LATTICE ENTHALPIES

1. a) Lattice dissociation enthalpy is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions.

   b) Lattice formation enthalpy is the enthalpy change when 1 mole of solid crystal is formed from its scattered gaseous ions.

2. a) Lattice dissociation enthalpy is a measure of the forces of attractions between the positive and negative ions. Bromide ions are bigger than chloride ions, and so the distance between the centres of the positive and negative ions in the lattice is greater in NaBr. Increasing distance weakens the forces of attraction between them, and hence the lattice enthalpy.

   b) There are two factors at work here.

   Magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the distance between the positive and negative ions is quite a lot less in MgO than in NaCl, and so the forces of attraction will be greater in MgO.

   But the main factor is the charge on the ions. In MgO, both positive and negative ions carry two charges. In NaCl, they only carry one. The strength of the attractions is much greater in MgO than in NaCl.

   (In fact, the strength of the attractions is proportional to the charges on the ions. If you double the charges on both positive and negative ions, the strength of the attractions will go up 4 times. The question says that the MgO lattice enthalpy is about 5 times greater than that of NaCl. The extra is due to the shorter distance between the ions in MgO.)

3. a) The standard atomisation enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state.

   b) $\frac{1}{2} Br_{2(l)} \longrightarrow Br_{(g)}$ $\Delta H^0_a = +112 \, kJ \, mol^{-1}$

      $Na_{(s)} \longrightarrow Na_{(g)}$ $\Delta H^0_a = +107 \, kJ \, mol^{-1}$
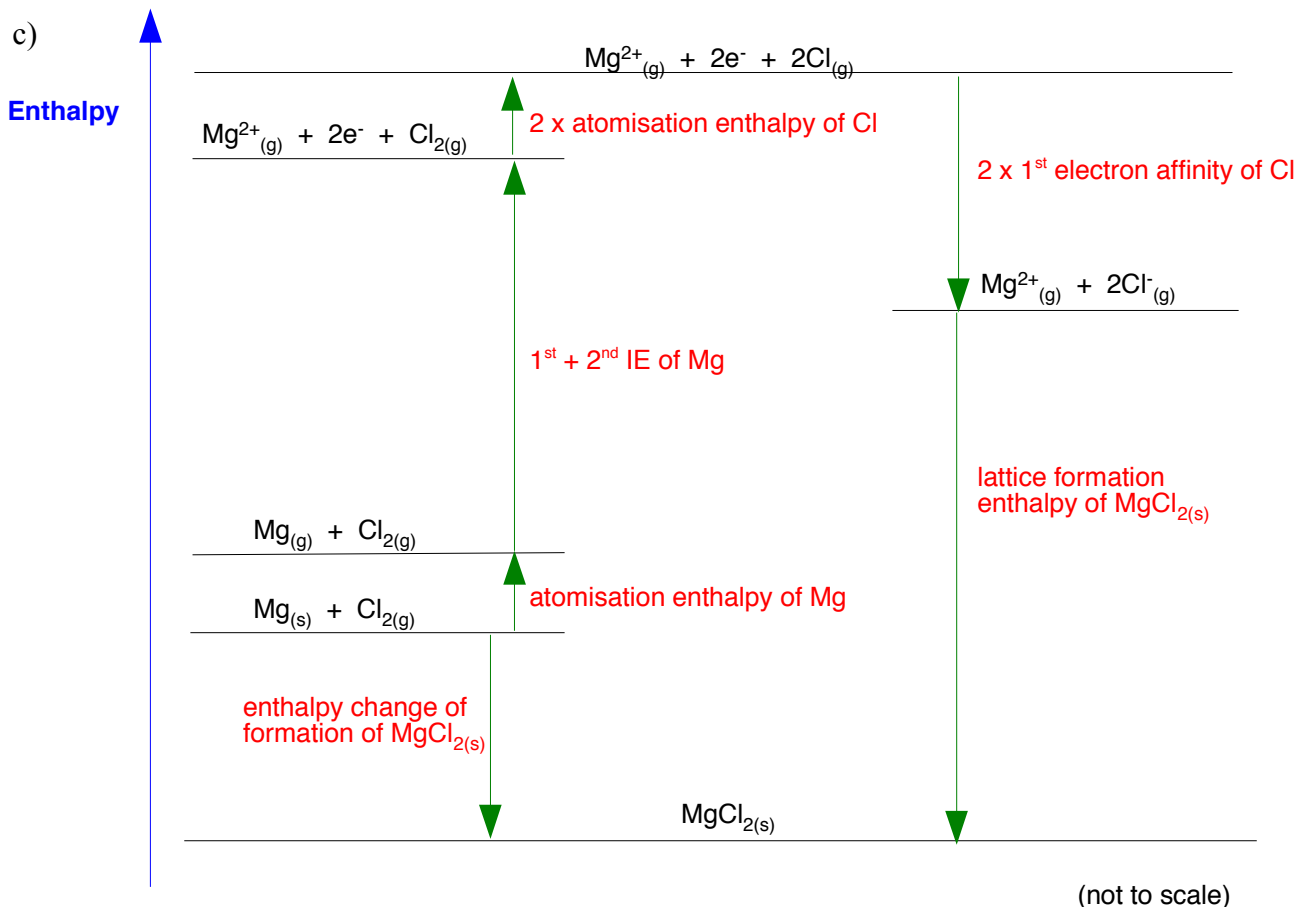
   (If you haven't got the state symbols written down, it is wrong. It is also wrong if you haven't ended up with just 1 mole of Br or Na.)

4. a)   +496 is the first ionisation energy of sodium.
         +122 is the atomisation enthalpy of chlorine.
         -349 is the first electron affinity of chlorine.
         -411 is the enthalpy change of formation of sodium chloride.

C h e m g u i d e – a n s w e r s

b) $-411 = +107 + 496 + 122 - 349 + LE$
      $LE = -787 \text{ kJ mol}^{-1}$

c)

Enthalpy

$Mg^{2+}_{(g)} + 2e^- + 2Cl_{(g)}$

2 x atomisation enthalpy of Cl

$Mg^{2+}_{(g)} + 2e^- + Cl_{2(g)}$

2 x 1st electron affinity of Cl

$Mg^{2+}_{(g)} + 2Cl^-_{(g)}$

1st + 2nd IE of Mg

lattice formation enthalpy of $MgCl_{2(s)}$

$Mg_{(g)} + Cl_{2(g)}$

$Mg_{(s)} + Cl_{2(g)}$

atomisation enthalpy of Mg

enthalpy change of formation of $MgCl_{2(s)}$

$MgCl_{2(s)}$

(not to scale)

(You could equally well have drawn two separate upward arrows for the first and second ionisation energies of magnesium. Check your diagram very carefully. Every single state symbol has to be correct.)

5. a) The theoretical value is based on assuming the substance has purely ionic bonding. If this agrees with the experimental value (as it does to within 1.5% for AgF), then you can assume that AgF is almost purely ionic.

    b) If there is a greater discrepancy (about 9% for AgI), then the bonding can't be entirely ionic, and must have covalent nature as well.

    c) As you go from AgF to AgI, the electronegativity of the halogen is falling. That means that the electronegativity difference between the silver and the halogen will be greatest with AgF, and least with AgI. The greater the difference, the more purely ionic the bonding will be. The fluorine will have the greatest tendency to pull bonding electrons to its end of the bond, and so form ions. Iodine doesn't have as strong a tendency, and so the bonding isn't so purely ionic.

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6. To make MgCl, you would need to remove 1 electron from the magnesium to produce Mg^+ ions. That just needs the first ionisation energy of the magnesium. However, the attractions between Mg^+ and Cl^- won't be all that strong, and so the lattice formation enthalpy won't be all that great either. The net effect of these (and the other) enthalpy changes is that the overall enthalpy change of formation of MgCl turns out to be slightly negative.

    To make $MgCl_2$, you would have to supply more energy to ionise the magnesium ($1^{st} + 2^{nd}$ ionisation energies), but you would also get a lot more energy released when the lattice forms, because of the greater attractions involving the 2+ ions. The net effect is that the enthalpy change of formation of $MgCl_2$ is more negative than that of MgCl, meaning that $MgCl_2$ is the more stable compound of the two.

    In making $MgCl_3$, you would get an even higher lattice formation energy because of the 3+ ions. But you would need to put in huge amounts of extra energy to make the Mg^{3+} ions, because the third electron to be removed comes from the 2-level instead of the 3-level. This is much closer to the nucleus, and so much more difficult to remove. The huge extra ionisation energy much more than counteracts any gain in lattice enthalpy, and so this compound would be very energetically unstable relative to $MgCl_2$.