Chapter 20

1

Thermodynamics

Thermodynamics

2

Thermodynamics involves situations in which the temperature of a system changes due to energy transfers.

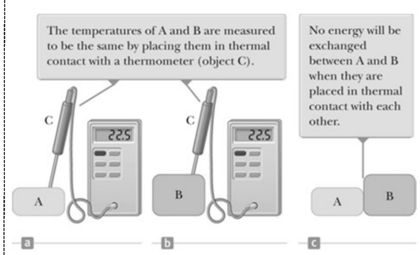
To describe thermal phenomena, careful definitions are needed:

- Temperature
- Heat
- Internal energy

Zeroth Law of Thermodynamics

3

- "If objects **A** and **B** are separately in thermal equilibrium with a third object **C**, then **A** and **B** are in thermal equilibrium with each other."
  - Let object **C** be the thermometer
  - Since they are in thermal equilibrium with each other, there is no energy exchanged among them.



Work in Thermodynamics

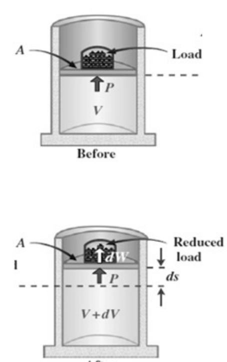
4

A gas confined to a cylinder with a movable frictionless piston of area A.

At equilibrium, the upward force on the piston due to the pressure of the confined gas is equal to the weight of the load on the top of the piston.

Now, assume we reduce the load from the piston in such a way that the piston will move upward through a displacement (Δy) with constant force (f).

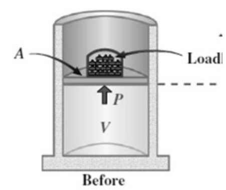
The process slow enough to keep the system in thermal equilibrium.



Work in Thermodynamics

5

- A gas confined to a cylinder with a movable frictionless piston of area A.
- At equilibrium, the upward force on the piston due to the pressure of the confined gas is equal to the weight of the load on the top of the piston.
- Now, assume we reduce the load from the piston in such a way that the piston will move upward through a displacement (Δy) with constant force (F).
- The process slow enough to keep the system in thermal equilibrium.



Work in Thermodynamics

6

- The work done by the gas is:

$$W = F\Delta r cos\theta = PA\Delta y$$

- P: pressure in N/m^2

$$P = \frac{F}{A}$$

- ($A\Delta y$) is the change in volume of the gas, (ΔV).
- Therefore, the work done on the gas is

$$W = P\Delta V = P(V_f - V_i)$$

Work in Thermodynamics

7

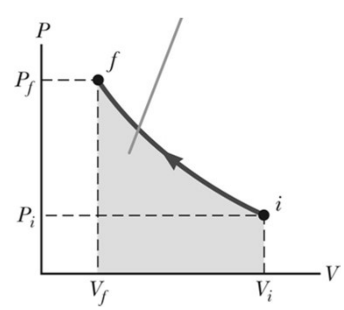
If the gas expands, then ΔV is positive and the work done by the gas is positive,
If the gas is compressed, ΔV is negative, indicating that the work done by the gas is negative (which can be interpreted as work done on the gas).

PV Diagrams

8

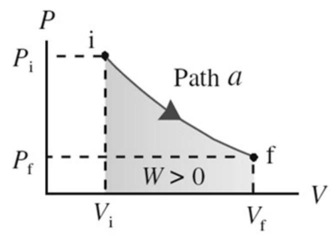
- Used when the pressure and volume are known at each step of the process.
- The work done in a process that takes the gas from an initial state to a final state is the area under the curve on the PV diagram, evaluated between the initial and final states.
  - This is true whether or not the pressure stays constant.
  - The work done does depend on the path taken.

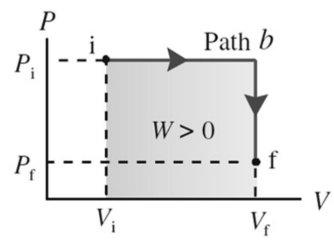
$$W = Area = \int_{V_i}^{V_f} PdV$$



Work Done By Various Paths

9

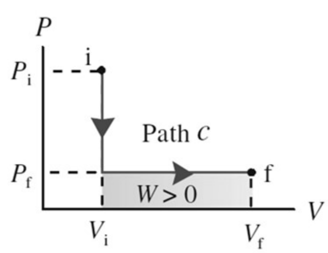


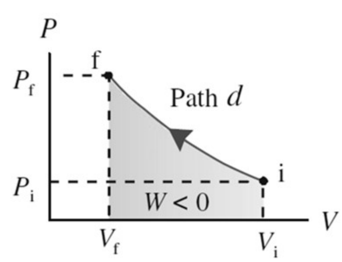


Mustafa Al-Zyout - Philadelphia University 23-Nov-20

Work Done By Various Paths

10

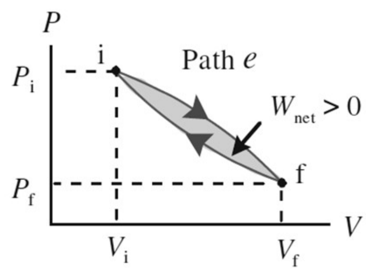




Mustafa Al-Zyout - Philadelphia University 23-Nov-20

Work Done By Various Paths

11



The First Law of Thermodynamics

12

The first law of thermodynamics is a special case of the law of conservation of energy.

The First Law of Thermodynamics

13

- The First Law of Thermodynamics states that:
  - "the change in internal energy of a system will be equal to the energy added to the system by heating minus the work done by the system":

$$\Delta U = Q - W$$

  - All quantities are in (Joule).
- U: is the internal energy for N monoatomic ideal gas molecules, and is directly proportional to the temperature:

$$U = \frac{3}{2} N k_B T$$

The First Law of Thermodynamics

14

- work is positive when it is done by the system and negative when it is done on the system,
- heat is positive when it is added to the system and negative when it is withdrawn from the system.
- Internal energy is positive when temperature is increased and negative when temperature is decreased.

Special Processes, Isolated Systems

15

- An isolated system is one that does not interact with its surroundings.
  - No energy transfer by heat takes place.
  - The work done on the system is zero.

$$Q = W = 0$$

- So, the internal energy of an isolated system remains constant.

$$\Delta U = 0$$

Special Processes, Cyclic Processes

16

- A cyclic process is one that starts and ends in the same state.
  - This process would not be isolated.
  - On a PV diagram, a cyclic process appears as a closed curve.
- The internal energy must be zero since it is a state variable.

$$\Delta U = 0$$

$$Q = W$$

- In a cyclic process, the net work done on the system per cycle equals the area enclosed by the path representing the process on a PV diagram.

Special Processes, Adiabatic Process

17

- An adiabatic process is one during which NO energy enters or leaves the system by heat.

This is achieved by Thermally insulating the walls of the system

$$Q = 0$$

$$\Delta U = -W$$

- If the gas is compressed adiabatically, W is negative so ΔU is positive and the temperature of the gas increases.
- If the gas expands adiabatically, W is positive so ΔU is negative and the temperature of the gas decreases.

Mustafa Al-Zyout - Philadelphia University 23-Nov-20

Special Processes, Isobaric Processes

18

- An isobaric process is one that occurs at a constant pressure.
  - May be accomplished by allowing the piston to move freely so that it is always in equilibrium
  - The values of the heat and the work are generally both nonzero.
- The work done is

$$W = P\left(V_f - V_i\right)$$

- where P is the constant pressure.

Mustafa Al-Zyout - Philadelphia University 23-Nov-20

Special Processes, Isovolumetric Processes (Isochoric Process)

19

- An isovolumetric process is one in which there is NO change in the volume.
  - This may be accomplished by clamping the piston at a fixed position.
- Since the volume does not change:

$$W = 0$$

$$\Delta U = Q$$

- If energy is added by heat to a system kept at constant volume, all of the transferred energy remains in the system as an increase in its internal energy.

Special Processes, Isothermal Process

20

- An isothermal process is one that occurs at a constant temperature.

  This can be accomplished by putting the cylinder in contact with some constant-temperature reservoir.
- Since there is no change in temperature,

$$\Delta U = 0$$

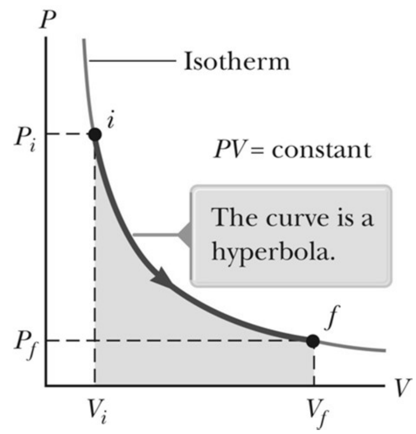
$$Q = W$$

- Any energy that enters the system by heat must leave the system by work.

Special Processes, Isothermal Process, cont

21

•At right is a PV diagram of an isothermal expansion.



The Second Law of Thermodynamics

22

•The macroscopic from of the second law is a statement that a quantity called the **entropy** tends to assume a maximum value. Like the internal energy, **the entropy of a system depends only on its state and not on how that state is achieved**.

- A **reversible process** is one in which the system can be returned to its original state with no net change in either the system or its surroundings. For example, if **no friction**, turbulence, or other dissipative effect is present, the **adiabatic expansion of a gas is reversible**. This is because an adiabatic compression can return the system to its original state. The work done on the gas during the compression is equal to that done by the gas during the expansion; the net work done by the gas and its surroundings is zero.
- **No known natural process is reversible**. When heat is transferred between objects at different temperatures, the heat can be returned to the higher temperature object, but to do so requires that the surroundings do work, as in a refrigerator. Thus the surroundings must be modified to return the system to its original state. Reversible processes, like frictionless systems in mechanics, are an idealization only approximately realized in real systems.

The Second Law of Thermodynamics

23

- We can now define the entropy of a system. **Suppose a small quantity of heat (ΔQ) is added to a system at a Kelvin temperature (T) during a reversible process**. We use (ΔQ) to emphasize the small changes involved. The entropy change of this system is then defined by:

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

If a large quantity of heat is transferred, it can be divided into many small amounts (ΔQ_i) such that the temperature (T_i) is nearly constant during the transfer of (ΔQ_i). Then, in a reversible process, the total change in entropy is found by summing the small entropy changes ($\Delta Q_i/T_i$). Note that when heat leaves a system, (ΔQ) is negative and so is the associated entropy change of the system. For an irreversible process, the entropy change of an isolates system can be evaluated by considering reversible processes that would bring the system to the same final state.

The Second Law of Thermodynamics

24

- We can now give **the macroscopic form of the second law. For any process, the total entropy of a system plus its surroundings may never decrease**:

$$\Delta S_{total} \geq 0$$

$$(\Delta S_{system} + \Delta S_{surrounding}) \geq 0$$

- **The total entropy change is zero for a reversible process and positive for an irreversible process**. This is called the second law of thermodynamics. Microscopically this is equivalent to saying that the molecular disorder of a system and its surroundings remains constant if the process is reversible and increases if it is not.