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Recap:

Canonical ensemble \rightarrow ideal gas \rightarrow thermodynamic cycles

Changing (exchanging) energy ΔE

$$\Delta E = Q + W \begin{cases} \rightarrow \text{change in volume} & W = -P dV \\ \rightarrow \text{change in entropy} & Q = T dS \end{cases}$$

PV diagrams

\rightarrow isotherms & adiabats

$$Q = T dS$$

In this case both the pressure and temperature change, while the entropy (and therefore $VT^{3/2}$) is constant. What are ΔP and the change in the temperature $\Delta T = T_f - T_0$ in terms of P_0, V_0, V_f and the fixed number of particles N ?

$$V_0 T_0^{3/2} = V_f T_f^{3/2} \rightarrow T_f = T_0 \left(\frac{V_0}{V_f} \right)^{2/3}$$

$$\Delta T = T_0 \left[\left(\frac{V_0}{V_f} \right)^{2/3} - 1 \right] = \frac{P_0 V_0}{N} \left[\left(\frac{V_0}{V_f} \right)^{2/3} - 1 \right] > 0$$

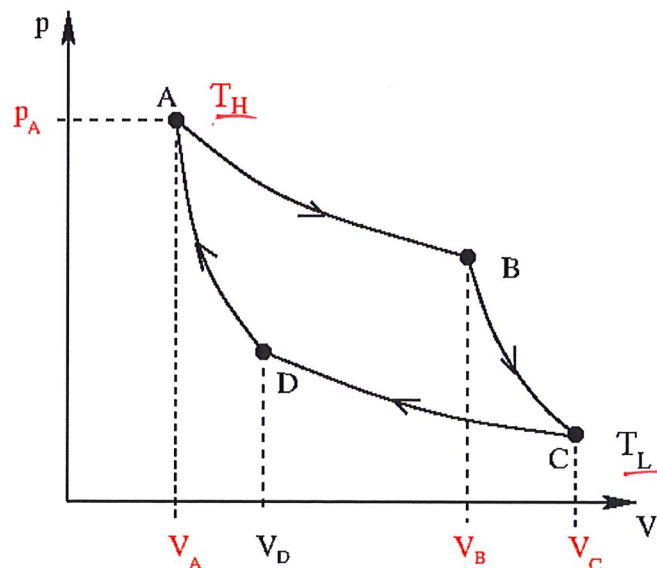
$$V_0^{2/3} \left(\frac{P_0 V_0}{N} \right) = V_f^{2/3} \left(\frac{P_f V_f}{N} \right) \rightarrow P_f = P_0 \left(\frac{V_0}{V_f} \right)^{5/3}$$

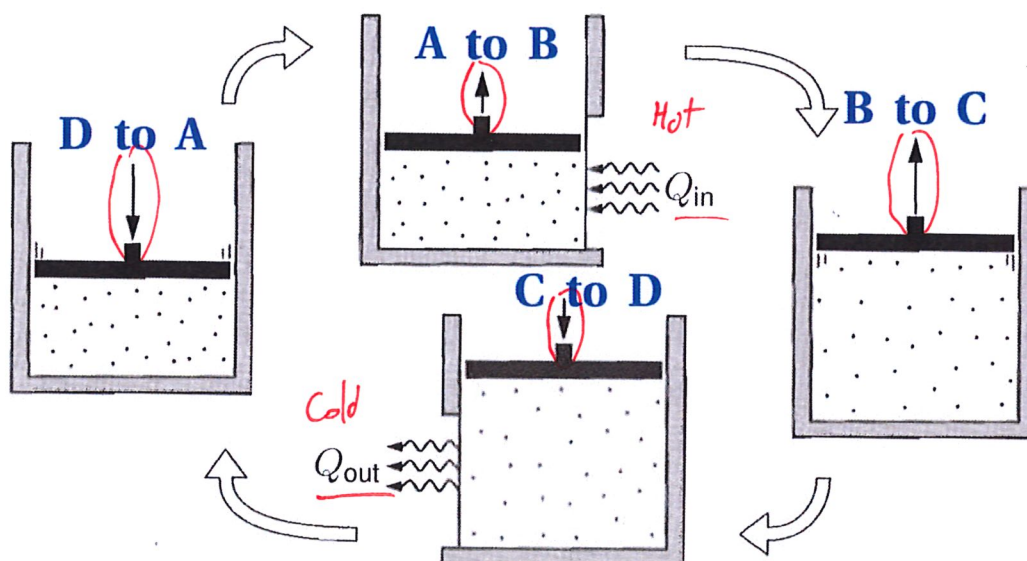
$$\Delta P = P_0 \left[\left(\frac{V_0}{V_f} \right)^{5/3} - 1 \right] > 0$$

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5.4 The Carnot cycle

A famous thermodynamic cycle was proposed by [Sadi Carnot](#) in 1824, and laid the groundwork for subsequent development of engines and refrigerators later in the nineteenth century. The key idea is to propose that the ideal gas in its container can exchange energy with either of two different thermal reservoirs: a 'hot' reservoir with temperature T_H and a 'cold' reservoir with temperature T_L . The Carnot cycle consists of four stages, which are first shown below in the form of a PV diagram, then illustrated in a sketch (adapted from Schroeder's *Introduction to Thermal Physics*) that provides a more concrete picture of the physical processes, and finally summarized in words.





The illustration above supposes that the hot reservoir is located to the right of the system, while the cold reservoir is located to its left. In words, the four stages are the following:

- From point A to point B the system undergoes slow isothermal expansion, bringing in heat Q_{in} from the hot reservoir in order to keep its temperature fixed at T_H .
- From point B to point C the system undergoes fast adiabatic expansion, with no heat exchange, until its temperature falls from T_H down to T_L .
- From point C to point D the system undergoes slow isothermal compression, expelling heat Q_{out} into the cold reservoir in order to keep its temperature fixed at T_L .
- From point D to point A the system undergoes fast adiabatic compression, with no heat exchange, until its temperature rises from T_L back up to T_H .

We need to make sure that these four processes really do produce a self-consistent closed cycle that our system could repeatedly follow. In a real experiment, we would have full control over the four variables $\{P_A, V_A, V_B, V_C\}$ coloured red in the PV diagram above. Specifically, we can prepare our N -particle system in initial macro-state A with our choice of pressure P_A and volume V_A , which through the ideal gas law specify the temperature $T_H = \frac{P_A V_A}{N}$ of the hot reservoir. We can then freely choose the volume $V_B > V_A$ at which to switch from isothermal expansion to adiabatic expansion, and similarly choose the volume $V_C > V_B$ at which we stop expanding and start compressing. (The choice of V_C is equivalent to choosing the temperature T_L of the cold reservoir.)

At this point, however, we are no longer free to choose an arbitrary volume $V_D < V_C$ at which to switch from isothermal compression to adiabatic compression — this switch needs to happen at precisely the correct point in order for the

final stage to bring the system back to its initial macro-state A . While we can expect that this will be possible for the Carnot cycle, a priori there is no guarantee that a given sequence of processes will close to form a self-consistent thermodynamic cycle.

In order to confirm the self-consistency of the Carnot cycle, we need to express the unknown quantities $\{P_B, P_C, T_L, P_D, V_D\}$ in terms of the four (red) inputs described above, along with the fixed number of particles N . At point B , we know the system's temperature remains $T_H = P_A V_A / N$. What is the pressure P_B in terms of $\{P_A, V_A, V_B, V_C, N\}$?

$$T_H = \frac{P_A V_A}{N} = \frac{P_B V_B}{N} \quad \rightarrow \quad P_B = P_A \left(\frac{V_A}{V_B} \right)$$

At point C , we know the system's entropy is the same as at point B . What are the temperature T_L and pressure P_C in terms of $\{P_A, V_A, V_B, V_C, N\}$?

$$V_B T_H^{3/2} = V_C T_L^{3/2} \quad \rightarrow \quad T_L = T_H \left(\frac{V_B}{V_C} \right)^{2/3} = \frac{P_A V_A}{N} \left(\frac{V_B}{V_C} \right)^{2/3} < T_H$$

$$N = \frac{P_A V_A}{T_H} = \frac{P_C V_C}{T_L} \quad \rightarrow \quad P_C = \frac{V_A}{V_C} \frac{T_L}{T_H} P_A = \frac{V_A}{V_C} \left(\frac{V_B}{V_C} \right)^{2/3} P_A < P_A$$

At point D , we know the system's temperature remains T_L . We have to demand that its entropy is the same as at point A , in order for the final adiabatic stage to connect points D and A . What are the resulting pressure P_D and volume V_D in terms of $\{P_A, V_A, V_B, V_C, N\}$?

$$V_A T_H^{3/2} = V_D T_L^{3/2} \quad \rightarrow \quad V_D = V_A \left(\frac{T_H}{T_L} \right)^{3/2} = V_A \left(\frac{V_C}{V_B} \right) > V_A$$

$$\frac{V_A V_C}{V_B} = V_D$$

$$N = \frac{P_A V_A}{T_H} = \frac{P_D V_D}{T_L} \quad \rightarrow \quad P_D = P_A \left(\frac{V_A}{V_D} \right) \left(\frac{T_L}{T_H} \right) = P_A \left(\frac{V_B}{V_C} \right) \left(\frac{V_B}{V_C} \right)^{2/3} = P_A \left(\frac{V_B}{V_C} \right)^{5/3} < P_A$$

You should find that all of $\{P_B, P_C, T_L, P_D, V_D\}$ can be consistently specified by the (red) inputs under our control, which establishes that the Carnot cycle is a valid thermodynamic cycle. This is not a surprising result, but does give us the

ingredients to address the question of how much net work (if any) this cycle can do on its surroundings, compared to the amount of heat it would transfer from the hot reservoir to the cold reservoir. It will simplify this calculation to use the following positive quantities, with subscripts (rather than negative signs) indicating whether energy is flowing into or out of the gas:

- When work is done on the system by its surroundings, $\underline{W_{in}} = W \geq 0$ from Eq. 59
- When work is done by the system on its surroundings, $\underline{W_{out}} = -W \geq 0$
- When heat enters the system, $\underline{Q_{in}} = Q \geq 0$ from Eq. 61
- When heat leaves the system, $\underline{Q_{out}} = -Q \geq 0$

We can now define a convenient combination of heat and work to consider.

The efficiency η of a thermodynamic engine is defined to be

$$\eta = \frac{W_{\text{done}}}{Q_{\text{in}}} = \frac{W_{\text{out}} - W_{\text{in}}}{Q_{\text{in}}}, \quad (64)$$

where $W_{\text{done}} = W_{\text{out}} - W_{\text{in}}$ is the net amount of work done by each repetition of the cycle, while Q_{in} is the total amount of heat that enters the system in each repetition.

By specifying a thermodynamic engine, we assume $\underline{W_{out}} > \underline{W_{in}}$, so that the overall cycle does more work on its surroundings than it requires as input to operate. This corresponds to $\underline{\eta} > 0$, and we can also put an upper bound on the efficiency, due to the first law of thermodynamics, Eq. 63. Because the system returns to its initial macro-state after each repetition of the cycle, we have

$$\begin{aligned} \Delta\langle E \rangle = 0 &= \underline{Q_{in}} - \underline{Q_{out}} + \underline{W_{in}} - \underline{W_{out}} \\ \implies \underline{W_{out}} - \underline{W_{in}} &= \underline{Q_{in}} - \underline{Q_{out}} \leq \underline{Q_{in}}, \end{aligned} \quad (65)$$

or $\underline{\eta} \leq 1$, with equality occurring when no 'waste' heat is expelled by the system throughout the entire cycle, $\underline{Q_{out}} = 0$. All together, $0 < \underline{\eta} \leq 1$ lets us interpret the efficiency as the fraction of the input heat that the engine is able to use to do work on its surroundings.

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Let's illustrate these ideas by computing the efficiency of the Carnot cycle. We can divide this calculation into smaller pieces by considering the contributions to W_{done} and Q_{in} from each of the cycle's four stages.