System, Surroundings, Types of Systems, Intensive and Extensive Properties

System

A thermodynamic system is defined as a definite quantity of matter or a region in space upon which attention is focussed in the analysis of a problem. We may want to study a quantity of matter contained with in a closed rigid walled chambers, or we may want to consider something such as gas pipeline through which the matter flows. The composition of the matter inside the system may be fixed or may change through chemical and nuclear reactions. A system may be arbitrarily defined. It becomes important when exchange of energy between the system and the everything else outside the system is considered. The judgement on the energetics of this exchange is very important.

Surroundings

Everything external to the system is surroundings. The system is distinguished from its surroundings by a specified boundary which may be at rest or in motion. The interactions between a system and its surroundings, which take place across the boundary, play an important role in thermodynamics. A system and its surroundings together comprise a universe.

Types of systems

Two types of systems can be distinguished. These are referred to, respectively, as closed systems and open systems or control volumes. A closed system or a control mass refers to a fixed quantity of matter, whereas a control volume is a region in space through which mass may flow. A special type of closed system that does not interact with its surroundings is called an **Isolated system** .

Two types of exchange can occur between the system and its surroundings:

1. energy exchange (heat or work) and
2. exchange of matter (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange, one can define

- **isolated systems:** no exchange of matter and energy
- **closed systems:** no exchange of matter but some exchange of energy
- **open systems:** exchange of both matter and energy

If the boundary does not allow heat (energy) exchange to take place it is called adiabatic boundary otherwise it is diathermal boundary.

Property

To describe a system and predict its behaviour requires a knowledge of its properties and how those properties are related. Properties are macroscopic characteristics of a system such as mass, volume, energy, pressure and temperature to which numerical values can be assigned at a given time without knowledge of the past history of the system. Many other properties are considered during the course of our study.

- The value of a property of a system is independent of the process or the path followed by the system in reaching a particular state.
- The change in the value of the property depends only on the initial and the final states.

The word state refers to the condition of a system as described by its properties.

Mathematically, if *P* is a property of the system, then the change in the property in going from the initial state 1 to the final state 2 is given by

$$\int_1^2 dP = P_2 - P_1$$

If *P = P (x, y)* then,

$$dP = \left(\frac{\partial P}{\partial x}\right)_y dx + \left(\frac{\partial P}{\partial y}\right)_x dy = a dx + b dy$$

where,

$$a = \left(\frac{\partial P}{\partial x}\right)_y \text{ and } b = \left(\frac{\partial P}{\partial y}\right)_x$$

If $\left(\frac{\partial a}{\partial y}\right)_x = \left(\frac{\partial b}{\partial x}\right)_y$, then *dP* is said to be an exact differential, and *P* is a point function. A thermodynamic property is a point function and not a path function. Pressure, temperature, volume or molar volume are some of the quantities which satisfy these requirements.

Intensive and Extensive Properties

There are certain properties which depend on the size or extent of the system, and there are certain properties which are independent of the size or extent of the system. The properties like volume, which depend on the size of the system are called extensive properties. The properties, like temperature and pressure which are independent of the mass of the system are called **intensive properties**. The test for an intensive property is to observe how it is affected when a given system is combined with some fraction of exact replica of itself to create a new system differing only by size. Intensive properties are those which are unchanged by this process, whereas those properties whose values are increased or decreased in proportion to the enlargement or reduction of the system are called extensive properties.

Assume two identical systems S_1 and S_2 as shown in Figure 1.1 . Both the systems are in identical states.
Let S_3 be the combined system. Is the value of property for S_3 same as that for S_1 (and S_2)?

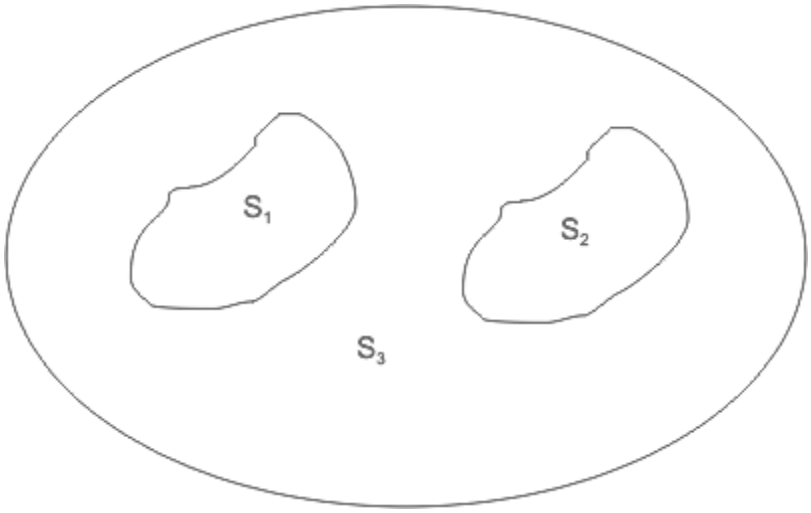

Figure 1.1

- If the answer is yes, then the property is intensive
- If the answer is no, then the property is extensive

The ratio of the extensive property to the mass is called the specific value of that property

specific volume, $v = V/m = 1/\rho$ (ρ is the density)

specific internal energy, $u = U/m$

Similarly, the molar properties are defined as the ratios of the properties to the mole number (N) of the substance

Molar volume = $\hat{v} = V/N$

Molar internal energy = $\hat{u} = U/N$

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