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Recap: Thermodynamic <u>cycles</u> (ideal gases (canonical ensemble))

PV diagrams

Carnot cycle between hot & cold reservoir
isotherms & adiabats

Efficiency $\eta = \frac{W_{done}}{Q_{in}}$

First law: $0 < \eta \leq 1$ "can't win"

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

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

The **efficiency** η of a thermodynamic engine is defined to be

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

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 $W_{\text{out}} > W_{\text{in}}$, so that the overall cycle does more work on its surroundings than it requires as input to operate. This corresponds to $\eta > 0$, 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

$$\begin{aligned} \Delta\langle E\rangle = 0 &= Q_{\text{in}} - Q_{\text{out}} + W_{\text{in}} - W_{\text{out}} \\ \Longrightarrow W_{\text{out}} - W_{\text{in}} &= Q_{\text{in}} - Q_{\text{out}} \leq Q_{\text{in}}, \end{aligned} \tag{65}$$

or $\eta \leq 1$, with equality occurring when no 'waste' heat is expelled by the system throughout the entire cycle, $Q_{\text{out}} = 0$. All together, $0 < \eta \leq 1$ 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.

can't win

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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.

First, in the isothermal expansion from point A to point B, the ideal gas law provides $P(V)$ to insert into Eq. 59:

$$W_{AB} = -\int_{V_A}^{V_B} P(V)\, dV = -NT_H \int_{V_A}^{V_B} \frac{dV}{V} = -NT_H \log\left(\frac{V_B}{V_A}\right)$$
$$= P_A V_A \log\left(\frac{V_A}{V_B}\right) < 0$$

You should find $W_{AB} < 0$, meaning the system does work on its surroundings during this stage. At the same time, the constant temperature means $\Delta\langle E\rangle \propto \Delta T = 0$ from Eq. 52, so that $Q_{AB} = -W_{AB} > 0$, in agreement with our earlier observation of heat flowing into the system during this stage.

Next, in the adiabatic expansion from point B to point C, we know $Q_{BC} = 0$, which lets us use the first law of thermodynamics to compute the work:

$$W_{BC} = \Delta\langle E\rangle = \frac{3}{2} N\Delta T = \frac{3}{2} N(T_L - T_H) = \frac{3}{2} NT_H\left(\frac{T_L}{T_H} - 1\right)$$
$$= \frac{3}{2} P_A V_A\left[\left(\frac{V_B}{V_C}\right)^{2/3} - 1\right] < 0$$

$$\frac{T_L}{T_H} = \left(\frac{V_B}{V_C}\right)^{2/3}$$

You should find that the system continues doing work on its surroundings during this stage, $W_{BC} < 0$.

Finally, the computations for the two compression stages are directly analogous to those above. For the isothermal compression from point C to point D, we have

$$W_{CD} = -\int_{V_C}^{V_D} P(V)\, dV = NT_L \log\left(\frac{V_C}{V_D}\right) = NT_H\left(\frac{T_L}{T_H}\right)\log\left(\frac{V_C}{V_D}\right)$$
$$= P_A V_A\left(\frac{V_B}{V_C}\right)^{2/3} \log\left(\frac{V_B}{V_A}\right) > 0$$

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

Now you should find $W_{CD} > 0$, meaning this compressions requires work to be done on the system by its surroundings, while $Q_{CD} = -W_{CD} < 0$ means heat flows out of the system. For the adiabatic compression from point D to point A, we know $Q_{DA} = 0$ while the change in temperature is exactly opposite the ΔT of the $B \to C$ adiabatic expansion. Therefore $W_{DA} = -W_{BC} > 0$ and more work has to be done on the system to complete the cycle.

Putting everything together,

$$
\begin{aligned}
W_{\text{out}} &= -W_{AB} - W_{BC} > 0 \\
W_{\text{in}} &= W_{CD} + W_{DA} = W_{CD} - W_{BC} \\
Q_{\text{in}} &= Q_{AB} = -W_{AB} \\
\eta &= \frac{-W_{AB} - \cancel{W_{BC}} - W_{CD} + \cancel{W_{BC}}}{-W_{AB}} = 1 + \frac{W_{CD}}{W_{AB}} = 1 - \frac{T_L}{T_H}.
\end{aligned} \tag{66}
$$

We can check that our result $\eta = 1 - \frac{T_L}{T_H}$ for the efficiency of the Carnot cycle makes sense. Since $T_L < T_H$, we have $\eta > 0$. If the temperatures of the hot and cold reservoirs approach each other, $\frac{T_L}{T_H} \to 1$, then the cycle would collapse to a single isotherm with $W_{\text{out}} = W_{\text{in}}$ and vanishing efficiency $\eta \to 0$. In the opposite limit of a large difference in the temperatures $T_L \ll T_H$, the efficiency would improve, with $\eta \to 1$ as $\frac{T_L}{T_H} \to 0$.

It turns out to be generic for heat engines to operate more efficiently as the temperature difference between their hot and cold reservoirs increases, and they always cease performing net work as $\frac{T_L}{T_H} \to 1$. The Carnot cycle is special because its efficiency $\eta = 1 - \frac{T_L}{T_H}$ is the theoretical maximum allowed by the second law of thermodynamics. We can show this by using Eq. 65 to rewrite

$$
\eta = \frac{Q_{\text{in}} - Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{Q_{\text{out}}}{Q_{\text{in}}} = 1 - \frac{T_L \Delta S_{\text{out}}}{T_H \Delta S_{\text{in}}},
$$

where the last equality uses Eq. 62 and the fact that the input heat $Q_{\text{in}} = T_H \Delta S_{\text{in}}$ enters the engine from the hot reservoir with temperature T_H, while the waste heat $Q_{\text{out}} = T_L \Delta S_{\text{out}}$ is expelled to the cold reservoir with temperature T_L. After each repetition of the cycle, the gas returns to its original macro-state, with its original entropy, after absorbing entropy ΔS_{in} from its surroundings and expelling ΔS_{out} back out again. The second law therefore demands $\Delta S_{\text{out}} \geq \Delta S_{\text{in}}$, so that

$$
\eta = 1 - \frac{T_L}{T_H} \frac{\Delta S_{\text{out}}}{\Delta S_{\text{in}}} \leq 1 - \frac{T_L}{T_H}
$$

can't break even

in principle, for any thermodynamic engine.

Finally, if we were to operate the Carnot cycle in reverse, with isothermal expansion at temperature T_L and compression at T_H, we would do work on the system in order to bring heat in from the cold reservoir (i.e., $Q_{\text{in}} \sim T_L$) and expel it to the hot reservoir ($Q_{\text{out}} \sim T_H$). In other words, we would have a refrigerator rather than an engine. The 'efficiency' of a refrigerator is called its *coefficient of performance*, and defined as

$$
\text{COP} = \frac{Q_{\text{in}}}{W_{\text{in}} - W_{\text{out}}} = \frac{Q_{\text{in}}}{Q_{\text{out}} - Q_{\text{in}}} = \frac{1}{Q_{\text{out}}/Q_{\text{in}} - 1} \leq \frac{1}{T_H/T_L - 1} = \frac{T_L}{T_H - T_L},
$$

$\sim 5 \to 6$

which can be greater than one. The reversed Carnot cycle provides the best possible COP for a refrigerator. Despite its efficiency, the Carnot cycle does not provide a practical engine or refrigerator, simply because its slow isothermal stages take too long! Real engines and refrigerators sacrifice efficiency for functionality.

Unit 6: Grand-canonical ensemble

6.1 The particle reservoir and chemical potential

Now that we have had some fun with applications of the canonical ensemble, we will complete our more formal development of statistical ensembles by considering the grand-canonical ensemble. Recall that statistical ensembles are probability spaces describing the micro-states that a system can adopt as it evolves in time, subject to certain constraints. Back in Unit 2 we first considered the micro-canonical ensemble, for which these constraints are conservation of the internal energy E and particle number N. We then introduced the canonical ensemble in Unit 3 by allowing the system's internal energy to fluctuate, while keeping its temperature T fixed through thermal contact with a large external thermal reservoir.

Building on this pattern, the next step is to allow *both* the system's energy and its particle number to fluctuate. Generalizing our earlier work on the canonical ensemble, these fluctuations occur through contact between the system and a large external reservoir. This is now a **particle reservoir**, with which the system can exchange both energy and particles.

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In the same way that energy exchange leads to a fixed temperature, we expect there to be some quantity that will be fixed due to particle exchange. Recall that we initially defined the temperature in the context of the micro-canonical ensemble in thermodynamic equilibrium (Eq. 22), as the dependence of the entropy on the internal energy for a fixed number of degrees of freedom:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_N .$$

The quantity we are now interested in comes from the complementary analysis interchanging the roles of E and N.

In thermodynamic equilibrium, the **chemical potential** in the micro-canonical ensemble is defined by

$$\mu = -T \left.\frac{\partial S}{\partial N}\right|_E . \tag{67}$$

This definition is not terribly intuitive, and unlike the temperature the chemical potential is not a familiar concept from everyday experiences. To gain some insight into the chemical potential, we can first note that μ has dimensions of energy. It is also an intensive quantity, like the temperature — it is independent of the extent of the system, and remains the same if we consider only a part of a larger system. Finally, we can expect the chemical potential to be negative, at least for 'natural' systems with positive temperatures. This is because the partial derivative $\frac{\partial S}{\partial N}$ is generally positive, since systems with more degrees of freedom typically have more entropy, reflecting the greater amount of information they can