Thermodynamics

Thermodynamics

- The study of processes in which energy is transferred as heat and as work.

System

- Object or set of objects we wish to consider
  – everything else in the universe is referred to as the “environment” or “surroundings”

Closed System

- No mass enters or leaves
- But energy may be exchanged with the environment

Open System

- Mass may enter and leave
- Energy may also be exchanged with the environment

Isolated

- A closed system is said to be isolated if no energy in any form passes across its boundaries

First Law of Thermodynamics

- The change in internal energy of a closed system will be equal to the heat added to the system minus the work done by the system

$$\Delta U = \Delta Q - \Delta W$$

internal energy, heat, work

$$\boxed{\Delta Q = \Delta U + \Delta W}$$

- This law is really just a statement of conservation of energy.
- Q and W represent energy transferred into and out of the system.

Notes:

- Work done on the system is negative
- Work done by the system is positive
- Heat added to the system is positive
- Heat lost by the system is negative

Thermodynamic Processes

- Any process that changes the state (pressure, volume, or temperature) of the system is called a thermodynamic process
  - Heating a gas
  - Compressing a gas

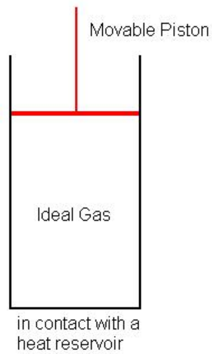
Isothermal Process

- Temperature is constant
- Internal energy does not change

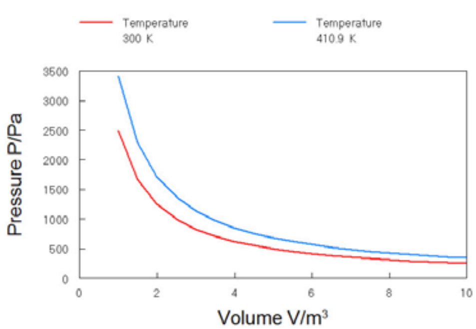
$$Q = \Delta U + W$$

$$\Delta U = 0$$

$$Q = W$$



Isothermal Process



Adiabatic Process

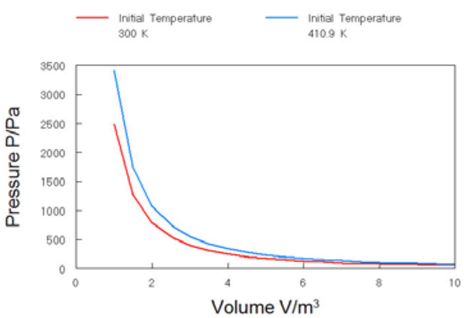
- No heat is transferred
- Well insulated container, quick compression or expansion

$$Q = \Delta U + W$$

$$Q = 0$$

$$\Delta U = -W$$

Adiabatic Process

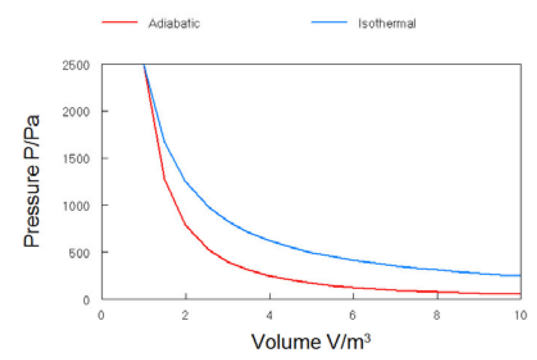


- It can be shown that the relationship between pressure and volume in an adiabatic system is

$$\boxed{pV^{\frac{5}{3}} = \text{constant}}$$

- This means that temperature will also change

$$TV^{\frac{2}{3}} = \text{constant}$$

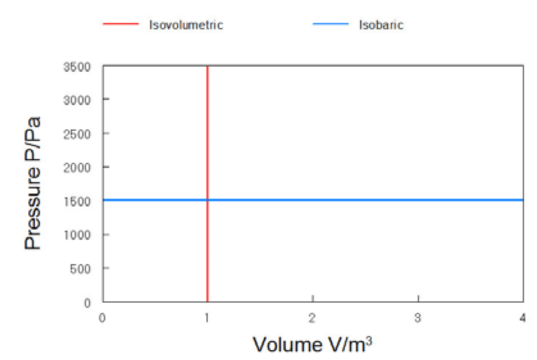


Isobaric

- Pressure is constant

Isovolumetric

- Volume is constant



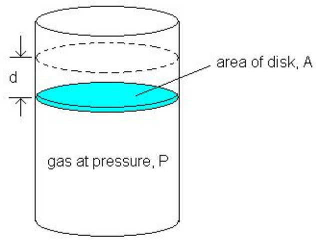
Work Done on a Gas

- Work is done on a piston moving the disk a distance d

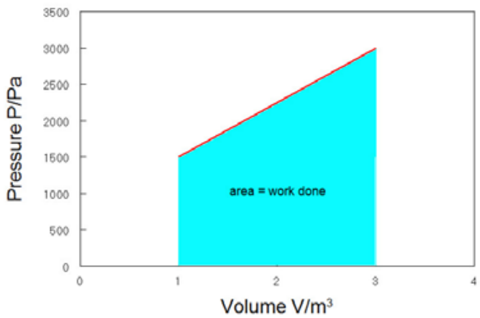
$$W = Fd \quad P = \frac{F}{A}$$

$$W = PAd$$

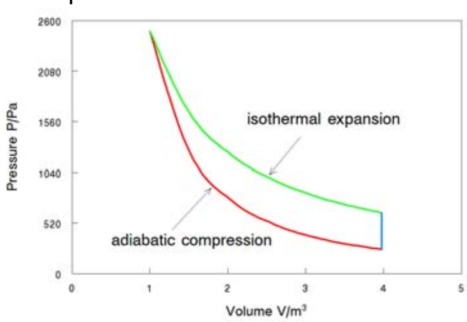
$$\boxed{W = P\Delta V}$$

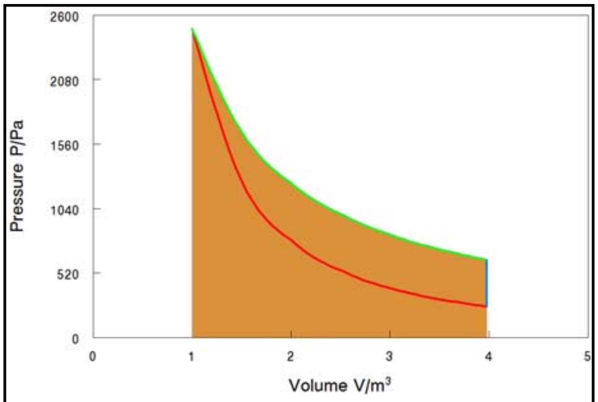


- If the pressure is not constant, then the work is the area under the pV curve

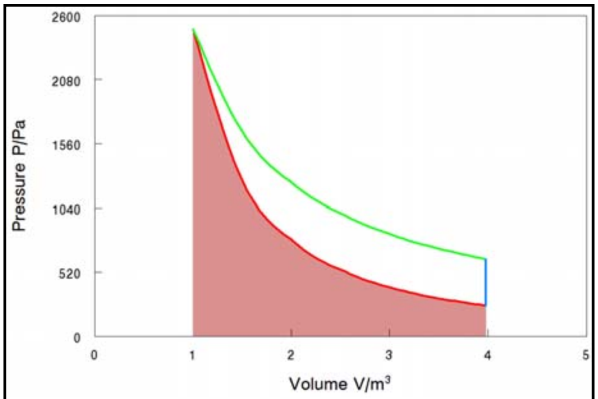


- In a closed loop, the work is the area within the loop

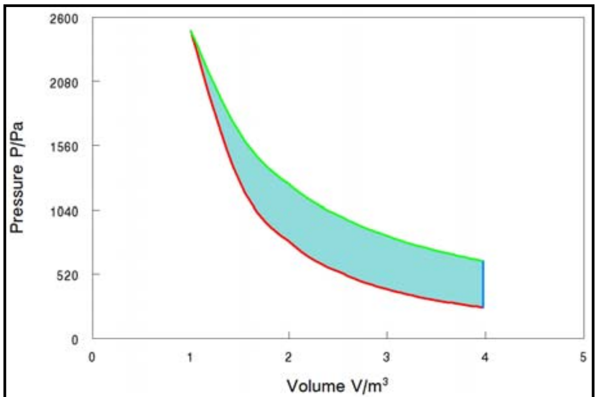




Work done by a gas as it expands



Work done on a gas as it is compressed



Net work done by the gas

Second Law of Thermodynamics

- The first law is a statement of conservation of energy
- However, there are examples of processes that do not violate that law but still do not occur
  - Heat moving from cold to hot
  - Rocks rising up from the ground
  - Broken glass putting itself back together

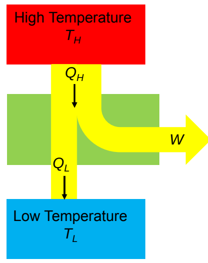
- The second law of thermodynamics is a statement about which processes occur in nature and which do not
- It can be stated in a number of equivalent ways

Second Law (Clausius statement)

- Heat can flow spontaneously from a hot object to a cold object; heat will not spontaneously flow from a cold object to a hot object

Heat Engine

- Mechanical energy can be obtained from thermal energy only when heat is allowed to flow from a high temperature to a low temperature



- For a heat engine to run continuously, it must be run in a cycle
- In each cycle the change in internal energy is zero since the system returns to its starting state

Efficiency

- The efficiency of a heat engine is defined as the ratio of work done to the heat (energy) input

$$\eta = \frac{\text{useful work done}}{\text{energy input}}$$

Example

- A car engine has an efficiency of 20% and produces an average of 23 000 J of mechanical work per second when it is running.
  - How much heat input is required?
  - How much heat is discharged as waste?

- Heat input required

$$\eta = \frac{\text{useful work done}}{\text{energy input}}$$

$$\text{energy input} = \frac{\text{useful work done}}{\eta} = \frac{23000\,\text{J}}{0.20} = 1.15\times10^{5}\,\text{J}$$

Heat input required = 1.15×10^{5} W

- Heat discharged as waste

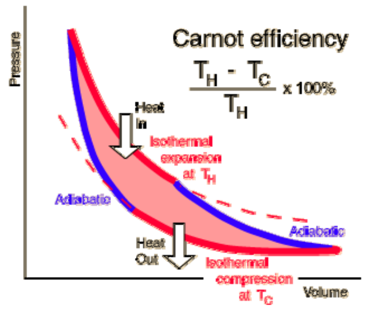
80% of the input

$$0.80(1.15\times10^{5}\,\text{J}) = 9.2\times10^{4}\,\text{J}$$

Waste heat discharged = 9.2×10^{4} W

Carnot Cycle

- Sadi Carnot (French) examined the characteristics of an ideal engine (now called a Carnot engine) to see how to improve efficiency
- This engine consists of four processes in a cycle (thus the name Carnot cycle)
  - Two adiabatic (Q=0)
  - Two isothermal (ΔT=0)



hyperphysics.phy-astr.gsu.edu/hbase/thermo/carnot.html

Carnot (ideal) Efficiency

- The efficiency of a Carnot cycle represents the fundamental upper limit to efficiency

$$\eta_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}}$$

- Real efficiency will always be less because of friction and the like

Example

- An engine manufacturer claims that that the heat input is 9.0 kW at 160°C and the exhaust is 4.0 kW at 20°C. Is this possible?

- Maximum efficiency

$$\eta_{Carnot} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{293\text{ K}}{433\text{ K}} = 0.323 = 32.3\%$$

- Claimed efficiency

$$\eta = \frac{\text{useful work done}}{\text{energy input}} = \frac{9.0\text{ kJ} - 4.0\text{ kJ}}{9.0\text{ kJ}} = 0.556 = 55.6\%$$

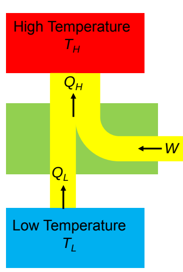
- Conclusion
  - Claim violates the second law of thermodynamics and therefore cannot be true

Second Law (Kelvin-Planck Statement)

- It is impossible, in a cyclic process, to completely convert heat into mechanical work

Refrigerators

- Refrigerators, air conditioners and heat pumps are the reverse of a heat engine
- Each transfers heat out of a cool environment into a warm environment



- The work is usually done by an electric compressor
- It is impossible to have a perfect refrigerator (one that requires no work)

Second Law (Clausius Statement)

- It is impossible for thermal energy to flow from a cold to a hot object without performing work

Entropy and the Second Law of Thermodynamics

- It was not until the latter half of the nineteenth century that the second law of thermodynamics was finally stated in a general way, in terms of entropy, introduced by Clausius in the 1860s

Entropy

- A function of the state of the system
- According to Clausius, the change in entropy S of a system when an amount of heat Q is added to it by a reversible process at constant temperature is given by

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

Example

- An ice cube of mass 56 g is taken from a storage compartment at 0°C and placed in a paper cup. Calculate the change in entropy of the ice when exactly half the ice has melted. ($L_{f\ water}$ = 333 $kJkg^{-1}$)

- Heat required to melt 28g of ice is

$$Q = mL = (0.028\,\text{kg})(333\,\text{kJkg}^{-1}) = 9.3\,\text{kJ}$$

- Temperature remains constant during the process so change in entropy is

$$\Delta S = \frac{Q}{T} = \frac{9.3\,\text{kJ}}{273\,\text{K}} = 34\ \text{JK}^{-1}$$

Second Law (General Statement)

- The total entropy of any system plus that of its environment increases as a result of any natural process

Order to Disorder

- The entropy of a system can be described as the amount of disorder in the system
  - The greater the disorder, the greater the entropy

What is disorder?

- A liquid is more disordered than a solid
  - In a solid the atoms are in a regular pattern whereas in a liquid they move around
- One mole of a gas in a large volume is more disordered than one mole of a gas in a small volume
  - We know less about the position of the molecules in the larger volume

- One mole of a gas in a given volume at high temperature is more disordered than one mole of a gas in the same volume at a low temperature
  - We know less about the position of the gas molecules at higher temperatures because the molecules have a greater velocity

Second Law (General Statement)

- Natural processes tend to move toward a state of greater disorder

Examples

- Mixing two substances together
- Falling rock
- Ripping a piece of paper
- Breaking a window

The Arrow of Time

- The Laws of Mechanics do not require that time move in a particular direction
- However, the Second Law of Thermodynamics requires a specific direction for time
- The most likely direction for any process is the one in which entropy or disorder increases

Heat Death

- In any natural process, some energy becomes unavailable to do work
- In any process, no energy is lost, it just becomes less useful
  - Energy is degraded
- Energy becomes more disordered
  - Mechanical energy transforms to thermal energy

- It is predicted that, as time goes on, the universe will approach a state of maximum disorder
- All heat will have flowed from high-temperature regions to low-temperature regions until the universe is one temperature
- All energy will have degraded to thermal energy
- No more work can be done
- The “heat death” of the universe