## Assignment 4 Week of September 28, 2009 Solutions

Chapter 9: Energy, Enthalpy, and Thermochemistry # 57, 62, 64,86

## Standard Enthalpies of Formation

57. 
$$4 \text{ Na(s)} + O_2(g) \rightarrow 2 \text{ Na}_2O(s), \quad \Delta H^\circ = 2 \text{ mol} \left(\frac{-416 \text{ kJ}}{\text{mol}}\right) = -832 \text{ kJ}$$
  
  $2 \text{ Na(s)} + 2 \text{ H}_2O(l) \rightarrow 2 \text{ NaOH(aq)} + \text{H}_2(g)$ 

$$\Delta H^{\circ} = \left[ 2 \operatorname{mol} \left( \frac{-470 \cdot \text{kJ}}{\text{mol}} \right) \right] - \left[ 2 \operatorname{mol} \left( \frac{-286 \text{ kJ}}{\text{mol}} \right) \right] = -368 \text{ kJ}$$

$$2Na(s) + CO_2(g) \rightarrow Na_2O(s) + CO(g)$$

$$\Delta \mathbf{H}^{\circ} = \left[1 \text{ mol} \left(\frac{-416 \text{ kJ}}{\text{mol}}\right) + 1 \text{ mol} \left(\frac{-110.5 \text{ kJ}}{\text{mol}}\right)\right] - \left[1 \text{ mol} \left(\frac{-393.5 \text{ kJ}}{\text{mol}}\right)\right] = -133 \text{ kJ}$$

In reactions 2 and 3, sodium metal reacts with the "extinguishing agent." Both reactions are exothermic and each reaction produces a flammable gas,  $H_2$  and CO, respectively.

62. a. 
$$C_2H_4(g) + O_3(g) \rightarrow CH_3CHO(g) + O_2(g)$$
,  $\Delta H^{\circ} = -166 \text{ kJ} - [143 \text{ kJ} + 52 \text{ kJ}] = -361 \text{ kJ}$ 

b. 
$$O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$$
,  $\Delta H^{\circ} = 34 \text{ kJ} - [90. \text{ kJ} + 143 \text{ kJ}] = -199 \text{ kJ}$ 

c. 
$$SO_3(g) + H_2O(1) \rightarrow H_2SO_4(aq)$$
,  $\Delta H^\circ = -909 \text{ kJ} - [-396 \text{ kJ} + (-286 \text{ kJ})] = -227 \text{ kJ}$ 

d. 
$$2 \text{ NO(g)} + \text{O}_2(\text{g}) \rightarrow 2 \text{ NO}_2(\text{g}),$$
  $\Delta \text{H}^{\circ} = 2(34) \text{ kJ} - 2(90.) \text{ kJ} = -112 \text{ kJ}$ 

64. 
$$C_2H_4(g) + 3 O_2(g) \rightarrow 2 CO_2(g) + 2 H_2O(l)$$
  $\Delta H^{\circ} = -1411 \text{ kJ}$ 

$$\Delta H^{\circ} = -1411.1 \text{ kJ} = 2(-393.5) \text{ kJ} + 2(-285.8) \text{ kJ} - \Delta H^{\circ}_{f, C_2H_4}$$

$$-1411.1 \text{ kJ} = -1358.6 \text{ kJ} - \Delta H^{\circ}_{f, C_3H_4}, \Delta H^{\circ}_{f, C_3H_4} = 52.5 \text{ kJ/mol}$$

## Challenge Problem

86. a. Using Hess's Law and the equation  $\Delta H = nC_p \Delta T$ :

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\begin{array}{c} \text{CH}_3\text{Cl}(248\,^\circ\text{C}) + \text{H}_2(248\,^\circ\text{C}) \to \text{CH}_4(248\,^\circ\text{C}) + \text{HCl}(248\,^\circ\text{C}) & \Delta\text{H}_1 = -83.3 \text{ kJ} \\ \text{CH}_3\text{Cl}(25\,^\circ\text{C}) \to \text{CH}_3\text{Cl}(248\,^\circ\text{C}) & \Delta\text{H}_2 = 1 \text{ mol } (48.5 \text{ J } ^\circ\text{C}^{-1} \text{ mol }^{-1}) \ (223\,^\circ\text{C}) \\ & = 10,800 \text{ J} = 10.8 \text{ kJ} \\ \text{H}_2(25\,^\circ\text{C}) \to \text{H}_2(248\,^\circ\text{C}) & \Delta\text{H}_3 = 1(28.9) \ (223) \ (1 \text{ kJ}/1000 \text{ J}) = 6.44 \text{ kJ} \\ \text{CH}_4(248\,^\circ\text{C}) \to \text{CH}_4(25\,^\circ\text{C}) & \Delta\text{H}_4 = 1(41.3) \ (-223) \ (1/1000) = -9.21 \text{ kJ} \\ \text{HCl}(248\,^\circ\text{C}) \to \text{HCl}(25\,^\circ\text{C}) & \Delta\text{H}_5 = 1(29.1) \ (-223) \ (1/1000) = -6.49 \text{ kJ} \end{array}
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 $\overline{\text{CH}_{3}\text{Cl}(25\,^{\circ}\text{C}) + \text{H}_{2}(25\,^{\circ}\text{C})} \rightarrow \text{CH}_{4}(25\,^{\circ}\text{C}) + \text{HCl}(25\,^{\circ}\text{C}) \quad \Delta \text{H}^{\circ} = \Delta \text{H}_{1} + \Delta \text{H}_{2} + \Delta \text{H}_{3} + \Delta \text{H}_{4} + \Delta \text{H}_{5}$ 

 $\Delta H^{\circ} = -83.3 \text{ kJ} + 10.8 \text{ kJ} + 6.44 \text{ kJ} - 9.21 \text{ kJ} - 6.49 \text{ kJ} = -81.8 \text{ kJ}$ 

b. 
$$\Delta H^{\circ} = [\Delta H_{f}^{\circ}(CH_{4}) + \Delta H_{f}^{\circ}(HCl)] - [\Delta H_{f}^{\circ}(CH_{3}Cl) + \Delta H_{f}^{\circ}(H_{2})]$$
  
-81.8 kJ = -75 kJ - 92 kJ -  $[\Delta H_{f}^{\circ}(CH_{3}Cl) + 0]$ ,  $\Delta H_{f}^{\circ}(CH_{3}Cl) = -85$  kJ/mol

Chapter 10: Spontaneity, Entropy, and Free Energy # 34, 35, 40, 47, 48

## Entropy and the Second Law of Thermodynamics: Free Energy

- 34. Living organisms need an external source of energy to carry out these processes. Green plants use the energy from sunlight to produce glucose from carbon dioxide and water by photosynthesis. In the human body, the energy released from the metabolism of glucose helps drive the synthesis of proteins. For all processes combined,  $\Delta S_{univ}$  must be greater than zero (2nd law).
- 35. No, living organisms need an outside source of matter (food) to survive.
- 40. a. Decrease in disorder;  $\Delta S^{\circ}(-)$

- b. Increase in disorder; ΔS°(+)
- c. Decrease in disorder ( $\Delta n < 0$ );  $\Delta S^{\circ}(-)$
- d. Decrease in disorder ( $\Delta n < 0$ );  $\Delta S^{\circ}(-)$
- e. HCl(g) is more disordered than two mol of ions in solution;  $\Delta S^{\circ}(-)$ .
- f. Increase in disorder;  $\Delta S^{\circ}(+)$

For c, d and e, concentrate on the gaseous products and reactants. When there are more gaseous product molecules than gaseous reactant molecules ( $\Delta n > 0$ ), then  $\Delta S^{\circ}$  will be positive (disorder increases). When  $\Delta n$  is negative then  $\Delta S^{\circ}$  is negative (disorder decreases).

47. a. 
$$NH_3(s) \rightarrow NH_3(l)$$
;  $\Delta G = \Delta H - T\Delta S = 5650 \text{ J/mol} - 200. \text{ K } (28.9 \text{ J K}^{-1} \text{ mol}^{-1})$ 

$$\Delta G = 5650 \text{ J/mol} - 5780 \text{ J/mol} = -130 \text{ J/mol}$$

Yes, NH<sub>3</sub> will melt since  $\Delta G < 0$  at this temperature.

b. At the melting point, 
$$\Delta G = 0$$
 so  $T = \frac{\Delta H}{\Delta S} = \frac{5650 \text{ J/mol}}{28.9 \text{ J K}^{-1} \text{ mol}^{-1}} = 196 \text{ K}.$ 

- 48. a.  $S_{thombic} \rightarrow S_{monoclinic}$ ; This phase transition is spontaneous ( $\Delta G < 0$ ) at temperatures above 95°C.  $\Delta G = \Delta H T\Delta S$ ; For  $\Delta G$  to be negative only above a certain temperature, then  $\Delta H$  is positive and  $\Delta S$  is positive (see Table 10.6 of text).
  - b. Since  $\Delta S$  is positive, then  $S_{\text{rhombic}}$  is the more ordered crystalline structure.