
Topic: The second law of Thermodynamics and the concept of entropy, Heat engine.

Entropy

Entropy (S) is a **measure of the disorder or randomness** of a system. The change in entropy (ΔS) for a process is defined as:

$$\Delta S = \int \frac{dQ}{T}$$

where: dQ is the heat added to the system, T is the temperature at which the heat is added.

Properties of Entropy

- Entropy is a state function, meaning that the change in entropy depends only on the initial and final states of the system, not on the path taken. - Entropy increases in a spontaneous process. If the entropy of a system increases, it indicates that the system is becoming more disordered.

Second Law of Thermodynamics

The second law of thermodynamics states that the total entropy of an isolated system can never decrease over time. In any spontaneous process, the entropy of the system and its surroundings always increases.

Entropy and the Second Law

The second law of thermodynamics implies that the entropy of the universe tends to increase over time. The change in the total entropy of an isolated system, considering both the system and its surroundings, is:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

For any spontaneous process, the total entropy change must be greater than zero. This is why processes that increase the disorder of the system (such as diffusion or mixing) are spontaneous.

Derivation of the Entropy Change Formula for an Isothermal Process

Consider an ideal gas undergoing an isothermal expansion or compression, where **the temperature remains constant**. We wish to derive the formula for the entropy change (ΔS) of the gas during this process.

First Law of Thermodynamics

The first law of thermodynamics is given by:

$$dU = dQ - dW$$

where: - dU is the change in internal energy, - dQ is the heat added to the system, - dW is the work done by the system.

For an **isothermal** process, the temperature of the system is constant, and the internal energy of an ideal gas depends only on temperature. Therefore, $dU = 0$ for an ideal gas during an isothermal process. This simplifies the first law to:

$$dQ = dW$$

Thus, the heat added to the system equals the work done by the system.

Work Done by an Ideal Gas

The work done by an ideal gas during an isothermal expansion or compression is given by:

$$dW = P dV$$

where P is the pressure and dV is the change in volume. From the ideal gas law, we know that:

$$P = \frac{nRT}{V}$$

where: - n is the number of moles, - R is the universal gas constant, - T is the temperature, - V is the volume.

Substituting the expression for pressure into the equation for work, we get:

$$dW = \frac{nRT}{V} dV$$

Heat Added to the System

Since $\delta Q = \delta W$ for an isothermal process, the heat added to the system is:

$$dQ = \frac{nRT}{V} dV$$

Now, to find the total heat added (Q) during the entire process, we integrate from the initial volume V_1 to the final volume V_2 :

$$Q = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

Since T is constant, it can be taken outside the integral:

$$Q = nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

The integral of $\frac{1}{V}$ is $\ln V$, so:

$$Q = nRT [\ln V]_{V_1}^{V_2}$$

This simplifies to:

$$Q = nRT (\ln V_2 - \ln V_1)$$

Using the logarithmic identity $\ln \frac{V_2}{V_1} = \ln V_2 - \ln V_1$, we get the final expression for the heat added during an isothermal process:

$$Q = nRT \ln \frac{V_2}{V_1}$$

Entropy Change

The entropy change ΔS for an ideal gas is related to the heat added to the system during a reversible process by the following formula:

$$\Delta S = \frac{Q_{\text{rev}}}{T}$$

Substituting the expression for Q into this equation:

$$\Delta S = \frac{nRT \ln \frac{V_2}{V_1}}{T}$$

The temperature T cancels out, and we are left with the formula for the entropy change of an ideal gas during an isothermal process:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

Problem 1:

Two identical copper blocks, each of mass $m = 1.5 \text{ kg}$, are placed in a thermally insulated box. Block L is initially at a temperature $T_{iL} = 60^\circ\text{C}$, and block R is at $T_{iR} = 20^\circ\text{C}$. The specific heat of copper is $c = 386 \text{ J/kg}\cdot\text{K}$. After removing an insulating shutter between the blocks, they come to thermal equilibrium at a final temperature $T_f = 40^\circ\text{C}$. Determine the net entropy change (ΔS_{net}) of the two-block system during this irreversible process.

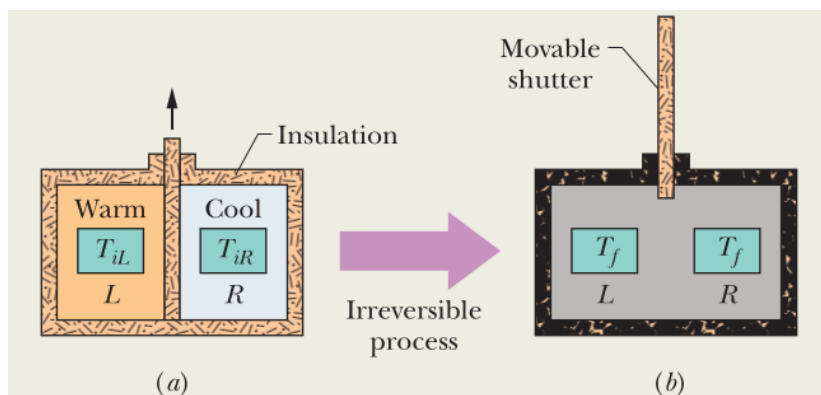


Figure 1: (a) In the initial state, two copper blocks L and R , identical except for their temperatures, are in an insulating box and are separated by an insulating shutter. (b) When the shutter is removed, the blocks exchange energy as heat and come to a final state, both with the same temperature T_f .

Solution

Initial temperatures and final temperature in Kelvin:

$$T_{iL} = 60^\circ\text{C} + 273 = 333 \text{ K}, \quad T_{iR} = 20^\circ\text{C} + 273 = 293 \text{ K}, \quad T_f = 40^\circ\text{C} + 273 = 313 \text{ K}.$$

Entropy change for block L :

Block L loses heat as it cools from T_{iL} to T_f . The entropy change is given by:

$$\Delta S_L = mc \ln \left(\frac{T_f}{T_{iL}} \right).$$

Substitute the given values:

$$\Delta S_L = (1.5)(386) \ln \left(\frac{313}{333} \right) \text{ J/K}.$$

Calculate:

$$\Delta S_L = 579 \ln(0.9402) \approx 579 \cdot (-0.0614) = -35.6 \text{ J/K}.$$

Entropy change for block R :

Block R gains heat as it warms from T_{iR} to T_f . The entropy change is:

$$\Delta S_R = mc \ln \left(\frac{T_f}{T_{iR}} \right).$$

Substitute the given values:

$$\Delta S_R = (1.5)(386) \ln \left(\frac{313}{293} \right) \text{ J/K}.$$

Calculate:

$$\Delta S_R = 579 \ln(1.0683) \approx 579 \cdot 0.0661 = 38.3 \text{ J/K}.$$

Net entropy change of the system :

The total entropy change is the sum of the entropy changes of blocks L and R :

$$\Delta S_{\text{net}} = \Delta S_L + \Delta S_R.$$

Substitute the values:

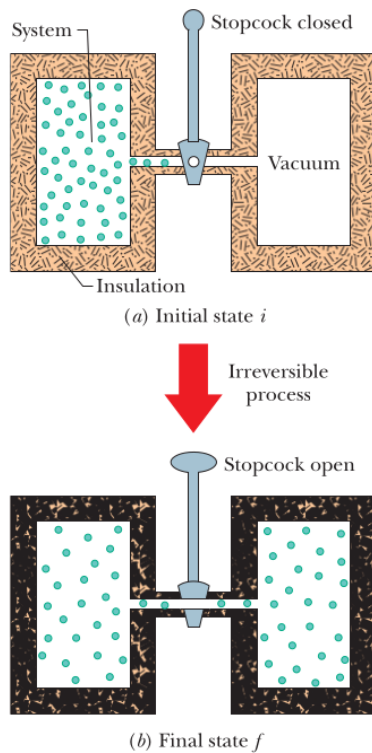
$$\Delta S_{\text{net}} = -35.6 + 38.3 = 2.7 \text{ J/K}.$$

Answer: The net entropy change of the two-block system is:

$$\boxed{\Delta S_{\text{net}} = 2.7 \text{ J/K}}.$$

Problem 2:

Suppose 1.0 mol of nitrogen gas is confined to the left side of a container. The stopcock is opened, and the volume of the gas doubles. Calculate the entropy change (ΔS) for this irreversible process. Treat the gas as ideal.



Solution

For an irreversible expansion of an ideal gas, the entropy change can be calculated using the formula:

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

where: n is the number of moles of gas, R is the universal gas constant ($R = 8.314 \text{ J/mol}\cdot\text{K}$), V_1 is the initial volume, V_2 is the final volume.

Given: - $n = 1.0 \text{ mol}$, - The volume of the gas doubles, so $V_2 = 2V_1$, - The process is irreversible, but the formula for entropy change in volume change of an ideal gas still holds.

Now, substitute $V_2 = 2V_1$ into the equation:

$$\Delta S = nR \ln \left(\frac{2V_1}{V_1} \right)$$

$$\Delta S = nR \ln 2$$

Substitute the known values:

$$\Delta S = (1.0 \text{ mol})(8.314 \text{ J/mol}\cdot\text{K}) \ln 2$$

Using $\ln 2 \approx 0.693$:

$$\Delta S \approx (1.0)(8.314)(0.693) \text{ J/K}$$

$$\Delta S \approx 5.76 \text{ J/K}$$

Answer: The entropy change for the nitrogen gas during this irreversible expansion is:

$$\boxed{\Delta S = 5.76 \text{ J/K}}.$$

Heat Engine

A **heat engine** is a device that takes in heat from a high-temperature reservoir, converts part of it into work, and expels the remaining heat to a lower-temperature reservoir. The general working cycle involves:

1. **Input Heat:** The engine absorbs heat, Q_H , from the hot reservoir at a high temperature T_H .
2. **Work Output:** The engine performs work, W , on the surroundings (e.g., moving a piston).
3. **Heat Rejection:** The engine rejects heat, Q_L , to the cold reservoir at a lower temperature T_L .

The efficiency of a heat engine is given by the equation:

$$\eta = \frac{Q_H - Q_L}{Q_H} = \frac{W}{Q_H} = 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

where:

η is the efficiency, Q_H is the heat absorbed, Q_L is the heat rejected.

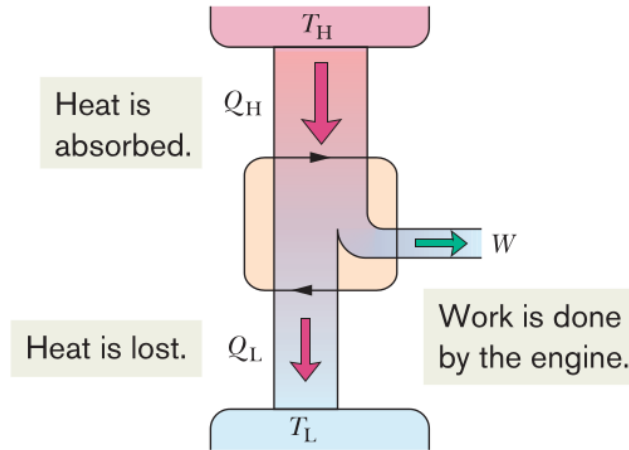


Figure 2: Schematic of a Heat engine

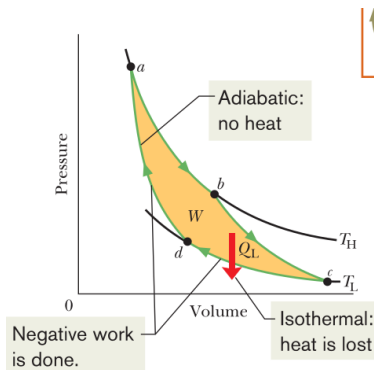
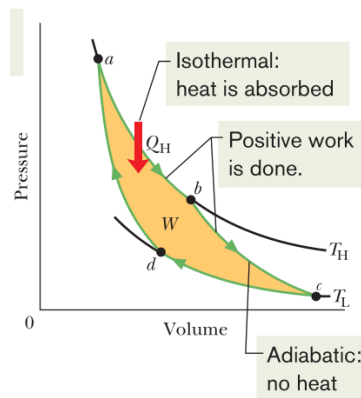
Carnot Engine

The **Carnot engine** is an idealized heat engine that operates between two heat reservoirs at temperatures T_H (hot) and T_L (cold). It is the most efficient engine possible for a given temperature difference.

Carnot Cycle

The Carnot engine operates on a four-step cycle:

1. **Isothermal Expansion:** The gas expands isothermally at temperature T_H , absorbing heat Q_H from the hot reservoir.
2. **Adiabatic Expansion:** The gas expands without heat exchange, and its temperature decreases from T_H to T_L .
3. **Isothermal Compression:** The gas is compressed isothermally at temperature T_L , rejecting heat Q_L to the cold reservoir.
4. **Adiabatic Compression:** The gas is compressed without heat exchange, and its temperature increases from T_L back to T_H .



Carnot Efficiency

The efficiency of a Carnot engine is given by the formula:

$$\eta_{\text{Carnot}} = 1 - \frac{T_L}{T_H}$$

where: T_H is the temperature of the hot reservoir, T_L is the temperature of the cold reservoir.

This formula shows that the efficiency depends only on the temperatures of the hot and cold reservoirs. A Carnot engine is the most efficient engine that can operate between two reservoirs.

Problem 3:

A Carnot engine operates between the temperatures $T_H = 850 \text{ K}$ and $T_L = 300 \text{ K}$. The engine performs $W = 1200 \text{ J}$ of work each cycle, which takes $t = 0.25 \text{ s}$. Solve the following:

- (a) What is the efficiency of this engine?
- (b) What is the average power of this engine?
- (c) How much energy Q_H is extracted as heat from the high-temperature reservoir every cycle?
- (d) How much energy Q_L is delivered as heat to the low-temperature reservoir every cycle?
- (e) By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?

Solution

(a) Efficiency of the engine

The efficiency of a Carnot engine is given by:

$$\eta = 1 - \frac{T_L}{T_H}$$

Substituting the given values:

$$\eta = 1 - \frac{300}{850} = 1 - 0.3529 = 0.6471 \text{ or } 64.71\%.$$

(b) Average power of the engine

The average power is the work done per unit time:

$$P = \frac{W}{t}$$

Substituting the given values:

$$P = \frac{1200}{0.25} = 4800 \text{ W.}$$

(c) Energy extracted as heat, Q_H

The work done by the engine is related to the heat extracted from the high-temperature reservoir by:

$$\eta = \frac{W}{Q_H}$$

Rearranging for Q_H :

$$Q_H = \frac{W}{\eta}$$

Substituting the values:

$$Q_H = \frac{1200}{0.6471} \approx 1854.4 \text{ J.}$$

(d) Energy delivered as heat, Q_L

The heat delivered to the low-temperature reservoir is:

$$Q_L = Q_H - W$$

Substituting the values:

$$Q_L = 1854.4 - 1200 \approx 654.4 \text{ J.}$$

(e) Entropy change

The entropy change for the energy transfer is calculated using:

$$\Delta S = \frac{Q}{T}$$

For the high-temperature reservoir:

$$\Delta S_H = \frac{Q_H}{T_H}$$

Substituting the values:

$$\Delta S_H = \frac{1854.4}{850} \approx 2.18 \text{ J/K.}$$

For the low-temperature reservoir:

$$\Delta S_L = \frac{Q_L}{T_L}$$

Substituting the values:

$$\Delta S_L = \frac{-654.4}{300} \approx -2.18 \text{ J/K}.$$

The total entropy change of the working substance is zero, as expected for a reversible Carnot cycle.