University of Science
Department of Materials science

Chapter 3
THE SECOND LAW OF THERMODYNAMICS

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Second Law of thermodynamics

The second law of thermodynamics can be understood through considering these processes:

- A rock will fall if you lift it up and then let go
- Hot pans cool down when taken out from the stove.
- Ice cubes melt in a warm room.

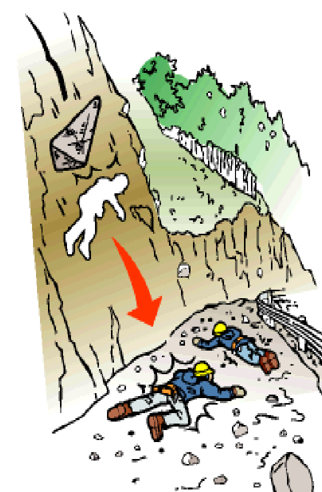
What's happening in every one of those?

Energy of some kind is changing from being localized (concentrated) somehow to becoming more spreed out.

i.e in example 1:

The potential energy localized in the rock is now totally spread out and dispersed in:

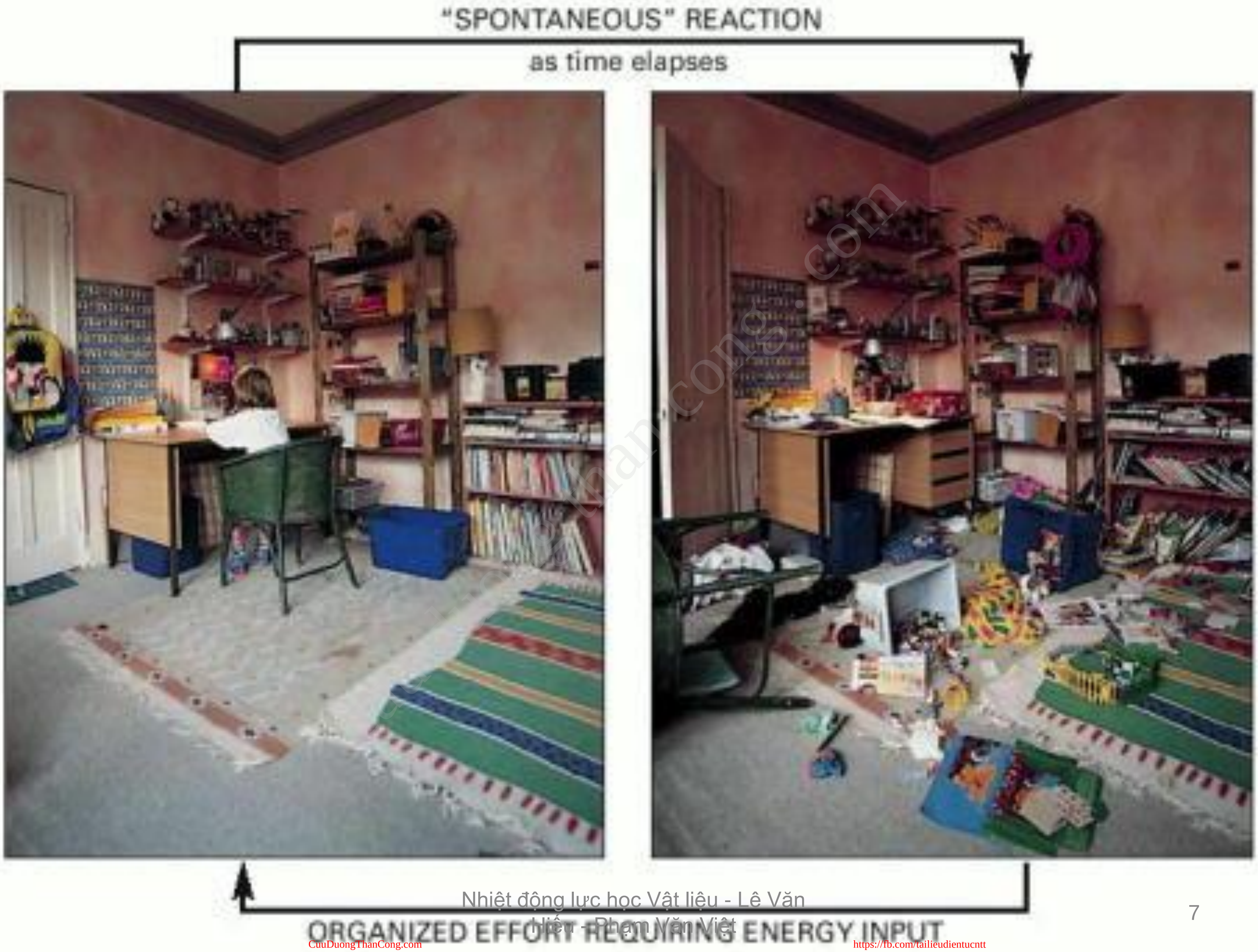
- A little air movement.
- Little heating of air and ground.



In the previous example

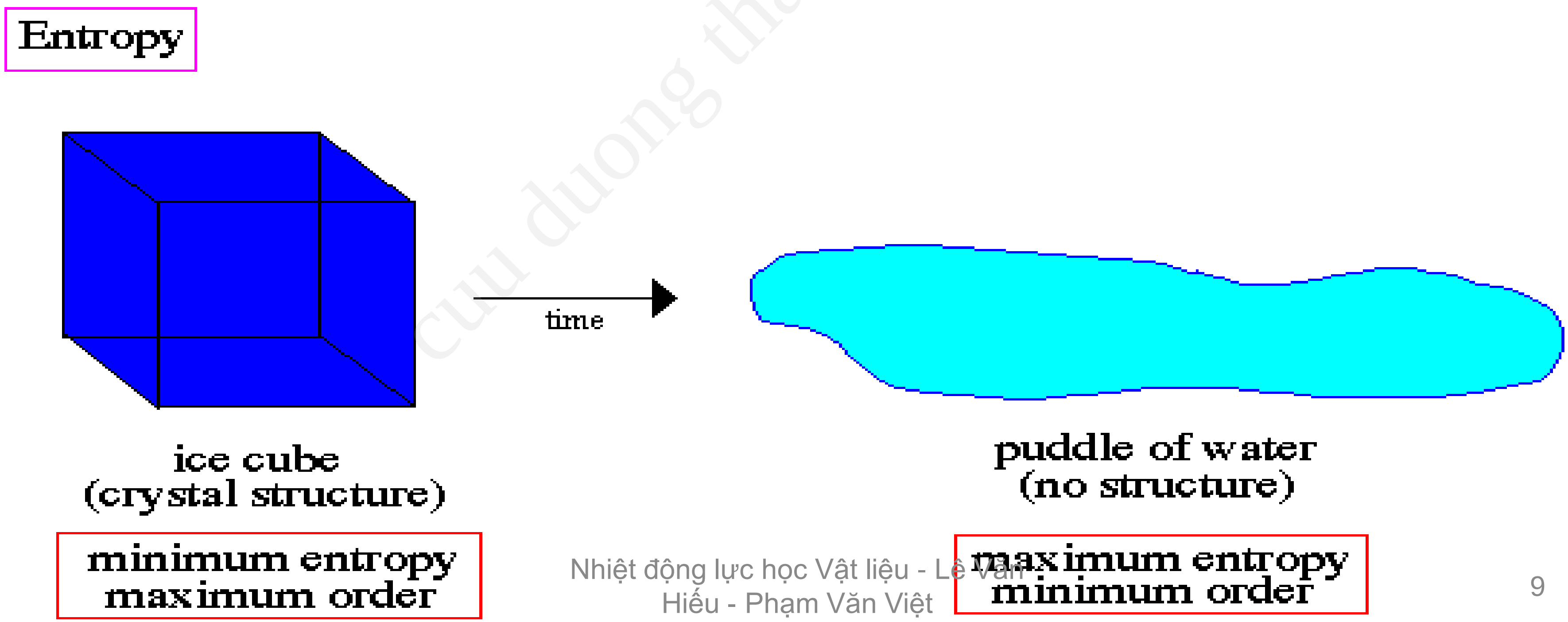
- System: rock above ground then rock on ground.
- Surroundings: air + ground

- The second law of thermodynamics states that energy (and matter) tends to become more evenly spread out across the universe.
- i.e to concentrate energy (or matter) in one specific place, it is necessary to spread out a greater amount of energy (as heat) across the remainder of the universe ("the surroundings").


"SPONTANEOUS" REACTION
as time elapses
ORGANIZED EFFORT REQUIRING ENERGY INPUT

What is entropy?

Entropy just measures the spontaneous dispersal of energy: or how much energy is spread out in a process as a function of temperature.



Follow the Entropy

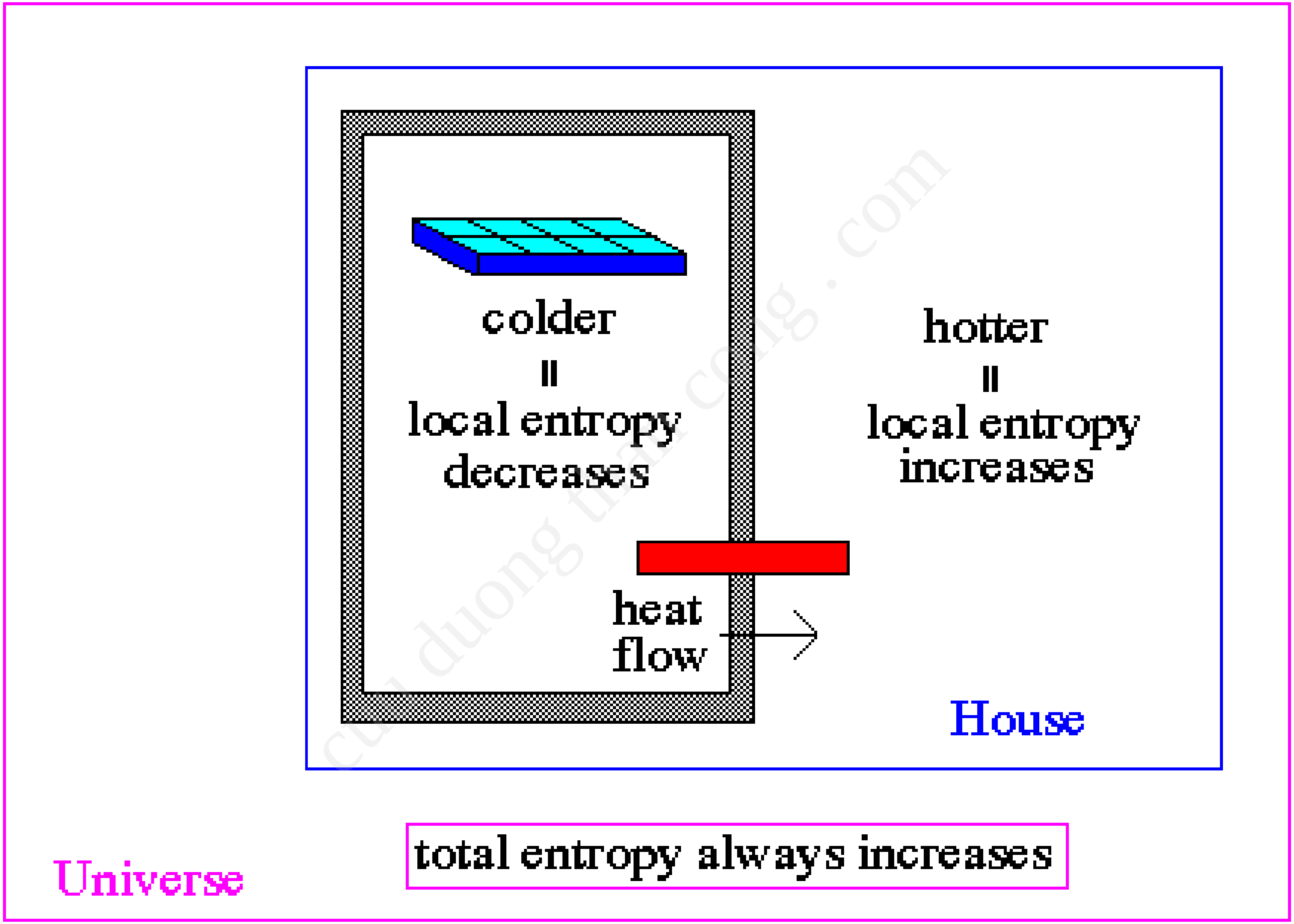
- *Entropy* a measure of disorder in the physical system.
- the *second law of thermodynamics* – the universe, or in any isolated system, the degree of disorder (entropy) can only increase.
- the movement towards a disordered state is a *spontaneous process*.

So in a simple equation:

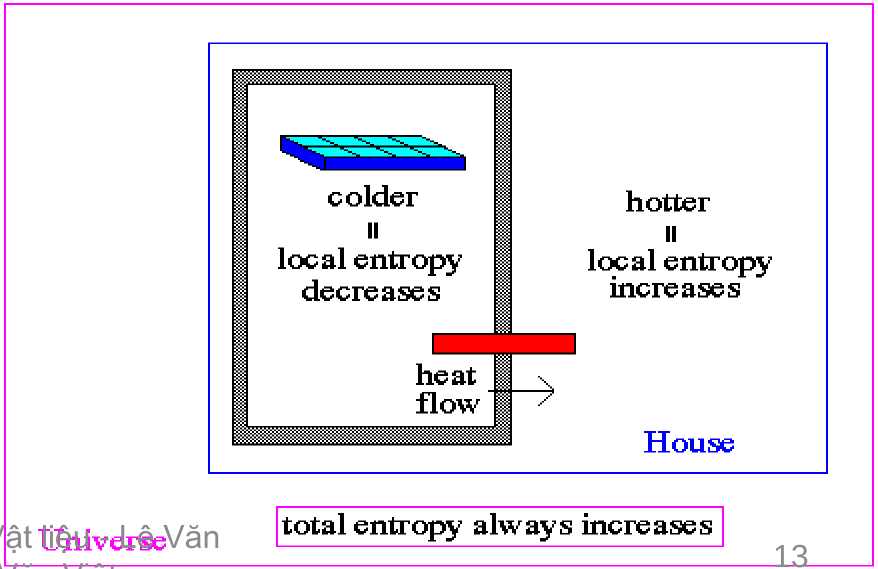
Entropy = “ energy dispersed” / T

Entropy couldn't be expressed without the inclusion of absolute temperature.

Entropy change ΔS shows us exactly how important to a system is a dispersion of a given amount of energy.


colder
=
local entropy
decreases
hotter
=
local entropy
increases
heat
flow
House
Universe
total entropy always increases

- i.e you can pump heat out of a refrigerator (to make ice cubes), but the heat is placed in the house and the entropy of the house increases, even though the local entropy of the ice cube tray decreases.



Entropy change ΔS

- In chemical terms entropy is related to the random movements of molecules and is measured by $T\Delta S$.
- When a system is at equilibrium, no net reaction occurs and the system has no capacity to do work.

$Q = T\Delta S$ This is a condition of maximum entropy.

- Work can be done by system proceeding to equilibrium and measure of the maximum useful work is given by the following equation

$$W = - \Delta H + T \Delta S$$

Is the second law of thermodynamics violated in the living cells?

NO!

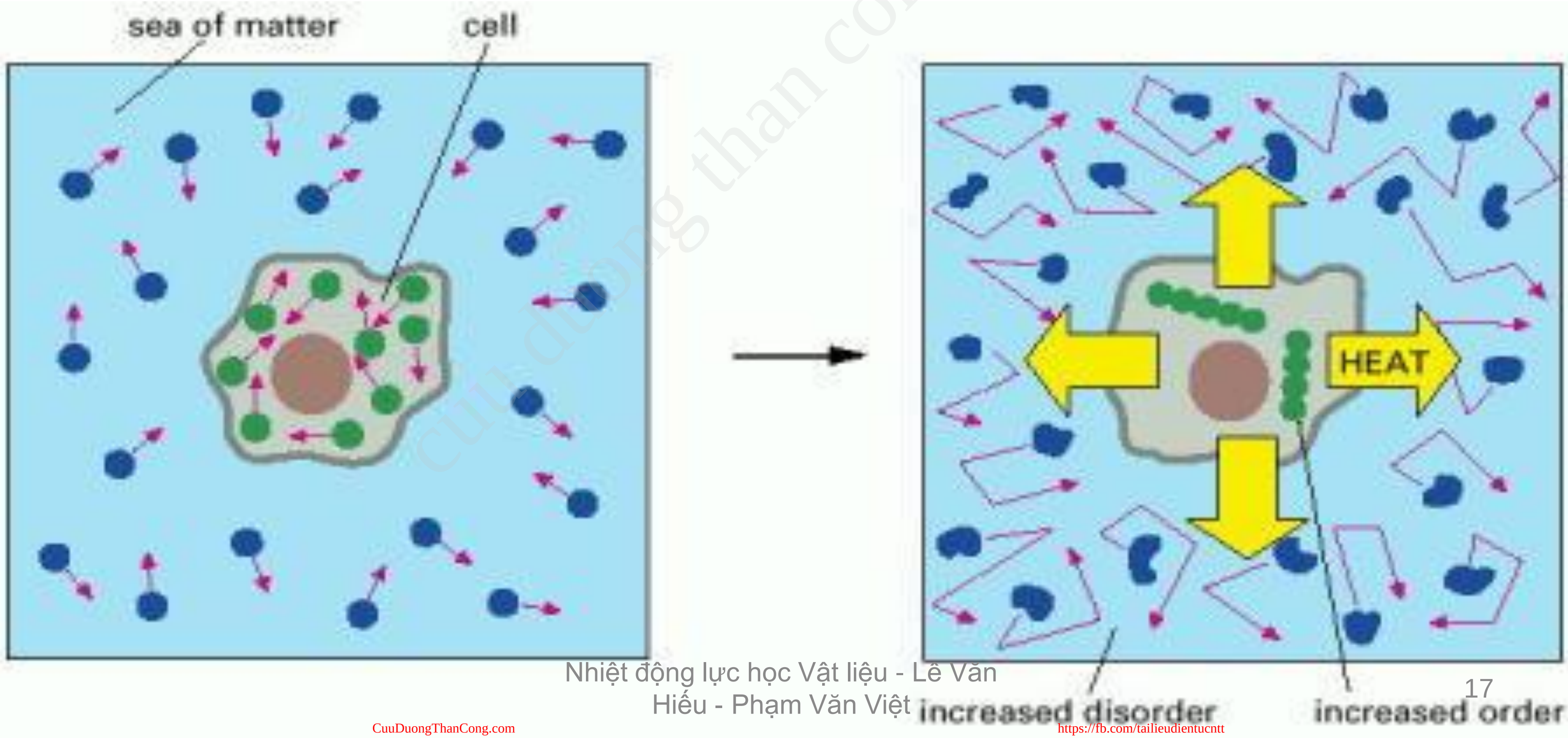
- Cell is not an isolated system: it takes energy from its environment to generate order within itself.
- Part of the energy that the cell uses is converted into heat.
- The heat is discharged into the cell's environment and disorders it.

The total entropy increases

Part of the energy that the cell uses is converted into heat.

The heat is discharged into the cell's environment and disorders it ►►

►► The total entropy increases



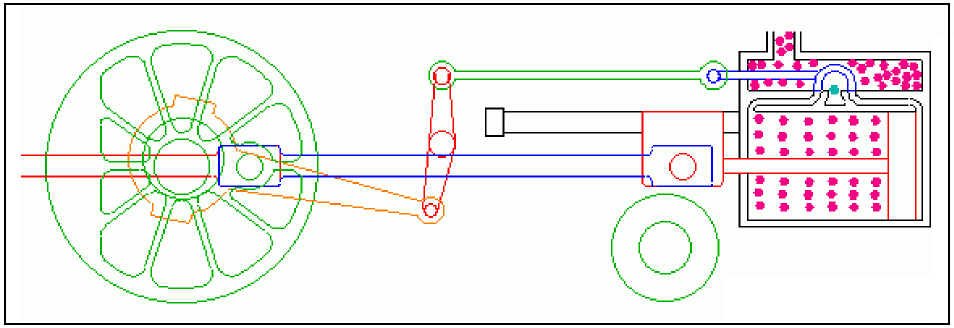
Carnot Cycle

Nicolas Leonard Sadi Carnot:

- French engineer and physicist

- Worked on early engines
- Tried to improve their efficiency

- Studied idealized heat engines, cyclic processes, and reversible processes



- Wrote his now famous paper, "A Reflection on the Motive Power of Fire" in 1824

- Introduced the "Carnot Cycle" for an idealized, cyclic and reversible process

http://en.wikipedia.org/wiki/Nicolas_L%C3%A9onard_Sadi_Carnot

Carnot Cycle

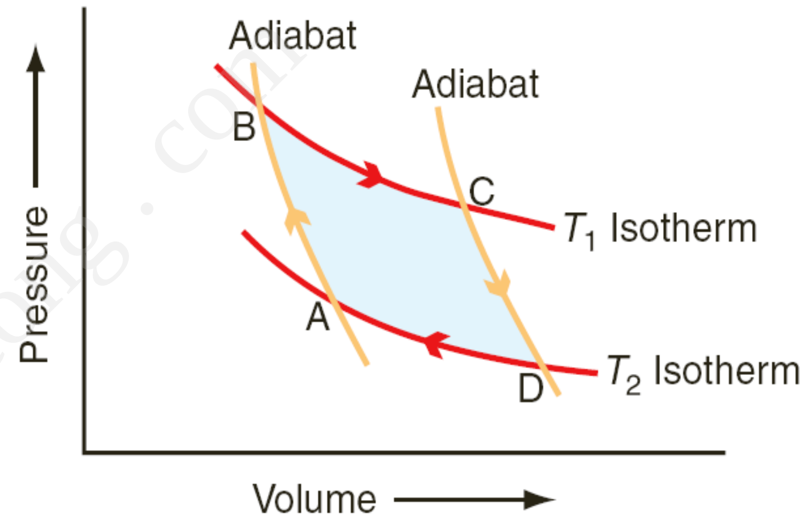
Basic Concepts:

Cyclic process:

- A series of transformations by which the state of a system undergoes changes but the system is eventually returned to its original state
- Changes in volume during the process may result in external work
- The **net** heat absorbed by the system during the cyclic process is equivalent to the **total** external work done

Reversible process:

- Each transformation in the cyclic process achieves an equilibrium state

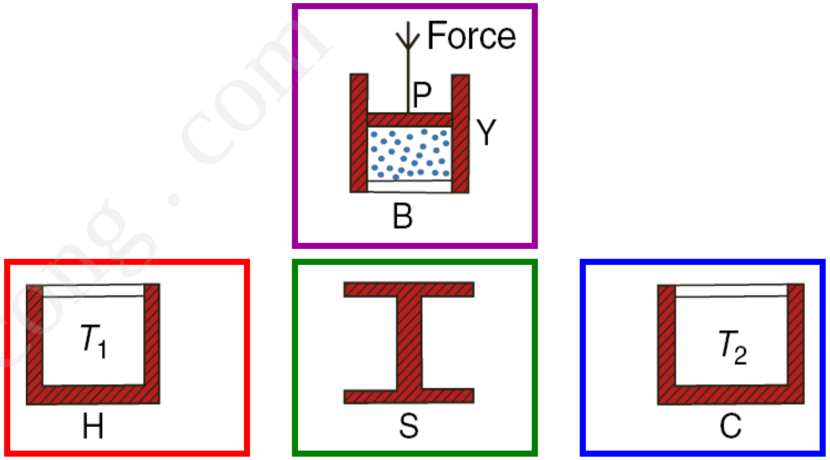


Transformations along A-B-C-D-A represents a cyclic process

The entire process is reversible since equilibirum is achieved for each state (A, B, C, and D)

Carnot Cycle

Carnot's Idealized Heat Engine:



<u>The Components</u>

- A "working substance" (blue dots) is in a **cylinder (Y)** with insulated walls and a conducting base (B) fitted with an insulated, frictionless piston (P) to which a variable force can be applied
- A **non-conducting stand (S)** upon which the cylinder may be placed to insulate the conducting base
- An infinite **warm reservoir of heat (H)** at constant temperature T_1
- An infinite **cold reservoir for heat (C)** at constant temperature T_2 (where $T_1 > T_2$)

Carnot Cycle

Carnot's Idealized Heat Engine:

<u>The Four Processes</u>:

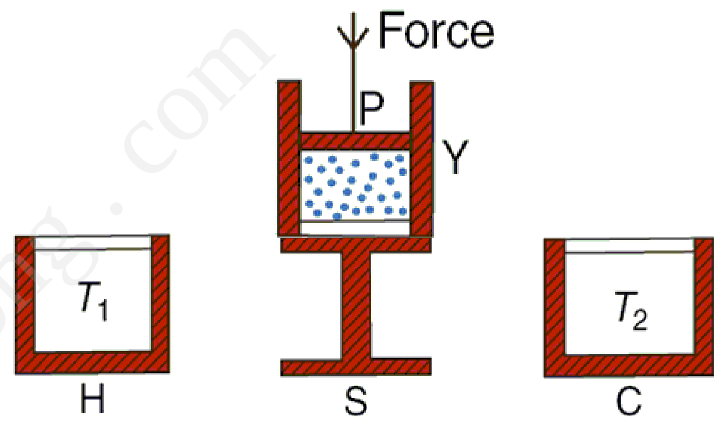
(1) Adiabatic Compression

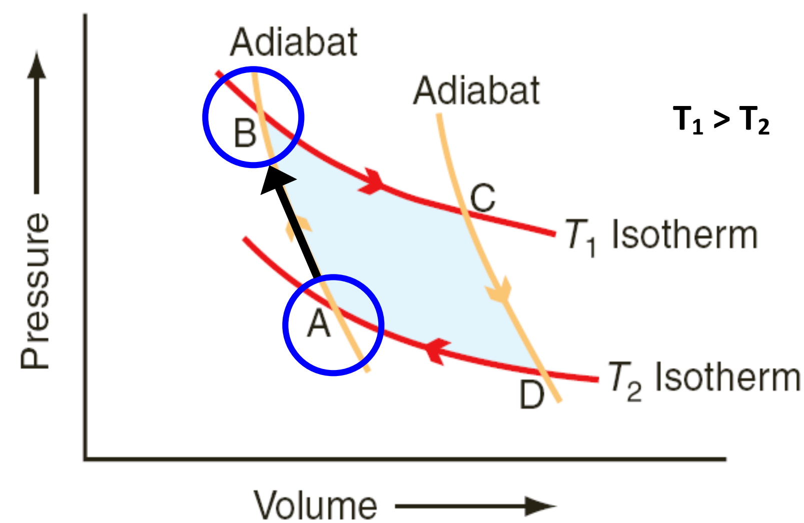
The substance begins at location A with a temperature of T_2

The cylinder is placed on the stand and the substance is compressed by increasing the downward force on the piston

Since the cylinder is insulated, no heat can enter or leave the substance contained inside

Thus, the substance undergoes adiabatic compression and its temperature increases to T_1 (location B)





$T_1 > T_2$

Carnot Cycle

Carnot's Idealized Heat Engine:

The Four Processes:

(1) Adiabatic Compression

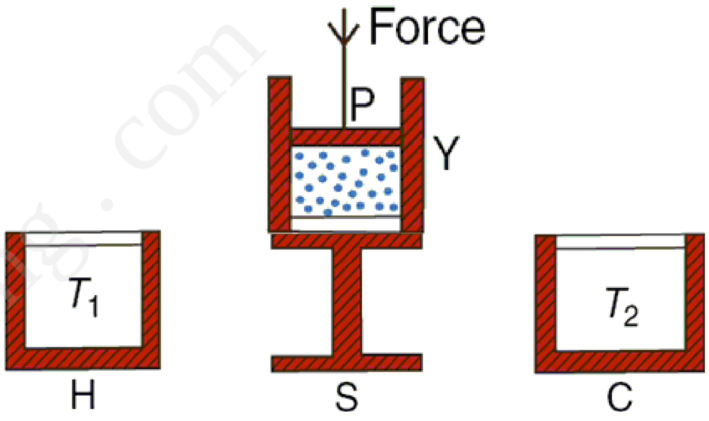
$$Q = \Delta U + W$$

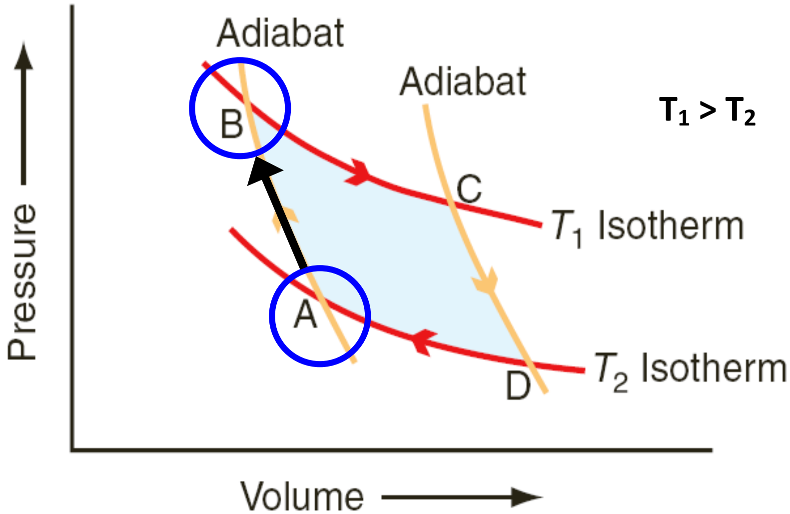
$$Q_{AB} = 0$$

$$\Delta U_{AB} = c_v (T_1 - T_2)$$

$$W_{AB} = -\Delta U_{AB}$$

$$W_{AB} = -c_v (T_1 - T_2)$$





Carnot Cycle

Carnot's Idealized Heat Engine:

The Four Processes:

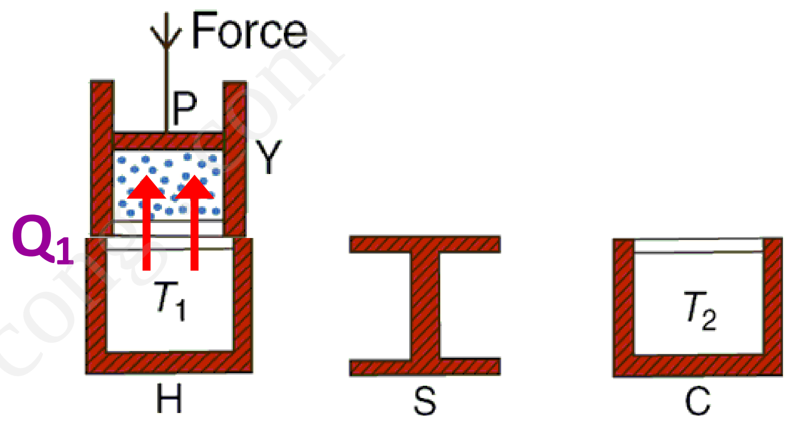
(2) Isothermal Expansion

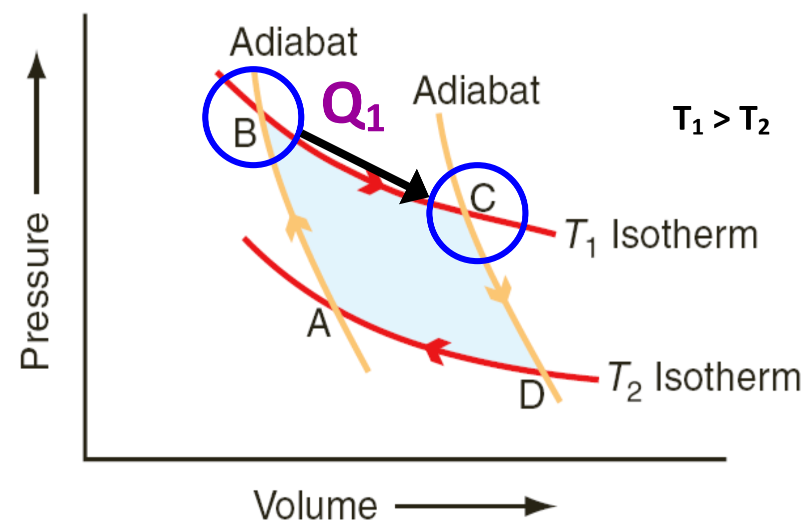
The cylinder is now placed on the warm reservoir

A quantity of heat Q_1 is extracted from the warm reservoir and thus absorbed by the substance

During this process the substance expands isothermally at T_1 to location C

During this process the substance does work by expanding against the force applied to the piston.

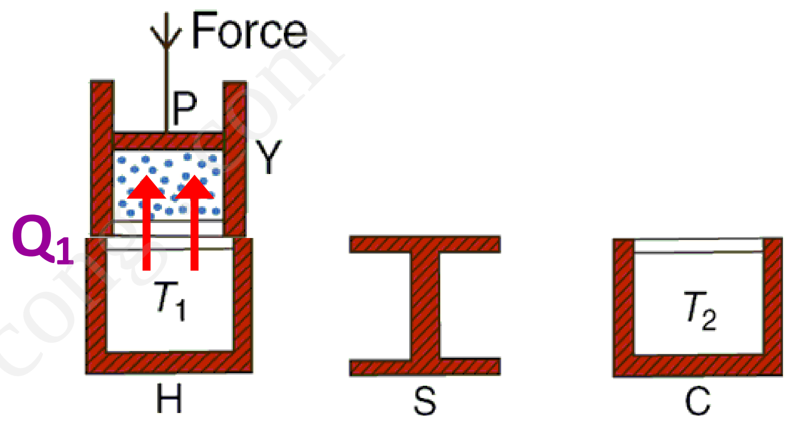




$T_1 > T_2$

Carnot Cycle

Carnot's Idealized Heat Engine:



The Four Processes:

(2) Isothermal Expansion

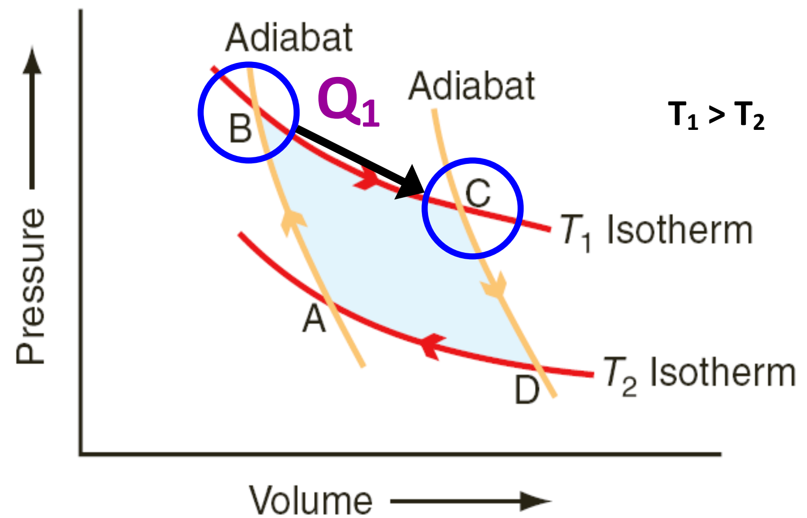
$$Q = \Delta U + W$$

$$\Delta T = 0 \qquad Q_{BC} = Q_1$$

$$\Delta U_{BC} = 0$$

$$W_{BC} = Q_{BC}$$

$$W_{BC} = R_d T_1 \ln\left(\frac{V_C}{V_B}\right)$$



Carnot Cycle

Carnot's Idealized Heat Engine:

The Four Processes:

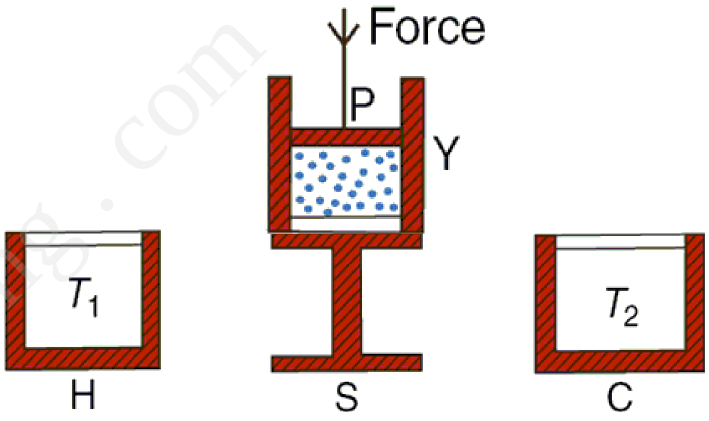
(3) Adiabatic Expansion

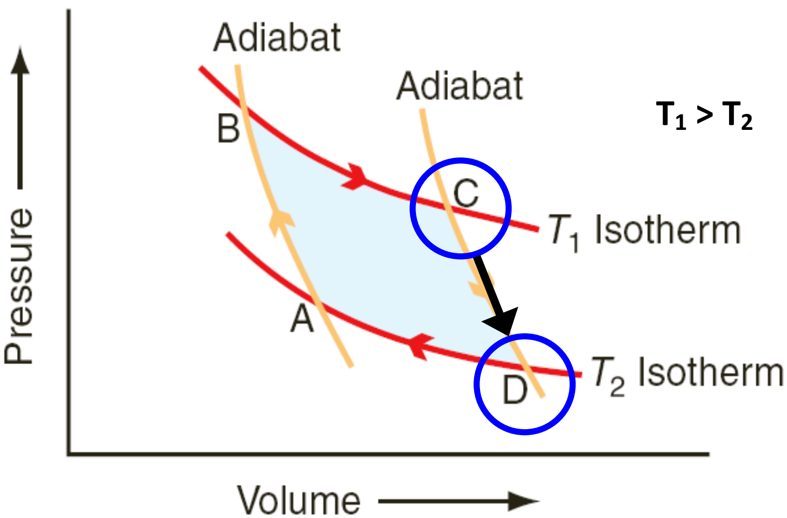
The cylinder is returned to the stand

Since the cylinder is now insulated, no heat can enter or leave the substance contained inside

Thus, the cylinder undergoes adiabatic expansion until its temperature returns to T_2 (location D)

Again, the cylinder does work against the force applied to the piston





Carnot Cycle

Carnot's Idealized Heat Engine:

<u>The Four Processes</u>:

(3) Adiabatic Expansion

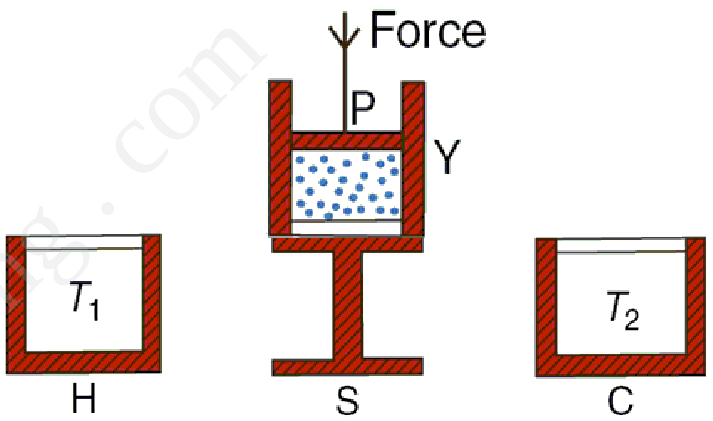
$$Q = \Delta U + W$$

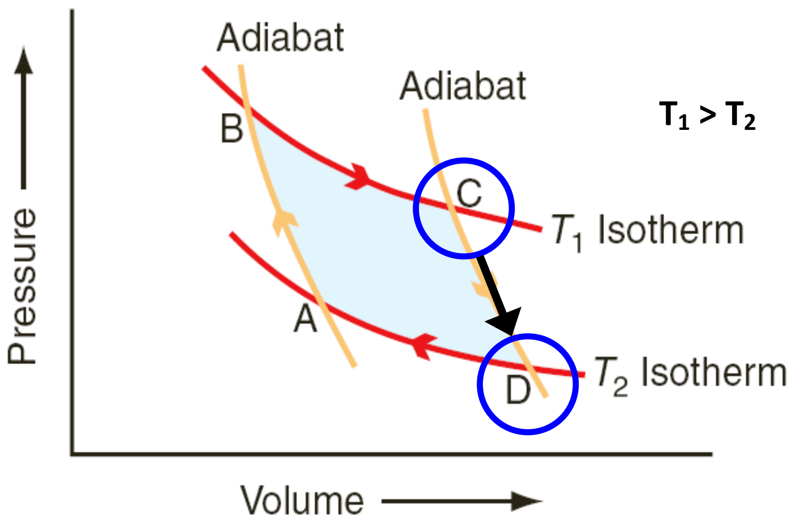
$$Q_{CD} = 0$$

$$\Delta U_{CD} = c_v (T_2 - T_1)$$

$$W_{CD} = -\Delta U_{CD}$$

$$W_{CD} = -c_v (T_2 - T_1)$$





Carnot Cycle

Carnot's Idealized Heat Engine:

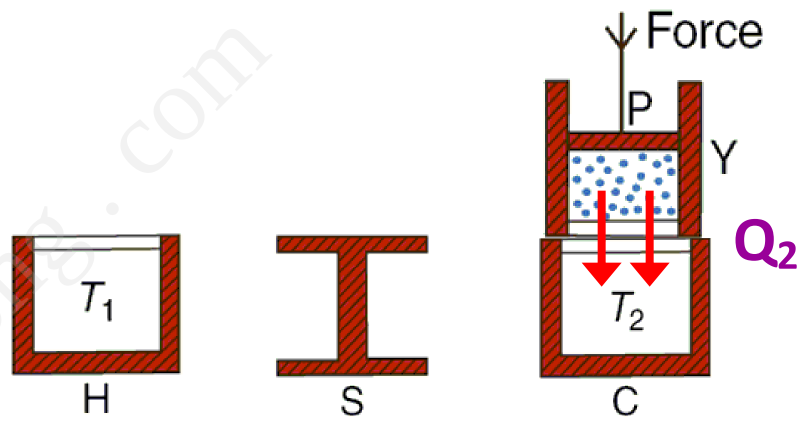
<u>The Four Processes</u>:

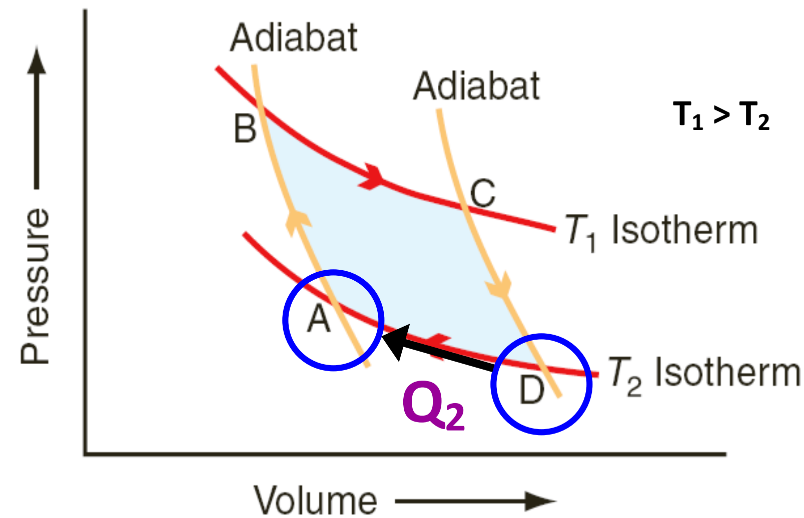
(4) Isothermal Compression

The cylinder is now placed on the cold reservoir

A force is applied to the piston and the substance undergoes isothermal compression to its original state (location A)

During this process the substance gives up the resulting compression heating Q_2 to the cold reservoir, allowing the process to occur isothermally





Carnot Cycle

Carnot's Idealized Heat Engine:

The Four Processes:

(4) Isothermal Compression

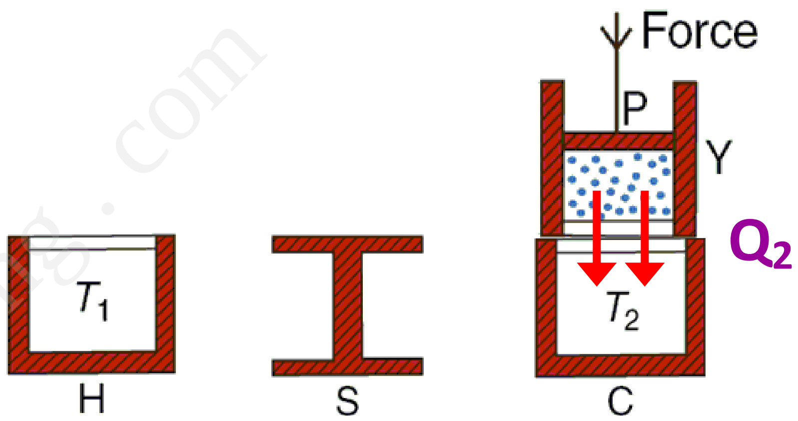
$$Q = \Delta U + W$$

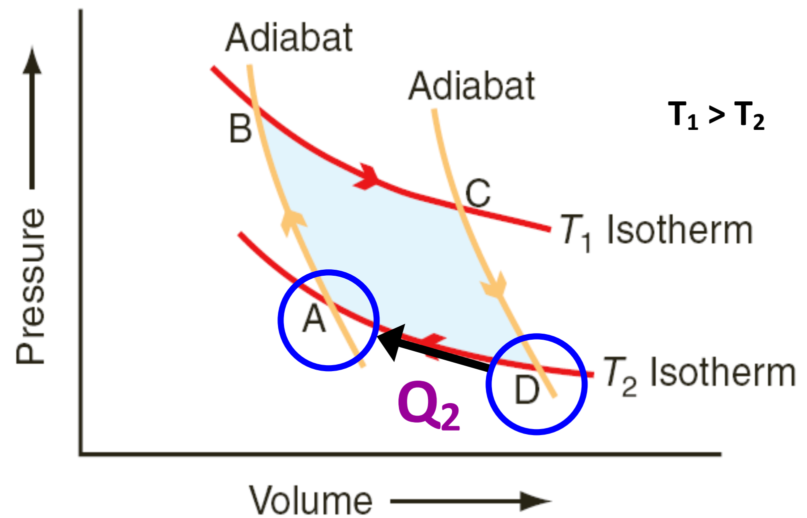
$$\Delta T = 0 \qquad Q_{DA} = Q_2$$

$$\Delta U_{DA} = 0$$

$$W_{DA} = Q_{DA}$$

$$W_{DA} = R_d T_2 \ln\left(\frac{V_A}{V_D}\right)$$





Carnot Cycle

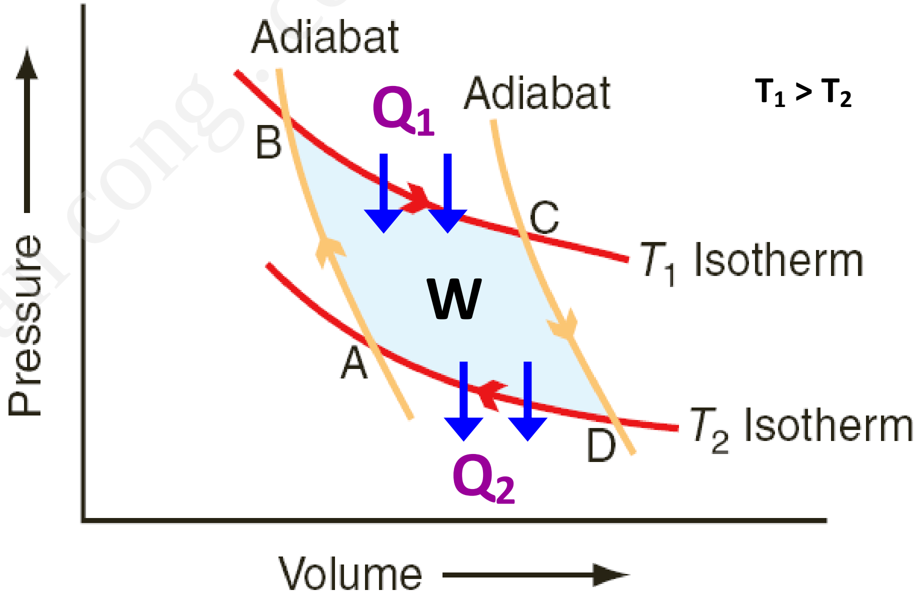
Carnot's Idealized Heat Engine:

Net Effect:

The **net** work done by the substance during the cyclic process is equal to the area enclosed within ABCDA

Since the process is cyclic, the **net** work done is also equal to Q_1+Q_2

The work is performed by transferring a fraction of the total heat absorbed from the warm reservoir to the cold reservoir



$$W_{NET} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$W_{NET} = Q_1 + Q_2$$

where: $Q_1 > 0$ and $Q_2 < 0$

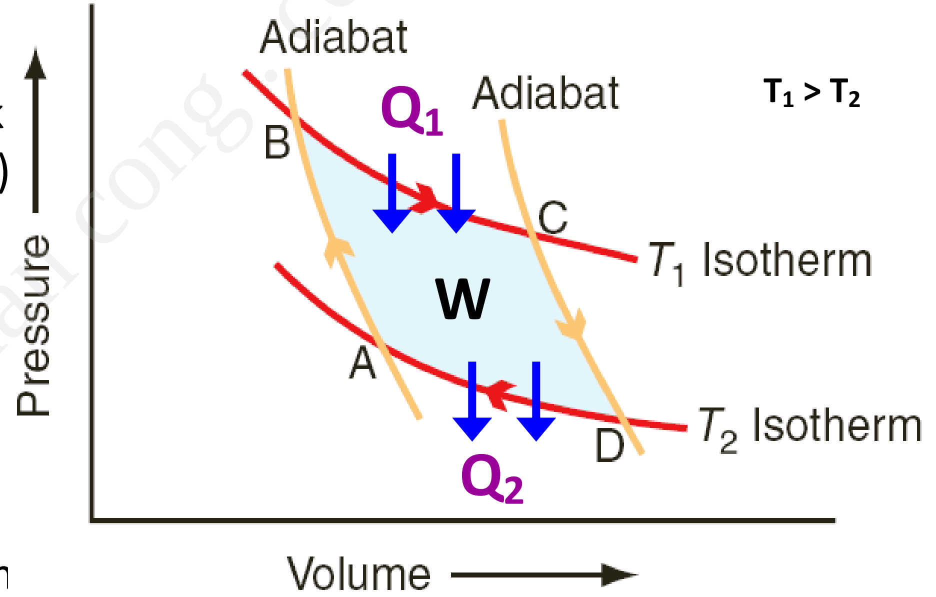
Carnot Cycle

Carnot's Idealized Heat Engine:

Efficiency:

We can define the efficiency of the heat engine (η) as the ratio between the net work done (W_{NET}) and the total heat absorbed (Q_1) or:

$$\eta = \frac{W_{NET}}{Q_1} = \frac{Q_1 + Q_2}{Q_1}$$



By considering the relations valid during each process, it can be shown that:

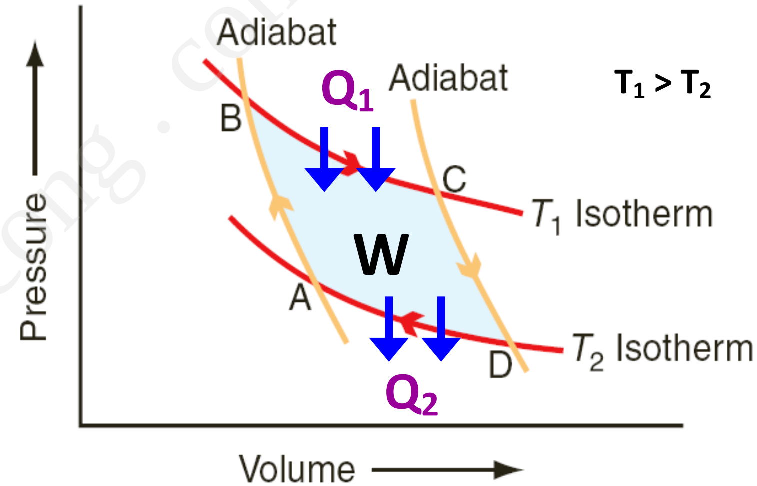
$$\eta = 1 - \frac{T_2}{T_1}$$

Carnot Cycle

Carnot's Idealized Heat Engine:

Important Lesson:

- It is <u>impossible</u> to construct a cyclic engine that transforms heat into work <u>without</u> surrendering some heat to a reservoir at a lower temperature



Examples of Carnot Cycles in Practice

- Steam Engine → has a radiator
- Power Plant → has cooling towers

Examples of Carnot Cycles in Nature

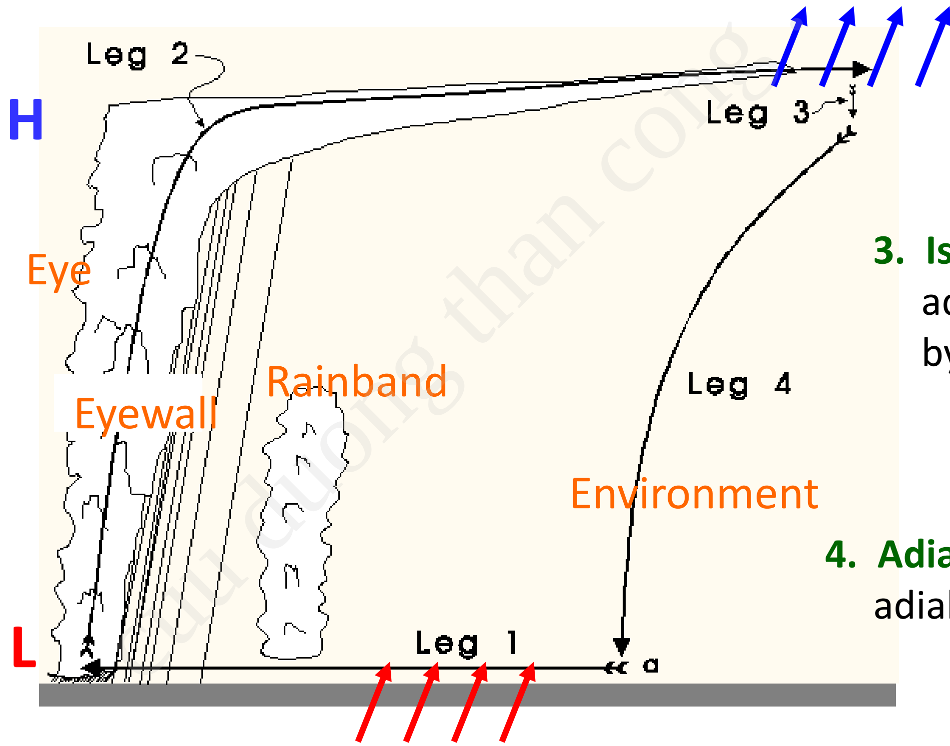
- Hadley Cell (??)
- Hurricane (??)**
- Thunderstorm (??)

Carnot Cycle

Example: A Hurricane

2. Adiabatic Expansion
cooling partially offset
by latent heat release

Heat Release (Q_2)
(Radiational Cooling)



3. Isothermal Compression
adiabatic warming offset
by radiational cooling

4. Adiabatic Compression
adiabatic warming

1. Isothermal Expansion
adiabatic cooling offset
by surface fluxes

Heat Absorbed (Q_1)
(Surface fluxes)
(from warm ocean)

Carnot Cycle

Example: A Hurricane

The National Hurricane Center closely monitors all hurricanes with a wide range of sensors, including buoys and satellites. On 27 August 2005, as Hurricane Katrina was approaching New Orleans, a buoy beneath the storm recorded a sea surface temperature of 29ºC. At the same time a satellite measured cloud top temperatures of -74ºC. Assuming Katrina was behaving like a Carnot cycle, how efficient was Katrina as a heat engine?

Warm reservoir → Ocean
Cold reservoir → Upper atmosphere

$$\eta = 1 - \frac{T_2}{T_1}$$

T_1 = 29ºC = 302 K
T_2 = -74ºC = 199 K

η = 0.34

Carnot Cycle

Example: A Thunderstorm

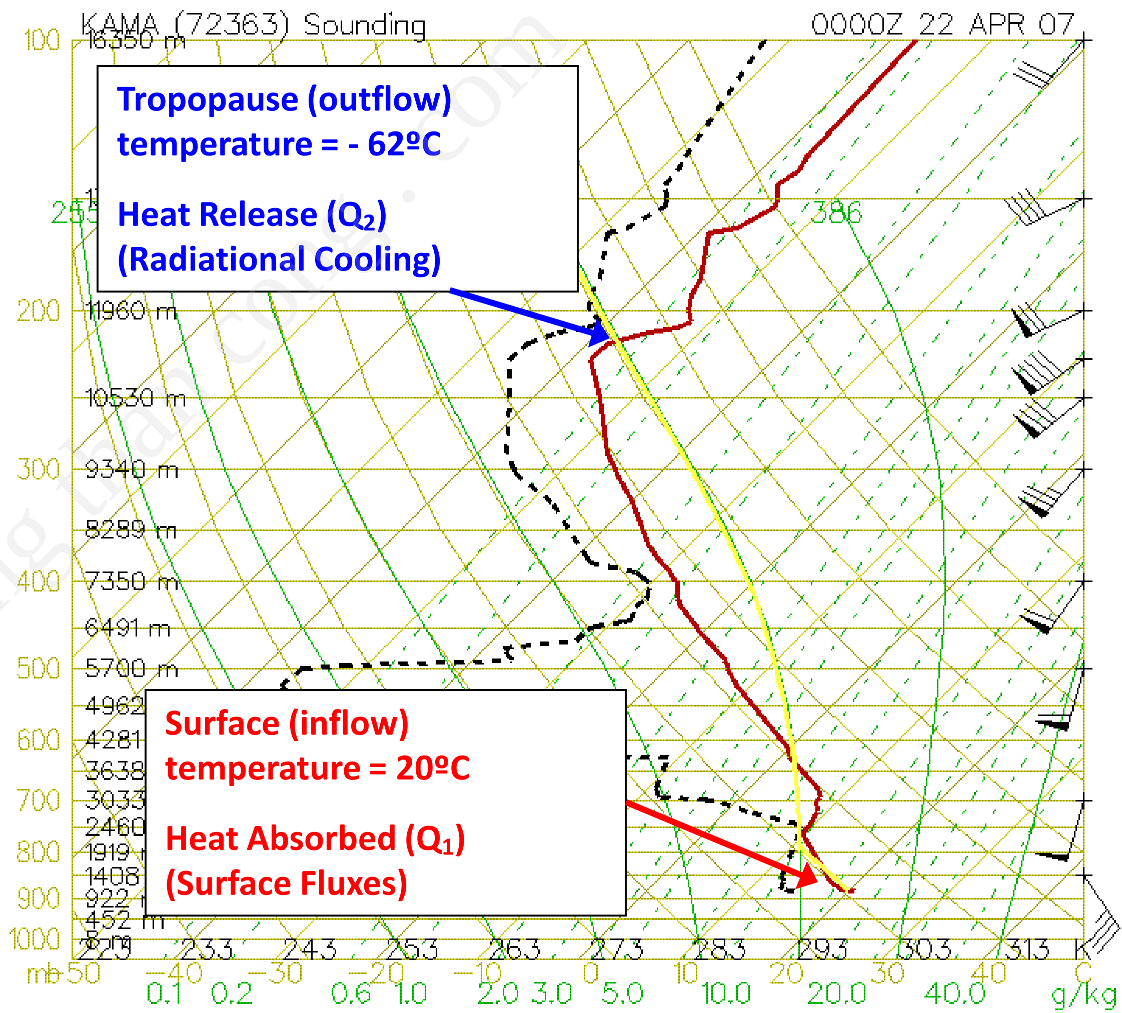
How efficient are typical thunderstorms assuming they behave like a Carnot cycle?

$$\eta = 1 - \frac{T_2}{T_1}$$

This sounding was very near some strong thunderstorms

T_1 = 20ºC = 293 K
T_2 = -62ºC = 211 K

η = 0.28



Combining the First and Second Laws

First Law of Thermodynamics

$$dQ = c_v dT + pdV$$

Second Law of Thermodynamics

$$dS \geq \frac{dQ_{rev}}{T}$$

↓

$$TdS \geq c_v dT + pdV$$

↓ ↓ ↓ ↓

There are many other forms since the First Law takes many forms

↓ ↓ ↓ ↓

$$TdS \geq c_p dT - Vdp$$

$$TdS \geq dU + dW$$

$$TdS \geq dH - dW$$

Combining the First and Second Laws

Special Processes:

$$TdS \geq c_v dT + pdV$$

Isothermal transformations

- Constant temperature
- Any irreversible (natural) work increases the entropy of a system

$$\Delta S \geq \frac{W}{T}$$

Adiabatic transformations

- No exchange of heat with the environment
- Entropy is constant

$$\Delta S = 0$$

Isentropic transformations

- Constant entropy
- Adiabatic and isentropic transformations are the exact same thing
- This is why "isentropes" and "dry adiabats" are the same on thermodynamic diagrams

$$\Delta S = 0$$

Combining the First and Second Laws

Special Processes:

$$TdS \geq c_v dT + pdV$$

Isochoric transformations

- Constant volume
- No work is done
- Entropy changes are a function of the initial and final temperatures

$$\Delta S \geq c_v \ln \frac{T_f}{T_i}$$

Isobaric transformations

- Constant pressure
- Entropy changes are a function of the initial and final temperatures

$$TdS \geq c_p dT - Vdp$$

$$\Delta S \geq c_p \ln \frac{T_f}{T_i}$$

Combining the First and Second Laws

Example: Air parcels rising through a cloud

- Most air parcels moving through the atmosphere experience an increase in entropy due to irreversible processes (condensation, radiational cooling, etc.)

- Assume an air parcel rising through a thunderstorm from 800 mb to 700 mb while its temperature remains constant. Calculate the change in entropy of the rising parcel.

p_1 = 800 mb
p_2 = 700 mb
dT = 0 (constant T)

$$TdS \geq c_p dT - Vdp$$

After some simplifications, using ideal gas law, and integrating from p_1 to p_2

$$\Delta S \geq -R_d \ln\left(\frac{p_2}{p_1}\right)$$

R_d = 287 J/kgK

ΔS = 38.3 J/kg K

Consequences of the Second Law

Entropy and Potential Temperature:

- Recall the definition of potential temperature:
  - Valid for adiabatic processes

$$\theta = T\left(\frac{p_0}{p}\right)^{R_d/c_p}$$

- By combining the first and second laws with potential temperature, it can easily be shown (see you text) that:

$$dS = c_p d\ln\theta$$

or:

$$\Delta S = c_p \ln\left(\frac{\theta_2}{\theta_1}\right)$$

- Therefore, **any reversible adiabatic process is also isentropic**

Consequences of the Second Law

Atmospheric Motions:

Recall:

- Reversible transformations do not occur naturally
- However, very slow transformations are almost reversible if a parcel is allowed to continually reach equilibrium with its environment at each successive "step" along it path.
- In the atmosphere, **vertical motions** are primarily responsible for **heat transfer** between the surface (a warm reservoir) and the top of the atmosphere, or outer space (a cold reservoir)

Therefore:

Synoptic vertical motions	Very slow (~0.01 m/s) Occur over large scale High and Low pressure systems	Minimal (or no) net heat transfer
Convective vertical motions	Very fast (~1-50 m/s) Occur over small scales Thunderstorms	Large heat transfer