

BROWNIAN MOTION

The constant erratic movement of tiny particles suspended in a fluid or gas is called Brownian motion. This phenomenon was discovered in 1827 by the British botanist Robert Brown when he observed a grain of pollen suspended in water shows a continuous random motion under a microscope. At first, these motions are considered a form of life but it is soon found that small inorganic particles behave similarly. There was no quantitative explanation of this phenomenon until the development of kinetic theory.

EINSTEIN'S THEORY OF BROWNIAN MOTION

Einstein developed a theory of Brownian motion in 1905. The basic assumption of this theory states that particles suspended in a liquid or a gas share thermal motions of the medium. The average translational kinetic energy of each particle is $\frac{3}{2} kT$ in accordance with principle of equipartition of energy. The Brownian motions result from impacts by molecules of the fluid and the suspended particles acquire the same mean kinetic energy as the molecules of the fluid.

The suspended particles are extremely large as compared to the molecules of the fluid and are continually bombarded on all sides by them. The equal numbers of molecules strike the particles on all sides at each instant if particles are sufficiently large and the number of molecules is sufficiently great.

For smaller particles and fewer molecules, the number of molecules striking various sides of the particle at any instant, being merely a matter of chance and may not be equal(i.e fluctuations occur). Hence, the particle at each instant suffers an unbalanced force causing it to move this way or that way.

Therefore, particles act just like very large molecules in the fluid and their motion should be the same as the motion of the fluid molecules. If Avogadro constant is infinite there would be no statistical imbalance and no Brownian motion. If Avogadro constant is very small, the Brownian motion would be very large. Hence we should be able to deduce the value of the Avogadro constant from observations of the Brownian motion. Deeply ingrained in this picture is the idea of molecular motion and the smallness of molecules. The Brownian motion therefore offers a striking experimental test of kinetic theory hypotheses.

The suspended particles are under the influence of gravity and settle to the bottom of the fluid. Since suspended particles behave like gas molecules, we are not surprised to learn that as for molecules in the atmosphere that density drops off exponentially with respect to height in the fluid. They form a miniature atmosphere.

Jean Perrin confirmed this prediction in 1908 by determining the number of particles of gum resin suspended at different heights in a liquid drop. From his data he deduced the value of the Avogadro constant. Perrin also made measurements of the displacement of Brownian particles during many equal time intervals and found that they have the statistical distribution required by the kinetic theory and the root mean square displacement predicted by Einstein. Perrin was awarded Physics Nobel prize 1926.

FIRST LAW OF THERMODYNAMICS

Statement: In any thermodynamic process, when heat Q is added to a system, this energy appears as an increase in the internal energy ΔU stored in the system plus the work W done by the system on its surroundings.

→ 1st law of thermodynamics is also called the law of conservation of energy.

Mathematically: $Q = \Delta U + W$

Explanation:

Consider some gas in cylinder to which heat Q is supplied. Due to the heat, the internal energy of the system changes from state ' U_1 ' to state ' U_2 ' & the system does some work ' W ' on the surrounding. Thus

$$Q = (U_2 - U_1) + W$$

or $Q = \Delta U + W$

which is the 1st law of thermodynamics

- APPLICATIONS OF 1st LAW OF THERMODYNAMICS

1. Isothermal process:

A process in which, the temperature of the system remains constant is called an isothermal process.

So for isothermal process, Boyle's law can be applied.

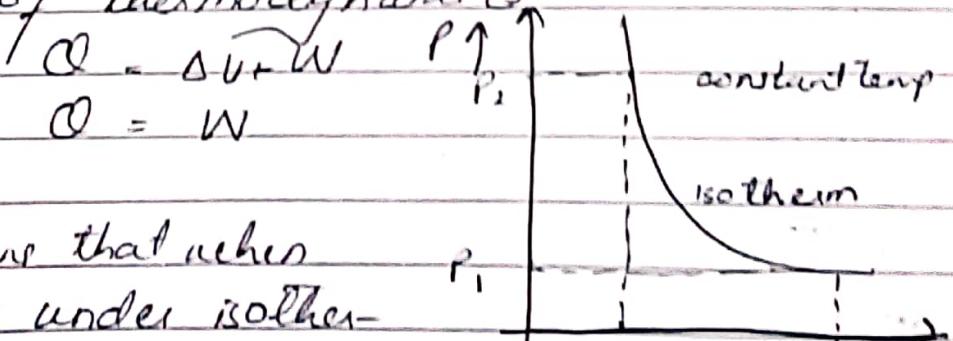
Explanation:-

Suppose during an isothermal change, pressure and volume changes from P_1, V_1 to P_2, V_2 .

Then according to Boyle's law

$$P_1 V_1 = P_2 V_2$$

Since the temperature of system remains constant, so there will be no change in the internal energy i.e. $\Delta U = 0$. Hence from first law of Thermodynamics



So it means that when gas expands under isothermal process, does external work 'W'; an amount of heat 'Q' has to be supplied

→ The graph b/w P & V is called PV diagram

Important: The curve obtained is called isotherm

Note: The transfer of heat from one place to another require time, so to keep temp of gas constant, the expansion or compression must be taken slowly

2. ADIABATIC PROCESS:

The process in which no heat enters or leaves the system is called Adiabatic process

Explanation:

Since no heat enters or leave the system
so $Q = 0$.

from 1st law of thermodynamics

$$Q = \Delta U + W$$

$$\text{so } 0 = \Delta U + W \Rightarrow W = -\Delta U$$

This equation can be expressed in two ways:

$$W = -\Delta U$$

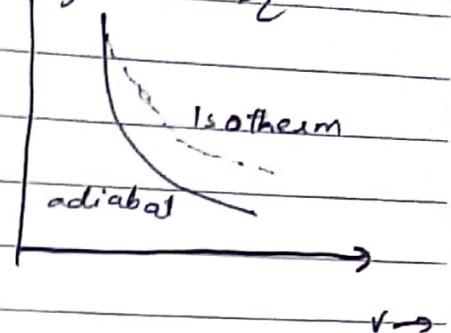
$$\Delta U = -W$$

If work is done by the gas, then it does it at the cost of its own internal energy. As a result the internal energy of the system of the system decreases. It is known as adiabatic expansion.

If work is done on the gas, then temperature of gas increases. As a result the internal energy of the system increases. It is known as adiabatic compression.

The graph b/w P & V is called PV diagram
Important: The curve obtained is called 'Adiabat'

This curve is represented by the eq.
 $PV^r = \text{constant.}$ if
where $r = C_p/C_v$



2ND LAW OF THERMODYNAMICS:

Need for 2nd law:

The 1st law of thermodynamics only tells that heat can be converted into equivalent amount of work but it does not tell the conditions under which heat can be converted into work & also the direction of flow of heat.

Working of a heat engine:

A heat engine absorbs heat Q_1 from the hot reservoir at temperature T_1 . It does work W and expels heat Q_2 to low temperature reservoir at temperature T_2 . As the working substance undergoes a cyclic process, returns to its initial state, the change in internal energy is zero.

Hence from first law of thermodynamics

$$\Delta Q = \Delta U + W$$

$$\Delta Q = W$$

$$W = Q_1 - Q_2$$

Hot reservoir

Q_1

Heat engine

Output work W

Cold reservoir

Important: