Chemguide – answers

GROUP 4: OXIDATION STATE TRENDS

1. a) CH_4: -4 (apart from in metal hydrides, hydrogen always has an oxidation state of +1 in its compounds)
   CO: +2
   CO_2: +4

   b) CO_2. Both the methane and carbon monoxide burn to form CO_2 – an exothermic reaction. Carbon dioxide is therefore lower on an energy "ladder" than either of the other two, and therefore the most the thermodynamically stable.

   c) For the elements carbon, silicon and germanium, the +4 state is the most stable. At tin, the +4 state is more stable than the +2, but tin(II) compounds are quite common. At lead, the +2 oxidation state is the more stable, although +4 compounds do exist.

   d) $$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$$

   At its simplest, the carbon monoxide reduces the iron(III) oxide by removal of oxygen, and is itself oxidised to carbon dioxide by gain of oxygen.

   Or: The iron in the iron oxide is reduced from +3 oxidation state to zero while the carbon is oxidised from an oxidation state of +2 to +4.

2. a) The Sn^{2+} ions convert to Sn^{4+} ions because the tin(IV) oxidation state is more stable than tin(II). This means the loss of two more electrons from the tin(II) ions, and these have to be given to something else, which gains them. Gain of electrons is reduction, and so tin(II) ions are reducing agents.

   b) $$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

   c) $$5Sn^{2+} + 2MnO_4^- + 16H^+ \longrightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$$

   You have to be able to work this out from electron-half-equations:

   $$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$
   $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

   For the second equation to gain the same number of electrons that the first one is losing, multiply the first one by 2 and the second one by 5 (to get a transfer of 10 electrons), and then add them:

   $$5 \times \quad Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$
   $$2 \times \quad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

   $$5Sn^{2+} + 2MnO_4^- + 16H^+ \longrightarrow 5Sn^{4+} + 2Mn^{2+} + 8H_2O$$

d) Working in the same way as above, but this time working out the half-equations as well:

You know that the IO_3^- ions end up as I_2, so write that down:

$$IO_3^- \longrightarrow I_2$$

Now balance the atoms, starting with the iodines. It is done in the presence of hydrogen ions, so the oxygens will end up as water.

$$2IO_3^- + 12H^+ \longrightarrow I_2 + 6H_2O$$

Now balance the charges. You need to add 10 electrons to the left-hand side.

$$2IO_3^- + 12H^+ + 10e^- \longrightarrow I_2 + 6H_2O$$

The tin half-equation is

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$$

That will have to happen five times to provide the 10 electrons for the IO_3^- equation. Add them up, and you get:

$$2IO_3^- + 12H^+ + 5Sn^{2+} \longrightarrow 5Sn^{4+} + I_2 + 6H_2O$$

Is this tedious? Yes! Do you have to be able to do it? Yes!

If you had trouble with the MnO_4^- equation in part (c), try it again using this same technique, and if you still aren't happy look at http://www.chemguide.co.uk/inorganic/redox/equations.html and don't give up until you can do it.

3. a) The simplest cases involve the effect of heat on lead(IV) chloride or lead(IV) oxide both of which decompose to form the corresponding lead(II) compound:

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

$$PbO_2 \longrightarrow PbO + O_2$$

b) The inert pair effect is an increasing reluctance of the s^2 pair of electrons in the bonding level to become involved in bonding as you get towards the bottom of Group 4. In other words the s^2 electrons behave as an "inert pair". In the lead case, the 6p electrons do become involved in bonding, but the 6s electrons are more reluctant. That means that it is easier to form lead(II) compounds than lead(IV) ones, and so lead(II) is the major oxidation state.

In tin, the inert pair effect is weaker, and although it does show itself in tin(II) compounds, these are not as stable as tin(IV) compounds where all four outer electrons are involved in bonding.