# BME 3711 - Biothermodynamics

## Course Overview

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- Thermodynamics: the science of heat and work.

$$\underbrace{\text{Thermo}}_{\text{Heat}}\underbrace{\text{dynamics}}_{\text{Motion}}$$

- Biothermodynamics: Thermodynamics of biological systems.

# Energy Conversion

- Thermodynamics is the study of energy and conversion of energy from one form to another.

Electrical Energy to Radiant Energy

Chemical energy to kinetic energy

Electrical energy to thermal energy

Solar Energy to Chemical Energy

Chemical energy to kinetic energy

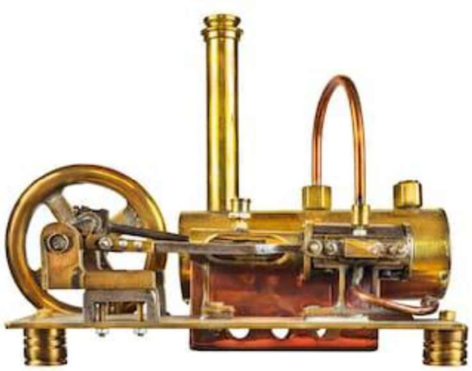
Kinetic energy to mechanical energy


GRIST MILL


AA
12-2026
ALKALINE BATTERY
Energizer

# Thermodynamic Revolution

- Thermodynamics deals with the relationships between heat and work.
- It was developed as a science out of an urge to increase the efficiency of steam engines.
- Maximum work by minimum coal
- Steam engines convert the heat energy to mechanical energy by using the pressure of the steam to push the pistons.

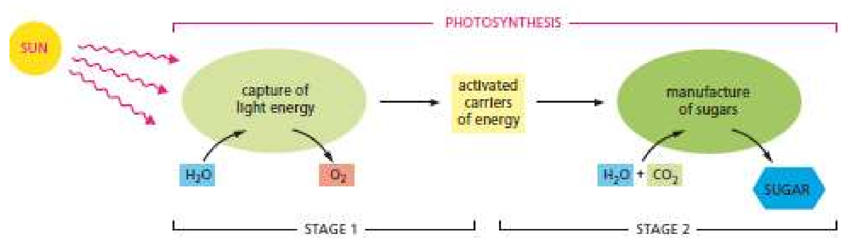


https://www.youtube.com/watch?v=9mhYnQGZJuM

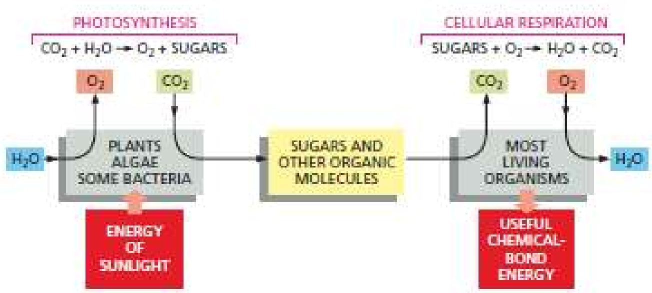
- Although humanity made use of large amount of thermal energy wasted as heat into some kind of mechanical work in 19th century, nature solved the issue much more earlier and the muscles, nerves and the metabolism evolved.
- Living cells and organisms must perform work to stay alive and to reproduce themselves.
- The synthetic reactions that occur within cells, like the synthetic processes in any factory, require the input of energy.
- Energy is also consumed in the motion and the storage and expression of information without which structures rich in information inevitably become disordered and meaningless.

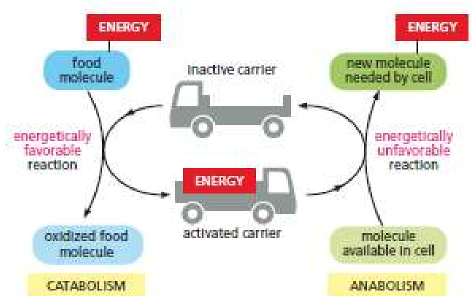
- Living systems are also about the stored, transformed and dissipated energy.
- Cells can be modelled as an adaptive thermal and chemical engines which convert energy in one form to another by coupling metabolic and chemical reactions.

- Living organisms must take in energy from their environment and convert it into to a form that their cells can use.
- The source of the energy that the organisms use is sun.
- Plants capture the energy from sunlight to make sugar and oxygen from carbon dioxide and water.

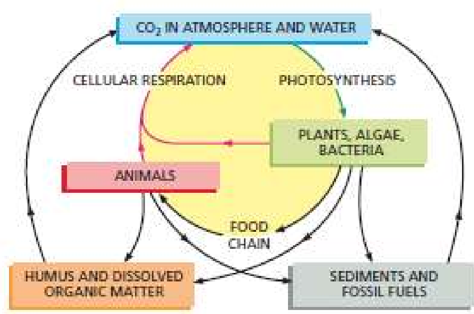


- Organisms ingest large molecules, like carbohydrates, proteins, and fats, and convert them into smaller molecules like carbon dioxide and water.
- This process is called cellular respiration, a form of catabolism, and makes energy available for the cell to use.
- The energy released by cellular respiration is temporarily captured by the formation of adenosine triphosphate (ATP) within the cell.
- ATP is the principle form of stored energy used for cellular functions and is frequently referred to as the energy currency of the cell.



- Carbon exists in the air largely as carbon dioxide ($CO_2$) gas.
- The $CO_2$ gas in the air is converted into organic molecules in plants.
- Those organic molecules are passed through food chains, and cellular respiration converts the organic carbon back into carbon dioxide gas.
- When organisms decay, carbon goes into the soil where in the long term they turn into fossil fuels.
- CO2 is released back in the air when the fossil fuels are burned.



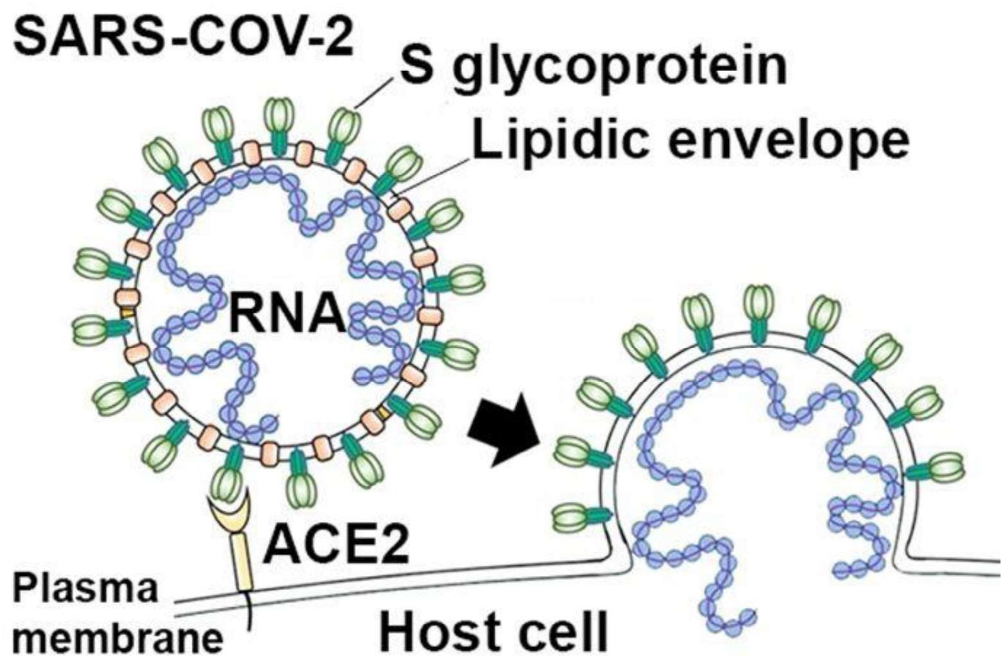
- Although the characteristic composition of an organism changes little through time, the population of molecules within the organism is far from static.
- Small molecules, macromolecules, and supramolecular complexes are continuously synthesized and then broken down in chemical reactions that involve a constant flux of mass and energy through the system.

- The constancy of this flux is the result of a *dynamic steady state,* a steady state that is far from equilibrium.
- Maintaining this steady state requires the constant investment of energy; when the cell can no longer generate energy, it dies and begins to decay toward equilibrium with its surroundings.

- Cells are transducers of energy, capable of interconverting chemical, electromagnetic, mechanical, and osmotic energy with great efficiency.
- All energy transductions in cells can be traced to this flow of electrons from one molecule to another, in a “downhill” flow from higher to lower electrochemical potential.
- This is formally analogous to the flow of electrons in a battery-driven electric circuit.

# Biothermodynamics

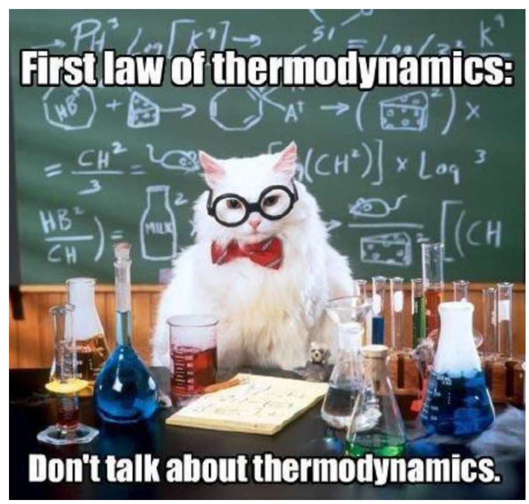
- Thermodynamics is summarized by a number of laws that allow us to account for the natural direction of physical and chemical change.
- Its principal relevance to biology is its application to the study of the deployment of energy by organisms.
  - Protein folding
  - Enzyme-Substrate Binding
  - Biological Energy Conversions
  - ATP Consumption
  - Drug Design can be identified by a thermodynamics approach.


SARS-COV-2
S glycoprotein
Lipidic envelope
RNA
ACE2
Plasma membrane
Host cell

- Living cells and organisms must perform **work W** to stay alive, to grow, and to reproduce:
  - Light → Chemical (by photosynthesis)
  - Chemical → Chemical (by cellular respiration)
  - Chemical → Electrical (by neurons)
  - Chemical → Mechanical (by muscles)
- The flow of energy maintains the order and life.

# Laws of Thermodynamics

- Zeroth Law: Thermal Equilibrium
- First Law: Energy Conversion
- Second Law: Entropy
- Third Law: Absolute Zero



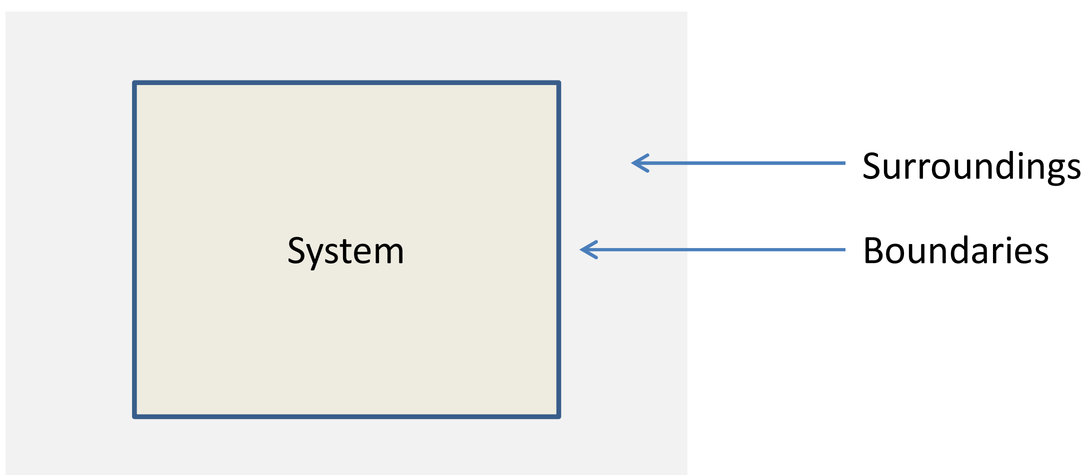
- Relationships between heat as an energy and work are the fundamentals for thermodynamics.
- **Work** is the measure of energy transfer that occurs when an object is moved over a distance d by an external force F.

$$W = F \times d \longrightarrow \text{Displacement work}$$

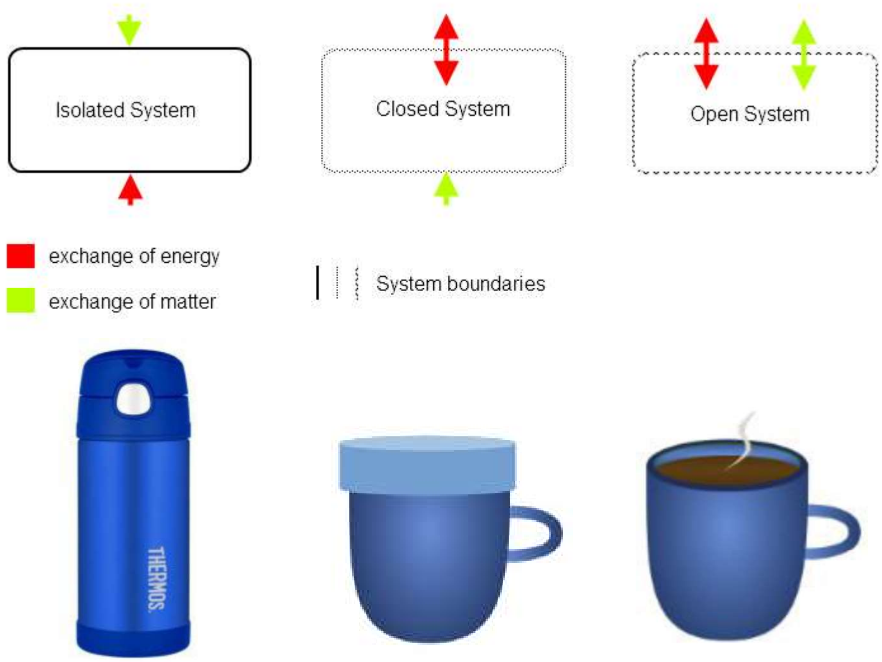
- **Energy** is the capacity to do work.
  - Kinetic energy, potential energy, electrical energy, thermal energy

# Some important definitions

- A thermodynamic **system** is defined as a quantity of matter of fixed mass and identity on which attention is focused for study.
- Everything external to the system is the **surroundings**, and the system is separated from the surroundings by the system **boundaries**.



- In thermodynamic systems energy can only be transferred by the boundaries.
  - Open Systems: Both mass and energy can be transferred through boundaries.
  - Closed Systems: Only energy can be transferred through boundaries but not mass.
  - Isolated Systems: No energy or mass can be transferred through boundaries.



- A living organism is an open system; it exchanges both matter and energy with its surroundings.
- Living organisms derive energy from their surroundings in two ways:
    1. They take up chemical fuels (such as glucose) from the environment and extract energy by oxidizing them.
    2. They absorb energy from sunlight.

# Properties of a system

- Any system can be specified by giving the values of the following properties:
  - Pressure (p)
  - Temperature (T)
  - Volume (V)
  - Moles of matter (n)

$\left.\begin{array}{l}\\ \\ \\ \end{array}\right\}$ *State Variables

**p = f (V, n, T)** ⟹

$$PV = nRT$$

$$P = nRT / V$$

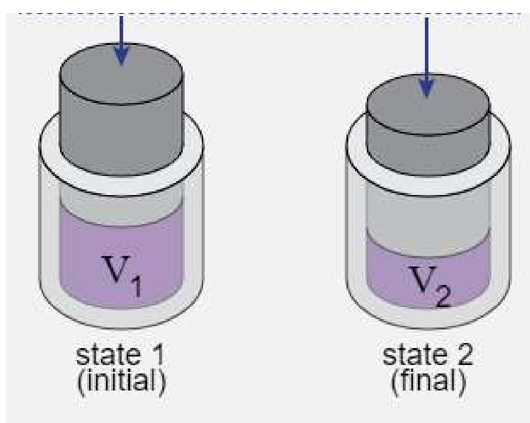
**Ideal Gas Law**

*State variables: measurable static properties that characterize the system.

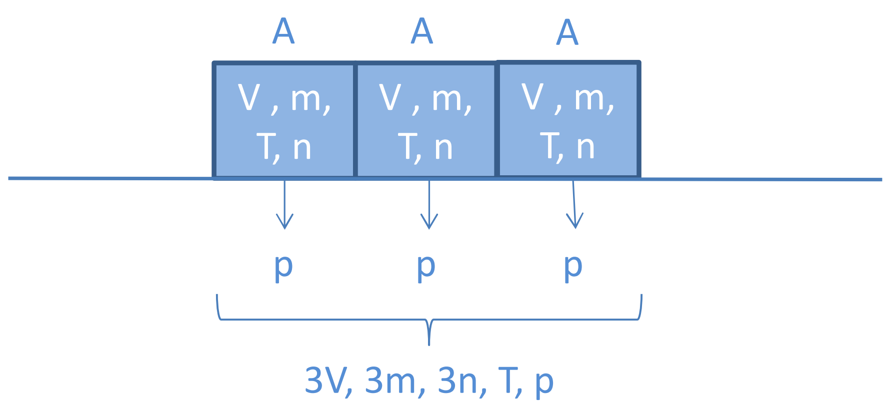
$$3H_2\ (g,\ 1\ bar,\ 50°C) = 3\ H_2\ (g,\ 5\ bar,\ 100°C)$$

Initial state $\xrightarrow{\text{Process Path}}$ Final State

2 Equilibrium States

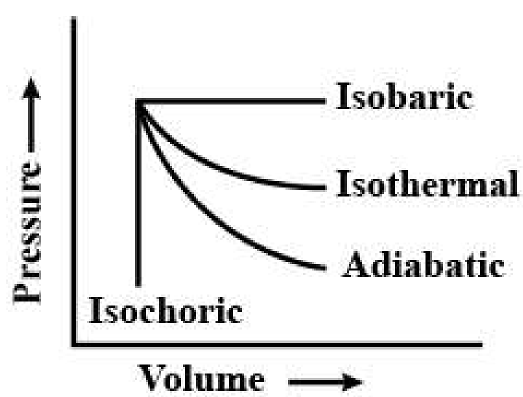


- Extensive Properties: depend on mass (V, n)
- Intensive Properties: do not depend on mass (p, T)



# Process Path

- The process of going from one equilibrium state to another, which is also called the path, can occur under several conditions:
  - Isobaric: under constant pressure ($\Delta P = 0$)
  - Isothermal: under constant temperature ($\Delta T = 0$)
  - Isochoric: under constant volume ($\Delta V = 0$)
  - Adiabatic: without heat transfer from or to the system ($\Delta Q = 0$)



# SI units

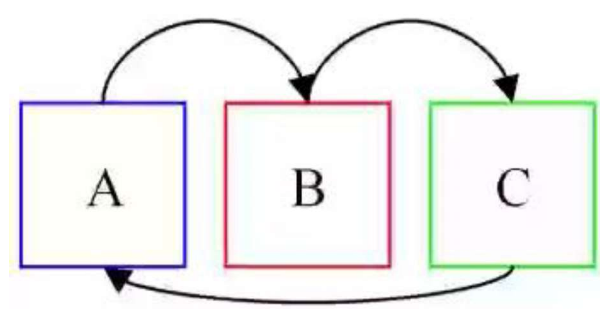
- SI units
  - Length: meter (m)
  - Mass: kilogram (kg)
  - Time: second (s)
  - Temperature: Kelvin (K)

$K = °C + 273.15$

- Derived Units:
  - Force: kg m $s^{-2}$ , Newton (N)
  - Pressure: kg $m^{-1}$ $s^{-2}$ , Pascal (Pa)
  - Energy: kg $m^2$ $s^{-2}$ , Joule (J)

# Zeroth Law of Thermodynamics: The Law of Thermal Equilibrium

- This law states that “If two systems are in thermal equilibrium with a third system, they are all in thermal equilibrium with each other.”
- Thus, if a system A is in thermal equilibrium with the system B, and the system B maintains thermal equilibrium with system C, then A and C are also in thermal equilibrium.



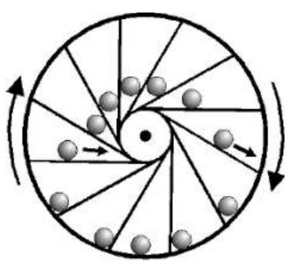
- In essence, the three bodies are all the same *temperature.*
- No matter how much energy two systems have, knowing how much energy they have doesn’t let the direction the heat will flow if they are in contact with each other.
- The Zeroth Law says that this number, which is the temperature, defines the direction of heat flow, and it does not depend directly on the amount of energy that’s involved.

# Perpetual Motion Machine

- People struggled for centuries to create energy from nothing, for they believed that if they could create energy, then they could produce work (and wealth) endlessly.
- However, without exception, they failed. As a result of their failed efforts, we have come to recognize that energy can be neither created nor destroyed but only converted from one form into another or transferred from place to place.

# Perpetual Motion Machine

- The idea of Perpetual Motion Machine is a product of those efforts that tries to create energy from no input.
- A perpetual motion machine is a hypothetical machine that can do work infinitely without an energy source.
- However, it is impossible to engineer such an engine since is violates the laws of thermodynamics.



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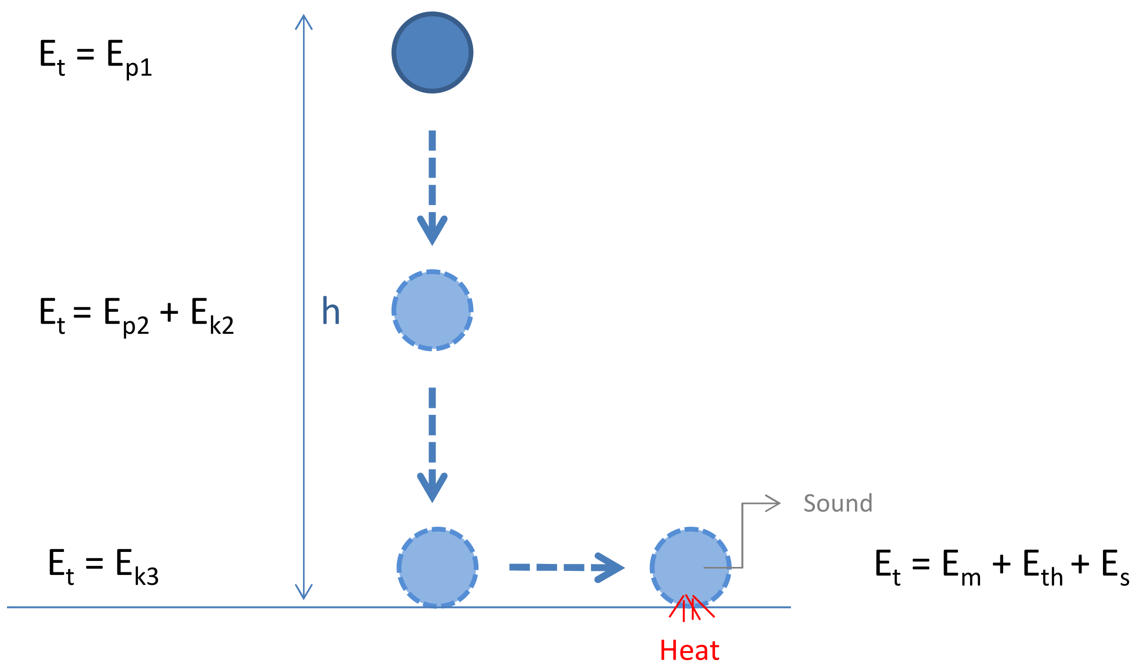


$E_t = E_{p1}$
$E_t = E_{p2} + E_{k2}$
h
Sound
$E_t = E_{k3}$
$E_t = E_m + E_{th} + E_s$
Heat

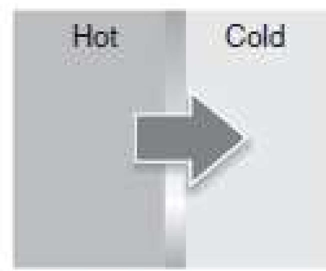
# First Law of Thermodynamics: The Law of Conservation of Energy

Energy can not be created nor destroyed can only be converted from one form to another.

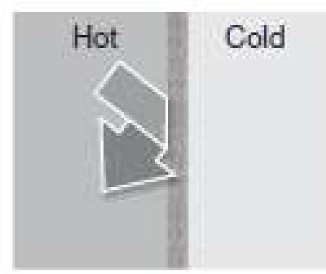
It deals with the relationship between energy and work and heat.

- Energy can be exchanged between a closed system and its surroundings by doing work or by the process called "heating."
- Heating is the process of transferring energy as a result of a temperature difference between the systems and its surroundings.
- It is common to say that "energy is transferred as work" when the system does work and "energy is transferred as heat" when the system heats its surroundings.

- Walls that permit heating as a mode of transfer of energy are called **diathermic**. A metal container is diathermic and so is our skin or any biological membrane.
- Walls that do not permit heating even though there is a difference in temperature are called **adiabatic**.
- The double walls of a thermos are adiabatic to a good approximation.




(a) Diathermic

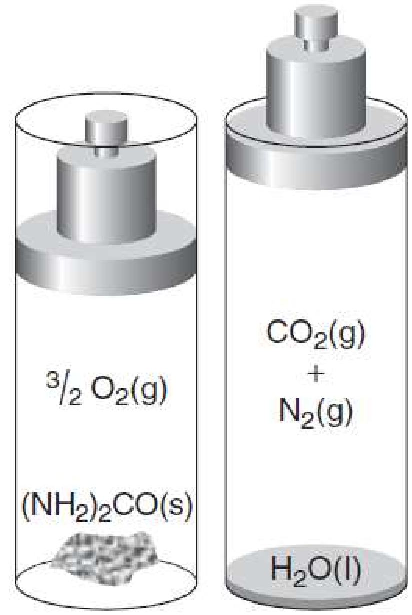



(b) Adiabatic

- As an example of these different ways of transferring energy, consider a chemical reaction that is a net producer of gas, such as the reaction between urea, $(NH_2)_2CO$, and oxygen to yield carbon dioxide, water, and nitrogen:

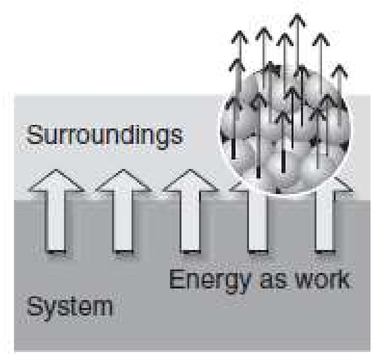
$$(NH_2)_2CO(s) + \tfrac{3}{2}\, O_2(g) \longrightarrow CO_2(g) + 2\, H_2O(l) + N_2(g)$$

- Suppose first that the reaction takes place inside a cylinder fitted with a piston, then the gas produced drives out the piston and raises a weight in the surroundings.
- In this case, energy has migrated to the surroundings as a result of the system doing work, because a weight has been raised in the surroundings: that weight can now do more work, so it possesses more energy.
- Some energy also migrates into the surroundings as heat. We can detect that transfer of energy by immersing the reaction vessel in an ice bath and noting how much ice melts.
- Alternatively, we could let the same reaction take place in a vessel with a piston locked in position. No work is done, because no weight is raised.
- However, because it is found that more ice melts than in the first experiment, we can conclude that more energy has migrated to the surroundings as heat.

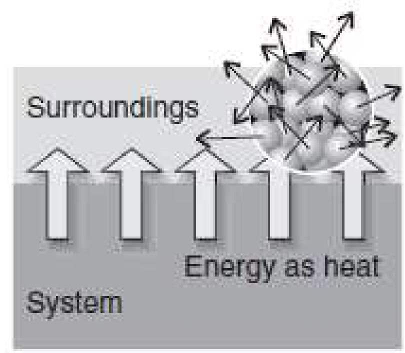



- A process in a system that heats the surroundings (we commonly say “releases heat into the surroundings”) is called **exothermic**.
- A process in a system that is heated by the surroundings (we commonly say “absorbs heat from the surroundings”) is called **endothermic**.

- The clue to the molecular nature of work comes from thinking about the motion of a weight in terms of its component atoms.
- When a weight is raised, all its atoms move in the same direction. This observation suggests that *work is the transfer of energy that achieves or utilizes uniform motion in the surroundings*.
- Electrical work, for instance, corresponds to electrons being pushed in the same direction through a circuit.
- Mechanical work corresponds to atoms being pushed in the same direction against an opposing force.



- When energy is transferred as heat to the surroundings, the atoms and molecules oscillate more rapidly around their positions or move from place to place more vigorously.
- The key point is that the motion stimulated by the arrival of energy from the system as heat is random, not uniform as in the case of doing work.
- This observation suggests that heat is the mode of transfer of energy that achieves or utilizes random motion in the surroundings.



- In bioenergetics, the most useful outcome of the breakdown of nutrients during metabolism is work, so we need to know how work is measured.

1) Displacement work
   - The work done when a force acts upon an object to cause a displacement x is W=Fx

2) Work done against gravity
   - The work done when the mass m is raised through a height h on the surface of the Earth against gravity is W=mgh

3) Electrical work
   - The work done to move a charge q between 2 points in a circuit with a potential difference V is W = q V

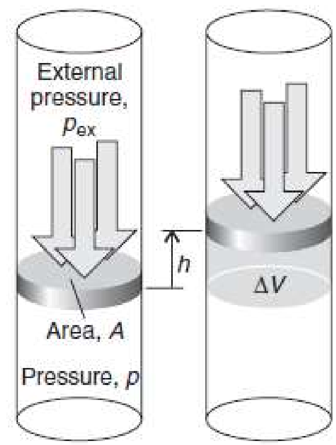
4) Boundary (Expansion) work
   - the work done when a system expands against an opposing pressure is $W= -p_{ex}\Delta V$

# Expansion work

Work done by the system = distance × opposing force

$$= h \times (p_{ex}A) = p_{ex} \times (hA) = p_{ex} \times \Delta V$$

Work done by system = $p_{ex}\Delta V$




Now consider the sign. A system does work and thereby loses energy (that is, *w* is negative) when it expands (when *V* is positive).

Therefore, we need a negative sign in the equation to ensure that *w* is negative (when *V* is positive).

# The work of exhaling air

- Exhalation of air during breathing requires work because air must be pushed out from the lungs against atmospheric pressure.
- Calculate the work of exhaling 0.50 L ($5.0 \times 10^{-4}$ $m^3$) of air, a typical value for a healthy adult, through a tube into the bottom of the apparatus and against an atmospheric pressure of 1.00 atm (101 kPa). (1 Pa $m^3$ = 1 J)

- The exhaled air lifts the piston so the change in volume is $\Delta V = 5.0 \times 10^{-4}$ m$^3$ and the external pressure is $p_{ex}$ 101 kPa.

$$w = -p_{ex}\Delta V = -(1.01 \times 10^5 \text{ Pa}) \times (5.0 \times 10^{-4} \text{ m}^3)$$

$$= -51 \text{ Pa m}^3 = -51 \text{ J}$$

# The work of moving nutrients through the trunk of a tree

- Nutrients in the soil are absorbed by the root system of a tree and then rise to reach the leaves through a complex vascular system in its trunk and branches.
- Calculate the work required to raise 10 g of liquid water (corresponding to a volume of about 10 mL) through the trunk of a 20 m tree from its roots to its topmost leaves.

- Work is done against Earth’s gravitational force.
- Gravitational force pulls down while water moves up towards the leaves.

$$\text{Work} = \text{Gravitational Force x Height}$$

$$Work = (1.0 \times 10^{-2}\ \text{kg}) \times (9.81\ \text{m s}^{-2}) \times (20\ \text{m})$$

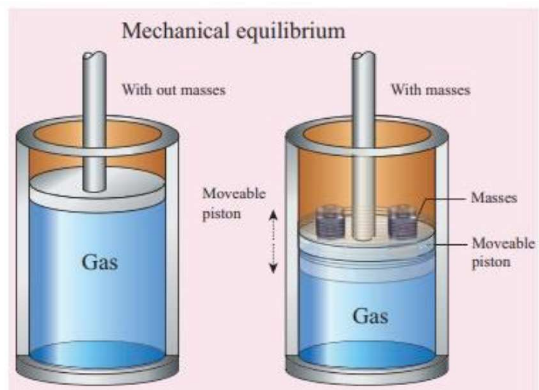
$$= 2.0\ \text{kg m}^2\ \text{s}^{-2} = 2.0\ \text{J}$$

# Maximizing the work obtained from a system

- The least expansion work from a system can be obtained when the external pressure is reduced—which provides the opposing force—to zero.
- The greatest expansion work for a given change in volume is done when the external pressure has its maximum value.
- The force opposing the expansion is then the greatest and the system must exert most effort to push the piston out. However, that external pressure cannot be greater than the pressure, p, of the gas inside the system, for otherwise the external pressure would compress the gas instead of allowing it to expand.
- Therefore, **maximum work is obtained when the external pressure is only infinitesimally less than the pressure of the gas in the system.**

https://www.youtube.com/watch?v=RKOPoJzqH94

- In effect, the two pressures must be adjusted to be the same at all stages of the expansion.
- This balance of pressures is a state of mechanical equilibrium.
- Therefore, we can conclude that ***a system that remains in mechanical equilibrium with its surroundings at all stages of the expansion does maximum expansion work***.

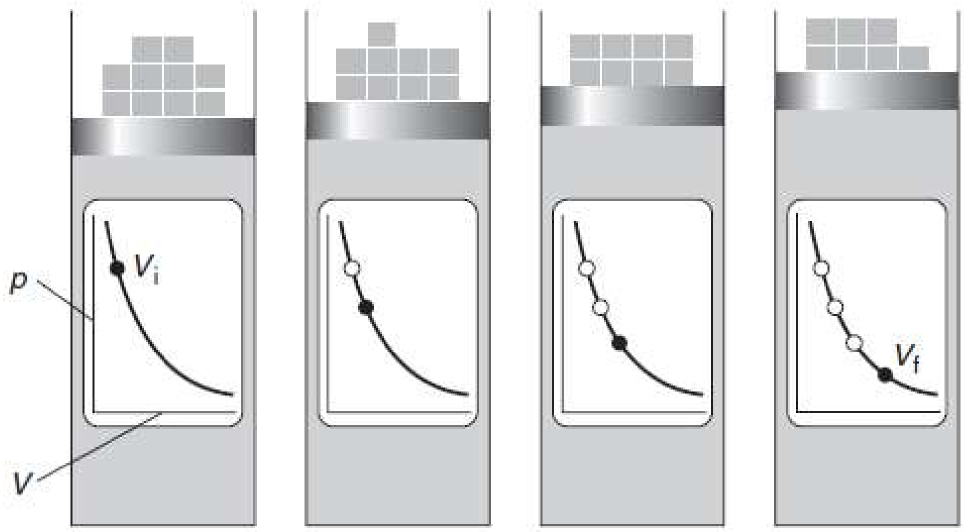


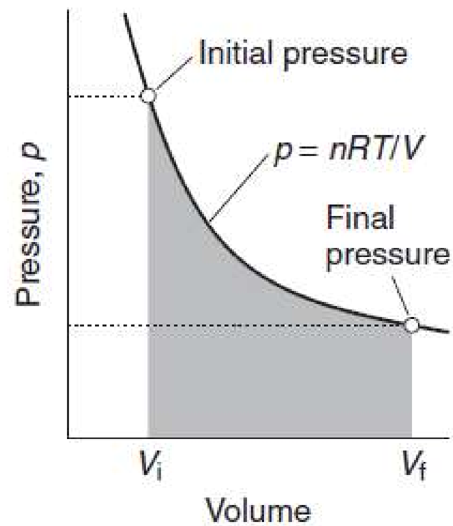
# Reversibility

- When the external pressure is infinitesimally less than the pressure of the gas at some stage of the expansion, the piston moves out.
- However, suppose we increase the external pressure so that it became infinitesimally greater than the pressure of the gas; now the piston moves in:
    - ***when a system is in a state of mechanical equilibrium, an infinitesimal change in the pressure results in opposite directions of change*.**
- **A change that can be reversed by an *infinitesimal* change in a variable**—in this case, the **pressure—is said to be reversible**.
- In thermodynamics it has a stronger meaning—reversibility means that a process can be reversed by an *infinitesimal* modification in some variable.

- Thus,
  1. A system does maximum expansion work when the external pressure is equal to that of the system at every stage of the expansion ($p_{ex} = p$).
  2. A system does maximum expansion work when it is in mechanical equilibrium with its surroundings at every stage of the expansion.
  3. Maximum expansion work is achieved in a reversible change.

# Reversible Expansion = Maximum Work




For a gas to expand reversibly, the external pressure must be adjusted to match the internal pressure at each stage of the expansion. When the weights are gradually unloaded from the piston as the piston is raised, the internal pressure falls. The procedure results in the extraction of the maximum possible work of expansion.

The work of reversible isothermal expansion of a gas is equal to the area beneath the curve p vs. V.

$$w = -nRT \ln \frac{V_f}{V_i}$$

- When the system expands through an infinitesimal volume d*V*, the infinitesimal work, d*w*, done is

$$dw = -p_{ex}dV$$

- At each stage, we ensure that the external pressure is the same as the current pressure, *p*, of the gas, thus $p_{ex} = p$

$$dw = -p dV$$

- The total work when the system expands from *V*i to *V*f is the sum (integral) of all the infinitesimal changes between the limits *V*i and *V*f,

$$w = -\int_{V_i}^{V_f} p dV$$

- From the perfect gas law (P V = n R T);

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

- *The **isothermal reversible** expansion of a perfect gas is*

$$w = -nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

- Since:

$$\int_{V_i}^{V_f} \frac{dV}{V} = \ln \frac{V_f}{V_i}$$

- We get

$$\boxed{w = -nRT \ln \frac{V_f}{V_i}}$$

$$w = -nRT \ln \frac{V_f}{V_i}$$

- In an expansion $V_f > V_i$, so $V_f / V_i > 1$ and the logarithm is positive (ln $x$ is positive if $x > 1$).
- Therefore, in an expansion, $w$ is negative. That is what we should expect: energy *leaves* the system as the system does expansion work.
- Second, for a given change in volume, we get more work the higher the temperature of the confined gas That is also what we should expect: at high temperatures, the pressure of the gas is high, so we have to use a high external pressure, and therefore a stronger opposing force, to match the internal pressure at each stage.

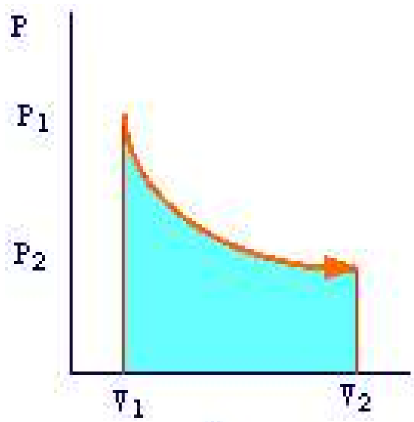
- Calculate the work done when 1.0 mol Ar(g) confined in a cylinder of volume 1.0 L at 25°C expands isothermally and reversibly to 2.0 L.

$$W = -nRT \ln V_f / V_i$$

$$W = - 1.0 \text{ mol} \times 8.314 \text{ J / mol K} \times 298.15 \text{ K} \times \ln 2 / 1$$

$$W = - 1718,19 \text{ J} = - 1.7 \text{ kJ}$$

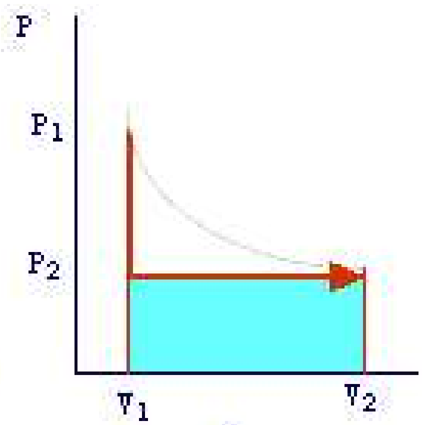
Which process is reversible and which one is irreversible?
What is the work done by each process?




A

Reversible

W = - nRT ln V2/V1



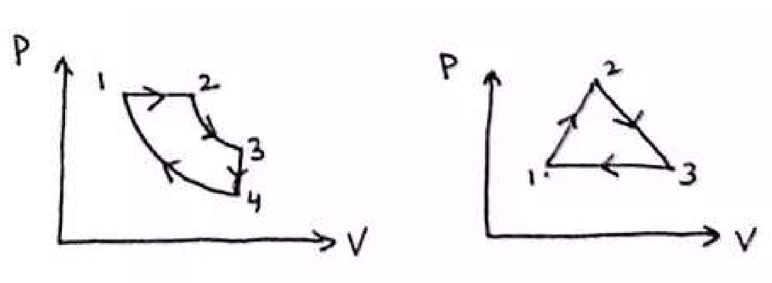

B

Irreversible

W = P2 (V2-V1)

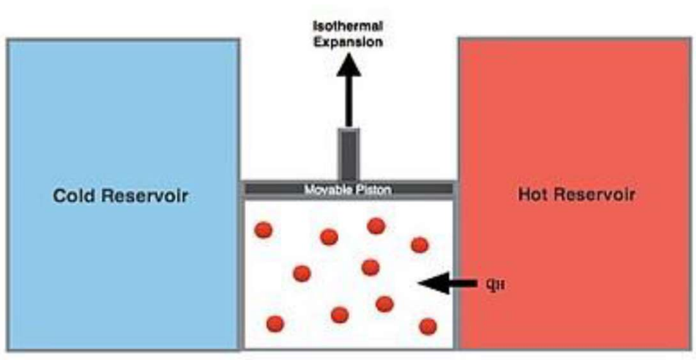
# Thermodynamic Cycle

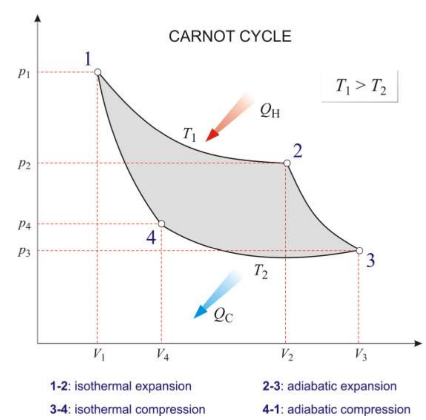
- A thermodynamic cycle occurs when a system is taken through a series of different states, and finally returned to its initial state.
- In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine.



# Carnot Cycle

- In 1824, S. Carnot devised a cycle comprising only of reversible processes which was named after him as Carnot cycle. It comprises of all reversible processes.
- This cycle, operating between two heat reservoirs, consists of an alternate series of two reversible isothermal and two reversible adiabatic processes.
- The system (1 mole of an ideal gas) is contained in a frictionless piston and cylinder arrangement. Out of the two heat reservoirs, one is at a higher temperature T2 (called the source) and the other at a lower temperature T1 (called the sink). The Carnot cycle performs four different operations which can be represented on a pressure-volume diagram:
  - Reversible Isothermal Expansion (process 1-2, T1 = constant)
  - Reversible Adiabatic Expansion (process 2-3, temperature drops from T1 to T2)
  - Reversible Isothermal Compression (process 3-4, T2 = constant)
  - Reversible Adiabatic Compression (process 4-1, temperature rises from T2 to T1)



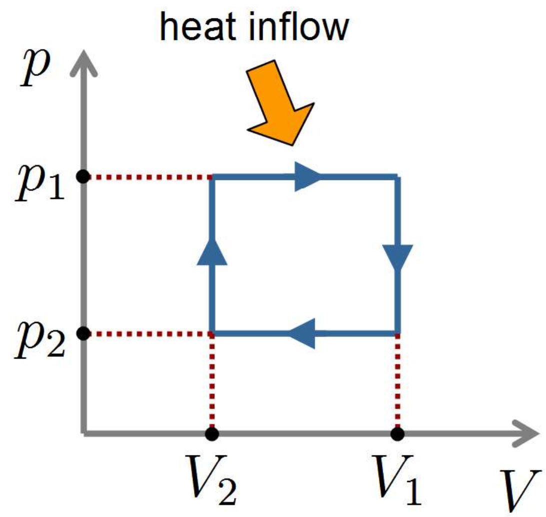



# Carnot Cycle

$W_{Total} = W_1 - W_2$

$W_T = P_2\,(V_1 - V_2) - P_1\,(V_1 - V_2)$

$$W_T = \underbrace{(P_2 - P_1)}_{-}\ \underbrace{(V_1 - V_2)}_{+}$$

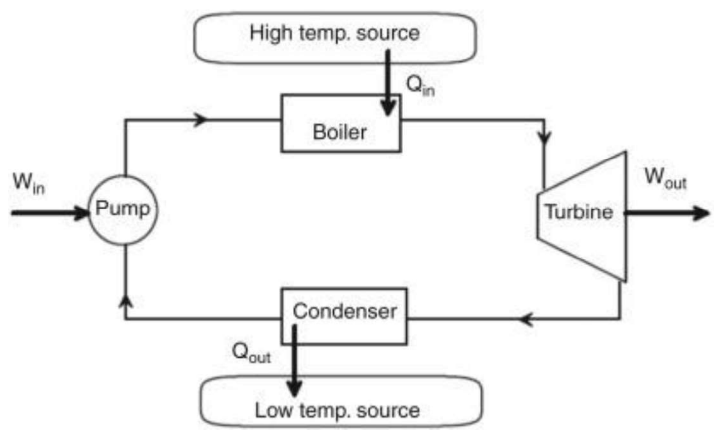



$W_T < 0$ work is done by the system on the environment. So this cycle produces energy.

**Do you think Carnot Cycle violates the First Law of thermodynamics? Why?**

# Rankine Cycle: Heat Engines

- Converting heat to work requires the use of a special device called a heat engine.
- Heat engines may vary considerably from one another, but share the following characteristics:
  - They operate on a cycle, they receive the driving heat from a high temperature source, they convert part of this heat to work, they reject the remaining waste heat to a low-temperature sink.




**Do you think it will be better not to release the heat in the condenser so that the efficiency of the system would be better?**

# Refrigeration Cycle

- In nature, heat flows in the direction of decreasing temperature. The reverse process, cannot occur spontaneously and requires the use of special devices called refrigerators.
- Like heat engines, refrigerators are cyclic devices. The working fluid used in the refrigeration cycle is called a refrigerant.
  - The refrigerant enters the compressor as a vapor and is compressed to the condenser pressure. It leaves the compressor at a relatively high temperature and cools down and condenses as it flows through the coils of the condenser by rejecting heat to the surrounding medium.
  - Next, the refrigerant enters an expansion valve, refrigerant's temperature and pressure decrease. The refrigerant then enters the evaporator, where it evaporates by absorbing heat from the refrigerated space (cooling effect).
  - The cycle is completed as the refrigerant leaves the evaporator and returns to the compressor.