HW 9-5: pg. 381 #69, 72, 88 (HINT: You are solving for the ΔH for the formation of CH_4. The formation of CH_4 is $C + 2\,H_2 \rightarrow CH_4$), 89

9.69 From the following data, calculate the average bond energy for the N–H bond.

$$\mathbf{NH_3(\mathit{g}) \rightarrow NH_2(\mathit{g}) + H(\mathit{g}) \qquad \Delta \mathit{H}° = 435\ kJ/mol}$$
$$\mathbf{NH_2(\mathit{g}) \rightarrow NH(\mathit{g}) + H(\mathit{g}) \qquad \Delta \mathit{H}° = 381\ kJ/mol}$$
$$\mathbf{NH(\mathit{g}) \rightarrow N(\mathit{g}) + H(\mathit{g}) \qquad \Delta \mathit{H}° = 360\ kJ/mol}$$

$$NH_3(g) \rightarrow N(g) + 3H(g) \qquad \Delta H° = 1176\ \text{kJ/mol}$$

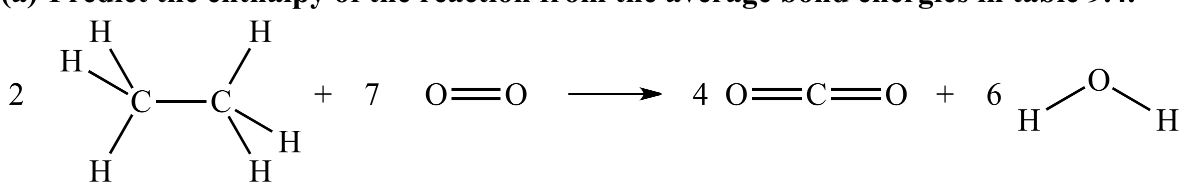
$$NH_3(g) \rightarrow N(g) + 3H(g) \qquad \Delta H° = 3\ D_{N-H}$$

$$\text{The average bond energy, } D_{\mathbf{N-H}} = \frac{1176\ kJ/mol}{3} = \mathbf{392\ kJ\ /\ mol}$$

9.72 For the reaction

$$\mathbf{2\ C_2H_6\ (g) + 7\ O_2\ (g) \rightarrow 4\ CO_2\ (g) + 6\ H_2O\ (g)}$$

(a) Predict the enthalpy of the reaction from the average bond energies in table 9.4.



Bonds Broken	*Number Broken*	*Bond Energy* (kJ/mol)	*Energy Needed* (kJ)
C – H	12	414	4968 (Endo)
C – C	2	347	694 (Endo)
O = O	7	498.7	3491 (Endo)

Bonds Formed	*Number Formed*	*Bond Energy* (kJ/mol)	*Energy Released* (kJ)
C = O	8	799	6392 (Exo)
O – H	12	460	5520 (Exo)

$$\Delta H° = \text{total energy input} - \text{total energy released}$$
$$= 4968 + 694 + 3491 - (6392 + 5520) = \mathbf{-2759\ kJ/mol}$$

(b) Calculate the enthalpy of reaction from the standard enthalpies of formation (see Appendix 3) of the reactant and product molecules.

$$\Delta H° = (4)(-393.5\ \text{kJ/mol}) + (6)(-241.8\ \text{kJ/mol}) - [(2)(-84.7\ \text{kJ/mol}) + (7)(0)]$$
$$= \mathbf{-2855\ kJ/mol}$$

(c) Why do the answers in parts (a) and (b) differ?

In (a), average bond energies are used, which may not reflect the actual bond energies in these specific compounds. In (b) exact thermodynamic values for these specific compounds are used.

9.88 Using the following information and the fact that the average C–H bond energy is 414 kJ/mol, estimate the standard enthalpy of formation of methane, CH_4.

$$C(s) \longrightarrow C(g) \qquad \Delta H^\circ_{rxn} = 716 \text{ kJ / mol}$$

$$2\ H_2(g) \longrightarrow 4\ H(g) \qquad \Delta H^\circ_{rxn} = 872.8 \text{ kJ / mol}$$

$$C(g) + 4H(g) \longrightarrow CH_4(g)$$

$$\Delta H = -4\ D_{C-H} = -4 \times 414 \text{ kJ/mol} = -1656 \text{ kJ/mol} \text{ (Exo because forming bonds)}$$

Therefore, $\Delta H^\circ_f(CH_4)$ would be approximately the sum of the enthalpy changes for the three steps.

$$\Delta H^\circ_f(CH_4) = 716 + 872.8 - 1656 \text{ kJ/mol} = \mathbf{-67 \text{ kJ / mol}}$$

This is close to the actual value. The $\Delta H^\circ_f(CH_4) = -74.85$ kJ/mol.

9.89 Based on energy considerations, which of the following reactions will occur more readily?
(*Hint*: Refer to table 9.4, and assume that the average bond energy of the C–Cl bond is 338 kJ/mol.)

(a) $Cl\ (g) + CH_4\ (g) \rightarrow CH_3Cl\ (g) + H(g)$

Bond(s) broken:
Bond(s) formed:

$$\Delta H^\circ_{rxn} = 414 - 338 = 76 \text{ kJ/mol}$$

(b) $Cl\ (g) + CH_4 \rightarrow CH_3(g) + HCl\ (g)$

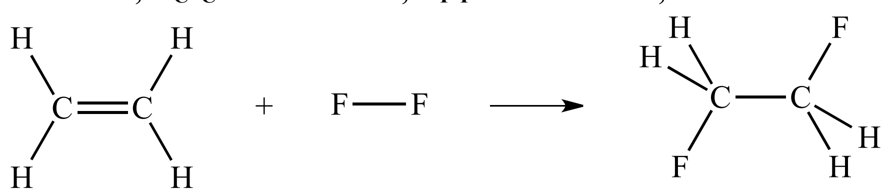
Bond(s) broken:
Bond(s) formed:

$$\Delta H^\circ_{rxn} = 414 - 431.9 = -18 \text{ kJ/mol}$$

Since reaction (b) is exothermic and (a) is endothermic, (b) will be more preferred.

Extra Problem: Consider the reaction: $C_2H_4(g) + F_2(g) \rightarrow C_2H_4F_2(g)$ $\qquad \Delta H^\circ_{rxn} = -549$ kJ

Given $D_{C\text{-}C} = 347$ kJ/mol, $D_{C=C} = 614$ kJ/mol, $D_{F\text{-}F} = 145$ kJ/mol, estimate the C-F bond energy.



$$\Delta H^\circ_{rxn} = \cancel{4\ D_{C\text{-}H}} + \underbrace{D_{C=C} + D_{F\text{-}F}}_{\text{Bonds broken}} - \cancel{4D_{C\text{-}H}} \underbrace{- D_{C\text{-}C} - 2D_{C\text{-}F}}_{\text{Bonds Formed}}$$

$$-549 \text{ kJ} = 614 \text{ kJ} + 145 \text{ kJ} - 347 \text{ kJ} - 2D_{C\text{-}F}$$

$$2D_{C\text{-}F} = 614 \text{ kJ} + 145 \text{ kJ} - 347 \text{ kJ} + 549 \text{ kJ}$$

$$D_{C\text{-}F} = \frac{961 \text{ kJ}}{2} = 481 \text{ kJ/mol}$$