- **Thermodynamics** is the study of the relationship between the energy transformation in the system and other physical quantities such as **temperature**, **pressure** and **volume** (P, V, T).

- **A thermodynamic equation of state** is a mathematical relationship of the thermodynamic or state variables, such as pressure, volume and temperature.

- For an ideal gas, \( pV = Nk_B T \) = nRT is the equation of state.

- P, V, T \( \rightarrow \) state variables.

### 3.1 Heat and Internal Energy

- **Internal energy** is the grand total of all the energy belonging to a system while it is stationary (neither translating nor rotating) including kinetic energy and potential energy.

- **Internal Energy, U** - of the system is the sum of all microscopic kinetic and potential energy of the molecules in the system.

  \[ U = \frac{3}{2} nRT \]

- **Thermal energy** is the portion of internal energy that changes when the temperature of the system changes (refer to KE: the higher the temperature of the gas, the greater the KE of the atoms and the greater the thermal energy of the gas).

- Changes in internal energy are detected when there is change in temperature.
Heat is the portion of internal energy that flows from one body to another body due to temperature difference between them. Once heat has been transferred to an object or substance, it ceases to be heat. It becomes internal energy.

### 3.2 Work and Heat

Consider a gas contained in a cylinder fitted with a movable piston. In equilibrium, the gas occupies a volume $V$ and exerts a uniform pressure on the cylinder walls and the piston. If the piston has a cross-sectional area of $A$, the force exerted by the gas on the piston is $F = PA$.

As the piston pushes up a distance of $\Delta y$, the work done on the piston by the gas is

$$W = F\Delta y = PA\Delta y = -P\Delta V$$

If gas expands, $\Delta V$ is $+ve$ $\rightarrow$ work done on the gas is $-ve$

$\rightarrow$ work done by gas.

If gas compressed, $\Delta V$ is $-ve$ $\rightarrow$ work done by the gas is $+ve$

$\rightarrow$ work done on the gas is positive

The work done on a gas at constant pressure is given by:

$$W = -P\Delta V$$

When volume is constant, work done by (or on) the system $= 0$
Calculation of work done can be obtained from PV diagram, where work done is area under the graph.

\[ W = P_f (V_f - V_i) \]

\[ W = P_i (V_f - V_i) \]

(c) Both P-V change continuously - the work done has some value intermediate between the values obtained in the first two processes.

3.3 The First Law of Thermodynamics - Relates internal energy, heat and work.

Energy can be transferred between a system and its surrounding in two ways:

1. via work done by (or on) the system
2. via heat transfer

Each of these represents a change of energy of the system results in changes: p,V and T of a gas.

If a system undergoes a change from an initial state to a final state, where Q is the energy transferred to the system by the heat and W is the work done on the system, the change in internal energy \( \Delta U \) is given by:

\[ \Delta U = U_f - U_i = Q + W \]

First law of Thermodynamics
\[
\begin{align*}
\Delta Q & \quad (\text{supplied/absorbed}) \\
\quad & - \quad (\text{lost}) \\
\Delta U & \quad (\text{increase}) \\
\quad & - \quad (\text{decrease}) \\
\Delta W & \quad \text{on the system} \\
\quad & - \quad \text{by the system}
\end{align*}
\]

- **First law of Thermodynamics** - describes how work and heat are related to a system's internal energy. (energy conservation in terms of thermodynamics variables).
- It relates the change in internal energy \((\Delta U)\) of a system to the work \((W)\) done by that system and the heat energy transferred \((Q)\) to or from that system.
- When heat (energy) is added, it either increases the internal energy of the system or does work on objects external to the system.
Internal Energy: \( U = \frac{3}{2} nRT \)

\( Cv = \frac{3}{2} R \)

\( \Delta U = nCv\Delta T \)

\( Cv \) = molar specific heat at constant volume

- **Isolated system**: system that does not interact with its surroundings.

  -- No heat transfer takes place → work done is zero → internal energy remains constant.

  \[ Q = W = 0, \Delta U = 0, U_i = U_f \]

  - For isolated systems, \( U \) remains constant.

- **Cyclic Process** – is a process that originates and ends at the same state. Thus, the change in internal energy has to be zero, thus the heat added is equal to the work done. The net work done equals the area enclosed by the path representing the process on a PV diagram.

  \[ \Delta U = 0, Q = -W \]

- If a closed system is supplied with heat (i.e. a can), all the heat will turn into internal energy, causing a rise in temperature.

- If a free moving piston is attached to it, expansion of gas causes piston to move. Work is done by gas to move the piston. The temperature rise in the second can is less than in the closed system. This is due to the heat being converted into internal energy (change in temperature) and work done.
- **Thermodynamic Processes** for an ideal gas can be divided into 4 types:

1. **Isobaric** (constant-pressure process)
2. **Adiabatic** (no heat is transferred into or out of the system)
3. **Isovolumetric/isometric** process (constant-volume process)
4. **Isothermal** Process (constant-temperature process)

In p-V diagram

1. **Isobaric Process** (iso for equal, and bar for pressure)
   - is a process where the pressure is constant. Pressure does not change during a process, while other quantities such as temperature and volume change.
   - the path of isobaric process is along horizontal line called an isobar.
   - \( W_{isobar} = F\Delta x = -p(V_2 - V_1) = -p\Delta V \)
   - From 1st law: \( Q = \Delta U - W = \Delta U + p\Delta V \)

An isobaric process is a **thermodynamic process** in which the pressure stays constant. The term derives from the Greek *isos*, (equal), and *barus*, (heavy). The heat transferred to the system does work but also changes the internal energy of the system:
According to the **first law of thermodynamics**, where $W$ is work done by the system, $U$ is internal energy, and $Q$ is heat. Pressure-volume work by the closed system is defined as:

$$W = \int p \, dV$$

where $\Delta$ means change over the whole process, whereas $d$ denotes a differential. Since pressure is constant, this means that

$$W = p \Delta V.$$

Applying the **ideal gas law**, this becomes

$$W = n \, R \, \Delta T$$

assuming that the quantity of gas stays constant, e.g., there is no phase change during a chemical reaction. According to the **equipartition theorem**, the change in internal energy is related to the temperature of the system by

$$\Delta U = n \, c_V \, \Delta T,$$

where $c_V$ is specific heat at a constant volume.

Substituting the last two equations into the first equation produces:

$$Q = n \, c_V \, \Delta T + n \, R \, \Delta T$$
$$= n \left( c_V + R \right) \Delta T$$
$$= n \, c_p \, \Delta T,$$
where \( c_P \) is specific heat at a constant pressure. (Cp=Cv+R)

Monatomic:

\[
c_V = \frac{3R}{2} \quad \text{and} \quad c_P = \frac{5R}{2}
\]

Diatomic:

\[
c_V = \frac{5R}{2} \quad \text{and} \quad c_P = \frac{7R}{2}
\]

2. **Adiabatic Process** - no heat is allowed to go in or out of system, \( Q=0 \).
- When the membrane is broken, the gas expands very rapidly into the vacuum until it occupies a volume \( V_f \) and is at a pressure of \( P_f \). The process has to occur very rapidly to avoid heat from entering or leaving the system. [heat flows very slowly].
- A curve called an adiabat, all three thermodynamics coordinates change (that is \( p, V \) and \( T \) would change)
- \( \Delta Q=0 \) is satisfied for a thermally isolated system

- In terms of 1st law of thermodynamics:

\[
Q = 0 = \Delta U - W
\]

\[
\Delta U = W
\]

The mathematical equation for an ideal fluid undergoing a reversible (i.e., no entropy generation) adiabatic process is

\[
P V^\gamma = \text{constant}
\]

where \( P \) is pressure, \( V \) is specific or molar volume, and
\[ \gamma = \frac{C_P}{C_V} : \]

\( C_P \) being the specific heat for constant pressure, \( C_V \) being the specific heat for constant volume, \( \gamma \) is the adiabatic index.

For a monatomic ideal gas, \( \gamma = \frac{5}{3} \), and for a diatomic gas (such as nitrogen and oxygen, the main components of air) \( \gamma = \frac{7}{5} \). Note that the above formula is only applicable to classical ideal gases and not Bose-Einstein or Fermi gases.

3. **Isovolumetric (Isochoric) Process**
   - is a process where the volume is kept constant while other quantities change.
   - the process is along the vertical line.\( (V_1=V_2) \)
   - No work done \( (W=p\Delta V=0, \text{ since } \Delta V=0) \)
   - In terms of 1st law of thermodynamics:
     \[ Q = \Delta U - W = \Delta U + 0 = \Delta U \]

An isochoric thermodynamic process is characterized by constant volume, i.e. \( \Delta V = 0 \). The process does no pressure-volume work, since such work is defined by

\[ \Delta W = -P\Delta V, \]

where \( P \) is pressure.

\[ Q = nC_v\Delta T \]

Isochoric Process in the [Pressure volume diagram](#). In this diagram, pressure increases, but volume remains constant.
4. **Isothermal Process** – is a process where the pressure and volume changes while the temperature remains constant, \( \Delta T = 0 \).

- Consider the gas enclosed in a container fitted with a movable piston and in contact with a heat reservoir. The process of compression or expansion is done very SLOWLY to ensure that gas stays in equilibrium with constant temperature.
- The ideal gas law may be written as

  \[
  P = \frac{nRT}{V} \quad \text{p constant} \rightarrow nRT \text{ constant} \rightarrow p \text{ inversely proportional to } V.
  \]

- The process path is along isotherm or line of constant temperature (hyperbola on p-V diagram).

  \[
  U \propto T
  \]

  Thus \( T_{\text{constant}} \rightarrow \Delta U = 0 \)

  From 1\textsuperscript{st} Law: \( \Delta Q = \Delta U - W = 0 - W = -W \)

  (no temperature change, no internal energy change)

**Details for an ideal gas**

![Diagram showing several isotherms on a p-V diagram](image-url)
For the special case of a gas to which Boyle's law applies, the product $pV$ is a constant if the gas is kept at isothermal conditions. The value of the constant is $nRT$, where $n$ is the number of moles of gas present and $R$ is the ideal gas constant. In other words, the ideal gas law $pV = nRT$ applies. This means that

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

holds. The family of curves generated by this equation is shown in the graph presented here. Each curve is called an isotherm. Such graphs are termed indicator diagrams and were first used by James Watt and others to monitor the efficiency of engines. The temperature corresponding to each curve in the figure increases from the lower left to the upper right.

**[edit] Calculation of work**

![Diagram](image)

The yellow area represents "work" for this isothermal change.

In thermodynamics, the work involved when a gas changes from state A to state B is simply

$$W_{A\rightarrow B} = \int_{V_A}^{V_B} p \, dV$$

For an isothermal, reversible process, this integral equals the area under the relevant pressure-volume isotherm, and is indicated in yellow in the figure at right for an ideal gas. Again $p = \frac{nRT}{V}$ applies and with $T$ being a constant (as this is an isothermal process), we have:

$$W_{A\rightarrow B} = \int_{V_A}^{V_B} p \, dV = \int_{V_A}^{V_B} \frac{nRT}{V} \, dV = nRT \int_{V_A}^{V_B} \frac{1}{V} \, dV = nRT \ln \frac{V_B}{V_A} = nRT \ln \frac{P_A}{P_B}$$