# UNIT 1 FUNDAMENTAL CONCEPTS AND DEFINITIONS

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# **1.1 INTRODUCTION**

Thermodynamics is, by and large, the study of Energy : its different forms and characteristics, the laws governing different energy transformations, the limitations imposed by nature on some types of transformations, and the methodologies for analyzing the different energy conversion phenomena. Like any other branch of science and technology, Thermodynamics has evolved its own grammar and rules ; unless you master them, you can not hope to apply Thermodynamic principles to solve engineering problems. In this Unit, you will learn about the nature and scope of Thermodynamics. You will also be introduced to the fundamental concepts and definitions employed in Thermodynamics.

# **Objectives**

After a study of this Unit, you should be able to

- define the nature and scope of Thermodynamics,
- understand how Thermodynamics is useful in different disciplines of Engineering,
- define and understand Energy from a thermodynamic viewpoint,

- distinguish between the macroscopic and microscopic approaches to the study of Thermodynamics,
- explain the nature and scope of physical laws and theories, as a prelude to the study of the Laws of Thermodynamics,
- understand the principal details of the SI system of units,
- define and distinguish between a system and a control volume,
- define and classify thermodynamic properties which are most commonly encountered,
- distinguish between different types of boundary or wall, and
- understand the concept of relaxation time and the application of thermodynamics to describe processes.

# **1.2 THE NATURE AND SCOPE OF THERMODYNAMICS**

#### **1.2.1 What is Thermodynamics?**

Thermodynamics may be concisely defined as the science of the relationships between heat, work and the properties of substances. Since heat and work are intimately connected through energy, thermodynamics involves the study of energy. It deals with :

- stored energy (chemical, potential, nuclear, etc.)
- energy fluxes (solar, wind, hydro, etc.)
- energy exchanges (heat and work); and
- the associated changes in properties (such as pressure, temperature etc.)

Thermodynamics literally means "heat-force-action". In so far as the I and II laws constitute the major content of thermodynamics, it is considered to deal with energy and entropy, the two properties unearthed by the two laws. Again, taking note of the essence of the two laws, thermodynamics is said to deal with the conservation and degradation of energy.

Dixon philosophizes about Thermodynamics thus: "The first law gave us a new property, energy, which is neither good nor bad but is there to be used or enjoyed - a little like life. The second law also has given us a new property, entropy, which limits our use of energy and is both bad and inevitable - a little like death. Energy and entropy - life and death. Everyday we use energy and we live a little. At the same time, we generate some entropy and die a little - not just we but our environment too".

#### **1.2.2 Why Should We Study Thermodynamics?**

Because man needs energy like he needs nothing else. Man's dependence on energy for the continued survival of the present civilization stems from his need to produce materials for his use which are not found in nature (through manufacturing processes), and to employ energy forms occurring in nature to do useful work for him (through energy conversion processes).

Man's use of energy has been increasing steadily and rapidly since the time of the industrial revolution, and currently it has assumed exponential rates of growth. This is due not only because of increasing per capita use but also because of population growth. One interesting feature of energy usage is its almost direct correlation with the degree of industrialization, gross national product and "standard of living".

A story told about Arnold Sommerfeld, a great physicist noted for his clarity of exposition, throws some light on the nature of the study of thermodynamics. During the course of his lifetime, Sommerfeld wrote a series of books, each book covering a particular area: mechanics, optics, electrodynamics, etc. When asked why he had never written a book on thermodynamics, he is reported to have answered in the following way: "Thermodynamics is a funny subject. The first time you go through the subject, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject it doesn't bother you any more". When Sommerfeld was killed in an accident, he was in the midst of writting a book on thermodynamics.

# 1.2.3 Utility of Thermodynamics in Different Disciplines of Engineering

In so far as energy is of vital concern to all of us, basic knowledge of energy should form part of literacy, at least science-literacy. As far as the different engineering disciplines are concerned, some typical applications of thermodynamics in each discipline are listed below:

aerospace engg.	:	propulsion systems for airplanes, rockets.	
chemical engg.	:	energetics of chemical reactions, petroleum refining, production of petrochemicals, air pollution abatement.	
civil engg.	:	hydro-electric power generation, power required for water pumping, energetics of water pollution abatement measures.	
electrical engg.	:	electric generators and motors, direct energy conversion.	
electronics and communication engg.	:	heat dissipation in electronic devices, information theory.	
mechanical engg.	:	thermal power generation, refrigerators and heat pumps, energy conservation, waste heat recovery.	
metallurgical engg.	:	steel making, phase transformations, alloying.	
naval architecture	:	ship propulsion.	
ocean engg.	:	wave energy, tidal energy, ocean thermal energy conversion (OTEC)	

It may be seen that thermodynamics is indispensable for chemical, mechanical and metallurgical engineering, and, in fact, these disciplines have their own specializations in thermodynamics, named chemical, mechanical and metallurgical engineering thermodynamics, respectively.

# **1.2.4 What is Energy?**

Most elementary texts on energy define it as "the capacity for performing work". This is not strictly correct. It will be obvious from considerations of energy "quality" through the Second Law of Thermodynamics (to be discussed later), that while high-quality energy is capable of complete (in the case of electrical energy) or partial (in the case of thermal energy) conversion into work, the same quantity of energy after "degradation" has less capacity for work. Equal amounts of energy do not possess the same "capacity for performing work". For example, one kJ of electrical energy possesses more capacity for doing work than one kJ of enthalpy of superheated system at high pressure, which, in turn, has more capacity for doing work than one kJ of internal energy of sea water. In fact, it is the ability of energy to do work which establishes its quality.

Energy can be fashioned into most of the other requirements of life. Technology today has advanced so far that there is almost no resource that can not be won, recycled or suitably substituted for, given sufficient energy and the means of safely dissipating the resultant thermal and other forms of pollution.

It is only in the past 20 years or so that the severely finite nature of the ("capital-type") energy resources, and the inevitable pollution resulting from energy utilization have begun to attract serious consideration by government, industry and the public.

# 1.2.5 Two Approaches to the Study of Thermodynamics

The macroscopic approach is empirical (i.e. based on experiment) and employs the continuum model for matter. It deals with observable properties, and either generalizes the "laws" from experiments or states them as axioms. The former approach is described as "inductive" or " operational-inductive", and employs the concept of "operational" definitions. This approach develops the laws as inductive inferences or generalizations from observation and experiments. It begins by defining basic quantities in terms of how they are measured. The operational definition eliminates the circularities that accompany other types of definitions, and was first introduced by P.W. Bridgeman. It then assesses the results of experience and conducts experiments among these quantities and generalizes the laws from the results. The laws are then used deductively to arrive at new conclusions.

In the axiomatic or "axiomatic-deductive" approach, some needed terms are defined, and the several laws are stated as axioms or first principles. The axioms are justified by the inability of anyone to disprove them, and the remaining content of the subject is deduced from the axioms. Fundamental Concepts and Definitions

Thus, the two macroscopic approaches are distinguished by :

- whether the laws are stated at the outset as axioms or whether the laws are arrived at inductively as generalizations from observations; and by
- the kind of definitions used for terms.

The microscopic approach is theoretical and employs the molecular model for matter. It applies statistical analyses to the assumed molecular model, and computes results which are then interpreted in terms of the macroscopic properties and laws. There are three principal microscopic approaches :

- kinetic theory and statistical mechanics
- quantum mechanics
- information theory

All of them assume that matter is made up of discrete particles. Kinetic theory is the oldest microscopic approach; it does not take into account the quantized nature of position and energy of particles, and hence has limited usefulness. Quantum mechanics utilizes the findings of quantum theory and probability theory to identify the most probable state as the macroscopically observed one. Information theory essentially does the same thing but postulates that the observed macroscopic state of a system corresponds to the one that yields the least information to an observer about the microscopic state of the system.

#### **1.2.6** Statistical Thermodynamics

The microscopic approach which combines kinetic theory and quantum mechanics is termed statistical thermodynamics. Its place and role within the framework of physical sciences may be described through a classification based on

- the number of particles involved,
- the particle size, and
- the particle velocity.

Newtonian mechanics is the study of a small number of particles of moderate size moving with moderate velocities. Quantum mechanics is the study of very small particles. Statistical mechanics is the study of very many particles. Astronomy is the study of very large particles. Relativity is the study of very rapidly moving particles.

Thus statistical thermodynamics, which is the study of very many very small particles, is a combination of statistical mechanics and quantum mechanics. Statistical mechanics asks, how are the particles distributed among a system's allowed energy levels? Quantum mechanics asks, what are these allowed energy levels?

#### **1.2.7** Physical Laws and Theories

There is a multitude of physical laws of varying degrees of complexity and detail, e.g. laws of motion, of electromagnetism, of nuclear interactions etc., but cutting across these laws there exist fundamental general principles which all the laws seem to follow. Examples are the principles of conservation, certain qualities of symmetry, the general form of quantum-mechanical principles, etc. Physical laws and theories are essentially strategies for systematizing facts of experience and observation to enable predictions about the future, and design of devices to bring about the effects one wants. Some physical theories even have the capacity and power to suggest new discoveries.

"Conservation" laws occupy a central place in many areas of physics; they imply the existence of a property or quantity which remains unchanged in time even as the system undergoes a multitude of changes in its state. Examples of such conserved properties are mass, momentum, angular momentum, energy, charge, etc.

There is a hierarchy of laws! For example, Newton's "laws" of motion and the "laws" of thermodynamics occupy a higher level, in terms of universality and comprehensiveness; there are other principles, loosely called "laws", which are of restricted applicability. These include:

- \* constitutive relations in continuum mechanics.
- flux-gradient relations of transport phenomena: Fick's law, Newton's law and Fourier's law.
- empirical gas laws, such as Boyle's law, Joule's law, Joule- Thomson law, Charles law etc., which are all consequences of the ideal gas law.

It will be noticed that almost all these statements are related to properties of matter.

Roger Penrose has formulated an arbitrary classification of three broad categories of basic physical theory : superb, useful and tentative. To qualify as "superb", he deems it necessary that the theory should apply without refutation to the phenomena of the world, but also requires that the range and accuracy with which it applies should, in some appropriate sense, be "phenomenal". Under this category, he lists Euclidean geometry, Newtonian mechanics, Maxwell's electromagnetic theory, Einstein's theory of general relativity, quantum theory, and quantum electrodynamics (QED).

Under "useful" theories, he lists the Gell Mann-Zweig quark model for hadrons, the Glashow - Salam - Ward - Weinberg theory for leptons, and the big-bang theory for the origin of the universe. Almost all others he classifies as "tentative". The important distinction between the useful and tentative categories is the lack of any significant experimental support for the theories in the latter category.

It is, of course, possible for a tentative theory to evolve into the useful category, and even into the superb category. It is not too surprising that the main superb theories are ancient ones, which have indeed evolved over the years from tentative beginnings.

Albert Einstein said : "A theory is more impressive the greater is the simplicity of its premises, the more different are the kinds of things it relates, and the more extended its range of applicability. Therefore, the deep impression which classical thermodynamics made on me. It is the only physical theory of universal content which I am convinced, that within the framework of the applicability of its basic concepts, will never be overthrown".

Arthur Eddington said "The laws of thermodynamics control, in the last resort, the rise and fall of political systems, the freedom or bondage of Nations, the movements of commerce and industry, the origins of wealth and poverty, and the general physical welfare of the human race".

## 1.2.8 The Laws of Thermodynamics

These are essentially four in number, and represent the summary and essence of our experience with nature. In common with other fundamental laws of nature (e.g. Newton's laws of motion), they can neither be derived nor proved. However, no single instance of disproof or violation of any of the laws of thermodynamics has been recorded, and these laws are regarded as among the most firmly established of all the laws of nature.

That even some scientists feel ill at ease with the grand generalizations of thermodynamics, and the embarrassingly elementary mathematical concepts applied throughout the discipline, is summarized succinctly by Bridgeman :

"It must be admitted, I think, that the laws of thermodynamics have a different feel from most of the other laws of physics. There is something more palpably verbal about them they smell more of their human origin. The guiding motif is strange to most of physics : namely, a capitalizing of the universal failure of human beings to construct perpetual motion machines of either the first or the second kind. Why should we expect nature to be interested either positively or negatively in the purposes of human beings, particularly purposes of such unblushingly economic tinge?".

## **1.2.9** Thermodynamics and Thermostatics

Some thermodynamicists are unhappy about calling their field of work as thermodynamics, but would prefer to call it "thermostatics". This is because, although it does deal with systems in motion, it does not deal with the rates at which processes, energy exchanges, etc. occur, or the mechanisms of changes in properties; these are the concern of transport phenomena and chemical kinetics.

# **1.3 THE S.I. SYSTEM OF UNITS**

## 1.3.1 A Review of Units

Everything we produce and consume, everything we buy and sell, and everything we see and feel, is measured and compared by means of units. Starting from arbitrary measures (the foot was defined as the length of 36 barleycorns strung end to end, and the yard was the distance from the tip of King Edgar's nose to the end of his outstretched hand), we have come a long way in standardizing our units. Many of these are now based upon the physical laws of nature, which are reproducible, invariable and neutral.

The CGS (esu) system was devised by scientists of the nineteenth century to measure the phenomena associated with capacitors and with static electricity. Subsequently they

proposed the CGS (emu) system to measure magnetism and electric currents. The two systems of units were used quite independently of each other, before it was suspected, and then definitely established, that they were related by the speed of light.

The MKS system then tried to unify the CGS (esu) and the CGS (emu) systems, while employing the practical units of electricity (volt, ampere and watt) which has gained favour in the electrical industry. Although this was an important step, it did not quite solve the problem of coherence (discussed later).

In 1954, at the X General Conference of Weights and Measures held at Sevres, France, the ampere (A) was chosen as the fourth base unit, and this system was often referred to as the MKSA system of units.

In 1960, at the XI General Conference of Weights and Measures, the system of units proposed in 1954 was officially named "Systeme International d'Unites", for which the universal abbreviation is SI. The SI or International System of units is a coherent system which is now used by over 80% of the world.

### **1.3.2** The SI Units

The SI units possess a number of remarkable features, which are shared by no other system of units:

- It is a decimal system.
- It employs many units which are commonly used in industry and commerce;
  e.g. volt, ampere, watt, kilogram etc.
- It is a coherent system which expresses with startling simplicity some of the most basic relationships which occur in electricity, in mechanics, and in electromechanics. (Briefly, a system is said to be coherent when products and quotients involving one unit of A, one unit of B, one unit of C, etc. yield one unit of X).
- It can be used by the research scientist, the technician, the practising engineer and the layman, thereby blending the theoretical and the practical world.

## **1.3.3** Base and Derived Units of the SI System

The foundation of the S I units rests upon seven base units and two supplementary units. These are listed in Table 1.1. From these base units we can derive other units to express quantities such as area, power, force and so on. There is really no limit to the number of units we can derive, but some occur so frequently that they have been given special names. Thus, instead of saying that the unit of force is kg.m/s<sup>2</sup>, we use the less cumbersome term "newton". Some of the derived units which have special names are listed in Table 1.2

BASE UNITS			
Unit	Symbol		
metre			
kilogram	kg		
second	S		
ampere	Α		
kelvin	K		
Candela	cd		
mole	mol		
SUPPLEMENTARY UNITS			
radian	täd		
steradian	sr		
	BASE UNITS Unit metre kilogram second ampere kelvin Candela mole SUPPLEMENTARY UNITS radian steradian		

#### Table 1.1 : BASE AND SUPPLEMENTARY UNITS

## Table 1.2 : DERIVED UNITS WITH SPECIAL NAMES

Quantity	Unit	Symbol	Units
Force	newton	N	kg.m/s <sup>2</sup>
Energy	joule	J	N.m
Power	watt	W	J/s
Pressure	pascal	Pa	N/m <sup>2</sup>
Electric potential	volt	v	W/A
Electric resistance	ohm	Ω	V/A
Electric conductance	siemens	S	1/요
Electric charge	coulomb	С	A.s
Electric capacitance	farad	F	C/V
Magnetic flux	weber	Wb	V.s
Magnetic flux density	tesla	Т	Wb/m <sup>2</sup>
Inductance	henry	H	Wb/A
Frequency	hertz	Hz	2π/s*
Illumination	lux	<b>1x</b>	cd.sr/m <sup>2</sup>
Luminious flux	lumen	lm	cd.sr

\* The dimension of the hertz is usually given as s<sup>-1</sup> but the complete formula is 2  $\pi$  since 1 Hz = 2 $\pi$  rad/s.

# 1.3.4 Multiples and Sub-multiples

Multiples and sub-multiples of S I units carry prefixes according to Table 1.3. It is interesting to note that the prefixes for positive powers of 10 have Greek roots while those for negative powers of 10 have Latin roots.

Multiplier	Exponent Form	Prefix	SI symbol
1 000 000 000 000	1012	tera	Т
1 000 000 000	10 <sup>9</sup>	ģiga	G
1 000 000	10 <sup>6</sup>	mega	М
1 000	10 <sup>3</sup>	kilo	k
100	10 <sup>2</sup>	hecto	h
10	<b>10</b> <sup>1</sup>	deca	da
0.1	10 <sup>-1</sup>	deci	d d
0.01	10-2	centi	С
0.001	10 <sup>-3</sup>	milli	m
0.000 001	10-6	micro	. u
0.000 000 001	10 <sup>-9</sup>	nano	n
0.000 000 000 001	10 <sup>-12</sup>	pico	р
0.000 000 000 000 001	10 <sup>-15</sup>	femto	f
0.000 000 000 000 000 001	10 <sup>-18</sup>	atto	a

Table 1.3 : MULTIPLES AND SUB-MULTIPLES

Fundamental Concepts and Definitions

#### **1.3.5** Definitions of Some Base Units

- The metre (m) is the length equal to 1 650 763.73 wavelengths in vacuum of the radiation corresponding to the transition between the  $2p_{10}$  and  $5d_5$  levels of the krypton 86 atom.
  - The kilogram (kg) is the unit of mass; it is equal to the mass of the international prototype of kilogram, which is a particular cylinder of platinum-iridium alloy which is preserved in a vault in Sevres, France by the International Bureau of Weights and Measures.
- The second (s) is the duration of 9 192 631 770 periods of the radiation corresponding to the transition between the two hyperfine levels of the grounc state of the Cesium - 133 atom.
- \* The kelvin (K), unit of thermodynamic temperature, is the fraction 1/273.16 o. the thermodynamic temperature of the triple point of water.

# **1.4 FUNDAMENTAL CONCEPTS AND DEFINITIONS**

Thermodynamics, like so many other disciplines, has developed its own vocabulary and its own characteristic usage of common words. Two consequences result from this. Words coined for thermodynamics enter the dictionary and often become common usage with time; examples are 'entropy', 'enthalpy', 'exergy', 'anergy' etc. We have to carefully define terms when we borrow them from common usage to represent thermodynamic concepts; examples are 'work', 'heat', 'energy', 'property', 'equilibrium', 'reversibility', 'availability', etc. In this process, frequent mis-use occurs, either because of a lack of understanding or because of perpetuation of outmoded concepts as a matter of convenience. For example, the following statements are thermodynamically incorrect, but still continue to flourish even among engineers:

- \* Turn the 'heat' up in an oven. ('Temperature' is the correct word).
- Heat 'flows' from a higher temperature to a lower temperature. (Heat is not a fluid like water to 'flow'; this is a legacy of the now-discredited 'caloric' theory of heat, which is responsible for other mis-statements, such as 'heat capacity', even 'heat transfer').
- Specific' heat, heat 'contained' in a body or exhaust gases. (Heat is not a property, like energy, for example, to be possessed by a system).

### **1.4.1** System, Surroundings and the Boundary

The careful and explicit definition of the system by means of its boundaries is of utmost importance in solving problems in thermodynamics. It is equivalent to isolating a free body in statics for a force balance.

Any prescribed and identifiable collection of matter, whose behaviour is being studied is called the thermodynamic system, or just system, for short; this is shown in fig.1.1. All other matter that is outside is called the surroundings or environment. The system and the surroundings together make up the universe.

Surroundings

System

System+Surroundings = Universe

Figure 1.1 : Definition of system

The boundary completely encloses the system and separates it from the surroundings. The boundary may be a material envelope or a tangible and visible interface between the system and its surroundings, as for example, the piston face and inside cylinder walls in an automobile engine enclosing the gas in the cylinder. The boundary may also be an imaginary closed surface which contains (prescribes and identifies) the collection of matter under consideration; as for example, the imaginary closed surface enclosing a small volume of a fluid within a larger volume of fluid.

No matter crosses the boundary of a system, by definition. Often the system will change position and shape, but the boundary then moves so as always to hold the same collection of matter. This means that a system has constant mass.

# 1.4.2 Control Volume

While the system concept focusses attention on the processes undergone by a fixed body of material, in many engineering problems, the focus of attention is a piece of equipment through which material flows continuously. Some examples are a hydro- electric plant, steam or gas turbine, gasoline or diesel engine, heat exchanger, nozzle, diffuser etc.

In such a case, it is useful to define the control volume. A control volume is any volume of fixed shape, and of fixed position and orientation relative to the observer.

# 1.4.3 Comparison between System and Control Volume

- Similarities :
- Both are defined by careful description of their boundaries.
- \* Both concepts are useful in permitting the interactions at the boundaries to be related to the changes occurring within them.
- \* Differences :
- A system denotes a prescribed collection of matter, while a control volume denotes a particular region of space.
- The system boundary may, and usually does, change shape, position and orientation relative to the observer. The control volume boundary does not, by definition.
- Matter may, and usualy does, flow across the control volume boundary.
  Material does not cross a system boundary, by definition.

In view of the above comparison, some texts on thermodynamics designate the control volume as an open system, while the system is termed a closed system. In this Course, we will use the terms system and control volume in preference to closed and open systems.

#### Example 1.1 :

Classify, with reasons, the following as either a system or a control volume, or neither a system nor a control volume ; or both a system and a control volume.

- (a) I.C.engine
- (b) Gases inside the cylinder of an I.C.engine when both valves are closed, and the piston is moving.
- (c) A steam power plant, including only the water + steam circuit.
- (d) The boiler in a steam power plant.
- (e) The contents of a toy balloon when there is leakage from the balloon to the atmosphere.
- (f) The contents of a rigid pressure vessel when there is neuner inflow nor outflow from the vessel.

#### Solution :

- (a) **Control Volume.** Fuel and air enter the I.C.engine, while exhaust gases leave the engine; the engine is of fixed shape, and of fixed position and orientation relative to the observer.
- (b) System. No matter crosses the boundary of the I.C.engine, while the system boundary is moving.
- (c) System and Control Volume. The combination of steam generator, steam turbine, condenser and boiler feed pump (excluding such things as the furnace and the cooling water circuit of the condenser) contains the same amount of

matter. All the components are of fixed shape, and of fixed position and orientation relative to the observer.

- (d) **Control Volume.** Fuel and air enter the furnace, while combustion products leave through the stack. Concurrently, water is pumped in by the boiler feed pump and steam leaves the boiler. All the components are of fixed shape, and of fixed position and orientation relative to the observer.
- (e) Neither a system nor a control volume. The mass inside the balloon is changing, as also the shape of the boundary.
- (f) Both a system and a control volume. System, since the pressure vessel is rigid, and no matter crosses the boundary; also a control volume, since the boundary is of fixed shape, position and orientation.

## SAQ1

Choose the correct answer(s). (There may be more than one correct answer).

#### (i) For a thermodynamic system :

- (a) there can be flow of matter across the system boundary.
- (b) there can not be any flow of matter across the system boundary.
- (c) its volume, shape, position and orientation relative to an observer may change.
- (d) its volume, shape, position and orientation relative to an observer can not change.

#### (ii) For a control volume :

- (a) there can be flow of matter across the system boundary.
- (b) there can not be any flow of matter across the system boundary.
- $a_{1}$  =  $a_{2}$  volume, shape, position and orientation relative to an observer may change.
- (d) its volume, shape, position and orientation relative to an observer can not change.

## 1.4.4 Isolated System

An isolated system is characterized by the fact that it has no interaction with its surroundings. The combination of system plus surroundings, making up the universe, is an example of an isolated system.

In summary, the permissible interactions for the three classes of regions defined above may be stated as follows:

- System : heat and / or work
- Control Volume : heat and / or work and / or mass
- Isolated System : No interaction permissible

This is illustrated in Figure 1.2.

#### Fund-mental Concepts and Definitions





# **1.4.5** Different Types of Boundaries (or Walls)

The classification into system, control volume a id isolated system is closely connected with the type of boundary or wall involved. In a system, the boundary is impermeable to matter, but can exchange energy with its surroundings in the form of heat or work. In a control volume, the boundary permits the transfer of mass and / or energy (in the form of heat or work); while in the case of an isolated system, the boundary is impervious to both mass and energy (either in the form of heat or work).

Three types of walls that separate the system from its surroundings are rigid walls, diathermal walls and adiabatic walls:

- A rigid wall will not permit a change in the volume of the system.
- \* A diathermal wall will permit the system to communicate thermally with its surroundings.
- \* An adiabatic wall is one which is impermeable to thermal energy.

### **1.4.6 Thermodynamic Properties**

A property is any (macroscopic) observable characteristic of a system. These distinguishing characteristics of a system are quantities that need to be specified in order to give a macroscopic description of the system. A property may be either directly observable or indirectly determinable. Many such quantities are familiar to us from other branches of science, such as mass, energy, pressure, volume, density, electric field, magnetic field, and magnetization of matter. Two other properties - temperature and entropy - are unique to thermodynamics.

Any combination of properties, such as, for example, the product of pressure and volume, may also be considered a property. Among the many such possible derived properties, three of them, viz. enthalpy, Gibbs function and Helmholtz function, are particularly useful.

The definition of a property in thermodynamics has a unique meaning. Taking the property pressure, when a system has a pressure of  $p_1$  at one instant and a value of  $p_2$  at another instant, the change in pressure  $(p_2 - p_1)$  is independent of how the change is accomplished. Mathematically speaking,

$$\Delta p = \int_{p_1}^{p_2} dp = (p_2 - p_1) \qquad \dots (1.1)$$

which means that dp is an exact differential, and the integral is independent of the path followed. For this reason, thermodynamic properties are called point functions or state functions. A quantity whose value depends on the particular path followed in going from one state to another is called a path function. The differential of such a quantity is inexact.

## **1.4.7** Classification of Properties

The properties of a system may be divided into essentially two types: intensive and extensive. Intensive properties are those which are independent of the amount of material in the system: they depend on the intensity of some effect in the system. Pressure, temperature and density are examples of intensive properties.

Those properties which are proportional to the mass of a system are called extensive properties; they depend on the extent or size of the system. Such properties are additive. Volume, energy and entropy are examples of such properties.

A new set of properties results when the extensive properties are divided by the mass of the system. Such properties are called specific properties. Examples are specific volume, specific energy and specific entropy. Conventionally, capital letters are employed to represent extensive properties, and the corresponding lower case letters for the corresponding specific properties. Thus V is volume and v is specific volume. Density (p) is defined as the mass of a system divided by its volume or the mass per unit volume. Thus p = 1 / v, and is an intensive property.

Although specific properties seem to be similar to intensive properties, there is a distinct difference between them. Specific properties, when multiplied by the mass of the system, result in extensive properties; the product of any intensive property and mass has no significance. For example, the product of specific volume and mass yields volume, while the product of density and mass has no significance.

#### **SAQ 2**

Classify the following properties as either intensive or extensive :

a) volume b) weight c) pressure d) temperature

e) density f) velocity g) elevation h) kinetic energy

## SAQ 3

Identify with reasons, the following properties as extensive or intensive :

a) weight b) molecular weight

## 1.4.8 State, Process, Path

The condition of a system at some instant of time is called its state. The state of a system is the totality of the properties of the system; it represents the complete description of the system. The state of a system is ultimately determined by the behaviour of the electrons and nuclear particles making up all matter. To an external observer, however, this behaviour manifests itself in a number of macroscopic characteristics, which can be measured without reference to the microscopic structure of matter. These measurable macroscopic quantities define the state of the system to a degree which has been shown to be entirely sufficient for the purposes of engineering thermodynamics. These measurable macroscopic characteristics of a system are the properties.

The state point is a point on a property diagram representing the properties of a system at any moment. A change of state of the system is the consequence of a process. The process consists of the succession of states passed through, which is known as the path of the process.

# 1.4.9 Thermodynamic Equilibrium

The concept of equilibrium is the cornerstone of classical thermodynamics. As many other things in thermodynamics, it is really an abstraction, since real systems are never strictly in equilibrium.

When a system has no unbalanced force within it and when the force it exerts on its boundary is balanced by external forces, the system is said to be in mechanical equilibrium. When the temperature of a system is uniform throughout and is equal to the temperature of the surroundings, the system is said to be in thermal equilibrium. When the chemical composition of a system remains unchanged, the system is said to be in chemical equilibrium.

It may also be seen that when two systems are in mechanical equilibrium the property that the systems have in common is pressure. Temperature is the property that two systems have in common when they are in thermal equilibrium.

There are other kinds of equilibrium as well. Two systems are said to be in electrostatic equilibrium if there is no tendency for a net charge flow between them when they are brought into contact. The electrostatic potential is the property that two systems have in common when they are in electrostatic equilibrium. Two phases of a substance (for example, solid and liquid) are said to be in phase equilibrium if there is no tendency for phase transformation (for example, melting) when they are brought into contact.

The term thermodynamic equilibrium is used to indicate a condition of equilibrium with respect to all possible macroscopic changes in a system. The concept of thermodynamic equilibrium is concerned with the static and time-invariant state of a system where no spontaneous processes take place and all macroscopic quantities remain unchanged.

It is important to distinguish between two kinds of idealized time-independent states. When the properties or state variables measured at any location in the system, and as a function of time on a time-scale which does not resolve individual molecular events, remain constant with time everywhere in the system, the system is said to be in a steady state. When, in addition, no changes appear in its surroundings, the system is said to be in a state of thermodynamic equilibrium. Thus, thermodynamic equilibrium is the time-invariant condition of an isolated system; steady state is the corresponding time-invariant condition of a system which can interact with its surroundings. In a sense, equilibrium is a special case of the more general steady state, being the limiting condition when the interaction with the surroundings approaches zero.

For example, if heat is supplied at a constant rate at one end of a piece of metal and removed at an equal rate at the other hand, the temperature at each point will approach a steady value. The system in question remains unchanged in time, but is not in a condition of thermodynamic equilibrium on account of the occurrence of the dissipative process. (i.e. changes occur in the surroundings.)

# 1.4.10 Equations of State

Experience has shown that not all the properties have to be measured to define the state of a system at equilibrium. There exist relations between equilibrium values of properties which are called equations of state. The ideal gas law relationship pv=RT is an example of an equation of state.

## 1.4.11 Mass, Force and Weight

The mass of a body is a measure of the amount of matter in the body. The mass of a given collection of matter is not altered by such things as:

- change of location
- deformation of shape
- change of temperature
- chemical reactions which the matter undergoes.

These facts express the content of the law of conservation of mass. Some of the processes which do alter the mass of a body are:

- nuclear reaction
- acceleration to velocities comparable to the speed of light.

Force is conceived as the pull and push that tend to make objects move. It has both magnitude and direction, and is treated mathematically as a vector. The vector sum of all forces acting on a body that is not accelerating must be zero.

The unit of force is defined by means of Newton's Second Law of Motion, which forms the foundation of the science of dynamics and is also an important part of thermodynamics :

"One newton (N) is the magnitude of the force, which acting on a body of one kilogram mass, causes it to accelerate at the rate of  $1 \text{ m/s}^2$  in the direction of the force".

The weight of a body on earth is related to the gravitational force exerted by the attraction of the earth. Whereas the mass of a body is constant, the weight of the body varies (by a few tenths of a per cent) with position on the earth's surface. It decreases considerably in outer space, soon becoming negligible compared with the gravitational attraction exerted by other heavenly bodies.

#### Example 1.2:

A spring balance, which is designed to measure weight, is to be employed for determining the mass of a sample of moon rocks on the moon's surface. The spring was originally calibrated for the earth's gravitational acceleration of  $9.8 \text{ m/s}^2$ . The scale reads 4.5 kg on the moon, where the gravitational acceleration is  $1.8 \text{ m/s}^2$ . Compute the mass of the sample. What would be the reading on a beam balance scale ?

#### Solution :

Since the spring was calibrated for the earth's gravitational field, the force corresponding to a reading of 1 kg on the spring balance is :

$$1 \text{ kg} \times 9.81 \text{ m/s}^2 = 9.81 \text{ N}$$

The force corresponding to a reading of 4.5 kg is :

Since the gravitational acceleration on the moon is  $1.8 \text{ m/s}^2$ ,

mass of sample = 
$$\frac{44.15}{1.8}$$
 = 24.53 kg ANSWER

Since a beam balance measures mass, it will indicate a reading of 24.53 kg ANSWER

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On the surface of the moon where the local gravity of g is  $1.67 \text{ m/s}^2$ , 2 kg of a gas occupy a volume of  $1 \text{ m}^3$ . Determine :

(i) the specific volume of the gas in  $m^3/kg$ 

(ii) the density in g/cm<sup>3</sup>

### **1.4.12** Pressure and its Measurement

The pressure p is defined as the normal force per unit area exerted by the system on its boundary. It is an intensive property, and may be looked upon as the driving force for volume change. It is a continuum concept. At the microscopic level, pressure may be explained as resulting from the impacts of particles on the wall. These impacts give rise to a force which is macroscopically measurable, and in the continuum view this force is considered to be uniformly distributed over the wall, not concentrated at particular points.

The pressure of a system is often measured with a gauge by employing the atmospheric pressure as the datum. In such a case, if the pressure is above atmospheric it is called gauge

pressure, and if it is below atmospheric it is called vacuum pressure. In engineering calculations, however, we must use absolute pressure.

The relations between gauge, vacuum and absolute pressures are given by the following two equations:

absolute pressure = atmospheric pressure + gauge pressure

absolute pressure = atmospheric pressure - vacuum pressure ....(1.3)

Figure 1.3 illustrates the relationships among absolute pressure, atmospheric pressure, gauge pressure and vacuum.



(a) Absolute pressure greater than atmospheric pressure (b) Absolute pressure smaller than atmospheric pressure

Figure 1.3 : Relationships among absolute pressure, atmospheric pressure, gauge pressure and vaccum

The following table gives some conversion factors for units of pressure:

 $1bar = 10^{5} \text{ N/m}^{2}$ 

1 pascal (Pa) =  $1 \text{ N/m}^2$ 

1 standard atmosphere (atm) = 760 mm Hg

= 1.013 250 bar



Figure 1.4 : Manometer

...(1.2)

#### The manometer

Figure 1.4 shows a manometer consisting of a U-tube, the two arms of which are connected to two systems in which the pressures are  $p_1$  and  $p_2$ . The purpose of the manometer is to provide a measure of the difference between  $p_1$  and  $p_2$ . The lower portion of the U- tube is filled with a liquid having a density which greatly exceeds the densities of the fluids in the two systems. The vertical distance z separating the two free liquid surfaces is measured by means of a suitably supported scale.

From the principles of hydrostatics, the pressure, density and height difference are related by:

$$(p_1 - p_2) = \rho gz$$
 ...(1.4)

Knowing  $\rho$ , measurement of z permits the pressure difference  $(p_1 - p_2)$  to be calculated. Additionally, if  $p_2$  is known,  $p_1$  can be determined.

It is interesting to note that the two arms of the U - tube need not be of equal, or even of uniform, cross - sectional area.

#### Example 1.3 :

Determine the pressure difference in Pa corresponding to one mm difference in liquid surface level in a manometer when the liquid is : (i) water, (ii) mercury. Take the densities of water and mercury to be 1000 and 13 568 kg/m<sup>3</sup>; and the gravitational acceleration to be  $9.81 \text{ m/s}^2$ .

Solution :

$$(p_1 - p_2) = \rho gz$$

(i) For water,  $(p_1 - p_2) = 1000 \text{ kg}/m^3 \times 0.001 \text{ m} \times 9.21 \text{ m/s}^2$ 

= 9.81 Pa ANSWER

(ii) For mercury, 
$$(p_1 - p_2) = 13568 \text{ kg/m}^3 \times 0.001 \text{ m} \times 9.81 \text{ m/s}^2$$

= 133.1 Pa ANSWER

### The Barometer

A barometer may take either of the forms shown in Figure 1.5; in both cases, the space above the liquid in the closed arm is evacuated. If the pressure in the open-ended arm is pand the difference of height of the two liquid columns is z, since the pressure in the closed end is zero,

$$\rho = \rho gz \qquad \dots (1.5)$$

Thus, the barometer is an instrument which measures absolute pressures, not pressure differences.

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Figure 1.5 : Barometer

SAQ 5

Choose the correct answer :

- (i) The vacuum in a vessel,  $p_v$  is given by :
- a)  $p_v = p p_{atm}$
- b)  $p_v = p + p_{atm}$
- c)  $p_v = p_{atm} p$
- $\mathbf{d}) \quad p_{v} = p$

where p is the absolute pressure in the vessel, and  $p_{alm}$  is the atmospheric pressure.

- (ii) The gauge pressure,  $p_g$  is given by :
- a)  $p_g = p p_{atm}$
- b)  $p_g = p + p_{aim}$
- c)  $p_g = p_{atm} p$
- d)  $p_g = p$

#### **The Bourdon Gauge**

The Bourdon Gauge is a dial instrument for measuring pressures both above and below the atmospheric pressure. It consists of a metal tube of oval cross section, bent into the form of a circular arc. One end of the tube is open, fixed rigidly to the casing, and is connected by means of rigid or flexibile tube to the pressure vessel in which the pressure is to be measured. The other end of the tube is closed, and connected through a gear-and-lever mechanism to a pointer moving over a suitably graduated scale. A change in pressure causes the oval section of the tube to tend to become circular, and this causes a deflection of the free end, proportional to the change in pressure.

Since the deformation of the tube cross section is caused by the pressure difference  $(p-p_{atm})$ , the Bourdon gauge measures gauge pressure, not absolute pressure. It may be employed for measuring pressures either above or below atmospheric pressure.

#### SAQ 6

A Bourdon gauge on a steam generator shows a pressure of 700 kPa. The barometer reads 755 mm Hg. What is the absolute pressure in kPa of the steam in the steam generator? Take the density of mercury to be  $13,600 \text{ kg/m}^3$ .

## 1.4.13 Thermodynamics and Processes

This sub-section can be skipped during the first reading, or in an elementary course, without loss of continuity. The concepts introduced in this section, however, are important to complete the picture, and to present a comprehensive treatment.

As a rule, the engineer is interested in employing thermodynamics more to describe processes than to study matter in thermodynamic equilibrium. This use of thermodynamics raises a basic question. It has been indicated earlier that the properties of a system at equilibrium do not change with time. Therefore, properties and relations between them which are defined only at equilibrium, can not apply to a system undergoing a process. How then is it possible to use thermodynamics to describe processes? The answer to this fundamental question is developed below.

## **Relaxation** Time

Each system responds differently when changes in its properties are imposed by some external agency. For example, consider a system for which the equation z = f(x,y) is the equation of state which relates the equilibrium values of the properties x, y and z. If this

system is suddenly subjected to change  $\Delta x$  in x, with y kept constant, z eventually reaches the new value predicted by the equation of state, namely

$$z + \Delta z = f(x + \Delta x, y) \qquad \dots (1.6)$$

The key word in the last sentence is eventually. The change  $\Delta z$  takes time. A definite time T elapses before equilibrium is restored to the extent that no further change in the properties is measurable anywhere in the system. T is called the relaxation time. The process by which a system resumes equilibrium after a sudden change in one of its properties is called the relaxation process.



Figure 1.6 : Illustration of the definition of relaxation time

Figure 1.6 illustrates the definition of T. There are many systems which approach equilibrium at the same rate as the function  $\exp(-t/T_e)$  approaches zero. In most cases T and  $T_e$  are of the same order of magnitude.

In general, the relaxation time T is a complicated function of all the properties of the system, of the magnitude of the impressed change  $\Delta x$ , and of the location where  $\Delta x$  is impressed. In some cases T may be calculated from suitable mathematical models, but in most cases it is a measured quantity.

The science of gas dynamics provides several examples of relaxation processes in gas systems subjected to step changes in temperature, pressure and volume. For the purpose of thermodynamics it is only necessary to know that a finite time, called the relaxation time, elapses before a system returns to equilibrium after a sudden change in any of its properties.

#### Slow Processes

When a system is caused to undergo a process, at least one of its measurable properties, say x, is subjected to a change x in some time interval,  $t_p$ . This interval can be called the process time. If  $t_p$  is zero,  $\Delta x$  is impressed as a step function and the system resumes equilibrium only after the relaxation time T has elapsed.

If  $t_p$  is increased and the same  $\Delta x$  is impressed more gradually, smaller deviations from equilibrium are observed during the process. Eventually, if  $t_p$  is made long enough for a given x, the state of the system at each instant of the process is so nearly the equilibrium state corresponding to the instantaneous value of x that deviations from any of the equations of state cannot be detected by measurement. Under these conditions, the process is called slow. Thus all the properties of a system are defined and all equations of state are satisfied at every instant during a slow process.

We are now in a position to answer the question raised earlier in this sub-section. Thermodynamics can be used to describe a process only if it is slow in the sense discussed above. Processes which are not slow are called fast. An application of thermodynamics to fast processes will lead to error since, by definition, there are measurable deviations from the equilibrium relations on which thermodynamics is based.

We will summarize the above conclusions as follows:

A process is slow when  $t_p$  greatly exceeds T, when both refer to the same x, that is,  $t_p >> T$  in a slow process.

It must be emphasized that fast and slow processes are defined in relation to the corresponding relaxation times of the systems under study. For one system a process with  $t_p$  of 1 ms may be slow. For another, a fast process could have  $t_p$  equal to many hours.

In many texts on thermodynamics, slow processes are alternatively called quasi-static or fully-resisted. The quasi-static process is also sometimes called a quasi-equilibrium process, and represents a process carried out in such a manner that at every instant the system departs only infinitesimally from an equilibrium state. If there are finite departures from equilibrium, the process is non-quasi-static. It will be seen later that a quasi-static process is an internally reversible process. A fully-resisted process is also described as one in which the speed of motion of the system boundary is much less than the velocity of sound in the fluid, permitting the fluid pressure at any instant to be very nearly uniform throughout the system.

# 1.5 SUMMARY

This Unit provides an introduction to the nature and scope of Thermodynamics, the rationale for studying it, a classification of the methodologies for studying it, and an overview of the laws of thermodynamics. It shows how the principles of thermodynamics are applicable in different branches of Engineering. The SI units are reviewed, and the fundamental concepts and definitions necessary for the subsequent development are introduced in this Unit.

Thermodynamics is the science of the relationships between heat, work, and the properties of substances.

The macroscopic approach to the study of Thermodynamics is empirical, employs the continuum model for matter, and deals with observable properties.

The microscopic approach is theoretical, employs the molecular model for matter, applies statistical analyses to the assumed molecular model, and computes results which are then interpreted in terms of the macroscopic properties and laws.

Statistical Thermodynamics is a microscopic approach which combines kinetic theory and quantum mechanics.

The Laws of Thermodynamics represent the summary and essence of our experience with nature, and deal with the concepts of Temperature, Energy, Entropy, and the Absolute Zero of Temperature.

The SI system of units possesses features not shared by any other system of units, viz., decimal, coherent, versatile and comprehensive.

The Thermodynamic system is any prescribed and identifiable collection of matter, whose behaviour is being investigated. All other matter that is outside is called the surroundings or environment. The system and the surroundings together make up the universe. The boundary completely encloses the system and separates it from the surroundings.

The control volume is any volume of fixed shape, and of fixed position and orientation relative to the observer.

An isolated system has no interaction whatsoever with its surroundings.

A thermodynamic property is any (macroscopic) observable characteristic of a system. An intensive property is independent of the amount of material in the system; it depends on the intensity of some effect in the system. Examples are pressure, temperature and density. An extensive property is proportional to the mass of the system; it depends on the extent or size of the system. Examples are volume, energy and entropy. A specific property is obtained when an extensive property is divided by the mass of the system. Examples are specific volume, specific energy and specific entropy.

The state of a system is the totality of the properties of the system, and represents the complete description of the system. A change of state of the system is the consequence of a process. The process consists of the succession of states passed through, which is known as the path of the process.

The concept of thermodynamic equilibrium is concerned with the static and time-invariant state of a system where no spontaneous processes take place and all macroscopic quantities remain unchanged.

Equations of state are relations between equilibrium values of properties. The ideal gas law relationship pv = RT is an example of an equation of state.

The mass of a body is a measure of the amount of matter in the body. It is not altered by change of location, deformation of shape, change of temperature, or chemical reactions which the matter undergoes. These facts express the content of the law of conservation of mass.

Force is conceived as the pull and push that tends to make objects move ; it has both magnitude and direction.

Pressure is the normal force per unit area exerted by the system on its boundary; it may be looked upon as the driving force for volume change.

Gauge pressures are pressures reckoned above the atmospheric pressure, while vacuum pressures are pressures reckoned below the atmospheric pressure. Absolute pressures are reckoned above a datum of zero pressure.

A manometer measures pressure differences ; a barometer measures absolute pressures.

A relaxation process is the process by which a system resumes equilibrium after a sudden change in one of its properties. The relaxation time is the time elapsed before equilibrium is restored.

Thermodynamics can be used to describe a process only if it is slow; i.e. when the process time greatly exceeds the relaxation time. Such processes are alternatively called quasi-static or fully-resisted.

# **1.6 KEY WORDS AND PHRASES**

Thermodynamics	:	The science of the relationships between heat, work and the properties of substances.
System	:	Any prescribed and identifiable collection of matter, whose behaviour is being studied.
Surroundings	:	All matter outside the system.
Universe	.:	System plus surroundings.
Boundary	:	A real or imaginary closed surface around the system which separates it from the surroundings.
Control Volume	:	Any volume of fixed shape, and of fixed position and orientation relative to the observer.
Isolated System	* :	A system characterized by the absence of any interaction with its surroundings.
Rigid wall	<b>:</b> .	A wall preventing any change in the volume of the system.
Diathermal wall	:	A wall permitting thermal communication between system and surroundings.
Adiabatic wall	j.	A wall preventing thermal communication between system and surroundings.
Property	:	Any macroscopic observable characteristic of a system.
Intensive Property	:	A property that is independent of the amount of material in the system.
Extensive Property	:	A property which is proportional to the mass of the system.
Specific Property	:	An extensive property divided by the mass of the system.
State	:	The condition of a system at some instant of time; it is represented by the totality of the properties of the system.
Process	:	Cause of a change of state of the system.
Path	. <b>.</b>	The succession of states passed through during a process.
Thermodynamic Equilibrium	:	The static and time-invariant state of a system where no spontaneous processes take place and all macroscopic quantities remain unchanged.
Equation of State	:	The relation between equilibrium values of properties at a given state.
Mass	:	A measure of the amount of matter.
Weight	<b>:</b>	The gravitational force exerted on a body by the attraction of the earth.

1.4

Pressure	:	The normal force per unit area exerted by a system on its boundary.
Gauge Pressure	:	The amount of pressure above the atmospheric pressure.
Vacuum Pressure	:	The amount of pressure below the atmospheric pressure.
Absolute Pressure	:	The pressure reckoned with respect to a datum of zero pressure.
Manometer	:	An instrument for measuring a pressure difference.
Barometer	:	An instrument for measuring absolute pressure.
Relaxation Process	:	The process by which a system resumes equilibrium after a sudden change in one of its properties.
Quasi-static Process	:	A process during which the system departs only infinitesimally from an equilibrium state.
Fully-resisted Process	:	A process during which the speed of motion of the system boundary is much less than the velocity of sound in the fluid.

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# **1.8 ANSWERS/SOLUTIONS TO SAQs**

- SAQ 1
  - (i) b and c
  - (ii) a and d

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a)	volume	· •	extensive property
b)	weight	-	extensive property
c)	pressure		intensive property
d)	temperature	-	intensive property
e)	density	-	intensive property
f)	velocity	-	intensive property
g)	elevation	-	intensive property
h)	kinetic energy	-	extensive property

# SAQ 3

a)

b)

weight - extensive property; W = mg

molecular weight - intensive property; it is independent of the mass of the system, depending only on the nature of the molecule.

# SAQ 4

i) specific volume =  $V/m = 1/2 = 0.5 \text{ m}^3/\text{kg}$ 

ii) density = 
$$m/V = 2 \text{ kg}/\text{m}^3 = \frac{2 \times 10^3}{10^6} \text{ g}/\text{cm}^3$$
  
=  $2 \times 10^{-3} \text{ g}/\text{cm}^3$ 

SAQ 5

- (i) c :  $p_v = p_{atm} p$
- (ii) a :  $p_g = p p_{atm}$

SAQ 6

 $p_{abs} = p_g + p_{atm}$ = 700 + [13,600 kg / m<sup>3</sup> × 9.81 m / m<sup>3</sup> × 0.755 m × 10<sup>-3</sup>] kPa = 700 + 100.73 = 800.73 kPa