

Thermodynamics and statistical mechanics

GRE · GRE Subject Test · GRE Physics

Two engines can obey energy conservation, yet only one obeys the entropy limit on efficiency.

Prerequisites: 19, 20, 34, 35, 36.

- Apply the first and second laws with a sign convention
- Relate ensembles, Boltzmann factors and entropy
- Analyse ideal gases, heat engines and quantum statistics

Choose the system and model

State the first-law sign convention: $\Delta U = Q - W$ when W is work done by the system.

Use the governing relation

For a reversible engine between reservoirs, efficiency is bounded by $1 - T_c/T_h$ using absolute temperatures.

Apply the conditions

Boltzmann weights are $\exp(-E/kT)$. Probabilities require division by the partition function.

Check the conclusion

Distinguish Maxwell–Boltzmann, Bose–Einstein and Fermi–Dirac assumptions. Fermions cannot share an identical single-particle state.

Worked method

Use work W done by the gas as positive. The first law is

$$\Delta U = Q - W.$$

For reversible isothermal expansion of an ideal gas, U depends only on T , so

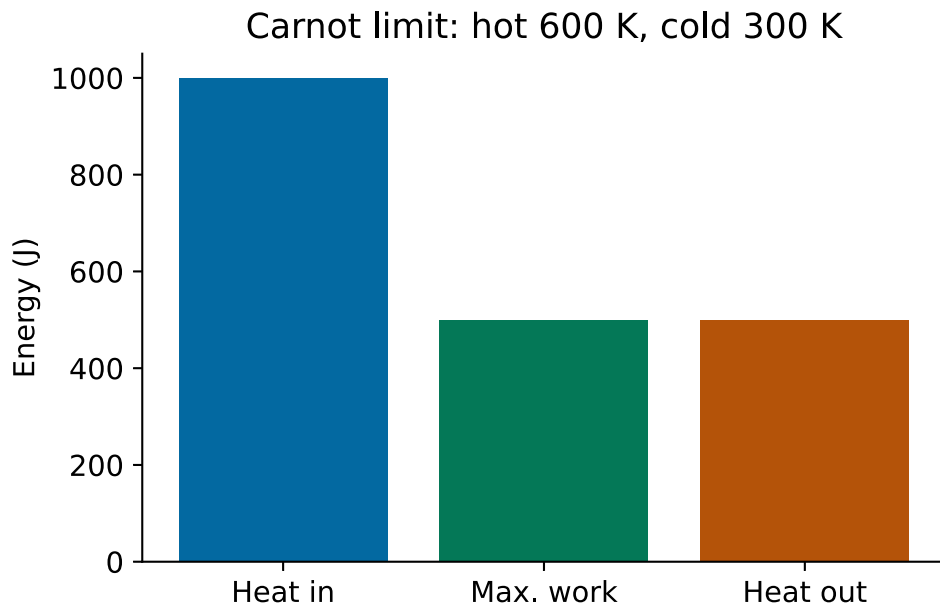
$$W = \int_{V_i}^{V_f} p dV = nRT \ln(V_f/V_i), \quad Q = W.$$

For $n = 0.50$ mol, $T = 300$ K and doubled volume,

$$W = nRT \ln 2 = (0.50 \text{ mol})(8.314 \text{ J/(mol K)})(300 \text{ K}) \ln 2 = 864 \text{ J}.$$

$$\Delta S = Q_{rev}/T = (864 \text{ J})/(300 \text{ K}) = 2.88 \text{ J/K}.$$

The gas expands and receives heat. The reservoir loses the same entropy in this reversible limit.



Thermodynamics and statistical mechanics: original GRE teaching diagram.

Check conditions and vocabulary

Celsius temperature ratios cannot be used in the Carnot efficiency formula.

entropy: A state quantity connected to multiplicity and reversible heat transfer.

partition function: The sum of statistical weights used to normalise probabilities.