CHM225 Problem Set #2– October 6, 2008

1. Compute the efficiency of a Carnot cycle engine using a Van der Waals gas as the working substance. How does your result compare with that for a Carnot cycle using an ideal gas as the working substance? Discuss your results.

2. Prove that two reversible adiabatic lines in a PV-diagram cannot intersect. Hint: assume they do intersect and show there is a contradiction.

3. Suppose that Kelvin's statement of the second law is false and Clausius' statement is true. The false Kelvin engine #1 converts heat $q'^{(a)}$ taken from a reservoir completely to work $-w$ on the surroundings. The true Clausius heat engine #2 takes heat $q^{(a)}$ from a hot reservoir, performs work $-w$ on the surroundings, and rejects heat $-q^{(b)}$ into the cold reservoir. Use the work produced in the Kelvin heat engine #1 to drive the Clausius engine #2 in reverse and show there is a violation of Clausius' statement of the second law.

4. A nonideal Van der Waals gas undergoes a reversible isothermal expansion from V_1 to V_2. Compute the entropy change and compare it with that for an ideal gas undergoing a reversible isothermal expansion between the same volumes.

5. Consider a reaction $R \rightleftharpoons P$ and suppose a catalyst is able to shift the equilibrium towards products P. Furthermore, suppose the reaction $R \to P$ is exothermic. If the above is true, then, starting with the reacting system at equilibrium with no catalyst present, the addition of catalyst will cause the system to evolve to a new equilibrium state with the evolution of heat. Given these conditions, construct a cycle and show that Kelvin's statement of the second law is violated.

6. We discussed the fact that the heat and work in a process that takes the system from state 1 to state 2 depend on the path taken between the system states. The integrals of dq and dw that we perform are line integrals since their values depend on the path or "line" that connects the states. To illustrate this concept consider the differential,

$$df = ydx + x^2dy,$$

and calculate its line integral from state $1 = (x_1, y_1)$ to state $2 = (x_2, y_2)$ along two different paths:

(a) increase x from x_1 to x_2 at fixed $y = y_1$, then increase y from y_1 to y_2 at fixed $x = x_2$;

(b) increase y from y_1 to y_2 at fixed $x = x_1$, then increase x from x_1 to x_2 at fixed $y = y_2$.

Is f a state function? Next consider $df/(x^2y)$ and repeat the calculation. Is $df/(x^2y)$ the differential of a state function? If so, what is it?