**Lecture #2**

# THE FIRST LAW OF THERMODYNAMICS

## Internal Energy

Every system in a definite state has a definite energy. This energy is called "internal energy" and designated by **E**.

- Internal energy arises due to the motions of the atoms or the molecules in the system.
- Internal energy is the accumulated energy in the system.
- Internal energy depends upon the properties of the system. If there is no change in the state of the system, E remains the same. It changes only when the system undergoes a change.
- Change in E is;

  $\Delta E = E_1 - E_2$

  where  $E_1$ and $E_2$ are the initial and final values of E.

## The First Law of Thermodynamics

When a system absorbs heat from the surroundings its internal energy increases. When it produces work in the surroundings internal energy decreases. The change in E may be expressed as;

$\Delta E = Q - W$

This equation is known as the first law of thermodynamics. The law can only calculate the change in E, not E itself.

- If there is no change in E, then $\Delta E = 0$. In this case, either $Q = W$ or there is no heat or work flows.
- If $\Delta E < 0$, the system loses energy, either by producing work in the surroundings or emitting heat to the surroundings.
- If  $\Delta E > 0$, the system gains energy, either by absorbing heat from the surroundings or destroying work in the surroundings.
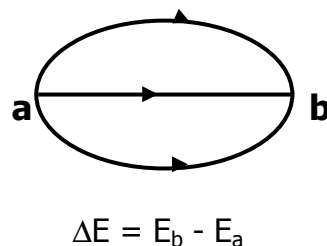
No matter how these transfers occur, the total energy of the universe remains the same.

$E_{universe} = E_{system} + E_{surroundings}$

According to the 1$^{st}$ law;

- Energy may be transformed from one form to the other, however it can never be created nor destroyed.
- The energy of the universe remains constant.
- 1$^{st}$ law is also known as the "Law of Conservation of Energy".

## State and Path Functions



$$\Delta E = E_b - E_a$$

Internal energy is a "**state function**". It depends upon the state of the system. For a specified change in state, the change in energy depends only on the initial and final states of the system, not upon the path connecting those states.

- The differential of a state function is an "**exact differential**".
- The integral of an exact differential is equal to the difference between the initial and final values of the function.

$$\int_{a}^{b} dE = E_a - E_b$$

- The value does not depend upon the path of integration.

Heat Q and work W are not state functions. They depend upon the path from a to b. dQ and dW are "**inexact differentials**". Q and W are "**path functions**".

- The sum of two inexact differentials is an exact differential.

$$dE = dQ \ - \ dW$$

- A "***cyclic process***" is a process that causes a series of changes in the properties of the system, but finally it brings the system to its initial state.

- Since dE is an exact differential, its cyclic integral is zero.

$$\int_{a}^{b} dE = \oint dE = 0$$

- Cyclic integrals of dQ and  dW are not zero.
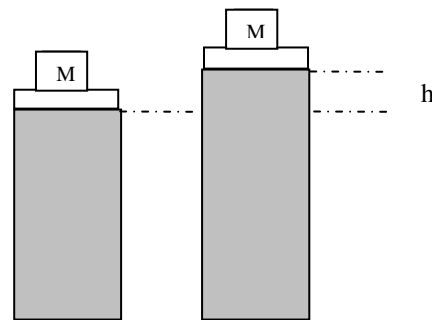
## Reversible Processes

Reversible processes are processes in which the system can be brought back to its initial state by changing an independent variable infinitesimally.

- Reversible processes consist of a sequence of equilibrium states.
- Maximum amount of work can only be obtained in a reversible process.
- In irreversible processes, the equilibrium of the system is completely destroyed. A finite length of time is required to establish a new equilibrium state.
- Reversible processes are not real processes, but ideal ones.
- Real processes are irreversible.

## Reversible Isothermal Expansion of an Ideal Gas

Suppose we have an ideal gas confined in a cylinder having a movable piston. If the external pressure acting on the piston is decreased infinitesimally, the gas expands infinitesimally. Finally, when the gas pressure equals external pressure piston stops.
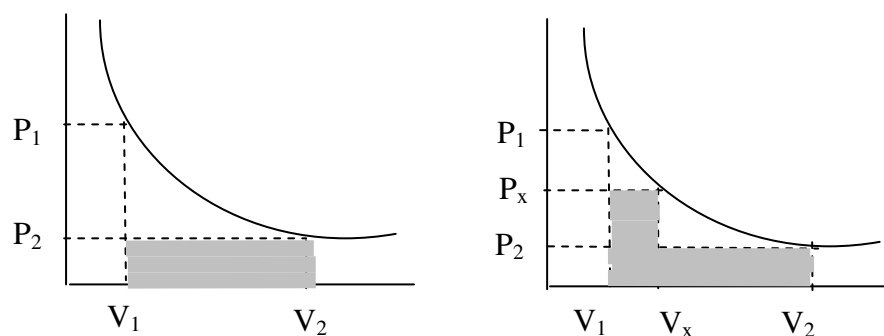
- Equilibrium of the gas is disturbed only infinitesimally.
- At any stage, the system does not depart from equilibrium.

- During expansion, M is raised to a height h.
- Work produced by the gas is W = Mgh
- Force acting on the piston is F = Mg
- Pressure acting on the piston is Mg/A, A is the cross-sectional area of the piston. Mg/A is the external pressure P'.
- Work produced by the gas;

  W = P' A h = P' dV

- Since the process is reversible, since the gas does not depart from equilibrium P' = P
- P can be expressed in terms of volume. P = nRT / V
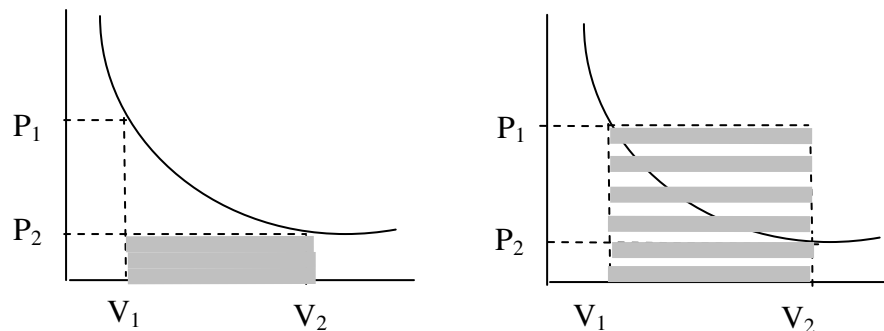- Work produced by the gas may be written as;

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln \frac{V_2}{V_1}$$

## One-stage vs Two-stage Expansion

Work obtained in two-stage expansion is greater than the work obtained in one-stage expansion. If the expansion were done in many stages, even more work should be produced.
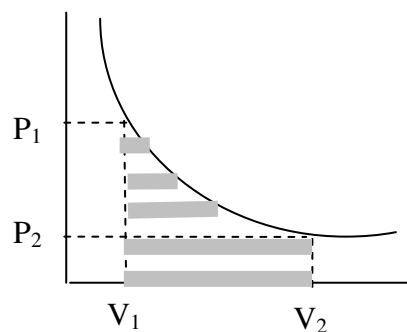
## One-stage Expansion vs One-stage Compression

Work obtained in one-stage expansion: $W = P_2 (V_2 - V_1)$

Work destroyed in one-stage compression: $W = P_1 (V_1 - V_2)$

More work is destroyed in compression than is produced in expansion.

## Maximum and Minimum Work

$$W_{max,min} = \int_{V_1}^{V_2} PdV$$

For the ideal gas, the maximum quantity of work produced in the reversible expansion or the minimum work destroyed in reversible compression is equal to the shaded area under the isotherm.

## Molecular Motions

Each atom in a molecule is described by 3 coordinates. A molecule containing N atoms has 3N independent modes of motion. We call this number "degrees of freedom".

Molecular motions are of three kinds;

- Translational motion
- Rotational motion
- Vibrational motion

### Translational Motion

Translational motion is the motion of the molecule as a whole along the three mutually perpendicular axes passing through its center of mass. Each molecule has 3 translational degrees of freedom. Due to this motion, the molecule gains kinetic energy only. Kinetic energy may be written as a sum of three components;
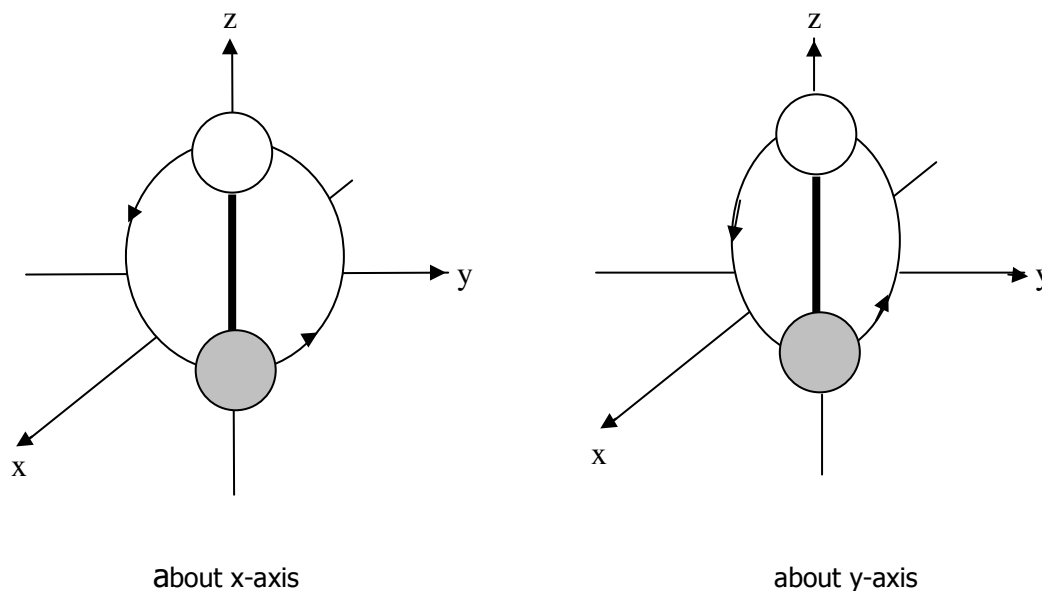
$$E_{trans} = (E_t)_x + (E_t)_y + (E_t)_z$$

$$E_{trans} = \frac{1}{2}mv_x^{\,2} + \frac{1}{2}mv_y^{\,2} + \frac{1}{2}mv_z^{\,2}$$

Each of these terms contains the square of the velocity component. Therefore, each contributes ½ kT to the energy of the molecule. So, it may be concluded that each molecule spends 3 degrees of freedom for translational motion and gains energy equal to 3/2 kT.

### Rotational Motion

Rotational motion is the motion of the molecule as a whole around the three mutually perpendicular axes passing through its center of mass. This motion depends upon the geometry of the molecule. If the molecule is linear, then the molecular axis coincides with one of the main axes, the molecule can rotate about the two remaining axes. Two modes of rotation are possible. Linear molecules have 2

rotational degrees of freedom, but nonlinear molecules can rotate about the three main axes.



about x-axis                                    about y-axis

Molecules gain kinetic energy only due to their rotational motions. For linear molecules the rotational energy has two components, whereas for nonlinear molecules it has three components.

$$E_{rot} = \frac{1}{2}I_x\omega_x^{\,2} + \frac{1}{2}I_y\omega_y^{\,2} \dots\dots\dots\dots\dots\dots\dots\dots \textit{linear molecule}$$

$$E_{rot} = \frac{1}{2}I_x\omega_x^{\,2} + \frac{1}{2}I_y\omega_y^{\,2} + \frac{1}{2}I_z\omega_z^{\,2} \dots\dots\dots\dots\textit{nonlinear molecule}$$

In these equations, $\omega$'s are angular velocities and I s are moments of inertia about the three main axes. Since each term in the energy expression is proportional to the square of a velocity component, each term contributes ½ kT to the energy of the molecule. Thus, linear molecules use their 2 degrees of freedom for the rotational motion and gain a kinetic energy equal to kT. Nonlinear molecules spend their 3 degrees of freedom for the  rotational motion and gain 3/2 kT.


**Vibrational Motion**

        Molecules spend their remaining degrees of freedom for their vibrational motions. Vibrational motions are internal motions. The atoms in the molecule change

their  positions periodically with respect to the others. Vibrational coordinates are bond distances and bond angles. There are two types of vibrational motions;

- **_Stretching Motions:_**  are the vibrations along the bonds. The atoms move along the bonds. The bond stretches and then relaxes.
- **_Bending Vibrations:_** change the magnitude of bond angles. Three atomsa re associated with this motion. The angle widens and it gets narrow.

The energy for each vibrational mode may be written as;

$$E_v = \frac{1}{2}\mu(\frac{dr}{dt})^2 + \frac{1}{2}k(r - r_o)^2$$

In this equation $\mu$ is the reduced mass, k is the force constant, r is the coordinate, ro is the equilibrium value of the coordinate and t is time. So, the molecule gains kinetic and potential energy for each vibrational mode. Since each term in the above expression is proportional to the square of velocity and coordinate, each contributes ½ kT to the energy. Thus, contribution of each vibrational mode is kT. The energy of vibrations is (3N − 5) kT for linear molecules and (3N − 6) kT for nonlinear molecules.

The total energy per molecule is;

$$E = \frac{3}{2}kT + \frac{2}{2}kT + (3N - 5)kT \ ..............................linear\ molecule$$

$$E = \frac{3}{2}kT + \frac{3}{2}kT + (3N - 6)kT \ ...........................nonlinear\ molecule$$

If we multiply these values by the Avagadro number, we obtain molar energies;

$$E = \frac{3}{2}RT + \frac{2}{2}RT + (3N - 5)RT \ ..........................linear\ molecule$$

$$E = \frac{3}{2}RT + \frac{3}{2}RT + (3N-6)RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots nonlinear\ molecule$$

By definition, the constant volume heat capacity is;

$$C_v = (\frac{\partial E}{\partial T})_v$$

By differentiating the molar energies with respect to temperature, we obtain molar heat capacities.

$$\overline{C}_v = \frac{3}{2}R + \frac{2}{2}R + (3N-5)R \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. linear\ molecule$$

$$\overline{C}_v = \frac{3}{2}R + \frac{3}{2}R + (3N-6)R \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots nonlinear\ molecule$$

### Monatomic Molecule

N = 1

$\sum$d.f. = 3

$$E = \frac{3}{2}kT \qquad\qquad \overline{E} = \frac{3}{2}RT \qquad\qquad \overline{C}_v = \frac{3}{2}R$$

### Diatomic Molecule

N = 2

$\sum$d.f. = 3x2 = 6

$$E = \frac{3}{2}kT + \frac{2}{2}kT + kT = \frac{7}{2}kT$$

$$\overline{E} = \frac{3}{2}RT + \frac{2}{2}RT + RT = \frac{7}{2}RT \qquad\qquad \overline{C}_v = \frac{7}{2}R$$