General Physics II at EPFL

(2018-2019 SS, Wed 17:15-19:00 and Thu 8:15-10:00, Exercise Thu 10:15-12:00)

Thermodynamic (8th week)

Heat, Work, Entropy and Internal Energy

In general, heat, Q, is incoming flow of thermal energy associated with a temperature change ΔT and given by

$$Q = m \cdot c \cdot \Delta T$$

c is a specific heat and m mass of the object. For an infinitesimal change in the temperature $\mathrm{d}T$, it leads to

$$\tilde{\mathrm{d}}Q = m \cdot c \cdot \mathrm{d}T$$

and Q is obtained by

$$Q = \int_{\text{initial}}^{\text{final}} \tilde{\mathrm{d}}Q = m \int_{T_{\text{initial}}}^{T_{\text{final}}} c \cdot \mathrm{d}T$$

When a gas changes its volume by ΔV under **a constant pressure** P, work is given by

$$W = P \cdot \Delta V$$

For a more general case, we consider that the volume of the gas changes only an infinitesimally small amount, $\mathrm{d}V$, quasistatically, and during this period P can be considered as unchanged and

$$\tilde{\mathrm{d}}W = P \cdot \mathrm{d}V$$

The total work is then given by

$$W = \int_{\text{initial}}^{\text{final}} \tilde{\mathrm{d}}W = m \int_{V_{\text{initial}}}^{V_{\text{final}}} P \cdot \mathrm{d}V$$

where $P = P(V)$. The first law of thermodynamics can then leads to

$$\Delta E_{\text{int}} = Q - W \;\Rightarrow\; dE_{\text{int}} = \tilde{d}Q - \tilde{d}W,\; \Delta E_{\text{int}} = \int_{\text{initial}}^{\text{final}} dE_{\text{int}}$$

Similarly for the entropy changes in a reversible process, we have

$$\Delta S = \frac{Q_{\text{reversible}}}{T} \;\Rightarrow\; dS = \frac{\tilde{d}Q_{\text{reversible}}}{T},\; \Delta S = \int_{\text{initial}}^{\text{final}} dS = \int_{\text{initial}}^{\text{final}} \frac{\tilde{d}Q_{\text{reversible}}}{T}$$

For a process with a constant volume, W=0, and from the first law of thermodynamics

$$\left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{V=\text{const}} = \left(\frac{\tilde{\partial} Q}{\partial T}\right)_{V=\text{const}} \equiv nC_V$$

for an n-mol gas.

Let us select T and V as state variables describing a gas state, it follows that

$$dE_{\text{int}} = \left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{V=\text{const}} dT + \left(\frac{\partial E_{\text{int}}}{\partial V}\right)_{T=\text{const}} dV$$

Since the internal energy is a function of T only,

$$dE_{\text{int}} = \left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{V=\text{const}} dT = nC_V dT$$

For a process with a constant pressure, work is not 0 and we have

$$\left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{P=\text{const}} = \left(\frac{\tilde{\partial} Q}{\partial T}\right)_{P=\text{const}} - \left(\frac{\tilde{\partial} W}{\partial T}\right)_{P=\text{const}} \equiv nC_P - \left(\frac{\tilde{\partial}\left(PV\right)}{\partial T}\right)_{P=\text{const}}$$

For the ideal gas case, $PV=nRT$, it follows that

$$\left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{P=\text{const}} = n\cdot C_P - nR\left(\frac{\tilde{\partial} T}{\partial T}\right)_{P=\text{const}} = n\left(C_P - R\right) = nC_V$$

Therefore, for the case of selecting P and T, we obtain as before

$$dE_{\text{int}} = \left(\frac{\partial E_{\text{int}}}{\partial T}\right)_{P=\text{const}} dT + \left(\frac{\partial E_{\text{int}}}{\partial P}\right)_{T=\text{const}} dP = nC_V dT$$

Entropy changes for heat cycles

Consider a reversible cycle of n-mol ideal gas. After one cycle, the internal energy comes back to the original state,

$$\oint dE_{\text{int}} = 0$$

Using $dE_{\text{int}} = TdS - PdV$ we obtain

$$\frac{dE_{\text{int}}}{T} = dS - \frac{P}{T}dV$$

Using $dE_{\text{int}} = nC_V dT$, it follows that

$$\oint \frac{dE_{\text{int}}}{T} = nC_V \oint \frac{dT}{T} = 0$$

Similarly, using the ideal gas law,

$$\oint \frac{PdV}{T} = nR\oint \frac{dV}{V} = 0$$

Therefore,

$$\oint dS = \oint \frac{dE_{\text{int}}}{T} + \oint P\,dV = 0$$

i.e. the entropy increase on the cycle is 0.

Heat Engine

A heat engine takes heat, $Q_1 > 0$, from a reservoir with temperature T_1, and coverts to work. The fact that the work, W, done by change the state of the system depends on the path it takes, is used to extract the work. In order to extract work continuously, the path has to come back to the original state making a cycle. Since the state of the heat engine comes back to the original one, the entropy of the heat engine remains unchanged after the cycle. On the other hand, the Entropy change of the heat reservoir after one cycle is given by

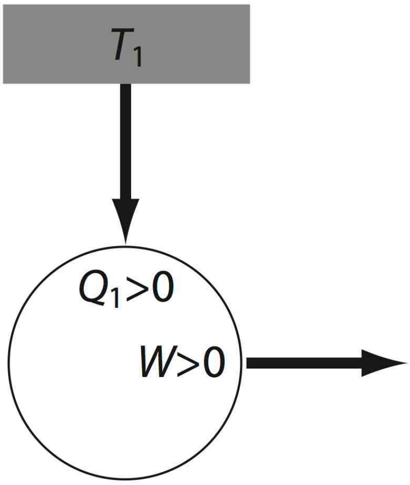
$$\Delta S_1 = \frac{-Q_1}{T_1} < 0$$

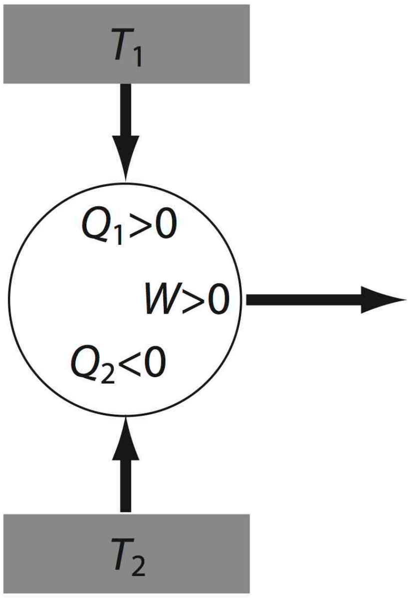
and the total entropy change is given by

$$\Delta S_{\text{total}} = \Delta S_1 = \frac{-Q_1}{T_1} < 0$$

which does not agree with the second law of thermodynamic, $\Delta S_{\text{total}} \geq 0$. In order to fulfil the second law, we need to introduce another heat reservoir with a temperature T_2, where $T_2 < T_1$ and the engine ejects heat, $Q_2 < 0$, to the second reservoir. The entropy change of the second reservoir is then

$$\Delta S_2 = \frac{-Q_2}{T_2} > 0$$





In this case, the first law gives, $\Delta E_{\text{int}} = Q_1 + Q_2 - W = 0$, i.e.

$$Q_2 = -Q_1 + W$$

and the total entropy change is given by

$$\Delta S_{\text{total}} = \Delta S_1 + \Delta S_2 = \frac{-Q_1}{T_1} + \frac{-Q_2}{T_2}$$

From the second law, we have

$$\Delta S_{\text{total}} = -\frac{Q_1}{T_1} - \frac{Q_2}{T_2} \geq 0.$$

leads to

$$\frac{Q_2}{T_2} \leq -\frac{Q_1}{T_1}, \text{ i.e. } \frac{Q_2}{Q_1} \leq -\frac{T_2}{T_1}$$

The efficiency of the heat engine is given by

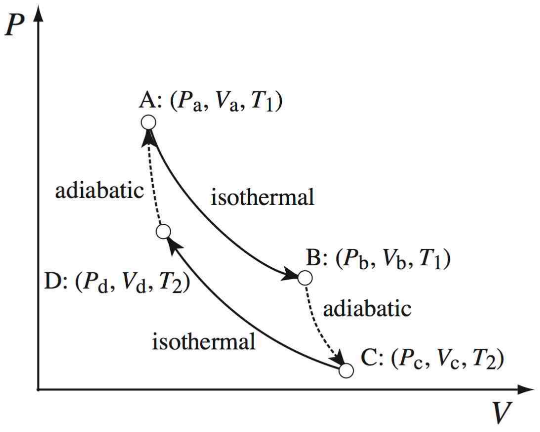
$$\varepsilon = \frac{W}{Q_1} = \frac{Q_1 + Q_2}{Q_1} = 1 + \frac{Q_2}{Q_1} \le 1 - \frac{T_2}{T_1}$$

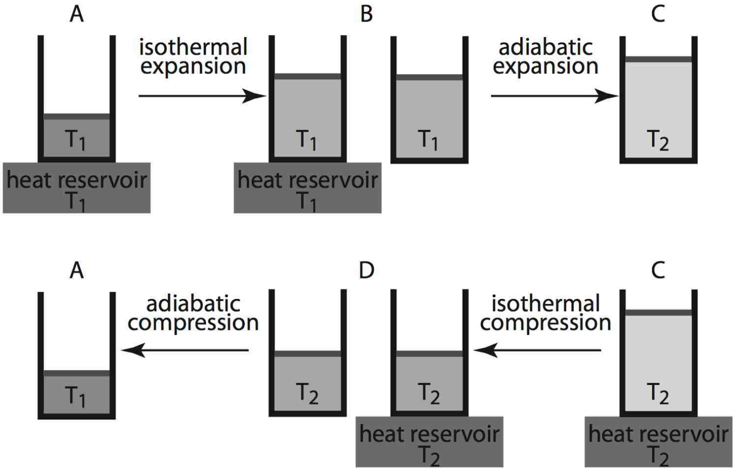
While a perfect engine has $\varepsilon = 1$, a real engine has efficiency less than 1, i.e.

$$\varepsilon \le 1 - \frac{T_2}{T_1} < 1.$$

Carnot Cycle

To demonstrate the argument above, Carnot cycle, a combination of isothermal and adiabatic processes, was invented. There is no real engine using the Carnot cycle, but it can be used to demonstrate the second law of thermodynamic, with four states, A, B, C, and D,





$A(V_a, P_a, T_1)$: A cylinder with an ideal gas is attached to a heat reservoir with a temperature T_1.
A→B: Isothermal expansion with a constant temperature T_1, heat $Q_1 > 0$ into the cylinder from the reservoir, and work $W_{ab} > 0$ being done.
$B(V_b, P_b, T_1)$: The cylinder is removed from the heat reservoir and thermally isolated.
B→C: Adiabatic expansion ($Q = 0$) till the temperature drops to T_2 and work done, $W_{bc} > 0$
$C(V_c, P_c, T_2)$: The cylinder is attached to another heat reservoir with a temperature T_2.
C→D: Isothermal compression with a constant temperature T_2, heat $Q_2 < 0$ out of the cylinder to the reservoir, and work $W_{cd} < 0$ being done.
$D(V_d, P_d, T_2)$: The cylinder is removed from the heat reservoir and thermally isolated.
D→A: Adiabatic compression ($Q = 0$) till the temperature raise to T_1 and work, $W_{da} < 0$, done from the outside.

As done previously for the isothermal process, we have

$$W_{ab} = \int_{V_a}^{V_b} P dV = nRT_1 \int_{V_a}^{V_b} \frac{dV}{V} = nRT_1 \ln \frac{V_b}{V_a}$$

and $\Delta E_{int} = 0$, leading to $\Delta E_{int} = Q - W = 0$, leading to

$$Q_1 = W_{ab} = nRT_1 \ln \frac{V_b}{V_a} > 0$$

Equally,

$$Q_2 = W_{cd} = nRT_2 \ln \frac{V_d}{V_c} < 0$$

In the adiabatic expansion, we have $PV^{\gamma} = P_b V_b^{\gamma}$, thus the work between B→C is given by

$$W_{\mathrm{bc}} = \int_{V_{\mathrm{b}}}^{V_{\mathrm{c}}} P dV = P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma} \int_{V_{\mathrm{b}}}^{V_{\mathrm{c}}} V^{-\gamma} dV = \frac{P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma}}{1-\gamma} V^{1-\gamma} \Big]_{V_{\mathrm{b}}}^{V_{\mathrm{c}}} = \frac{P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma}}{1-\gamma} \left(V_{\mathrm{c}}^{1-\gamma} - V_{\mathrm{b}}^{1-\gamma} \right) = \frac{P_{\mathrm{b}} V_{\mathrm{b}}}{1-\gamma} \left[\left(\frac{V_{\mathrm{c}}}{V_{\mathrm{b}}} \right)^{1-\gamma} - 1 \right]$$

Equally for the adiabatic compression, the work for D→A is given by

$$W_{\mathrm{da}} = \int_{V_{\mathrm{d}}}^{V_{\mathrm{a}}} P dV = P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma} \int_{V_{\mathrm{d}}}^{V_{\mathrm{a}}} V^{-\gamma} dV = \frac{P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma}}{1-\gamma} V^{1-\gamma} \Big]_{V_{\mathrm{d}}}^{V_{\mathrm{a}}} = \frac{P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma}}{1-\gamma} \left(V_{\mathrm{a}}^{1-\gamma} - V_{\mathrm{d}}^{1-\gamma} \right) = \frac{P_{\mathrm{a}} V_{\mathrm{a}}}{1-\gamma} \left[1 - \left(\frac{V_{\mathrm{d}}}{V_{\mathrm{a}}} \right)^{1-\gamma} \right]$$

For the isothermal processes, we have $P_{\mathrm{a}} V_{\mathrm{a}} = P_{\mathrm{b}} V_{\mathrm{b}}$ and $P_{\mathrm{c}} V_{\mathrm{c}} = P_{\mathrm{d}} V_{\mathrm{d}}$. And for the adiabatic processes it follows that $P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma} = P_{\mathrm{c}} V_{\mathrm{c}}^{\gamma}$ and $P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma} = P_{\mathrm{d}} V_{\mathrm{d}}^{\gamma}$. Furthermore, the ideal gas law gives

$$\frac{P_{\mathrm{a}} V_{\mathrm{a}}}{T_1} = \frac{P_{\mathrm{b}} V_{\mathrm{b}}}{T_1} = \frac{P_{\mathrm{c}} V_{\mathrm{c}}}{T_2} = \frac{P_{\mathrm{d}} V_{\mathrm{d}}}{T_2}.$$

It follows that

$$\begin{aligned} P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma} &= P_{\mathrm{c}} V_{\mathrm{c}}^{\gamma} \\ P_{\mathrm{b}} V_{\mathrm{b}}^{\gamma} \frac{T_1}{P_{\mathrm{b}} V_{\mathrm{b}}} &= P_{\mathrm{c}} V_{\mathrm{c}}^{\gamma} \frac{T_2}{P_{\mathrm{c}} V_{\mathrm{c}}} \\ V_{\mathrm{b}}^{\gamma-1} T_1 &= V_{\mathrm{c}}^{\gamma-1} T_2 \\ \frac{T_1}{T_2} &= \left(\frac{V_{\mathrm{c}}}{V_{\mathrm{b}}} \right)^{\gamma-1} \end{aligned}$$

and

$$\begin{aligned} P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma} &= P_{\mathrm{d}} V_{\mathrm{d}}^{\gamma} \\ P_{\mathrm{a}} V_{\mathrm{a}}^{\gamma} \frac{T_1}{P_{\mathrm{a}} V_{\mathrm{a}}} &= P_{\mathrm{d}} V_{\mathrm{d}}^{\gamma} \frac{T_2}{P_{\mathrm{d}} V_{\mathrm{d}}} \\ V_{\mathrm{a}}^{\gamma-1} T_1 &= V_{\mathrm{d}}^{\gamma-1} T_2 \\ \frac{T_1}{T_2} &= \left(\frac{V_{\mathrm{d}}}{V_{\mathrm{a}}} \right)^{\gamma-1} \end{aligned}$$

giving

$$\begin{aligned} W_{\mathrm{bc}} + W_{\mathrm{da}} &= \frac{P_{\mathrm{b}} V_{\mathrm{b}}}{1-\gamma} \left[\left(\frac{V_{\mathrm{c}}}{V_{\mathrm{b}}} \right)^{1-\gamma} - 1 \right] + \frac{P_{\mathrm{a}} V_{\mathrm{a}}}{1-\gamma} \left[1 - \left(\frac{V_{\mathrm{d}}}{V_{\mathrm{a}}} \right)^{1-\gamma} \right] \\ &= \frac{P_{\mathrm{a}} V_{\mathrm{a}}}{1-\gamma} \left[\frac{T_1}{T_2} - 1 + 1 - \frac{T_1}{T_2} \right] \\ &= 0 \end{aligned}$$

i.e. the adiabatic parts of works cancel each other. This conclusion can be reached in a much simpler way. As indicated before, $\Delta E_{\mathrm{int}} = n C_V \Delta T$ and for an adiabatic process, $Q = 0$ leads to $\Delta E_{\mathrm{int}} = -W$. It follows that

$$W_{\mathrm{bc}} = -\Delta E_{\mathrm{int}}^{\mathrm{bc}} = -n C_{\mathrm{V}} \left(T_2 - T_1 \right) \text{ and } W_{\mathrm{da}} = -\Delta E_{\mathrm{int}}^{\mathrm{da}} = -n C_{\mathrm{V}} \left(T_1 - T_2 \right),$$

which leads to

$$W_{\mathrm{bc}} + W_{\mathrm{da}} = 0.$$

The total work is now given by

$$W = W_{\mathrm{ab}} + W_{\mathrm{cd}} = n R T_1 \ln \frac{V_{\mathrm{b}}}{V_{\mathrm{a}}} + n R T_2 \ln \frac{V_{\mathrm{d}}}{V_{\mathrm{c}}} = n R T_1 \ln \frac{V_{\mathrm{b}}}{V_{\mathrm{a}}} - n R T_2 \ln \frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}$$

Note that the first law of thermodynamic is valid and $W = Q_1 + Q_2$. Using

$$\frac{T_1}{T_2} = \left(\frac{V_c}{V_b}\right)^{\gamma-1} = \left(\frac{V_d}{V_a}\right)^{\gamma-1}$$

we obtain

$$\frac{V_c}{V_b} = \frac{V_d}{V_a}, \text{ i.e. } \frac{V_b}{V_a} = \frac{V_c}{V_d}$$

thus

$$W = W_{ab} + W_{cd} = nR\left(T_1 - T_2\right)\ln\frac{V_b}{V_a}$$

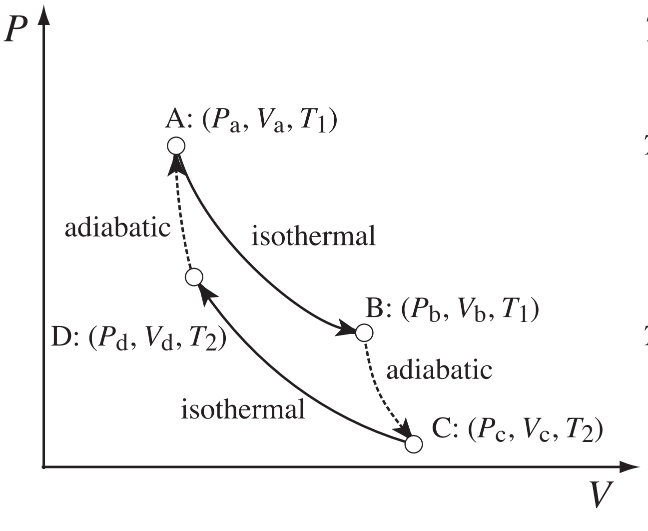
and the efficiency is given by

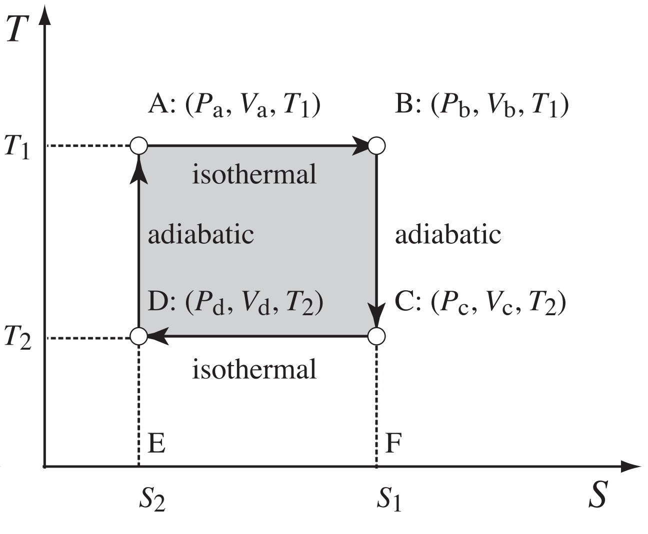
$$\varepsilon = \frac{W}{Q_1} = \frac{nR\left(T_1 - T_2\right)\ln V_b/V_a}{nRT_1 \ln V_b/V_a} = 1 - \frac{T_2}{T_1}$$

i.e the Carnot cycle gives the maximum efficiency allowed by the second law of thermodynamic.

Carnot cycle and *T*-*S* plot

In the previous section, Carnot cycle was drawn on the pressure (P) versus volume (V) plane. From the relation, $\tilde{d}W = PdV$, valid for a reversible process, the area surrounded by the Carnot cycle, A→B→C→D, on the P-V plane gives the total work of the Carnot engine. By recalling the expression, $\tilde{d}Q = TdS$, for a reversible process, let us draw the Carnot cycle on the temperature (T) versus entropy (S) plane. On this plane, an isothermal process, T constant, is a horizontal line and an adiabatic process, $Q = 0$ thus S constant, is a vertical line. Therefore, a Carnot cycle is a rectangular box on the T-S plane. Similar for the work, the area surrounded by A→B→C→D on the T-S plane give the total heat of the Carnot engine.





As introduced in “Entropy and the first law of thermodynamic”, the infinitesimal change in the internal energy can be given from the first law of thermodynamics as

$$\mathrm{d}E_{\mathrm{int}} = T\mathrm{d}S - P\mathrm{d}V$$

By recalling that the internal energy depends only on the temperature, i.e.

$$dE_{\mathrm{int}} = \left(\frac{\partial E_{\mathrm{int}}}{\partial T}\right)dT = nC_V dT\ ,$$

it follows that

$$dS = \frac{\mathrm{d}E_{\text{int}}}{T} + \frac{P}{T}\mathrm{d}V = nC_V\frac{dT}{T} + nR\frac{dV}{V}$$

For a change of state from $(P_1,\, V_1,\, T_1)$ to $(P_2,\, V_2,\, T_2)$, the change of the entropy, ΔS, is given by the integration as

$$\Delta S = nC_V\int_{T_1}^{T_2}\frac{dT}{T} + nR\int_{V_1}^{V_2}\frac{dV}{V} = nC_{\text{V}}\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$$

The entropy change for the isothermal expansion A→B, ΔS, is given by

$$\Delta S = nR\ln\frac{V_{\text{b}}}{V_{\text{a}}}$$

thus the area of the rectangular box is given by

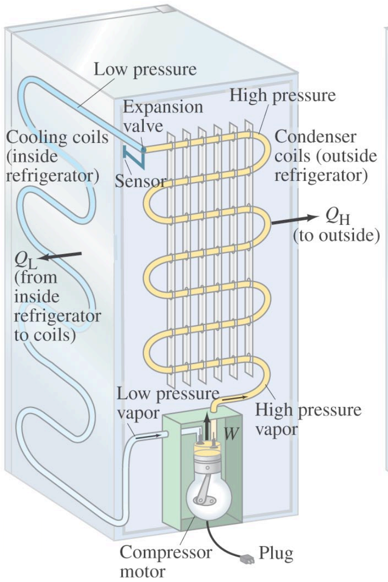
$$Q_{\text{total}} = \Delta S \times (T_1 - T_2) = nR(T_1 - T_2)\ln\frac{V_{\text{b}}}{V_{\text{a}}}$$

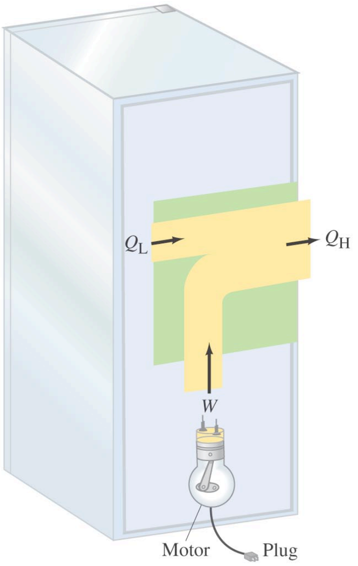
in agreement with the analysis before without using the entropy.

Refrigerators

The operation principle of refrigerators and heat pumps are the reverse of a heat engine, transferring heat from a cool environment to a warm environment by work. In order to demonstrate how the refrigerator works, we operate the Carnot cycle in the reversed order: A→D→C→B→A. In this case, the upper and lower limits for the integration in the heat and work calculations must be exchanged, thus the sign of the heat and work should be flipped. The efficiency of a refrigerator is defined as

$$\varepsilon_{\text{refrigerator}} = \frac{\text{thermal energy extracted from the heat reservoir with } T = T_2}{\text{total work given to the refrigerator}}$$





From the Carnot engine calculations, heats for A→D and B→A, Q_{dc} and Q_{ba}, respectively are given by

$$Q_{\text{dc}} = nRT_2\ln\frac{V_{\text{c}}}{V_{\text{d}}} > 0 \text{ and } Q_{\text{ba}} = nRT_1\ln\frac{V_{\text{a}}}{V_{\text{b}}} < 0$$

and similarly for the work, A→D, D→C, C→B, and B→A

$$W_{\mathrm{ad}} = \frac{P_{\mathrm{b}}V_{\mathrm{b}}}{1-\gamma}\left[\left(\frac{V_{\mathrm{c}}}{V_{\mathrm{b}}}\right)^{1-\gamma} - 1\right],\ W_{\mathrm{dc}} = nRT_2 \ln\frac{V_{\mathrm{c}}}{V_{\mathrm{d}}},\ W_{\mathrm{cb}} = \frac{P_{\mathrm{b}}V_{\mathrm{b}}}{1-\gamma}\left[1 - \left(\frac{V_{\mathrm{c}}}{V_{\mathrm{b}}}\right)^{1-\gamma}\right],\ W_{\mathrm{ba}} = nRT_1 \ln\frac{V_{\mathrm{d}}}{V_{\mathrm{c}}}.$$

The total work is given by

$$W_{\mathrm{total}} = W_{\mathrm{ad}} + W_{\mathrm{dc}} + W_{\mathrm{cb}} + W_{\mathrm{ba}} = nR(T_2 - T_1)\ln\frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}$$

The thermal energy extracted from the heat reservoir with $T = T_2$ is given by Q_{dc}, and the work given to the refrigerator is $-W_{\mathrm{total}}$. Thus the efficiency is then given by

$$\varepsilon_{\mathrm{refrigerator}} = \frac{Q_{\mathrm{dc}}}{-W_{\mathrm{total}}} = \frac{nRT_2 \ln\frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}}{nR(T_1 - T_2)\ln\frac{V_{\mathrm{c}}}{V_{\mathrm{d}}}} = \frac{T_2}{T_1 - T_2}.$$