Homework Assignment 3
Solution to Even Numbered Problems 7.36 and 7.68

Problem 7.36:
For all cases $\Delta H^\circ = \sum \Delta H^\circ_{\text{products}} - \sum \Delta H^\circ_{\text{reactants}}$
All values for $\Delta H^\circ$ can be found in Oxtoby’s Appendix D (entries are per mole of substance)

a) $2\text{NO}(g)+\text{O}_2(g) \rightarrow 2\text{NO}_2(g)$
   $\Delta H^\circ = 2\Delta H^\circ_{\text{NO}_2} - 2\Delta H^\circ_{\text{NO}} - \Delta H^\circ_{\text{O}_2} = (2 \text{ moles})(33.18 \text{ kJ/mole}) - (2 \text{ moles})(90.25 \text{ kJ/mole}) - (1 \text{ mole})(0 \text{ kJ/mole}) = -114.14 \text{ kJ}$

b) $\text{C}(s)+\text{CO}_2(g) \rightarrow 2\text{CO}(g)$
   $\Delta H^\circ = 2\Delta H^\circ_{\text{CO}} - \Delta H^\circ_{\text{C}} - \Delta H^\circ_{\text{CO}_2} = (2 \text{ moles})(-110.52 \text{ kJ/mole}) - (1 \text{ mole})(0 \text{ kJ/mole}) - (1 \text{ mole})(-393.51 \text{ kJ/mole}) = +172.47 \text{ kJ}$

c) $2\text{NH}_3(g)+(7/2)\text{O}_2(g) \rightarrow 2\text{NO}_2(g)+3\text{H}_2\text{O}(g)$
   $\Delta H^\circ = 2\Delta H^\circ_{\text{NO}_2} + 3\Delta H^\circ_{\text{H}_2\text{O}} - 2\Delta H^\circ_{\text{NH}_3} - (7/2)\Delta H^\circ_{\text{O}_2} = (2 \text{ moles})(33.18 \text{ kJ/mole}) + (3 \text{ moles})(-241.82 \text{ kJ/mole}) - (2 \text{ moles})(-46.11 \text{ kJ/mole}) - ((7/2) \text{ mole})(0 \text{ kJ/mole}) = -566.88 \text{ kJ}$

d) $\text{C}(s)+\text{H}_2\text{O}(g) \rightarrow \text{CO}(g)+\text{H}_2(g)$
   $\Delta H^\circ = \Delta H^\circ_{\text{CO}} + \Delta H^\circ_{\text{H}_2} - \Delta H^\circ_{\text{C}} - \Delta H^\circ_{\text{H}_2\text{O}} = (1 \text{ mole})(-110.52 \text{ kJ/mole}) + (1 \text{ mole})(0 \text{ kJ/mole}) - (1 \text{ mole})(0 \text{ kJ/mole}) - (1 \text{ mole})(-241.82 \text{ kJ/mole}) = +131.30 \text{ kJ}$

Problem 7.68
As in class we want to write the reaction at two different temperatures and then connect reactants and products at one temperature to reactants and products at the second temperature using heat capacities:

SO$_2$(g) + (1/2)O$_2$(g) $\rightarrow$ SO$_3$(g)  $T_1= 298.15$ K  $\Delta H_1^\circ$

\[\downarrow \Delta H_{\text{reactants}} \quad \uparrow \Delta H_{\text{products}}\]

SO$_2$(g) + (1/2)O$_2$(g) $\rightarrow$ SO$_3$(g)  $T_2= 500$ K  $\Delta H_2^\circ$

Since enthalpy changes are independent of path:

$\Delta H_1^\circ = \Delta H_{\text{reactants}} + \Delta H_2^\circ + \Delta H_{\text{products}}$

$\Delta H_2^\circ = \Delta H^\circ_{\text{SO}_3} - \Delta H^\circ_{\text{SO}_2} - (1/2)\Delta H^\circ_{\text{O}_2} = (1 \text{ mole})(-395.72 \text{ kJ/mole}) - (1 \text{ mole})(-296.83 \text{ kJ/mole}) - ((1/2) \text{ mole})(0 \text{ kJ/mole}) = -98.89 \text{ kJ}$
ΔH_{products} = C_p(SO_3) \cdot (298-500) = (1 \text{ mole}) \times (50.7 \text{ J/mole-K}) \cdot (298-500) = -10.24 \text{ kJ}

ΔH_{reactants} = C_p(SO_2) \cdot (500-298) + (1/2)C_p(O_2) \cdot (500-298) = (1 \text{ mole}) \times (39.9 \text{ J/mole-K}) \cdot (500-298) + ((1/2) \text{ mole}) \times (29.4 \text{ J/mole-K}) \cdot (500-298) = +11.03 \text{ kJ}

Using: \ ΔH^\circ_1 = ΔH_{reactants} + ΔH^\circ_2 + ΔH_{products}

-98.89 \text{ kJ} = +11.03 \text{ kJ} + ΔH^\circ_2 -10.24 \text{ kJ}

ΔH^\circ_2 = -99.68 \text{ kJ}

Note that the effect of the heat capacity terms is to nearly cancel each other. In fact the enthalpy hardly changes over this T range because the heat capacities of the products and reactants are nearly equal. (Look carefully at the sign of ΔT in the calculations for the reactants and products!)