

4.1 Thermodynamics and statistical mechanics

Name: _____ Class: _____ Date: _____

Total: 11 marks

KEY WORDS entropy • partition function

Objective

Apply the first and second laws with a sign convention; Relate ensembles, Boltzmann factors and entropy ; Analyse ideal gases, heat engines and quantum statistics. Original public practice; not an ETS paper.

1 Key knowledge and worked examples

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

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

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

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

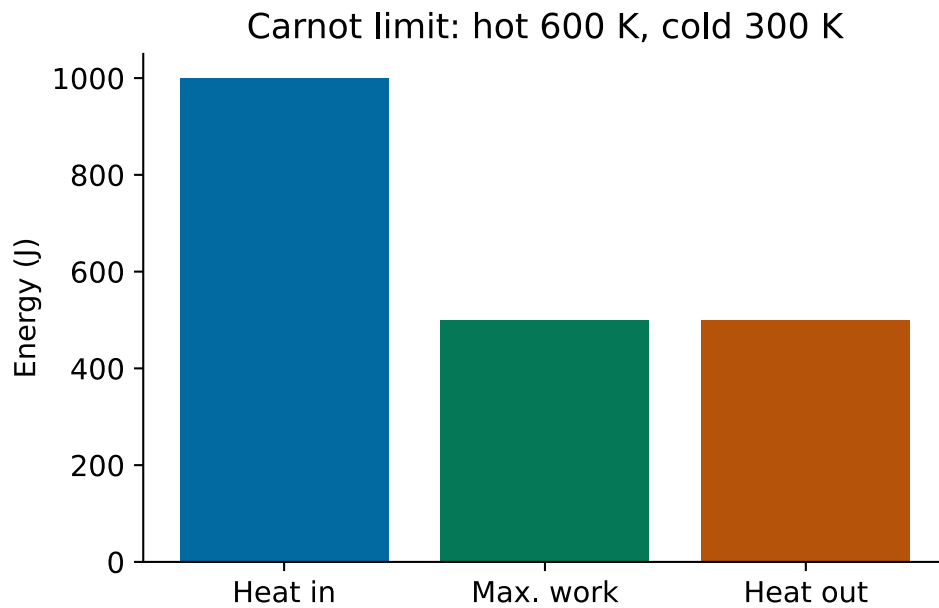
$$W = \int_{V_i}^{V_f} p dV = nRT \ln(V_f/V_i), \quad Q = W.$$

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.



2 Practice

2.1 Choose one answer. A Carnot engine between 400 K and 300 K has efficiency: [1]

- A 0.25
- B 0.75
- C 1.33

2.2 Choose one answer. A higher-energy state's Boltzmann weight at fixed T is: [1]

- A greater
- B smaller
- C always identical

2.3 A system receives 100 J heat and does 40 J work. $\Delta U =$ _____ J. Show your relation and units. [2]

Solutions

2.1 A $1 - 300/400 = 0.25$.

Compare the rejected options: 0.75; 1.33. Use the stated model and conditions.

2.2 B The negative exponential decreases with energy.

Compare the rejected options: greater; always identical. Use the stated model and conditions.

2.3 60. $\Delta U = Q - W = 100 - 40$.

2.4 False. That violates the second law.

3.1 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; $Q_{\text{actual}}/T = 0$ 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.