The Richard Stockton College of New Jersey
*Chemistry Program, School of Natural Sciences and Mathematics*
*PO Box 195, Pomoma, NJ*

CHEM 3410: Physical Chemistry I — Fall 2009

# Homework 5— Model Solutions

1. At constant temperature, we can write $dG$ as:

$$dG = VdP$$

Integrating this by applying the ideal gas law:

$$\Delta G = \int_{10.5}^{0.500} VdP = \int_{10.5}^{0.500} \frac{nRT}{P} dP = (2.5\ mol)(8.314\ J/molK)(350\ K)\ln\frac{0.500}{10.5}$$

$$\boxed{\Delta G = -22.1 \text{ kJ}}$$

2. The reaction of interest is:

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$$

The maximum other work possible (in this case, electrical work) is equal to $\Delta G_{rxn}$.

We can do this problem several ways. We can find $\Delta H_{rxn}$ and $\Delta S_{rxn}$ and use $\Delta G_{rxn} = \Delta H_{rxn} + T\Delta S_{rxn}$. However, most data tables also contain $\Delta G_f$ for the compounds in this reaction. We could therefore take $\Delta G_f$ of the products minus $\Delta G_f$ of the reactants.

$$\Delta G_{rxn} = [\Delta G_f(CO_2) + 2\Delta G_f(H_2O)] - \Delta G_f(CH_4)$$

$$\Delta G_{rxn} = (-394.4 + 2 * -237.1) - (-50.5)\ kJ/mol$$

$$\boxed{\text{Max Electrical Work} = \Delta G_{rxn} = -818.1 \text{ kJ/mol}}$$

3. Assuming everything behaves ideally:

$$\Delta\overline{G}_{mix} = RT(X_a \ln X_a + X_b \ln X_b)$$

$$\Delta\overline{S}_{mix} = -R(X_a \ln X_a + X_b \ln X_b)$$

(a) Forming one mole of air

$$\Delta G_{mix} = (8.314\ J/molK)(298.15\ K)(0.8 \ln 0.8 + 0.2 \ln 0.2)$$

$$\boxed{\Delta G_{mix} = -1240\ J = -1.24\ kJ}$$

$$\Delta S_{mix} = -(8.314\ J/molK)(0.8 \ln 0.8 + 0.2 \ln 0.2)$$

$$\boxed{\Delta S_{mix} = 4.16\ J}$$

(b) Mixing a total of 3 moles of gas

$$\Delta\overline{G}_{mix} = (8.314\ J/molK)(298.15\ K)(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3})$$

$$\boxed{\Delta G_{mix} = -1578\ J/mol \times 3\ mol = -4.74 \text{ kJ}}$$

$$\Delta\overline{S}_{mix} = -(8.314\ J/molK)(\frac{2}{3}\ln\frac{2}{3} + \frac{1}{3}\ln\frac{1}{3})$$

$$\boxed{\Delta S_{mix} = 5.29\ J/molK \times 3\ mol = 15.87\ \text{J/K}}$$

4. (a) We are at constant temperature, so:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 35\ kJ/mol - (310\ K)(0.088\ kJ/molK)$$

$$\boxed{\Delta G^\circ = 7.72\ \text{kJ/mol} > 0 \text{ so the process is not spontaneous}}$$

(b) If $\Delta H^\circ$ and $\Delta S^\circ$ don't change much with temperature, by increasing the temperature the $-T\Delta S^\circ$ term will become larger and eventually overcome the positive value of $\Delta H^\circ$. At that point, $\Delta G$ will become negative and the process will be spontaneous.

(c) At 39°C :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -4.0\ kJ/mol - (312\ K)(-0.012\ kJ/molK)$$

$$\boxed{\Delta G^\circ = -0.256\ \text{kJ/mol} < 0 \text{ so the process is spontaneous}}$$

(d) If again we assume that $\Delta H^\circ$ and $\Delta S^\circ$ don't change much with temperature, then as we increase the temperature the entropy term is going to get larger and remain positive. Therefore, at higher temperatures we would not expect the transition to be spontaneous.

(e) When the two phases are in equilibrium, $\Delta G = 0$. Using this and solving for $T$:

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-4000\ J/mol}{12\ J/molK}$$

$$\boxed{T = 333\ \text{K}}$$