Problem 4.2–3 Free Expansion of Ideal Gas

In general:

$$dS = \frac{1}{T}dU - \frac{P}{T}dV + \frac{\mu}{T}dN$$

Since U of ideal gas is independent on volume (dU=0), and N = const in the process:

$$dS = \frac{P}{T}dV = \frac{NR}{V}dV$$

In a series of infinitesimal free expansions, entropy changes by:

$$\Delta S == \int_{V_i}^{V_f} \frac{NR}{V}dV = NR\ln\left(\frac{V_f}{V_i}\right)$$

Note that free expansion is always irreversible ΔS>0.

Problem 4.2 – 4 Temperature and entropy change in free expansion

The equations of state: $$T = \frac{Av^2}{s} \qquad P = -2Av\ln\left(\frac{s}{s_0}\right)$$

Given the initial temperature T_0, molar volume v_0, and final molar volume v_f, find the final temperature and increase in molar entropy Δs.

Solution:

Since equations of state involve v and s as independent extensive variables, it is convenient to find the fundamental relation in the *energy* representation:

$$du = Tdu - Pdv$$

$$du = \frac{Av^2}{s}ds + 2Av\ln\left(\frac{s}{s_0}\right)dv \xrightarrow{\text{integrating}} \boxed{u = Av^2\ln\left(\frac{s}{s_0}\right) + C}$$

Problem 4.2 – 4 Temperature and entropy change in free expansion

$$\boxed{u = Av^2 \ln\left(\frac{s}{s_0}\right) + C}$$

In the free expansion process, no work is done on the system and no heat is transferred to the system if it is adiabatically insulated form the environment. Therefore, the energy of the system does not change in the free expansion process:

$$\boxed{u_f = u_i}$$

$$Av_0^2 \ln\left(\frac{s_i}{s_0}\right) = Av_f^2 \ln\left(\frac{s_f}{s_0}\right)$$

Note that s_0 is not the initial entropy, it is just a constant (this may be a source of some confusion). Otherwise we would get $s_f = s_0$ in the irreversible free expansion process.

Problem 4.2 – 4 Temperature and entropy change in free expansion

$$Av_0^2 \ln\left(\frac{s_i}{s_0}\right) = Av_f^2 \ln\left(\frac{s_f}{s_0}\right) \Rightarrow \ln\left(\frac{s_i}{s_0}\right)^{v_0^2} = \ln\left(\frac{s_f}{s_0}\right)^{v_f^2} \Rightarrow$$

$$\left(\frac{s_i}{s_0}\right)^{v_0^2} = \left(\frac{s_f}{s_0}\right)^{v_f^2} \Rightarrow \left(\frac{s_i}{s_0}\right)^{\frac{v_0^2}{v_f^2}} = \frac{s_f}{s_0} \Rightarrow s_f = s_0\left(\frac{s_i}{s_0}\right)^{\frac{v_0^2}{v_f^2}}$$

$$T_f = \frac{Av_f^2}{s_f} \Rightarrow T_f = \frac{Av_f^2}{s_0}\left(\frac{s_0}{s_i}\right)^{\frac{v_0^2}{v_f^2}} \Rightarrow \boxed{T_f = \frac{Av_f^2}{s_0}\left(\frac{T_0 s_0}{Av_0^2}\right)^{\frac{v_0^2}{v_f^2}}}$$

$$\Delta s = s_f - s_i = \frac{Av_f^2}{T_f} - \frac{Av_0^2}{T_0} \Rightarrow \boxed{\Delta s = s_0\left(\frac{Av_0^2}{T_0 s_0}\right)^{\frac{v_0^2}{v_f^2}} - \frac{Av_0^2}{T_0}}$$

Problem 4.4 – 1 Heat Exchange between Two Identical Objects

Conservation of energy demands:

$$\Delta U = \int_{T_{10}}^{T_f} C_1(T_1)\,dT_1 + \int_{T_{20}}^{T_f} C_2(T_2)\,dT_2 = 0$$

where T_f is the final temperature of each body. Therefore:

$$AT_{10} + \frac{B}{2}T_{10}^2 + AT_{20} + \frac{B}{2}T_{20}^2 = 2\left(AT_f + \frac{B}{2}T_f^2 \right)$$

Solving for T_f

$$T_f = \frac{1}{2}\sqrt{\left(\frac{2A}{B} + T_{10} + T_{20}\right)^2 + (T_{10} - T_{20})^2} - \frac{A}{B} = 307.1[K]$$

Note that T_f is not the average temperature since the heat capacities depend on T

Problem 4.4 – 1 Heat Exchange between Two Identical Objects

The change of entropy of the two systems in this process can be found from the expression below, where we have taken into account that no work is done in the process

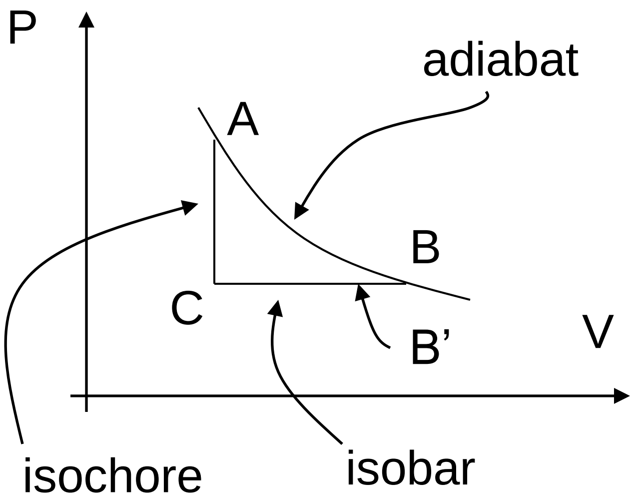
$$\Delta S = \int_{T_{10}}^{T_f} \frac{\delta Q_1}{T_1}{}_1 + \int_{T_{20}}^{T_f} \frac{\delta Q_2}{T_2} = \int_{T_{10}}^{T_f} \frac{C_1 dT_1}{T_1} + \int_{T_{20}}^{T_f} \frac{C_2 dT_2}{T_2} = \int_{T_{10}}^{T_f} \frac{A + BT_1}{T_1} dT_1 + \int_{T_{20}}^{T_f} \frac{A + BT_2}{T_2} dT_2$$

Integrating, we obtain:

$$\Delta S = A \ln\left(\frac{T_f}{T_{10}}\right) + B\left(T_f - T_{10}\right) + A \ln\left(\frac{T_f}{T_{20}}\right) + B\left(T_f - T_{20}\right)$$

$$\Delta S = A \ln\left(\frac{T_f^2}{T_{10} T_{20}}\right) + B\left(2T_f - T_{10} - T_{20}\right) = 1.6\left[\frac{J}{K}\right]$$

Problem 4.5 – 6 Maximum work theorem



1. The system delivers a non-zero work during the adiabatic process A – B: $W_{AB} > 0$.

2. Since the process is adiabatic, no heat flows between the system and the reversible heat source (RHS): $Q_{AB} = 0$.

3. From the conservation of energy and the above two statements, the internal energy of the system decreases in this process $\Delta U_{AB} < 0$.

4. Since energy is a monotonically increasing function of temperature, temperature of the system decreases in the process A – B: $T_B < T_A$.

5. Since temperature is a function of the state only, it also decreases in the process A – C – B.

6. Since $W_{ACB} < W_{AB}$ and $\Delta U_{AB} = \Delta U_{ACB}$, we conclude from the conservation of energy that heat flows from the system to the reversible heat sink during the A-C-B process $Q_{ACB}>0$.

7. Entropy of the composite system (system + reversible heat source) increases every time there is heat transfer between the system and the RHS and $T_{system} \neq T_{RHS}$ (irreversible process).

8. For example, at point B' on the isobar close to point B, $T_{system} < T_A \leq T_{RHS}$ because positive heat has been transferred to the RHS during the ACB' process $Q_{ACB}>0$.

9. Since $T_{system} \neq T_{RHS}$ during the B' - B process, the B' – B process is irreversible and thus the whole A-C-B process is irreversible.

Problem 4.5 – 11 Heat Flow between Two Different Objects

Maximum work can be obtained from the two bodies in a reversible process where the total change of entropy of the two bodies is zero:

$$0 = \Delta S = \Delta S_1 + \Delta S_2 = \int_{T_{10}}^{T_f} \frac{\delta Q_1}{T_1} + \int_{T_{20}}^{T_f} \frac{\delta Q_2}{T_2} = \int_{T_{10}}^{T_f} \frac{C_1}{T_1} dT_1 + \int_{T_{20}}^{T_f} \frac{C_2}{T_2} dT_2 = a\left(T_f - T_{10}\right) + 2b\left(T_f - T_{20}\right)$$

In the above expression we replaced δQ with dU since the process was carried out at constant volumes of both bodies, so no work was done by the bodies ***directly***. The bodies act as hot and cold bodies of a typical heat engine.

Solving for T_f:

$$T_f = \frac{aT_{10} + 2bT_{20}}{a + 2b}$$

The change of energy of the two bodies only depends on the initial and final states and is given by:

$$\Delta U = \int_{T_{10}}^{T_f} C\left(T_1\right) dT_1 + \int_{T_{20}}^{T_f} C\left(T_2\right) dT_2 = \int_{T_{10}}^{T_f} aT_1 dT_1 + \int_{T_{20}}^{T_f} 2bT_2 dT_2 = \frac{a}{2}\left(T_f^2 - T_{10}^2\right) + b\left(T_f^2 - T_{20}^2\right)$$

Substituting the expression for T_f

$$\Delta U = -\frac{ab}{a + 2b}\left(T_{10} - T_{20}\right)^2$$

The maximum work is negative of ΔU:

$$W_{\max} = \frac{ab}{a + 2b}\left(T_{10} - T_{20}\right)^2 > 0$$

Problem 4.6 – 2 Efficiency of the heat pump

Efficiency of a reversible heat pump:

$$\varepsilon = \frac{\delta Q}{\delta W} = \frac{T_h}{T_h - T_c}$$

$$T_h = 294.26K$$

$$T_c = 283.15K$$

$$\varepsilon = 26.5$$

When calculating efficiencies (and many other quantities) in thermodynamics, one needs to use the absolute temperature scale (Kelvin scale).

Indeed, there is nothing special about zero Celsius of Fahrenheit, but if you use Celsius or Fahrenheit in the equation above, your efficiency always turns to zero if the hot system is at zero degrees independent on the temperature of the cold body. This is unphysical because zero of Celsius or Fahrenheit temperature scale is to a large degree arbitrary.

The Kelvin scale is the absolute temperature scale (zero Kelvin is the lowest temperature possible) and should always be used in thermodynamics. Convert temperature to Kelvins before using it in a thermodynamic equation.