7. (a) $\Delta H_f = D_{\text{bonds broken}} - D_{\text{bonds formed}} = 0 - 950\ ^{\text{kJ}}/_{\text{mol}}$

$$\boxed{\Delta H_f = -950\ ^{\text{kJ}}/_{\text{mol}}}$$

(b) ΔS^o will be negative because the total number of gas molecules is less as products than reactants, therefore, the entropy of the system which depends on positional probabilities will decrease as the reaction proceeds to the right.

(c) The change in Gibbs free energy can be calculated from the equation $\Delta G^o = \Delta H^o - T\Delta S^o$. The sign of ΔH^o is negative so the change in enthalpy tends to make ΔG^o negative. However, the sign of ΔS^o is also negative but it is preceded by a negative sign in the equation $\Delta G^o = \Delta H^o - T\,\Delta S^o$. Therefore, $T\Delta S^o$ tends to make ΔG^o positive in this reaction. At lower temperatures, the ΔH^o, which is not temperature-dependent and is negative, is the dominant factor so ΔG^o is negative. At higher temperatures $T\Delta S^o$, which is temperature-dependant and makes ΔG^o positive, is the dominant factor so ΔG^o is positive.

(d) Although at low temperatures the thermodynamics predicts a spontaneous reaction (ΔG^o is negative), it says nothing about the rate of the reaction. The kinetics indicates the rate of the reaction and is determined, in part, by the effectiveness of collisions between the reactant molecules. The triple bond of nitrogen is very strong as indicated by the high enthalpy of formation calculated above. At low temperatures, these molecules do not have enough kinetic energy on average to overcome this bond energy of nitrogen and break this triple bond during collisions. Since temperature is a measure of the **AVERAGE** kinetic energy of the molecules of a gas, some molecules may have enough energy for the reaction to occur, but they are relatively few. Thus, the kinetics predict a very slow reaction--so slow that there is no measurable amount of $NH_3(g)$ produced.

5. (a) q-Joules (J)

m-grams (g)

c-$\dfrac{\text{Joules}}{\text{gram}\cdot\text{Centigrade degree}}\left(\dfrac{\text{J}}{\text{g}\cdot\text{C}^\circ}\right)$

ΔT-Centigrade degrees (C°)

(b) The mass of each solution must be measured. However, it is easier to measure the volume of each solution and use the density of water (1.0 g/mL) to determine the mass of each solution (the mass of each solution is assumed to be the same as water as outlined in the assumptions of this question).
The temperature of each solution (assumed that both solutions have the same temperature) before they are mixed, and then again a few minutes after they are mixed.

(c) (i) Since the density of each solution is the same as that of water, the two solutions are have equal volumes, both solutions are considered to completely dissociate (one is a strong acid and one is a strong base, and the balanced equation shows a 1:1:1 mole ratio in the reaction, the volume of water produced (from combining these two solutions) is the volume of either solution before they are mixed. Using the density of water, the mass of water produced from this reaction can be calculated from the volume of water produced.
Take this mass of water produced and divide by the molar mass of water (18.0 g) to determine the number of moles of water produced.

(ii) The heat produced from this reaction is determined by $q = mc\Delta T$ and the number of moles of water (n_{water}) is determined as described in part (c) (i) above. Use these values in the relationship: $\Delta H_{neut} = \dfrac{q}{n_{\text{water}}}$

(d) (i) q will increase in this reaction because the concentrations of each reactant as doubled so twice as much water will be produced, which means twice the heat.

(ii) ΔH_{neut} will stay the same because this the heat produced **PER** mole of water produced so this is a constant.

(e) ΔH_{neut} would be less because the solutions will not undergo as great of a temperature change since some of the heat from the reaction went into the air. Therefore, the calulated heat of the reaction from $q = mc\Delta T$ would be less, but the same number of moles of water would be assummed to have formed.

2. (a) $? \text{ kJ} = 73.1 \text{ g NO}\left(\frac{1 mole NO}{30.0 g NO}\right)\left(\frac{-114.1 kJ}{2 moles NO}\right)$

$$\boxed{\Delta H = -278 \text{ kJ}}$$

(b) (i) $\Delta G° = -RT\ln K$

$-70.4 \text{ kJ} = -(0.008315 \text{ kJ/K•mol})(298\text{K})\ln K$

$$\boxed{K_{eq} = 2.18 \times 10^{12}}$$

(ii) $\Delta G° = \Delta H° + T\Delta S°$

$\Delta G° = -114.1 \text{ kJ} - T(-0.1465 \text{ kJ/K})$

$\Delta G° = -114.1 \text{ kJ} + T(0.1465 \text{ kJ/K})$

$$\boxed{\text{Therefore, as T increases, } \Delta G \text{ becomes less negative.}}$$

(c) $\Delta S° = \Sigma S°\text{products} - \Sigma S°\text{reactants}$

$\Delta S^o = n_{NO_2} S^o{}_{NO_2} - [n_{NO} S^o{}_{NO} + n_{O_2} S^o{}_{O_2}]$

$-146.5 \text{ J/K} = (2 \text{ moles})•(240.1 \text{ J/K•mol}) - [(2 \text{ moles})•(210.8 \text{ J/K•mol}) + (2 \text{ moles})•S^o{}_{O_2}]$

$$\boxed{S^o{}_{O_2} = 87.9 \text{ J/K•mol}}$$

(d) $\Delta H^o = \Sigma H_f^o products - \Sigma H_f^o reac\tan ts$

$\Delta H^o = n_{NO_2} H^o_{f\,NO_2} - [n_{NO} H^o_{f\,NO} + n_{O_2} H^o_{f\,O_2}]$

$-114.1 \text{ kJ} = (2 \text{ moles})•H^o_{f\,NO_2} - [(2 \text{ moles})•(607 \text{ kJ/K•mol}) + (1 \text{ mole})•(495 \text{ kJ/K•mol})]$

$$\boxed{H^o_{f\,NO_2} = 797.5 \text{ kJ/mol}}$$

6. (a) $\Delta H^\circ = \Sigma\Delta H_f^o \text{products} - \Sigma\Delta H_f^o \text{reactants}$

$$\Delta H^\circ = \left[\Delta H_f^o(O_2) + \Delta H_f^o(NO_2)\right] - \left[\Delta H_f^o(O_3) + \Delta H_f^o(NO)\right]$$

ΔH° = (0 kJ/mol + 33 kJ/mol) - (143 kJ/mol + 90 kJ/mol)

$$\boxed{\Delta H^\circ = -200 \text{ kJ}}$$

(b) ΔS° for the reaction will be zero because there is no increase in entropy (disorder). There are the same number of gas particles on the reactant side as the product side.

(c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ Since ΔS° is zero and ΔH° is negative, ΔG° should be negative.

(d) Compare experiment number 3 to 1.

$$\left(\frac{[O_3]_3}{[O_3]_1}\right) = \left(\frac{Rate_3}{Rate_1}\right)^m$$

$$\left(\frac{0.0020M}{0.0010M}\right) = \left(\frac{2x}{x}\right)^m$$

$2 = 2^m$

$m = 1$

Compare experiment number 2 to 1.

$$\left(\frac{[NO]_2}{[NO]_1}\right) = \left(\frac{Rate_2}{Rate_1}\right)^n$$

$$\left(\frac{0.0020M}{0.0010M}\right) = \left(\frac{2x}{x}\right)^n$$

$2 = 2^n$

$n = 1$

Rate = $k[O_3]^m[NO]^n = k[O_3]^1[NO]^1$

$$\boxed{\text{Rate} = k[O_3][NO]}$$

(e) Step I is the rate-determining (the slowest step) since the rate law written from its molecularity matches the rate law determined from experimentation in part (c.) above.