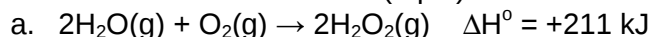


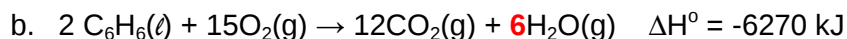
## Quiz 8 – Due in class Monday, November 6, 2017

Complete the following problems. You may work with one other student in the class, but you **may not** use your book, your notes, the Internet, or other human assistance. You may also turn in a single quiz for both students, for which each student will receive the same grade.

1. For each of the reactions below, determine which of the following applies: (1) spontaneous at all temperatures, (2) nonspontaneous at all temperatures, (3) spontaneous only at high temperatures, (4) spontaneous only at low temperatures. No calculations are necessary, but justify your answers in sentence or two. (9 pts)



The number of moles of gas decreases as reactants form products, therefore  $\Delta S^\circ$  is negative. Since  $\Delta H^\circ$  is positive, the reaction is nonspontaneous at all temperatures.



There was a typo in the quiz. There should have been 6 mol  $\text{H}_2\text{O}$  instead of 3, resulting in more moles of gas going to products and a positive  $\Delta S^\circ$ . Since  $\Delta H^\circ$  is negative as well, the reaction is spontaneous at all temperatures.



The number of moles of gas decreases as reactants form products, therefore  $\Delta S^\circ$  is negative. Since  $\Delta H^\circ$  is also negative, the reaction is spontaneous at low temperatures.

2. The conversion of ethanol to methanol is **not** spontaneous at all temperatures. Use the data below to determine at what temperature the spontaneity of the reaction changes. Is the reaction spontaneous at high temperatures or at low temperatures? (8 pts)



| Species                             | $\Delta H^\circ_f$ , kJ/mol | $S^\circ_f$ , J/mol K | $\Delta G^\circ_f$ , kJ/mol |
|-------------------------------------|-----------------------------|-----------------------|-----------------------------|
| C(g)                                | +716.7                      | +158.0                | +671.3                      |
| CO(g)                               | -110.5                      | +197.7                | -137.2                      |
| CH <sub>3</sub> OH(g)               | -200.7                      | +239.8                | -162.0                      |
| C <sub>2</sub> H <sub>5</sub> OH(g) | -235.1                      | +282.7                | -168.5                      |
| H <sub>2</sub> (g)                  | 0                           | +130.7                | 0                           |
| H <sub>2</sub> O(g)                 | -241.8                      | +188.8                | -228.6                      |

$$\begin{aligned}\Delta H^\circ_{\text{rxn}} &= \Delta H^\circ_{f, \text{CO}} + 2\Delta H^\circ_{f, \text{H}_2} + \Delta H^\circ_{f, \text{CH}_3\text{OH}} - (\Delta H^\circ_{f, \text{C}_2\text{H}_5\text{OH}} + \Delta H^\circ_{f, \text{H}_2\text{O}}) \\ \Delta H^\circ_{\text{rxn}} &= -110.5 \text{ kJ} + 2(0 \text{ kJ}) + (-200.7 \text{ kJ}) - ((-235.1 \text{ kJ}) + (-241.8 \text{ kJ})) \\ \Delta H^\circ_{\text{rxn}} &= +165.7 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ_{\text{rxn}} &= S^\circ_{f, \text{CO}} + 2S^\circ_{f, \text{H}_2} + S^\circ_{f, \text{CH}_3\text{OH}} - (S^\circ_{f, \text{C}_2\text{H}_5\text{OH}} + S^\circ_{f, \text{H}_2\text{O}}) \\ \Delta S^\circ_{\text{rxn}} &= +197.7 \text{ J/K} + 2(+130.7 \text{ J/K}) + (+239.8 \text{ J/K}) - ((+282.7 \text{ J/K}) + (+188.8 \text{ J/K})) \\ \Delta S^\circ_{\text{rxn}} &= +227.4 \text{ J/K}\end{aligned}$$

Since both  $\Delta H^\circ_{\text{rxn}}$  and  $\Delta S^\circ_{\text{rxn}}$  are positive, the reaction is spontaneous at high temperature. The spontaneity changes when  $\Delta H^\circ_{\text{rxn}} = T \Delta S^\circ_{\text{rxn}}$

$$T = \frac{\Delta H^\circ_{\text{rxn}}}{\Delta S^\circ_{\text{rxn}}} = \frac{+165.7 \text{ kJ}}{0.2274 \text{ J/K}} = 729 \text{ K}$$

3. The following data were obtained for the reaction  $2\text{NO}(g) + 2\text{H}_2(g) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(g)$ . Use the initial rate data to determine the rate law for the reaction, including the value of the rate constant, with units. (8 pts)

| Experiment | $[\text{NO}]_0$ (M) | $[\text{H}_2]_0$ (M) | Initial Rate (M/min) |
|------------|---------------------|----------------------|----------------------|
| 1          | 0.0100              | 0.0100               | 0.00600              |
| 2          | 0.0200              | 0.0300               | 0.144                |
| 3          | 0.0100              | 0.0200               | 0.0120               |

Comparing reactions 1 and 3:  $[\text{NO}]$  remains constant, but  $[\text{H}_2]$  changes by  $(0.0200/0.0100) = 2$  times. The rate changes by  $(0.0120/0.00600) = 2$  times. Since the change in rate is the same as the change in concentration, the reaction must be **first order in  $\text{H}_2$** .

We don't have a pair of experiments where  $\text{NO}$  changes and  $\text{H}_2$  stays the same, so we will have to work a little harder. Compare experiments 1 and 2 and write the rate expressions for each as  $\text{rate} = k[\text{NO}]^x[\text{H}_2]^1$ :

$$\frac{0.144 \text{ Mmin}^{-1}}{0.00600 \text{ Mmin}^{-1}} = \frac{k(0.0200)^x(0.0300)^1}{k(0.0100)^x(0.0100)^1}$$

$$24 = \frac{(0.0200)^x(3)}{(0.0100)^x}$$

$$8 = \frac{(0.0200)^x}{(0.0100)^x} = (2)^x$$

$$\begin{aligned} \log(8) &= x\log(2) \\ x &= \log(8)/\log(2) = 3 \end{aligned}$$

Therefore, the rate law must be:  $\text{Rate} = k[\text{NO}]^3[\text{H}_2]$

We can use any experiment to find the value of the rate constant. Let's use experiment 3:

$$k = \frac{\text{Rate}}{[\text{NO}]^3[\text{H}_2]} = \frac{0.012 \text{ Mmin}^{-1}}{(0.0100\text{M})^3(0.0200\text{M})} = 6.0 \times 10^5 \text{ M}^{-3}\text{min}^{-1}$$

**So, the overall rate law is:  $\text{Rate} = 6.0 \times 10^5 \text{ M}^{-3}\text{min}^{-1} [\text{NO}]^3[\text{H}_2]$**

|                                                                                  |                                          |                                                     |
|----------------------------------------------------------------------------------|------------------------------------------|-----------------------------------------------------|
| $\frac{a^x}{b^x} = \left(\frac{a}{b}\right)^x$                                   | $K = ^\circ\text{C} + 273.15$            | $q_{\text{lost}} = -q_{\text{gained}}$              |
| $q = mc\Delta T$                                                                 | $q = n_{\text{LR}}\Delta H_{\text{rxn}}$ | $q = m\Delta H$                                     |
| $\Delta S_{\text{universe}} = \Delta S_{\text{system}} - \Delta S_{\text{surr}}$ | $\Delta G = \Delta H - T\Delta S$        | $\Delta S_{\text{surr}} = -\Delta H_{\text{sys}}/T$ |