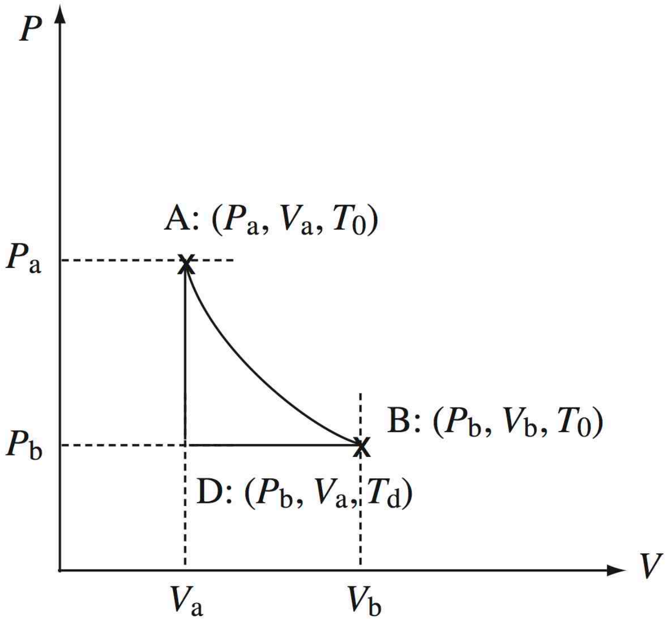
General Physics II: Tutorial Material 10

1) Let us consider an isothermal change of the state $\mathrm{A}(V_\mathrm{a}, P_\mathrm{a}, T_0) \rightarrow \mathrm{B}(V_\mathrm{b}, P_\mathrm{b}, T_0)$ in a closed system, where $V_\mathrm{a} < V_\mathrm{b}$.

   a) Calculate work and heat of the system taking this path.

   b) The system now takes another path for A to B, namely an isovolumetric process from A to $\mathrm{D}(V_\mathrm{a}, P_\mathrm{b}, T_d)$ first, followed by an isobaric process from D to B. Calculate the work and heat for the two processes. Is the total heat of the path equal to the total work of the path? Is the result what one expects?



a) From the ideal gas law,

$$P = \frac{nRT_0}{V}$$

the work for the isothermal process is given by

$$W = \int_{V_\mathrm{a}}^{V_\mathrm{b}} P\,dV = \int_{V_\mathrm{a}}^{V_\mathrm{b}} \frac{nRT_0}{V} dV = nRT_0 \int_{V_\mathrm{a}}^{V_\mathrm{b}} \frac{dV}{V} = nRT_0 \ln V \Big]_{V_\mathrm{a}}^{V_\mathrm{b}} = nRT_0 \ln \frac{V_\mathrm{b}}{V_\mathrm{a}} > 0$$

Note that from the ideal gas law, $P_\mathrm{a} > P_\mathrm{b}$. Since no change in the temperature between A and B, there is no change in the internal energy and the first law of thermodynamics gives $\Delta E_\mathrm{int} = Q - W = 0$, thus

$$Q = W = nRT_0 \ln \frac{V_\mathrm{b}}{V_\mathrm{a}}$$

b) Since no change is made in volume for A to D,

$$W_{ad} = 0.$$

The temperature of B is given by the ideal gas law to be

$$T_d = \frac{V_a P_b}{nR}$$

and since

$$T_0 = \frac{V_a P_a}{nR}$$

$T_0 > T_b$, i.e. the temperature decreases. The temperature difference is given by

$$\Delta T = T_d - T_0 = \frac{V_a(P_b - P_a)}{nR}$$

and heat by

$$Q_{ad} = nC_{\mathrm{V}}\Delta T = \frac{V_a(P_b - P_a)}{R} C_{\mathrm{V}}$$

For D to B, the work is given by

$$W_{db} = P_b \Delta V = P_b(V_b - V_a)$$

and heat

$$Q_{db} = nC_{\mathrm{P}}\Delta T = \frac{P_b(V_b - V_a)}{R} C_{\mathrm{P}}$$

Therefore, the total work is given by

$$W = W_{ad} + W_{db} = P_b(V_b - V_a)$$

and total heat

$$Q = Q_{ad} + Q_{db} = P_b(V_b - V_a)$$

where $C_{\mathrm{P}} = C_{\mathrm{V}} + R$ and $P_a V_a = P_b V_b = nRT_0$ are used. The result shows that $Q = W$ as expected, since the change in the internal energy does not depend on the path, but given only by the difference in the internal energies of the final and of the initial states.

2) Lets us considers a very large heat reservoir at a temperature T_{R}, and a small thermal system at T_{S}. The specific heat of the small system is C. By putting them into thermal contact, they reach a thermal equilibrium at T_{R}, since the heat reservoir has such a large heat capacity and stays at the same temperature.

a) Calculate the entropy changes of the heat reservoir.
b) Calculate the entropy changes of the small system.
c) Calculate the entropy changes of the total system.
b) Show that the change of the entropy of the total system is $\Delta S \geq 0$.

Heat of the small system and that of reservoir are given by $Q_{\mathrm{system}} = C(T_{\mathrm{R}} - T_{\mathrm{S}})$ and $Q_{\mathrm{reservoir}} = -Q_{\mathrm{system}}$, respectively. So the thermal energy flows from the reservoir to the small system when $T_{\mathrm{R}} > T_{\mathrm{S}}$. Process of the transferring of thermal energy from the heat reservoir itself can be considered as a reversible process since the process can be reversed by attaching another system with a temperature of $2T_{\mathrm{R}} - T_{\mathrm{S}}$. A similar argument can be valid for the system, since the process can be reversed by attaching the system to another heat reservoir with a temperature of T_S. However, the combined process of the heat reservoir and the system is irreversible.

a) Since the process of the heat reservoir alone is reversible, entropy change of the heat reservoir is given by

$$\Delta S_{\text{reservoir}} = \frac{Q_{\text{reseroir}}}{T_R} = C\frac{\left(T_S - T_R\right)}{T_R}$$

thus change of the reservoir entropy is negative when $T_R > T_S$.

b) Since the process of the system alone is reversible, entropy of the small system is given by

$$\Delta S_{\text{system}} = C\int_{T_S}^{T_R}\frac{dT}{T} = C\ln\frac{T_R}{T_S}$$

thus change of the system entropy is positive when $T_R > T_S$.

c) Entropy of the total system is given by

$$\Delta S = \Delta S_{\text{reservoir}} + \Delta S_{\text{system}} = C\frac{\left(T_S - T_R\right)}{T_R} + C\ln\frac{T_R}{T_S}$$

d) Let us rewrite the change of the entropy as

$$\Delta S = C\left(\frac{T_S}{T_R} - 1 - \ln\frac{T_S}{T_R}\right)$$

For $T_S/T_R = 0$ we obtain $\Delta S = +\infty$, for $T_S/T_R = 1$ $\Delta S = 0$. From the derivative,

$$\frac{d\Delta S}{d\left(T_S/T_R\right)} = C\left(1 - \frac{T_R}{T_S}\right)$$

we learn that ΔS is monotonically decreasing function of T_S/T_R for $T_S/T_R = 0$ to $T_S/T_R = 1$. For $T_S/T_R = 1$ to $T_S/T_R = \infty$, ΔS is monotonically increasing as a function of T_S/T_R. Therefore, we can conclude that $\Delta S \geq 0$, and it is 0 when $T_R = T_S$.

3) Show that the entropy difference of an n-mol ideal gas, ΔS, when the state $A\left(P_1, V_1, T_1\right)$ is changed to $B\left(P_2, V_2, T_2\right)$ quasi-statically, is given by

$$\Delta S = nC_V\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}.$$

Show that this leads to ΔS=0 for an adiabatic process, as expected from the definition.

From the first law of the thermodynamics, $Q = \Delta E_{\text{int}} + W$, where $W = P\Delta V$, and with the ideal gas law, $PV = nRT$ and $\Delta E_{\text{int}} = nC_V\Delta T$, heat can be written as

$$Q = \Delta E_{\text{int}} + P\Delta V = nC_V\Delta T + \frac{nRT}{V}\Delta V$$

For an infinitesimal quasi-static change of the state, this leads to

$$\tilde{d}Q = nC_V dT + \frac{nRT}{V}dV,$$

and the change in the entropy becomes

$$\mathrm{d}S = \frac{\tilde{\mathrm{d}}Q}{T} = \frac{nC_{\mathrm{V}}}{T}\mathrm{d}T + \frac{nR}{V}\mathrm{d}V$$

The entropy change for A to B is now given by

$$\Delta S = \int_A^B dS \,.$$

thus

$$\Delta S = \int_A^B \left(nC_{\mathrm{V}}\frac{dT}{T} + nR\frac{dV}{V} \right) = \left[nC_{\mathrm{V}} \ln T + nR \ln V \right]_A^B = nC_{\mathrm{V}} \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$$

For an adiabatic process, we have $PV^{\gamma} = \text{constant}$. Using $PV=nRT$, we have

$$V_1^{\gamma-1}T_1 = V_2^{\gamma-1}T_2$$

thus

$$\ln\frac{T_2}{T_1} = \ln\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\gamma-1\right)\ln\frac{V_1}{V_2} = \frac{C_{\mathrm{P}}-C_{\mathrm{V}}}{C_{\mathrm{V}}}\ln\frac{V_1}{V_2} = \frac{R}{C_{\mathrm{V}}}\ln\frac{V_1}{V_2}$$

It follows that

$$\Delta S = 0$$

which makes sense since Q=0 in the adiabatic process.

4) An n-mole ideal gas with a volume V_1 expands adiabatically (Q = 0) into the vacuum (free expansion) and its volume becomes V_2. Is this process reversible process? Show that the entropy change is positive, i.e. $\Delta S > 0$. Is this result paradoxical? How can we explain this?

The free expansion of the gas into vacuum is not reversible process since it cannot be controlled to proceed through a succession of many infinitesimally small quasi-statistical paths. Thus, the entropy change cannot be obtained by

$$\Delta S = \int \frac{\tilde{\mathrm{d}}Q_{\mathrm{reverse}}}{T} \,.$$

On the other hand, the final state is well defined: Since it is an adiabatic process, Q = 0. The pressure of the vacuum is zero, thus no work is done during the expansion and $W = 0$. It follows that

$$\Delta E_{\mathrm{int}} = Q - W = 0 \,,$$

thus no change in the temperature during the expansion: Thus the final state has the same temperature, T, as the initial state with a volume V_2.

Since the entropy difference between the two states does not depend on the path, ΔS calculated between the initial and final states with a reversible isothermal expansion of volume $V_1 \rightarrow V_2$ is identical to ΔS for the free expansion process. Therefore, we can use the previous solution with $T_1 = T_2$. It follows that

$$\Delta S = nR\ln\frac{V_2}{V_1} \,.$$

Since $V_1 < V_2$, we have $\Delta S > 0$, increase of the entropy.

From a usual expression of $\Delta S = Q/T$, one wants to conclude $\Delta S = 0$ for the free expansion. However, with the exact formula

$$\Delta S = \int_A^B \frac{\tilde{\mathrm{d}}Q_{\mathrm{reversible}}}{T} > \int_A^B \frac{\tilde{\mathrm{d}}Q_{\mathrm{irreversible}}}{T}$$

we have

$$\int_A^B \frac{\tilde{\mathrm{d}}Q_{\mathrm{irreversible}}}{T} = 0$$

but not ΔS.