

Thermodynamics

Part-1

NCERT short Notes-PHYSICS

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INTRODUCTION

- Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy.
- Thermodynamics is a macroscopic science. It deals with bulk systems and does not go into the molecular constitution of matter.

THERMAL EQUILIBRIUM

A **thermo dynamical system** is said to be in equilibrium state if the macroscopic variables that characterize the system do not change in time.

- When two bodies are placed in thermal contact. Heat flows from the body at a higher temperature to the one at lower temperature. The flow stops when the temperatures equalise; the two bodies are then in thermal equilibrium.
- **For example**, a gas inside a closed rigid container completely insulated from its surroundings, with fixed values of pressure, volume, temperature, mass and composition that do not change with time, is in a state of thermodynamic equilibrium.

ZEROth LAW OF THERMODYNAMICS

‘Two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other’

- The physical quantity that determines whether or not given system A is in thermal equilibrium with another system B is called **Temperature**.

HEAT, INTERNAL ENERGY AND WORK

- **Internal energy** is the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest.
- Internal energy U of a system is an example of a thermodynamic **‘state variable’** – its value depends only on the given state of the system, not on history i.e. not on the ‘path’ taken to arrive at that state.
- Thus, the internal energy of a given mass of gas depends on its state

described by specific values of pressure, volume and temperature.

- Pressure, volume, temperature, and internal energy are thermodynamic state variables of the system (gas). If we neglect the small intermolecular forces in a gas, the internal energy of a gas is just the sum of kinetic energies associated with various random motions of its molecules.
- **Heat** is defined as the transfer of energy across the boundary of a system due to a temperature difference between the system and its surroundings.
- **Heat and work in thermodynamics are not state variables.** They are modes of energy transfer to a system resulting in change in its internal energy, which, as already mentioned, is a state variable.

Units of Heat

- **One calorie** is the amount of heat required to raise the temperature of 1g of water by 1°C.

Or

- **One calorie** is defined to be the amount of heat required to raise the temperature of 1g of water from 14.5 °C to 15.5 °C.

Since heat is just a form of energy, it is preferable to use the unit joule, J.

The Mechanical Equivalent of Heat

- In SI units, the specific heat capacity of water is 4186 J kg⁻¹ K⁻¹ i.e. 4.186 J g⁻¹ K⁻¹.
- The mechanical equivalent of heat is defined as the amount of work needed to produce 1 cal of heat; i.e. 1 cal = 4.186 J.

FIRST LAW OF THERMODYNAMICS

The energy (ΔQ) supplied to the system goes in partly to increase the internal energy of the system (ΔU) and the rest in work on the environment (ΔW).

Let

- ΔQ = Heat supplied to the system by the surroundings
- ΔW = Work done by the system on the surroundings

- ΔU = Change in internal energy of the system

The general principle of conservation of energy then implies that

$$\Delta Q = \Delta U + \Delta W \dots \dots \dots (1)$$

Equation (1) is known as the **First Law of Thermodynamics**.

- **Isolated system**— A system that does not interact with its surroundings. In this case, no energy transfer by heat takes place and the value of the work done by the system is zero; hence, the internal energy remains constant.

For **isothermal expansion** of an ideal gas

- Heat supplied to the system is used up entirely by the system in doing work on the environment. (as $\Delta U = 0$)

i.e.
$$\Delta Q = \Delta W$$

- If the system is a gas in a cylinder with a movable piston, the gas in moving the piston does work. Since force = pressure x area, and area x displacement = volume, work done by the system against a constant pressure P is

$$\Delta W = P \Delta V$$

Where ΔV is the change in volume of the gas.

Thus, for this case, Eq. (1) gives

$$\Delta Q = \Delta U + P \Delta V \dots \dots \dots (2)$$

For gases, for example, we can define two specific heats: **specific heat capacity at constant volume and specific heat capacity at constant pressure**.

Relation between C_p and C_v (Mayer's Formula)

For Ideal gas,

$$C_p - C_v = R$$

Where C_p and C_v are molar specific heat capacities of an ideal gas at constant pressure and volume respectively and R is the universal gas constant.

Proof: we begin with Eq. (2) for 1 mole of the gas :

$$\Delta Q = \Delta U + P \Delta V$$

If ΔQ is absorbed at constant volume, $\Delta V = 0$

$$C_v = \left(\frac{\Delta Q}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right)_v = \left(\frac{\Delta U}{\Delta T}\right) \dots \dots \dots (3)$$

Since U of an ideal gas depends only on temperature.

If, on the other hand, ΔQ is absorbed at constant pressure,

$$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_p = \left(\frac{\Delta U}{\Delta T}\right) + P \left(\frac{\Delta V}{\Delta T}\right)_p \dots\dots\dots(4)$$

Now, for a mole of an ideal gas

$$PV = RT$$

Which gives

$$P \left(\frac{\Delta V}{\Delta T}\right)_p = R \dots\dots\dots(5)$$

Put Eqn (3) & (5) in (4)

We get

$$C_p - C_v = R$$

EQUATION OF STATE

- Thermodynamic state variables describe equilibrium states of systems.
- The connection between the state variables is called the **equation of state**.
- For example, for an ideal gas, the equation of state is the ideal gas relation

$$P V = \mu R T$$

- For a fixed amount of the gas i.e. given μ , there are thus, only two independent variables, say P and V or T and V .
- The pressure-volume curve for a fixed temperature is called an **isotherm**.

THERMODYNAMIC STATE VARIABLES

The thermodynamic state variables are of two kinds: **extensive** and **intensive**.

- **Extensive variables** indicate the 'size' of the system. Internal energy U , volume V , total mass M is extensive variables.
- **Intensive variables** such as pressure and temperature do not indicate size. Pressure P , temperature T , and density ρ are intensive variables.

For example, in the equation

$$\Delta Q = \Delta U + P \Delta V$$

Quantities on both sides are extensive. (The product of an intensive variable like P and an extensive quantity ΔV is extensive.)

THERMODYNAMIC PROCESSES

Quasi-static process

For a process to be **Quasi-static** the pressure and temperature of the system must differ

from those of its surroundings by only an infinitesimal amount at all times during the process; the process must take place slowly, so that the system passes through an infinite succession of quasi-equilibrium states. The prefix "quasi" is often translated as "almost".

Isothermal process

A process in which the temperature of the system is kept fixed throughout is called an **isothermal process**.

- For example, the expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature. of an isothermal process.

Adiabatic process

If the system is insulated from the surroundings and no heat flows between the system and the surroundings, the process is **adiabatic**

Isochoric process

- In an isochoric process, V is constant. No work is done on or by the gas.
- From Eq. (1), the heat absorbed by the gas goes entirely to change its internal energy and its temperature.
- The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant volume.

Isobaric process

- In an isobaric process, P is fixed. Work done by the gas is
- $$W = P (V_2 - V_1) = \mu R (T_2 - T_1)$$
- With temperature change internal energy also changes.
 - The heat absorbed goes partly to increase internal energy and partly to do work.
 - The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant pressure.

Cyclic process

- In a cyclic process, the system returns to its initial state. Since internal energy is a state variable, $\Delta U = 0$ for a cyclic process. The total heat absorbed equals the work done by the system.

Second Law of Thermodynamics

Kelvin-Planck statement

No process is possible whose sole result is the absorption of heat from a reservoir and the complete conversion of the heat into work.

Clausius statement

No process is possible whose sole result is the transfer of heat from a colder object to a hotter object.

NOTE:-

It can be proved that the two statements above are completely equivalent.

REVERSIBLE PROCESSES

A process is reversible if it can be reversed such that both the system and the surroundings return to their original states, with no other change anywhere else in the universe.

or

A process is reversible only if it is quasi-static (system in equilibrium with the surroundings at every stage) and there are no dissipative effects. For example, a quasi-static isothermal expansion of an ideal gas in a cylinder fitted with a frictionless movable piston is a reversible process.

IRREVERSIBLE PROCESSES

Irreversibility arises mainly from two causes:

1. Many processes (like a free expansion, or an explosive chemical reaction) take the system to non-equilibrium states;
2. Most processes involve friction, viscosity and other dissipative effects. Since dissipative effects are present everywhere and can be minimized but not fully eliminated, most processes that we deal with are irreversible.

PUZZLER

Biting into a hot piece of pizza can be either a pleasant experience or a painful one, depending on how it is done. Eating the crust doesn't usually cause a problem, but if you get a mouthful of hot cheese, you can be left with a burned palate. Why does it make so much difference whether your mouth touches the crust or the cheese when both are at the same temperature? (Charles D. Winters)



Taken from ***Fundamentals of Physics, by Resnik & Halliday***