

Thermodynamics and statistical mechanics

GRE undergraduate preparation · local supported objectives

Choose the physical question

Reasoning

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

Reasoning

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

Use the governing relation

Reasoning

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

Apply the conditions

Reasoning

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

Check the conclusion

Reasoning

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

Worked reasoning 1

Reasoning

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

Worked relation 2

Reasoning

Apply this relation only under the conditions just stated.

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

Worked reasoning 3

Reasoning

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

Worked relation 4

Reasoning

Apply this relation only under the conditions just stated.

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

Worked reasoning 5

Reasoning

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

Worked relation 6

Reasoning

Apply this relation only under the conditions just stated.

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

Worked relation 8

Reasoning

Apply this relation only under the conditions just stated.

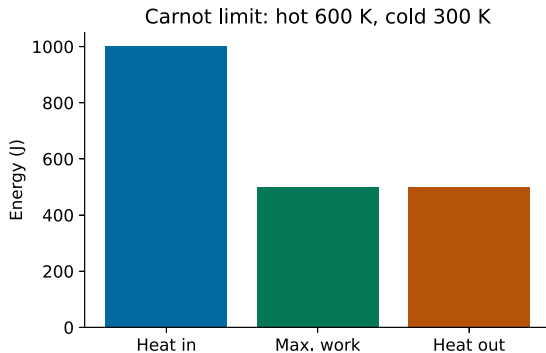
$$\Delta S = Q_{\text{rev}}/T = (864 \text{ J})/(300 \text{ K}) = 2.88 \text{ J/K}.$$

Worked reasoning 9

Reasoning

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

Read the original diagram



- Original GRE teaching diagram: Thermodynamics and statistical mechanics
- Identify the axes, units, directions and the stated model.

Independent transfer · attempt

Reasoning

An insulated rigid vessel contains ideal gas confined initially to half its volume. Remove the internal partition into vacuum. Compare Q , W , temperature change and gas entropy change with reversible isothermal expansion to the same final volume. **[5]**

Independent transfer · reasoning

Reasoning

Free expansion has $Q = 0$ by insulation and $W = 0$ because external pressure is zero. Thus $\Delta U = 0$ and ideal-gas temperature is unchanged. Entropy is a state function: $\Delta S = nR \ln 2 > 0$, evaluated on an imagined reversible isothermal path. The actual process is irreversible; $Q_{actual}/T = 0$ is not its entropy change. Reversible expansion has $Q = W = nRT \ln 2$ and the same gas entropy increase, with a matching reservoir entropy decrease. Award the four quantities and comparison.

Check assumptions and limits

Reasoning

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

Keep the technical distinctions

Reasoning

entropy : A state quantity connected to multiplicity and reversible heat transfer.
partition function : The sum of statistical weights used to normalise probabilities.

Check yourself

- Define entropy and give its condition of use.
- Define partition function and give its condition of use.
- Redo the original transfer with a changed parameter; check a limiting case.