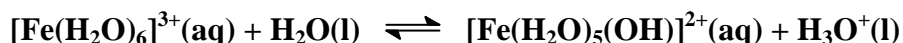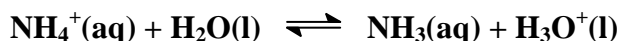1. (a) **HNO$_3$ is a very strong acid so the NO$_3^-$(aq) ion is not basic. A solution of KNO$_3$ contains K$^+$(aq) and NO$_3^-$(aq) ions and is neutral.**

   (b) **FeCl$_3$ dissolves to give Fe^{3+}(aq) and 3Cl$^-$(aq) ions. The small and high charged Fe^{3+} ion is surrounded by six water molecules in aqueous solution and acts as a weak acid because of the equilibrium:**

   $$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(l)$$

   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.

   (c) **Ca(OH)$_2$ is a strong base and dissolves to give Ca^{2+}(aq) and OH$^-$(aq) ions. A solution of Ca(OH)$_2$ is thus basic.**

   (d) **(NH$_4$)$_2$SO$_4$ dissolves to give SO$_4^{2-}$(aq), the anion of a strong acid, H$_2$SO$_4$, and NH$_4^+$, the cation of a weak base, NH$_3$. SO$_4^{2-}$(aq) does not react but NH$_4^+$ is a weak acid and the solution is acidic because of the equilibrium:**

   $$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(l)$$

   (e) **NaN$_3$ dissolves to give Na$^+$(aq) and N$_3^-$(aq), the anion of a weak acid. This anion is thus a weak base and the solution is basic because of the equilibrium:**

   $$N_3^-(aq) + H_2O(l) \rightleftharpoons HN_3(aq) + OH^-(aq)$$
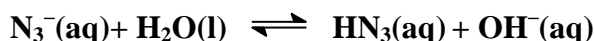
   (f) **BaCl$_2$ dissolves to give Ba^{2+}(aq) and 2Cl$^-$(aq) ions. HCl is a very strong acid so the Cl$^-$(aq) ion is not basic. The Ba^{2+} ion is large and is not acidic.**

2. **The solubility equilibrium is:**

   $$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

   for which the solubility product is:

   $$K_{sp} = [Ca^{2+}(aq)]^3[PO_4^{2-}(aq)]^2$$

   (a) **If the molar solubility is equal to S then, from the equilibrium equation, [Ca^{2+}(aq)] = 3S and [PO$_4^{3-}$(aq)] = 2S and the solubility product becomes:**

   $$K_{sp} = [Ca^{2+}(aq)]^3[PO_4^{3-}(aq)]^2 = (3S)^3 \times (2S)^2 = 108S^5 = 1.3 \times 10^{-32}$$

   molar solubility = S = 1.6 × 10^{-7} M

   The molar mass of Ca$_3$(PO$_4$)$_2$ is:

$$(3 \times 40.08 \text{ (Ca)}) + 2 \times (30.97 \text{ (P)} + 4 \times 16.00 \text{ (O)})) \text{ g mol}^{-1} = 310.18 \text{ g mol}^{-1}$$

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) Na_3PO_4 dissolves completely to give $[PO_4^{3-}\text{(aq)}] = 0.20$ M. The amount of $PO_4^{3-}\text{(aq)}$ from $Ca_3(PO_4)_2$ is tiny in comparison to that from Na_3PO_4. Denoting the molar solubility by S again, K_{sp} is, as above:

$$K_{sp} = [Ca^{2+}\text{(aq)}]^3[PO_4^{3-}\text{(aq)}]^2 = (3S)^3 \times ([PO_4^{2-}\text{(aq)}])^2$$

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

3.   The solubility equilibrium for $Ag_2SO_4\text{(s)}$ is:

$$Ag_2SO_4\text{(s)}) \rightleftharpoons 2Ag^{+}\text{(aq)} + SO_4^{2-}\text{(aq)}$$

for which the solubility product is:

$$K_{sp} = [Ag^{+}\text{(aq)}]^2[SO_4^{2-}\text{(aq)}] = 2 \times 10^{-5}$$

As $[Ag^{+}] = 0.01$ M and $[SO_4^{2-}\text{(aq)}] = 0.01$ M before mixing and equal volumes are mixed, the concentrations will halve: $[Ag^{+}] = 0.005$ M and $[SO_4^{2-}\text{(aq)}] = 0.005$ 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) K$\underline{\text{Mn}}$O$_4$ $K^{+} Mn^{7+} 4O^{2-}$ Mn is +7

(b) $\underline{\text{S}}O_4^{2-}$ $S^{6+} 4O^{2-}$ S is +6

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

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

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

(f) $\underline{\text{Br}}F_3$ $Br^{3+} 3F^{-}$ Br is +3

(g) [$\underline{\text{Ni}}$(NH$_3$)$_6$]$^{2+}$ $Ni^{2+} 6NH_3$ Ni is +2 (ammonia is a neutral ligand)

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

5. K_{stab} refers to the equilibrium:

$$Zn^{2+}\text{(aq)} + 4NH_3\text{(aq)} \rightleftharpoons [Zn(NH_3)_4]^{2+}\text{(aq)}$$
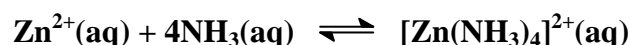
As $K_{stab} = 8 \times 10^8$ and is *very* large, the reaction essentially goes to completion. The reaction requires a 4:1 ratio $NH_3 : Zn^{2+}(aq)$ ions and as 3.0 mol of NH_3 and 0.10 mol of $Zn^{2+}(aq)$ is present, NH_3 is in excess.

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

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

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

The amount of $[Zn(NH_3)_4]^{2+}(aq)$ formed is therefore:

amount of $[Zn(NH_3)_4]^{2+}(aq) = (0.10 - x)$ mol

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

amount of $[Zn(NH_3)_4]^{2+}(aq) = (0.10 - x) \sim 0.10$ mol

$$[[Zn(NH_3)_4]^{2+}(aq)] \sim \frac{0.10}{1.5} \text{ M}$$

Formation of 0.10 mol of $[Zn(NH_3)_4]^{2+}(aq)$ requires 0.40 mol of ammonia, leaving:

amount of $NH_3 = (3.0 - 4 \times 0.10) = 2.6$ mol and

$$[NH_3(aq)] = \frac{2.6}{1.5} \text{ M}$$

Hence,

$$K_{stab} = \frac{[[Zn(NH_3)_4]^{2+}(aq)]}{[Zn^{2+}(aq)][NH_3(aq)]^4} = \frac{(\frac{0.10}{1.5})}{(\frac{x}{1.5})(\frac{2.6}{1.5})^4} = 8 \times 10^8$$

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

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

$$\text{number of moles of haemoglobin} = \frac{\text{mass}}{\text{molar mass}} = \frac{15.0\,\text{g}}{6.45 \times 10^4\,\text{g mol}^{-1}}$$
$$= 2.33 \times 10^{-4} \text{ mol}$$

As each haemoglobin can bind 4 molecules of O_2:

number of moles of $O_2 = 4 \times 2.33 \times 10^{-4}$ mol $= 9.30 \times 10^{-4}$ 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 $= \dfrac{0.061}{0.0155} = 4$

Each iron atom binds one O_2 molecule.

(c)   **Fe is in Group 8 so has 8 valence electrons with a configuration $[Ar]4s^2 3d^6$. Possible oxidation states include Fe^+, Fe^{2+}, Fe^{3+}, Fe^{4+} and Fe^{6+}. As the 4s electrons are lost first, these oxidation states correspond to the following electron arrangments:**

	4s	3d					number of unpaired electrons
Fe	↑↓	↑↓	↑	↑	↑	↑	4
Fe^+	↑	↑↓	↑	↑	↑	↑	5
Fe^{2+}		↑↓	↑	↑	↑	↑	4
Fe^{3+}		↑	↑	↑	↑	↑	5
Fe^{4+}		↑	↑	↑	↑		4
Fe^{6+}		↑	↑				2

The magnetic studies are consistent with an Fe^{2+} or an Fe^{4+} being present. Fe^{2+} is much more common and it is this oxidation state which is actually present in haemoglobin.