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Homework Assignment 3

Solution to Oxtoby Even Numbered Problems 7.36 and 7.68

Problem 7.36:

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

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

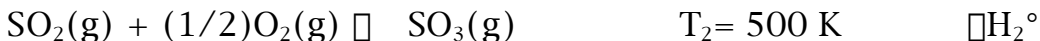
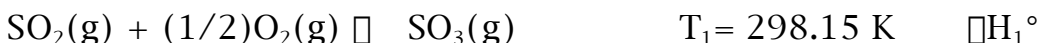
b) $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow 2\text{CO}(\text{g})$ $\Delta H^\circ = 2\Delta H_f^\circ (\text{CO}) - \Delta H_f^\circ (\text{C}) - \Delta H_f^\circ (\text{CO}_2)$
 $= (2 \text{ moles}) \times (-110.52 \text{ kJ/mole}) - (1 \text{ mole}) \times (0 \text{ kJ/mole}) - (1 \text{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

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

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

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:



Since enthalpy changes are independent of path:

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

$$\begin{aligned} \Delta H_1^\circ &= \Delta H_f^\circ(\text{SO}_3) - \Delta H_f^\circ(\text{SO}_2) - (1/2)\Delta H_f^\circ(\text{O}_2) = (1 \text{ mole}) \times (-395.72 \text{ kJ/mole}) \\ &- (1 \text{ mole}) \times (-296.83 \text{ kJ/mole}) - ((1/2)\text{mole}) \times (0 \text{ kJ/mole}) \\ &= \\ &\quad -98.89 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{products}} &= C_p(\text{SO}_3) (298-500) = (1 \text{ mole}) \times (50.7 \text{ J/mole-K}) (298-500) \\ &= \\ &\quad -10.24 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta H_{\text{reactants}} &= C_p(\text{SO}_2) (500-298) + (1/2)C_p(\text{O}_2) (500-298) = (1 \text{ mole}) \times (39.9 \text{ J/mole-K}) (500-298) \\ &+ ((1/2)\text{mole}) \times (29.4 \text{ J/mole-K}) (500-298) = \\ &\quad +11.03 \text{ kJ} \end{aligned}$$

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

$$-98.89 \text{ kJ} = +11.03 \text{ kJ} + \Delta H_2^\circ - 10.24 \text{ kJ}$$

$$\Delta H_2^\circ = -99.68 \text{ kJ}$$

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!)