1. (a) HNO₃ is a very strong acid so the NO₃⁻(aq) ion is not basic. A solution of KNO₃ contains K⁺(aq) and NO₃⁻(aq) ions and is neutral.

(b) FeCl₃ dissolves to give Fe³⁺(aq) and 3Cl⁻(aq) ions. The small and high charged Fe³⁺ ion is surrounded by six water molecules in aqueous solution and acts as a weak acid because of the equilibrium:

\[ \text{[Fe(H}_2\text{O)}₆]³⁺(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{[Fe(H}_2\text{O)}₅(\text{OH})]²⁺(aq) + \text{H}_3\text{O}⁺(l) \]

The Cl⁻ ion, the anion of a strong acid HCl, does not react and stays in solution as Cl⁻(aq). The solution is therefore acidic.

(b) Ca(OH)₂ is a strong base and dissolves to give Ca²⁺(aq) and OH⁻(aq) ions. A solution of Ca(OH)₂ is thus basic.

(c) (NH₄)₂SO₄ dissolves to give SO₄²⁻(aq), the anion of a strong acid, H₂SO₄, and NH₄⁺, the cation of a weak base, NH₃. SO₄²⁻(aq) does not react but NH₄⁺ is a weak acid and the solution is acidic because of the equilibrium:

\[ \text{NH}_4⁺(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}⁺(l) \]

(e) NaN₃ dissolves to give Na⁺(aq) and N₃⁻(aq), the anion of a weak acid. This anion is thus a weak base and the solution is basic because of the equilibrium:

\[ \text{N}_3⁻(aq) + \text{H}_2\text{O(l)} \rightleftharpoons \text{HN}_3(aq) + \text{OH}⁻(aq) \]

(f) BaCl₂ dissolves to give Ba²⁺(aq) and 2Cl⁻(aq) ions. HCl is a very strong acid so the Cl⁻(aq) ion is not basic. The Ba²⁺ ion is large and is not acidic.

2. The solubility equilibrium is:

\[ \text{Ca}_3(\text{PO}_4)₂(s) \rightleftharpoons 3\text{Ca}²⁺(aq) + 2\text{PO}_4³⁻(aq) \]

for which the solubility product is:

\[ K_{sp} = [\text{Ca}²⁺(aq)]³[\text{PO}_4³⁻(aq)]² \]

(a) If the molar solubility is equal to \( S \) then, from the equilibrium equation, \([\text{Ca}²⁺(aq)] = 3S\) and \([\text{PO}_4³⁻(aq)] = 2S\) and the solubility product becomes:

\[ K_{sp} = [\text{Ca}²⁺(aq)]³[\text{PO}_4³⁻(aq)]² = (3S)³ × (2S)² = 108S⁵ = 1.3 \times 10^{-32} \]

molar solubility = \( S = 1.6 \times 10^{-7} \) M

The molar mass of Ca₃(PO₄)₂ is:
Therefore, the solubility in g L^{-1} is:

\[
\text{solubility} = \text{molar solubility} \times \text{formula mass} = (1.6 \times 10^{-7} \text{ mol L}^{-1}) \times (310.18 \text{ g mol}^{-1}) = 5.0 \times 10^{-3} \text{ g L}^{-1}
\]

(b) \( \text{Na}_3\text{PO}_4 \) dissolves completely to give \([\text{PO}_4^{3-}(aq)] = 0.20 \text{ M} \). The amount of \( \text{PO}_4^{3-}(aq) \) from \( \text{Ca}_3(\text{PO}_4)_2 \) is tiny in comparison to that from \( \text{Na}_3\text{PO}_4 \). Denoting the molar solubility by \( S \) again, \( K_{sp} \) is, as above:

\[
K_{sp} = [\text{Ca}^{2+}(aq)]^3[\text{PO}_4^{3-}(aq)]^2 = (3S)^3 \times ([\text{PO}_4^{3-}(aq)])^2
\]

\[
27S^3 \times (0.20)^2 = 1.3 \times 10^{-32} \text{ so molar solubility} = S = 2.3 \times 10^{-11} \text{ M}
\]

3. The solubility equilibrium for \( \text{Ag}_2\text{SO}_4(s) \) is:

\[
\text{Ag}_2\text{SO}_4(s) \rightleftharpoons 2\text{Ag}^+(aq) + \text{SO}_4^{2-}(aq)
\]

for which the solubility product is:

\[
K_{sp} = [\text{Ag}^+(aq)]^2[\text{SO}_4^{2-}(aq)] = 2 \times 10^{-5}
\]

As \([\text{Ag}^+] = 0.01 \text{ M} \text{ and } [\text{SO}_4^{2-}(aq)] = 0.01 \text{ M} \) before mixing and equal volumes are mixed, the concentrations will halve: \([\text{Ag}^+] = 0.005 \text{ M} \text{ and } [\text{SO}_4^{2-}(aq)] = 0.005 \text{ M} \) the reaction quotient or ionic product is:

\[
Q_{sp} = (0.005)^2 \times (0.005) = 1 \times 10^{-7}
\]

As \( Q_{sp} < K_{sp} \), the equilibrium will proceed to the right and the solid will dissolve – no precipitate will form.

4. (a) \( \text{KMnO}_4 \quad \text{K}^+ \text{ Mn}^{7+} \text{ 4O}^{2-} \quad \text{Mn is +7} \)

(b) \( \text{SO}_4^{2-} \quad \text{S}^{6+} \text{ 4O}^{2-} \quad \text{S is +6} \)

(c) \( \text{Na}_2\text{O}_2 \quad 2\text{Na}^+ \text{ 2O}^- \quad \text{O is -1 (oxygen in a peroxide)} \)

(d) \( \text{MgH}_2 \quad \text{Mg}^{2+} \text{ 2H}^- \quad \text{H is -1 (hydrogen as a hydride with a metal)} \)

(e) \( \text{NH}_4^+ \quad \text{N}^3- \text{ 4H}^+ \quad \text{H is +1 (hydrogen in combination with a non-metal)} \)

(f) \( \text{BrF}_3 \quad \text{Br}^{3+} \text{ 3F}^- \quad \text{Br is +3} \)

(g) \( [\text{Ni(NH}_3)_6]^{2+} \quad \text{Ni}^{2+} \text{ 6NH}_3 \quad \text{Ni is +2 (ammonia is a neutral ligand)} \)

(h) \( \text{K}_4[\text{Fe(CN)}_6] \quad 4\text{K}^+ \text{ Fe}^{2+} \text{ 6CN}^- \quad \text{Fe is +2 (cyanide is an anionic ligand)} \)

5. \( K_{stab} \) refers to the equilibrium:
\[ \text{Zn}^{2+}(aq) + 4\text{NH}_3(aq) \rightleftharpoons [\text{Zn(NH}_3)_4]^{2+}(aq) \]

As \( K_{\text{stab}} = 8 \times 10^8 \) and is very large, the reaction essentially goes to completion. The reaction requires a 4:1 ratio \( \text{NH}_3 : \text{Zn}^{2+}(aq) \) ions and as 3.0 mol of \( \text{NH}_3 \) and 0.10 mol of \( \text{Zn}^{2+}(aq) \) is present, \( \text{NH}_3 \) is in excess.

Let the tiny amount of \( \text{Zn}^{2+}(aq) \) and its concentration in 1.5 L after complexation be:

amount of \( \text{Zn}^{2+}(aq) = x \) mol and

\[
[Zn^{2+}(aq)] = \frac{\text{number of moles}}{\text{volume}} = \frac{x}{1.5} \text{ M}
\]

The amount of \([\text{Zn(NH}_3)_4]^{2+}(aq)\) formed is therefore:

amount of \([\text{Zn(NH}_3)_4]^{2+}(aq) = (0.10 - x) \) mol

As \( x \) is so small, this amount and hence the concentration can be approximated as:

amount of \([\text{Zn(NH}_3)_4]^{2+}(aq) = (0.10 - x) \sim 0.10 \text{ mol}

\[
[[\text{Zn(NH}_3)_4]^{2+}(aq)] \sim \frac{0.10}{1.5} \text{ M}
\]

Formation of 0.10 mol of \([\text{Zn(NH}_3)_4]^{2+}(aq)\) requires 0.40 mol of ammonia, leaving:

amount of \( \text{NH}_3 = (3.0 - 4 \times 0.10) = 2.6 \) mol and

\[
[\text{NH}_3(aq)] = \frac{2.6}{1.5} \text{ M}
\]

Hence,

\[
K_{\text{stab}} = \frac{[[\text{Zn(NH}_3)_4]^{2+}(aq)]}{[\text{Zn}^{2+}(aq)][\text{NH}_3(aq)]^4} = \frac{0.10}{x (\frac{2.6}{1.5})^4} = 8 \times 10^8
\]

\( x = 1.4 \times 10^{-11} \text{ mol and } [\text{Zn}^{2+}(aq)] = 9.2 \times 10^{-12} \text{ M} \)

6. (a) 100 mL of blood contains 15.0 g of haemoglobin corresponding to:

number of moles of haemoglobin = \frac{\text{mass}}{\text{molar mass}} = \frac{15.0 \text{ g}}{6.45 \times 10^4 \text{ g mol}^{-1}}

= 2.33 \times 10^{-4} \text{ mol}

As each haemoglobin can bind 4 molecules of \( \text{O}_2 \):
number of moles of O₂ = 4 × 2.33 × 10⁻⁴ mol = 9.30 × 10⁻⁴ mol

As 101.3 kPa = 1 atm, using the ideal gas equation, \( PV = nRT \), at 311 K and 101.3 kPa, this will occupy a volume of:

\[
V = \frac{nRT}{P} = \frac{(9.30 \times 10^{-4} \text{ mol}) \times (0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}) \times (311 \text{ K})}{1 \text{ atm}} = 0.0237 \text{ L}
\]

(b) 1 kg of haemoglobin corresponds to:

\[
\text{number of moles of haemoglobin} = \frac{1000 \text{ g}}{6.45 \times 10^4 \text{ g mol}^{-1}} = 0.0155 \text{ mol}
\]

3.4 g of iron corresponds to:

\[
\text{number of moles of iron} = \frac{\text{mass}}{\text{atomic mass}} = \frac{3.4 \text{ g}}{55.85 \text{ g mol}^{-1}} = 0.061 \text{ mol}
\]

Therefore, the number of iron atoms per haemoglobin is \( \frac{0.061}{0.0155} = 4\). Each iron atom binds one O₂ molecule.

(c) Fe is in Group 8 so has 8 valence electrons with a configuration \([\text{Ar}]4s^23d^6\). Possible oxidation states include Fe⁺, Fe²⁺, Fe³⁺, Fe⁴⁺ and Fe⁶⁺. As the 4s electrons are lost first, these oxidation states correspond to the following electron arrangements:

<table>
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<tr>
<th>4s</th>
<th>3d</th>
<th>number of unpaired electrons</th>
</tr>
</thead>
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<td>(\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
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</tr>
<tr>
<td>(\uparrow)</td>
<td>(\uparrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
<td>5</td>
</tr>
<tr>
<td>(\uparrow\uparrow\downarrow)</td>
<td>(\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
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<tr>
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</tr>
<tr>
<td>(\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
<td>(\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
<td>4</td>
</tr>
<tr>
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<td>(\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow)</td>
<td>2</td>
</tr>
</tbody>
</table>

The magnetic studies are consistent with an Fe²⁺ or an Fe⁴⁺ being present. Fe²⁺ is much more common and it is this oxidation state which is actually present in haemoglobin.