Problem Set 12 Solutions

1. *What is the increase in entropy of one gram of ice at $O^o C$ is melted and heated to $50^o C$?*

   The change in entropy is given by $dS = \frac{dQ}{T}$. In this case, the dQ must be calculated in two pieces. First there is the heat needed to melt the ice, and then there is the heat needed to raise the temperature of the system. Therefore,

   $$\Delta Q = mL_f + mc_w \Delta T$$

   where $m = 1\,g$ is the total mass of the system, $L_f = 80\,cal/g$ is the heat of fusion, and $c_w = 1\,cal/(g \cdot K)$ is the specific heat of water. Thus, the total change in entropy is

   $$\Delta S = \frac{mL_f}{T_i} + \int_{T_i}^{T_f} mc_w \frac{dT}{T}$$

   where $T_i = 0^o C = 273K$ and $T_f = 50^o C = 323K$. Plugging in numbers, and remembering that we always use temperatures in Kelvin,

   $$\Delta S = \frac{(1\ g)(80\ cal/g)}{273K} + \int_{273}^{323} (1\ cal/g)(1\ g)\frac{dT}{T}$$
   $$= \frac{80}{273}\ cal/K + \ln\left(\frac{323}{273}\right)\ cal/K$$
   $$\Delta S = 0.461\ cal/K$$

2. *Find the change in entropy if $500\ g$ of water at $80^o\ C$ is added to $300\ g$ of water at $20^o\ C$.*

   The total amount of water is $800g$, so the final temperature of the system is given by

   $$\left(\frac{5}{8}\right)353K + \left(\frac{3}{8}\right)293K = 330.5K$$

   For $m_1 = 500\ g$ and $m_2 = 300\ g$, the entropy change is given by

   $$\Delta S = \int \frac{dQ}{T}$$
   $$= \int_{353}^{330.5} c_w m_1 \frac{dT}{T} + \int_{293}^{330.5} c_w m_2 \frac{dT}{T}$$
   $$= c_w \left(m_1 \ln \frac{330.5}{353} + m_2 \ln \frac{330.5}{293}\right).$$

   c_w is the specific heat of water which is $1\ cal/(g \cdot K)$, so substituting in numbers,

   $$\Delta S = 3.20\ cal/K.$$

   (Please note this answer is very sensitive to roundoff. Changing $330.5K$ to $331K$ gives $4.4\ cal/K$.)

3. *Consider a mole of a gas initially at $1 \equiv (P_1, V_1)$ and finally at $2 \equiv (P_2, V_2)$. Since $S_2 - S_1$ is path independent, choose the simple path shown in Figure (1) by first changing pressure at constant volume and then volume at constant pressure. Let $0 = (P_0, T_0)$ be the intermediate point you go through. Show that*

   $$S_2 - S_1 = C_P \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right).$$

   Show that if 1 and 2 lie on an adiabatic curve, this difference vanishes. Assume $C_p = C_V + R$, but not a particular value to C_V.

We know from the first law of thermodynamics that

$$dU = dQ - PdV.$$

Therefore, $dQ = dU + PdV$. For an ideal gas, $dU = C_v NdT$ and $P = NRT/V$. For one mole of gas we have that

$$dQ = C_v dT + RT\frac{dV}{V}.$$

Now, $dS = dQ/T$, so dividing the above equation by T we have

$$dS = C_v\frac{dT}{T} + R\frac{dV}{V}. \tag{1}$$

From here, you could plug in that $T = PV/(NR)$ and $dT = \frac{1}{NR}(PdV + VdP)$ to get

$$dS = C_v\frac{dP}{P} + (C_v + R)\frac{dV}{V}.$$

Then you could first integrate along constant pressure ($dP = 0$) and then constant volume ($dV = 0$) and simplify the resulting expression to find the answer. However, there is no reason we cannot directly integrate equation 1 from point 1 to point 2 to find that

$$S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}.$$

Now, we know that $\frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2}$ by the ideal gas law. Plugging this in for $\frac{V_2}{V_1}$ we have

$$S_2 - S_1 = C_v \ln\frac{T_2}{T_1} + R\ln\frac{T_2 P_1}{T_1 P_2}$$
$$= C_v \ln\frac{T_2}{T_1} + R\ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2}$$
$$S_2 - S_1 = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

where $C_p = C_v + R$..

If 1 and 2 are on an adiabatic curve, then $dQ = 0$ which means that we know dS must equal zero. We see this by remembering that then $PV^\gamma = constant$ where $\gamma = C_p/C_v$. Therefore,

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^\gamma$$
$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}.$$

Plugging this into the equation for $S_2 - S_1$ we find that

$$S_2 - S_1 = C_p \ln\left(\frac{V_1}{V_2}\right)^{\gamma-1} - R\ln\left(\frac{V_1}{V_2}\right)^\gamma$$
$$= C_p(\gamma - 1)\ln\frac{V_1}{V_2} - R\gamma\ln\frac{V_1}{V_2}$$
$$= C_p(\frac{C_p - C_v}{C_v})\ln\frac{V_1}{V_2} - R\gamma\ln\frac{V_1}{V_2}$$
$$= R(\frac{C_p}{C_v})\ln\frac{V_1}{V_2} - R\gamma\ln\frac{V_1}{V_2}$$
$$= R\gamma\ln\frac{V_1}{V_2} - R\gamma\ln\frac{V_1}{V_2}$$
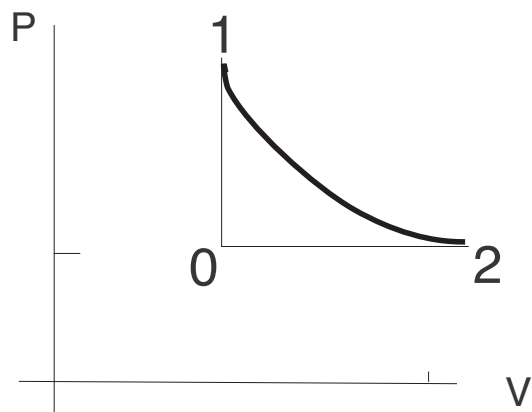$$S_2 - S_1 = 0$$

as desired.

FIG. 1: To compute entropy difference $S_2 - S_1$ go from 1 to 0 at constant volume and then from 0 to 2 at constant pressure.