

Homework Assignment # 3 (Due April 9, 2020)

Chapter 5

1) Beginning with Equation (5.5), use Equation (5.6) to eliminate V_c and V_d to arrive at the result

$$w_{cycle} = -nR(T_{hot} - T_{cold}) \ln \frac{V_b}{V_a}$$

2) Consider the reversible Carnot cycle shown in Figure 5.2 with 1 mol of an ideal gas with $C_{V,m} = \frac{3}{2}R$ as the working substance. The initial isothermal expansion occurs at the hot reservoir temperature of $T_{hot} = 600$ °C from an initial volume of 3.50 L (V_a) to a volume of 10.0 L (V_b). The system then undergoes an adiabatic expansion until the temperature falls to $T_{cold} = 150$ °C. The system then undergoes an isothermal compression and a subsequent adiabatic compression until the initial state described by $T_a = 600$ °C and $V_a = 3.50$ L is reached.

- Calculate V_c and V_d .
- Calculate w for each step in the cycle and for the total cycle.
- Calculate ε and the amount of heat that is extracted from the hot reservoir to do 1.00 kJ of work in the surroundings.
- Calculate q , ΔU , and ΔH for each step in the cycle and for the total cycle.

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3) Calculate ΔS if the temperature of 1 mol of an ideal gas with $C_{V,m} = \frac{3}{2}R$ is increased from 150 to 350 K under conditions of (a) constant pressure and (b) constant volume.

4) One mole of an ideal gas with $C_{V,m} = \frac{3}{2}R$ undergoes the transformations described in the following list from an initial state described by $T = 300$ K and $P = 1.00$ bar. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- The gas is heated to 450 K at a constant external pressure of 1.00 bar.
- The gas is heated to 450 K at a constant volume corresponding to the initial volume.
- The gas undergoes a reversible isothermal expansion at 300 K until the pressure is half of its initial value.

5) One mole of an ideal gas with $C_{V,m} = \frac{5}{2}R$ undergoes the transformations described in the following list from an initial state described by $T = 250$ K and $P = 1.00$ bar. Calculate q , w , ΔU , ΔH , and ΔS for each process.

- a. The gas undergoes a reversible adiabatic expansion until the final pressure is half its initial value.
- b. The gas undergoes an adiabatic expansion against a constant external pressure of 0.500 bar until the final pressure is half its initial value.
- c. The gas undergoes an expansion against a constant external pressure of zero bar until the final pressure is equal to half of its initial value.

6) One mole of $\text{H}_2\text{O}(l)$ is supercooled to $-2.25\text{ }^\circ\text{C}$ at 1 bar pressure. The freezing temperature of water at this pressure is $0.00\text{ }^\circ\text{C}$. The transformation $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s)$ is suddenly observed to occur. By calculating ΔS , $\Delta S_{\text{surroundings}}$ and ΔS_{total} , verify that this transformation is spontaneous at $-2.25\text{ }^\circ\text{C}$. The heat capacities are given by $C_P(\text{H}_2\text{O}(l)) = 75.3\text{ J K}^{-1}\text{ mol}^{-1}$ and $C_P(\text{H}_2\text{O}(s)) = 37.7\text{ J K}^{-1}\text{ mol}^{-1}$, and $\Delta H_{\text{fusion}} = 6.008\text{ kJ mol}^{-1}$ at $0.00\text{ }^\circ\text{C}$. Assume that the surroundings are at $-2.25\text{ }^\circ\text{C}$. [*Hint*: Consider the two pathways at 1 bar: (a) $\text{H}_2\text{O}(l, -2.25\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25\text{ }^\circ\text{C})$ and (b) $\text{H}_2\text{O}(l, -2.25\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(l, 0.00\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, 0.00\text{ }^\circ\text{C}) \rightarrow \text{H}_2\text{O}(s, -2.25\text{ }^\circ\text{C})$. Because S is a state function, ΔS must be the same for both pathways.]

7) An ideal gas sample containing 2.50 mol for which $C_{V,m} = \frac{3}{2}R$ undergoes the following reversible cyclical process from an initial state characterized by $T = 450\text{ K}$ and $P = 1.00\text{ bar}$:

- a. It is expanded reversibly and adiabatically until the volume doubles.
- b. It is reversibly heated at constant volume until T increases to 450 K.
- c. The pressure is increased in an isothermal reversible compression until $P = 1.00\text{ bar}$.

Calculate q , w , ΔU , ΔH , ΔS , $\Delta S_{\text{surroundings}}$, and ΔS_{total} for each step in the cycle, and for the total cycle. The temperature of the surroundings is 300 K.

8) One mole of a van der Waals gas at $27\text{ }^\circ\text{C}$ is expanded isothermally and reversibly from an initial volume of 0.020 m^3 to a final volume of 0.060 m^3 . For the van der Waals gas,

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V_m^2}. \text{ Assume that } a = 0.556\text{ Pa m}^6\text{ mol}^{-2}, \text{ and that}$$

$b = 64 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$. Calculate q , w , ΔU , ΔH , and ΔS for the process.

9) 15.0 grams of steam at 373 K is added to 250.0 g of $\text{H}_2\text{O}(l)$ at 298 K at a constant pressure of 1 bar. Is the final state of the system steam or liquid water? Calculate ΔS for the process.

Chapter 6

1) A sample containing 2.50 mol of an ideal gas at 298 K is expanded from an initial volume of 10.0 L to a final volume of 50.0 L. Calculate ΔG and ΔA for this process for (a) an isothermal

reversible path and (b) an isothermal expansion against a constant external pressure of 0.750 bar. Explain why ΔG and ΔA do or do not differ from one another.

2) Calculate $\Delta G_{\text{reaction}}^{\circ}$ for the reaction $\text{CO}(g) + \frac{1}{2} \text{O}_2(g) \leftrightarrow \text{CO}_2(g)$ at 298.15 K. Calculate $\Delta G_{\text{reaction}}^{\circ}$ at 650 K assuming that $\Delta H_{\text{reaction}}^{\circ}$ is constant in the temperature interval of interest.

3) Consider the equilibrium $\text{NO}_2(g) \leftrightarrow \text{NO}(g) + 1/2\text{O}_2(g)$. One mole of $\text{NO}_2(g)$ is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the contents of the vessel gives the following results:

T	700 K	800 K
$\frac{P_{\text{NO}}}{P_{\text{NO}_2}}$	0.872	2.50

a. Calculate K_P at 700 and 800 K.

b. Calculate $\Delta G_{\text{reaction}}^{\circ}$ and $\Delta H_{\text{reaction}}^{\circ}$ for this reaction at 298.15 K. Assume that $\Delta H_{\text{reaction}}^{\circ}$ is independent of temperature.

4) If the reaction $\text{Fe}_2\text{N}(s) + 3/2\text{H}_2(g) \leftrightarrow 2\text{Fe}(s) + \text{NH}_3(g)$ comes to equilibrium at a total pressure of 1 bar, analysis of the gas shows that at 700 and 800 K, $\frac{P_{\text{NH}_3}}{P_{\text{H}_2}} = 2.165$ and 1.083, respectively, if only $\text{H}_2(g)$ was initially present in the gas phase and $\text{Fe}_2\text{N}(s)$ was in excess.

a. Calculate K_P at 700 and 800 K.

b. Calculate $\Delta S_{\text{reaction}}^{\circ}$ at 700 and 800 K and $\Delta H_{\text{reaction}}^{\circ}$, assuming that it is independent of temperature.

c. Calculate $\Delta G_{\text{reaction}}^{\circ}$ for this reaction at 298.15 K.

5) The pressure at the center of the earth is probably greater than 3×10^6 atm, and the temperature there is about 4000 °C. What is the change in the Gibbs function of reaction on going from crust to core for a reaction in which $\Delta V_m = 1 \text{ cm}^3 \text{ mol}^{-1}$ and $\Delta S_m = 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$? Does the pressure or temperature effect dominate in determining the change?

6) A sample containing 2.25 moles of He (1 bar, 298 K) is mixed with 3.00 mol of Ne (1 bar, 298 K) and 1.75 mol of Ar (1 bar, 298 K). Calculate ΔG_{mixing} and ΔS_{mixing} .