Thermodynamics and statistical mechanics

GRE undergraduate preparation · local supported objectives

Thermodynamics and statistical mechanics

- Use the **first law 热力学第一定律** with a stated sign convention.
- Apply Carnot limits and entropy changes.
- Weight states with Boltzmann factors and a **partition function**.
- Choose Fermi–Dirac, Bose–Einstein or Maxwell–Boltzmann statistics.

The first law and its signs

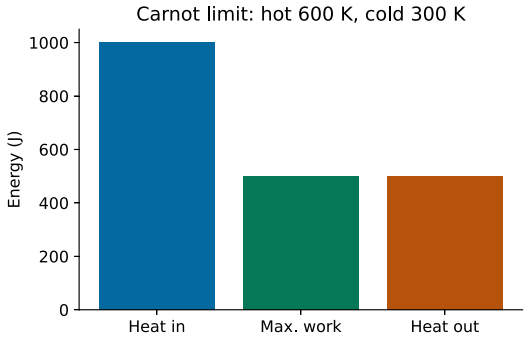
- Isothermal ideal gas: $\Delta U = 0$, so $Q = W = nRT\ln(V_f/V_i)$.
- Isochoric (constant volume): $W = 0$, so $Q = \Delta U = nC_V\Delta T$.
- **Adiabatic 绝热的** ($Q = 0$): PV^γ is constant, and the gas cools as it expands.
- On a P–V diagram, the work is the area under the path.

Carnot limits

- Between 600 K and 300 K, at most half of the heat input becomes work.
- A refrigerator works better when the two temperatures are close.

$$\eta \le 1 - \frac{T_c}{T_h}, \qquad \mathrm{COP}_{\mathrm{fridge}} \le \frac{T_c}{T_h - T_c}$$

Figure: Carnot limits



- Carnot efficiency $1 - 300/600 = 1/2$ caps the work at half the heat input
- Read the axes and units first.

Entropy

- Entropy is a state function. For an irreversible process, find ΔS along any reversible path between the same states.
- Free expansion of an ideal gas to double its volume: $W = 0$ and $Q = 0$, yet $\Delta S = nR\ln 2 > 0$.
- Statistically, $S = k\ln\Omega$, where Ω is the number of microstates.

Boltzmann factors

- Z is the **partition function** 配分函数; g_i counts states with the same energy.
- Two levels a gap ΔE apart: $N_2/N_1 = (g_2/g_1)\, e^{-\Delta E/kT}$.
- At room temperature, $kT \approx 0.025$ eV.

$$P(E_i) = \frac{g_i\, e^{-E_i/kT}}{Z}, \qquad Z = \sum_i g_i\, e^{-E_i/kT}$$

Which statistics?

- Plus sign: **fermions** 费米子 (electrons, protons), at most one per state.
- Minus sign: **bosons** 玻色子 (photons, helium-4 atoms), which can pile into one state.
- When $\overline{n} \ll 1$ (a hot, dilute gas), both reduce to Maxwell–Boltzmann.

$$\overline{n} = \frac{1}{e^{(E-\mu)/kT} \pm 1}$$

Worked example: an impossible engine

- Carnot limit: $\eta_{\max} = 1 - 300/600 = 0.50$. The claim breaks the second law, though not the first.
- Best case, per 1000 J taken in: 500 J of work and 500 J rejected.
- Entropy check: $\Delta S_{\text{hot}} = -1000/600 = -1.67$ J/K and $\Delta S_{\text{cold}} = +500/300 = +1.67$ J/K. The total is zero, as a reversible engine needs. The claimed engine would reject only 300 J, giving a total of -0.67 J/K: impossible.

Worked example: expansion and level populations

- Work: $W = nRT\ln 2 = (1)(8.31)(300)(0.693) = 1.73$ kJ, and $Q = W$ because $\Delta U = 0$.
- Entropy: $\Delta S = Q/T = 1730/300 = 5.76$ J/K, the same as $R\ln 2$.
- Two levels 0.10 eV apart at 300 K ($kT = 0.0259$ eV): $N_2/N_1 = e^{-3.87} = 0.021$, so about 2% are excited.

Common errors

- Using degrees Celsius in $1 - T_c/T_h$.
- Mixing the two sign conventions for work.
- Saying free expansion has no entropy change because $Q = 0$.

Common errors (2)

- Forgetting the degeneracy g_i in a Boltzmann ratio.
- Putting two electrons in the same quantum state.

Key terms

- **reservoir**: A body large enough that heat flow does not change its temperature.
- **entropy**: A state function that measures the number of ways a state can be arranged; $\Delta S = Q/T$ for reversible heat flow.
- **first law**: Energy conservation for heat and work: $\Delta U = Q - W$.
- **adiabatic**: With no heat exchanged.

Check yourself

- What is the best possible COP of a refrigerator between 270 K and 300 K?
- Two moles of ideal gas expand freely into a vacuum, doubling their volume. What is ΔS?
- Which statistics describe the conduction electrons in a metal?