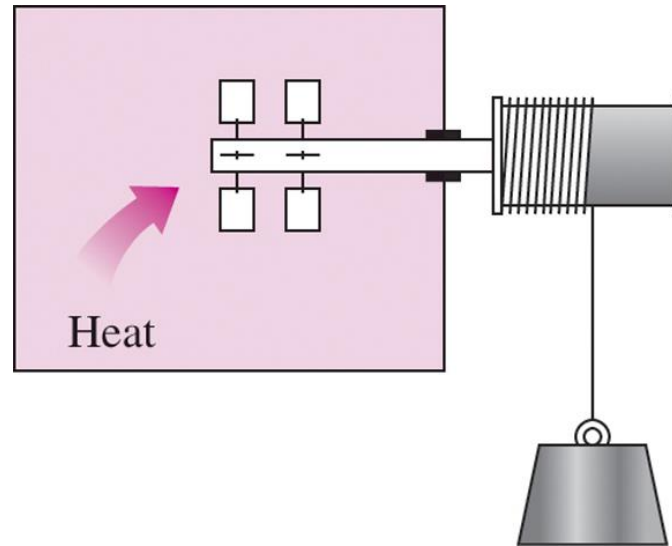# Second Law of Thermodynamics

Introduction

➢ **A process must satisfy the first law in order to occur.**

➢ **Satisfying the first law alone does not ensure that the process will take place.**

❑ **Second law is useful:**

➢ *provide means for predicting the direction of processes,*

➢ *establishing conditions for equilibrium,*

➢ *determining the best theoretical performance of cycles, engines and other devices.*

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A cup of hot coffee does not get hotter in a cooler room.

HOT COFFEE → Heat

Heat

Transferring heat to a paddle wheel will not cause it to rotate.
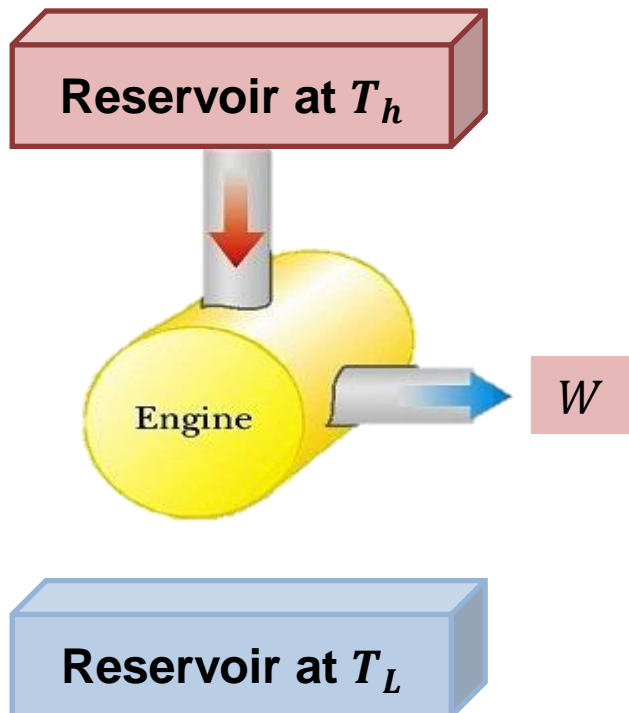
Heat

$I = 0$
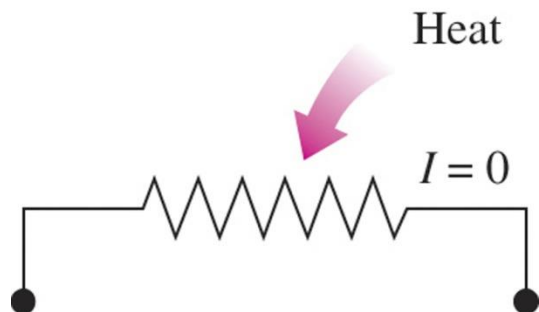
Transferring heat to a wire will not generate electricity.

These processes cannot occur even though they are not in violation of the first law.

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Second Law of Thermodynamics

Reservoir at T_h

Engine

W

Reservoir at T_L

Impossible Heat engine

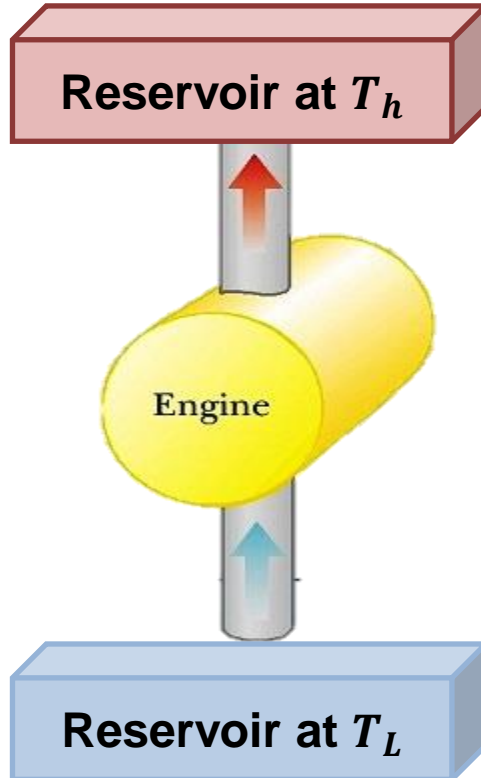*Kelvin-Planck statement*

Kelvin-Planck statement

❑ It is impossible for any device (heat engine) that operates on a cycle to receive heat from a single reservoir and produce a net amount of work

❑ it is impossible to build a heat engine that has 100% thermal efficiency.

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Second Law of Thermodynamics

Reservoir at T_h

Engine

Reservoir at T_L

## *Clausius statement*

❑ **It is impossible to construct a device that operates on a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher-temperature body.**

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Third Law of Thermodynamics

❑ **The 2nd law states that process occur in a certain direction, not in any direction.**

❑ **This relates to the 2nd law since the 2nd law predicts that not all heat provided to a cycle can be transformed into an equal amount of work, some heat rejection must take place.**

❑ **It often leads to the definition of a new property called *entropy*, which in qualitative terms, it can be viewed as a *measure of the randomness or disorder* of the atoms & molecules in a system.**

Increasing entropy →

$\Delta S > 0$
$\Delta S < 0$

$\Delta S > 0$
$\Delta S < 0$

Crystalline solid   Liquid   Gas

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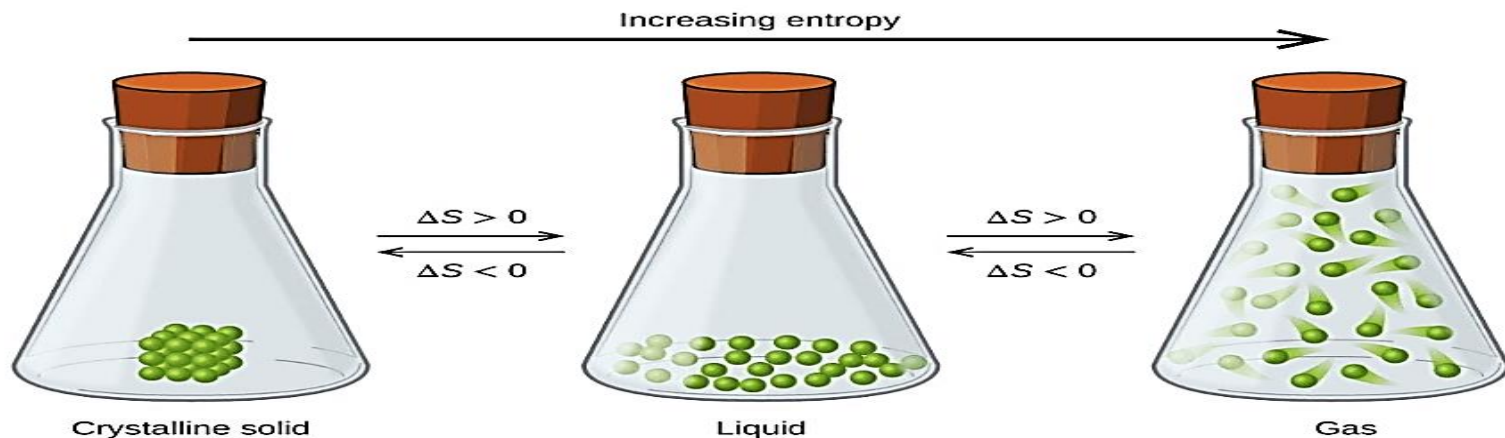
Third Law of Thermodynamics

❑ *The third law of thermodynamics* is concerned with the behavior of systems in equilibrium as temperature approaches absolute zero.

❑ *The third law of thermodynamics* states that the *entropy* of a perfect crystal at a temperature of zero Kelvin (absolute zero) is equal to zero.

❑ The Nernst statement of *the third law of thermodynamics* implies that it is not possible for a process to bring the *entropy* of a given system to zero in a finite number of processes.

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Entropy Change

➢ **Clausius found through his laboratory observations of any real process of a system that is in contact thermally with the surrounding medium at temperature *T* that the quantity**

$$dS = \frac{dQ}{T} \qquad\qquad dQ = T\, dS$$

$$S_2 - S_1 = \int_1^2 \frac{dQ}{T} \qquad Cal/\,^0K$$

• **During the reversible process, it is found that the change in entropy follows a change in the amount of heat transferred to the system and its absolute temperature.**

So, The first law of thermodynamics refers to

$$dU = T\, dS - P\, dV$$

And from it we get the following relationships

$$T = \left(\frac{\partial U}{\partial S}\right)_V \quad \& \quad P = -\left(\frac{\partial U}{\partial V}\right)_S \quad \& \quad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_E$$

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Other thermodynamic functions

Helmholtz functions (Free energy) *F*

It is known as the following relationship

$$dU = TdS - PdV = d(TS) - SdT - PdV$$

$$d(U - TS) = -SdT - PdV$$

$$\boxed{F = U - TS}$$

$$\boxed{dF = -PdV - SdT}$$

❑ **it is concluded from the last equation that**

- **The change in *Helmholtz free energy* at a constant temperature is equal to the work done on the system**

- **In any reversible process, when temperature and pressure are constant, we find that** $dF = 0$

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Other thermodynamic functions

Gibbs functions *G* (thermodynamic potential) ϕ

It is known as the following relationship

$$dF = -PdV - SdT$$

$$= -d(VP) + VdP - SdT$$

$$d(F + PV) = VdP - SdT$$

$$\boxed{\phi = F + PV}$$

$$\boxed{d\phi = VdP - SdT}$$

➢ **it is note that the change in *Gibbs function* (the thermodynamic potential) is equal zero when pressure and temperature are constant, as in cases of evaporation, melting and sublimation.**

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Maxwell's Equations

- **The previous thermodynamic functions are independent and do not depend on the path by which the change took place. Therefore, we can apply the differentiation condition to the following equations**

$$dU = -PdV + TdS \qquad \& \qquad dH = VdP + TdS$$

$$dF = -PdV - SdT \qquad \& \qquad d\phi = VdP - SdT$$

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V}\right)_s = -\left(\frac{\partial P}{\partial S}\right)_v \rightarrow (1)$$

$$\frac{\partial^2 H}{\partial P \partial S} = \left(\frac{\partial V}{\partial S}\right)_p = \left(\frac{\partial T}{\partial P}\right)_s \rightarrow (2)$$

$$\frac{\partial^2 \phi}{\partial P \partial S} = \left(\frac{\partial S}{\partial P}\right)_v = -\left(\frac{\partial V}{\partial T}\right)_p \rightarrow (3)$$

$$\frac{\partial^2 F}{\partial V \partial T} = \left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T \rightarrow (4)$$

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Molecular Motion of Gases

Gases are composed of particles (with continuous movement or collisions) and the particle's kinetic energy depends on the temperature of the body *T*. The ideal gas, its molecules are constantly moving and colliding with the walls of the container that contains the gas, and we assume that it is an elastic collision. If we have a cubic container *(L)* and it contains N particles of the same type and The forces acting on the particles are negligible, and the particles collide with the walls of the container more than they collide with each other. Assume that the velocity of the molecule v and its components $\left(v_x, v_y, v_z\right)$ then

$$\frac{1}{N}\sum v^2 = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

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Since there is no preference between directions, we conclude

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \quad \Longrightarrow \quad \overline{v^2} = 3\,\overline{v_x^2}$$

If the mass of the molecule is m moving toward the wall, so its momentum back and forth

$$mv = mv_x - (-mv_x) = 2mv_x$$

If the particle path the cube in time (L/v). So, the time between any two collisions $(2L/v)$. The number of collisions per unit time is $(v/2L)$.

So, the change of momentum per unit time

$$2mv_x \left(\frac{v_x}{2L}\right)$$

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At the same time, it represents the average force on the wall as a result of particle collisions

$$f = 2mv_x \left(\frac{v_x}{2L}\right) = \left(\frac{mv_x^2}{L}\right)$$

The total force

$$F = \sum f = \frac{m}{L} \sum v_x^2$$

$$F = \frac{Nm}{L} \left(\frac{1}{N}\right) \sum v_x^2 = \frac{Nm}{L} \overline{v_x^2} \qquad \rightarrow \quad (1)$$

Since pressure is the force per unit area

$$P = \frac{F}{L^2} = \frac{Nm}{L^3} \overline{v_x^2} \qquad \rightarrow (2)$$

But L^3 is the volume of the container because it is a cube.

$$P = \frac{Nm}{V}\overline{v_x^2} \quad \rightarrow \quad PV = Nm\overline{v_x^2} \quad \rightarrow \quad (3)$$

Where,

$$\overline{v_x^2} = \frac{\bar{v}^2}{3}$$

$$PV = \frac{Nm\bar{v}^2}{3} \quad \rightarrow \quad (4)$$

If we assume that the number of molecules of one mole of this gas N_0 and the molar mass M then,

$$Nm = nN_0m = nM$$

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$$PV = \frac{nM\bar{v}^2}{3} \implies PV = \frac{2}{3}\left(\frac{nM\bar{v}^2}{2}\right) = \frac{2}{3} U \rightarrow (5)$$

Where, $U = 1/2 \ (nM\bar{v}^2)$ **represents the internal energy**

$$PV = nRT = \frac{2}{3} U \rightarrow (6)$$

The ideal gas law

Where P, V and T are the pressure, volume and temperature; n is the number of moles; and R is the ideal gas constant

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