Entropy, First Law, Energy, and Work

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1 Quiz Review

- **Question 1:** State the fundamental assumption of Statistical Mechanics.
- **Answer:** For an isolated system in equilibrium, all accessible microstates are equally likely.
- **Question 2:** In one sentence, state the Second Law of Thermodynamics.
- **Answer:** Entropy always increases. Any large system in equilibrium will be found in the macrostate with the largest multiplicity.

2 Boltzmann Entropy and Information

So far, we have seen the Boltzmann entropy:

$$S(E, N, V) = k_B \ln \Omega(E, N, V) \tag{1}$$

If all accessible microstates are equally likely, just by simple probability, the system will find itself in the macrostate with the largest multiplicity. This maximizes entropy by construction.

This also minimizes the information we have about the system:

- **High Entropy ↔ Low Information**
- Entropy is often said to be associated with *disorder* within a physical system. This disorder is associated with all the possible microstates corresponding to a given macrostate.

3 Temperature and Pressure Definitions

Once we know the entropy, we can define equilibrium temperature T:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} \tag{2}$$

(Note: N and V are fixed when we differentiate).

We also introduce the pressure P:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{E,N} \tag{3}$$

Pressure is Force per unit Area ($P = F/A$), with units $[P] = N/m^2$.

3.1 Justification for the Pressure Definition

We can justify this by looking at the entropy of a combined system with volume V_{tot} and total energy E. Consider two systems separated by a movable partition (allowing volume exchange) but at the same temperature.

The multiplicity of the total system is:

$$\Omega(V_{\text{tot}}) = \sum_{\{V_i\}} \exp\left[\frac{S_1(V_i)}{k_B} + \frac{S_2(V_{\text{tot}} - V_i)}{k_B}\right] \tag{4}$$

Using the same argument that we used when defining temperature, this sum is dominated by its largest term, which happens when $V_i = V_*$ such $S_1(V_*) + S_2(V_{\text{tot}} - V_*)$ is a maximum. This maximum occurs when

$$\left.\frac{\partial S_1}{\partial V}\right|_{V_*} = \left.\frac{\partial S_2}{\partial V}\right|_{V_{\text{tot}}-V_*} \tag{5}$$

Substituting the definition of pressure ($P/T = \partial S/\partial V$):

$$\frac{P_1}{T} = \frac{P_2}{T} \implies P_1 = P_2 \tag{6}$$

This makes intuitive sense: the movable barrier will settle where the pressure is equal on both sides. Now, despite the above definition, pressure has little to do with entropy. To see this, use the definition of temperature in the definition of entropy:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{E,N} = \left(\frac{\partial E}{\partial S}\right)_{N,V}\left(\frac{\partial S}{\partial V}\right)_{E,N}. \tag{7}$$

We see that the dependence on entropy cancels out in the chain rule.

4 The First Law of Thermodynamics

To make the relationship formal, consider the total differential of entropy $S(E, V)$ (keeping N fixed):

$$dS = \left(\frac{\partial S}{\partial E}\right) dE + \left(\frac{\partial S}{\partial V}\right) dV \tag{8}$$

Substituting the definitions of temperature and pressure:

$$dS = \frac{1}{T} dE + \frac{P}{T} dV \tag{9}$$

Rearranging this gives the fundamental thermodynamic relation:

$$dE = TdS - PdV \tag{10}$$

This equation is a statement about energy conservation and is known as the **First Law of Thermodynamics**.

4.1 Work (-PdV)

Consider the second term, $-PdV$.

- Since $P = F/A$, then $PdV = (F/A)(Adx) = Fdx$.
- This represents mechanical **Work**.

Sign Convention:

- If $dV < 0$ (compression), then $-PdV > 0$. We are applying force on the system, doing work *on* it, and increasing its energy.
- If $dV > 0$ (expansion), then $-PdV < 0$. The system is doing work and losing energy.

4.2 Heat (TdS)

What about the TdS term? This must be a form of energy transferred (absorbed) from the surroundings.

- This energy is called **Heat**.
- Heat is associated with the random motion of atoms and molecules in a system.

5 Heat Capacity Revisited

Heat capacity is defined generally as $C = \frac{\partial E}{\partial T}$. However, because we have multiple state variables (like V), we must specify what is held constant.

5.1 Heat Capacity at Constant Volume (C_V)

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V \tag{11}$$

If V is constant, then $dV = 0$, so $dE = TdS$. Thus:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \tag{12}$$

Since TdS is the heat absorbed, the heat capacity measures the ability to absorb heat (as opposed to other forms of energy).

5.2 Heat Capacity at Constant Pressure (C_P)

Sometimes it is easier to compute heat capacity at constant pressure (this is typically what you find in tables):

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P \tag{13}$$

6 Reversible vs. Irreversible Processes

- **Irreversible Process:** A physical process that increases the total entropy of the Universe. This process cannot happen in reverse as it would violate the Second Law.
- **Reversible Process:** A process that leaves the entropy of the Universe unchanged. These are usually *quasistatic* (occurring very slowly).

7 Example Problem: Irreversible Compression

A cylinder contains one liter of air at room temperature (300 K) and atmospheric pressure (10^5 N/m^2). At one end is a massless piston with surface area 0.01 m^2. You push the piston in very suddenly, exerting a force of 2000 N. The piston moves 1 mm before stopping.

Solution

(a) Work Done on the System

Work is defined as the force applied multiplied by the displacement in the direction of the force.

$$F = 2000\,\text{N}$$
$$\Delta x = 1\,\text{mm} = 0.001\,\text{m}$$

The work done W is:

$$W = F \cdot \Delta x = (2000\,\text{N})(0.001\,\text{m}) = 2\,\text{J} \tag{14}$$

Answer: You have done **2 Joules** of work.

(b) Heat Added to the Gas

The problem states the piston is pushed "very suddenly." In thermodynamics, a sudden compression is treated as an **adiabatic** process because there is insufficient time for heat to flow through the cylinder walls.

$$Q = 0\,\text{J} \tag{15}$$

Answer: 0 Joules of heat has been added.

(c) Increase in Internal Energy

According to the First Law of Thermodynamics:

$$\Delta E = Q + W \tag{16}$$

Using the values from (a) and (b):

$$\Delta E = 0 + 2\,\text{J} = 2\,\text{J} \tag{17}$$

Answer: The energy of the gas increases by **2 Joules**.

(d) Change in Entropy

We assume the gas returns to equilibrium after the compression. Since the changes in volume and energy are small, we can use the **Thermodynamic Identity** in differential form:

$$dE = TdS - PdV \tag{18}$$

Rearranging to solve for entropy change dS:

$$dS = \frac{1}{T}dE + \frac{P}{T}dV \tag{19}$$

List of Values:

- $T = 300$ K
- $P = 10^5$ N/m^2
- $\Delta E = +2$ J
- $\Delta V = -(\text{Area} \times \Delta x) = -(0.01\,\text{m}^2)(0.001\,\text{m}) = -10^{-5}\,\text{m}^3$ (Negative due to compression)

Substituting these values:

$$\begin{aligned}\Delta S &\approx \frac{1}{300}(2) + \frac{10^5}{300}(-10^{-5}) \\ &= \frac{2}{300} - \frac{1}{300} \\ &= \frac{1}{300}\,\text{J/K} \approx 0.0033\,\text{J/K}\end{aligned}$$

Answer: The entropy increases by approximately **0.0033 J/K**.

Discussion: Why is $dS > 0$ if $Q = 0$?

It may seem contradictory that entropy increases ($\Delta S > 0$) even though no heat was added ($Q = 0$). This occurs because the process is **irreversible**.

The definition $dS = dQ/T$ applies only to reversible processes. In this case, the "sudden" pushing of the piston created turbulence and shock waves. The work done (2 J) exceeded the work required for quasistatic compression ($P_{\text{atm}}\Delta V = 1$ J), with P_{atm} being the atmospheric pressure here . This extra 1 Joule of energy dissipated into internal heat, generating entropy.