Homework #4

Chapter 21
1. McQuarrie and Simon Problems: 4,5,12,14,40,43
2. a) Given the partition function of a diatomic gas:
\[ q(V, T) = \left( \frac{2\pi M k_B T}{h^2} \right)^{3/2} V \frac{T}{\theta_{rot}} \frac{\Theta_{vib}}{1-e^{-\Theta_{vib}/T}} g_v e^{D_v/k_B T} \]
where \( Q(N, V, T) = \frac{q^N}{N!} \)

find an equation for the standard molar entropy.

b) Use your answer from part 2a) and the data in Chapter 18 to calculate the standard molar entropy of CO(g) at its standard boiling point, 81.6 K.

c) Compare your answer from part 2b) with the experimental value of 155.6 J·K\(^{-1}\)·mol\(^{-1}\). Why is there a discrepancy of about 5 J·K\(^{-1}\)·mol\(^{-1}\)?

Chapter 22
1. The molar enthalpy of vaporization of benzene at its normal boiling points (80.09 °C) is 30.72 kJ/mol. Assuming that \( \Delta_{vap} H \) and \( \Delta_{vap} S \) are temperature independent, calculate the value of \( \Delta_{vap} G \) at 75 °C, 80.09 °C, and 85.0 °C. Explain your results.

2. Use the van der Waals equation to derive an expression for \( \Delta (\bar{U}(T, \bar{V}) - \bar{U}_{id}(T, \bar{V})) \). Use your result along with the van der Waals equation to calculate the value of \( \bar{U}(T, \bar{V}) \) for ethane at 400 K given that \( \bar{U}_{id}(T, \bar{V}) = 14.55 \text{ kJ/mol} \). (Display results graphically like Fig 22-3). To do this, use a range of \( \bar{V} \) of 0.0700 L/mol to 7.00 L/mol and calculate both \( \bar{U}(T, \bar{V}) \) and \( P(T, \bar{V}) \).

3. Determine \( \bar{C}_p - \bar{C}_v \) for a gas that obeys the equation:
   a. \( P(\bar{V} - b) = RT \)
   b. \( PV = nRT \)

4. What are the natural variables of the entropy? Explain your answer briefly.

5. Starting from \( dU = TdS - PdV \) derive the Maxwell equation below:
\[ \left( \frac{\partial T}{\partial V} \right)_S = -\left( \frac{\partial P}{\partial S} \right)_V \]

6. How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37 °C (i.e., blood temperature)? The standard entropy of reaction is 182.4 J·K\(^{-1}\)·mol\(^{-1}\). [Hint: Find other necessary values on NIST.] How is this related to the maximum non-PV work?

7. Calculate \( \Delta_r G(375K) \) for the reaction \( 2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \) from the appropriate values of \( \Delta_r G(298K), \Delta_r H(298K) \), and the Gibbs-Helmholtz equation. [Again, you may need to use NIST or another thermodynamic table.]

8. When 2 moles of gas at 330 K and 3.50 atm is subjected to isothermal compression, the entropy drops by 25.0 J/K. Find the final pressure and the Gibbs free energy.
9. For each of the following processes, state which of the quantities $\Delta U$, $\Delta H$, $\Delta S$, $\Delta A$, and $\Delta G$ are equal to zero:
   a. Isothermal reversible expansion of an ideal gas
   b. Adiabatic reversible expansion of a non-ideal gas
   c. Vaporization of liquid water at 80 °C and 1 bar pressure.
   d. Vaporization of liquid water at 100 °C and 1 bar pressure.
   e. Reaction between $H_2$ and $O_2$ in a thermally insulated bomb.

For Presentation (Oct 26):
Group J: Chapter 21, M&S #14
Group A: Chapter 22, #2

Note to Group B: You’ll be presenting on the next set of homework, not this one.