Correlating Structures and Bonding with Thermochemical Principles

1. Predict the enthalpy of formation of water using only average bond energies. (The tabulated value for $\Delta H^\circ_{f,\text{water}}$ is –241.8 kJ/mol)

$$\mathbf{H_2(g) + \tfrac{1}{2}\, O_2(g) \rightarrow H_2O(g)}$$

Bond energy, H_2 = 436 kJ/mol
Bond energy, O_2 = 498 kJ/mol
Bond energy, OH = 463 kJ/mol

Approximate ΔH_f = (436 kJ + ½(498 kJ)) – 2(463 kJ) = -241 kJ (per mol H_2O)

(about 0.3% low from experimental value)

2. Using only average bond energies, calculate the enthalpy of combustion of methane, CH_4. The products are gaseous water and carbon dioxide. (The experimental value is –802.4 kJ/mol.)

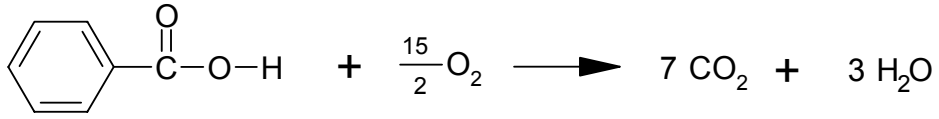
$$\mathbf{CH_4(g) + 2\, O_2(g) \rightarrow CO_2(g) + 2\, H_2O(g)}$$

Bond energy, C-H = 413 kJ/mol
Bond energy, O=O = 498 kJ/mol
Bond energy, C=O = 732 kJ/mol
Bond energy, O-H = 463 kJ/mol

Approximate $\Delta H_{combustion}$ = [4(413 kJ) + 2(498 kJ)] – [2(732 kJ) + 4(463 kJ)] = -668 kJ

Not quite as accurate as in problem 1 but not a bad estimate.

3. Calculate the enthalpy of combustion of benzoic acid, $C_7H_6O_2$. The experimental value is -26.42 kJ/g. Explain the difference between the calculated and experimental values.



Bond energy, C=C = 602 kJ/mol
Bond energy, C-C = 346 kJ/mol
Bond energy, C=O = 732 kJ/mol
Bond energy, C-O = 358 kJ/mol
Bond energy, O-H = 463 kJ/mol
Bond energy, O=O = 498 kJ/mol

Approx $\Delta H_{combustion}$ = [3(602 kJ) + 4(346 kJ) + 732 kJ + 358 kJ + 463 kJ + $\frac{15}{2}$ (498 kJ)] – [14(732 kJ) + 6(463 kJ)] = -4548 kJ (per mol)

Experimental value = -26.42 kJ/g x 122.12 g/mol = -3226 kJ/mol

The extreme difference (1322 kJ) between experiment and calculation here is due to "resonance stabilization"; it is the stabilization energy gained by the delocalization of the of the ring π electrons.