

PHY101: Introduction to Physics I

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Lecture 35

Department of Physics, School of Natural
Sciences,
Shiv Nadar Institution of Eminence, Delhi NCR

Previous Lectures

Second law of thermodynamics

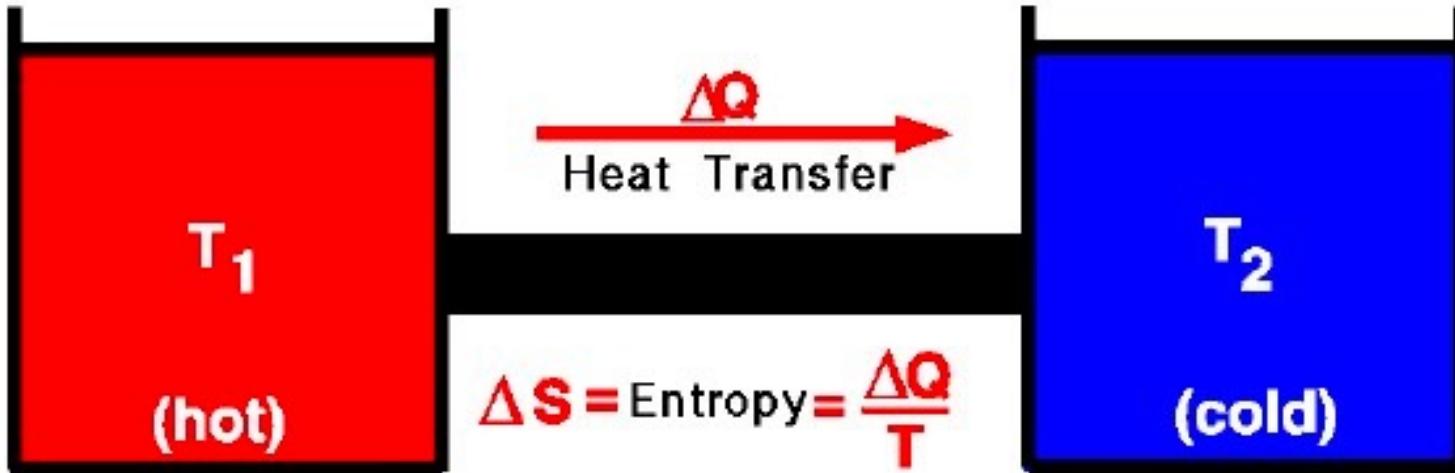
This Lecture

Entropy

**Reference book: Fundamental of physics
by Halliday, Resnick and Walker**

Second Law of Thermodynamics

- Heat cannot flow from a cold object to a hot object on its own.



There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

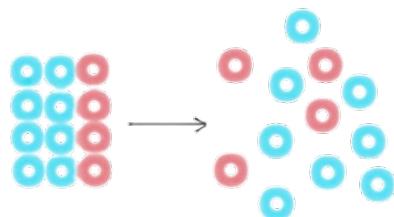
$$S_f = S_i \text{ (reversible)}$$

$$S_f > S_i \text{ (irreversible)}$$

- Direction of flow of energy. It's in the direction from less entropy (more order) to more entropy (less order)

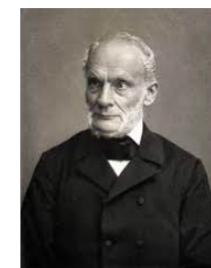
Entropy

- Entropy (S) was introduced as an important concept in thermodynamics.
- Similar to internal energy and temperature, it is a state function, i.e., it only depends on the thermodynamic state of a system and not on how the system reached that state.
- Statistical mechanics provides a connection of entropy with the microscopic configurations of constituents of a system.



Entropy (S)

Measure of disorder



Rudolf Clausius
(1822–1888)

German mathematician and physicist

Thermodynamic Entropy

- Thermodynamically entropy concerns with the transfer of energy by heat during a reversible process.
- If dQ_r is the amount of energy transferred by heat when the system follows a reversible path between two equilibrium states, then change in the entropy dS is given by

$$dS = \frac{dQ_r}{T},$$

where T is the constant temperature of the system during the infinitesimal process. We use the subscript r with Q to emphasize that the process considered is reversible.

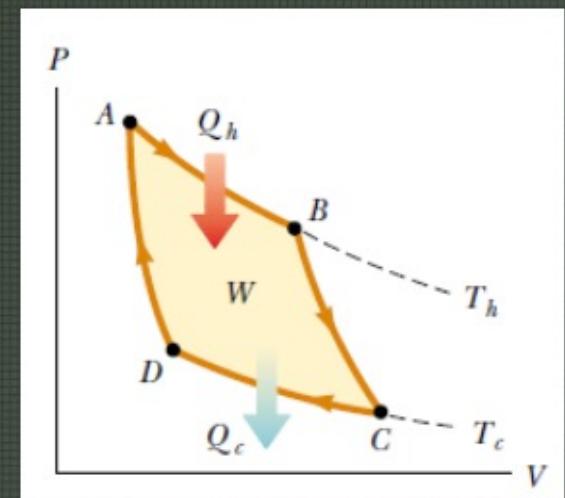
- For a finite process, we have

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

Entropy change in Carnot cycle

- The heat exchange in the Carnot cycle takes place only during the isothermal expansion and compression:
A → B and C → D in the figure.
- There is no heat exchange for the adiabatic
B → C and D → A processes.
- Thus

$$\begin{aligned}\Delta S &= \int_A^B \frac{dQ}{T} + \int_B^C \frac{dQ}{T} + \int_C^D \frac{dQ}{T} + \int_D^A \frac{dQ}{T} \\ \Rightarrow \Delta S &= \frac{1}{T_h} \int_A^B dQ + 0 + \frac{1}{T_c} \int_C^D dQ + 0 \\ \Rightarrow \Delta S &= \frac{|Q_h|}{T_h} - \frac{|Q_c|}{T_c}.\end{aligned}$$



Entropy change in Carnot cycle

But from the analysis of Carnot engine we know that

$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$, and hence $\frac{|Q_h|}{T_h} = \frac{|Q_c|}{T_c}$. As a result,

$$\Delta S = 0.$$

Actually this follows directly from the observation that Entropy is a state function, it depends on the initial and final states only. This holds true for arbitrary reversible cycles, including non-Carnot ones. Therefore, for a **reversible cycle** $\Delta S = 0$, i.e.,

$$\oint \frac{dQ_r}{T} = 0$$

The integration symbol \oint represents a closed path.

(Be careful to distinguish between a process and a cycle.)

Entropy: If a process occurs in a closed system, the entropy increases for irreversible process and remains constant for reversible process, but it never decreases.

Entropy change in Free Expansion

Consider the adiabatic free expansion of a gas occupying an initial volume V_i as shown in the figure. Now, a membrane separating the gas from an evacuated region is broken and the gas expands to a volume V_f .

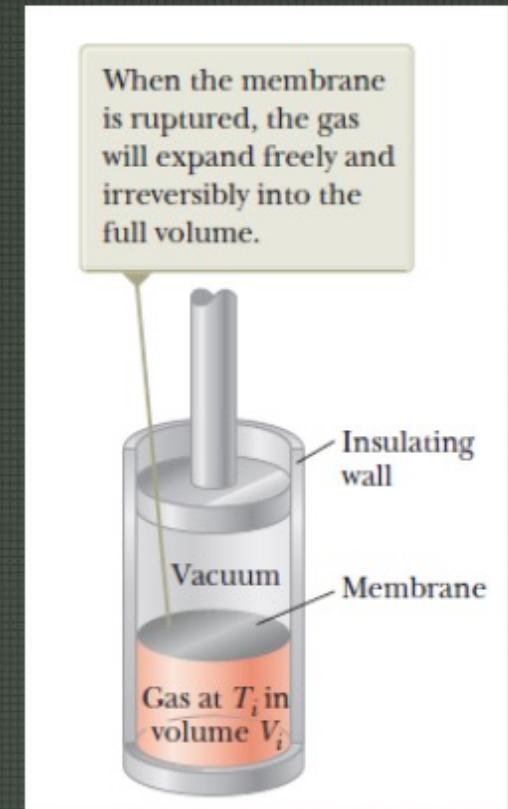
This process is irreversible; the gas would not spontaneously crowd into half the volume after filling the entire volume.

Now we have $\Delta Q = 0$ as the process is adiabatic. We cannot plug this into the expression

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

which holds for reversible processes.

When the membrane is ruptured, the gas will expand freely and irreversibly into the full volume.



Entropy change in Free Expansion

However, we can figure out the change in entropy for this irreversible process by considering an equivalent reversible process that shares the same initial and final states. *This is possible, since entropy is a state function.*

A simple choice is an isothermal (T constant) reversible expansion in which the gas pushes slowly against a piston while energy enters the gas by heat from a reservoir to hold the temperature constant.

$$\text{Thus, } \Delta S = \int_i^f dS = \frac{1}{T} \int_i^f dQ_r = \frac{1}{T} \int_i^f PdV$$

The last step follows from first law, as $dU = 0$ since T is fixed.

Entropy change in Free Expansion

Now ideal gas law gives $P = NkT/V = nRT/V$ (N is the total number and n is the number of moles (Don't confuse it with number density)). Thus

$$\Delta S = \frac{1}{T} \int_i^f \frac{nRT}{V} dV$$
$$\Rightarrow \Delta S = nR \ln\left(\frac{V_f}{V_i}\right)$$



Entropy change

For arbitrary transformations, bringing a **thermodynamic system** from state i to f , the change in entropy is given by

$$\Delta S \geq \int_i^f \frac{\delta Q}{T}$$

The equality holds if the process is reversible.

If the system is isolated, then there is no heat exchange with the surroundings (adiabatic) then

$$\Delta S \geq 0.$$

Second law of thermodynamics

(Entropy Statement)

- The entropy of the Universe (isolated) increases in all real process.

$$\Delta S \geq 0$$

- The equality holds when the process is reversible.
- The Universe always evolves toward a higher-probability* macrostate, corresponding to greater disorder.

* To define higher probability macrostate we will have to consider the microstates corresponding to a macrostate, as discussed ahead.

Second Law of Thermodynamics

- It is impossible to convert heat energy into work with 100 percent efficiency.
- It is impossible to build a machine that produces as much energy as it uses.
- The entropy of the universe tends to a maximum.
(Rudolf Clausius, 1865)
- You cannot break even.

Second Law of Thermodynamics

"Energy is most usable where it is most concentrated--as in highly structured chemical bonds (gasoline, sugar) or at high temperature (steam, incoming sunlight). *Since the second law of thermodynamics says that the overall tendency in all processes is away from concentration, away from high temperature, it is saying that, overall, more and more energy is becoming less and less usable.*"

"As one goes forward in time, the net entropy (degree of disorder) of any isolated or closed system will always increase (or at least stay the same)".

"The increase of disorder or entropy is what distinguishes the past from the future, giving a direction to time." — Stephen Hawking, A Brief History of Time

Third Law of Thermodynamics

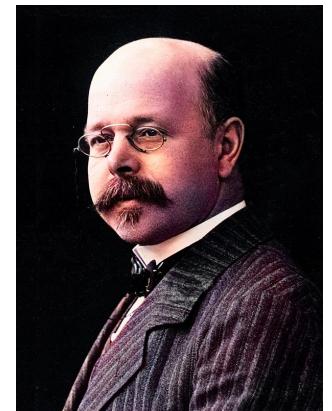
- So far we considered just the change in Entropy and not its absolute value.
- The second law does not determine uniquely the difference in entropy of two states if they refer to different substances.
- In 1905 Nernst proposed a rule for this determination which is referred to as the Third law of thermodynamics:

The entropy of a system at absolute zero is a universal constant, which may be taken to be zero.

Third Law of Thermodynamics

When the temperature reaches absolute zero (0K, -273.15°C), all the process comes to stop and the entropy shows no change. **(1906, heat theorem)**

The entropy of a pure, perfect crystalline substance at 0 K is zero.



Walther Nernst
(1864-1941)

It is impossible to achieve absolute zero (**Unattainability principle**)

Or in other words

Any process cannot reach absolute zero temperature in a finite number of steps and within a finite time.

Practice Problems

1. 5000 J of heat are added to two moles of an ideal monatomic gas, initially at a temperature of 500 K, while the gas performs 7500 J of work. What is the final temperature of the gas?

Solution

$$\Delta U = Q - W = 5000 \text{ J} - 7500 \text{ J} = -2500 \text{ J}$$

$$\Delta U = -2500 \text{ J} = (3/2)nR\Delta T = (3/2)(2)(8.31)\Delta T$$

$$\rightarrow \Delta T = -100 \text{ K}$$

$$\rightarrow T_f = \mathbf{500 \text{ K} - 100 \text{ K} = 400 \text{ K}}$$

comment: the gas does more work than it takes in as heat,
so it must use 2500 J of its internal energy.

Practice Problems

2. Compute the internal energy change and temperature change for the two processes involving 1 mole of an ideal monatomic gas.
- (a) 1500 J of heat are added to the gas and the gas does no work and no work is done on the gas
- (b) 1500 J of work are done on the gas and the gas does no work and no heat is added or taken away from the gas

Solution

(a)

$$\begin{aligned}\Delta U &= Q - W = 1500 \text{ J} - 0 = 1500 \text{ J} \\ \Delta U &= 1500 \text{ J} = (3/2)nR\Delta T = (3/2)(1)(8.31)\Delta T \\ \rightarrow \Delta T &= 120 \text{ K}\end{aligned}$$

(b)

$$\begin{aligned}\Delta U &= Q - W = 0 - (-1500 \text{ J}) = +1500 \text{ J} \\ \Delta U &= 1500 \text{ J} = (3/2)nR\Delta T = (3/2)(1)(8.31)\Delta T \\ \rightarrow \Delta T &= 120 \text{ K}\end{aligned}$$

Notice that in both processes, the change in internal energy is the same. We say that the internal energy is a “state function”. A state function depends only on the state of the system and not on the process that brings the system to that particular state.

Practice Problems

Q1. Practical steam engines utilize 450°C steam, which is later exhausted at 270°C. (a) What is the maximum efficiency that such a heat engine can have? (b) Since 270°C steam is still quite hot, a second steam engine is sometimes operated using the exhaust of the first. What is the maximum efficiency of the second engine if its exhaust has a temperature of 150°C? (c) What is the overall efficiency of the two engines? (d) Show that this is the same efficiency as a single Carnot engine operating between 450°C and 150°C.

5. (a)

$$Eff_1 = 1 - \frac{T_{c,1}}{T_{h,1}} = 1 - \frac{543 \text{ K}}{723 \text{ K}} = 0.249 \text{ or } 24.9\%$$

(b)

$$Eff_2 = 1 - \frac{423 \text{ K}}{543 \text{ K}} = 0.221 \text{ or } 22.1\%$$

(c)

$$Eff_1 = 1 - \frac{T_{c,1}}{T_{h,1}} \Rightarrow T_{c,1} = T_{h,1} (1, -, eff_1) \text{ similarly, } T_{c,2} = T_{h,2} (1 - Eff_2)$$

using $T_{h,2} = T_{c,1}$ in above equation gives

$$T_{c,2} = T_{h,1} (1 - Eff_1) (1 - Eff_2) \equiv T_{h,1} (1 - Eff_{\text{overall}})$$

$$\therefore (1 - Eff_{\text{overall}}) = (1 - Eff_1) (1 - Eff_2)$$

$$Eff_{\text{overall}} = 1 - (1 - 0.249) (1 - 0.221) = 41.5\%$$

(d)

$$Eff_{\text{overall}} = 1 - \frac{423 \text{ K}}{723 \text{ K}} = 0.415 \text{ or } 41.5$$

Practice Problems

Q1. Calculate the entropy change for 1.00 mol of an ideal gas expanding isothermally from a volume of 24.4 L to 48.8 L.

$$\begin{aligned}\Delta S &= nR \ln\left(\frac{V_2}{V_1}\right) \\ &= (1.00 \text{ mol})(8.314 \text{ J}/(\text{mol K})) \ln\left(\frac{44.8 \text{ L}}{22.4 \text{ L}}\right) \\ &= 5.76 \text{ J/K}\end{aligned}$$

Q2. The enthalpy of fusion for water is 6.01 kJ/mol. Calculate the entropy change for 1.0 mole of ice melting to form liquid at 273 K.

The entropy change for a phase change at constant pressure is given by

$$\Delta S = \frac{q}{T} = \frac{\Delta H_{phase}}{T}$$

$$\begin{aligned}\Delta S &= \frac{(1 \text{ mol})(6010 \text{ J/mol})}{273 \text{ K}} \\ &= 22 \text{ J/K}\end{aligned}$$

Q2. What is the increase in entropy if one gram of ice at 0°C is melted and heated to 50°C?

The change in entropy is given by $dS = \frac{dQ}{T}$. In this case, the dQ must be calculated in two pieces. First there is the heat needed to melt the ice, and then there is the heat needed to raise the temperature of the system. Therefore,

$$\Delta Q = mL_f + mc_w\Delta T$$

where $m = 1\text{ g}$ is the total mass of the system, $L_f = 80\text{ cal/g}$ is the heat of fusion, and $c_w = 1\text{ cal/(g}\cdot\text{K)}$ is the specific heat of water. Thus, the total change in entropy is

$$\Delta S = \frac{mL_f}{T_i} + \int_{T_i}^{T_f} mc_w \frac{dT}{T}$$

where $T_i = 0^\circ\text{C} = 273\text{ K}$ and $T_f = 50^\circ\text{C} = 323\text{ K}$. Plugging in numbers, and remembering that we always use temperatures in Kelvin,

$$\begin{aligned}\Delta S &= \frac{(1\text{ g})(80\text{ cal/g})}{273\text{ K}} + \int_{273}^{323} (1\text{ cal/g})(1\text{ g}) \frac{dT}{T} \\ &= \frac{80}{273} \text{ cal/K} + \ln\left(\frac{323}{273}\right) \text{ cal/K} \\ \Delta S &= 0.461 \text{ cal/K}\end{aligned}$$