Example Problem 6.1

Calculate the change in entropy of n moles of an ideal gas that undergo quasi-static processes a and b from an initial state (T_0, P_0, V_0) to a final state (T_0, P_1, V_1). Then redo the calculation for n moles of gas making the change via process c.

a. *isobaric quasi-static expansion, (T_0, P_0, V_0) to (T_1, P_0, V_1).*

b. *isochoric quasi-static heating, (T_1, P_0, V_1) to (T_0, P_1, V_1).*

c. *isothermal expansion, (T_0, P_0, V_0) to (T_0, P_1, V_1).*

Solution 6.1

Because processes a and b are quasi-static, any heat added to the gas is dq_{rev} and related to the entropy change by $dS = \frac{dq_{rev}}{T}$.

$$\Delta S = n\int_{T_0}^{T_1} \frac{\overline{C}_p dT}{T} + n\int_{T_1}^{T_0} \frac{\overline{C}_v dT}{T}$$

$$\Delta S = n\overline{C}_p \ln\frac{T_1}{T_0} + n\overline{C}_v \ln\frac{T_0}{T_1}$$

$$\Delta S = n(\overline{C}_p - \overline{C}_v) \ln\frac{T_1}{T_0}$$

For an ideal gas $\overline{C}_p - \overline{C}_v = R$ and using the ideal gas law $\frac{T_1}{T_0} = \frac{V_1}{V_0}$.

$$\Delta S = nR\ln\frac{V_1}{V_0}$$

Now for process c we can use the first law and the fact that the internal energy is only a function of temperature to write $dq = -w = PdV = \frac{nRTdV}{V}$. This is the same heat that would be added during reversible isothermal expansion.

$$dS = \frac{dq_{rev}}{T}$$

$$\Delta S = \int_{V_0}^{V_1} \frac{nRdV}{V}$$

$$\Delta S = nR\ln\frac{V_1}{V_0}$$

This illustrates that the entropy is indeed a state function for an ideal gas.

Example Problem 6.2

In class Professor Carter showed that the entropy of an ideal gas is a function of state as it is a perfect differential.

$$dS = \frac{C_v}{T}dT - \frac{nR}{V}dV$$

From this an alternate definition of the heat capacity at constant volume and molar volume are:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_v}{T} \text{ and } \left(\frac{\partial S}{\partial V}\right)_T = -\frac{R}{\overline{V}}$$

He also introduced the Gibbs Free energy $G = U - TS + PV$. Using the differential form of the Gibbs Free energy write alternate expressions for the entropy and volume.

Solution 6.2
First lets write the Gibbs Free energy in it's differential form for an ideal gas.

$$G = U - TS + PV$$
$$dG = dU - TdS - SdT + PdV + VdP$$
$$dG = (TdS - PdV) - TdS - SdT + PdV + VdP$$
$$dG = VdP - SdT$$

Now on examining the first derivatives we can see: $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$. There are many other consequences of the form of the Gibbs Free energy that will be examined later in the course.

Example Problem 6.3
A kilo of liquid water transforms to ice in a giant freezer at atmospheric pressure and the melting temperature. Given the latent heat of fusion, $L_f = 334 kJ/kg$, calculate the molar entropy of fusion for water, S_f.

Solution 6.3
The latent heat of fusion is the heat given off by a liquid when it transforms to a solid at the melting temperature and pressure. For the freezer: $\Delta S_{freezer} = \frac{L_f}{T}$.This is a reversible transformation. So $\Delta S_{universe} = 0$ and therefore $\Delta S_{water} = -\Delta S_{freezer}$. The latent entropy of fusion is the entropy change of the solid upon melting.

$$S_f = -\Delta S_{water} = \Delta S_{freezer} = \frac{334 kJ/kg}{273.15K} * \frac{0.018kg}{1mole} = 22\frac{J}{mole \ K}$$

It should be noted that the latent heat of fusion and entropy of fusion are reported as positive numbers. So the interpretation could be that each is the change in that property of the system on melting or the change in that property of the surroundings on freezing.