CHAPTER SIX

THERMOCHEMISTRY

For Review

1. Potential energy: energy due to position or composition
   
   Kinetic energy: energy due to motion of an object

   Path-dependent function: a property that depends on how the system gets from the initial state to the final state; a property that is path-dependent

   State function: a property that is independent of the pathway

   System: that part of the universe on which attention is to be focused

   Surroundings: everything in the universe surrounding a thermodynamic system

2. Plot a represents an exothermic reaction. In an exothermic process, the bonds in the product molecules are stronger (on average) than those in the reactant molecules. The net result is that the quantity of energy $\Delta(PE)$ is transferred to the surroundings as heat when reactants are converted to products.

   For an endothermic process, energy flows into the system from the surroundings as heat to increase the potential energy of the system. In an endothermic process, the products have higher potential energy (weaker bonds on average) than the reactants.

3. First law of thermodynamics: the energy of universe is constant. A system can change its internal energy by flow of work, heat, or both ($\Delta E = q + w$). Whenever a property is added to the system from the surroundings, the sign is positive; whenever a property is added to the surroundings by the system, the sign is negative.

4. As a gas expands, the system does work on the surroundings so $w$ is negative. When a gas contracts, the surroundings do work on the system so $w$ is positive. $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$; To boil water, heat must be added so $q$ is positive. The molar volume of a gas is huge compared to the molar volume of a liquid. As a liquid converts to a gas, the system will expand its volume, performing work on the surroundings; $w$ is negative.

5. $q_p = \Delta H$; $q_V = \Delta E$; A coffee-cup calorimeter is at constant (atmospheric) pressure. The heat released or gained at constant pressure is $\Delta H$. A bomb calorimeter is at constant volume. The heat released or gained at constant volume is $\Delta E$.

6. The specific heat capacities are: 0.89 J/°C g (Al) and 0.45 J/°C g (Fe) Al would be the better choice. It has a higher heat capacity and a lower density than Fe. Using Al, the same amount of heat could be dissipated by a smaller mass, keeping the mass of the amplifier down.
7. In calorimetry, heat flow is determined into or out of the surroundings. Because $\Delta E_{\text{univ}} = 0$ by the first law of thermodynamics, $\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$; what happens to the surroundings is the exact opposite of what happens to the system. To determine heat flow, we need to know the heat capacity of the surroundings, the mass of the surroundings that accepts/donates the heat, and the change in temperature. If we know these quantities, $q_{\text{surr}}$ can be calculated and then equated to $q_{\text{sys}}$ ($q_{\text{surr}} = q_{\text{sys}}$). For an endothermic reaction, the surroundings (the calorimeter contents) donates heat to the system. This is accompanied by a decrease in temperature of the surroundings. For an exothermic reaction, the system donates heat to the surroundings (the calorimeter) so temperature increases.

8. Hess’s law: in going from a particular set of products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps ($\Delta H$ is path independent). When a reaction is reversed, the sign of $\Delta H$ is also reversed but the magnitude is the same. If the coefficients in a balanced reaction are multiplied by a number, the value of $\Delta H$ is multiplied by the same number while the sign is unaffected.

9. Standard enthalpy of formation: the change in enthalpy that accompanies the formation of one mole of a compound from its elements with all substances in their standard states. The standard state for a compound has the following conventions:

   a. gaseous substances are at a pressure of exactly 1 atm.

   b. for a pure substance in a condensed state (liquid or solid), the standard state is the pure liquid or solid.

   c. for a substance present in solution, the standard state is a concentration of exactly 1 M.

The standard state of an element is the form in which the element exists under conditions of 1 atm and 25°C. $\Delta H^o$ values for elements in their standard state are, by definition, equal to zero.

   Step 1: reactants $\rightarrow$ elements in standard states
   \[ \Delta H_1 = -\sum n_r \Delta H^o_r(\text{reactants}) \]

   Step 2: elements in standard state $\rightarrow$ products
   \[ \Delta H_2 = \sum n_p \Delta H^o_r(\text{products}) \]

   reactants $\rightarrow$ products
   \[ \Delta H^o_{\text{reaction}} = \Delta H_1 + \Delta H_2 \]

   \[ \Delta H^o_{\text{reaction}} = \sum n_p \Delta H^o_r(\text{products}) - \sum n_r \Delta H^o_r(\text{reactants}) \]

10. Three problems are: there is only a finite amount of fossil fuels, fossil fuels can be expensive, and the combustion and exploration of fossil fuels can add pollution to the biosphere whose effects may not be reversible. Some alternative fuels are syngas from coal, hydrogen from the breakdown of water, and ethanol from the fermentation of sugar.