH_4^+] = 0.124\ M$

$[Ba^{2+}] = 0.0317\ M$

$[H^+] = 1.13 \times 10^{-9}\ M$

$[Cl^-] = 0.187\ M$

$[OH^-] = 8.85 \times 10^{-6}\ M$

c. 10.0 mmol HCl is added. Of this amount 6.34 mmol is neutralised by NH_3. Assuming that the volume is 110 mL, and ignoring the weak acid NH_4^+ we get:

$$[H^+] = \frac{3.66\ mmol}{110\ mL} = 0.0333\ M$$

$pH = -\log(0.0333) = 1.48$

d. In the strong acidic solution, $[NH_3]$ will be very low.

$$[NH_4^+] = \frac{18.7\ mmol}{110\ mL} = 0.170\ M$$

$$[NH_3] = \frac{K_a[NH_4^+]}{[H^+]} = \frac{10^{-9.24}\ M \times 0.170\ M}{0.0333\ M} = 2.9 \times 10^{-9}\ M$$
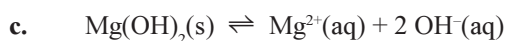
6 Magnesium Hydroxide

a. $pOH = 14.0 - 10.5 = 3.5$

$[OH^-] = 10^{-3.5}$ M $= 3.2 \times 10^{-4}$ M

This corresponds to a solubility of $Mg(OH)_2$ of 1.6×10^{-4} mol L^{-1} or

9.2×10^{-4} g/100 mL.

b. $K_{sp} = [Mg^{2+}] [OH^-]^2 = 1.6 \times 10^{-11}$ M^3

c. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2\ OH^-(aq)$

$[Mg^{2+}] = x;$ $[OH^-] = 0.010$ M $+ 2x \cong 0.010$ M

$$x = \frac{K_{sp}}{[OH^-]^2} = \frac{1.6 \times 10^{-11}\ \text{M}^3}{(0.010\ \text{M})^2} = 1.6 \times 10^{-7}\ \text{M}$$

The solubility is 1.6×10^{-7} mol L^{-1} or 9×10^{-7} g/100 mL.

d. $Mg(OH)_2$ is in large excess, and the hydrochloric acid will be completely neutralised due to the reaction:

$Mg(OH)_2(s) + 2\ H^+(aq) \rightarrow Mg^{2+}(aq) + 2\ H_2O(l)$
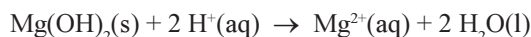
Assuming constant volume of 100 mL, this reaction produces a Mg^{2+} concentration of 0.050 M. Then $Mg(OH)_2$ dissolves in the solution:

$[Mg^{2+}] = 0.050$ M $+ x \cong 0.050$ M

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = \sqrt{\frac{1.6 \times 10^{-11}\ \text{M}^3}{0.050\ \text{M}}} = 1.8 \times 10^{-5}\ \text{M}$$

$pOH = -\log(1.8 \times 10^{-5}) = 4.7$

$pH = 14.0 - 4.7 = 9.3$

7 An Unstable Solid

a.

	NH$_4$HS(s)	$\rightleftharpoons$	NH$_3$(g)	+	H$_2$S(g)
$H^{\ominus}$/(kJ mol^{-1})	−156.9		− 45.9		−20.4
$S^{\ominus}$/(J K^{-1} mol^{-1})	113.4		192.6		205.6

$\Delta H^{\ominus} = -45.9$ kJ mol^{-1} $- 20.4$ kJ mol^{-1} $- (-156.9)$ kJ mol^{-1} $= 90.6$ kJ mol^{-1}

$\Delta S^{\ominus} = 192.6$ J K^{-1} mol^{-1} $+ 205.6$ J K^{-1} mol^{-1} $- 113.4$ J K^{-1} mol^{-1} $= 284.8$ J K^{-1} mol^{-1}

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\,\Delta S^{\ominus} = (90600 - 298.15 \times 284.8)$ J mol^{-1} $= 5687$ J mol^{-1}

$= 5.7$ kJ mol^{-1}

b.

$\Delta G^{\ominus} = - RT \ln K_a$

at 25 °C: -5687 J mol^{-1} = $- 8.3145$ J K^{-1} mol^{-1} × 298.15 K ln K_a

$K_a = 0.1008$

$K_a = (p(NH_3)/\text{bar}) (p(H_2S)/\text{bar})$

$K_p = p(NH_3)\ p(H_2S) = 0.1008$ bar^2

c.

at 35 °C: $\Delta G^{\ominus} = \Delta H^{\ominus} - T \Delta S^{\ominus} = (90600 - 308.15 \times 284.8)$ J mol^{-1}

$= 2839$ J mol^{-1}

K_a $= 0.3302$

K_p $= p(NH_3)\,p(H_2S) = 0.3302$ bar^2

d.

$p(\text{total}) = p(NH_3) + p(H_2S)$

$p(NH_3) = p(H_2S) = 0.5\, p(\text{total})$ (equal amounts)

$K_p = p(NH_3)\, p(H_2S) = 0.5\, p(\text{total}) \times 0.5\, p(\text{total}) = (0.5\, p(\text{total}))^2 = 0.1008$ bar^2

$p(\text{total}) = 0.635$ bar

$n(\text{gas}) = p\, V / (R\, T) = 0.635$ bar × 25.00 L /(0.083145 L bar mol^{-1} K^{-1} × 298.15 K)

$= 0.64$ mol

$n(NH_4HS) = 1.00$ mol $-\ 0.5 \times 0.64$ mol $= 0.68$ mol   *i.e.* there is still solid present

e.

$n(\text{gas}) = p\, V / (R\, T) = 0.635$ bar × 100.00 L /(0.083145 L bar mol^{-1} K^{-1} × 298.15 K)

$= 2.56$ mol

$n(NH_4HS) = 1.00$ mol $-\ 0.5 \times\ 2.56$ mol $= -\ 0.28$ mol !   *i.e.* there is no solid left

1.00 mole of solid converted to 2.00 moles of gas

$p(\text{total}) = n(\text{total})\, R\, T / V = 2.00 \times 0.083145$ L bar mol^{-1} K^{-1} × 298.15 K / 100.00 L

$= 0.50$ bar

8 Electrochemistry

a. Cell diagram: $Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$

This cell diagram implies a cell reaction with oxidation (electron production) on the left-hand side (IUPAC convention):

left, oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

right, reduction: $Ag^+(aq) + e^- \rightarrow Ag(s)$ (to be multiplied by 2)

Cell reaction: $Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$
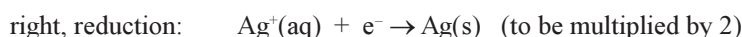
b. $E^\ominus(cell) = E^\ominus(right) - E^\ominus(left) = 0.80\ V - (-0.76\ V) = 1.56\ V$

The Nernst equation corresponding to cell reaction above:

(Some may prefer to focus on half-cells and half-reactions)

The activity a of a solute is approximated by its concentration (divided by the standard concentration).

The activity of a solid substance is equal to 1.

$$E(cell) = E^\ominus(cell) - \frac{0.05916\ V}{n} \log \frac{a(Zn^{2+})\,a(Ag)^2}{a(Zn)\,a(Ag^+)^2}$$

$$= 1.56\ V - \frac{0.05916\ V}{2} \log \frac{0.200}{0.100^2} = 1.52\ V$$

The positive sign of $E(cell)$ implies that the cell reaction as written above is the spontaneous reaction which takes place during discharge of the cell.

Spontaneous reaction: $Zn(s) + 2\,Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2\,Ag(s)$
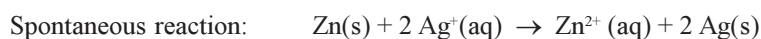
c. At complete discharge $E(cell) = 0$ and the cell reaction has reached chemical equilibrium.

$$0 = 1.56\ V - \frac{0.05916\ V}{2} \log K$$

$K = 5.5 \times 10^{52}$, *i.e.* the cell reaction has an equilibrium position to the far right with practically no Ag^+ ions left in solution. The amount of transported Ag^+ and electrons:

$n(Ag^+) = [Ag^+]\,V(solution) = 0.100\ \text{M} \times 1.00\ \text{L} = 0.100\ mol$

$n(e^-) = n(Ag^+) = 0.100\ mol$

The Faraday constant F is the (numeric) electric charge of 1 mole of electrons.

$Q = n(e^-)\,F = 0.100\ mol \times 96485\ C\ mol^{-1} = 9649\ C$

d. x designates the resultant $[Ag^+]$

the left-hand electrode is unchanged, *i.e.* $[Zn^{2+}]$ remains 0.200 M

$$1.04\ V = 1.56\ V - \frac{0.05916\ V}{2} \log \frac{0.200}{x^2}$$

$x = 7.3 \times 10^{-10}\ \text{M}$

e. [Cl$^-$] = amount added per volume – amount in AgCl precipitate per volume

= 0.300 M – (0.100 M – 7.3 × 10^{-10} M) = 0.200 M

K_{sp} (AgCl) = [Ag$^+$] [Cl$^-$] = 7.3 × 10^{-10} M × 0.200 M = 1.5 × 10^{-10} M^2

9 Cyanide in Waste

a. $Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2\ OH^-(aq)$

$K_{sp} = [Cd^{2+}][OH^-]^2 = s\ (2s)^2 = 4\ s^3 = 5.9 \times 10^{-15}\ M^3$

$s = 1.14 \times 10^{-5}\ M$

b. $K_{sp} = s(s + 0.010)^2$; $s < 1.14 \times 10^{-5}\ M$; $s << 0.010\ M$

$s(0.010)^2 = 5.9 \times 10^{-15}\ M^3$; $s = 5.9 \times 10^{-11}\ M$

c. $s = 0.5\ [OH^-] = c(Cd)$

$c(Cd) = [Cd^{2+}] + [Cd(CN)^+] + [Cd(CN)_2] + [Cd(CN)_3^-] + [Cd(CN)_4^{2-}]$

$0.5\ [OH^-] = [Cd^{2+}](1 + K_1\ [CN^-] + \beta_2[CN^-]^2 + \beta_3[CN^-]^3 + \beta_4[CN^-]^4\ )$

$0.5\ [OH^-] = \dfrac{K_{sp}}{[OH^-]^2}\ (1 + K_1\ [CN^-] + \beta_2[CN^-]^2 + \beta_3[CN^-]^3 + \beta_4[CN^-]^4\ )$

$[OH^-] = \sqrt[3]{2 \times K_{sp}(1 + K_1[CN^-] + \beta_2[CN^-]^2 + \beta_3[CN^-]^3 + \beta_4[CN^-]^4)}$

$[OH^-] = \sqrt[3]{2 \times K_{sp}(1 + K_1[CN^-] + K_1K_2[CN^-]^2 + K_1K_2K_3[CN^-]^3 + K_1K_2K_3K_4[CN^-]^4)}$

$[OH^-] = \sqrt[3]{2 \times 5.9 \times 10^{-15}(1 + 3.02 \times 10^2 + 3.99 \times 10^4 + 1.70 \times 10^6 + 7.59 \times 10^6)}\ M$

$[OH^-] = \sqrt[3]{2 \times 5.9 \times 10^{-15} \times 9.32 \times 10^6}\ M = 4.79 \times 10^{-3}\ M$

$s = 2.4 \times 10^{-3}\ M$

d. $[OH^-] = \sqrt[3]{2 \times 5.9 \times 10^{-15}(1 + K_1K_2K_3K_4[CN^-]^4)}$

$[OH^-] = 4.47 \times 10^{-3}\ M$

$s = 2.24 \times 10^{-3}\ M$

Percentage deviation: $\dfrac{(2.40 - 2.24) \times 10^{-3}}{2.40 \times 10^{-3}} \times 100\% = 6.7\ \%$

10 Age of Greenland Rock

a. The gain in ^{206}Pb must equal the loss in ^{238}U, thus

$n_t(^{206}Pb) - n_0(^{206}Pb) = n_0(^{238}U) - n_t(^{238}U)$

Since $n_t(^{238}U) = n_0(^{238}U)e^{-kt}$ and substituting for $n_0(^{238}U)$ we obtain

$n_t(^{206}Pb) = n_t(^{238}U)(e^{kt} - 1) + n_0(^{206}Pb)$

b. From the above equation,

$$\{n_t(^{206}Pb)/n(^{204}Pb)\} = \{n_t(^{238}U)/n(^{204}Pb)\}(e^{kt} - 1) + \{n_0(^{206}Pb)/n(^{204}Pb)\}$$

relating $n_t(^{206}Pb)/n(^{204}Pb)$ as a linear function of $n_t(^{238}U)/n(^{204}Pb)$. From the data, least-squares fitting yields a slope of $0.769 = e^{kt} - 1$, which with

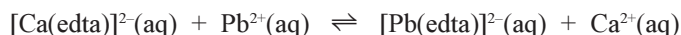$k = \ln 2/(4.468\ \text{Ga}) = 1.551\ \text{Ga}^{-1}$ result in $t = 3.7$ Ga.

c. The y-axis intercept represents the $n_0(^{206}Pb)/n(^{204}Pb)$ ratio at the time of crystallization of the analysed minerals.

11 Lead Poisoning

a. 83 µg / (207.2 g mol^{-1} × 0.10 L) = 4.00 µM (M(Pb) = 207.2 g mol^{-1}).

b. It is relevant to consider the reaction

$$[Ca(edta)]^{2-}(aq) + Pb^{2+}(aq) \rightleftharpoons [Pb(edta)]^{2-}(aq) + Ca^{2+}(aq)$$

with equilibrium constant $K = K(Pb) / K(Ca) = 10^{7.3}$. Due to the strong complexation and excess of Ca^{2+} ion over total edta^{4-} ligand, essentially all ligand will be tied as the lead or calcium complexes. Since $[[Pb(edta)]^{2-}] \ll [[Ca(edta)]^{2-}]$, the real concentrations of Ca^{2+} and $[Ca(edta)]^{2-}$ ions would be very close to the formal concentrations, and the expression for K then gives

$[Pb(edta)^{2-}]/[Pb^{2+}] = K \times [Ca(edta)^{2-}]/[Ca^{2+}]$
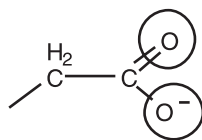
$= 10^{7.3} \times (1.0\ \text{mM} / 2.5\ \text{mM}) = 8.0 \times 10^6$.

c. The $[Pb(edta)]^{2-}$ complex concentration is 40 % of the original after 2 h. Thus, $0.4 = e^{-k \times 2\ h}$, yielding $k = 0.458$ h^{-1} and, consequently, $t_{1/2} = \ln 2 / 0.458$ h^{-1} = 1.5 h.

12 Nickel Enzyme

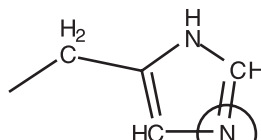**a.** $$H_2NCOO^-(aq) + H_2O(l) \rightarrow NH_3(aq) + HCO_3^-(aq)$$

b.

Aspartate   Histidine

c.

d. $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$.

e.   Upper energy level: d_{z^2} and $d_{x^2-y^2}$. Lower energy level: d_{xy}, d_{xz} and d_{yz}.
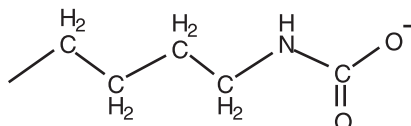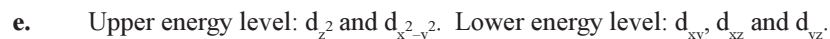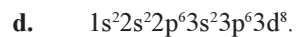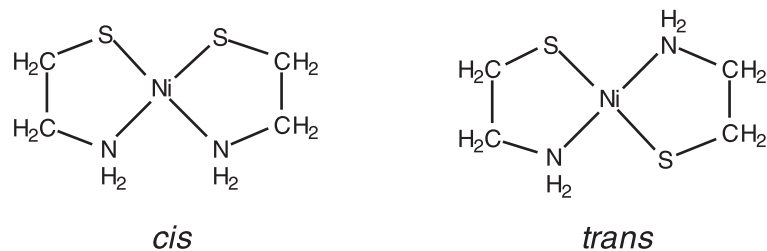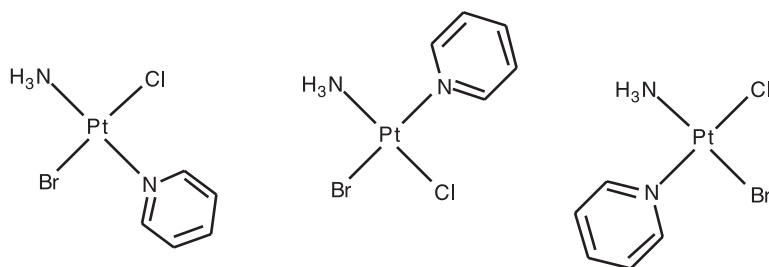
In an octahedral ligand field the mutually orthogonal y, x and z axes (origin at the metal centre) are oriented such that the six ligating atoms each fall on these axes. Thus, the electrons of the ligating atoms generate an arrangement of negative charge around the metal atom. This arrangement affects the different d orbitals differently. The d_{xy}, d_{xz} and d_{yz} orbitals all have their electron density concentrated mainly in areas between the charges of the ligands whereas, by comparison, the d_{z^2} and $d_{x^2-y^2}$ orbitals have their electron density concentrated in areas closer to the ligand charges. Qualitatively, this repulsive interaction raises the energy of the d_{z^2} and $d_{x^2-y^2}$ orbitals compared with that of the d_{xy}, d_{xz} and d_{yz} orbitals.
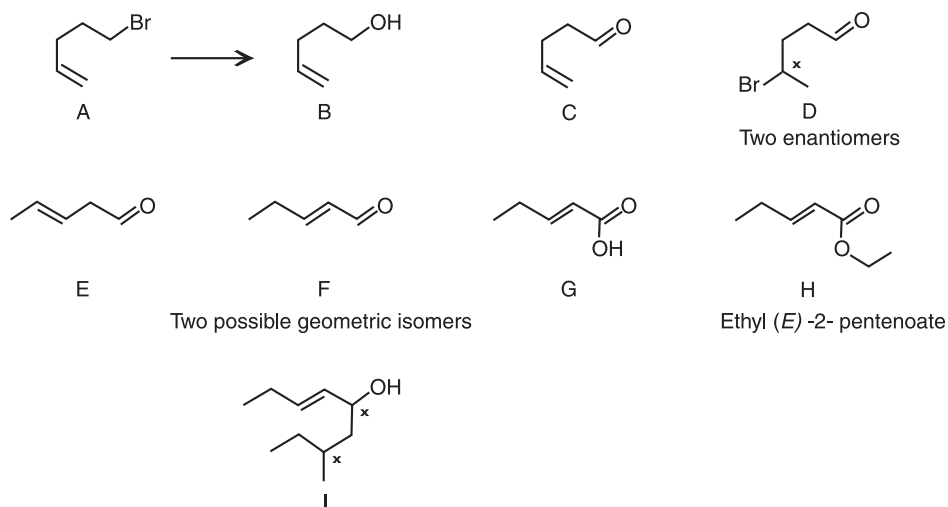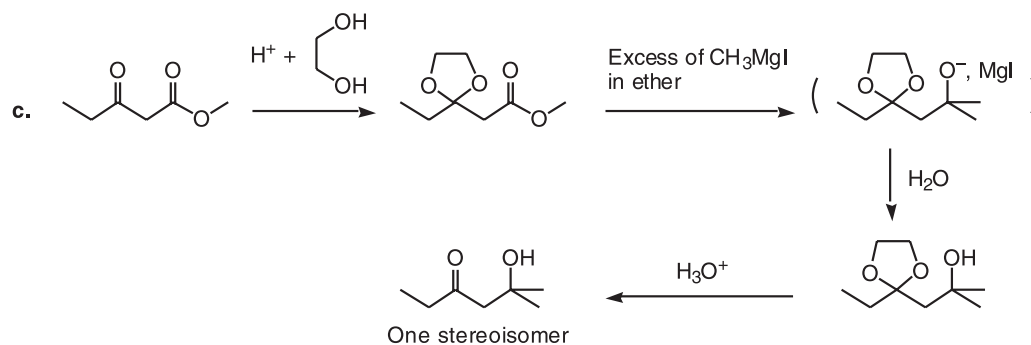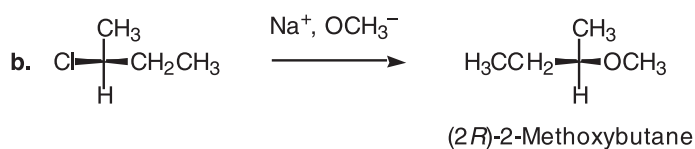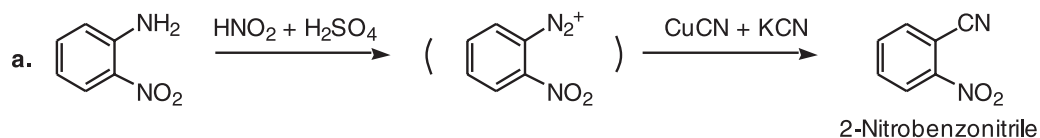
f.

cis   *trans*

g.

13 Killer Thistle for use in Medical Treatment ?

A   B   C   D
Two enantiomers

E   F   G   H
Two possible geometric isomers   Ethyl (*E*)-2- pentenoate

I

I   Four isolated stereiosomers
II   The diastereomeric pair is formed in unequal amounts
  The enantiomeric pairs are formed in equal amounts
  i.e. Box No. 2
III   The diastereomeric pair have different melting points
  The enantiomeric pairs have identical melting points
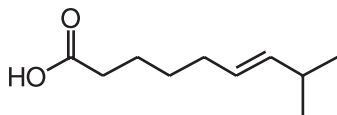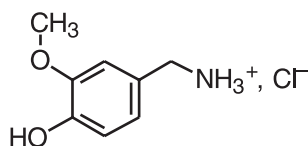 i.e. Box No. 3

14 Application of Organic Synthesis

a.   HNO$_2$ + H$_2$SO$_4$ CuCN + KCN   2-Nitrobenzonitrile

b.   Na$^+$, OCH$_3^-$ (2*R*)-2-Methoxybutane

c.   H$^+$ +   Excess of CH$_3$MgI in ether   O$^-$, MgI

  H$_2$O

  H$_3$O$^+$

One stereoisomer

15 Cayenne

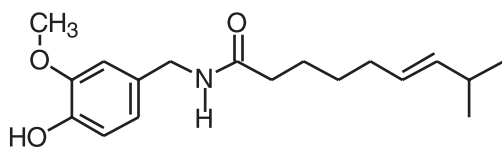**a.** $C_{18}H_{27}NO_3$

b.


c.

d.

e. Two isomers of A exist.

16 An Organic Compound

a. The isotopic pattern at $m/Z = 234$, 236 and 238 mass units with relative intensities 25:50:25% corresponds to 2 bromine atoms (in bromine ^{79}Br and ^{81}Br have almost the same occurrence).

b. Since only carbon and hydrogen are present besides bromine, the molecular formula must be $C_6H_4Br_2$. The possible isomers are *ortho*-, *meta*- and *para*-dibromobenzene.
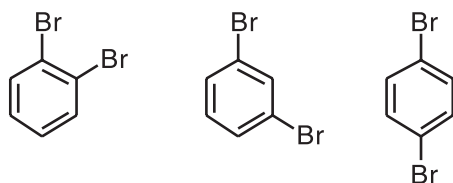
**c.** 155 and 157 correspond to the monobromobenzene cation: $C_6H_4Br^+$, and 76 is the $C_6H_4^+$ ion.

d. Because the intensity ratios are 1:2:1 and the masses only differ by one unit. A fragment with a single charge corresponding to half of the molecule would have given two peaks of equal intensity at 117 and 119 mass units.

e. The ^1H NMR spectrum consists of two signals. The compound must be the *ortho*-isomer, since this has two kinds of hydrogen atoms. The *meta*- and *para*-isomers would have given 3 signals and 1 signal, respectively.

f. Since the *ortho* compound contains 3 kinds of carbon atoms, 3 signals are expected.

17 Heather

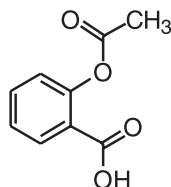**a.** The derivative is the methyl ester:
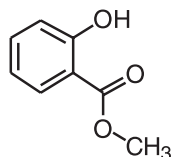
b. Because of a change in the strength of the intramolecular bond.

c. The molar absorptivity is calculated from:

$$\log \frac{100}{50} = \frac{\varepsilon \times 1 \times 4.9 \times 10^{-3}}{152}$$

The result is 9338 M^{-1} cm^{-1}

d. The compound is:

Acetylsalicylic acid

18 DNA – the PCR-method

a. $2^{30} - 1$ copies = 1073741823 copies

b. $2^{60} - 1$ copies = 1.15×10^{18} copies

dNTP average molar mass = 483 g mol^{-1}; $M(HP_2O_7^{3-})$ = 175 g mol^{-1};

M (1000 bp double-stranded DNA) = $((483 - 175) \times 2 \times 1000 + 2 \times 175)$g mol^{-1}

= 616350 g mol^{-1}

Total mass of DNA:

m(DNA) = $1.15 \times 10^{18}/N_A \times 616350$ g = 1.18 g

c. No, since the [γ-^{32}P] will be lost with the pyrophosphate in the polymerase reaction.

d. $k = \dfrac{\ln 2}{t_{1/2}}$; $k = \dfrac{0.693}{14.2 \text{ d}} = 0.0488 \text{ d}^{-1}$

$A = A_0 e^{-kt}$

$A = 1 \text{ }\mu\text{Ci/pmol} \times e^{-0.0488 \cdot 92} = 0.011 \text{ }\mu\text{Ci/pmol}$

1 μCi = 3.7×10^4 Bq = 2.22×10^6 dpm (decays per min)

0.011 μCi/pmol = 24420 dpm/pmol

## 19   Proteins, UV spectra and light absorption

a. $\varepsilon_{\text{Tryptophan}} \approx 5600 \text{ M}^{-1}\text{cm}^{-1};\ \varepsilon_{\text{Tyrosine}} \approx 1400 \text{ M}^{-1} \text{cm}^{-1}$

$\varepsilon_{\text{Lysozyme}} \approx (6 \times 5600 + 3 \times 1400) \text{ M}^{-1}\text{cm}^{-1} \approx 37800 \text{ M}^{-1} \text{cm}^{-1}$

b. $c = \dfrac{A}{\varepsilon \times l} = \dfrac{1.05}{37800 \text{ M}^{-1} \text{ cm}^{-1} \times 1\text{cm}} = 27.8\ \mu\text{M}$

c. $c_{\text{mass}} = 14313 \text{g/mol} \times 27.8\ \mu\text{M} = 0.398 \text{ g/L}$

d. $1 \text{ g/L} = \dfrac{1}{14313} \text{ M} = 69.8\ \mu\text{M}$
$A = 37800 \text{ M}^{-1} \text{cm}^{-1} \times 69.8\ \mu\text{M} \times 1 \text{ cm} = 2.64$

Amino acid frequency in lysozyme: tryptophan: 4.65%; tyrosine: 2.33%

$\varepsilon_{\text{100 amino acids in lysozyme}} = (4.65 \times 5600 + 2.33 \times 1400) \text{ M}^{-1} \text{cm}^{-1} = 29302 \text{ M}^{-1} \text{cm}^{-1}$

$\varepsilon_{\text{100 amino acids in average protein}} = (1.3 \times 5600 + 3.4 \times 1400) \text{ M}^{-1} \text{cm}^{-1} = 12040 \text{ M}^{-1} \text{cm}^{-1}$

$A_{\text{1 g/L average protein}} = 2.64\ \dfrac{12040 \text{ M}^{-1} \text{cm}^{-1}}{29302 \text{ M}^{-1} \text{cm}^{-1}} = 1.08$

e. $\varepsilon_{\text{unknown protein}} = (2 \times 5600 + 11 \times 1400) \text{ M}^{-1} \text{cm}^{-1} = 26600 \text{ M}^{-1} \text{cm}^{-1}$

$A_{\text{0,24 g/L lysozyme}} = 0.24 \times 2.64 = 0.63$

$A_{\text{unknown protein}} = 1.85 - 0.63 = 1.22$

$c_{\text{unknown protein}} = \dfrac{1.22}{26600 \text{ M}^{-1} \text{cm}^{-1} \times 1\text{cm}} = 45.9\ \mu\text{M}$
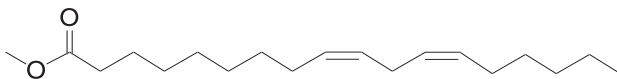
20   Sunflower Oil

a.   The molecules of constituent **S** exist as two enantiomers.
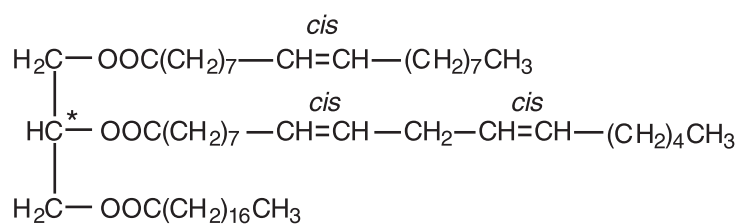
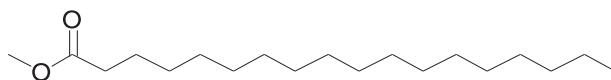**b.**   The structures and names of the methyl esters are
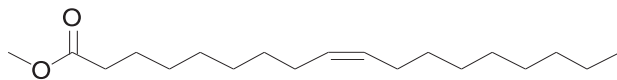
(Z)-methyl octadec-9-enoate   or
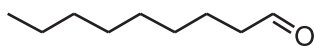(Z)-octadec-9-enoic acid methyl ester

(9Z, 12Z)-methyl octadec-9,12-dienoate   or
(9Z, 12Z)-octadec-9,12-dienoic acid methyl ester

methyl octadecanoate   or
octadecanoic acid methyl ester

c.   Ozonolysis of **S** followed by treatment of zinc gives the following aldehydes
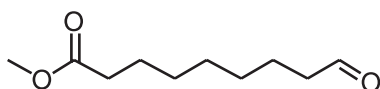

nonal

hexanal   methane dicarbaldehyde

methyl nonalate or
nonanaloic acid methyl ester

d.   The amount of used potassium hydroxide is 3 times the amount of the triacylglycerol **S** (a triglyceride).

$n(\mathbf{S}) = 10.0$ g/885.402 g mol^{-1} = 11.29 mmol

$V(\text{KOH}) = 3 \times n/c = 3 \times 11.29$ mmol/0.996 M = 34.0 mL

e.   SapVal = 3.40 mmol/g $\times$ 56.11 g mol^{-1} = 191

f.   112.9 mmol **S** contains 3×112.9 mmol C = C double bonds.

$m(\text{I}_2) = 0.3388$ mol $\times$ 253.8 g mol^{-1} = 85.98 g; Iodine no. = 86

21 Experimental   Preparation of Hydrobenzoin

a. For example:

$$
\begin{array}{ccc}
\text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 \\
\text{H}\!-\!\text{OH} & \text{H}\!-\!\text{OH} & \text{HO}\!-\!\text{H} \\
\text{H}\!-\!\text{OH} & \text{HO}\!-\!\text{H} & \text{H}\!-\!\text{OH} \\
\text{C}_6\text{H}_5 & \text{C}_6\text{H}_5 & \text{C}_6\text{H}_5
\end{array}
$$

or ... or

b.

$$
\text{H}\!-\!\overset{\displaystyle \text{H}}{\underset{\displaystyle \text{H}}{\overset{|}{\underset{|}{\text{B}}}}}\!-\!\text{H} \quad \text{Na}^+
$$
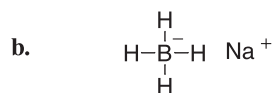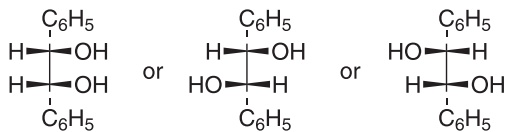
c. 1,2-Dihydroxy-1,2-diphenylethane

d II. Theoretical yield from 100 mg of benzil is 102 mg.

f. 3

g. 2

h. Pour it slowly into diluted hydrochloric acid then into the container for inorganic chemical waste.