

CHEM 3410: Physical Chemistry I — Fall 2009

Homework 3 — Model Solutions

1. We defined enthalpy as $H \equiv U + PV$. We can then write the change in enthalpy as:

$$\Delta H = \Delta U + \Delta(PV)$$

But for an ideal gas, $PV = nRT$. Substituting this in to the above equation yields:

$$\Delta H = \Delta U + \Delta(nRT)$$

At constant temperature this further simplifies to:

$$\Delta H = \Delta U + \Delta nRT = 9400 \text{ J/mole} + (0.27 \text{ mol})(8.314 \text{ J/mole} \cdot \text{K})(300 \text{ K})$$

$$\boxed{\Delta H = 10.1 \text{ kJ}}$$

2. At constant pressure, $\Delta H = q$ and we can solve for them both using the heat capacity:

$$\Delta H = q = \int_{T_i}^{T_f} nC_p dT = R \int_{348}^{1623} 3.093 + 6.967 \times 10^{-3}T - 45.81 \times 10^{-7}T^2 + 1.035 \times 10^{-9}T^3$$

$$\Delta H = q = R \left[3.093T + 6.967 \times 10^{-3} \frac{T^2}{2} - 45.81 \times 10^{-7} \frac{T^3}{3} + 1.035 \times 10^{-9} \frac{T^4}{4} \right]_{348}^{1623}$$

Evaluating the term in the brackets at the final temperature minus the initial temperature (as indicated with the notation) we get:

$$\boxed{\Delta H = q = 66.6 \text{ kJ}}$$

We can find the change in internal energy since (1) the number of moles remains the same and (2) we know the temperature change and it is an ideal gas:

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - nR\Delta T = 66.6 \times 10^3 \text{ J} - (1)(8.314 \text{ J/mol} \cdot \text{K})(1623 - 348 \text{ K})$$

$$\boxed{\Delta U = 56.0 \text{ kJ}}$$

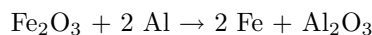
Since we now know the internal energy change and the heat flow, we can find the work done using the first law:

$$w = \Delta U - q = 56.0 \text{ kJ} - 66.6 \text{ kJ}$$

$$\boxed{w = -10.6 \text{ kJ}}$$

The sign of our answer does make sense since the gas is being heated and is expanding, thus work is being done by the gas and the sign of w should be negative.

3. (a) The balanced chemical reaction would look like this:



The enthalpy change for this reaction at 298 K can be calculated using standard enthalpies of formation of the products and reactants:

$$\Delta H_{rxn}^\circ = [\Delta H_f^\circ(\text{Al}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Fe})] - [\Delta H_f^\circ(\text{Fe}_2\text{O}_3) + 2\Delta H_f^\circ(\text{Al})]$$

The standard enthalpies of formation of elements are zero, so using available thermochemical data:

$$\Delta H_{rxn}^{\circ} = -851.5 \text{ kJ/mole}$$

- (b) To answer this part of the question we need to determine how much heat needs to be supplied to the solid iron to melt it. This will require heating the solid α -iron to the transition temperature, transforming from α to γ , heating the solid γ -iron to the melting temperature, and then transformation the solid to a liquid at the melting temperature.

According to the reaction, for each mole of "reaction", 2 moles of iron are produced. We therefore need to do these calculations based on 2 moles of Fe. In part (a) we determined 851 kJ of heat are released during this reaction. We need to compare that amount of heat to the heat required to melt the iron as described above.

$$q = \int_{298}^{1185} nC_p^{\alpha} dT + n\Delta H^{\alpha \rightarrow \gamma} + \int_{1185}^{1808} nC_p^{\gamma} dT + n\Delta H_{melting}$$

Assuming that the heat capacities are independent of temperature:

$$q = 2C_p^{\alpha}(1185 - 298 \text{ K}) + 2\Delta H^{\alpha \rightarrow \gamma} + 2C_p^{\gamma}(1808 - 1185 \text{ K}) + 2\Delta H_{melting}$$

$$q = 2 \text{ mol}(38 \text{ J/molK})(887 \text{ K}) + 2 \text{ mol}(900 \text{ J/mol}) + 2 \text{ mol}(34 \text{ J/molK})(623 \text{ K}) + 2 \text{ mol}(14900 \text{ J/mol})$$

$$q = 141.4 \text{ kJ}$$

Since 851 kJ are liberated during this reaction there is indeed enough heat to melt the iron. Note that we assumed that all the liberated heat would go into heating the iron, but there is also solid aluminum oxide as well. However, this is a first-approximation and agrees with the observations made during the reaction.