

Solutions to Homework Problem Set 9

Reif 4.1

(a) We use the second law $dS = dQ/T$ to derive the entropy change. For the water, the net entropy change is given by $\Delta S = \int \frac{C}{T} dT = \int \frac{mc}{T} dT = m \ln \frac{T_f}{T_i} = m \ln \frac{373\text{K}}{273\text{K}} = 1.31 \times 10^3 \text{ J/K}$. Here the mass of water $m = 1000\text{g}$ and the specific heat of water $c = 4.18\text{J/K/g}$.

The entropy change in the heat reservoir can be approximated by $\Delta S' = \frac{Q'}{T'}$ where $Q' = -Q = -C\Delta T$. As $\Delta T = 100\text{K}$, $Q' = -Q = -418000\text{J}$. The entropy change in the heat reservoir is then $\Delta S' = \frac{-418000\text{J}}{373\text{K}} = -1.12 \times 10^3 \text{ J/K}$.

So the net change of entropy of the combined system is $\Delta S_0 = \Delta S + \Delta S' = 190 \text{ J/K}$.

(b) For the water, the net entropy change in the two stages can be derived by $\Delta S = \int_{T=273\text{K}}^{T=323\text{K}} dS + \int_{T=323\text{K}}^{T=373\text{K}} dS = \int_{T=273\text{K}}^{T=323\text{K}} \frac{C_V dT}{T} + \int_{T=323\text{K}}^{T=373\text{K}} \frac{C_V dT}{T}$. As the heat capacity of water is nearly constant independent of temperature variations, the above integral can be written as $\Delta S = C \ln(373/323) + C \ln(323/273) = C \ln(373/273) = m \ln(373/273) = 1.31 \times 10^3 \text{ J/K}$.

The entropy change in the heat reservoir can be approximated by $\Delta S' = \frac{Q'}{T'}$ where $Q' = -Q = -C\Delta T$. As $\Delta T = 50\text{K}$ in both stages, $Q' = -Q = -209000\text{J}$ is the same in both stages. The total entropy change in the heat reservoir in the two stages is then $\Delta S' = \frac{-209000\text{J}}{323\text{K}} + \frac{-209000\text{J}}{373\text{K}} = -1.21 \times 10^3 \text{ J/K}$

The net entropy change in the combined systems is then $\Delta S_0 = \Delta S + \Delta S' = 100 \text{ J/K}$.

(c) Comparing the results from (a) and (b), it is seen intuitively that, if the water is gradually heated by letting it in contact successively with many heat reservoirs with infinitesimally increasing temperatures, the net entropy change in the combined systems will reduce to zero.

A more rigorous mathematical proof is as such: during the above process, at each step, the water and the heat reservoir is nearly in thermal equilibrium, $T' = T + dT$, where dT is the infinitesimal temperature difference between the system and heat reservoir, and $dQ = -dQ'$. Therefore,

$$dS' = \frac{dQ'}{T'} = \frac{-dQ}{T + dT} = -\frac{dQ}{T} \left(1 - \frac{dT}{T} + O\left(\frac{dT}{T}\right)\right)$$

Note that in the last step Taylor expansion is used, and $O\left(\frac{dT}{T}\right)$ includes all higher (≥ 2) order terms. As both dQ and dT/T are first order terms, $dQ \times dT/T$ are second order terms. We can discard all higher than first-order terms to arrive at

$$dS' = -\frac{dQ}{T} = -dS$$

Therefore, the net entropy change in the entire system is $dS_0 = dS + dS' = 0$. This is the quasi-static process of heating the system.

Reif 5.3

(a) The molar heat capacity is $c_V = \frac{1}{n} \partial E / \partial T)_V = \frac{5}{2} R$.

(b) The work done by the gas is the total area covered under the curve A-B-C, which is the sum area of 6.5 square cells, each having an area of 2×10^9 dynes cm = 200 J. So $W = 6.5 * 200 \text{ J} = 1300 \text{ J}$. As the gas is expanding, it does the work, so W is positive.

(c) First we need to find the change in internal energy. For an ideal gas, the internal energy is only a function of temperature, so $\Delta E = \int c_V dT$ (for one mole gas). As c_V is a constant, $\Delta E = c_V \Delta T = \frac{5}{2} R (T_C - T_A) = \frac{5}{2} R (P_C V_C - P_A V_A) / R = \frac{5}{2} (P_C V_C - P_A V_A) = 1500 \text{ J}$. Note that the ideal gas law (equation of state) $PV = RT$ is used to derive the above result.

(d) Since c_V is a constant, for one mole ideal gas, we can directly use the result

$$\Delta S = c_V \ln\left(\frac{T_C}{T_A}\right) + R \ln\left(\frac{V_C}{V_A}\right) = \frac{5}{2} R \ln\left(\frac{P_C V_C}{P_A V_A}\right) + R \ln\left(\frac{V_C}{V_A}\right) = \frac{5}{2} R \ln\left(\frac{P_C}{P_A}\right) + \frac{7}{2} R \ln\left(\frac{V_C}{V_A}\right) = 2.83 R = 23.5 \text{ J/K}$$