Notes on Carnot Cycle

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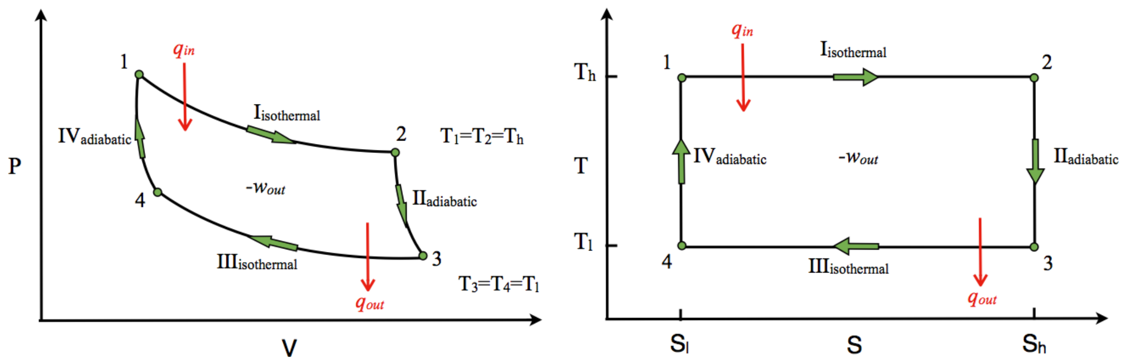

Figure 1. Carnot cycle in P-V and T-S diagram.[1]

The Carnot cycle provides an upper limit on the efficiency that any classical thermodynamic engine can achieve during the conversion of heat into work. It is not an actual thermodynamic cycle, but is a theoretical construct. The whole change of entropy of the cycle is zero. The maximum efficiency of the heat engine is achieved if and only if no new entropy is created in the cycle. According to Figure 1, the total entropy change in the cycle is

$$\Delta S = \Delta S_I + \Delta S_{III} = -nR\ln\left(\frac{V_2}{V_1}\right) - nR\ln\left(\frac{V_4}{V_3}\right) \tag{1.1}$$

Due to the fact that $V_3/V_4 = V_2/V_1$, Eq. (1.1) equals to zero. The efficiency is

$$\eta = \frac{nRT_h\ln\left(V_2/V_1\right) + nRT_l\ln\left(V_4/V_3\right)}{nRT_h\ln\left(V_2/V_1\right)} = 1 - \frac{T_l}{T_h} \tag{1.2}$$

Usually due to the friction and collision of molecules, the process is irreversible (because dissipated energy cannot be recovered), and entropy increases. In this case, the efficiency of the engine will be lower than the upper limit. If the total change of entropy is decreasing, the efficiency of the heat engine could surpass the upper limits set by the Carnot cycle.

[1] Figure taken from https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/Thermodynamic_Cycles/Carnot_Cycle

Such process has been created in microscopic scale, called Brownian Carnot engine[2]. Now, due to $\Delta S < 0$, Eq. (1.1) becomes

$$nR\ln\left(\frac{V_4}{V_3}\right) > -nR\ln\left(\frac{V_2}{V_1}\right) \tag{1.3}$$

The efficiency of the heat engine now becomes

$$\eta = \frac{nRT_h \ln\left(V_2/V_1\right) - knRT_l \ln\left(V_2/V_1\right)}{nRT_h \ln\left(V_2/V_1\right)} = 1 - k\frac{T_l}{T_h} \tag{1.4}$$

where k<1. Obviously, efficiency in Eq. (1.4) is larger than that in Eq. (1.2) and Carnot limits is violated.

[2] https://www.nature.com/articles/nphys3518#ref8. As described by stochastic thermodynamics, energy transfers in microscopic systems are random and thermal fluctuations induce transient decreases of entropy, allowing for possible violations of the Carnot limit