CHEME 3130: Converting heat to work: Introduction and Analysis of the Carnot Cycle

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Introduction

Just like complex chemical processes can be decomposed into many interconnected unit operations, processes that have been devised to convert heat to work e.g., a steam engines or a steam powered turbines can also thought of as interconnected operations. These thermodynamic operations, called *paths*, are composed of two types of physical operations, isothermal expansion (or contraction) and adiabatic expansion (or contraction). Let's start our discussion of these processes for *closed* systems. Recall, that our general energy and material balances can be written in differential form as:

$$d\left(mu\right)\Big|_{sys} = \delta Q + \delta W + \sum_{s=1}^{\mathcal{S}} \nu_s u_s \delta m_s + \sum_{r=1}^{\mathcal{R}} \delta E_r \qquad (1)$$

$$dm = \sum_{s=1}^{\mathcal{S}} \nu_s \delta m_s \qquad (2)$$

where we have neglected changes in kinetic and potential energy in the system. For a closed system with no chemical reactions, our general differential balances reduce to:

$$dU = \delta Q + \delta W \qquad (3)$$

and dm = 0. Eqn (3) is the first-law of thermodynamics for a closed system with no chemical reactions, where we have neglected changes in kinetic and potential energy. For each stage of our process, we'll apply the first law and then sum the work that is generated from the cycle.

Carnot heat cycle for a closed system. The Carnot cycle, named after the French engineer Sadi Carnot, is a hypothetical set of reversible expansion/compression operations developed in 1824 as a model for the conversion of heat to work [1]. The Carnot cycle involves two heat reservoirs, a hot reservoir maintained at T_H and a cold reservoir maintained at T_L, along with two reversible isothermal operations, and two reversible adibatic operations (Fig. 1). Starting from $\mathbb{P}_1$, a working fluid is isothermally expanded from $\mathbb{P}_1$ to $\mathbb{P}_2$, and then adibatically expanded from $\mathbb{P}_2$ to $\mathbb{P}_3$. The working fluid is then isothermally compressed from $\mathbb{P}_3$ to $\mathbb{P}_4$, and then adiabatically compressed from $\mathbb{P}_4$ back to the starting point $\mathbb{P}_1$. If we assume the working fluid in the cycle is an
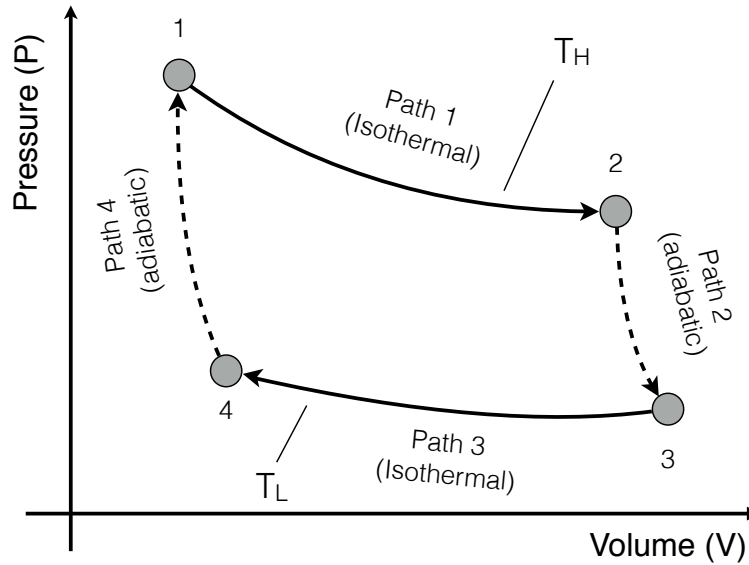
Fig. 1: Schematic of the Carnot cycle. A working fluid is isothermally expanded from $\mathbb{P}_1$ to $\mathbb{P}_2$, and then adiabatically expanded from $\mathbb{P}_2$ to $\mathbb{P}_3$. The working fluid is then isothermally compressed from $\mathbb{P}_3$ to $\mathbb{P}_4$, and then adiabatically compressed from $\mathbb{P}_4$ back to the starting point $\mathbb{P}_1$.

ideal gas, whose internal energy is given by:

$$U = \frac{3}{2}Nk_BT \tag{4}$$

we can then derive the work generated by this cycle using the first-law for a closed system.

- **Path 1**: Isothermal expansion $\mathbb{P}_1 \rightarrow \mathbb{P}_2$. The first-law for path 1 is given by:

$$dU_1 = \delta Q_1 + \delta W_1 \tag{5}$$

or:

$$dU_1 = \delta Q_1 - PdV \tag{6}$$

after substitution of the expansion work. We know (from statistical mechanics) that the internal energy of an ideal gas is given by Eqn (4). Thus, the change in internal energy for path 1 is zero because $\mathbb{P}_1 \rightarrow \mathbb{P}_2$ is isothermal:

$$\Delta U_{\mathbb{P}_1 \rightarrow \mathbb{P}_2} = \frac{3}{2}Nk_B\left(T_H - T_H\right) = 0 \tag{7}$$

Constant internal energy along path 1 reduces the first law to:

$$\delta Q_1 = PdV \tag{8}$$

Subsituting the ideal-gas relationship for pressure $P = nRT_H/V$, and integrating between

$\mathbb{P}_1 \to \mathbb{P}_2$ gives an expression for the heat:

$$Q_1 = nRT_H \ln\left(\frac{V_2}{V_1}\right) \tag{9}$$

However, we know that

$$\delta Q_1 = -\delta W_1 \tag{10}$$

thus the expansion work done in path 1 is given by:

$$W_1 = -nRT_H \ln\left(\frac{V_2}{V_1}\right) \tag{11}$$

- **Path 2**: Adiabatic expansion $\mathbb{P}_2 \to \mathbb{P}_3$. The first-law for path 2 is given by:

$$dU_2 = \delta Q_2 - PdV \tag{12}$$

after substitution of the expansion work. However, path 2 is *adiabatic* which means $\delta Q_2 = 0$. Thus, the first law for path 2 reduces to:

$$dU_2 = -PdV \tag{13}$$

To estimate the work down by the adiabatic expansion, lets expand the internal energy:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{14}$$

which gives:

$$\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = -PdV \tag{15}$$

or after collecting like differential terms:

$$\left(\frac{\partial U}{\partial T}\right)_V dT = -\left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \tag{16}$$

Eqn (16) can be applied for a general working fluid; however, we are analyzing the Carnot cycle for an ideal gas. Thus, we can simply Eqn (16) by first realizing that:

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \tag{17}$$

and second:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{18}$$

which gives:

$$C_V dT = -PdV \tag{19}$$

or:

$$\delta W_2 = C_V dT \tag{20}$$

Eqn (20) says that we can directly relate the work done to the temperature change in the working fluid of the system. Integrating both sides of Eqn (20) gives the work done by path 2:

$$W_2 = \int_{T_H}^{T_L} C_V dT \tag{21}$$

or:

$$W_2 = C_V (T_L - T_H) \tag{22}$$

- **Path 3**: Isothermal compression $\mathbb{P}_3 \to \mathbb{P}_4$. Following the derivation for path 1, the work generated by isothermal expansion from $\mathbb{P}_3 \to \mathbb{P}_4$ is given by:

$$W_3 = -nRT_L \ln \left(\frac{V_4}{V_3} \right) \tag{23}$$

- **Path 4**: Adiabatic compression $\mathbb{P}_4 \to \mathbb{P}_1$. Following the derivation of path 2, the work generated by adibatic expansion from $\mathbb{P}_4 \to \mathbb{P}_1$ is given by:

$$W_4 = C_V (T_H - T_L) \tag{24}$$

Change in a state function for a cyclic process. Beyond its efficiency, one of the other interesting things about Carnot is that it nicely demonstrates one of the central properties of *state functions*:

$$dU = \sum_{j=\mathbb{P}_1}^{\{\mathbb{P}\}} dU_j = 0 \tag{25}$$

The net change in a state function, such as internal energy, temperature, pressure or volume (irrespective of the working fluid) is zero around a closed path. This has important consequences later, and is easy to see from our first law analysis of the Carnot cycle: where

$$dU = dU_1 + dU_2 + dU_3 + dU_4 \tag{26}$$

If we ignore the fact that our working fluid is an ideal gas (assume its some arbitrary fluid), we simply need to integrate the dU expression around the path:

$$\int_{\mathbb{P}_1}^{\mathbb{P}_1} dU = \int_{\mathbb{P}_1}^{\mathbb{P}_2} dU_1 + \int_{\mathbb{P}_2}^{\mathbb{P}_3} dU_2 + \int_{\mathbb{P}_3}^{\mathbb{P}_4} dU_3 + \int_{\mathbb{P}_4}^{\mathbb{P}_1} dU_4 \tag{27}$$

or:

$$U_1 - U_1 = (U_2 - U_1) + (U_3 - U_2) + (U_4 - U_3) + (U_1 - U_4) = 0 \tag{28}$$

Even if we consider an ideal gas, we know that both $dU_1 = 0$ and $dU_3 = 0$ which gives:

$$dU = dU_2 + dU_4 \tag{29}$$

or:

$$dU = C_V dT\Big|_{\mathbb{P}_2 \to \mathbb{P}_3} + C_V dT\Big|_{\mathbb{P}_4 \to \mathbb{P}_1} \tag{30}$$

Integrating both sides of the differential internal energy equation gives:

$$\Delta U = C_V \int_{T_H}^{T_L} dT + C_V \int_{T_L}^{T_H} dT \tag{31}$$

or:

$$\Delta U = C_V \left[(T_H - T_L) + (T_L - T_H) \right] = 0 \tag{32}$$

Interestingly, non-state variables, such as heat and work, are *not* conserved along a closed path. To see that, lets compute the net work done by the cycle:

$$\delta W_{net} = \sum_{j=\mathbb{P}_1}^{\{\mathbb{P}\}} \delta W_j \neq 0 \tag{33}$$

or after integration and substitution of work definitions:

$$W_{net} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) + C_V \left(T_L - T_H\right) - nRT_L \ln\left(\frac{V_4}{V_3}\right) + C_V \left(T_H - T_L\right) \tag{34}$$

which reduces to:

$$W_{net} = -nRT_H \ln\left(\frac{V_2}{V_1}\right) - nRT_L \ln\left(\frac{V_4}{V_3}\right) \neq 0 \tag{35}$$

Efficiency of the Carnot cycle. One of the interesting features of the Carnot cycle is it's efficiency, denoted by the symbol η. The efficiency of a Carnot cycle is defined as the net work done by the system, divided by the net input heat:

$$\eta = -\frac{W_{net}}{Q_{in}} \tag{36}$$

Using our first law results, we can put the efficiency in terms of the two operating parameters we control, the temperature of the hold and cold reservoirs:

$$\eta = 1 - \frac{T_L}{T_H} \tag{37}$$

We can increase the efficiency by allowing $T_H \to \infty$ or by having a small value for T_L. As we shall see, the Carnot cycle is the *most* efficient cycle for converting heat to work. However, unfortunately Carnot is imaginary but it can serve as a useful model system to measure real results against.

References

1. Carnot S (1824) Reflections on the Motive Power of Fire and on Machines Fitted to Develop that Power. Paris, France: Bachelier.