THERMODYNAMICS PROBLEMS

1. Calculate ΔH°_{rxn} for the following reaction at 25 °C.

$4NH_3(g) + 5O_2(g) \rightarrow 4NO(g) + 6H_2O(g)$

$\Delta H^\circ_f [NO(g)] = 90.4 \frac{kJ}{mol}$ $\Delta H^\circ_f [H_2O(g)] = -241.8 \frac{kJ}{mol}$ $\Delta H^\circ_f [NH_3(g)] = -46.3 \frac{kJ}{mol}$

$\Delta H^\circ_{rxn} = (4)(90.4 \frac{kJ}{mol}) + (6)(-241.8 \frac{kJ}{mol}) - [(4)(-46.3 \frac{kJ}{mol}) + (5)(0)] =$ **$-904.0 \frac{kJ}{mol}$**

If you include moles as units for your coefficients: $\Delta H^\circ_{rxn} = -904.0$ kJ

2. Calculate the entropy change for $2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$

S° values: Na(s) = 51.05 J/mol•K, Cl_2(g) = 223.0 J/mol•K, NaCl(s) = 72.38 J/mol•K

$\Delta S^\circ_{rxn} = (2)\left(72.38 \frac{J}{K \cdot mol}\right) - (2)\left(51.05 \frac{J}{K \cdot mol}\right) - (1)\left(223.0 \frac{J}{K \cdot mol}\right) =$ **$-180.3 \frac{J}{K \cdot mol}$**

If you include moles as units for your coefficients: $\Delta S^\circ_{rxn} = -180.3 \frac{J}{K}$

3. a) Calculate ΔG, given ΔH = -227 kJ, ΔS = -309 J/K, T = 1450 K.

$\Delta G = \Delta H - T\Delta S$ $\Delta G = -227kJ - (1450K)\left(\frac{-309J}{K}\right)\left(\frac{1kJ}{1000J}\right) =$ **+221 kJ**

b) Is this process spontaneous at this temperature? If not, calculate the temperature (in °C) at which this reaction becomes spontaneous.

No, it is not spontaneous at 1450 K (ΔG is +)

Set ΔG = 0: $0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$

$T = \frac{-227kJ}{\left(-309\frac{J}{K}\right)\left(\frac{1kJ}{1000J}\right)}$ = 735 K -273 = 462 °C ⇐ T at equilibrium

ΔH and ΔS are both negative, so it is spontaneous at temperatures below 462 °C.

Spontaneous at T < 462 °C

3. **ΔG_f° in kJ/mol:**

CaO(s) -604.2 $Ca(OH)_2$(s) -896.8 H_2O(g) -228.6 H_2O(l) -237.2

Calculate ΔG° for these reactions and predict whether they will be spontaneous or not.

a) $2H_2O(g) \leftrightarrows 2H_2(g) + O_2(g)$

$\Delta G^\circ = -(2)\left(-228.6 \frac{kJ}{mol}\right) =$ **$457.2 \frac{kJ}{mol}$** (or **457.2 kJ**) +ΔG° so it is not spontaneous

b) $CaO(s) + H_2O(l) \leftrightarrows Ca(OH)_2(s)$

$\Delta G^\circ = (1)\left(-896.8 \frac{kJ}{mol}\right) - (1)\left(-604.2 \frac{kJ}{mol}\right) - (1)\left(-237.2 \frac{kJ}{mol}\right) =$ **$-55.4 \frac{kJ}{mol}$** (or **-55.4 kJ**)

b is spontaneous under standard state conditions (ΔG° is -)

4. ΔG^o is -24.7 kJ/mol for the formation of methanol.

   $C(s) + \frac{1}{2} O_2(g) + 2H_2(g) \leftrightarrows CH_3OH(g)$

   Calculate the equilibrium constant, K, at 25 °C for this reaction.

$$K = e^{\frac{-\Delta G}{RT}} = e^{\frac{-\left(-24.7\frac{kJ}{mol}\right)}{\left(8.314\frac{J}{K\cdot mol}\right)\left(\frac{1kJ}{1000J}\right)(298K)}} = e^{9.969} = \mathbf{2.14\times10^4}$$

5. a) At 25 °C, K_a for acetic acid is 1.8×10^{-5}. Predict the sign of ΔG^o at 25 °C for $CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$. Calculate ΔG^o at 25 °C.

   K < 1 so ΔG° will be +

   $\Delta G° = -RT \ln K = -(8.314\ \frac{J}{K\cdot mol})(298\ K)(\ln 1.8\times10^{-5}) =$ **$2.7\times10^4\ \frac{J}{mol}$ or $27\ \frac{kJ}{mol}$**

   b) Calculate ΔG at 25 °C for the acetic acid equilibrium reaction, when $[H_3O^+] = 0.020$ M, $[CH_3COO^-] = 0.010$ M, and $[CH_3COOH] = 0.10$ M. (Use ΔG^o from part b.)

   $\Delta G = \Delta G° + RT\ln Q \qquad Q = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$

$$\Delta G = 27\frac{kJ}{mol} + (8.314\times10^{-3}\ \frac{kJ}{K\cdot mol})(298\ K)\left(\ln\frac{[0.020][0.010]}{[0.10]}\right)$$

$$\Delta G = 27\frac{kJ}{mol} + (2.478\ \frac{kJ}{mol})(\ln 2.0\times10^{-3}) = 27\frac{kJ}{mol} + (2.478\ \frac{kJ}{mol})(-6.215)$$

$$\Delta G = 27\frac{kJ}{mol} - 15.4\ \frac{kJ}{mol} \quad \mathbf{\Delta G = 12\ \frac{kJ}{mol}\ or\ 1.2\times10^4\ \frac{J}{mol}}$$

   ⇒ Since $Q = 2.0\times10^{-3} > K = 1.8\times10^{-5}$, the reaction shifts left

   ⇒This is consistent with the **+ΔG value which tells us the reaction is not spontaneous in the forward direction**.

6. ΔG° for the reaction $H_2(g) + I_2(g) \leftrightarrows 2\ HI(g)$ is 2.60 kJ/mol at 25°C.
   In one experiment, the initial pressures are $P_{H_2} = 4.3$ atm, $P_{I_2} = 0.34$ atm, and $P_{HI} = 0.23$ atm. Calculate ΔG and predict the direction that this reaction will proceed.

   $\Delta G = \Delta G° + RT\ln Q \qquad Q = \frac{P_{HI}^2}{P_{H_2}P_{I_2}}$

$$\Delta G = 2.60\ \frac{kJ}{mol} + (8.314\times10^{-3}\ \frac{kJ}{K\cdot mol})(298\ K)\left(\ln\frac{(0.23)^2}{(4.3)(0.34)}\right)$$

$$\Delta G = 2.60\ \frac{kJ}{mol} + (2.478\ \frac{kJ}{mol})(\ln 0.0362) = 2.60\ \frac{kJ}{mol} + -8.22\frac{kJ}{mol} = \mathbf{-5.62\ \frac{kJ}{mol}}$$

Since ΔG is negative it will be spontaneous in the forward direction