D - Using Average Bond Enthalpies

- Bond enthalpies are defined as the energy change when one mole of a covalent bond in the gaseous state is formed from its gaseous atoms.

  Eg. $A(g) + B(g) \rightarrow A\text{-}B(g)$
- The enthalpy change will be ________________ because bonds are being formed.
- The opposite process (breaking the bonds) would be ____________________, giving a positive enthalpy change, but the number will still be the same.
- The following table gives some values for average bond enthalpies. Note that for most cases these are averaged values from several compounds containing similar bonds. For some molecules (eg. F_2, H_2) the bond enthalpy can be known fairly accurately (since the specific bond only occurs in one molecule)

Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						

Multiple Bonds

C = C	614	N = N	418	O = O	495	(O_2)
C ≡ C	839	N ≡ N	941			
C = N	615			S = O	523	
C ≡ N	891			S = S	418	
C = O	799					
C ≡ O	1072					

- When calculating the enthalpy change for a reaction, we need to determine how much energy is put in to break existing bonds and how much energy is given off when new bonds are formed.

Example #1 – Calculate ΔH for the reaction $N_2 + 3H_2 \rightarrow 2NH_3$

Energy in

Energy out

Example #2 – Calculate ΔH for the reaction $2\ CO + O_2 \rightarrow 2\ CO_2$

Example #3 – Calculate ΔH for the reaction $C_2H_2 + Br_2 \rightarrow CHBrCHBr$

E – Using Standard enthalpies of Formation and Combustion (HL topic)

- $\Delta H_f°$ (standard enthalpy of formation) is the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states.
- $\Delta H_c°$(standard enthalpy of combustion) is the change in enthalpy when one mole of a substance is burned under standard conditions.
- **Standard states**:
  - For an element, the standard state is the form in which the element exists under conditions of one atmosphere and 25°C
  - For gases, pressure = 1 atmosphere
  - For solids and liquids, substances must be pure
- By using standard enthalpies of formation, we can calculate the enthalpy change of a given reaction
- **Example #1** – combustion of methane:
  $CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

Given: $\Delta H_f°$ = -75 kJ/mol for CH_4, -394 kJ/mol for CO_2, -286 kJ/mol for H_2O

Step 1 – write the formation equation for each compound

Step 2 – manipulate equations to obtain the desired overall reaction

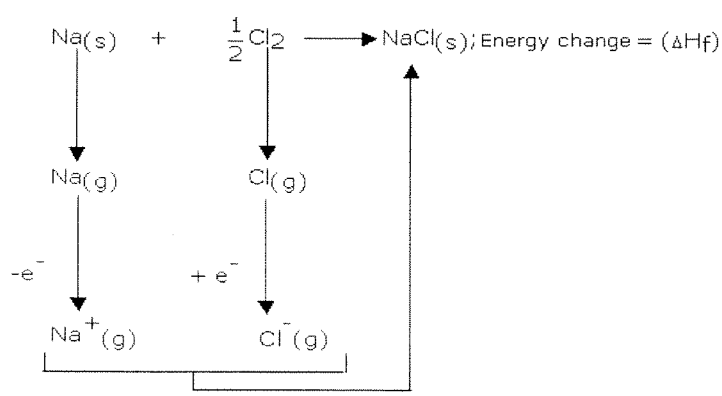
- **Example #2** – Calculate the enthalpy change for the reaction:
  $3F_2(g) + NH_3(g) \rightarrow 3\ HF(g) + NF_3(g)$
  given the standard enthalpies of formation:
  F_2 = 0 kJ/mol, NH_3 = -46 kJ/mol, HF = -269 kJ/mol, NF_3 = -114 kJ/mol

F – The Born-Haber cycle (HL topic)

- The Born-Haber cycle is a method that relates the enthalpy change of forming an ionic compound from its elements to its **lattice enthalpy**. Because the lattice enthalpy is generally very high, the entire process is exothermic although many of the steps are endothermic.
- For example, we will consider the formation of sodium chloride.

$$Na(s) + \frac{1}{2}Cl_{2(g)} \longrightarrow NaCl;\ \Delta H_f$$

  - The overall reaction can be broken down into several steps as shown in the energy cycle (the Born-Haber cycle) below



  - The steps involved are:
    1. Changing 1 mol of sodium atoms (solid) to the gas phase
       - Enthalpy required for this is called standard enthalpy of atomization (or vaporization)
       - Reaction is endothermic

- ΔH_{at}^{o} for sodium = + 108 kJ/mol

2. The sodium atoms are ionized to form Na^+ ions
   - First ionization energy (ΔH_{IE}^{o}) for Na is +494 kJ/mol

3. ½ mol of chlorine molecules are broken into chlorine atoms
   - This involves breaking the Cl-Cl bond
   - Energy required is equal to half of the bond enthalpy and is usually known as the standard enthalpy of atomization because 1 mol of atoms is produced.
   - ΔH_{at}^{o} for chlorine = +121 kJ/mol

4. Gaseous chlorine atoms each gain one electron
   - First electron affinity (ΔH_{EA}^{o}) for Cl is -364 kJ/mol

   - Note – for atoms that must gain more than one electron to form stable ions, we must consider both the first and second electron affinities, which can be very different.

5. Formation of crystalline solid from gaseous ions
   - This is known as **lattice enthalpy** – which can be defined either as the enthalpy change when one mole of a solid ionic salt is formed from its gaseous ions under standard conditions or the enthalpy change when one mole of a solid ionic salt is decomposed into its gaseous ions under standard conditions.
   - In this case, we will use the first definition and the value ΔH_{latt}^{o}(NaCl) = -771 kJ/mol (what difference would it make if we used the second definition?)

6. Put all the steps together and calculate ΔH° for the reaction

Practice question #1 - Calculate the lattice enthalpy of magnesium fluoride (MgF_2) can be calculated from the atomization enthalpy of Mg =146.4 kJ mol^{-1}; IE_1 and IE_2 values of Mg=737 and 1449 kJ mol $^{-1}$ respectively; atomization energy of fluorine = 158.8 kJ mol $^{-1}$; EA of fluorine = - 328 kJ mol $^{-1}$ and ΔH_f^o of MgF_2 = - 1096.5 kJ mol ^{1}. The Born-Haber cycle is shown below.